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Synthesis and Rearrangement of Diphosphorus Analogues of Amidinium Salts

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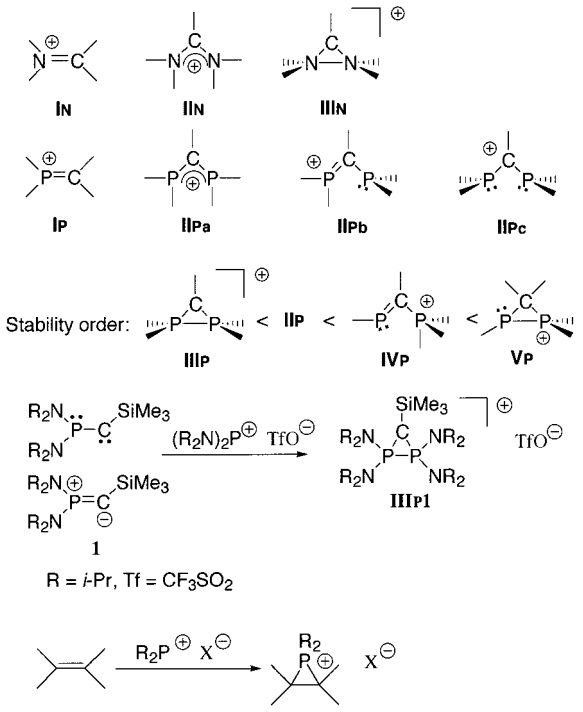
Abstract: Transient diphosphinocarbocations **IIP** are generated either by addition of phosphenium salts to the stable [bis(diisopropylamino)phosphino](silyl)carbene or by chloride abstraction from *C*-phosphino-*P*-chloro phosphorus ylides. In contrast to their nitrogen anlogues (amidinium salts) **IIN**, which feature a planar 3-center−4p-electron system, calculations show that **IIP** should exist as **IIPb**, in which one phosphorus is planar, while the other remains pyramidal. With small substituents at phosphorus, derivatives of type **IIP** rearrange by a 1,3-shift of a phosphorus substituent to the other phosphorus center to give *C*-phosphoniophosphaalkenes. When bulky substituents are present at phosphorus, derivatives **IIP** undergo ring closure, giving rise to the corresponding cyclic valence isomers **IIIP**, in which the carbon atom bears a negative charge. Diphosphinocarbocations **IIP** can be trapped by acetonitrile giving regioselectively the corresponding [2 + 3] cycloadduct.

Introduction

Nitrogen-substituted carbocations, namely the iminium **IN**, amidinium **IIN**, and guanidinium ions, are well-known stable species, which have found widespread use in synthetic chemistry, biological processes, and molecular materials science[1] (Scheme 1). Contrastingly, for the heavier analogues, only the "monophosphorus"-substituted cations, the highly reactive methylenephosphonium ions **IP**, have been isolated;[2] no experimental studies had been undertaken before this work[3] concerning the bis- and trisphosphinocarbenium ions.[4]

The origin of the stability of the aminocarbocations lies in the π-donation of the nitrogen lone pair into the formally unfilled 2p(π)-orbital of the adjacent carbon center, which overcompensates the σ-attracting effect due to the electronegativity of nitrogen. According to Schleyer et al.,[5] "the inherent π donor capabilities of the heavier elements are as large as or larger

Scheme 1



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(3) For a preliminary account of this work, see: Kato, T.; Gornitzka, H.; Baceiredo, A.; Schoeller, W. W.; Bertrand, G. *Science* **2000**, *289*, 754.
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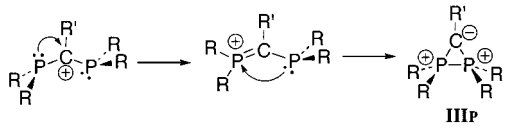
than their second row counterparts", and since phosphorus is more electropositive than carbon, and of course nitrogen, phosphinocarbocations should be more stable than their amino analogues. However, Schleyer et al also stated that "the apparently superior ability of nitrogen to act as a π donor is due, in part, to the ease in achieving the optimum planar configurations with sp^2 hybridization" (inversion barriers at B3LYP/6-31g* level: PH_3, 37.3 kcal mol^{-1}; NH_3, 5.8 kcal mol^{-1}).

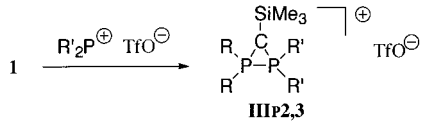
On the basis of calculated energies of isodesmic reactions, replacing one hydrogen atom of **IN** by an additional amino group further stabilizes the amidinium salt **IIN** by about 44 kcal/mol.[6] Interestingly, introduction of a second phosphino group only stabilizes **IIP** over **IP** by 12 kcal/mol.[7] Amidinium salts **IIN** adopt a planar structure due to the 3-center−4π-electron system, while it was predicted for **IIP** that a similar structure, **IIPa**, would not even be a minimum on the potential energy surface. Depending on the level of calculation, it was found that either one (**IIPb**)[8] or two phosphorus centers (**IIPc**)[7b] would be pyramidalized (Scheme 1). This is due to the electropositivity of the phosphino groups, which shifts a surplus of electron density to the central atom, preventing the π-donation and therefore the planarization of the phosphorus atom(s). Interestingly, calculations on the parent compounds showed that **IIP** was not the global minimum on the P_2CH_5 hypersurface.[7b] The unsymmetrical three-membered ring **VP** and the phosphoniophosphaalkene **IVP**[9] were found to be lower in energy than **IIP**, while the symmetrical three-membered heterocycle **IIIP** was predicted to be by far the least stable isomer. Surprisingly, we have recently found[3] that when a dichloromethane solution of bis(diisopropylamino)phosphenium trifluoromethanesulfonate[10] was added to a pentane solution of the carbene **1**[11] at 0 °C, neither **IIP1** nor its rearranged isomers **IVP1** and **VP1** were obtained, but instead, their three-membered heterocycle isomer **IIIP1** was isolated as extremely air-sensitive white crystals (66% yield) (Scheme 1).

This experimental observation is at first glance in total contradiction to the theoretical predictions drawn from the parent system P_2CH_5. Therefore, it was of interest to investigate the role of the substituents on the fate of the reaction. Moreover, two mechanisms could account for the formation of **IIIP1**. Indeed, phosphenium salts are known to react with multiple bonds to give the corresponding three-membered rings.[12] Since the phosphinocarbene **1** features phosphorus−carbon multiple bond character,[11c] the formation of compounds **IIIP1** might result from a concerted [2 + 1] cycloaddition. Alternatively, **IIIP1** could come from the ring closure of the primary formed allylic type cation **IIP1**. The demonstration of the latter hypothesis would prove that derivative **IIIP1** results from a "cascade stabilization" of the electron deficient carbocation center: the first phosphorus atom gives electrons to the carbocationic center and becomes positively charged and, therefore, highly electrophilic, and the second phosphorus atom then acts as a Lewis base toward the first. The overall process transforms the carbocationic center into a carbanionic center. Since this type of transformation is unlikely to be unique, it should be of significant synthetic utility (Scheme 2).

Scheme 2

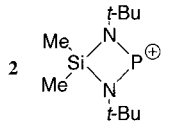


Scheme 3



IIIP2: R = N(*i*-Pr)$_2$, R' = N(*c*-hex)$_2$

IIIP3: R = N(*i*-Pr)$_2$, R' R' = -N(*t*-Bu)-SiMe$_2$-N(*t*-Bu)-



Here, we report evidence for the transient formation of bis(phosphino)carbocations of type **IIP**, as well as their rearrangement into isomers of types **IIIP** and **IVP**.

Results

Bis(dicyclohexylamino)phosphenium triflate and the cyclic phosphenium salt **2**[13] react with carbene **1** to give **IIIP2** and **IIIP3**, respectively (Scheme 3). Salt **IIIP2** was not stable enough to be isolated but was identified in solution by ^{31}P NMR spectroscopy. Indeed, its three-membered ring structure was clearly indicated by a characteristic high field[14] AB system centered at 8.0 ppm ($^1J_{PP}$ = 130 Hz). The triflate salt of heterocycle **IIIP3** was isolated as a yellow oil in 30% yield. Its ionic nature was indicated by its very low solubility in nonpolar solvents. Apart from the characteristic high-field ^{31}P NMR AB system at 7.5 ppm ($^1J_{PP}$ = 164 Hz), a doublet of doublets corresponding to the carbon bonded to the two phosphorus atoms was observed in the ^{13}C NMR spectrum (d_C = 67.7 ppm, J_{PC} = 5.2 and 7.1 Hz), confirming the presence of two magnetically nonequivalent phosphorus nuclei. A single-crystal X-ray diffraction analysis of the corresponding gallium tetrachloride salt definitively proved the structure (vide infra).

Since the abstraction of chloride from P-chloro phosphorus ylides is a known method for obtaining the corresponding methylenephosphonium salts **IP**,[2c] the *C*-phosphino-*P*-chloro phosphorus ylide **3** was prepared by adding 1 equiv of the corresponding chlorophosphine to a pentane solution of the carbene **1** (Scheme 4). [Note that the more crowded bis(diisopropylamino) and bis(dicyclohexylamino)chloro phosphines do not react with the carbene **1**.] Addition of aluminum

(6) Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1993**, *115*, 2362.
(7) (a) Frenking, G.; Fau, S.; Marchand, C. M.; Grützmacher, H. *J. Am. Chem. Soc.* **1997**, *119*, 6648. (b) Grützmacher, H.; Marchand, C. M. *Coord. Chem. Rev.* **1997**, *163*, 287.
(8) This work.
(9) A few examples of phosphoniophosphaalkenes **IVP** have been synthesized: Grützmacher, H.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 740.
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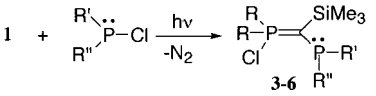
(12) Sanchez, M.; Mazières, M. R.; Lamandé, L.; Wolf, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M.; Schere, O., Eds.; Thieme: Stuutgart, 1990; pp 129−148.
(13) Veith, M.; Bertsch, B.; Huch, V. *Z. Anorg. Allg. Chem.* **1988**, *559*, 73.
(14) Mathey, F. *Chem. Rev.* **1990**, *90*, 997.

Scheme 4



R = *i*-Pr_2N

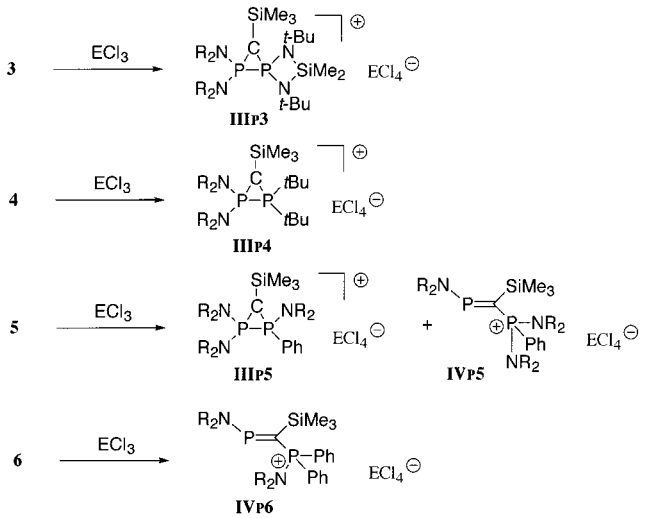
3: R′ R″ = -N(*t*-Bu)-$SiMe_2$-N(*t*-Bu)-

4: R′ = R″ = *t*-Bu

5: R′ = *i*Pr_2N, R″ = Ph

6: R′ = R″ = Ph

Scheme 5



R = *i*-Pr, E = Al or/and Ga

and gallium trichloride to phosphorus ylide **3** again leads to the formation of heterocyclic salts **IIIP3(AlCl$_4$)** and **IIIP3-(GaCl$_4$)**, respectively, which feature spectroscopic data identical with those of the previously isolated triflate salt (Scheme 5). The gallium salt was characterized by a single-crystal X-ray diffraction study (Figure 1, Table 1). Not surprisingly, the geometric parameters observed for **IIIP3** are very similar to those previously observed for **IIIP1**.[3] The carbon center is planar (sum of bond angles 359.9°), the P−P (2.12 Å) and P−C (1.74 and 1.71 Å) bond lengths being slightly shorter than would be expected for single bonds. The electronic structure of **IIIP1** has been discussed in details in the primary account of this work.[3]

The *C*-phosphino-*P*-chloro phosphorus ylides **4**−**6** were also synthesized in good yields by adding 1 equiv of the desired chlorophosphine to carbene **1** (Scheme 4). In the case of $Pr_2N(Ph)P-Cl$ and $^tBu_2P-Cl$, the reaction requires 3 days at room temperature and 1 week at 40 °C, respectively, while the diphenylchlorophosphine-derived ylide **6** was readily formed at low temperature. The di-*tert*-butylphosphino derivative **4** reacts at −78 °C with $GaCl_3$ to give, once again, the corresponding three-membered ring **IIIP4**. This compound has been fully characterized by multinuclear NMR spectroscopy. In contrast, addition of 1 equiv of $GaCl_3$ to the (diisopropylamino)-phenylphosphino derivative **5** afforded a mixture of three-membered ring **IIIP5** and *C*-phosphoniophosphaalkene **IVP5** in a 20/80 ratio (according to ^{31}P NMR spectroscopy). Both compounds were characterized in solution by NMR spectroscopy. In the ^{31}P NMR spectrum, the three-membered ring **IIIP5** displays a characteristic high-field AX-system at δ 8.5 and −68.5 ppm ($^2J_{PP}$ = 254.6 Hz), while **IVP5** gives the expected low-field AX-system at 66.7 (σ^4-P) and 343.3 ppm (σ^2-P) ($^2J_{PP}$ = 162.2 Hz). In the ^{13}C NMR spectrum, the signal for the P=C−P carbon atom is a doublet of doublets at 104.8 ppm ($^1J_{PC}$ = 70.6 and 72.4 Hz), lying in the range observed previously for similar compounds.[9,15] Last, in the case of the diphenylphosphino derivative **6**, the *C*-phosphonio phosphaalkene **IVP6** has been isolated in 55% yield as colorless crystals, with no trace of the isomeric three-membered ring of type **IIIP6** detectable (Scheme 5). The ^{31}P NMR spectrum for **IVP6** exhibited an AX system at 52.0 (σ^4-P) and 341.0 (σ^2-P) ppm ($^2J_{PP}$ = 154.2 Hz), while in the ^{13}C NMR spectrum the carbon atom bonded to the two phosphorus centers was observed as a doublet of doublets at 107.7 ($^1J_{PC}$ = 74.8 and 49.8 Hz).

In none of the reactions described above could the formation of the open form **IIP** be detected. However, when a dichloromethane solution of *C*-phosphino-*P*-chloro phosphorus ylide **6** was treated at −78 °C with gallium trichloride, in the presence of a large excess of acetonitrile, five-membered heterocycle **7** was cleanly obtained and isolated in 75% yield (Scheme 6). This compound was fully characterized in solution and by a single-crystal X-ray diffraction study (Figure 2, Table 1). We

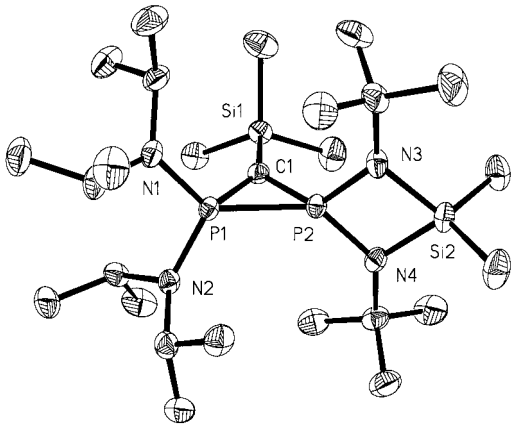


Figure 1. Solid-state structure of compound **IIIP3**. Selected bond lengths (Å) and angles (deg): P(1)−P(2), 2.1209(12); P(1)−C(1), 1.737(3); P(2)−C(1), 1.706(3); C(1)−Si(1), 1.872(3); P(1)−N(1), 1.664(3); P(1)−N(2), 1.661(3); P(2)−N(3), 1.671(3); P(2)−N(4), 1.669(3); P(1)−C(1)−P(2), 76.05(14); P(1)−C(1)−Si(1), 147.3(2); P(2)−C(1)−Si(1), 136.6(2); C(1)−P(1)−P(2), 51.30(11); C(1)−P(2)−P(1), 52.65(12).

Table 1. Crystallographic Data for Compounds **IIIP3** and **7**

	IIIP3	7
formula	$C_{26}H_{61}Cl_4GaN_4Si_2P_2$	$C_{30}H_{50}Cl_4GaN_3P_2Si$
formula weight	759.43	754.28
cryst system, space group	monoclinic, $P2_1/c$	triclinic, P-1
a, Å	9.9435(4)	11.103(2)
b, Å	21.9177(8)	12.865(3)
c, Å	18.3228(7)	14.354(3)
α, deg		93.476(3)
β, deg	90.2780(10)	104.064(3)
γ, deg		107.433(3)
V, Å^3	3993.2(3)	1877.8(7)
Z	4	2
d_{calcd}, Mg/m^3	1.263	1.334
absorp coeff, mm^{-1}	1.119	1.158
no. total reflections	52994	17042
no. unique reflections	5716	9383
R_1 ($I > 2\sigma(I)$)	0.0469	0.0316
wR2,[a] (all data)	0.1192	0.0834
(Δ/ρ)$_{max}$ [e Å^{-3}]	0.453 and −0.604	0.922 and −0.643

[a] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$.

(15) Markovskii, L. N.; Romanenko, V. D.; Ruban, A. V. *Chemistry of Acyclic Compounds of Two-Coordinate Phosphorus*; Naukova Dumka: Kiev, 1988.

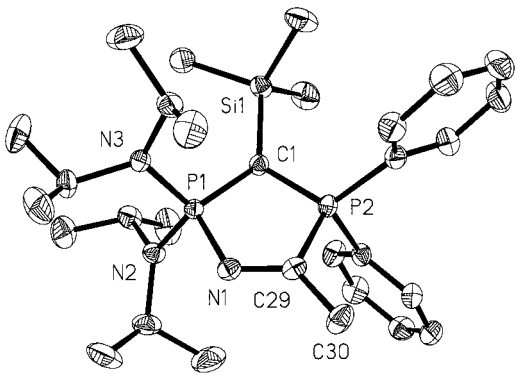
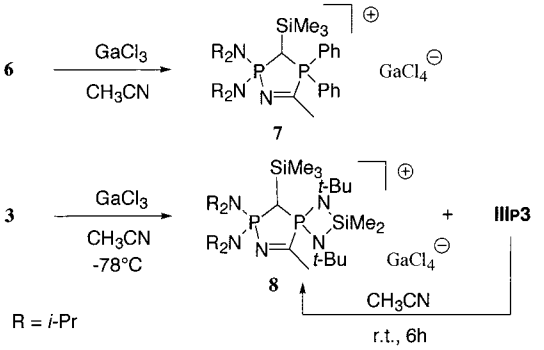


Figure 2. Solid-state structure of compound **7**. Selected bond lengths (Å) and angles (deg): P(1)−C(1), 1.7274(16); P(2)−C(1), 1.7046(16); C(1)−Si(1), 1.8653(16); P(1)−N(1), 1.7102(14); P(2)−C(29), 1.8613(17); N(1)−C(29), 1.273(2); C(29)−C(30), 1.492(2); P(1)−C(1)−P(2), 105.95(8); P(1)−C(1)−Si(1), 131.04(9); P(2)−C(1)−Si(1) 122.56(9); P(1)−N(1)−C(29), 114.55(11); N(1)−C(29)−P(2), 113.79(12); C(29)−P(2)−C(1), 99.60(7).

Scheme 6



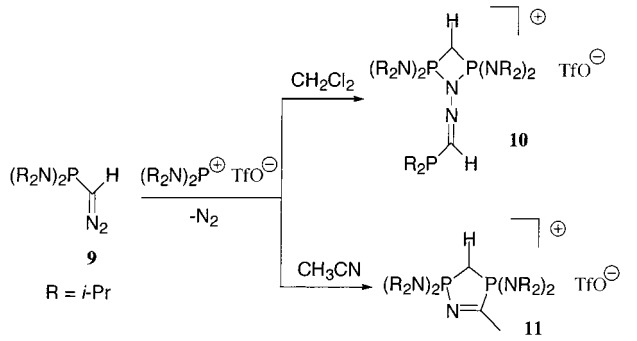
have checked that the *C*-phosphoniophosphaalkene **IVP6** did not react with acetonitrile.

When the reaction of *C*-phosphino-*P*-chloro phosphorus ylide **3** with gallium trichloride, in the presence of a large excess of acetonitrile, was monitored at −78 °C by ^{31}P NMR spectroscopy, a 1/1 mixture of **IIIP3** and the five-membered heterocycle **8** was obtained (Scheme 6). After stirring of the reaction mixture at room temperature for 6 h, the three-membered heterocycle **IIIP3** was totally transformed into **8**. We have checked that **IIIP3** does not react with acetonitrile at −78 °C, but it appears that it does react at room temperature, cleanly affording **8** after 6 h. Note that **IIIP1** (diisopropylamino substituents at both phosphorus) does not react with acetonitrile, even under heating at 50 °C for 12 h; under more drastic conditions, decomposition of **IIIP1** occurred.

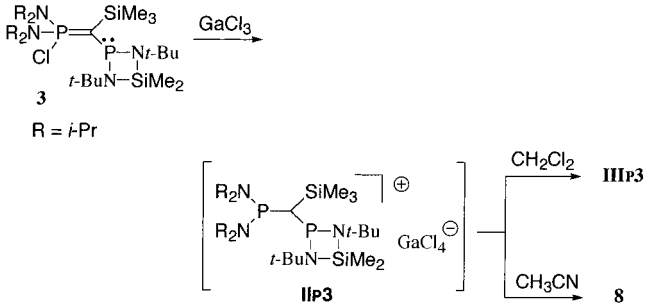
Evolution of nitrogen was observed when the bis(diisopropylamino)phosphenium salt was added at −78 °C to a dichloromethane solution of the bis(diisopropylamino)phosphinodiazomethane **9**. After workup, the heterocyclic salt **10** was isolated in 62% yield (Scheme 7). The ^{31}P NMR spectrum show two singlets at 53.1 and 46.0 ppm in a 1/2 ratio, while in the ^{13}C NMR spectrum, a triplet at 17.0 ppm (J_{PC} = 148.1 Hz) suggested the presence of an ylidic carbon bonded to two magnetically equivalent phosphorus nuclei. The PC(H)P skeleton was confirmed by a triplet at 1.64 ppm (J_{PH} = 12.5 Hz) in the ^{1}H NMR spectrum. The azine proton was apparent by the presence of a doublet at 7.85 ppm (J_{PH} = 148.1 Hz), while the corresponding carbon atom gave a broad doublet at 159.6 ppm.

When the same reaction was carried out in acetonitrile, the formation of **10** was totally inhibited and the adduct **11** was

Scheme 7



Scheme 8



cleanly obtained (66% yield). Note that, as in the previous reactions leading to **7** and **8**, only one regioisomer is formed.

Discussion

As mentioned in the Introduction, the formation of **IIIP2** and **IIIP3** by addition of a phosphenium salt to the carbene **1** could have been rationalized by a concerted [2 + 1] cycloaddition involving the multiple bond character of the carbene. However, the formation of **IIIP3** by chloride abstraction from the *C*-phosphino-*P*-chloro phosphorus ylide **3** (Scheme 5) clearly demonstrates that the open form of type **IIP** is indeed the intermediate leading to the heterocyclic system. This is confirmed by the formation of the five-membered heterocycle **8** (Scheme 6), which results from a [3 + 2] cycloaddition of **IIP3** with acetonitrile (Scheme 8). Note that although **IIIP3** slowly reacts at room temperature with acetonitrile to give **8**, no reaction occurred at −78 °C, which proves the involvement of **IIP3** in the low-temperature experiment, but does not exclude a possible equilibrium between **IIP3** and **IIIP3**, at room temperature.

To gain more insight into the electronic structure of species **IIP**, ab initio calculations at the B3LYP/6-31 g* level[16] with additional zero-point vibrational energy correction were performed on the model compound **IIIP7** (SiH_3 at carbon and NH_2 at phosphorus). As predicted by the previous calculations on the parent compounds, we found that the open planar form (C_{2v} symmetry) of type **IIP7a**, analogous to that of amidinium salts

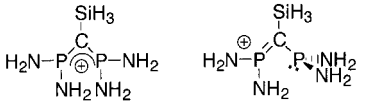
(16) All quantum chemical calculations were performed at the B3LYP/6-31g* level with the Gaussian-98 set of programs: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Gammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J. Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.

Table 2. Energy between Both Valence Isomers: **IIPb** and **IIIP**

C substituent	P substituents	ΔE (kcal/mol)[a]
NH_2	NH_2	only **IIPb** is stable
H	H	34.6
H	NH_2	3.7
CH_3	NH_2	6.5
SiH_3	NH_2	5.8
$SiMe_3$	N^iPr_2	−6.1

[a] $E_{ring} - E_{allyl}$.

IIN, is not a minimum on the potential energy surface. This illustrates the striking difference between the chemistry of phosphorus and nitrogen (Scheme 1). However, pyramidalization of one of the phosphorus atoms leads to **IIP7b**, which is not only an energy minimum but also lower in energy than the cyclic form **IIIP7** by 5.8 kcal/mol.



IIP7a **IIP7b**

From Scheme 5, it is clear that the evolution of the open form of type **IIP** is strongly dependent on the nature of the substituents. The calculations indicate that **IIP7** prefers to rearrange to the *C*-phosphoniophosphaalkene form **IVP7**, which is much lower in energy than **IIIP7**. To understand the factors that allow for the formation of the cyclic isomer of type **IIIP**, calculations were performed with varying substitution patterns (Table 2). The given values have been verified by the corresponding vibrational analysis (at the density functional level) as energy minima on the electronic hypersurfaces (except for $SiMe_3$ at carbon and N^iPr_2 at phosphorus, for which a vibrational analysis is prohibited due the size of the structure). Somewhat surprising is the almost negligible effect of the carbon substituent on going from H to CH_3 and SiH_3; of course, with an amino group at carbon, the three-membered ring is no longer a minimum, because of stabilization of the positive charge by the amino group, giving rise to an iminium structure. Amino substituents at the phosphorus atoms favor the ring structure. This is due to the σ-withdrawing effect of the amino group, which increases the tendency for pyramidalization at phosphorus. As a consequence, the open structure is destabilized and the energy difference between structures **IIP** and **IIIP** decreases; isomers **IIP** stay lower in energy than **IIIP**, except for **IIIP1** (observed experimentally). The only reasonable explanation to rationalize the reverse order of stability of **IIP** and **IIIP**, when replacing NH_2 by the bulky N^iPr_2 substituents at phosphorus, is to believe that the steric demand in the linear form is larger than in the cyclic system (Figure 3). This is in line with the experimental observation of cyclic derivatives **IIIP2**−**5**.

From the calculations and the experimental results, it appears that intermediates **IIP** easily rearrange via 1,3-shift of a P-substituent to the other phosphorus atom, giving **IVP**, except when bulky substituents are present at both phosphorus, since the phosphorus centers cannot accommodate a further substituent anymore. However, in this case, the three-membered ring structure **IIIP** is favored with respect to the open form **IIP**. Since the carbon substituent has apparently no effect on the relative stability of compounds **IIP** and **IIIP**, a possibility to enable the isolation of the open form was to decrease the steric

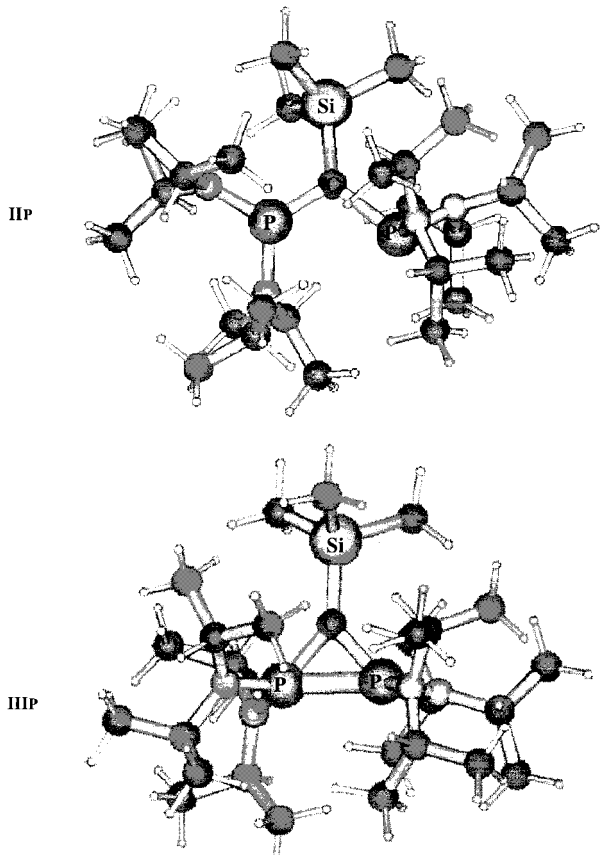


Figure 3. Optimized geometries of **IIP1** and **IIIP1**.

hindrance at the carbon center. The results described in Scheme 7 demonstrate the difficulty of the task, which is due to the high reactivity of the diphosphinocarbocation **IIP**. Indeed, **10** obviously results from a [3 + 1] cycloaddition reaction involving the open form **IIP9** and the starting diazo precursor **9**. This is further demonstrated by the reaction in acetonitrile, which leads to the [3 + 2] cycloadduct **11**. All attempts to spectroscopically observe **IIP9** failed, but in agreement with our hypothesis, no 1,3-shift is observed, nor is the formation of the corresponding three-membered heterocycle.

The regioselectivity of the cycloaddition reations leading to **7** and **8** can be explained by the different nature of the two phosphorus atoms. The amino substituents stabilize the positive charge at phosphorus, and therefore, the amino-substituted phosphorus is the electrophilic site of the molecule and reacts with the nitrogen end of acetonitrile. This is also true for **8**, for which the silicon atom of the four-membered ring makes the nitrogen less of a π-donor.

Conclusion

Diaminocarbocations **IIN** (amidinium salts) have a planar allylic-type structure featuring a 3-center−4p-electron system. In contrast, the diphosphinocarbocations **IIP** should exist as **IIPb**, in which one phosphorus is planar, while the other remains pyramidal.

Whenever one of the phosphorus ends can accommodate a further substituent, derivatives **IIP** rearrange into the thermodynamically more stable phosphoniophosphaalkenes **IVP**. This 1,3-shift is prevented when sterically hindered substituents are used at both phosphorus atoms, but in this case the diphosphi-

nocarbocations **IIP** undergo a ring closure into three-membered heterocycles **IIIP** featuring a carbanionic center. This is due to the fact that the steric demand in the linear form is larger than in the cyclic system. This type of transformation of a cationic into an anionic center is unlikely to be unique and should be of significant synthetic utility.

Interestingly, intermediates **IIP** appear to be highly reactive 1,3-dipoles, which can be efficiently trapped by acetonitrile, leading regioselectively to the corresponding five-membered heterocycles. Since intermolecular trapping reactions are faster than both the 1,3-shift and the ring closure, one can conclude that diphosphinocarbocations possess a non-negligible lifetime. However, all our attempts to spectroscopically characterized a compound of type **IIP** failed, and this remains an exciting challenge.

Experimental Section

All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^{1}H, ^{13}C, ^{19}F, ^{29}Si, and ^{31}P NMR spectra were recorded on Bruker AC200, WM250, or AMX400 spectrometers. ^{1}H, ^{13}C, and ^{29}Si chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to an external standard of 85% H_3PO_4.

Synthesis of Three-Membered Heterocycles IIIP1−3, by Addition of the Corresponding Phosphenium Salts to the Carbene 1. In a typical experiment, a CH_2Cl_2 solution (2.5 mL) of 1 equiv of phosphenium trifluoromethane sulfonate was added to a pentane solution (5 mL) of the carbene **1** (0.3 mmol) at 0 °C. After the solution mixture had been stirred for 30 min at room temperature, the solvent was removed under vacuum. Derivative **IIIP1** was isolated as a white powder by adding Et_2O (5 mL) to the residue and recrystallized from a THF solution at −5 °C (66% yield). Heterocycle **IIIP2** was only characterized in solution, while **IIIP3** was isolated as a yellow oil in 30% yield. The latter compound was fully characterized with $GaCl_4^-$ as counterion (vide infra).

IIIP1: mp 89−90 °C;^{31}P{^{1}H} NMR ($CDCl_3$) δ 7.3; ^{29}Si{^{1}H} NMR ($CDCl_3$) δ −10.7 (t, $^2J_{PSi}$ = 10.6 Hz); ^{1}H NMR ($CDCl_3$) δ 0.22 (s, 9 H, $SiCH_3$), 1.34 (d, $^3J_{HH}$ = 6.7 Hz, 24 H, $CHCH_3$), 1.38 (d, $^3J_{HH}$ = 6.7 Hz, 24 H, $CHCH_3$), 3.83 (sept t, $^3J_{HH}$ = 6.7 Hz, $^3J_{HP}$ = $^4J_{HP}$ = 6.9 Hz, 8 H, NCH); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 2.9 (t, $^3J_{PC}$ = 4.1 Hz, $SiCH_3$), 23.9 (t_{like}, $^3J_{PC}$ = $^4J_{PC}$ = 3.1 Hz, $CHCH_3$), 25.1 (t_{like}, $^3J_{PC}$ = $^4J_{PC}$ < 2 Hz, $CHCH_3$), 49.3 (s, NCH), 49.6 (t, $^1J_{PC}$ = 7.3 Hz, C−$SiMe_3$), 120.6 (q, $^1J_{FC}$ = 320.1 Hz, CF_3). Anal. Calcd for $C_{29}H_{65}N_4O_3F_3SiP_2S$: C, 49.98; H, 9.40; N, 8.04. Found: C, 50.17; H, 9.48; N, 8.24.

IIIP2: ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 9.0 and 7.1 ($^1J_{PP}$ = 130 Hz).

IIIP3: vide infra.

Preparation of *C*-Phosphino-*P*-Chloro Phosphorus Ylides 3−6. In a typical experiment, a pentane solution (2 mL) of 1 equiv of chlorophosphine was added to a pentane solution (3 mL) of the carbene **1** (0.3 mmol) at −78 °C. The reaction was monitored by ^{31}P NMR spectroscopy. Ylides **3** and **6** were readily obtained after the solution mixture was warmed to room temperature. In the case of the more crowded chlorophosphines [(^{i}Pr$_2$N)PhPCl and ^{t}Bu$_2$PCl], the reaction was complete after 3 days at room temperature and 1 week at 40 °C, respectively. After filtration, the solution mixture was concentrated and the corresponding ylides **3**, **4**, and **6** were obtained by slow crystallization at −20 °C, and derivative **5** was obtained as an oil.

3: white crystals (52%); mp 175 °C (dec);^{31}P{^{1}H} NMR ($CDCl_3$) δ 84.2 and 143.8 ($^2J_{PP}$ = 189.6 Hz); ^{1}H NMR ($CDCl_3$) δ 0.30 (s, 3 H, $SiCH_3$), 0.37 (s, 9 H, $SiCH_3$), 0.39 (s, 3 H, $SiCH_3$), 1.18−1.45 (m, 42 H, CH_3), 3.86−4.41 (m, 4 H, NCH); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 6.1 (d, J_{PC} = 4.5 Hz, $SiCH_3$), 6.3 (s, $SiCH_3$), 7.6 (d, J_{PC} = 5.1 Hz, $SiCH_3$), 23.2−26.5 (m, $CHCH_3$), 32.2 (d, J_{PC} = 5.3 Hz, CCH_3), 48.6 and 49.4 (s broad, CHN), 50.9 (d, J_{PC} = 14.8 Hz, CCH_3), 58.3 (dd, J_{PC} = 115.5 and 92.9 Hz, PCP). Anal. Calcd for $C_{26}H_{61}N_4Si_2P_2Cl$: C, 53.53; H, 10.54; N, 9.60. Found: C, 53.68; H, 10.46; N, 9.48.

4: ^{31}P{^{1}H} NMR ($CDCl_3$) δ 40.2 and 90.1 (AX system, $^2J_{PP}$ = 257.4 Hz).

5: yellow oil. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 50.5 and 84.2 ($^2J_{PP}$ = 246.3 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 5.9 (d, J_{PC} = 4.7 Hz, $SiCH_3$), 23.7 (s, J_{PC} = 6.4 Hz, $CHCH_3$), 24.2 (d, J_{PC} = 7.3 Hz, $CHCH_3$), 24.7 (d, J_{PC} = 3.1 Hz, $CHCH_3$), 24.8 (d, J_{PC} = 2.3 Hz, $CHCH_3$), 24.9 (s, $CHCH_3$), 35.6 (dd, J_{PC} = 119.4 and 45.3 Hz, PCP), 46.3(s, CHN), 49.0 (d, J_{PC} = 6.8 Hz, CHN), 49.3 (d, J_{PC} = 5.4 Hz, CHN), 125.2 (d, J_{PC} = 1.7 Hz, C_{aro}), 126.8 (d, J_{PC} = 3.4 Hz, C_{aro}), 131.3 (d, J_{PC} = 19.5 Hz, C_{aro}), 148.0 (t_{like}, J_{PC} = 20.0 Hz, C_{aro}).

6: white crystals (82%); mp 65−69 °C; ^{31}P{^{1}H} NMR ($CDCl_3$) δ 0.3 and 86.5 ($^2J_{PP}$ = 228.6 Hz); ^{1}H NMR ($CDCl_3$) δ −0.11 (s, 9 H, $SiCH_3$), 1.20 (d, $^3J_{HH}$ = 7.0 Hz, 12 H, $CHCH_3$), 1.44 (d, $^3J_{HH}$ = 7.0 Hz, 12 H, $CHCH_3$), 4.21 (sept d, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 14.0 Hz, 4 H, NCH), 7.20−7.47 (m, 10 H, H_{aro}); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 4.3 (s, $SiCH_3$), 23.8 (d, J_{PC} = 3.3 Hz, $CHCH_3$), 23.9 (d, J_{PC} = 3.1 Hz, $CHCH_3$), 24.5 (d, J_{PC} = 3.8 Hz, $CHCH_3$), 24.6 (d, J_{PC} = 3.9 Hz, $CHCH_3$), 26.3 (dd, J_{PC} = 134.6 and 23.4 Hz, PCP), 49.2 (d, $^2J_{PC}$ = 5.3 Hz, CHN), 127.4 (d, J_{PC} = 4.0 Hz, C_{aro}), 132.1 (d, J_{PC} = 19.6 Hz, C_{aro}), 134.3 (t, J_{PC} = 13.0 Hz, C_{aro}), 143.0 (t, J_{PC} = 19.4 Hz, C_{aro}). Anal. Calcd for $C_{28}H_{47}N_2SiP_2Cl$: C, 62.61; H, 8.82; N, 5.21. Found: C, 62.42; H, 8.71; N, 5.25.

Synthesis of Three-Membered Heterocycles IIIP3−5 and Phosphoniophosphaalkene IVP5,6 by Chloride Abstraction from Ylides 3−6. In a typical experiment, a CH_2Cl_2 solution (3 mL) of 1 equiv of $AlCl_3$ or $GaCl_3$ was added to a CH_2Cl_2 solution (5 mL) of ylide (0.3 mmol) at −78 °C. After the mixture had been stirred for 1 h at room temperature, the solvent was removed under vacuum. Heterocycle **IIIP3** was slowly crystallized from a CH_2Cl_2 solution at −30 °C, while **IIIP4** was obtained as an oil. Derivatives **IIIP5** and **IVP5** were characterized in the solution mixture. The phosphoniophosphaalkene **IVP6** was crystallized from a CH_2Cl_2/toluene solution at −20 °C.

IIIP3($GaCl_4$): colorless crystals (39%); mp 100 °C (dec);^{31}P{^{1}H} NMR (CD_2Cl_2) δ 8.0 and 6.9 ($^1J_{PP}$ = 164.0 Hz); ^{29}Si{^{1}H} NMR ($CDCl_3$) δ −10.4 (t_{like}, $^2J_{PSi}$ = 10.6 Hz $CSiCH_3$), 6.3 (t_{like}, $^2J_{PSi}$ = 2.5 Hz $NSiCH_3$); ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 9 H, $CSiCH_3$), 0.60 (s, 3 H, $NSiCH_3$), 0.62 (s, 3 H, $NSiCH_3$), 1.39 (s, 18 H, CCH_3), 1.41 (d, $^3J_{HH}$ = 7.0 Hz, 12 H, $CHCH_3$), 1.43 (d, $^3J_{HH}$ = 7.0 Hz, 12 H, $CHCH_3$), 3.71 (sept, $^3J_{HH}$ = 7.0 Hz, NCH); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 2.5 (t_{like}, $^3J_{PC}$ = 4.3 Hz, $CSiCH_3$), 4.2 (s, $NSiCH_3$), 5.2 (dd, J_{PC} = 5.0 and 7.9 Hz, $NSiCH_3$), 23.4 (t_{like}, $^3J_{PC}$ = 3.4 Hz, $CHCH_3$), 24.8 (t_{like}, $^3J_{PC}$ = 2.6 Hz, $CHCH_3$), 32.7 (t_{like}, $^3J_{PC}$ = 3.6 Hz, $NCCH_3$), 49.6 (s, NCH), 54.1 (s, $NCCH_3$), 67.7 (dd, $^1J_{PC}$ = 5.2 and 7.1 Hz, PC). Anal. Calcd for $C_{26}H_{61}N_4Si_2P_2GaCl_4$: C, 41.12; H, 8.10; N, 7.38. Found: C, 41.33; H, 8.15; N, 7.35.

IIIP4($GaCl_4$): yellow oil (60%). ^{31}P{^{1}H} NMR ($CDCl_3$) δ −21.5 and 10.4 ($^1J_{PP}$ = 136.0 Hz); ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 9 H, $CSiCH_3$), 1.40 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $CHCH_3$), 1.43 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $CHCH_3$), 1.44 (s, 9 H, CCH_3), 1.53 (s, 9 H, CCH_3), 3.95 (sept d, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 1.8 Hz, NCH); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 3.4 (dd, $^3J_{PC}$ = 1.8 and 2.8 Hz, $SiCH_3$), 23.5 (d, $^3J_{PC}$ = 6.4 Hz, $CHCH_3$), 24.9 (dd, $^3J_{PC}$ = 2.8 and 4.6 Hz, $CHCH_3$), 29.9 (t_{like}, $^3J_{PC}$ < 1.8 Hz, CCH_3), 50.6 (d, $^2J_{PC}$ = 5.5 Hz, NCH), 43.9 (dd, J_{PC} = 8.3 and 2.7 Hz, $PCCH_3$).

IIIP5($AlCl_4$): ^{31}P{^{1}H} NMR ($CDCl_3$) δ −68.0 and 8.5 ($^1J_{PP}$ = 254.5 Hz).

IVP5($AlCl_4$): ^{31}P{^{1}H} NMR ($CDCl_3$) δ 66.7 and 343.3 ($^1J_{PP}$ = 162.2 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 104.8 (dd, J_{PC} = 70.6 and 72.4 Hz, PCP),

IVP6($AlCl_4$): Colorless crystals (55% yield); mp 96−97 °C; ^{31}P-{^{1}H} NMR ($CDCl_3$) δ 52.0 and 341.0 ($^2J_{PP}$ = 152.6 Hz); ^{1}H NMR ($CDCl_3$) δ −0.10 (s, 9 H, $SiCH_3$), 1.11 (d, 12 H, J_{HH} = 6.8 Hz, CH_3), 1.38 (d, 12 H, J_{HH} = 6.7 Hz, CH_3), 3.47 (d sept, 2 H, J_{HH} = 6.8 Hz, J_{PH} = 15.4 Hz, NCH), 4.38 (m, 2 H, NCH), 7.70−8.13 (m, 10 H, H_{aro});

$^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 3.4 (s, Si*C*H_3), 23.5 (dd, J_{PC} = 3.3 and 1.9 Hz, CH*C*H_3), 24.9 (m, CH*C*H_3), 51.1 (dd, J_{PC} = 1.9 and 3.6 Hz, CHN), 53.5 (m, CHN), 102.7 (dd, J_{PC} = 49.8 and 74.8 Hz, PCP), 126.5 (dd, J_{PC} = 105.4 and 3.8 Hz, C_i), 129.7 (d, J_{PC} = 11.1 Hz, C_o), 133.0 (s broad, C_m), 134.5 (s, C_p). Anal. Calcd for $C_{28}H_{47}N_2SiP_2AlCl_4$: C, 50.15; H, 7.06; N, 4.18. Found: C, 50.20; H, 7.14; N, 4.24.

Five-Membered Heterocycle 7. To a CH_2Cl_2 solution (2 mL) of ylide **6** (0.11 g, 0.21 mmol) was added a CH_3CN solution of $GaCl_3$ (0.04 g, 0.23 mmol) at −78 °C. After the solution was warmed slowly to room temperature, the solvent was removed under vacuum, and the residue was washed with ether. Derivative **7** was recrystallized from a CH_2Cl_2/ether solution at −20 °C. (0.12 g, 75%): mp 77−78 °C; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 40.1 and 87.9 ($^2J_{PP}$ = 124.4 Hz); ^1H NMR ($CDCl_3$) δ 0.06 (s, 9 H, $SiCH_3$), 1.34 (d, $^3J_{HH}$ = 7.1 Hz, 12 H, CHC*H*$_3$), 1.38 (d, $^3J_{HH}$ = 7.1 Hz, 12 H, CHC*H*$_3$), 2.60 (dd, J_{PH} = 7.1 and 2.1 Hz, 3 H, N=CC*H*$_3$), 4.15 (sept d, $^3J_{HH}$ = 7.1 Hz, $^3J_{PH}$ = 13.9 Hz, 4 H, NCH), 7.60−7.80 (m, 10 H, H_{aro}); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 1.0 (s, Si*C*H_3), 2.3 (d, $^3J_{PC}$ = 3.4 Hz, N=C*C*H_3), 24.3 (d, J_{PC} = 3.0 Hz, CH*C*H_3), 24.7 (d, J_{PC} = 3.0 Hz, CH*C*H_3), 48.9 (d, $^2J_{PC}$ = 5.7 Hz, CHN), 122.9 (dd, J_{PC} = 79.3 and 8.1 Hz, C_i), 130.3 (d, J_{PC} = 12.0 Hz, C_o), 133.0 (d, J_{PC} = 10.9 Hz, C_m), 134.9 (d, J_{PC} = 3.3 Hz, C_p), 181.0 (d, J_{PC} = 33.5 Hz, C=N), PCP carbon was not observed.

Five-Membered Heterocycle 8. To a CH_2Cl_2 solution (2 mL) of ylide **3** (0.16 g, 0.27 mmol) was added an acetonitrile solution of $GaCl_3$ (0.05 g, 0.27 mmol) at −78 °C. The cold bath was removed and the solution mixture was stirred at room temperature for 6 h. Then, the solvent was removed under vacuum, and the residue was washed with ether. Derivative **8** was recrystallized from a CH_2Cl_2/ether solution at −20 °C (0.05 g, 25%): mp 192 °C (dec); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 50.7 and 79.3 ($^2J_{PP}$ = 129.0 Hz); ^1H NMR ($CDCl_3$) δ 0.04 (s, 9 H, $SiCH_3$), 0.71 (s, 3 H, $NSiCH_3$), 0.83 (s, 3 H, $NSiCH_3$), 1.30 (s, 18 H, $NCCH_3$), 1.36 (d, $^3J_{HH}$ = 7.1 Hz, 12 H, CHC*H*$_3$), 1.40 (d, $^3J_{HH}$ = 7.1 Hz, 12 H, CHC*H*$_3$), 2.57 (dd, J_{PH} = 7.1 and 2.0 Hz, 3 H, N=CC*H*$_3$), 3.93 (sept d, $^3J_{HH}$ = 7.1 Hz, $^3J_{PH}$ = 10.7 Hz, 4 H, NCH); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 3.3 (t, J_{PC} = 4.3 Hz, $CSiCH_3$), 4.6 (s, Si*C*H_3), 5.1 (m, NSi*C*H_3), 20.7 (t, J_{PC} = 29.4 Hz, N=C*C*H_3), 24.8 (d, J_{PC} = 3.7 Hz, CH*C*H_3), 25.0 (d, J_{PC} = 5.5 Hz, CH*C*H_3), 32.4 (d, J_{PC} = 2.6 Hz, C*C*H_3), 49.0 (d, $^2J_{PC}$ = 6.4 Hz, CHN), 53.3 (s, N*C*CH_3), 189.0 (dd, J_{PC} = 48.7 and 1.8 Hz, C=N), PCP carbon was not observed.

Four-Membered Heterocycle 10. To a CH_2Cl_2 solution (5 mL) of bis(diisopropylamino)phosphinodiazomethane **9** (0.14 g, 0.48 mmol) was added a dichloromethane solution (1 mL) of bis(diisopropylamino)-phosphenium salt (0.09 g, 0.24 mmol) at 0 °C. After the solution was warmed slowly to room temperature, the solvent was removed under vacuum, and the residue was washed with ether. Heterocycle **10** was recrystallized from a CH_2Cl_2/toluene solution at −30 °C (0.11 g, 62%): mp 118−120 °C; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 46.0 (s, 2 P) and 53.1 (s, 1 P); ^1H NMR ($CDCl_3$) δ 1.09 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, CHC*H*$_3$), 1.18 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, CHC*H*$_3$), 1.34 (d, $^3J_{HH}$ = 7.0 Hz, 24 H, CHC*H*$_3$), 1.36 (d, $^3J_{HH}$ = 7.0 Hz, 24 H, CHC*H*$_3$), 1.64 (t, $^2J_{PH}$ = 12.5 Hz, 1 H, PCHP), 3.33 (sept d, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 14.0 Hz, 8 H, NCH), 3.98 (sept, $^3J_{HH}$ = 6.6 Hz, 4 H, NCH), 7.85 (d, $^2J_{PH}$ = 29.6 Hz, 1 H, N=CH); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 17.0 (t, J_{PC} = 148.1 Hz, PCP), 23.4−25.6 (m, CH*C*H_3), 48.0 (s br, CHN), 49.5 (s, CHN), 120.6 (q, J_{FC} = 320.1 Hz, CF_3), 159.8 (s br, C=N).

Five-Membered heterocycle 11. To a CH_2Cl_2 solution (5 mL) of bis(diisopropylamino)phosphinodiazomethane **9** (0.13 g, 0.48 mmol) was added an acetonitrile solution (1 mL) of solution of bis-(diisopropylamino)phosphenium salt (0.18 g, 0.48 mmol) at 0 °C. After the solution was warmed slowly to room temperature, the solvent was removed under vacuum, and the residue was washed with ether. Derivative **11** was recrystallized from a CH_2Cl_2/toluene solution at −30 °C (0.21 g, 66%): mp 313 °C (dec); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 60.0 and 66.2 ($^2J_{PP}$ = 196.5 Hz); ^1H NMR ($CDCl_3$) δ 1.26 (d, $^3J_{HH}$ = 7.0 Hz, 12 H, CHC*H*$_3$), 1.30 (d, $^3J_{HH}$ = 7.0 Hz, 12 H, CHC*H*$_3$), 1.35 (d, $^3J_{HH}$ = 7.0 Hz, 12 H, CHC*H*$_3$), 1.40 (d, $^3J_{HH}$ = 7.0 Hz, 12 H, CHC*H*$_3$), 1.78 (t, $^2J_{PH}$ = 8.9 Hz, 1 H, PCHP), 2.63 (dd, J_{PH} = 5.5 and 1.1 Hz, 3 H, N=CCH_3), 3.81 (sept d, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 14.0 Hz, 4 H, NCH), 3.92 (sept d, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 14.0 Hz, 4 H, NCH); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 1.0 (t, J_{PC} = 2.7 Hz, N=C*C*H_3), 13.4 (dd, J_{PC} = 151.5 and 156.6 Hz, PCP), 23.1 (d, J_{PC} = 3.6 Hz, CH*C*H_3), 24.0 (d, J_{PC} = 3.9 Hz, CH*C*H_3), 24.3 (s, CH*C*H_3), 25.1 (d, J_{PC} = 2.5 Hz, CH*C*H_3), 47.8 (d, J_{PC} = 6.1 Hz, CHN), 48.4 (d, J_{PC} = 6.1 Hz, CHN), 120.6 (q, J_{FC} = 320.1 Hz, CF_3), 186.6 (d, J_{PC} = 69.1 Hz, C=N).

X-ray Crystallographic Studies of Compounds IIIP3 and 7. Crystal data for both structures are presented in Table 1. Data were collected at low temperatures on a Bruker-AXS CCD 1000 diffractometer with Mo Ka (λ = 0.71073 Å). The structures were solved by direct methods by means of SHELXS-97[17] and refined with all data on F^2 by means of SHELXL-97.[18] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the molecules were geometrically idealized and refined using a riding model. A disorder of three chlorine atoms of the $GaCl_4$ anion in **IIIP3** was refined on two positions with the help of 92 ADP and distances restraints.

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Supporting Information Available: X-ray crystallographic data for compounds **IIIP3** and **7** (print/PDF). This material is available free of charge via the Internet at http/::pubs.acs.org.

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