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Article

An Investigation of Staudinger Reactions Involving *cis*-1,3,5-Triazidocyclohexane and Tri(alkylamino)phosphines

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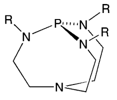
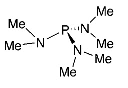
The reaction of 1,3,5-*cis*-triazidocyclohexane with the electron-rich tris(dialkylamino)phosphines $P(NMe_2)_3$ (**1**) and $N(CH_2CH_2NMe)_3P$ (**2b**) in acetonitrile for 3 h furnished the corresponding tris-phosphazides 1,3,5-*cis*-$(R_3PN_3)_3C_6H_9$, **3a** (R_3P = **1**) and **3b** (R_3P = **2b**), in 90% and 92% yields, respectively. The same reaction with the relatively electron-poor tris(dialkylamino)phosphine $MeC(CH_2NMe)_3P$ (**4**) for 2 days gave the tris-iminophosphorane, 1,3,5-*cis*-$(R_3PN)_3C_6H_9$, **5a** (R_3P = **4**), in 60% yield. Compound **3b** is a thermally stable solid that did not lose dinitrogen when refluxed in toluene for 24 h or when heated as a neat sample at 100 °C /0.5 Torr for 10 h. By contrast, tris-phosphazide **3a** decomposed to the tris-iminophosphorane 1,3,5-*cis*-$(R_3PN)_3C_6H_9$, **5b** (R_3P = **1**), in 3 h in quantitative yield upon heating to 100 °C in toluene. Factors influencing the formation of the phosphazides or the iminophosphoranes in these reactions are discussed. The reaction of **3b** with 4 equiv of benzoic acid gave $[N(CH_2CH_2NMe)_3P{=}NH_2]PhCO_2$ {[**6b**H]$PhCO_2$} in quantitative yield along with benzene (56% yield) and dinitrogen. The same reaction with **3a** gave $[(Me_2N)_3P{=}NH_2]PhCO_2$ {[**7a**H]$PhCO_2$} (quantitative yield), benzene (15% yield), and dinitrogen. Treatment of [**6b**H]$PhCO_2$ with KO^tBu afforded $N(CH_2CH_2NMe)_3P{=}NH$ (**6b**) in 40% overall yield. Compound **6b** upon treatment with $PhCH_2CH_2Br$ produced [**6b**H]Br in 90% yield along with styrene. The new compounds were characterized by analytical and spectroscopic methods, and selected compounds (**3b**, **5a**, and [**6b**H]Br) were structured by X-ray crystallography. A special feature of **3b** is its capability to function as a starting material for **6b**, which was not accessible by other synthetic routes.

Introduction

Tris-dialkylaminophosphines such as **1** have been known for decades. Over the past 10 years, we have been exploring the chemistry of bicyclic analogues of these compounds such as proazaphosphatranes **2a**−**2g**, some of which are potent catalysts, promoters, and strong nonionic bases that efficiently facilitate a wide variety of useful organic transformations.[1]



	R
2a	H
2b	Me
2c	Et
2d	^iPr
2e	^iBu
2f	Piv
2g	$CHMe(CH_2Ph)$



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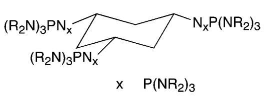
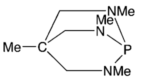


	x	$P(NR_2)_3$
3a	3	**1**
3b	3	**2b**
5a	1	**4**
5b	1	**1**



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Acyclic phosphazides of the type $RN_3P(NR_2)_3$ and acyclic iminophosphoranes of the type $RN{=}P(NR_2)_3$ are well-known, and recently, such derivatives have also been reported for proazaphosphatranes.[2,3] As part of an ongoing investigation of derivatives of this type,[4] we were curious to see if

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(1) (a) For recent reviews, see: Verkade, J. G. *Top. Curr Chem*. **2003**, *223*, 1−44. (b) Verkade, J. G.; Kisanga, P. *Tetrahedron* **2003**, *59*, 7819−7858. (c) Verkade, J. G.; Kisanga, P. *Aldrichimica Acta* **2004**, *37*, 3−14.

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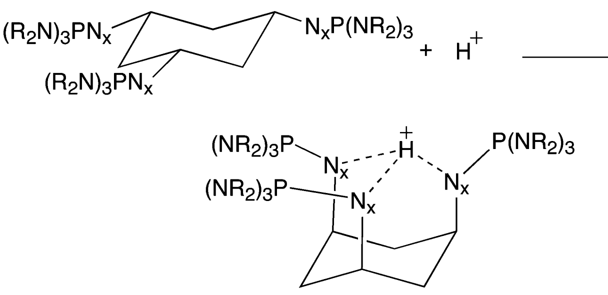
compounds of type **3** could be induced to invert their conformation in the presence of electron pair acceptors such as protons and transition metals, to form adamantane-like structures in which compounds **3** would function as tris-chelating ligands via their N−C-bound nitrogens. Although no evidence for reaction 1 was observed, a surprising decomposition reaction occurred when benzoic acid was added to **3b** and to **3a** in which {[**6b**H]PhCO$_2$} and {[**7a**H]-PhCO$_2$} were formed, respectively, along with dinitrogen and benzene.[5] Here we give further details on these reactions,



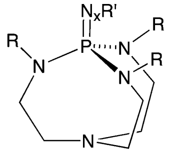
(1)

and we report on reactions of 1,3,5-*cis*-triazidocyclohexane with tris(dialkylamino)phosphines **1** and **4** that gave **3a** and **5a**, respectively. The presence of the phosphazido (PN$_3$−) group in **3b** and the iminophosphoryl (P═N−) moiety in **5a** and [**6b**H]PhCO$_2$ was unambiguously confirmed by X-ray means.

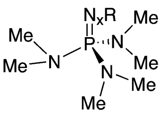
Windus et al.[6] and more recently Schwesinger and co-workers[7] predicted that **6a** would be more basic than its parent **2a**. Unfortunately, **2a** polymerizes readily and must be derivatized in situ.[8] Therefore, one of our goals was to synthesis **6b** and to compare its basicity with its parent **2b**. Further, the presence of the NH functionality in **6b** would allow us to synthesize a range of new bicyclic iminophosphoranes of the type N(CH$_2$CH$_2$NMe)$_3$P═NR (R = alkyl or aryl) which are not accessible by the usual Staudinger reaction involving **2b** with RN$_3$ because of the unusually great thermal stability of phosphazide intermediates containing sterically hindered basic phosphines (see Results and Discussion).

Results and Discussion

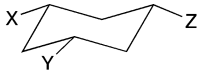
Synthesis of Staudinger Products. The Staudinger reaction of 1,3,5-*cis*-triazidocyclohexane with **1** in acetonitrile afforded **3a** in 92% yield, and the same reaction with **2b** gave **3b** in 90% yield. Compound **3b** did not decompose to the corresponding tris-iminophosphorane even in refluxing toluene after 24 h, and a neat sample of **3b** survived for 10 h at 100 °C/0.5 Torr. On the other hand, **3a** upon heating in toluene at 100 °C for 3 h gave **5b** quantitatively. In order to illuminate factors that could contribute to the stability of phosphazides **3a** and **3b**, an acetonitrile solution of 1,3,5-*cis*-triazidocyclohexane was treated with **4** at ambient temperature for 2 days followed by solvent evaporation to give a colorless residue that upon crystallization from diethyl ether/pentane gave tris-iminophosphorane **5a** in 60% yield. ESI/MS spectral data recorded during the reaction of 1,3,5-*cis*-triazidocyclohexane with **4** were consistent with the formation of intermediates **8a**−**8f** which apparently decomposed over the 2 day reaction period.



	R	R'	x
6a	H	H	1
6b	Me	H	1
6c	Me	Me	3
6d	Me	Me	1
6e	Me	Ph	3
6f	Me	Ph	1
6g	Me	CH$_2$Ph	3
6h	Me	CH$_2$Ph	1
6i	Me	alkyls	3
6j	Me	alkyls	1
6k	CHMe(CH$_2$Ph)	alkyls	3
6l	CHMe(CH$_2$Ph)	alkyls	1



	R	x
7a	H	1
7b	CH$_2$Ph	1
7c	SO$_2$C$_6$H$_4$Me-*4*	3
7d	SO$_2$C$_6$H$_4$Me-*4*	1
7e	(CH$_2$)$_3$OH	3
7f	CPh$_3$	3



	X	Y	Z
8a	NP(NR$_2$)$_3$	N$_3$	N$_3$
8b	NP(NR$_2$)$_3$	NP(NR$_2$)$_3$	N$_3$
8c	NP(NR$_2$)$_3$	N$_3$P(NR$_2$)$_3$	N$_3$
8d	NP(NR$_2$)$_3$	NP(NR$_2$)$_3$	N$_3$P(NR$_2$)$_3$
8e	NP(NR$_2$)$_3$	N$_3$P(NR$_2$)$_3$	N$_3$P(NR$_2$)$_3$
8f	N$_3$P(NR$_2$)$_3$	N$_3$P(NR$_2$)$_3$	N$_3$P(NR$_2$)$_3$

P(NR$_2$)$_3$ = **4**

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(4) The phosphazides **6g**, **6i**, and **6k** were erroneously reported earlier to be iminophosphoranes **6h**, **6j**, and **6l**.[2a−c]

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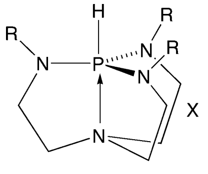
The facile formation of **5a** compared to **5b** in the aforementioned decomposition reaction is ascribed to the poorer basicity of **4** relative to **1**, as is discussed in a subsequent paragraph.

The Staudinger reaction is a two step process involving the electrophilic addition of an alkyl or aryl azide to a P(III) center followed by dinitrogen elimination from the intermediate phosphazide **A** to give iminophosphorane **B** as depicted in reaction 2. Both sterically hindered and electron-rich phosphorus compounds and/or electron-withdrawing substituents on the azides have been shown to stabilize intermediate **A**.[9,10]

$$R_3P + N_3R' \rightarrow \underset{\mathbf{A}}{R_3PN_3R'} \rightarrow \underset{\mathbf{B}}{R_3P{=}NR'} + N_2 \qquad (2)$$

Proazaphosphatranes **2b**−**2g** are more basic than their acyclic $P(NR_2)_3$ analogues because of (i) the stability of the three-center, four-electron $H-P-N_{ax}$ bond in the corresponding azaphosphatrane cations **9a**−**9f**, (ii) the "chelate" effect of the three five-membered rings in cations **9a**−**9f**, (iii) the electron richness of the phosphorus owing to donation of electron density from the bridgehead nitrogen, and (iv) donation of p lone pair electron density from the planar nitrogen in all three $RNCH_2$ moieties to the phosphorus.[11] It has been determined that, in **1**, two of the nitrogens are planar and can donate electrons to phosphorus via their lone pairs which reside in unhybridized p orbitals, whereas the third nitrogen (which is pyramidal) directs its hybridized lone pair anti to the phosphorus lone pair and therefore acts merely as an electron-withdrawing group.[12,13] Because of the constrained nature of proazaphosphatranes, this type of conformational behavior cannot occur.



9a - 9f, X = anion

Basicity Considerations for Staudinger Product Components. That the phosphorus in **4** is less basic than the same atom found in **1** and **2a**−**2g** based on evidence is now briefly summarized. We have recently shown that **1**, **2b**, and **2d** upon reaction with 4-toluenesulfonyl azide form the stable ionic phosphazides **10** and **11a**−**11b**, respectively, whereas the same reaction with **4** gave the neutral phosphazide **12c** which subsequently decomposed to **12d**, analogously to the decomposition of **12a** to **12b**.[14] The formation of ionic phosphazides **10**, **11a**, and **11b** in the aforementioned reaction was attributed to the relatively basic nature of phosphorus in **1**, **2b**, and **2d**, respectively, compared with the weaker basicity of **4**.[15] The poorer basicity of the phosphorus in **4** is further supported by the preferential formation of di-adduct **13** in the reaction of **4** with B_2H_6 in 1:1 molar ratio[16] and also from the observation that a complex reaction mixture of adducts formed when **4** was treated with MeI[17] whereas **1** and **2b**, for example, gives only PBH_3 and PMe^+ products, respectively, in these reactions.[12,18−20]

$(Me_2N)_3PN_3]SO_2C_6H_4Me\text{-}4$

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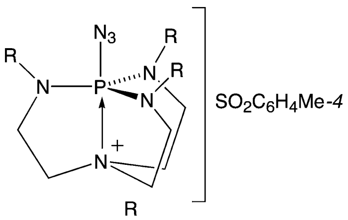
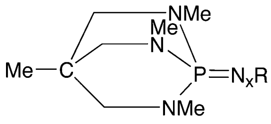
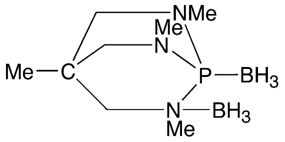


	R
11a	Me
11b	ⁱPr



	R	x
12a	Ph	3
12b	Ph	1
12c	$SO_2C_6H_4Me$-*4*	3
12d	$SO_2C_6H_4Me$-*4*	1



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These results are consistent with the idea that donation of electron density from N → P in **4** is not as large as it is in the $(-N)_3P$ moiety of **1** and **2**. This smaller N → P donator ability can be associated with the H_2C-N-P angle narrowing (from an sp^2 nitrogen toward sp^3) upon P → BH_3 or PMe^+

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formation (owing to NPN angle widening from ca. 104° toward sp^3) which in turn would facilitate adduct formation at an sp^3 nitrogen. This notion is also supported by earlier IR spectroscopic studies of derivatives of the related bicyclic phosphite $P(OCH_2)_3CMe$.[21] Thus, electron rich proazaphosphatrane **2b** gave a thermally stable phosphazide **3b**, relatively electron-rich **1** gave tris-phosphazide **3a** that can be isolated, but upon thermolysis gave tris-iminophosphorane **5b**, and electron-poor **4** gave tris-iminophosphorane **5a** at room temperature. From an examination of three-dimensional molecular models, the steric bulk at the phosphorus increases in the order **4** < **1** < **2b**. Thus, steric bulk acts in concert with the basicity order of this series of tris(dialkylamino)-phosphines in determining the thermal stability of the azide product in the Staudinger reaction of these phosphines with 1,3,5-*cis*-triazidocyclohexane. It may be added in this respect that phosphazides **12a** and **12c** are stable compared with **8f** because of the presence of an electron-withdrawing Ph and Ts group in **12a** and **12c**, respectively, whereas the cyclohexyl moiety in **8f** is electron-donating.[9,10]

Structural Characterization of Staudinger Products. Compounds **3a**, **3b**, **5a**, and **5b** were characterized by mass and NMR spectroscopic methods, and X-ray diffraction structural data were obtained for **3b** and **5a**. The ESI/MS technique has been shown to be a valuable tool for detecting transient intermediates in reactions of phosphines.[22] ESI/MS spectra of tris-phosphazides **3a** and **3b** showed clean single peaks at *m*/*z* 697.7 and at *m*/*z* 856 for their respective molecular ions. However, HRMS spectra of **3a** and **3b** displayed peaks at *m*/*z* 612.45232 and *m*/*z* 771.53235 which are characteristic for tris-iminophosphoranes (**3a** $-$ 3N$_2$ molecules)$^+$ and (**3b** $-$ 3N$_2$ molecules)$^+$, respectively, indicating decomposition of the tris-phosphazides into their corresponding tris-iminophosphoranes under HRMS spectral conditions. The ^{31}P NMR spectrum of **3a** and **3b** showed peaks at 41.5 and 37.1 ppm, respectively, that are in the expected region for phosphazides derived from tris(dialkylamino)phosphines [i.e., **6e** (δ_P 38.1 ppm),[3b] **6g** (δ_P 37.8 ppm),[2a] **6i** (δ_P 35.7, 36.2 and 38.0 ppm),[2b] and **7c** (δ_P 36.2 ppm)].[15,23] The ^{1}H NMR spectra of **3a** and **3b** are also consistent with their proposed structures.

Tris-iminophosphorane **5b** displayed an upfield-shifted ^{31}P signal at 21.6 ppm relative to tris-phosphazide **3a** (δ_P 41.5 ppm), and the former chemical shift is comparable to those reported for **7b** (δ_P 23.2 ppm)[24] and **7d** (δ_P 25.3 ppm).[15] Interestingly, the δ_P value for iminophosphorane **5a** is -1.7 ppm, which is shifted considerably upfield compared with those reported for iminophosphoranes **12b** (δ_P 11.5 ppm)[14] and **12d** (δ_P 16.7 ppm).[15] However, the upfield δ_P value for **5a** compared with that of **5b** is consistent with the relative δ_P values for their respective parent compounds, namely, **4** (δ_P 83.5 ppm)[14] and **1** (δ_P 123.0 ppm).[25] The difference in δ_P between **5a** and **5b** on one hand and **12b** and **12d** on the other presumably arises because of the variation in substitutents on the imino nitrogen. A notable feature of the ^{13}C NMR spectrum of **5a** is the (through-bond) coupling between phosphorus and the bridgehead carbon of the cage moiety ($^3J_{PC}$ = 27.0 Hz). Similar through-bond couplings were reported for **12c** ($^3J_{PC}$ = 30.3 Hz) and **12d** ($^3J_{PC}$ = 31.8 Hz).[15]

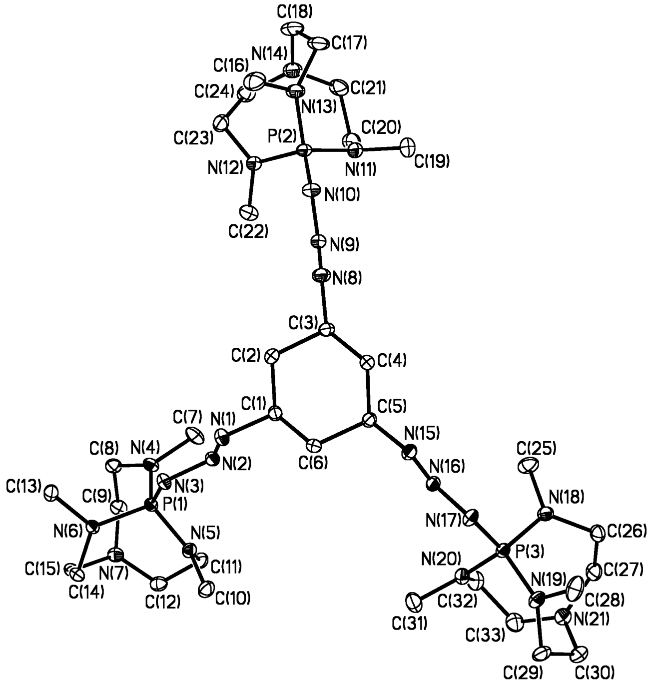

Figure 1. Computer drawing of the molecular structure of **3b**. Hydrogen atoms have been omitted for clarity.

Figure 1 depicts the molecular structure of **3b** which features an approximately C_3 axis passing through the center of the cyclohexane ring, and azidophosphoryl moieties that are bonded to the cyclohexane ring in equatorial positions, giving the molecule a bowl-like appearance. All three P$-$N$-$N$-$N moieties in this molecule exhibit the *E*-configuration with respect to their central $-$N$=$N$-$ linkages. Selected structural parameters of **3b** and of structurally related **7e**[26] and **7f**[27] are given in Table 1. The geometry of the phosphorus atoms in **3b** is approximately tetrahedral (av N$_{eq}$-PN$_{azido}$ = 109.85$-$110.46°) while that of the "equatorial" PN$_3$ nitrogens and the "axial" C$_3$N nitrogen in the cage is planar. The av P$-$N$_{eq}$ distance in **3b** [1.642(1) Å] is somewhat short relative to that in **2d** [1.703(1) Å] as is also the P$-$N$_{ax}$ transannular distance in **3b** [3.155(1), 3.061(2), 3.100(1) Å] versus that in **2d** (3.293 Å).[11] The three equatorial nitrogens in **3b** and **2d** are essentially planar. The PN$-$N and the PNN$=$N distances in **3b** are comparable to those found in **7e** and in **7f**.

The conformation of the cyclohexyl ring and the disposition of the iminophosphoryl moieties in **5a** (Figure 2) are

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Table 1. Comparison of Salient Structural Features of Azidophosphoranes **3b**, **7e**,[a] and **7f**[b]

param	3b fragment 1	3b fragment 2	3b fragment 3	**7e**[c]	**7f**[c]
			Distances, Å		
av $P-N_{eq}$	1.643(1)	1.644(1)	1.637(1)	$1.639(1)_{oop}$ $1.651(1)_{ip}$	$1.640(2)_{oop}$ $1.647(2)_{ip}$
$P-N_{azido}$	1.613(1)	1.616(1)	1.619(1)	1.615(1)	1.620(2)
$PN-N$	1.372(2)	1.366(2)	1.368(2)	1.375(2)	1.376(2)
$PNN-N$	1.256(2)	1.255(2)	1.261(2)	1.256(2)	1.261(2)
$P\cdots N_{ax}$	3.155(1)	3.061(2)	3.100(1)		
			Angles, deg		
PNN	113.8(1)	112.1(1)	110.4(1)	111.7(1)	107.3(1)
NNN	112.6(1)	113.1(1)	113.1(1)	112.1(1)	112.6(1)
$N_{eq}PN_{azido}$	110.5(7)	109.8(7)	110.1(7)	$107.3(1)_{oop}$ $120.2(1)_{ip}$	$104.55(9)_{oop}$ $115.46(9)_{ip}$
			Angle Sums around Nitrogen, deg		
N_{eq}	358.4, 359.0, 358.3	358.5, 358.2, 358.9	358.5, 358.7, 359.4	357.7_{oop}, 357.2_{oop}, 353.6_{ip}	359.7_{oop}, 354.0_{ip}, 352.6_{ip}
N_{ax}	359.3	360.0	359.79		

[a] Reference 26. [b] Reference 27. [c] ip = in plane, no multiple bonding between phosphorus and nitrogen. oop = out of plane, multiple bonding between phosphorus and nitrogen.

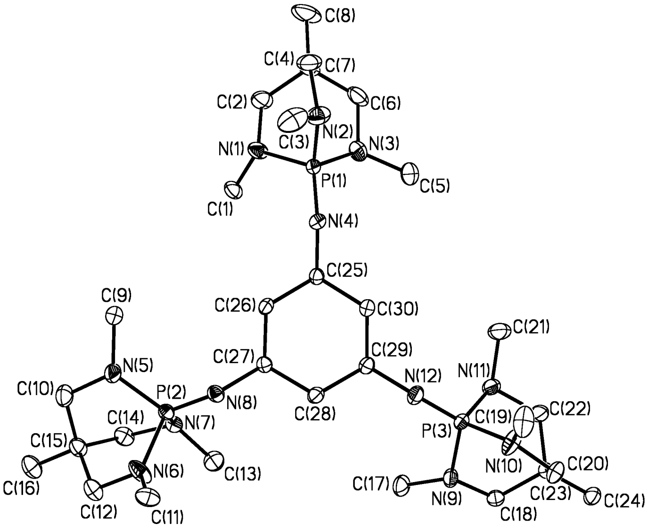
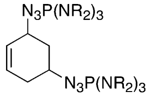


Figure 2. Computer drawing of the molecular structure of **5a**. Hydrogen atoms have been omitted for clarity.

similar to those observed in **3b**. The exocyclic P═N distances in **5a** [1.520−1.524(3) Å] are shorter than those reported for the same link in **7a** [1.557(1) Å][12] and in **12d** [1.576(1) Å][15] (see Table 2) for reasons that are not clear. The bonding environment around the phosphorus in **7a** is different from that in **5a** and **12d**. In **7a**, only two of the Me_2N moieties engage in multiple bonding with phosphorus while the third Me_2N moiety does not.[12] Therefore, we refrain from comparing their structural parameters (Table 2).

Products of the Reaction of 3a and 3b with Benzoic Acid. Compound **3b** upon treatment with 3 equiv of benzoic acid at room temperature in acetonitrile resulted in an exothermic reaction that produced dinitrogen (confirmed by GC/MS), benzene (56% confirmed by GC/MS and ^{1}H NMR spectroscopy), and [**6b**H]$PhCO_2$. The mechanistic pathway proposed for this reaction (summarized in Scheme 1) was discussed in our previous communication.[5] In order to elucidate the formation of benzene in this transformation, we treated **3a** with 3 equiv of benzoic acid under similar conditions, giving a lower conversion to benzene (15%) but a quantitative conversion to [**7a**H]$PhCO_2$ as revealed by ^{31}P NMR spectroscopy. The identity of [**7a**H]$^+$ formed in this reaction was confirmed by comparing its δ_P value measured in the reaction mixture (δ_P 42.1 ppm) with those of [**7a**H]X (X = Cl, δ_P 42.6 ppm, and 7,8-$C_2B_9H_{12}$, δ_P 43.2 ppm) which were characterized earlier by others.[28] The constitution of [**7a**H]$^+$ was also confirmed by ESI/MS spectroscopy that showed a peak at *m/z* 179.7 for the parent ion. The reaction of **14b** with benzoic acid also gave complete conversion to benzene, dinitrogen, and [**6b**H]$PhCO_2$ as indicated by ^{31}P NMR spectroscopy (see Experimental Section).



14a, $P(NR_2)_3$ = **1**

14b, $P(NR_2)_3$ = **2b**

The competition of **3a** and **3b** for benzoic acid was investigated by employing an equimolar ratio of **3a** and **3b** in the presence of 3.0 equiv of benzoic acid in acetonitrile-d_3 at 20 °C. After 3 h, more than 95% of the **3b** had decomposed to [**6b**H]$PhCO_2$ while less than 5% of **3a** had reacted to give [**7a**H]$PhCO_2$ as determined by NMR (^{1}H and ^{31}P) and ESI/MS spectroscopies on the reaction mixture. We attribute the faster decomposition of **3b** compared with **3a** to the more basic nature of the proazaphosphatrane phosphorus in the former. This larger basicity is attributable to the fact that all three "equatorial" nitrogens in the **2b** moiety of **3b** are planar, thus allowing the unhybridized p orbitals on these sp^2 nitrogens to donate electron density to the phosphorus via π bonding.[29] In **3a**, only two of the nitrogens of its **1** moiety are likely to have this favorable conformation while the third nitrogen is more pyramidal, with its lone pair pointed away from the phosphorus, as has been determined to be the case for the structure of **1**.[12,13] The axial nitrogen in the **2b** moiety of **3b** is too far away from the phosphorus [3.1053(15) Å] to engage in any significant transannular interaction that might be expected to enhance the basicity of the phosphorus. These arguments are also consistent with the higher basicity we found for reaction product **6b** compared with **7a** (see below). Thus, abstraction of a proton from the β carbon of the cyclohexyl ring is faster with **3b** (Scheme 1).

Compound [**6b**H]$PhCO_2$ was converted to air- and moisture-sensitive **6b** by treating it with KO^{t}Bu in THF followed by pentane extraction, pentane evaporation, and sublimation of the residue to give **6b** in 40% yield. Further characterization of **6b** was carried out by treating it with $PhCH_2CH_2Br$ to obtain [**6b**H]Br in 90% yield and by X-ray crystallographic

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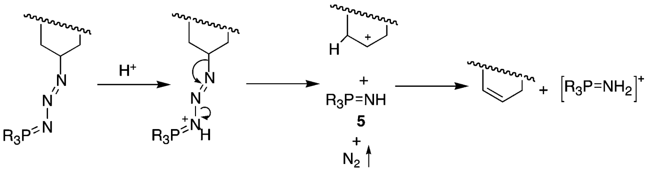
Table 2. Comparison of Salient Structural Features of Iminophosphoranes **5a**, **7a**,[a] and **12d**[b]

	5a				
param	fragment 1	fragment 2	fragment 3	**7a**[c]	**12d**
		Distances, Å			
av P—N	1.674(3)	1.666(3)	1.667(3)	1.677(1)$_{ip}$ 1.656(1)$_{oop}$	1.645(1)
P═N	1.520(3)	1.522(3)	1.524(3)	1.557(1)	1.576(1)
P···CMe	2.722(4)	2.732(4)	2.730(3)		
av N$_{ring}$PN$_{imine}$, deg	116.2(2)	116.5(2)	116.3(2)	120.2(1)$_{ip}$ 110.4(1)$_{oop}$	114.18(8)
		Angle Sums around Nitrogen, deg			
	345.9, 345.4, 347.1	358.5, 356.9, 339.4	349.4, 358.2, 341.6	343.5$_{ip}$, 358.3$_{oop}$, 357.0$_{oop}$	352.3, 345.4, 346.0

[a] Reference 12. [b] Reference 15. [c] ip = in plane, no multiple bonding between phosphorus and nitrogen. oop = out of plane, multiple bonding between phosphorus and nitrogen.

Scheme 1



experiments on [**6b**H]Br (see below). The ^{31}P NMR spectrum of **6b** revealed a peak at 36.9 ppm which is shifted upfield compared with that reported for **7a** (δ_P 42.3 ppm)[30] but is shifted significantly downfield with respect to **6d** (δ_P 26.7 ppm) and **6f** (δ_P 16.2 ppm),[31] again revealing the strong dependency of this parameter on the R substituent of the P═NR group.

^{31}P NMR spectra of [**6b**H]X [X = PhCO$_2$ and Br] revealed peaks at 34.9 and 34.4 ppm, respectively, which are shifted upfield compared to these shifts reported for [**6d**H][CF$_3$CO$_2$] (δ_P 37.9 ppm) and [**7a**H]X [X = Cl (δ_P 42.6 ppm) and 7,8-C$_2$B$_9$H$_{12}$ (δ_P 43.2 ppm)] but were shifted significantly downfield in comparison to the shift reported for [**6f**H]CF$_3$CO$_2$ (δ_P 18.4 ppm).[28,31] Although we strongly hesitate to interpret the upfield δ_P value for [**6f**H][CF$_3$CO$_2$] relative to that of [**6b**H]Br and [**6d**H][CF$_3$CO$_2$] as an indication of a phosphorus geometry in [**6f**H]$^+$ that is closer to TBP owing to incipient transanulation, it is interesting that the P—N$_{ax}$ distance in the [**6f**H]$^+$cation [2.551(3) Å[31]] is shorter than that in [**6b**H]$^+$ [2.859(2) Å], the structural features of which are now discussed.

The molecular structure of [**6b**H]$^+$ in Figure 3 is reminiscent of that of the [**6f**H]$^+$ cation,[31] revealing a roughly tetrahedral phosphorus geometry (av N$_{eq}$PN$_{eq}$ = 112.03°), planar equatorial nitrogens (angle sums = 358.9°, 357.3°, and 357.0°), and a planar axial nitrogen (angle sum = 358.8°). The average N$_{eq}$PN$_{eq}$ angle in [**6f**H]$^+$ [115.1(2)°][31] is closer to conferring a TBP geometry on the phosphorus atom than in [**6b**H]$^+$, and this is also reflected in the deviation from planarity of the axial nitrogen in [**6f**H]$^+$ (angle sum = 351.2°). It appears that the Ph moiety in [**6f**H]$^+$ polarizes the N$_{ax}$ lone pair toward the phosphorus atom more effectively than the proton in [**6b**H]$^+$. The P═N distance of 1.626(2) Å in [**6b**H]$^+$ is but barely shorter than 3 × σ compared with this distance in [**6f**H]$^+$ [1.644(4) Å], but it is distinctly longer than that in **7a** [1.557(1) Å].[12] The average P—N distance in [**6b**H]$^+$ [1.631(2) Å] is comparable to that in [**6f**H]$^+$ [1.636(4) Å][31] but is shorter than that found in **7a** [P—N$_{oop}$ = 1.656(1) Å[12]]. There are both intra- and intermolecular NH$_2$···Br hydrogen bonds in [**6b**H]Br forming a linear polymer as shown in Figure 4.

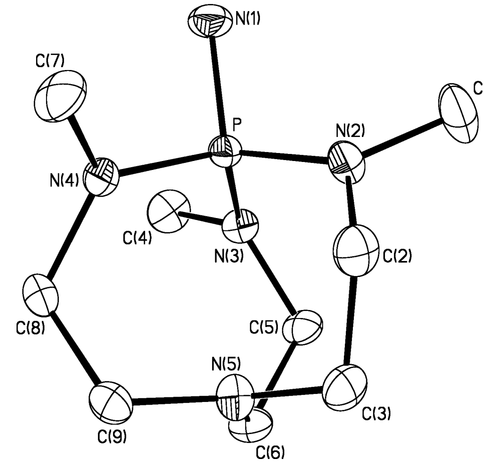


Figure 3. Computer drawing of the molecular structure of **6b**H$^+$. Hydrogen atoms and anion have been omitted for clarity.

Although we obtained **6b** by a rather indirect route, it is possible to envisage other pathways to this compound, such as the reaction of (R$_2$N)$_3$PX$_2$ with ammonia to give (R$_2$N)$_3$PNH$_2$X followed by treatment with base to give (R$_2$N)$_3$P═NH.[32] However, we found that no reaction occurred when **15** was treated with ammonia owing to decreased reactivity of the P—Cl bond caused by transannular P—N bonding in the cation of **15**.[33]

A second approach is analogous to the reaction of(Me$_2$N)$_3$P═O with triflic anhydride to give $\{[(\mathrm{Me_2N})_3\mathrm{P}]_2\mathrm{O}\}^{2+}$-2[OTf]$^-$ which on treatment with ammonia gave (Me$_2$N)$_3$P═NH.[30] Although oxide **16** reacted with triflic anhydride to

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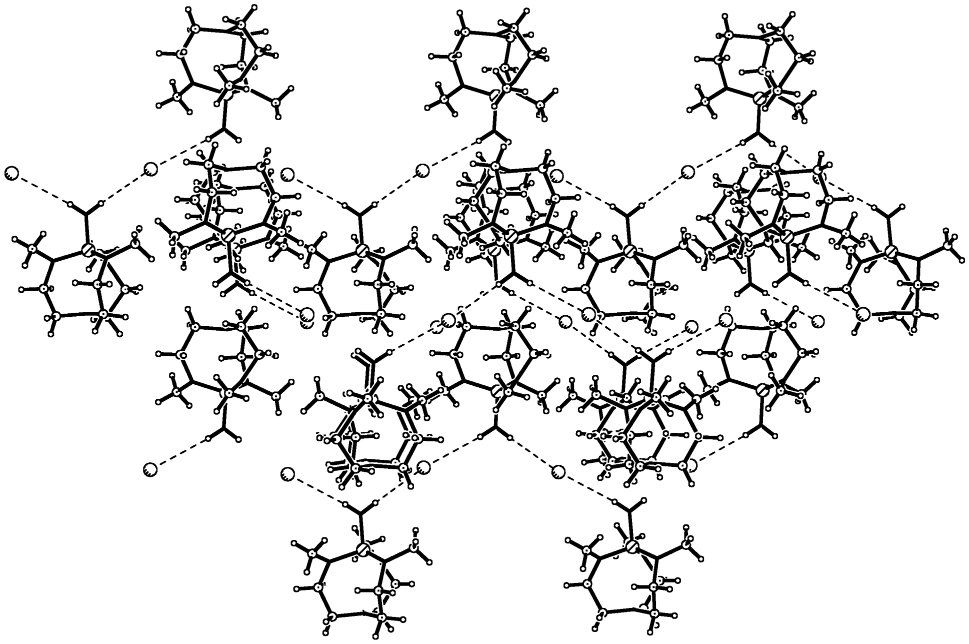
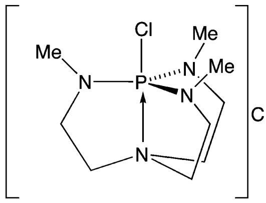
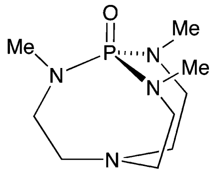


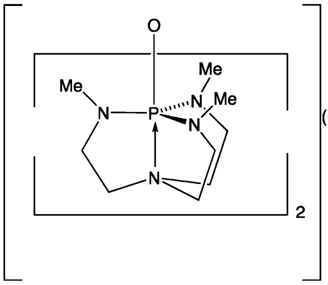
Figure 4. Computer drawing of the molecular structure of [**6b**H]Br with NH_2···Br intra- and intermolecular hydrogen bond network.



15



16



17

give stable **17**, this product was refractory to ammonia.[34] Again, transannulation in **17** may well be responsible for this failure. A third approach involves the Staudinger reaction of R_3P with Me_3SiN_3 to give $R_3P{=}NSiMe_3$ which upon hydrolysis with 2 equiv of acid gave $R_3P{=}NH$ (R = Me_2N and Ph).[35] However, the reaction of **2b** or **2d** with Me_3SiN_3 gave [**2b**H]N_3 and [**2d**H]N_3, respectively, instead of $N(CH_2CH_2NR)_3P{=}NSiMe_3$ (probably owing to the highly basic nature of phosphorus in **2b** and **2d**) along with as yet unidentified products.[36] One could also envisage the Staudinger reaction of **2b** with (hazardous) HN_3 to give **6b** as an alternative approach, but we believe this reaction would result in simple deprotonation of the HN_3 to give [**2b**H]N_3.

Comparison of the Basicities of 2b and 6b. Because theoretical studies indicated that **6a** would be more basic than **2a**,[6,7] we undertook an experimental comparison of the basicities of **6b** and **2b**, since **2a** could not be employed because of its severe tendency to polymerize.[8] The ^{31}P NMR spectrum of a reaction mixture containing **2b** with [**6b**H]Br in acetonitrile-d_3 revealed the formation of two additional species, namely, **6b** (δ_P 36.9 ppm) and [**2b**H]Br (δ_P −10.6 ppm).[37] However, no additional species were formed when an acetonitrile-d_3 solution of [**2b**H]Br was treated with **6b**. This indicates that, contrary to expectation based on theory, **2b** is more basic than **6b**. The probable reason for the lower basicity of **6b** relative to **2b** is that the polarizing proton is more distant from the lone pair on N_{ax} in [**6b**H]Br than in [**2b**H]X (X = Br or Cl) which is fully transannulated.[1] The reasons for contradictory results obtained from the present ^{31}P NMR experiments and the theoretical studies carried out by Windus et al.[6] and Schwesinger and co-workers[7] is presently unclear although solvation effects probably play a significant role. The aforementioned theory groups[6,7] also predicted that **18a** would be more basic than **2a**. We were recently able to provide confirmatory evidence for this conclusion in a ^{31}P NMR spectroscopic study in which equilibrium experiments were carried out with **18b** and [**2b**H]$^+$.[17]

Summary and Conclusions

The reaction of 1,3,5-*cis*-triazidocyclohexane with **1** and **2b** gives the tris-phosphazides **3a** and **3b**, respectively, in high yields, and the greater thermal stability of **3b** compared with **3a** presumably arises mainly from the presence of a more electron-rich as well as a sterically crowded phosphorus in **3b**. The slow reaction of 1,3,5-*cis*-triazidocyclohexane

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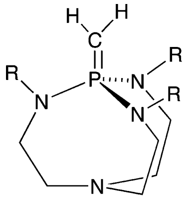

18a, R = H

18b, R = Me

with relatively electron poor **4** affords **5a** via several detectable intermediates (**8a**−**8f**) under mild conditions. The presence of an electron-rich sterically crowded phosphorus in compounds of type **3b** promotes protonation of a nitrogen in the azido group, thus facilitating departure of [**6b**H]$^+$, benzene formation, and dinitrogen evolution. This process, followed by the conversion of [**6b**H]$^+$ to **6b**, appears to be a unique albeit circuitous route to **6b** which may be useful as a precursor to [**6b**R]$^+$ species upon reaction with organic halides. Contrary to expectation from theory, **2b** is more basic than **6**.

Experimental Section

Materials and General Methods. All reactions were carried out under argon. Solvents were distilled by standard procedures prior to use,[38] and the following compounds were prepared by published methods: 1,3,5-*cis*-triazidocyclohexane,[39] **2b**,[3b] **4**,[40] and the triamine $MeC(CH_2NMeH)_3$[41] that was used to prepare **4**. Compound **1** was purchased from Acros Organics. All other chemicals were purchased from Aldrich and were used without further purification. HRMS spectra were recorded on a KRATOS MS-50 spectrometer, and ESI/MS, CI/MS, and GC/MS spectra were obtained with a Finnigan TSQ700 spectrometer. Elemental analyses were performed in the Instrument Services Laboratory of the Chemistry Department at Iowa State University. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR 300, a VXR 400, or a Bruker DRX-400 NMR spectrometer. ^{31}P{^{1}H} NMR spectra were recorded on a Bruker WM-200, a VXR 400, or a Bruker DRX-400 NMR spectrometer using 85% H_3PO_4 as the external standard. X-ray data collections and structure solutions were conducted at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment Micro VAX 3100 computer using SHELXTL-Plus and SHELXL-93 programs.

Synthesis of 3a. To a solution of *cis*-1,3,5-triazidocyclohexane (104 mg, 0.500 mmol) in acetonitrile (10 mL) was added all at once a solution of **1** (245 mg, 1.50 mmol) in acetonitrile (2 mL) at 0 °C. The resulting clear solution was stirred at ambient temperature for 3 h, and then, volatiles were removed under reduced pressure to give a white solid. The solid was washed with diethyl ether and dried under reduced pressure for 10 h to give **3a** in 90% yield (312 mg). ^{31}P{^{1}H} NMR (CD_3CN): δ 41.5 (s). ^{1}H NMR (CD_3CN): δ 1.76−1.98 (m, 6H, Cy-CH_2), 2.62 (d, $^3J_{PH} = 9.2$ Hz, 54H, NCH_3), 3.57 (m, 3H, Cy-CH). ^{13}C{^{1}H} NMR (CD_3CN): δ 37.4 (d,$^2J_{PC} =$ 2.4 Hz, 18C, NCH$_3$), 37.7 (s, 3C, Cy-CH$_2$), 65.4 (s, 3C, Cy-CH). Anal. Calcd for $C_{24}H_{63}N_{18}P_3$: C, 41.36; H, 9.11; N, 36.18%. Found: C, 41.20; H, 9.27; N, 35.01. Attempts to improve the nitrogen analysis by further purification were not successful. ESI/MS (*m/z*): 697.7 (M$^+$). HRMS Calcd for $C_{24}H_{63}N_{12}P_3$ (*m/z*): 612.45156. Found: 612.45232 (M − 3N$_2$)$^+$.

Synthesis of 3b. To a solution of 1,3,5-*cis*-triazidocyclohexane (104 mg, 0.500 mmol) in acetonitrile (10 mL) was added all at once a solution of **2b** (324 mg, 1.50 mmol) in acetonitrile (5 mL) at 0 °C. The resulting clear solution was stirred at ambient temperature for 3 h followed by removal of volatiles under reduced pressure. Compound **3b** was obtained as a colorless solid in 92% yield (394 mg) upon washing with diethyl ether and drying under reduced pressure for 10 h. Crystals of **3b** suitable for X-ray diffraction were grown from hot acetonitrile. ^{31}P{^{1}H} NMR (CD_3CN): δ 37.1 (s). ^{1}H NMR (CD_3CN): δ 1.56−1.60 (m, 6H, Cy-CH_2), 2.65 (d, $^3J_{PH} = 7.6$ Hz, 27H, NCH_3), 2.77 (t, $^3J_{HH} = 4.8$ Hz, 18H, N$_{ax}$CH_2), 2.88 (dt, $^3J_{PH} = 12.8$ Hz; $^3J_{HH} = 4.8$ Hz, 18H, N$_{eq}$CH_2), 3.38 (m, 3H, Cy-CH). ^{13}C{^{1}H} NMR (CD_3CN): δ 35.7 (d, $^2J_{PC} = 3.5$ Hz, 9C, NCH$_3$), 39.4 (s, 3C, Cy-CH$_2$), 50.3 (s, 9C, N$_{ax}$$CH_2$), 52.3 (s, 9C, N$_{eq}$$CH_2$), 66.3 (s, 3C, Cy-$C$H). Anal. Calcd for $C_{33}H_{72}N_{21}P_3$: C, 46.30; H, 8.48; N, 34.36%. Found: C, 46.29; H, 8.57; N, 34.07. ESI/MS (*m/z*): 856 (M$^+$). HRMS Calcd for $C_{33}H_{72}N_{15}P_3$ (*m/z*): 771.53121. Found: 771.53235 (M − 3N$_2$)$^+$.

Synthesis of 5a. A solution of *cis*-1,3,5-triazidocyclohexane (109 mg, 0.526 mmol) in acetonitrile (10 mL) was added to a stirred acetonitrile (10 mL) solution of **4** (312.0 mg, 1.666 mmol). After the addition was complete, the resulting mixture was stirred for 2 days at room temperature. Solvent was removed under reduced pressure to give an oil that was dissolved in a minimum amount of diethyl ether, followed by diffusion of pentane into the solution. Colorless crystals of **5a** were obtained in 60% yield after several days. ^{31}P{^{1}H} NMR (C_6D_6): δ −1.7 (s). ^{1}H NMR (C_6D_6): δ 0.36 (s, 9H, C−CH_3), 2.07 (m, 3H, Cy-CH_2), 2.66 (d, $^3J_{PH} = 7.2$ Hz, 18H, NCH_2), 2.70 (d,$^3J_{PH} = 12.0$ Hz, 27H, NCH_3), 2.80 (br, 3H, Cy-CH_2), 3.89 (br, 3H, Cy-CH). ^{13}C{^{1}H} NMR (C_6D_6): δ 21.8 (s, 3C, C-CH$_3$), 33.4 (d, $^3J_{PC} = 27.0$ Hz, 3C, C-CH$_3$), 37.8 (s, 9C, NCH$_3$), 51.3 (m, 3C, Cy-CH$_2$), 54.0 (m, 3C, Cy-CH), 64.4 (s, 9C, NCH$_2$). Anal. Calcd for $C_{30}H_{63}N_{12}P_3$: C, 52.61; H, 9.27; N, 24.54%. Found: C, 51.95; H, 9.37; N, 24.87. Repeated crystallization of the sample did not improve the carbon analysis. ESI/MS (*m/z*): 686 (M + H$^+$). EI/MS (*m/z*): 685 (M$^+$).

A reaction of *cis*-1,3,5-triazidocyclohexane with **4** in acetonitrile-*d*$_3$ was monitored by ESI/MS spectroscopy at 6 h time intervals. After 6 h, ESI/MS spectroscopy showed peaks at *m/z* 405, 554, 741, and 791 which correspond to (**8a** + K), **8c**, **8e**, and (**8f** + Na), respectively. After 12 h, ESI/MS spectroscopy showed signals at *m/z* 405, 526, 554, 685, 713, 741, and 791 which correspond to (**8a** + K), **8b**, **8c**, **4**, **8d**, **8e**, and (**8f** + Na), respectively.

Synthesis of 5b. Compound **3a** (349 mg, 0.500 mmol) was dissolved in toluene (20 mL) followed by stirring at 100 °C for 3 h. Compound **5b** was isolated as a white solid (291 mg, 95%) upon removing the volatiles under reduced pressure. ^{31}P{^{1}H} NMR (CD_3CN): δ 21.6 (s). ^{1}H NMR (CD_3CN): δ 0.86−0.95 (m, 3H, Cy-CH_2), 1.74 (d, $^2J_{HH} = 11.6$ Hz, 3H, Cy-CH_2), 2.56 (d, $^3J_{PH} =$ 9.2 Hz, 54H, NCH_3), 2.88 (m, 3H, Cy-CH). ^{13}C{^{1}H} NMR (CD_3CN): δ 38.1 (d, $^2J_{PC} = 1.8$ Hz, 18C, NCH$_3$), 51.4 (s, 3C, Cy-CH$_2$), 54.7 (m, 3C, Cy-CH). ESI/MS (*m/z*): 612 (M$^+$). HRMS Calcd for $C_{24}H_{63}N_{12}P_3$ (*m/z*): 612.45156. Found: 612.45232 (M$^+$).

Synthesis of 6b. To a solution of **3b** (428 mg, 0.500 mmol) in acetonitrile (20 mL) was added a solution of benzoic acid (183 mg, 1.500 mmol) in acetonitrile (10 mL) at 0 °C. The resulting mixture was stirred at ambient temperature for 4 h followed by removal of all the volatiles under reduced pressure to give [**6b**H]-

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$PhCO_2$ as a pale yellow oil in quantitative yield which was then dissolved in THF (20 mL) and treated with KO^{t}Bu (336 mg, 3.00 mmol). After the reaction mixture stirred at ambient temperature for 2 h, the volatiles were removed under reduced pressure followed by extraction of the residue with pentane (50.0 mL). Compound **6b** was obtained as a colorless solid (156 mg, 40%) upon sublimation (120 °C/0.50 Torr) of the residue left upon evaporation of the pentane.

Spectroscopic Data for [6bH]PhCO$_2$. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 34.9 (s). ^1H NMR (C_6D_6): δ 2.67 (t, $^3J_{HH} = 5.6$ Hz, 6H, $N_{ax}CH_2$), 2.70 (d, $^3J_{PH} = 10.0$ Hz, 9H, NCH_3), 2.83 (dt, $^3J_{PH} = 14.6$ Hz; $^3J_{HH} = 5.6$ Hz, 6H, $N_{eq}CH_2$), 3.07 (br, 2H, NH_2), 7.61 (m, 5H, C_6H_5). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 35.0 (d, $^2J_{PC} = 4.6$ Hz, 3C, NCH_3), 49.1 (s, 3C, $N_{ax}CH_2$), 51.0 (d, $^2J_{PC} = 3.3$ Hz, 3C, $N_{eq}CH_2$), 127.4, 129.2, 129.3, 139.3, and 169.9 (s, C_6H_5, 6C). CI/MS for $C_9H_{23}N_5P$ (*m/z*): 232 (**6b**H$^+$). HRMS Calcd for $C_9H_{23}N_5P$ (*m/z*): 232.16911. Found: 232.16995 (M$^+$).

Spectroscopic Data for 6b. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 36.9 (s). ^1H NMR (C_6D_6): δ 2.43 (t,$^3J_{HH} = 4.8$ Hz, 6H, $N_{ax}CH_2$), 2.58 (dt, $^3J_{PH} = 12.0$ Hz; $^3J_{HH} = 4.8$ Hz, 6H, $N_{eq}CH_2$), 2.71 (d, $^3J_{PH} = 7.6$ Hz, 9H, NCH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 35.6 (d, $^2J_{PC} = 6.3$ Hz, 3C, NCH_3), 49.7 (s, 3C, $N_{ax}CH_2$), 51.6 (d,$^2J_{PC} = 2.3$ Hz, 3C, $N_{eq}CH_2$). HRMS Calcd for $C_9H_{22}N_5P$ (*m/z*): 231.16231. Found: 231.16257 (M$^+$).

Synthesis of [6bH]Br from 6b. To a solution of **6b** (232 mg, 1.00 mmol) in C_6D_6 (5.0 mL) was added $PhCH_2CH_2Br$ (190 mg, 1.00 mmol) at room temperature. A white precipitate began to form after 1 min, and the resulting mixture was kept at room temperature with occasional shaking. After 3 h, the ^1H NMR spectrum indicated the virtual disappearance of peaks corresponding to $PhCH_2CH_2Br$ while that of styrene took its place. A GC/MS spectrum was recorded to confirm the identity of styrene. The precipitate was filtered and washed with diethyl ether to give pure [**6b**H]Br as a colorless solid (290 mg, 90%) upon drying under reduced pressure for 6 h. Crystals suitable for X-ray data collection were obtained by diffusing diethyl ether into a chloroform solution of [**6b**H]Br. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.4 (s). ^1H NMR ($CDCl_3$): δ 2.69 (t, $^3J_{HH} = 4.8$ Hz, 6H, $N_{ax}CH_2$), 2.82 (m, 6H, $N_{eq}CH_2$), 2.86 (d, $^3J_{PH} = 7.5$ Hz, 9H, NCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 36.3 (d, $^2J_{PC} = 4.8$ Hz, 3C, NCH_3), 49.7 (s, 3C, $N_{ax}CH_2$), 50.3 (d, $^2J_{PC} = 3.7$ Hz, 3C, $N_{eq}CH_2$). Anal. Calcd for $C_9H_{23}N_5PBr$: C, 34.63; H, 7.43; N, 22.43%. Found: C, 34.66; H, 7.41; N, 22.11. ESI/MS (*m/z*): 232 (for **6b**H$^+$).

Comparison of the Basicities of 2b and 6b. To a solution of [**6b**H]Br (31 mg, 0.10 mmol) in acetonitrile-d_3 (0.40 mL) in a 5 mm NMR tube was added a solution of **2b** (22 mg, 0.10 mmol) in acetonitrile-d_3 (0.30 mL). The reaction mixture was kept at room temperature with occasional shaking. ^1H and ^{31}P NMR spectroscopies were used to monitor the reaction (see Results and Discussion section).

To a solution of [**2b**H]Cl (25 mg, 0.10 mmol) in acetonitrile-d_3 (0.40 mL) in a 5 mm NMR tube was added a solution of **6b** (23 mg, 0.10 mmol) in acetonitrile-d_3 (0.30 mL). The reaction mixture was kept at room temperature with occasional shaking. ^1H and ^{31}P NMR spectroscopies were used to monitor the reaction (see Results and Discussion section).

Synthesis of 3,5-*cis*-Diazidohex-1-ene. During the synthesis of 1,3,5-*cis*-triazidocyclohexane,[39] 3,5-*cis*-diazidohex-1-ene was formed as a minor product as shown by TLC (eluent = hexanes and ethyl acetate) and ^1H NMR spectroscopy of the crude product. Silica gel column chromatography carried out using a mixture of hexanes and ethyl acetate (50:1) as the eluent gave the title compound as a clear yellow oil in 10% yield, along with the previously reported 1,3,5-*cis*-triazidocyclohexane in 55% yield.[5,39] ^1H NMR ($CDCl_3$): δ 1.65 (m, 1H), 2.13 (m, 1H), 2.38 (m, 2H), 3.65 (m, 1H), 4.06 (m, 1H), 5.70 (m, 1H), 5.90 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 30.7, 33.9, 55.1, 56.6, 126.2, and 128.3 (all singlets). ESI/MS (*m/z*): 164 (M$^+$).

Synthesis of 14a and 14b. To a solution of 3,5-*cis*-diazidohex-1-ene (82 mg, 0.500 mmol) in acetonitrile (10 mL) was added all at once a solution of **1** (or **2b**) (1.00 mmol) in acetonitrile (5 mL) at 0 °C. The resulting clear solution was stirred at ambient temperature for 3 h followed by removal of volatiles under reduced pressure. Compound **14a** (or **14b**) was obtained as a colorless solid (204 mg, 83% for **14a**; 253 mg, 85% for **14b**) upon washing with diethyl ether and drying under reduced pressure for 10 h at room temperature.

Spectroscopic Data for 14a. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 41.15, 41.18 (all singlets). ^1H NMR (C_6D_6): δ 2.42 (m, 2H), 2.43 (d, $^3J_{PH} = 8.8$ Hz, 36H, NCH_3), 2.63 (m, 1H), 2.81 (m, 1H), 4.28 (br, 1H), 4.84 (br, 1H), 5.96 (m, 1H), 6.23 (m, 1H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 32.2 (s), 36.3 (s), 37.1 (d, $^2J_{PC} = 2.1$ Hz, 12 C, NCH_3), 65.2 (s), 67.1 (s), 126.3 (s), and 131.6 (s). ESI/MS (*m/z*): 491 (M$^+$).

Spectroscopic Data for 14b. $^{31}P\{^1H\}$ NMR (CD_3CN): δ 37.0, 37.2 (all singlets). ^1H NMR (CD_3CN): δ 1.69 (m, 2H), 2.05 (m, 1H), 2.17 (m, 1H), 2.65 (d, $^3J_{PH} = 7.6$ Hz, 18H, NCH_3), 2.77 (t, $^3J_{HH} = 4.8$ Hz, 12H, $N_{ax}CH_2$), 2.90 (dt, $^3J_{PH} = 7.6$ Hz; $^3J_{HH} = 4.8$ Hz, 12H, $N_{eq}CH_2$), 3.56 (m, 1H), 4.02 (m, 1H), 5.53 (m, 1H), 5.74 (m, 1H). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 31.4, 34.6, 35.8, 49.3, 51.2, 63.5, 65.7, 126.1, and 130.9 (all singlets). ESI/MS (*m/z*): 597 (M$^+$).

^1H and ^{31}P NMR Monitoring of the Reaction of 3a, 3b, 14a, and 14b with Benzoic Acid. To a solution of **3b** or **14b** (0.02 mmol) in acetonitrile-d_3 (0.70 mL) in a 5 mm NMR tube at −10 °C was added benzoic acid (3.0−9.0 equiv). After briefly shaking the NMR tube, 50 ^1H (or ^{31}P) NMR spectra were recorded at −10 °C at the following time intervals. The first 10 spectra were recorded with 60 s intervals, the second 10 spectra with 300 s intervals, the third 10 spectra with 600 s intervals, the fourth 10 spectra with 1200 s intervals, and the fifth 10 spectra with 1800 s intervals. A 60 s time period was required to complete each ^1H NMR acquisition, and 300 s was required to finish each ^{31}P NMR acquisition. This process was repeated for **3a** and **14a** except that the respective reactions were carried out at 20 °C and all the NMR spectra were recorded at the same temperature.

ESI/MS Monitored Reaction of 3a and 3b with Benzoic Acid. To a solution of **3a** or **3b** (0.500 mmol) in acetonitrile (20.0 mL) at room temperature was added a solution of benzoic acid (183 mg, 1.50 mmol) in acetonitrile (5.0 mL). The reaction mixture was stirred at room temperature, and then, a sample (1 μL) of the reaction mixture was syringed out for ESI/MS measurement at the following time intervals: 1, 5, 10, 30 min, 1, 1.5, 2, 3 and 24 h.

Samples were introduced into the electrospray interface through an untreated fused-silica capillary of 50 μm i.d. and 190 μm o.d. A myoglobin and MRFA mixture was used for tuning and routine calibration of the instrument. The mass spectrometer was used in the positive ion Q1MS mode. Quadrupoles Q2 and Q3 were maintained in the RF only mode. The scan range was maintained from *m/z* 100 to 2000 with a scan rate of 3 s per scan. The voltage on the ESI needle tip was about 5 kV in all the experiments.

GC/MS Detection of Benzene from the Reaction of 3a and 3b with Benzoic Acid. To a solution of **3a** or **3b** (0.500 mmol) at room temperature in acetonitrile (20 mL) was added a solution of benzoic acid (183 mg, 1.50 mmol) in acetonitrile (5 mL). The reaction mixture was stirred at room temperature, and toluene (46 mg, 0.500 mmol) was introduced as the internal reference for the GC/MS experiment. A sample (1 μL) of the reaction mixture was

Table 3. Crystal Data and Structure Refinement for **3b**, **5a**, and [**6b**H]Br

	3b	**5a**	[**6b**H]Br
empirical formula	$C_{41}H_{84}N_{25}P_3$	$C_{30}H_{63}N_{12}P_3$	$C_9H_{23}BrN_5P$
fw	1020.24	684.83	312.2
T, K		173(2)	
wavelength, Å		0.71073	
cryst syst	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$
unit cell dimensions			
a, Å	10.9785(5)	11.2306(5)	8.0902(4)
b, Å	11.2183(5)	15.4844(7)	12.3661(7)
c, Å	24.454(1)	21.695(1)	13.6035(7)
α, deg	77.900(1)		
β, deg	83.510(1)	98.379(1)	
γ, deg	73.715(1)		
V, Å^3	2822.0(2)	3732.5(3)	1360.9(1)
Z	2	4	4
d(calcd), Mg/m^3	1.201	1.219	1.524
abs coeff, mm^{-1}	0.159	0.198	3.123
F(000)	1100	1488	648
cryst size, mm^3	0.50 × 0.50 × 0.50	0.50 × 0.50 × 0.10	0.30 × 0.30 × 0.10
θ range for data collection, deg	1.71−26.37	1.62−25.00	2.23−28.25
reflns collected	22528	26998	11748
indep reflns	11169 [*R*(int) = 0.0181]	6562 [*R*(int) = 0.0557]	3199 [*R*(int) = 0.0346]
abs correction	*a*	*a*	*a*
max and min transm	0.9247 and 0.9247	0.9805 and 0.9074	0.7453 and 0.4543
refinement method	*b*	*b*	*b*
data/restraints/params	11169/0/635	6562/0/418	3199/1/154
GOF on F^2	1.065	1.037	1.064
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.038 wR2 = 0.105	R1 = 0.065 wR2 = 0.151	R1 = 0.024 wR2 = 0.063
R indices (all data)	R1 = 0.046 wR2 = 0.110	R1 = 0.089 wR2 = 0.159	R1 = 0.025 wR2 = 0.063
largest diff peak and hole	0.414 and −0.317 e Å^{-3}	0.447 and −0.376 e Å^{-3}	0.309 and −0.589 e Å^{-3}
Flack *x* parameter	N/A	N/A	0.006(8)

[a] Multiscan with SADABS. [b] Full-matrix least-squares on F^2.

syringed out for GC/MS measurement at time intervals of 1, 3, and 24 h. A solution of benzene (39 mg, 0.500 mmol) and toluene (46 mg, 0.500 mmol) in acetonitrile (25 mL) was used as a standard. The system was configured in the electron impact ionization mode, and the first quadrupole was used as the analyzer and scanned from $m/z = 10$ to 200 at a rate of 0.5 s per scan. The second and the third quadrupoles were kept at RF-only mode. Unit mass resolution was achieved using FC43 as a calibration and tuning reference. Oven temperature was maintained at 35 °C for 1 min and increased to 299 °C at a rate of 10 °C per min. A blank experiment was carried out before the sample analysis. A DB-1 GC column (J&W Scientific) was used in all the experiments. The injector and transfer line temperatures were fixed at 250 °C.

X-ray Crystallography. Data Collection. Crystals of **3b**, **5a**, and [**6b**H]Br of appropriate size were selected under oil under ambient conditions and attached to the tip of a glass capillary. Crystals were mounted in a stream of cold nitrogen at 173(2) K and centered in the X-ray beam by using a video camera. Crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo Kα ($\lambda = 0.71073$ Å) radiation and the diffractometer to crystal distance of 4.9 cm. The data were collected by using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of a full sphere to a resolution of 0.80 Å. Data were harvested by collecting three sets of frames with 0.3° scans in ω with an exposure time 30 s per frame. These highly redundant data sets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[42]

Structure Solution and Refinement. The systematic absences in the diffraction data were uniquely consistent for the space group $P2_1/n$ for **5a**, for the space group $P2_12_12_1$ for [**6b**H]Br, and for the space groups $P\bar{1}$ and $P1$ for **3b**. In the case of **3b**, the *E*-statistics strongly suggested the centrosymmetric space group $P\bar{1}$ which was subsequently chosen, and in all cases, the selected space groups yielded chemically reasonable and computationally stable results of refinement.[42] In all cases, a successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients, unless otherwise specified. In the case of **3b**, there were also four solvate molecules of acetonitrile present in the asymmetric unit. In the case of [**6b**H]Br, hydrogens H(1n) and H(2n) were found from the difference map and refined with constrained N−H distances. The ORTEP diagrams are drawn with 30% probability ellipsoids. Crystal data and structure refinement for **3b**, **5a**, and [**6b**H]Br are collected in Table 3.

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Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for compounds **3b**, **5a**, and [**6b**H]Br. This material is available free of charge via the Internet at http://pubs.acs.org.

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(42) *SADABS V.2.05, SAINT V.6.22, SHELXTL V.6.10 & SMART 5.622 Software Reference Manuals*; Bruker-AXS: Madison, WI, 2000−2003.