# Synthesis and Reactivity of Cyclic 6-Membered Six-$\pi$- and Four-Membered Four-$\pi$-Electron Ylides

**Klaus Bieger, Juan Tejeda, Régis Réau, Françoise Dahan, and Guy Bertrand***

*Contribution from the Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cêdex, France*

*Received March 9, 1994*®

**Abstract:** *N*-Phosphinonitrilimine **1** and phosphine azides **4** react with dimethyl acetylenedicarboxylate via formal [4 + 2] cycloadditions affording 1,2,3$\lambda^5$-diazaphosphinine **2** (90% yield) and 1,2,3,4$\lambda^5$-triazaphosphinines **5** (63–75% yield), respectively. Although **2** is reluctant toward dinitrogen extrusion, derivatives **5** afford 1,2$\lambda^5$-azaphosphetes **6** (80–90% yield) by heating in refluxing toluene. Four-$\pi$-electron four-membered rings **6** react via the ring nitrogen atom with a variety of electrophiles. The four-membered ring structure is preserved by addition of boron trifluoride or iodomethane, while ring-opening reactions are observed with water, pentafluorobenzonitrile, and carbon disulfide; ring expansion reactions occurred with dimethyl acetylenedicarboxylate, methyl isothiocyanate, phenyl isocyanate, trimethylsilyl isocyanate, and isothiocyanate.

## Introduction

For more than a century, the synthesis and bonding description of six-$\pi$-electron six-membered rings and four-$\pi$-electron four-membered rings have attracted considerable attention.[1] The former are often associated with aromaticity and stability, and the latter with antiaromaticity and high reactivity. Whereas benzene was dicovered in 1825 by Faraday,[2] for a long time all efforts to obtain stable cyclobutadienes failed.[3] The crucial breakthrough was achieved in 1965, when Petit stabilized the parent cyclobutadiene with the organometallic fragment Fe(CO)$_3$.[4] Since then, a very few substituted cyclobutadienes, stabilized by push-pull effects or bulky substituents, have been isolated.[5]

The aromatic and antiaromatic character of these systems is perturbed when one or more second-row heteroatoms are present in the ring.[6] With a third-row element (or heavier), possessing available p-orbitals to build the $\pi$-system, the comparison is even more striking:[6] for example, neither silabenzene[7] or germabenzene[8] is stable. When the heteroatom has no p-orbital available for the $\pi$-system, the six-membered ring is no longer a Hückel aromatic system and, of course, the four-membered ring is not antiaromatic.[9]

Our aim was to synthesize new non-antiaromatic four-$\pi$-electron four-membered rings and to elucidate their reactivity with a view to opening new pathways to further heterocycles. Here we report our first attempts to prepare the prototype of such compounds, namely the $\lambda^5$-phosphete, and the synthesis and reactivity of related 1,2$\lambda^5$-azaphosphetes.[10]

## Results and Discussion

The only two known four-$\pi$-electron four-membered heterocycles featuring third-row elements, namely the 1$\lambda^5$,3$\lambda^5$-diphosphetes **B**[11] and 1,3,2$\lambda^5$,4$\lambda^5$-diazadiphosphetes (cyclodiphosphazenes) **D**,[12] have been prepared by dimerization of the corresponding transient $\lambda^5$-phosphaalkynes **A** and $\lambda^5$-phosphonitriles **C**, respectively. Having in hand thermodynamically stable but reactive $\lambda^5$-phosphaalkynes **A**[13] and transient $\lambda^5$-phosphonitriles **C**,[12] we first tried to synthesize the desired 1$\lambda^5$-phosphetes **E** and 1,2$\lambda^5$-azaphosphetes **F** by reacting **A** and **C** with various alkynes. These attempts led to complex mixtures of products as detected by $^{31}$P NMR spectroscopy, from which no product was isolable (Scheme 1).

Since the thermal and photochemical elimination of dinitrogen from cyclic azoalkanes is an efficient method for the preparation of strained or even antiaromatic species,[14] it was tempting to study the thermal behavior of 1,2,3$\lambda^5$-diazaphosphinine **2**, which is easily available from *N*-phosphinonitrilimine **1** and dimethyl acetylenedicarboxylate.[15] However, all attempts to eliminate

* Abstract published in *Advance ACS Abstracts*, August 15, 1994.

(1) (a) Kekulé, A. *Justus Liebigs Ann. Chem.* **1872**, *162*, 77. (b) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960. (c) Hoffmann, R. *J. Chem. Soc., Chem. Commun.* **1969**, 240. (d) Dewar, M. J. S.; Kohn, M. C.; Trinajstic', M. *J. Am. Chem. Soc.* **1971**, *93*, 3437. (e) Schaad, L. J.; Hess, A. B., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 3068. (f) Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1993**, *115*, 11153. (g) Schultz, P. A.; Messmer, R. P. *J. Am. Chem. Soc.* **1993**, *115*, 10943. (h) Toda, F.; Garratt, P. *Chem. Rev.* **1992**, *92*, 1685.

(2) Heany, H. In *Comprehensive Organic Chemistry. The Synthesis and Reactions of Organic Compounds*; Stoddart, J. F.; Ed.; Pergamon Press: Oxford, U.K., 1979; Vol. 1, pp 241.

(3) Maier, G. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 425.

(4) (a) Emerson, G. F.; Watts. L.; Petit, R. *J. Am. Chem. Soc.* **1965**, *87*, 313. (b) Emerson, G. F.; Fitzpatrick, J. D.; Petit, R. *J. Am. Chem. Soc.* **1965**, *87*, 3253. (c) Efraty, A. *Chem. Rev.* **1977**, *77*, 691.

(5) (a) Lindner, H. J.; von Gross, B. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 490. (b) Masamune, S.; Nakamura, N.; Suda, M.; Ona, H. *J. Am. Chem. Soc.* **1973**, *95*, 8481. (c) Kimling, H.; Krebs, A. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 932. (d) Irngartinger, H.; Nixdorf, M. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 403. (e) Gompper, R.; Seybold, G. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 824. (f) Delbaere, L. T. J.; James, M. N. G.; Nakamura, N.; Masamune, S. *J. Am. Chem. Soc.* **1975**, *97*, 1973.

(6) Schoeller, W. W.; Busch, T. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 617.

(7) (a) Solouki, B.; Rosmus, P.; Bock, H.; Maier, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 51. (b) Maier, G.; Mihn, G.; Reisenauer, P. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 523.

(8) Märkl, G.; Rudnick, D.; Schulz, R.; Schweig, A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 221.

(9) Barton, D. H. R.; Hall, M. B.; Lin, Z.; Parekh, S. I. *J. Am. Chem. Soc.* **1993**, *115*, 955.

(10) For a preliminary account see: Tejeda, J.; Réau, R.; Dahan, F.; Bertrand, G. *J. Am. Chem. Soc.* **1993**, *115*, 7880.

(11) (a) Svara, J.; Fluck, E.; Riffel, H. *Z. Naturforsch.* **1985**, *40b*, 1258. (b) Neumüller, B.; Fluck, E. *Phosphorus and Sulfur* **1986**, *29*, 23. (c) Keller, H.; Maas, G.; Regitz, M. *Tetrahedron Lett.* **1986**, *27*, 1903.

(12) (a) Baceiredo, A.; Bertrand, G.; Majoral, J.-P.; Sicard, G.; Jaud, J.; Galy, J. *J. Am. Chem. Soc.* **1984**, *106*, 6088. (b) Baceiredo, A.; Bertrand, G.; Majoral, J.-P.; El Anba, F.; Manuel, G. *J. Am. Chem. Soc.* **1985**, *107*, 3945. (c) Granier, M.; Baceiredo, A.; Dartiguenave, Y.; Dartiguenave, M.; Menu, M. J.; Bertrand, G. *J. Am. Chem. Soc.* **1990**, *112*, 6277.

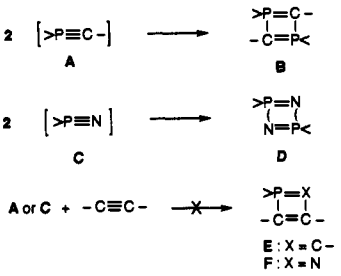
(13) (a) Igau, A.; Grützmacher, H.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1988**, *110*, 6463. (b) Igau, A.; Baceiredo, A.; Trinquier, G.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 621. (c) Soleilhavoup, M.; Baceiredo, A.; Treutler, O.; Ahlrichs, R.; Nieger, M.; Bertrand, G. *J. Am. Chem. Soc.* **1992**, *114*, 10959. (d) Gillette, G. R.; Baceiredo, A.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1429.

(14) Adam, W.; De Lucchi, O. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762.

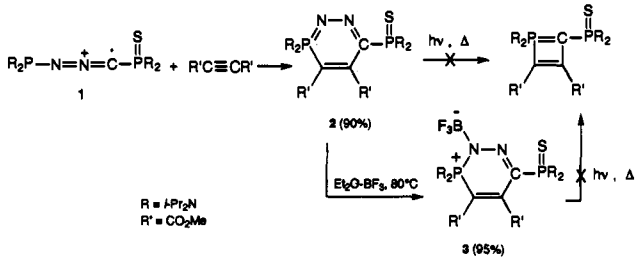
(15) (a) Granier, M.; Baceiredo, A.; Nieger, M.; Bertrand, A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1123. (b) Castan, F.; Granier, M.; Straw, T.; Baceiredo, A.; Dillon, K.; Bertrand, G. *Chem. Ber.* **1991**, *124*, 1739.

0002-7863/94/1516-8087$04.50/0 

**Scheme 1**



**Scheme 2**



dinitrogen from the six-membered heterocycle **2** by photolysis or thermolysis failed. We then tried to initiate the elimination of $N_2$ by adding boron trifluoride etherate. In this case, compound **3** was obtained in 95% yield after recrystallization. It is noteworthy that this Lewis acid adduct **3** is also stable in refluxing toluene or under photolytic conditions (Scheme 2).

The reluctance of **2** to loose $N_2$ is consistent with the high stability of phosphazo derivatives. Indeed, **2** features the same $R_3P{=}N{-}N{=}C<$ sequence as Staudinger–Meyer adducts (phosphines + diazo derivatives), which are not precursors of phosphorus ylides.[16] In marked contrast, it is well known that the phosphazides (the Staudinger adducts of phosphines with azido derivatives, $R_3P{=}N{-}N{=}N{-}$) easily decompose into dinitrogen and iminophosphoranes.[17] Therefore, it was of interest to prepare 1,2,3,4$\lambda^5$-triazaphosphinines **5**, as potential precursors of 1,2$\lambda^5$-azaphosphetes **6**. As a synthetic route, we extended the formal 1,4-dipolar reactivity of phosphanyl-substituted 1,3-dipoles[15,18] to phosphanyl azides. Bis(diisopropylamino)- and bis(dicyclohexylamino)phosphanyl azides (**4a**[19] and **4b**)[20] cleanly reacted with dimethyl acetylenedicarboxylate, affording the desired six-membered rings **5a** (75% yield) and **5b** (63% yield), respectively. The ORTEP view of **5a** is shown in Figure 1, and the pertinent metric parameters are collected in Table 1. As expected, extrusion of dinitrogen occurred in refluxing toluene giving 1,2$\lambda^5$-azaphosphetes **6a** and **6b** in 80 and 90% yield, respectively (Scheme 3).

On comparison of the molecular structures of **2**,[15a] **5a**, and **6a** (Figure 2), the first remarkable feature is the similarity between the two six-membered rings **2** and **5a**. Both exhibit a very flat boat conformation with the phosphorus and the para-X atoms lying outside the plane. Comparable bond lengths and angles were observed; for instance a (P)N–N length for **2** of 1.316(5) Å and for **5a** of 1.296(4) Å. In other words, solid-state structural parameters do not give any information on the dramatic difference in the behavior of these two heterocycles with respect to $N_2$ elimination. For both the six-membered rings **2** and **5a** and the

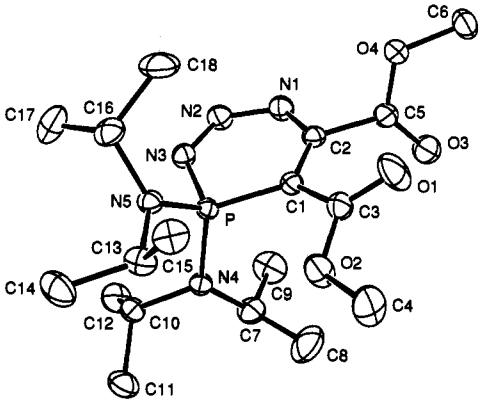
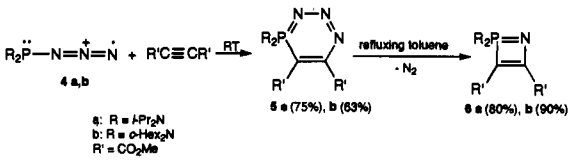


**Figure 1.** ORTEP plot of 1,2,3,4$\lambda^5$-triazaphosphinine **5a** showing the numbering scheme used.

**Table 1.** Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for **5a**

| | | | |
|---|---|---|---|
| P–C1 | 1.744(3) | P–N4 | 1.638(2) |
| P–N3 | 1.666(2) | P–N5 | 1.636(2) |
| C1–C2 | 1.375(4) | N1–N2 | 1.335(3) |
| C2–N1 | 1.356(4) | N2–N3 | 1.296(4) |
| C1–C3 | 1.478(4) | C2–C5 | 1.508(4) |
| C3–O1 | 1.197(4) | C5–O3 | 1.197(4) |
| C3–O2 | 1.329(4) | C5–O4 | 1.319(4) |
| C1–P–N3 | 103.1(1) | N3–P–N4 | 110.0(1) |
| C1–P–N4 | 113.8(1) | N3–P–N5 | 106.1(1) |
| C1–P–N5 | 116.1(1) | N4–P–N5 | 107.3(1) |
| P–C1–C2 | 115.4(2) | C2–N1–N2 | 120.2(2) |
| C1–C2–N1 | 129.9(3) | N1–N2–N3 | 124.0(2) |
| N2–N3–P | 126.4(2) | C7–N4–C10 | 115.0(2) |
| P–N4–C7 | 122.3(2) | P–N5–C13 | 121.8(2) |
| P–N4–C10 | 117.2(2) | P–N5–C16 | 122.1(2) |
| C13–N5–C16 | 115.2(2) | P–C1–C2–N1 | 2.3(4) |
| N1–N2–N3–P | –4.5(4) | C1–C2–N1–N2 | 5.6(5) |
| N2–N3–P–C1 | 10.3(3) | C2–N1–N2–N3 | –4.6(4) |
| N3–P–C1–C2 | –8.6(2) | | |

**Scheme 3**



four-membered ring **6a**, it appears that the exocyclic P–N bond lengths are slightly shorter than the endocyclic ones, especially in the case of **6a**, and are comparable to those observed in bis(diisopropylamino)phosphenium salts (1.61 Å).[21] This is an indication of a positive charge delocalization on the exocyclic N–P–N fragment, which is confirmed by the planarity of these N atoms. Moreover, the endocyclic C–C, C–N, and N–N bond lengths of **2**, **5a**, and **6a** have values that lie halfway between single and double bonds, indicating that in these compounds the N–N–X–C–C and N–C–C parts of the ring can be regarded as anionic pentadienyl and propenyl systems, respectively. Thus, the six-$\pi$-electron six-membered rings **2** and **5a** are best described by the "nonaromatic" structure **G**, while the four-$\pi$-electron four-membered ring **6a** is best illustrated by the "nonantiaromatic" structure **H**. Note that the structure of type **H** is significantly different from those of 1$\lambda^5$,3$\lambda^5$-diphosphetes **B**[11] and 1,3,2$\lambda^5$,4$\lambda^5$-diazadiphosphetes (cyclodiphosphazenes) **D**,[12] where the $\pi$-systems basically follow the "island model"[22] (Scheme 4). However, there is a common feature to all these cyclic four-$\pi$-electron ylides **B**, **D**, and **H**: the distance between the phosphorus atom and the

(16) Bestmann, H. J.; Zimmermann, R. In *Methoden der Organischen Chemie (Houben-Weyl)*; Regitz, M., Ed.; Thieme: Stuttgart, Germany, 1982; Vol. E1, pp 616–617.
(17) (a) Gololobov, Y. G.; Kasukhin, L. F. *Tetrahedron* **1992**, *48*, 1354. (b) Bock, H.; Schnöller, M. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 636.
(18) Facklam, T.; Wagner, O.; Heydt, H.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 314.
(19) Scherer, O. J.; Glabel, W. *Chem.-Ztg.* **1975**, *99*, 246.
(20) Alcaraz, G.; Baceiredo, A.; Dahan, F.; Bertrand, G. *J. Am. Chem. Soc.*, in press.
(21) Cowley, A. H.; Cushner, M. C.; Szobota, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 7784.
(22) (a) Trinquier, G. *J. Am. Chem. Soc.* **1986**, *108*, 568. (b) Ahlrichs, R.; Schiffer, H. *J. Am. Chem. Soc.* **1985**, *107*, 6494.

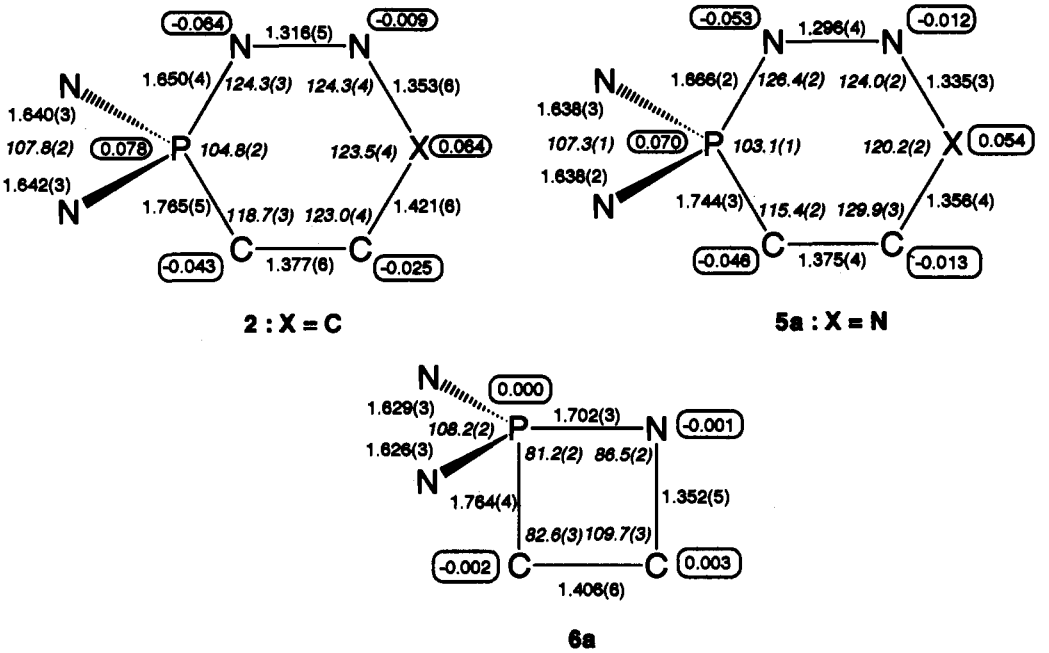
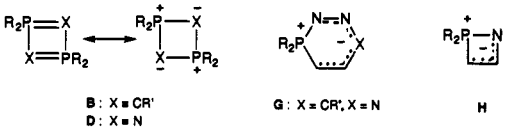



**Figure 2.** Comparison of X-ray data for **2**, **5a**, and **6a**. Values of bond lengths (Å) are in roman type, values of angles (deg) in italics, and the maximum deviations (Å) are circled.

**Scheme 4**



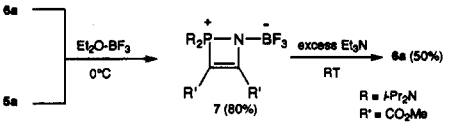

opposite atom is short [**B**, P–P 2.410 Å;[11a] **D**, P–P 2.22 Å;[12a] **6a**, P–C 2.109(4) Å]; so far, this experimental fact has not been rationalized.

It is also of interest to compare the NMR data for compounds **5** and **6**. There is a deshielding of the $^{31}P$ chemical shift from **5** to **6** ($\Delta\delta = 47$), which seems to be a general phenomenon going from six-π-electron six-membered to four-π-electron four-membered rings (i.e. from cyclotriphosphazenes to cyclodiphosphazenes $\Delta\delta = 20$).[12b] In the same way, the deshielding of the CN $^{13}C$ chemical shift from **5** to **6** ($\Delta\delta \sim 30$) is comparable to that observed in going from triazine[23] to azete[24] ($\Delta\delta \sim 40$).

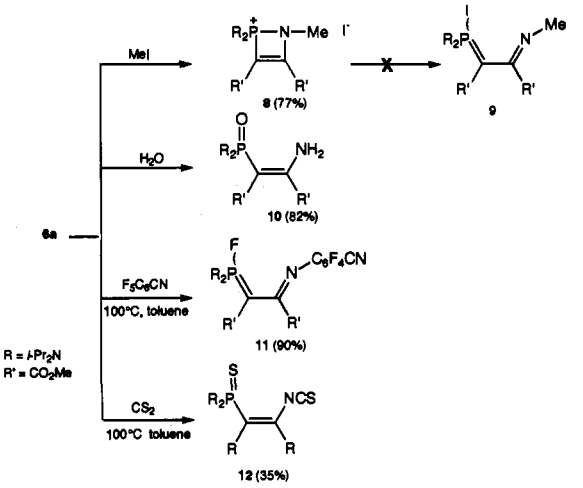
Although 1,2λ⁵-azaphosphetes **6** are highly thermally stable (they only start to decompose in solution at 170 °C, giving rise to a complicated mixture of products), they are quite reactive. These cyclic four-π-electron ylides **6** are inert toward nucleophiles but readily react with inorganic and organic electrophiles. As expected, the most reactive site is the nitrogen atom. Derivatives **6a** and **6b** being very similar, we only studied in detail the reactivity of **6a**.

Addition of Lewis acids, such as boron trifluoride, gave rise to a new type of phosphorus heterocycle, the unsaturated four-membered phosphonium ring **7** (80% yield), already demonstrating the synthetic potential of **6**. Addition of an excess of triethylamine to **7** gave back the starting azaphosphete **6a** (50% yield). This route is reminiscent of the preparation of the first stable cyclobutadiene by deprotonation of cyclobutenium salts.[5e] Interestingly, addition of boron trifluoride etherate at 0 °C to 1,2,3,4λ⁵-triazaphosphinine **5a** directly led to the zwitterionic heterocycle **7** in quantitative yield; it is therefore possible to prepare

**Scheme 5**




**Scheme 6**




the azaphosphete **6a** under very mild experimental conditions (Scheme 5).

In the same way, addition of a stoichiometric amount of iodomethane to **6a** afforded cyclic phosphonium salt **8** (77% yield), which surprisingly did not rearrange into the ylidic opened form **9**. In contrast, compound **6a** was readily hydrolyzed into (*Z*)-1-amino-2-phosphoranylalkene **10** (82% yield), when exposed to air. This can be rationalized by the formation of the strong covalent phosphorus–oxygen bond, converting the phosphonium center into a pentacoordinated phosphorus atom, which favors a ring opening reaction. A similar mechanism also explains the formation of **11** (90% yield), in the reaction of 1,2λ⁵-azaphosphete **6a** with pentafluorobenzonitrile at 100 °C. A classical aza-Wittig reaction was observed by adding carbon disulfide to **6a**, in refluxing toluene, giving (*Z*)-1-(isothiocyanato)-2-(thiophosphoranyl)-alkene **12** (35% yield) (Scheme 6). The ORTEP view of **12** is

(23) Katritzky, A. R.; Rees, C. W. *Comprehensive Heterocyclic Chemistry*; Pergamon Press: Oxford, U.K., 1984.

(24) (a) Vogelbacher, U. J.; Regitz, M.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 842. (b) Ledermann, M.; Regitz, M.; Angermund, K.; Binger, P.; Krüger, C.; Mynott, R.; Gleiter, R.; Hyla-Kryspin, I. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1559.

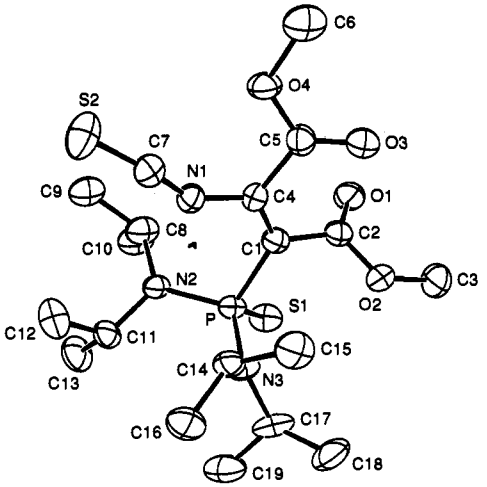



**Figure 3.** ORTEP plot of (*Z*)-1-(isothiocyanato)-2-(thiophosphoranyl)-alkene **12** showing the numbering scheme used.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for **12**

| | | | |
|---|---|---|---|
| P–S1 | 1.942(2) | P–N2 | 1.660(3) |
| P–C1 | 1.844(4) | P–N3 | 1.642(4) |
| C1–C2 | 1.489(6) | C4–C5 | 1.504(6) |
| C2–O1 | 1.197(6) | C5–O3 | 1.196(5) |
| C2–O2 | 1.335(5) | C5–O4 | 1.301(5) |
| O2–C3 | 1.442(6) | O4–C6 | 1.450(6) |
| C1–C4 | 1.342(6) | C4–N1 | 1.360(5) |
| N1–C7 | 1.183(5) | C7–S2 | 1.561(4) |
| P–C1–C4 | 128.3(3) | C1–C4–N1 | 123.4(4) |
| C4–N1–C7 | 145.4(4) | N1–C7–S2 | 173.3(4) |

shown in Figure 3, and the pertinent metric parameters are collected in Table 2. Note that the molecule is arranged in a propeller fashion to minimize the steric interaction; all the bond lengths as well as the angles are usual.

All these reactions show that **6a** behaves as a classical aza-Wittig reagent, and since dimethyl acetylenedicarboxylate is known to insert into a P=N bond,[17a] it was tempting to extrapolate this reaction to **6a** as a new route to 1,4λ⁵-azaphosphinines.[25] According to $^{31}P$ NMR spectroscopy, the reaction performed at 100 °C required 2 equivalents of alkyne and afforded two main products in a 1/1 ratio (broad singlets at +42.62 and +37.85); all attempts to separate these two products by fractional crystallization or column chromatography failed. Mass spectroscopy confirmed that these adducts arrose from the addition of two molecules of dimethyl acetylenedicarboxylate to **6a**. Single crystals were grown from a toluene solution and subjected to an X-ray diffraction study. The thermal ellipsoid plot of the molecule is shown in Figure 4, and pertinent structural parameters are listed in Table 3. Indeed, compound **13** is a 1,4λ⁵-azaphosphinine but not the expected one (Scheme 7). It is clear that the mechanism leading to **13** is very complicated, and all hypotheses would be pure speculation. The initial diisopropylamino phosphorus substituents have migrated, whereas the phosphorus atom now bears substituents coming from dimethyl acetylenedicarboxylate. The ring is almost planar, and the values of intracyclic bond lengths are halfway between those for single and double bonds. The cyclic skeleton is almost symmetrical [P–C 1.729(4), 1.723(4) Å; C–C 1.406(5), 1.397(5) Å] with a small discrepancy between the two CN bonds [1.371(5), 1.311(5) Å]. It is important to note that the melting points of several single crystals were identical (180 °C) and that the $^{31}P$ NMR spectrum of a toluene solution of these crystals exhibits the same broad signals as the crude reaction mixture, demonstrating that in solution **13** exists as two isomers.

(25) Märkl, G. In *Methoden der Organischen Chimie (Houben-Weyl)*; Regitz, M., Ed.; Thieme: Stuttgart, Germany, 1982; Vol. E1, pp 96.

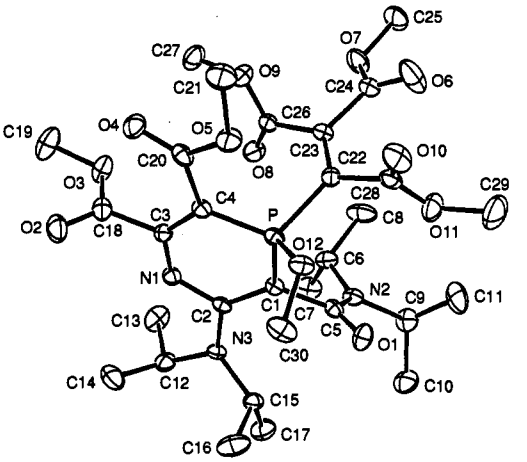



**Figure 4.** ORTEP plot of six-π-electron phosphorus ylide **13** showing the numbering scheme used.

**Table 3.** Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for **13**

| | | | |
|---|---|---|---|
| P–C1 | 1.729(4) | P–C22 | 1.829(4) |
| P–C4 | 1.723(4) | P–O12 | 1.587(3) |
| C1–C2 | 1.406(5) | C2–N1 | 1.371(5) |
| C3–C4 | 1.397(5) | N1–C3 | 1.311(4) |
| C1–C5 | 1.522(5) | C5–O1 | 1.218(5) |
| C5–N2 | 1.361(5) | C2–N3 | 1.363(4) |
| C3–C18 | 1.513(6) | C4–C20 | 1.460(5) |
| C18–O2 | 1.198(5) | C20–O4 | 1.197(5) |
| C22–C23 | 1.331(6) | C22–C28 | 1.526(6) |
| C23–C24 | 1.496(6) | C23–C26 | 1.514(6) |
| C24–O6 | 1.180(6) | C26–O8 | 1.187(5) |
| C24–O7 | 1.301(6) | C26–O9 | 1.317(5) |
| C28–O10 | 1.188(5) | C28–O11 | 1.310(6) |
| C1–P–C4 | 105.8(2) | C4–P–C22 | 111.8(2) |
| C1–P–C22 | 113.5(2) | C4–P–O12 | 115.9(2) |
| C1–P–O12 | 113.8(2) | C22–P–O12 | 96.1(2) |
| P–C1–C2 | 118.9(3) | N1–C3–C4 | 129.6(3) |
| C1–C2–N1 | 123.5(3) | C3–C4–P | 116.9(3) |
| C2–N1–C3 | 122.2(3) | P–C1–C2–N1 | 21.7(5) |
| N1–C3–C4–P | 6.6(6) | C1–C2–N1–C3 | –12.3(6) |
| C3–C4–P–C1 | 2.9(3) | C2–N1–C3–C4 | –3.4(6) |
| C4–P–C1–C2 | –15.6(3) | | |

This unexpected reactivity of **6a** led us to study in greater depth its behavior toward electrophiles. Isocyanates and isothiocyanates have been widely employed in aza-Wittig reactions, giving unsymmetrical carbodiimides and the corresponding phosphine oxides and sulfides, respectively.[17a,26] In marked contrast, methyl isothiocyanate reacted with **6a**, giving heterocycle **14** in 90% yield. The presence of the P–N($CH_3$)–C(S)–N sequence is supported by the presence of a doublet for the $NCH_3$ group in $^1H$ (3.21, $J_{PH}$ = 6.2 Hz) and $^{13}C$ NMR (38.53, $J_{PC}$ = 4.4 Hz), the CS group giving a doublet at 188.88 ($J_{PC}$ = 3.6 Hz); the P=C(R)—C(R)=N skeleton is indicated by the $^{13}C$ NMR data [81.51, $J_{PC}$ = 153.6 Hz, P=C; 158.90, $J_{PC}$ = 7.4 Hz, C=N; 165.61, $J_{PC}$ = 12.9 Hz, CO; 166.49, $J_{PC}$ = 18.8 Hz, CO). In the same way, phenyl isocyanate added to **6a** affords the analogous oxo compound **15** (66% yield). These results are reminiscent of the Dimroth rearrangement[17a,26b] and demonstrate the applicability of four-π-electron four-membered rings in heterocyclic synthesis (Scheme 7).

Clean reactions also occurred with trimethylsilyl isocyanate, and isothiocyanate leading, after hydrolysis, to heterocycles **16** and **17**, which were isolated in 50 and 40% yield, respectively (Scheme 7). The spectroscopic data for these two compounds **16**

(26) (a) Williams, A.; Ibrahim, I. T. *Chem. Rev.* **1981**, *81*, 589. (b) Molina, P.; Arques, A.; Vinader, M. V. *J. Org. Chem.* **1988**, *53*, 4654. (c) Murahashi, S. I.; Tanogushi, Y.; Imada, Y.; Tanigawa, Y. *J. Org. Chem.* **1989**, *54*, 3292. (d) Tsuge, O.; Kanemasa, S.; Matsuda, K. *J. Org. Chem.* **1984**, *49*, 2688. (e) Scriven, E. F. V.; Turnbull, K. *Chem. Rev.* **1988**, *88*, 297.

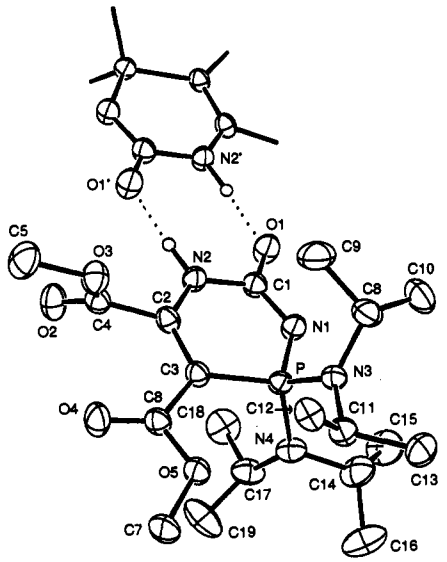
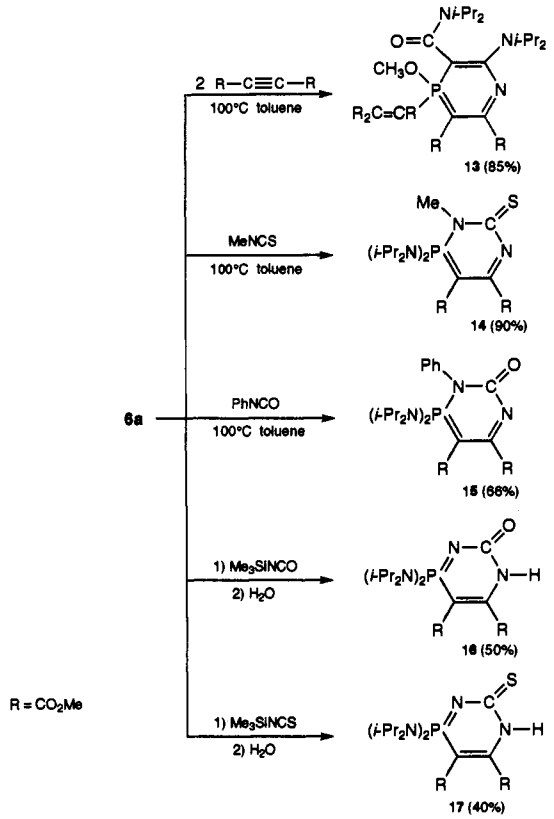



**Figure 5.** ORTEP plot of heterocycle **16** showing the numbering scheme used. Hydrogen atoms are not shown for clarity, except the NH involved in the hydrogen bond illustrated by dotted lines.

**Scheme 7**

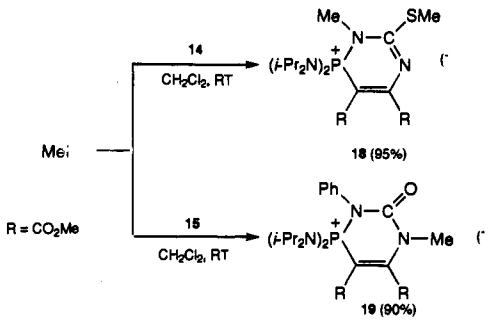



and **17** were very similar but did not fit with the expected structure of type **14–15**. In particular, no coupling was observed between the phosphorus and the NH hydrogen (**16**, 10.68; **17**, 10.07; singlets), indicating the absence of a PNH sequence; the presence of the NH bonds was confirmed by the observation of a classical absoption in the IR spectrum (**16**, 3387 $cm^{-1}$; **17**, 3362 $cm^{-1}$). The proposed structures have been clearly established by a single-crystal X-ray diffraction study performed on **16**. The thermal ellipsoid plot of the molecule is shown in Figure 5, with the pertinent metric parameters listed in Table 4. The hydrogen atom is located on the N(2) atom, and as usually observed for 2-pyridone type compounds,[27] **16** exists as a hydrogen-bonded dimer in the solid state [H(N2)–N2, 0.97(2) Å; N2···O1′, 2.784-(3) Å; H(N2)···O1′, 1.83(2) Å; N2–H(N2)···O1′, 169(2)°]. It is of interest to note that **16** has a structure comparable to that of cytosine,[28] the $C(NH_2)$ being replaced by a $P(NiPr_2)_2$ group; both rings are planar, and the bond lenghts in the NC(O)NH skeleton lie in the same range [N1–C1, 1.320(3) vs 1.364 Å; C1–N2, 1.427(3) vs 1.368 Å; C1–O1, 1.236(3) vs 1.241 Å].

**Table 4.** Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for **16**

| | | | |
|---|---|---|---|
| P–C3 | 1.780(2) | P–N3 | 1.643(2) |
| P–N1 | 1.602(2) | P–N4 | 1.648(2) |
| N1–C1 | 1.320(3) | C1–O1 | 1.236(3) |
| C1–N2 | 1.427(3) | N2–C2 | 1.357(3) |
| C2–C3 | 1.368(4) | C2–C4 | 1.525(4) |
| C3–C6 | 1.482(4) | C4–O2 | 1.185(3) |
| C6–O4 | 1.196(3) | C3–P–N1 | 105.8(1) |
| N1–P–N3 | 108.3(1) | C3–P–N3 | 113.3(1) |
| N1–P–N4 | 112.5(1) | C3–P–N4 | 110.6(1) |
| N3–P–N4 | 106.5(1) | P–N1–C1 | 127.4(2) |
| N1–C1–O1 | 124.8(2) | N1–C1–N2 | 119.2(2) |
| N2–C1–O1 | 116.0(2) | C1–N2–C2 | 124.9(2) |
| N2–C2–C3 | 125.2(2) | P–C3–C2 | 116.5(2) |
| P–N3–C8 | 121.3(2) | P–N4–C14 | 117.6(2) |
| P–N3–C11 | 122.6(2) | P–N4–C17 | 121.3(2) |
| C8–N3–C11 | 114.4(2) | C14–N4–C17 | 114.7(3) |
| P–N1–C1–N2 | 5.5(4) | N2–C2–C3–P | 9.0(3) |
| N1–C1–N2–C2 | –7.1(4) | C2–C3–P–N1 | –8.8(2) |
| C1–N2–C2–C3 | –1.0(4) | C3–P–N1–C1 | 1.9(3) |

**Scheme 8**




The readily available heterocycles **14** and **15** are highly functionalized and have a high synthetic potential, as shown by the reaction with iodomethane giving the corresponding cationic heterocycles **18** (95% yield) and **19** (90% yield) (Scheme 8). As indicated by NMR spectroscopy, the methylation of **14** occurs at the sulfur atom of the thiocarbonyl function ($^1H$ NMR 2.52; $^{13}C$ NMR 16.49), whereas with **15** the methylation takes place at the nitrogen atom of the imine moiety ($^1H$ NMR: 3.22; $^{13}C$ NMR 36.31).

These results show that the 1,2λ⁵-azaphosphetes are not laboratory curiosities only demonstrating that the presence of one σ⁴-phosphorus atom is sufficient to stabilize four-π-electron four-membered rings but also versatile precursors for highly functionalized neutral and cationic heterocycles. Synthetic routes to other "heterocyclobutadienes" merit investigation.

## Experimental Section

All experiments were performed in an atmosphere of dry argon. Melting points are uncorrected. $^1H$, $^{13}C$, $^{11}B$, $^{19}F$, and $^{31}P$ NMR spectra were recorded on Brucker AC80, AC200, or WM250 spectrometers. $^1H$ and $^{13}C$ chemical shifts are reported in ppm relative to $Me_4Si$ as external standard. $^{11}B$, $^{19}F$, and $^{31}P$ NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external $BF_3{\cdot}Et_2O$, $CF_3CO_2H$, and 85% $H_3PO_4$, respectively. Infrared spectra were recorded on a Perkin-

(27) (a) Nethaji, M.; Pattabhi, V. *Acta Crystallogr., Sect. C* **1989**, *C45*, 509. (b) Ohms, U.; Guth, H. E.; Dannöhl, H.; Schweig, A. *Z. Kristallogr.* **1984**, *169*, 185. (c) Low, J. N.; Wilson, C. C. *Acta Crystallogr. Sect. C* **1983**, *C39*, 1688.

(28) McClure, R. J.; Craven, B. M. *Acta Crystallogr. Sect. B* **1973**, *B29*, 1234.

Elmer FT-IR spectrometer 1725 X. Mass spectra were obtained on a Ribermag R10 10E instrument. Liquid chromatography was done on silica gel or neutral alumina. Conventional glassware was used.

**Six-Membered Heterocycle 3.** Neat boron trifluoride etherate (0.31 mL, 2.52 mmol) was added dropwise, at −80 °C, to a THF solution (8 mL) of **2**[15] (1.62 g, 2.40 mmol). The solution was allowed to warm to room temperature, and the solvent and excess $BF_3{\cdot}Et_2O$ were removed under vacuum. After crystallization in chloroform at room temperature, **3** was obtained as a yellow solid (1.70 g, 95% yield): mp 154 °C dec; $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$ 1.18 (d, $J_{HH}$ = 6.9 Hz, 12 H, C$H_3$CHN), 1.26 (d, $J_{HH}$ = 6.9 Hz, 12 H, C$H_3$CHN), 1.31 (d, $J_{HH}$ = 6.9 Hz, 12 H, C$H_3$CHN), 1.37 (d, $J_{HH}$ = 6.9 Hz, 12 H, C$H_3$CHN), 3.77 (s, 3 H, $CH_3O$), 3.83 (s, 3 H, $CH_3O$), 3.86 (m, $J_{HH}$ = 6.9 Hz, 8 H, $CH_3CHN$); $^{13}$C NMR ($CDCl_3$, 50.323 MHz) $\delta$ 22.54 (d, $J_{PC}$ = 2.7 Hz, $CH_3CHN$), 23.71 (d, $J_{PC}$ = 4.2 Hz, $CH_3CHN$), 23.98 (s, $CH_3CHN$), 47.80 (d, $J_{PC}$ = 5.8 Hz, $CH_3CHN$), 49.11 (d, $J_{PC}$ = 5.7 Hz, $CH_3CHN$), 53.18 (s, $CH_3O$), 54.02 (s, $CH_3O$), 118.27 (dd, $J_{PC}$ = 135.9 Hz, $J_{PC}$ = 9.9 Hz, PCCO), 145.24 (dd, $J_{PC}$ = 145.2 Hz, $J_{PC}$ = 25.5 Hz, P(S)CN), 145.38 (d, $J_{PC}$ = 28.4 Hz, PC$C$), 162.60 (d, $J_{PC}$ = 9.6 Hz, CO), 162.88 (d, $J_{PC}$ = 13.9 Hz, CO); $^{31}$P NMR ($CDCl_3$, 32.438 MHz) $\delta$ +11.25, +64.81 ($J_{PP}$ = 2.4 Hz); $^{11}$B NMR ($CDCl_3$, 25.709 MHz) $\delta$ −0.68; IR (THF) 1745, 1723 cm$^{-1}$ (CO). Anal. Calcd for $C_{31}H_{62}BF_3N_6O_4P_2S$: C, 50.00; H, 8.39; N, 11.29. Found: C, 50.12; H, 8.48; N, 11.35.

**Synthesis of 1,2,3,4λ$^5$-Triazaphosphinine 5a.** Dimethyl acetylenedicarboxylate (0.85 mL, 6.92 mmol) was added dropwise to a pentane solution (125 mL) of bis(diisopropylamino)phosphanyl azide **4a**[19] (1.89 g, 6.92 mmol) at room temperature. The solution was stirred for 12 h, and **5a** precipitated as a pale-yellow solid which was washed several times with pentane and dried *in vacuo*. **5a** was recrystallized from an ether solution at −20 °C (2.16 g, 75% yield): mp 122–123 °C; $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$ 1.08 (d, $J_{HH}$ = 6.9 Hz, 12 H, C$H_3$CHN), 1.27 (d, $J_{HH}$ = 6.9 Hz, 12 H, C$H_3$CHN), 3.71 (s, 3 H, $CH_3O$), 3.85 (sept d, $J_{PH}$ = 16.9 Hz, $J_{HH}$ = 6.9 Hz, 4 H, $CH_3CHN$), 3.87 (s, 3 H, $CH_3O$); $^{13}$C NMR ($CDCl_3$, 50.323 MHz) $\delta$ 22.93, 23.62 (s, $CH_3CHN$), 47.62 (d, $J_{PC}$ = 4.7 Hz, $CH_3CHN$), 51.70, 52.62 (s, $CH_3O$), 81.77 (d, $J_{PC}$ = 113.2 Hz, PC), 150.44 (d, $J_{PC}$ = 2.4 Hz, CN), 166.23 (d, $J_{PC}$ = 11.6 Hz, CO), 166.81 (d, $J_{PC}$ = 2.7 Hz, CO); $^{31}$P NMR (THF, 32.438 MHz) $\delta$ +5.74; IR (THF) 1748, 1716 cm$^{-1}$ (CO). Anal. Calcd for $C_{18}H_{34}N_5O_4P$: C, 52.04; H, 8.25; N, 16.86. Found: C, 52.34; H, 8.27; N, 17.03.

**Synthesis of 1,2,3,4λ$^5$-Triazaphosphinine 5b.** The procedure described for **5a** was used starting from **4b**[20] (0.69 g, 1.59 mmol), and **5b** was obtained as a pale-yellow solid (2.5 g, 63% yield): mp 139–140 °C; $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$ 1.01–1.85 (m, 40 H, $CH_2$), 3.30–3.37 (m, 4 H, NCH), 3.67 (s, 3 H, $CH_3O$), 3.84 (s, 3 H, $CH_3O$); $^{13}$C NMR ($CDCl_3$, 50.323 MHz) $\delta$ 25.09, 26.72 (s, $CH_2$), 33.70 (d, $J_{PC}$ = 2.0 Hz, $CH_2$), 34.76 (s, $CH_2$), 51.98 (s, $CH_3O$), 52.77 (s, $CH_3O$), 57.65 (d, $J_{PC}$ = 4.5 Hz, NCH), 82.58 (d, $J_{PC}$ = 114.0 Hz, PC), 150.29 (d, $J_{PC}$ = 2.4 Hz, CN), 166.49 (d, $J_{PC}$ = 11.4 Hz, CO), 166.97 (d, $J_{PC}$ = 3.0 Hz, CO); $^{31}$P NMR ($CH_2Cl_2$, 32.438 MHz) $\delta$ +6.01; IR ($CH_2Cl_2$) 1743, 1708 cm$^{-1}$ (CO); CIMS *m/e* 548 ($M^+$ + 1 − $N_2$). Anal. Calcd for $C_{30}H_{50}N_5O_4P$: C, 62.59; H, 8.75; N, 12.16. Found: C, 62.51; H, 8.78; N, 12.08.

**Synthesis of 1,2λ$^5$-Azaphosphete 6a.** A toluene solution (20 mL) of **5a** (1.44 g, 3.48 mmol) was heated at 110 °C for 12 h. The solvent was removed under vacuum, and the residue was washed three times with ether (3 × 10 mL). Compound **6a** crystallized at −80 °C from a pentane solution as pale-yellow crystals (1.08 g, 80% yield): mp 109–110 °C; $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$ 1.24 (d, $J_{HH}$ = 6.8 Hz, 12 H, C$H_3$CHN), 1.26 (d, $J_{HH}$ = 6.8 Hz, 12 H, C$H_3$CHN), 3.52 (s, 3 H, $CH_3O$), 3.68 (sept d, $J_{PH}$ = 18.4 Hz, $J_{HH}$ = 6.8 Hz, 4 H, $CH_3CHN$), 3.82 (s, 3 H, $CH_3O$); $^{13}$C NMR ($CDCl_3$, 50.323 MHz) $\delta$ 21.83, 22.12 (s, $CH_3CHN$), 47.50 (d, $J_{PC}$ = 4.9 Hz, $CH_3CHN$), 49.63 (d, $J_{PC}$ = 2.1 Hz, $CH_3O$), 52.16 (s, $CH_3O$), 91.88 (d, $J_{PC}$ = 81.6 Hz, PC), 158.30 (s, CO), 164.05 (d, $J_{PC}$ = 64.3 Hz, CO), 182.37 (d, $J_{PC}$ = 28.0 Hz, CN); $^{31}$P NMR (THF, 32.438 MHz) $\delta$ +52.46; IR (THF) 1743, 1660 cm$^{-1}$ (CO). CIMS ($M^+$ + 1) 388. Anal. Calcd for $C_{18}H_{34}N_3O_4P$: C, 55.80; H, 8.85; N, 10.85. Found: C, 55.79; H, 8.79; N, 10.82.

**Synthesis of 1,2λ$^5$-Azaphosphete 6b.** The procedure described for **6a** was used starting from **5b** (0.58 g, 1.0 mmol). Compound **6b** was obtained as a very viscous oil (0.49 g, 90% yield): $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$ 0.97–1.72 (m, 40 H, $CH_2$), 3.23–3.30 (m, 4 H, NCH), 3.51 (s, 3 H, $CH_3O$), 3.86 (s, 3 H, $CH_3O$); $^{13}$C NMR ($CDCl_3$, 50.323 MHz) $\delta$ 25.21 (s, $CH_2$), 26.52 (d, $J_{PC}$ = 2.9 Hz, $CH_2$), 32.52, 32.83 (s, $CH_2$), 49.85 (d, $J_{PC}$ = 2.0 Hz, $CH_3O$), 52.98 (s, $CH_3O$), 57.31 (d, $J_{PC}$ = 4.5 Hz, NCH), 92.44 (d, $J_{PC}$ = 82.0 Hz, PC), 158.16 (s, CO), 163.90 (d, $J_{PC}$ = 64.5 Hz, CO), 181.66 (d, $J_{PC}$ = 23.7 Hz, CN); $^{31}$P NMR ($CH_2Cl_2$, 32.438 MHz) $\delta$ +52.60; IR ($CH_2Cl_2$) 1756, 1672 cm$^{-1}$ (CO); CIMS *m/e* 548 ($M^+$ + 1). Anal. Calcd for $C_{30}H_{50}N_3O_4P$: C, 65.79; H, 9.20; N, 7.67. Found: C, 65.82; H, 9.18; N, 7.59.

**Four-Membered Heterocycle 7.** Neat boron trifluoride etherate (0.20 mL, 1.60 mmol) was added dropwise, at room temperature, to an ethereal solution (8 mL) of **6a** (0.58 g, 1.50 mmol). The solution was stirred for 30 min at room temperature, and **7** precipitated as a pale yellow solid, which was washed two times with ether (2 × 8 mL). **7** was recrystallized from a toluene solution at −80 °C (0.54 g, 80% yield): mp 175 °C dec; $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$ 1.33 (d, $J_{HH}$ = 6.9 Hz, 12 H, C$H_3$CHN), 1.39 (d, $J_{HH}$ = 6.9 Hz, 12 H, C$H_3$CHN), 3.68 (s, 3 H, $CH_3O$), 3.83 (sept d, $J_{PH}$ = 19.4 Hz, $J_{HH}$ = 6.9 Hz, 4 H, $CH_3CHN$), 3.94 (s, 3 H, $CH_3O$); $^{13}$C NMR ($CDCl_3$, 50.323 MHz) $\delta$ 21.58 (d, $J_{PC}$ = 1.8 Hz, $CH_3CHN$), 49.08 (d, $J_{PC}$ = 5.0 Hz, $CH_3CHN$), 52.28 (d, $J_{PC}$ = 1.7 Hz, $CH_3O$), 53.13 (s, $CH_3O$), 100.00 (d, $J_{PC}$ = 108.8 Hz, PC), 159.43 (d, $J_{PC}$ = 7.5 Hz, CO), 160.01 (d, $J_{PC}$ = 44.5 Hz, CO), 169.77 (d, $J_{PC}$ = 15.5 Hz, $J_{BC}$ = 1.5 Hz, CN); $^{31}$P NMR ($CDCl_3$, 32.438 MHz) $\delta$ +45.66; $^{11}$B NMR ($CDCl_3$, 25.709 MHz) $\delta$ −0.51 (qua, $J_{BF}$ = 14.4 Hz); $^{19}$F NMR ($CDCl_3$, 188.296) −66.05 (qua, $J_{BF}$ = 14.4 Hz); IR (THF) 1758, 1703 cm$^{-1}$ (CO); CIMS *m/e* 408 ($M^+$ + 2-$BF_2$). Anal. Calcd for $C_{18}H_{34}BF_3N_3O_4P$: C, 47.49; H, 7.53; N, 9.23. Found: C, 47.51; H, 7.58; N, 9.18.

**Four-Membered Heterocycle 8.** Neat iodomethane (0.2 mL, 3.20 mmol) was added dropwise, at room temperature, to a dichloromethane solution (5 mL) of **6a** (1.00 g, 2.58 mmol). The solution was stirred overnight at room temperature, and after the solvent and excess iodomethane were removed under vacuum, the residue was washed three times with ether (3 × 10 mL). **8** was purified by recrystallization at room temperature from a $CH_2Cl_2$/THF solution as pale brown crystals (1.05 g, 77% yield): mp 135 °C dec; $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$ 0.94 (d, $J_{HH}$ = 6.8 Hz, 12 H, C$H_3$CHN), 0.99 (d, $J_{HH}$ = 6.8 Hz, 12 H, C$H_3$CHN), 2.82 (d, $J_{PH}$ = 14.1 Hz, 3 H, $NCH_3$), 3.35 (s, 3 H, $CH_3O$), 3.54 (sept d, $J_{PH}$ = 20.8 Hz, $J_{HH}$ = 6.8 Hz, 4 H, $CH_3CHN$), 3.63 (s, 3 H, $CH_3O$); $^{13}$C NMR ($CDCl_3$, 50.323 MHz) $\delta$ 21.66 (d, $J_{PC}$ = 1.6 Hz, $CH_3CHN$), 23.10 (d, $J_{PC}$ = 1.1 Hz, $CH_3CHN$), 32.76 (d, $J_{PC}$ = 3.7 Hz, $NCH_3$), 49.90 (d, $J_{PC}$ = 4.2 Hz, $CH_3CHN$), 52.47 (s, $CH_3O$), 54.74 (d, $J_{PC}$ = 2.5 Hz, $CH_3O$), 104.41 (d, $J_{PC}$ = 104.1 Hz, PC), 157.15 (d, $J_{PC}$ = 40.6 Hz, CO), 158.01 (d, $J_{PC}$ = 8.2 Hz, CO), 163.33 (d, $J_{PC}$ = 7.2 Hz, CN); $^{31}$P NMR ($CH_2Cl_2$, 32.438 MHz) $\delta$ +49.51; IR ($CH_2Cl_2$) 1751, 1715 cm$^{-1}$ (CO). Anal. Calcd for $C_{19}H_{37}IO_4N_3P$: C, 43.11; H, 7.04; N, 7.94. Found: C, 43.44; H, 7.40; N, 7.97.

**(*Z*)-1-Amino-2-phosphoranylalkene 10.** A THF solution (8 mL) of **6a** (0.97 g, 2.5 mmol) was exposed to air for 3 h at room temperature. The solvent was removed under vacuum, and **10** was isolated by crystallization from ether/pentane at −10 °C as a colorless solid (0.83 g, 82% yield): mp 128 °C; $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$ 1.17 (d, $J_{HH}$ = 6.8 Hz, 12 H, C$H_3$CHN), 1.25 (d, $J_{HH}$ = 6.8 Hz, 12 H, C$H_3$CHN), 3.58 (s, 3 H, $CH_3O$), 3.80 (s, 3 H, $CH_3O$), 3.74 (sept d, $J_{PH}$ = 15.7 Hz, $J_{HH}$ = 6.8 Hz, 4 H, $CH_3CHN$), 7.33 (s, 2 H, $NH_2$); $^{13}$C NMR ($CDCl_3$, 50.323 MHz) $\delta$ 23.00 (d, $J_{PC}$ = 2.5 Hz, $CH_3CHN$), 23.18 (d, $J_{PC}$ = 2.9 Hz, $CH_3CHN$), 46.05 (d, $J_{PC}$ = 5.8 Hz, $CH_3CHN$), 50.37 (s, $CH_3O$), 52.23 (s, $CH_3O$), 91.86 (d, $J_{PC}$ = 151.0 Hz, PC), 157.33 (d, $J_{PC}$ = 7.3 Hz, $CNH_2$), 166.48 (d, $J_{PC}$ = 19.0 Hz, CO), 167.35 (d, $J_{PC}$ = 10.4 Hz, CO); $^{31}$P NMR ($CDCl_3$, 32.438 MHz) $\delta$ +31.18, IR ($C_7H_8$) 3474 ($NH_2$), 1740, 1701 cm$^{-1}$ (CO); CIMS *m/e* 406 ($M^+$ + 1). Anal. Calcd for $C_{18}H_{36}O_5N_3P$: C, 53.33; H, 8.95; N, 10.36. Found: C, 53.43; H, 8.98; N, 10.23.

**P-Fluorinated Phosphorus Ylide 11.** A toluene solution of **6a** (1.00 g, 2.58 mmol) and pentafluorobenzonitrile (0.340 mL, 2.70 mmol) was heated at 110 °C for 2 h. After the solvent was removed under vacuum, the residue was dissolved in pentane (10 mL) and **11** crystallized at −20 °C as a light brown solid (1.35 g, 90% yield): mp 107 °C; $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$ 1.29 (d, $J_{HH}$ = 6.9 Hz, 24 H, C$H_3$CHN), 3.59 (s, 6 H, $CH_3O$), 3.83 (sept d, $J_{PH}$ = 16.9 Hz, $J_{HH}$ = 6.9 Hz, 4 H, $CH_3CHN$); $^{13}$C NMR ($CDCl_3$, 50.323 MHz) $\delta$ 22.07 (s, $CH_3CHN$), 23.78 (s, $CH_3CHN$), 48.63 (d, $J_{PC}$ = 4.6 Hz, $CH_3CHN$), 50.39 (s, $CH_3O$), 51.85 (s, $CH_3O$), 72.48 (dd, $J_{PC}$ = 191.9 Hz, $J_{FC}$ = 24.6 Hz, PC), 84.90 (t-like, $J_{FC}$ = 15.3 Hz, *C*CN), 108.43 (s, C≡N), 137.92 (t, $J_{FC}$ = 34.3 Hz, C=N—*C*), 139.04 (m d, $J_{FC}$ = 239.5 Hz, CF), 147.06 (m d, $J_{FC}$ = 249.3 Hz, CF), 164.73 (d, $J_{PC}$ = 19.0 Hz, CO), 167.45 (d, $J_{PC}$ = 16.6 Hz, CO), the *C*=N was not observed, probably hidden by one of the CF signals; $^{31}$P NMR ($CDCl_3$, 32.438 MHz) $\delta$ +64.90 (d, $J_{FP}$ = 1535.4 Hz); IR (neat) 2238 (C≡N), 1740, 1684 cm$^{-1}$ (CO); FABMS (MNBA) *m/e* 581 ($M^+$ + 1) . Anal. Calcd for $C_{25}H_{34}O_4N_4F_5P$: C, 51.72; H, 5.90; N, 9.65. Found: C, 51.33; H, 6.17; N, 9.66.

**(*Z*)-1-(Isothiocyanato)-2-(thiophosphoranyl)alkene 12.** A toluene solution of **6a** (1.00 g, 2.58 mmol) and carbon disulfide (0.31 mL, 5.16

**Table 5.** Crystallographic Data[a] for 1,2,3,4λ⁵-Triazaphosphinine **5a**, 1-(Isothiocyanato)-2-(thiophosphoranyl)alkene **12**, Six-π-Electron Phosphorus Ylide **13**, and Heterocycle **16**

| | **5a** | **12** | **13** | **16** |
|---|---|---|---|---|
| chem formula | $C_{18}H_{34}N_5O_4P$ | $C_{19}H_{34}N_3O_4PS_2$ | $C_{30}H_{46}N_3O_{12}P$ | $C_{19}H_{35}N_4O_5P$ |
| fw | 415.47 | 463.6 | 671.68 | 430.48 |
| cryst syst | monoclinic | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/n$ (no. 14) | $P2_1/c$ (no. 14) | $P2_1/c$ (no. 14) | $P2_1/n$ (no. 14) |
| $a$, Å | 9.475(1) | 16.570(3) | 11.443(1) | 9.814(1) |
| $b$, Å | 15.018(2) | 12.520(2) | 8.180(1) | 15.208(2) |
| $c$, Å | 16.226(2) | 11.697(1) | 37.334(3) | 16.186(2) |
| $\beta$, deg | 98.53(1) | 92.27(2) | 90.69(1) | 90.55(1) |
| $V$, Å$^3$ | 2283.3(5) | 2425(1) | 3494(1) | 2415.7(5) |
| $F(000)$ | 896 | 992 | 1432 | 928 |
| $Z$ | 4 | 4 | 4 | 4 |
| $D_{calc}$, g cm$^{-3}$ | 1.209 | 1.270 | 1.277 | 1.184 |
| $\mu$(Mo K$\alpha$), mm$^{-1}$ | 0.15 | 0.30 | 0.13 | 0.14 |
| $T_{min}$–$T_{max}$[b] | 0.952–1.000 | 0.937–0.999 | 0.971–0.999 | 0.968–1.000 |
| $2\theta$ range, deg | 3–52 | 3–48 | 3–46 | 3–56 |
| no. of data collected | 4739 | 3987 | 4835 | 6115 |
| no. of observed data[c] | 2917 | 2539 | 2986 | 3651 |
| no. of params varied | 253 | 262 | 415 | 266 |
| $R$[d] | 0.039 | 0.028 | 0.042 | 0.040 |
| $R_w$[e] | 0.043 | 0.032 | 0.041 | 0.046 |

[a] All data collected at $T$ = 293 K on an Enraf-Nonius CAD4 diffractometer with graphite monochromatized Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) using $\omega$–$2\theta$ scans. [b] From empirical absorption corrections: North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A21*, 351. [c] $F_o^2 > 3\sigma(F_o^2)$ for **5a** and **16**, $F_o^2 > 2\sigma(F_o^2)$ for **12** and **13**. [d] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [e] $R_w = [\sum(w|F_o| - F_c|)^2/\sum w|F_o|^2]^{1/2}$.

mmol) was heated at 90 °C for 12 h in a sealed tube. After the solvent and excess carbon disulfide were removed under vacuum, the residue was extracted with ether (10 mL). **12** was obtained as yellow crystals from a $Et_2O$/THF mixture at room temperature (0.418 g, 35% yield): mp 141 °C; $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$ 1.34 (d, $J_{HH}$ = 6.8 Hz, 12 H, C$H_3$CHN), 1.37 (d, $J_{HH}$ = 6.8 Hz, 12 H, C$H_3$CHN), 3.75 (s, 3 H, $CH_3O$), 3.83 (s, 3 H, $CH_3O$), 3.94 (sept d, $J_{PH}$ = 15.4 Hz, $J_{HH}$ = 6.8 Hz, 4 H, $CH_3CHN$); $^{13}$C NMR ($CDCl_3$, 50.323 MHz) $\delta$ 23.94 (s, $CH_3$CHN), 24.43 (s, $CH_3$CHN), 48.17 (d, $J_{PC}$ = 4.0 Hz, $CH_3CHN$), 52.87 (s, $CH_3O$), 53.93 (s, $CH_3O$), 126.34 (s, NCS), 139.26 (d, $J_{PC}$ = 96.4 Hz, PC), 145.43 (s, CNCS), 160.76 (d, $J_{PC}$ = 8.6 Hz, CO), 165.28 (d, $J_{PC}$ = 5.5 Hz, CO); $^{31}$P NMR ($CH_2Cl_2$, 32.438 MHz) $\delta$ +62.75; IR (neat) 2029 (NCS), 1739, 1693 cm$^{-1}$ (CO); EIMS *m/e* 463 ($M^+$). Anal. Calcd for $C_{19}H_{34}O_4N_3PS_2$: C, 49.22; H, 7.39; N, 9.06. Found: C, 49.20; H, 7.43; N, 9.03.

**Six-π-Electron Phosphorus Ylide 13.** A toluene solution of **6a** (1.00 g, 2.58 mmol) and dimethyl acetylenedicarboxylate (1 mL, 8.13 mmol) was heated at 110 °C for 12 h. After the solvent and excess dimethyl acetylenedicarboxylate were removed under vacuum, the oily residue was treated with ether (10 mL). **13** was obtained as an orange powder which was recrystallized from a toluene solution at room temperature (1.48 g, 85% yield): mp 180 °C dec; $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 2.12 (d, $J_{HH}$ = 6.5 Hz, C$H_3$CHN), 2.22 (d, $J_{HH}$ = 6.6 Hz, C$H_3$CHN), 2.37 (d, $J_{HH}$ = 6.5 Hz, C$H_3$CHN), 2.43 (d, $J_{HH}$ = 6.5 Hz, C$H_3$CHN), 2.59 (d, $J_{HH}$ = 6.5 Hz, C$H_3$CHN), 2.70 (d, $J_{HH}$ = 6.6 Hz, C$H_3$CHN), 2.85 (d, $J_{HH}$ = 6.6 Hz, C$H_3$CHN), 2.98 (d, $J_{HH}$ = 6.6 Hz, C$H_3$CHN), 4.39, 4.42 (s, $CH_3O$), 4.66 (d, $J_{PH}$ = 9.8 Hz, $CH_3OP$), 4.78 (d, $J_{HH}$ = 10.0 Hz, $CH_3OP$), 4.88, 4.90, 5.00, 5.22 (s, $CH_3O$), the $CH_3CHN$ cannot be described because of the $CH_3O$; $^{13}$C NMR ($CDCl_3$, 50.323 MHz) $\delta$ 19.18, 20.02, 20.34, 20.97, 21.16, 21.18, 21.50, 21.63, 22.44, 23.23, 23.31, 25.5 (s, $CH_3$CHN), 46.56, 49.47, 49.80, 50.28, 50.94, 51.15 (s, $CH_3$CHN), 51.52 (d, $J_{PC}$ = 4.8 Hz, $CH_3OP$), 53.53, 52.06, 52.20, 52.30, 52.43, 52.54, 52.75, 52.94, 53.27, 53.53 (s, $CH_3O$), 70.95 (d, $J_{PC}$ = 86.0 Hz), 73.61 (d, $J_{PC}$ = 108.9 Hz), 138.34 (d, $J_{PC}$ = 10.6 Hz), 140.67 (d, $J_{PC}$ = 134.2 Hz), 157.29 (d, $J_{PC}$ = 11.5 Hz), 161.32 (d, $J_{PC}$ = 13.5 Hz), 161.66 (d, $J_{PC}$ = 24.0 Hz), 161.97 (d, $J_{PC}$ = 10.8 Hz), 162.17 (d, $J_{PC}$ = 4.5 Hz), 163.81 (d, $J_{PC}$ = 6.2 Hz), 165.15 (d, $J_{PC}$ = 7.4 Hz), 165.86 (d, $J_{PC}$ = 3.3 Hz), 167.38 (d, $J_{PC}$ = 17.2 Hz), 167.56 (d, $J_{PC}$ = 16.2 Hz); $^{31}$P NMR ($CDCl_3$, 32.438 MHz) $\delta$ +42.62, +37.85; IR ($CDCl_3$) 1751, 1735, 1694 cm$^{-1}$ (CO); EIMS *m/z* 671 ($M^+$). Anal. Calcd for $C_{30}H_{46}N_3O_{12}P$: C, 53.64; H, 6.90; N, 6.25. Found: C, 53.54; H, 6.91; N, 6.30.

**Heterocycle 14.** A toluene solution of **6a** (0.90 g, 2.32 mmol) and methyl isothiocyanate (0.5 g, 6.8 mmol) was heated at 110 °C for 1 h. The solution was concentrated until a yellow solid precipitated (1–2 mL). After addition of ether (15 mL), the mixture was filtered and the residue was washed four times with ether (4 × 10 mL). **14** was obtained as a yellow powder (0.96 g, 90% yield): mp 157 °C; $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 1.12 (d, $J_{HH}$ = 7.0 Hz, 24 H, C$H_3$CHN), 3.21 (d, $J_{PH}$ = 6.2 Hz, 3 H, $NCH_3$), 3.53 (s, 3 H, $CH_3O$), 3.63 (sept d, $J_{PH}$ = 15.7 Hz, $J_{HH}$ = 7.0 Hz, 4 H, $CH_3CHN$), 3.64 (s, 3 H, $CH_3O$); $^{13}$C NMR ($CDCl_3$, 50.323 MHz) $\delta$ 23.04 (d, $J_{PC}$ = 3.0 Hz, $CH_3$CHN), 23.17 (d, $J_{PC}$ = 3.4 Hz, $CH_3$CHN), 38.53 (d, $J_{PC}$ = 4.4 Hz, $NCH_3$), 49.11 (d, $J_{PC}$ = 5.3 Hz, $CH_3$CHN), 51.13 (s, $CH_3O$), 52.10 (s, $CH_3O$), 81.51 (d, $J_{PC}$ = 153.6 Hz, PC), 158.90 (d, $J_{PC}$ = 7.4 Hz, CN), 165.61 (d, $J_{PC}$ = 12.9 Hz, CO), 166.49 (d, $J_{PC}$ = 18.8 Hz, CO), 188.88 (d, $J_{PC}$ = 3.6 Hz, CS); $^{31}$P NMR ($C_7H_8$, 32.438 MHz) $\delta$ +38.06; IR (neat) 1745, 1707 cm$^{-1}$ (CO); EIMS *m/e* 460 ($M^+$). Anal. Calcd for $C_{20}H_{37}N_4O_4PS$: C, 52.16; H, 8.10; N, 12.16. Found: C, 52.10; H, 8.02; N, 12.10.

**Heterocycle 15.** A toluene solution of **6a** (1.15 g, 2.97 mmol) and phenyl isocyanate (0.5 mL, 4.6 mmol) was heated at 110 °C for 15 h. After the solvent was removed under vacuum, the residue was washed four times with ether (4 × 10 mL). **15** was obtained as colorless crystals from a toluene-THF solution (0.99 g, 66% yield): mp 206–207 °C (dec); $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$ 0.98 (d, $J_{HH}$ = 6.8 Hz, 12 H, C$H_3$CHN), 1.21 (d, $J_{HH}$ = 6.8 Hz, 12 H, C$H_3$CHN), 3.59 (d, $J_{PH}$ = 0.3 Hz, 3 H, $CH_3O$), 3.74 (s, 3 H, $CH_3O$), 3.82 (sept d, $J_{PH}$ = 13.2 Hz, $J_{HH}$ = 6.8 Hz, 4 H, $CH_3CHN$), 7.15–7.32 (m, 5 H, $C_6H_5$); $^{13}$C NMR ($CDCl_3$, 50.323 MHz) $\delta$ 23.18 (d, $J_{PC}$ = 3.4 Hz, $CH_3$CHN), 23.97 (d, $J_{PC}$ = 4.4 Hz, $CH_3$CHN), 49.80 (d, $J_{PC}$ = 5.9 Hz, $CH_3CHN$), 50.85 (s, $CH_3O$), 52.14 (s, $CH_3O$), 79.90 (d, $J_{PC}$ = 153.1 Hz, PC), 127.61 (s, *p*-CH), 128.12 (d, $J_{PC}$ = 2.4 Hz, *m*-CH), 129.09 (s, *o*-CH), 137.25 (s, *i*-C), 158.76 (d, $J_{PC}$ = 1.8 Hz, CCN), 165.31 (d, $J_{PC}$ = 14.1 Hz, CO), 165.75 (d, $J_{PC}$ = 10.6 Hz, CO), 167.08 (d, $J_{PC}$ = 21.7 Hz, NCO); $^{31}$P NMR ($CH_2Cl_2$, 32.438 MHz) $\delta$ +43.80; IR (neat) 1739, 1693 (CO), 1660 cm$^{-1}$ (NCO). EIMS *m/e* 507 ($M^+ + 1$). Anal. Calcd for $C_{25}H_{39}N_4O_5P$: C, 59.27; H, 7.75; N, 11.05. Found: C, 59.26; H, 7.79; N, 11.10.

**Heterocycle 16.** A toluene solution of **6a** (1.00 g, 2.58 mmol) and trimethylsilyl isocyanate (0.380 mL, 2.80 mmol) was heated at 110 °C for 15 h. After exposure to air at room temperature for 24 h, the solvent was removed under vacuum. **16** was obtained as colorless crystals from a toluene/THF solution (0.55 g, 50% yield): mp 197 °C dec; $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 1.05 (d, $J_{HH}$ = 6.8 Hz, 12 H, C$H_3$CHN), 1.22 (d, $J_{HH}$ = 6.8 Hz, 12 H, C$H_3$CHN), 3.57 (s, 3 H, $CH_3O$), 3.79 (s, 3 H, $CH_3O$), 3.63 (sept d, $J_{PH}$ = 16.9 Hz, $J_{HH}$ = 6.9 Hz, 4 H, $CH_3CHN$), 10.68 (s, 1 H, NH); $^{13}$C NMR ($CDCl_3$, 50.323 MHz) $\delta$ 23.60 (d, $J_{PC}$ = 2.0 Hz, $CH_3$CHN), 23.80 (d, $J_{PC}$ = 2.0 Hz, $CH_3$CHN), 47.47 (d, $J_{PC}$ = 5.6 Hz, $CH_3CHN$), 51.73 (s, $CH_3O$), 53.75 (s, $CH_3O$), 89.03 (d, $J_{PC}$ = 118.8 Hz, PC), 153.69 (d, $J_{PC}$ = 4.7 Hz, CN), 154.73 (d, $J_{PC}$ = 11.3 Hz, NCO), 163.86 (d, $J_{PC}$ = 16.9 Hz, CO), 165.83 (d, $J_{PC}$ = 5.8 Hz, CO); $^{31}$P NMR ($CDCl_3$, 32.438 MHz) $\delta$ +23.88; IR ($CH_2Cl_2$) 3387 (NH), 1751, 1702 (CO), 1649 cm$^{-1}$ (NCO); FABMS (gly) *m/e* 431 (M + 1). Anal. Calcd for $C_{19}H_{35}N_4O_5P$: C, 53.01; H, 8.20; N, 13.02. Found: C, 52.91; H, 8.26; N, 12.91.

**Heterocycle 17.** A toluene solution of **6a** (1.00 g, 2.58 mmol) and trimethylsilyl isothiocyanate (0.395 mL, 2.80 mmol) was allowed to react at room temperature for 15 h. After exposure to air at room temperature for 24 h, the solvent was removed under vacuum. **17** was obtained as

pale-yellow crystals from a $CH_2Cl_2/Et_2O$ solution (0.54 g, 40% yield): mp 154 °C dec; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 1.05 (d, $J_{HH}$ = 6.8 Hz, 12 H, C$H_3$CHN), 1.22 (d, $J_{HH}$ = 6.8 Hz, 12 H, C$H_3$CHN), 3.67 (s, 3 H, $CH_3O$), 3.77 (sept d, $J_{PH}$ = 17.3 Hz, $J_{HH}$ = 6.9 Hz, 4 H, $CH_3CHN$), 3.87 (s, 3 H, $CH_3O$), 10.07 (s, 1 H, NH); $^{13}C$ NMR ($CDCl_3$, 50.323 MHz) $\delta$ 23.06 (d, $J_{PC}$ = 2.7 Hz, $CH_3CHN$), 23.53 (d, $J_{PC}$ = 2.4 Hz, $CH_3CHN$), 47.40 (d, $J_{PC}$ = 5.7 Hz, $CH_3CHN$), 51.72 (s, $CH_3O$), 53.66 (s, $CH_3O$), 90.55 (d, $J_{PC}$ = 116.7 Hz, PC), 150.06 (d, $J_{PC}$ = 7.5 Hz, CN), 162.31 (d, $J_{PC}$ = 14.9 Hz, CO), 165.15 (d, $J_{PC}$ = 4.9 Hz, CO), 176.60 (broad s, CS); $^{31}P$ NMR ($CDCl_3$, 32.438 MHz) $\delta$ +13.30; IR ($CH_2Cl_2$) 3362 (NH), 1750, 1707 $cm^{-1}$ (CO). Anal. Calcd for $C_{19}H_{35}N_4O_4PS$: C, 51.10; H, 7.90; N, 12.55. Found: C, 51.02; H, 7.82; N, 12.49.

**Cyclic Phosphonium Salt 18.** A dichloromethane solution of **14** (0.55 g, 1.20 mmol) and iodomethane (0.10 mL, 1.08 mmol) was allowed to react for 5 min at room temperature. After the solvent and excess iodomethane were removed under vacuum, the residue was washed three times with ether (3 × 10 mL). After crystallization in $CH_2Cl_2$ at −20 °C, **18** was obtained as a yellow solid (0.69 g, 95% yield): mp 119 °C dec; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 1.21 (d, $J_{HH}$ = 7.4 Hz, 12 H, C$H_3$-CHN), 1.25 (d, $J_{HH}$ = 7.3 Hz, 12 H, C$H_3$CHN), 2.52 (s, 3 H, $CH_3S$), 3.48 (d, $J_{PH}$ = 7.2 Hz, 3 H, $CH_3N$), 3.68 (sept d, $J_{PH}$ = 16.6 Hz, $J_{HH}$ = 7.3 Hz, 4 H, $CH_3CHN$), 3.72 (s, 3 H, $CH_3O$), 3.78 (s, 3 H, $CH_3O$); $^{13}C$ NMR ($CDCl_3$, 50.323 MHz) $\delta$ 16.49 (s, $CH_3S$), 23.13 (d, $J_{PC}$ = 3.1 Hz, $CH_3CHN$), 23.36 (d, $J_{PC}$ = 2.2 Hz, $CH_3CHN$), 37.00 (s, $NCH_3$), 50.30 (d, $J_{PC}$ = 5.0 Hz, $CH_3CHN$), 53.04 (s, $CH_3O$), 53.16 (s, $CH_3O$), 93.36 (d, $J_{PC}$ = 145.3 Hz, PC), 159.14 (d, $J_{PC}$ = 3.1 Hz, CN), 163.16 (d, $J_{PC}$ = 11.7 Hz, CO), 164.60 (d, $J_{PC}$ = 17.0 Hz, CO), 173.78 (s, $CSCH_3$); $^{31}P$ NMR ($CH_2Cl_2$, 32.438 MHz) $\delta$ +33.67; IR ($CDCl_3$) 1752, 1726, 1709 $cm^{-1}$ (CO). Anal. Calcd for $C_{21}H_{40}I\,N_4O_4PS$: C, 41.86; H, 6.69; N, 9.29. Found: C, 41.78; H, 6.74; N, 9.14.

**Cyclic Phosphonium Salt 19.** A dichloromethane solution of **15** (0.50 g, 0.99 mmol) and iodomethane (0.10 mL, 1.08 mmol) was allowed to react for 2 h at room temperature. After the solvent and excess iodomethane were removed under vacuum, **19** was obtained in pure form, according to NMR spectroscopy, as a yellow oil (0.58 g, 90% yield): $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 1.00 (d, $J_{HH}$ = 6.9 Hz, 12 H, C$H_3$CHN), 1.11 (d, $J_{HH}$ = 6.9 Hz, 12 H, C$H_3$CHN), 3.22 (s, 3H, $CH_3N$), 3.63 (sept d, $J_{PH}$ = 13.1 Hz, $J_{HH}$ = 6.9 Hz, 4 H, $CH_3CHN$), 3.67 (s, 3 H, $CH_3O$), 3.80 (s, 3 H, $CH_3O$), 7.20 (m, 5 H, $C_6H_5$); $^{13}C$ NMR ($CDCl_3$, 50.323 MHz) $\delta$ 23.55 (d, $J_{PC}$ = 3.7 Hz, $CH_3CHN$), 24.05 (d, $J_{PC}$ = 3.8 Hz, $CH_3CHN$), 36.31 (s, $NCH_3$), 50.97 (d, $J_{PC}$ = 5.7 Hz, $CH_3CHN$), 53.95 (s, $CH_3O$), 54.97 (s, $CH_3O$), 96.12 (d, $J_{PC}$ = 155.0 Hz, PC), 127.68 (s, *m*-CH), 129.81 (s, *i*-CH), 130.45 (s, *o*-CH), 133.90 (s, *p*-CH), 151.39 (d, $J_{PC}$ = 3.9 Hz, CN), 153.65 (d, $J_{PC}$ = 1.1 Hz, NCO), 160.63 (d, $J_{PC}$ = 18.8 Hz, CO), 161.72 (d, $J_{PC}$ = 10.3 Hz, CO); $^{31}P$ NMR ($CH_2Cl_2$, 32.438 MHz) $\delta$ +35.84.

**Solution and Refinement of Structures 5a, 12, 13, and 16.** Atomic scattering factors ($f'$,$f''$) were taken from a standard source.[29] The initial structural solutions were obtained by the SHELXS-86 direct method analysis. Atoms not located from the initial structure solution were found by successive difference Fourier maps with intervening cycles of least-squares refinement (SHELX-76). Crystallographic data are provided in Table 5. All non-hydrogen atoms were treated anisotropically. Full-matrix least-squares refinements were used in all cases. All hydrogen atoms were located by difference Fourier maps, and their positions were idealized in the subsequent cycles of refinement, except for the H atom bonded to N2 in **16**, which is involved in hydrogen bond donation to O1 of the centrosymmetric molecule. Final $R$ values are provided in Table 5.

**Acknowledgment.** Thanks are due to the DFG (Germany) and the University of Castilla-La-Mancha (Spain) for grants to K.B. and J.T., respectively, and to the CNRS for financial support of this work.

**Supplementary Material Available:** Tables of crystal and intensity collection data, positional and thermal parameters, interatomic distances and angles, least-squares planes equations, and torsion angles for **5a**, **12**, **13**, and **16** (28 pages); tables of observed and calculated structure factors, (53 pages). for **5a**, **12**, **13**, and **16** This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(29) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.