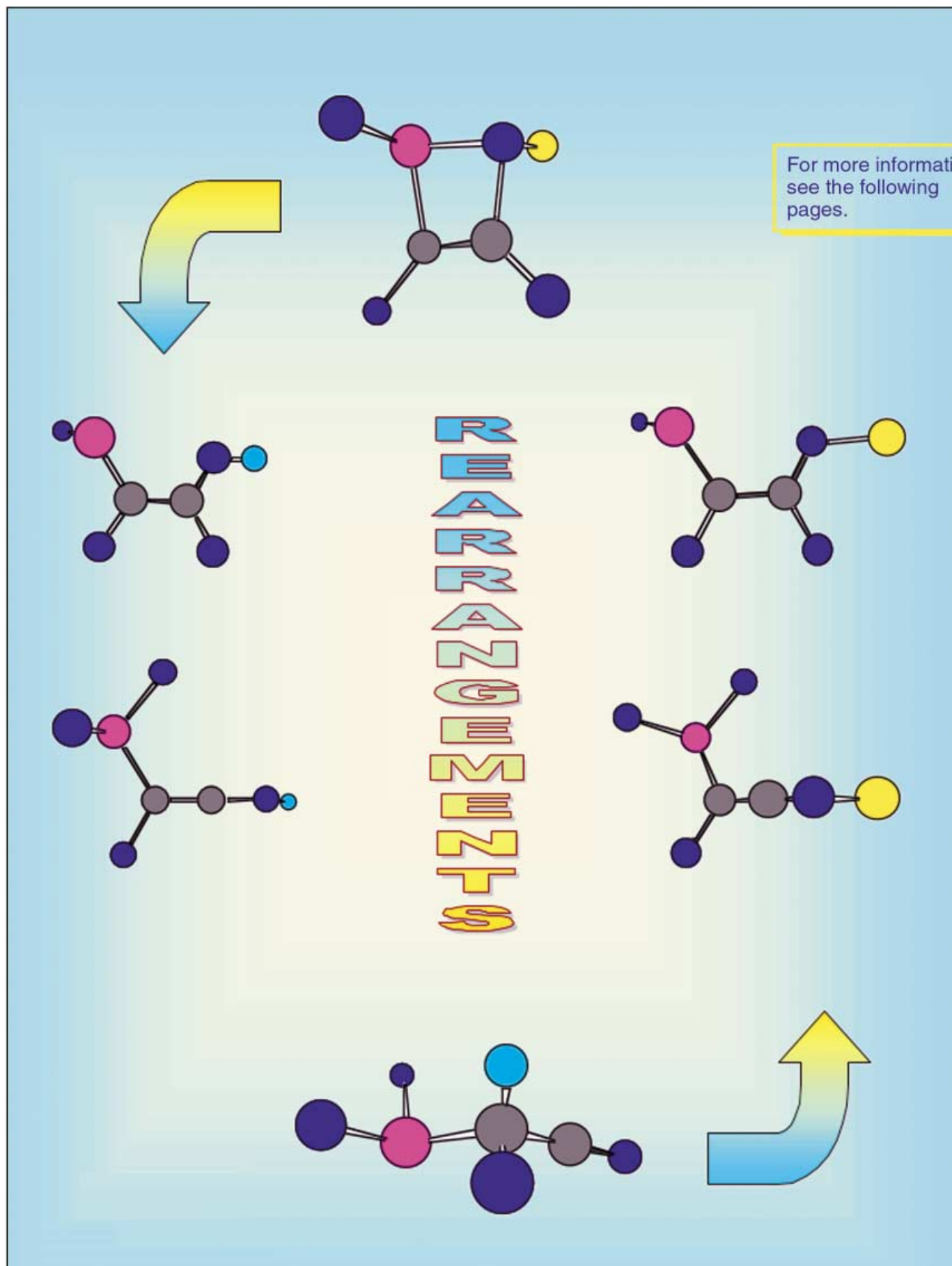




A Rare Example of a Rearrangement Involving Four Structural Isomers: α -Phosphinonitrile/*C*-Phosphinoketenimine/1-Aza-4-phosphabutadiene/1,2-Dihydro-1,2-azaphosphete

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Abstract: The stable compound [bis(dicyclohexylamino)phosphino](trimethylsilyl)carbene (**1**) reacts with dimethyl cyanamide to afford the original 1,2-dihydro-1,2-azaphosphete **4a** (51 % yield). The surprising formation of this heterocycle involves the transient formation of a nitrile, a keteneimine, and a 1-aza-4 λ^3 -phosphabutadiene derivative. By using substituent effects and different synthetic routes, all of these structural isomers have been isolated.

Keywords: cumulenes • heterocycles • phosphorus • rearrangements

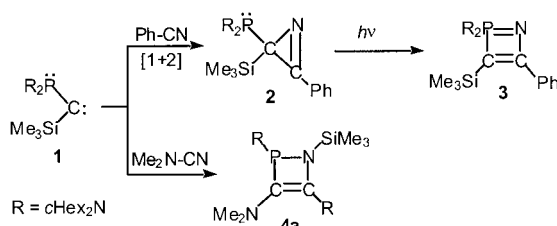
Introduction

Advances in synthetic methodology continue to afford access to new classes of small heterocycles, which in turn opens the route to structure and reactivity studies of these often-unusual compounds. In the course of our study concerning the reactivity of stable (phosphino)(silyl)carbenes,^[1] we have shown that the carbene **1** undergoes a [1+2] cycloaddition reaction with benzonitrile giving rise to the corresponding 2-phosphino-2*H*-azirine **2**, which can be isomerized to the 1,2- λ^5 -azaphosphete **3** (Scheme 1).^[2,3] Since the cycloaddition of transient carbenes with nitriles has never been described, it is

of interest to investigate the scope and limitation of such a route for the synthesis of azirines. Here we report a detailed study of the reaction of **1** with dimethyl cyanamide, which surprisingly cleanly affords the 1,2-dihydro-1,2 λ^3 -azaphosphete **4a** instead of the expected azirine (Scheme 1). Note that although the chemistry of 1,2-dihydro-1,2-diphosphetes is well developed,^[4] only a few examples of dihydroazaphosphetes have been reported.^[5] Of particular interest, rearrangements involving four different structural isomers of dihydroazaphosphetes are described.

Results and Discussion

Synthesis of the 1,2-dihydro-1,2 λ^3 -azaphosphete **4a:** [Bis(dicyclohexylamino)phosphino](trimethylsilyl)carbene (**1**)^[6] readily reacts with Me₂N–C≡N at room temperature to give the original four-membered heterocycle **4a**, which was isolated in 51 % yield (Scheme 1). The ³¹P NMR spectrum (proton coupled) shows a broad triplet at δ = 58.7 ppm (³*J*(P,H) = 14.6 Hz) consistent with the presence of only one cyclohexylamino (*c*-Hex₂N) group directly bonded to the phosphorus atom. Indeed, in the ¹³C NMR spectrum two CHN groups appear as two doublets with rather large phosphorus–carbon coupling constants^[7] at δ = 54.1 (²*J*(P,C) = 16.5 Hz) and 54.0 ppm (²*J*(P,C) = 12.5 Hz), which supports the presence of a chiral λ^3 -phosphorus center, while the two other CHN groups appear as a singlet at δ = 58.0 ppm confirming the migration of a dicyclohexylamino group from phosphorus to a carbon atom. The unsaturated nature of **4a** was deduced from the signals at δ = 124.0 (¹*J*(P,C) = 0 Hz) and 146.0 ppm (²*J*(P,C) = 19.0 Hz) in the ¹³C NMR spectrum. The



Scheme 1.

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structure of **4a** was unequivocally established by a single-crystal X-ray diffraction analysis (Table 1). The solid-state structure of the molecule is illustrated in Figure 1. The four-membered ring is planar (maximum deviation 6 pm), and both phosphorus and nitrogen atoms are strongly pyramidalized (sum of the angles: 291.94° and 329.46°, respectively). The P1–N1 (1.81 Å), P1–C2 (1.82 Å), C1–N1 (1.45 Å), and C1–C2 (1.35 Å) bond lengths are consistent with three single and one double bond, respectively.

Evidently, a multistep mechanism has to be postulated for the formation of **4a**. Indeed, from the starting reagents to the formation of **4a** 1) the silyl group migrates from the car-

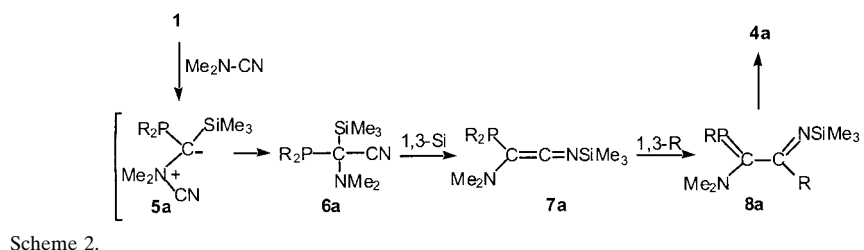


Table 1. Crystallographic data for compounds **4a** and **9a**.

	4a	9a
formula	C ₃₁ H ₅₀ N ₄ PSi	C ₂₈ H ₅₁ N ₄ PS
<i>M_r</i>	546.88	506.76
crystal system	triclinic	orthorhombic
space group	<i>P</i> $\bar{1}$	<i>Pbca</i>
<i>a</i> [Å]	9.625 (1)	10.470(1)
<i>b</i> [Å]	11.270 (1)	19.106(3)
<i>c</i> [Å]	16.127(2)	29.001(3)
β [°]	103.650(10)	90
<i>V</i> [Å ³]	1628.4(3)	5801.40(12)
<i>F</i> (000)	604	2224
<i>Z</i>	2	8
ρ_{calcd} [g cm ⁻³]	1.115	1.160
<i>T</i> [K]	173	193
μ (MoK α) [mm ⁻¹]	0.146	0.190
<i>2</i> θ range [°]	3.78–47.06	4.48–46.52
data collected	18996	47089
unique data	4571	3991
<i>R</i> (int)	0.0536	0.0715
parameters	339	328
goodness-of-fit	0.884	1.009
<i>R</i> 1	0.0312	0.0439
<i>wR</i> 2	0.0663	0.1165
($\Delta\rho$) max/min [e Å ⁻³]	0.169/–0.180	0.568/–0.204

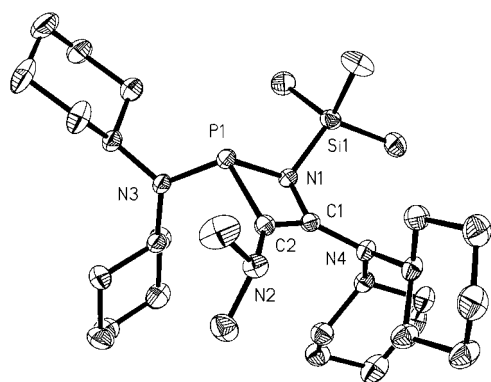
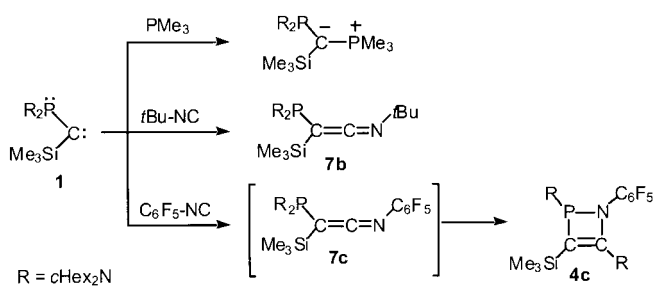


Figure 1. Thermal ellipsoid diagram (30% probability) of **4a** showing the atom numbering scheme. Pertinent bond lengths (Å) and bond angles (deg) are as follows: P1–C2 1.8183(17), P1–N1 1.8096(14), P1–N3 1.6742(15), C1–C2 1.347(2), C1–N1 1.452(2), N1–Si1 1.7610(14), C1–N4 1.393(2), C2–N2 1.423(2), N1–P1–N3 109.37(7), N1–P1–C2 74.69(7), N3–P1–C2 107.88(8), C1–N1–Si1 123.65(11), C1–N1–P1 88.85(9), Si1–N1–P1 116.96(8).

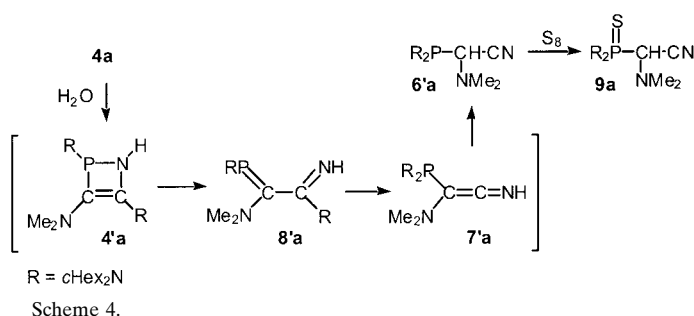
bene carbon atom to the nitrogen end of the cyanamide, 2) a dicyclohexylamino shifts from the phosphorus atom to the carbene carbon atom, and 3) the Me₂N–C fragment inserts into the phosphorus–carbon bond of **1**. Scheme 2 summarizes our working hypothesis, which was based on recent observations. We have shown that Lewis bases such as phosphines react with **1** to give the corresponding phosphorus ylide

(Scheme 3);^[8] therefore the first step might be the transient formation of the nitrogen ylide **5a**, which would easily rearrange by a Stevens rearrangement^[9] into the α -phosphinonitrile **6a**. Then a 1,3-silyl migration would lead to the



keteneimine **7a**, which could rearrange into the 1-aza-4-phosphabutadiene **8a**. Lastly an electrocyclic ring closure would give the isolated 1,2-dihydro-1,2λ³-azaphosphete **4a**. Indeed, carbene **1** reacts with *tert*-butyl isonitrile to give the corresponding stable keteneimine **7b**,^[10] whereas with the pentafluorophenyl isonitrile the 1,2-dihydro-1,2-azaphosphete **4c** was obtained^[11] (Scheme 3). Therefore, it is reasonable to postulate that the formation of **4a** and **4c** involves the rearrangement of the initially formed keteneimine **7a** and **7c**. Lastly, in the related diphosphete system, the existence of an equilibrium between the 1,4-diphosphadiene and the 1,2-dihydro-1,2-diphosphete has been demonstrated.^[12]

Hydrolysis of the 1,2-dihydro-1,2λ³-azaphosphete 4a: Compound **4a** is extremely moisture sensitive and its hydrolysis in toluene at room temperature, in the presence of Bu₄NF, resulted in the formation of the α -phosphinonitrile **6'a**, which has been isolated after addition of an excess of elemental sulfur as the corresponding thioxophosphoranyl derivative **9a** in 55% yield (Scheme 4). The ³¹P NMR spectrum (proton coupled) for **9a** shows a doublet of quintuplets at δ = 64.8 ppm (³*J*(P,H) = 17.2 Hz, ²*J*(P,H) = 16.1 Hz) in agreement with the presence of two dicyclohexylamino groups directly bonded to the phosphorus atom. The ¹³C NMR spectrum revealed a doublet for both the PCH group (δ = 63.7 ppm,



$^1J(\text{P,C}) = 115.3 \text{ Hz}$) and the nitrile carbon ($\delta = 113.1 \text{ ppm}$, $^2J(\text{P,C}) = 11.3 \text{ Hz}$). The presence of the $\text{C}\equiv\text{N}$ group was confirmed by an IR absorption at $\tilde{\nu} = 2210 \text{ cm}^{-1}$. The formation of **6'a** was so unexpected, that we confirmed its structure by an X-ray diffraction study of **9a** (Table 1, Figure 2).

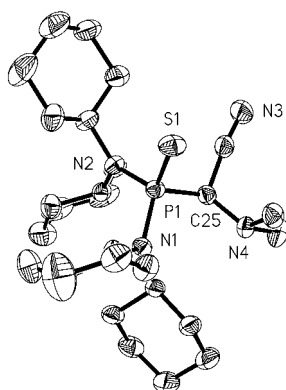


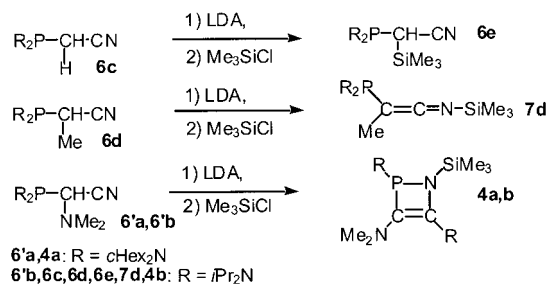
Figure 2. Thermal ellipsoid diagram (30% probability) of **9a** showing the atom numbering scheme. Pertinent bond lengths (Å) and bond angles (deg) are as follows: P1–C25 1.865(3), P1–S1 1.9399(9), P1–N1 1.662(2), P1–N3 1.670(2), N1–P1–N2 112.58(11), N1–P1–C25 104.18(11), N2–P1–C25 102.31(11), N1–P1–S1 114.38(8), N2–P1–S1 112.32(8), C25–P1–S1 110.01(9).

Derivative **6'a** is analogous to the postulated intermediate **6a** in the formation of the 1,2-dihydro-1,2-azaphosphete **4a** (Scheme 2), the silyl group being replaced by a proton. Therefore, its formation probably involves the reverse steps of the formation of the four-membered ring **4a**. The initial cleavage of the N–Si bond would destabilize the corresponding azaphosphete **4'a** as well as the open form, the 1-aza-4-phosphabutadiene **8'a**, which would rearrange into a transient keteneimine **7'a** by a 1,3-migration of a dicyclohexylamino group from C to P;^[13] lastly a 1,3-hydrogen shift would give the isolated α -phosphinonitrile **6'a** (Scheme 4).

Metalation–silylation of α -phosphinonitriles **6'a, **6'b**, **6c**, and **6d**:** These results as a whole seem to indicate that the α -phosphinonitriles **6a** and **6'a** are in equilibrium with the corresponding dihydroazaphosphetes **4a** and **4'a** via the keteneimines **7a** and **7'a** and the azaphosphabutadienes **8a** and **8'a**. To confirm this hypothesis, the sequential metalation–silylation of α -phosphinonitriles **6'a,b** and **6c,d** was performed. Indeed, there are many examples in the literature that demonstrate the ambident character of carbanions α to nitriles;^[14] this offers two potential sites for electrophilic

attack (*C*- or *N*-alkylation), despite the fact that they exist as *N*-lithio, rather than *C*-lithio derivatives, both in solution and in the solid state.^[15] Consequently, the silylation of α -phosphinonitriles **6** should give in a first step either the corresponding α -silylated nitriles or the isomeric *N*-silylketeneimines **7**, which according to our hypothesis could ultimately rearrange into the dihydroazaphosphetes **4**.

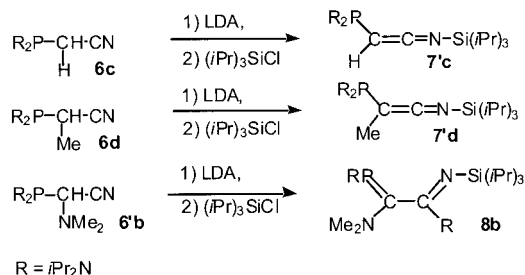
The lithium salts of **6'a,b** and **6c,d** have been prepared by using one equivalent of *n*BuLi or LDA in THF at -78°C , and were first silylated by addition of trimethylsilyl chloride (Scheme 5). In the case of the non-*C*-substituted α -phosphinonitrile **6c**, the new phosphinonitrile **6e** was isolated in 92 %



Scheme 5.

yield. The presence of the nitrile group was confirmed by IR absorption $\nu(\text{CN}) = 2210 \text{ cm}^{-1}$ and by the ^{13}C NMR signal for CN ($\delta = 121 \text{ ppm}$). The silylation of the lithium salt of *C*-methylated α -phosphinonitrile **6d** led to the formation of *N*-trimethylsilyl keteneimine **7d**. The structure of **7d** was unambiguously established by the two characteristic ^{13}C NMR resonances at $\delta = 185.2$ ($J(\text{PC}) = 9.4 \text{ Hz}$) and 38.6 ppm ($J(\text{PC}) = 8.8 \text{ Hz}$) for the α and β carbons of keteneimines,^[16] and the $\nu(\text{CCN})$ absorption located at 2028 cm^{-1} in the IR spectrum.^[17] Finally, in the case of the *C*-dimethylamino-substituted phosphinonitriles **6'a,b**, the dihydroazaphosphetes **4a,b** were cleanly obtained. The structure of **4a** was confirmed by comparison with an authentic sample, and the data for **4b** compared well with those for **4a**.

These results leave no doubt on the possible rearrangement of *N*-silylketeneimines of type **7** into dihydroazaphosphetes **4**. To demonstrate the possible involvement of 1-aza-4-phosphabutadienes of type **8** in the rearrangement of keteneimines **7** into heterocycles **4**, we performed triisopropyl silylation reactions of the lithium salts of **6'b** and **6c,d** (Scheme 6). Indeed, it has been shown that bulky substituents prevent the ring closure of the related 1,4-diphosphabutadiene into 1,2-dihydrodiphosphete.^[18] With **6c** and **6d** keteneimines **7c** and



Scheme 6.

7'd were isolated in 91% and 69% yield, respectively. However, in the case of the lithium salt of the *C*-dimethyl-amino-substituted α -phosphinonitrile **6'b**, the formation of the desired 1-aza-4-phosphabutadiene **8b** was observed. The ^{31}P [^1H]NMR spectrum for **8b** a singlet at $\delta = 111.7$ ppm, in the region expected for this type of σ^2 -phosphorus atom,^[19] was observed. In the ^{13}C NMR spectrum, the signals for the dicoordinate carbon atoms appeared as doublets at $\delta = 180.5$ [$J(\text{P},\text{C}) = 97.5$ Hz ($\text{P}=\text{C}$)] and 152.7 ppm [$J(\text{P},\text{C}) = 34.1$ Hz ($\text{N}=\text{C}$)].

Conclusion

These results, as a whole, suggest the existence of reversible rearrangements between four structural isomers, namely α -phosphinonitriles **6**, *C*-phosphino ketenimines **7**, 1-aza-4 λ^3 -phosphabutadienes **8**, and 1,2-dihydro-1,2-azaphosphete **4**. Smaller substituents favored the nitrile form **6** over the ketenimine isomer **7**, which has already been demonstrated.^[14] Similarly, smaller substituents favor the formation of the 1,2-dihydro-1,2-azaphosphete **4** over the 1-aza-4 λ^3 -phosphabutadiene **8**, which is reminiscent of the already reported 1,2-dihydro-1,2diphosphete/1 λ^3 ,4 λ^3 -diphosphabutadiene system. More difficult to rationalize are the factors governing the 1,3-amino group migration from P to C, which allows the formation of the butadiene system **8** from the ketenimine **7** and vice-versa. Our observations seem to indicate that the ketenimines rearrange into **8** when a *p*- or σ -donor at C (NMe_2 or SiMe_3) and a π -electron-withdrawing group at N are present (SiR_3 or C_6F_5), in other words in the case of push–pull substituted ketenimines.

Work is in progress to study the possible peculiar reactivity of a variety of push–pull ketenimines.

Experimental Section

General remarks: All manipulations were performed under an inert atmosphere of argon by using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^1H , ^{13}C , ^{31}P , and ^{29}Si NMR spectra were recorded on Bruker AC80, AC200, WM250, or AMX400 spectrometers. ^1H , ^{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 external 85% H_3PO_4 . Infrared spectra were recorded on a Perkin–Elmer FT-IR Spectrometer 1725X. Mass spectra were obtained on a Ribermag R10 10E instrument.

1,3-Bis(dicyclohexylamino)-4-dimethylamino-2-trimethylsilyl-1,2-dihydro-1,2-azaphosphete (4a) from carbene 1: Dimethylcyanamide (2 equiv, 1.56 mL, 19.44 mmol) was added to solution of **1** (4.63 g, 9.72 mmol) in toluene (30 mL) at room temperature. The solvent was removed under vacuum, and the residue was extracted with pentane. After filtration, derivative **4a** slowly crystallizes at -20°C as colorless crystals (2.71 g, 51%). M.p. 129–130 $^\circ\text{C}$; ^{31}P [^1H] NMR (CDCl_3): $\delta = 58.7$ ppm; ^1H NMR (CDCl_3): $\delta = 3.15$ (m, 4H; CHN), 2.50 (s, 6H; CH_3N), 1.96–1.01 (m, 40H; CH_2), 0.13 ppm (s, 9H; CH_3Si); ^{13}C [^1H] NMR (CDCl_3): $\delta = 146.0$ (d, $J_{\text{PC}} = 19.0$ Hz; $\text{P}=\text{C}=\text{C}$), 124.0 (s; $\text{P}=\text{C}=\text{C}$), 58.0 (s; $\text{CHN}=\text{C}$), 54.1 (d, $J_{\text{PC}} = 16.5$ Hz; $\text{CHN}=\text{P}$), 54.0 (d, $J_{\text{PC}} = 12.5$ Hz; $\text{CHN}=\text{P}$), 46.0 (d, $J_{\text{PC}} = 4.2$ Hz; CH_3N), 38.4 (d, $J_{\text{PC}} = 10.0$ Hz; CH_2), 36.0 (d, $J_{\text{PC}} = 16.0$ Hz; CH_2), 33.0, 31.0, 27.0, 26.5, 26.4, 26.1 (s; CH_2), 1.85 ppm (d, $J_{\text{PC}} = 5.8$ Hz; CH_3Si); ^{29}Si [^1H] NMR (CDCl_3): $\delta = 0.7$ ppm (d, $J_{\text{PSi}} = 8.9$ Hz); elemental analysis calcd (%) for $\text{C}_{31}\text{H}_{50}\text{N}_4\text{SiP}$: C 68.08, H 10.87, N 10.24; found: C 68.01, H 10.95, N 10.20.

α -Phosphinonitrile 6a via hydrolysis of 4a: A solution of azaphosphete **4a** (0.22 g, 0.39 mmol) in toluene (3 mL) was treated at room temperature with Bu_4NF (1 equiv, 3.9 μL of a 1 M solution in THF). After the solution mixture was stirred at room temperature for 1 h, ^{31}P NMR spectroscopy indicated the quantitative formation of the α -phosphinonitrile **6a**, which was characterized in solution. ^{31}P [^1H] NMR (CDCl_3): $\delta = 55.9$ ppm; ^1H NMR (CDCl_3): $\delta = 3.95$ (d, $J(\text{P},\text{H}) = 6.2$ Hz, 1H; $\text{CH}=\text{P}$), 2.74 (m, 4H; CHN), 2.33 (s, 6H; CH_3N), 1.27–0.98 (m, 40H; CH_2); ^{13}C [^1H] NMR (CDCl_3): $\delta = 116.6$ (d, $J_{\text{PC}} = 27.0$ Hz, CN), 57.9 (d, $J_{\text{PC}} = 10.0$ Hz, CHN), 57.5 (d, $J_{\text{PC}} = 15.0$ Hz, CHN), 57.2 (s, $\text{CH}=\text{P}$), 43.2 (d, $J_{\text{PC}} = 7.4$ Hz, CH_3N), 35.1, 34.7, 27.0, 26.8, 25.7, 25.6 ppm (s, CH_2); IR (toluene): $\tilde{\nu} = 2210$ cm^{-1} (CN).

α -Thioxophosphoranylnitrile (9a): Treatment of a solution of nitrile **6a** (0.19 g, 0.4 mmol) in toluene (5 mL) with an excess of elemental sulfur led after 24 h at 80°C to the corresponding thioxophosphoranyl derivative **9a**. After the solvent was removed under vacuum, the residue extracted with hexane, and after filtration, compound **9a** was crystallized from a solution in Et_2O at -20°C as colorless crystals (0.11 g; 55%). M.p. 213–215 $^\circ\text{C}$; ^{31}P [^1H] NMR (CDCl_3): $\delta = 64.8$ ppm; ^1H NMR (CDCl_3): $\delta = 4.01$ (d, $J_{\text{PH}} = 19.3$ Hz, 1H; $\text{CH}=\text{P}$), 3.39 (m, 4H; CHN), 2.56 (s, 6H; CH_3N), 1.33–1.12 ppm (m, 40H; CH_2); ^{13}C [^1H] NMR (CDCl_3): $\delta = 113.1$ (d, $J_{\text{PC}} = 11.3$ Hz, CN), 63.7 (d, $J_{\text{PC}} = 115.3$ Hz, $\text{CH}=\text{P}$), 58.9 (d, $J_{\text{PC}} = 2.7$ Hz, CHN), 57.9 (d, $J_{\text{PC}} = 1.9$ Hz, CHN), 44.0 (d, $J_{\text{PC}} = 6.6$ Hz, CH_3N), 35.2, 34.5, 34.3, 34.0, 27.5, 27.4, 27.2, 25.7, 25.5 ppm (s, CH_2); MS (EI): m/z : 506 [M^+]; elemental analysis calcd (%) for $\text{C}_{28}\text{H}_{51}\text{N}_4\text{PS}$: C 66.36, H 10.14, N 11.05; found: C 66.41, H 10.20, N 11.06.

Synthesis of α -phosphinonitrile 6'b from an iminium salt: A solution of the [bis(diisopropylamino)phosphanyl] (dimethylamino)carbenium salt^[20] (5.67 g, 13.4 mmol) in THF (50 mL) was added to a solution of KCN (16.9 mmol) and [18]crown-6 (4.5 g, 17.0 mmol) in THF (15 mL). After the solution mixture was stirred at room temperature for 18 h, the solvent was removed under vacuum, and the residue was extracted with diethyl ether (20 mL). Compound **6'b** was crystallized from a solution in Et_2O at -20°C as white crystals (2.58 g, 61%). M.p. 94–95 $^\circ\text{C}$; ^{31}P [^1H] NMR (CDCl_3): $\delta = 48.9$ ppm; ^1H NMR (CDCl_3): $\delta = 4.04$ (d, $J_{\text{PH}} = 5.7$ Hz, 1H; $\text{CH}=\text{P}$), 3.36 (sept d, $J_{\text{HH}} = 6.6$ Hz, $J_{\text{PH}} = 1.4$ Hz, 4H; CHN), 2.37 (s, 6H; CH_3N), 1.23 (d, $J_{\text{HH}} = 6.6$ Hz, 6H; CH_3CH), 1.22 (d, $J_{\text{HH}} = 6.6$ Hz, 6H; CH_3CH), 1.20 (d, $J_{\text{HH}} = 6.6$ Hz, 6H; CH_3CH), 1.13 ppm (d, $J_{\text{HH}} = 6.6$ Hz, 6H; CH_3CH); ^{13}C [^1H] NMR (CDCl_3): $\delta = 117.0$ (d, $J_{\text{PC}} = 26.8$ Hz, CN), 56.8 (s, $\text{CH}=\text{P}$), 47.5 (d, $J_{\text{PC}} = 11.2$ Hz, CHN), 47.4 (d, $J_{\text{PC}} = 11.2$ Hz, CHN), 43.4 (d, $J_{\text{PC}} = 7.7$ Hz, CH_3N), 24.5 (d, $J_{\text{PC}} = 5.3$ Hz, CH_3C), 24.3 (d, $J_{\text{PC}} = 7.7$ Hz, CH_3C), 23.9 ppm (d, $J_{\text{PC}} = 6.9$ Hz, CH_3C); IR (pentane): $\tilde{\nu} = 2212$ cm^{-1} (CN); MS (EI): m/z : 314 [M^+]; elemental analysis calcd (%) for $\text{C}_{16}\text{H}_{35}\text{N}_4\text{P}$: C 61.11, H 11.22, N 17.82; found: C 61.02, H 11.16, N 17.78.

α -Phosphinonitrile 6c from a chlorophosphine: A solution of bis(diisopropylamino)chlorophosphine (2.6 g, 9.7 mmol), ClCH_2CN (0.75 g, 10 mmol), and zinc powder (0.69 g, 10.7 mmol) in THF (15 mL) was sonicated at room temperature for 6 h. After the reaction was completed (the evolution of the reaction was monitored by ^{31}P NMR spectroscopy), the solvent was removed under vacuum, and the residue was extracted with Et_2O (20 mL). From the concentrated Et_2O solution, compound **6c** crystallized at -20°C as white crystals (1.75 g, 66%). M.p. 78–79 $^\circ\text{C}$; ^{31}P [^1H] NMR (CDCl_3): $\delta = 44.0$ ppm; ^1H NMR (CDCl_3): $\delta = 3.40$ (sept d, $J_{\text{HH}} = 6.7$ Hz, $J_{\text{PH}} = 4.9$ Hz, 4H; CHN), 2.60 (d, $J_{\text{PH}} = 8.7$ Hz, 2H; PCH_2), 1.20 (d, $J_{\text{HH}} = 6.7$ Hz, 12H; CH_3CH), 1.16 ppm (d, $J_{\text{HH}} = 6.7$ Hz, 12H; CH_3CH); ^{13}C [^1H] NMR (CDCl_3): $\delta = 118.8$ (d, $J_{\text{PC}} = 14.1$ Hz, CN), 46.9 (d, $J_{\text{PC}} = 11.7$ Hz, CHN), 24.1 (d, $J_{\text{PC}} = 8.1$ Hz, CH_3C), 23.9 (d, $J_{\text{PC}} = 6.5$ Hz, CH_3C), 16.9 ppm (d, $J_{\text{PC}} = 23.3$ Hz, PCH_2); IR (pentane): $\tilde{\nu} = 2236$ cm^{-1} (CN); elemental analysis calcd (%) for $\text{C}_{14}\text{H}_{30}\text{N}_3\text{P}$: C 61.96, H 11.14, N 15.48; found: C 61.89, H 11.07, N 15.52.

Phosphinonitrile 6d by methylation of 6c: $n\text{BuLi}$ in hexanes (1 equiv) was added to a solution of **6c** (0.25 g, 0.9 mmol) in THF (10 mL) at -78°C . After warming up to 0°C , the solution mixture was stirred at this temperature for 45 min. The mixture was then cooled again to -78°C , and CH_3I (1 equiv, 0.13 g, 0.9 mmol) was added. After the solution was allowed to warm to room temperature, the solvent was removed under vacuum, and the residue was extracted with pentane (20 mL). Compound **6d** crystallized at -20°C from the concentrated pentane solution as white crystals (0.216 g, 82%). M.p. 88–9 $^\circ\text{C}$; ^{31}P [^1H] NMR (CDCl_3): $\delta = 56.0$ ppm; ^1H NMR (CDCl_3): $\delta = 3.30$ (sept d, $J_{\text{HH}} = 6.6$ Hz, $J_{\text{PH}} = 11.4$ Hz, 2H; CHN), 3.00 (sept d, $J_{\text{HH}} = 6.6$ Hz, $J_{\text{PH}} = 11.1$ Hz, 2H;

CHN), 2.64 (dq, $^2J_{\text{PH}} = 3.6$ Hz, $^3J_{\text{HH}} = 7.1$ Hz, 2H; PCH_2), 1.32 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H; CH_3CH), 1.22 (d, $^3J_{\text{HH}} = 7.1$ Hz, 3H; CH_3CP), 1.11 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H; CH_3CH), 1.07 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H; CH_3CH), 0.90 ppm (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H; CH_3CH); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 123.4$ (d, $^2J_{\text{PC}} = 12.0$ Hz, CN), 47.7 (d, $^2J_{\text{PC}} = 11.7$ Hz, CHN), 47.1 (d, $^2J_{\text{PC}} = 11.2$ Hz, CHN), 24.7 (d, $^2J_{\text{PC}} = 6.6$ Hz, CH_3C), 24.5 (d, $^2J_{\text{PC}} = 6.7$ Hz, CH_3C), 24.4 (d, $^2J_{\text{PC}} = 6.4$ Hz, CH_3C), 22.6 (d, $^2J_{\text{PC}} = 16.9$ Hz, CH_3CP), 16.1 ppm (d, $^2J_{\text{PC}} = 24.3$ Hz, PCH); IR (pentane): $\tilde{\nu} = 2232\text{ cm}^{-1}$ (CN); MS (EI): m/z : 285 [M^+]; elemental analysis calcd (%) for $\text{C}_{15}\text{H}_{32}\text{N}_3\text{P}$: C 63.12, H 11.30, N 14.72; found: C 63.18, H 11.38, N 14.70

General procedure for the metalation–silylation of phosphonitriles 6'a, 6'b, 6c, and 6d: One equivalent of base (*n*-BuLi or LDA) was added to a solution of the nitrile **6'a**, **6'b**, **6c**, or **6d** (1 mmol) in THF (10 mL) at -78°C . After the temperature increased to 0°C , the solution mixture was stirred at this temperature for 45 min. The mixture was then cooled again at -78°C , and one equivalent of R_3SiCl ($\text{R} = \text{Me}$ or *i*Pr) was added. After the solution was slowly heated to room temperature (30 min), the solvent was removed under vacuum, and the residue was extracted with pentane (20 mL).

α -Phosphonitrile 6e: Yellow oil (92% yield); $^3\text{P}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 47.4$ ppm; ^1H NMR (C_6D_6): $\delta = 3.57$ (sept d, $^3J_{\text{HH}} = 6.6$ Hz, $^3J_{\text{PH}} = 12.1$ Hz, 2H; CHN), 3.38 (sept d, $^3J_{\text{HH}} = 6.6$ Hz, $^3J_{\text{PH}} = 11.9$ Hz, 2H; CHN), 1.89 (d, $^2J_{\text{PH}} = 2.5$ Hz, 1H; PCH), 1.25 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H; CH_3CH), 1.14 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H; CH_3CH), 1.07 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H; CH_3CH), 0.99 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H; CH_3CH), 0.22 ppm (s, 9H; CH_3Si); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 121.1$ (s, CN), 48.3 (d, $^2J_{\text{PC}} = 5.7$ Hz, CHN), 48.0 (d, $^2J_{\text{PC}} = 7.0$ Hz, CHN), 25.1 (d, $^2J_{\text{PC}} = 6.5$ Hz, CH_3C), 24.4 (d, $^2J_{\text{PC}} = 8.5$ Hz, CH_3C), 24.1 (d, $^2J_{\text{PC}} = 8.8$ Hz, CH_3C), 24.0 (d, $^2J_{\text{PC}} = 9.1$ Hz, CH_3C), 21.3 (d, $^2J_{\text{PC}} = 56.6$ Hz, PCH), -1.3 ppm (d, $^2J_{\text{PC}} = 6.3$ Hz, CH_3Si); IR (C_6D_6): $\tilde{\nu} = 2210\text{ cm}^{-1}$ (CN).

Ketenimine 7d: Yellow oil (89% yield); $^3\text{P}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 61.4$ ppm; ^1H NMR (C_6D_6): $\delta = 3.57$ (sept d, $^3J_{\text{HH}} = 6.6$ Hz, $^3J_{\text{PH}} = 12.1$ Hz, 2H; CHN), 3.38 (sept d, $^3J_{\text{HH}} = 6.6$ Hz, $^3J_{\text{PH}} = 11.9$ Hz, 2H; CHN), 1.89 (d, $^2J_{\text{PH}} = 9.0$ Hz, 3H; PCCH_3), 1.21 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H; CH_3CH), 1.19 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H; CH_3CH), 1.06 (d, $^3J_{\text{HH}} = 6.6$ Hz, 12H; CH_3CH), 0.38 ppm (s, 9H; CH_3Si); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 185.2$ (d, $^2J_{\text{PC}} = 9.4$ Hz, $\text{P}-\text{C}=\text{C}$), 48.1 (d, $^2J_{\text{PC}} = 8.1$ Hz, CHN), 47.3 (d, $^2J_{\text{PC}} = 10.9$ Hz, CHN), 38.6 (d, $^1J_{\text{PC}} = 8.8$ Hz, $\text{P}-\text{C}$), 25.3 (d, $^2J_{\text{PC}} = 6.0$ Hz, CH_3C), 24.9 (d, $^2J_{\text{PC}} = 6.7$ Hz, CH_3C), 24.8 (d, $^2J_{\text{PC}} = 6.8$ Hz, CH_3C), 24.3 (d, $^2J_{\text{PC}} = 6.5$ Hz, CH_3C), 22.0 (d, $^2J_{\text{PC}} = 63.5$ Hz, PCCH_3), 1.7 ppm (s, CH_3Si); IR (C_6D_6): $\tilde{\nu} = 2028\text{ cm}^{-1}$ ($\text{C}=\text{C}=\text{N}$).

1,2-Dihydro-1,2-azaphosphete 4b: $^3\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 59.1$ ppm; ^1H NMR (CDCl_3): $\delta = 3.61$ (sept, $^3J_{\text{HH}} = 6.6$ Hz, 2H; CHN), 3.34 (sept d, $^3J_{\text{HH}} = 6.6$ Hz, $^3J_{\text{PH}} = 8.6$ Hz, 2H; CHN), 2.34 (s, 6H; CH_3N), 1.19 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H; CH_3CH), 1.18 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H; CH_3CH), 1.17 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H; CH_3CH), 1.11 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H; CH_3CH), 0.12 ppm (s, 9H; CH_3Si); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 146.9$ (d, $^2J_{\text{PC}} = 19.1$ Hz, $\text{P}-\text{C}=\text{C}$), 123.6 (s, $\text{P}-\text{C}=\text{C}$), 49.0 (s, $\text{CHN}-\text{C}=\text{N}$), 46.7 (d, $^2J_{\text{PC}} = 4.2$ Hz, $\text{CHN}-\text{P}$), 43.7 (br d, CH_3N), 23.2 (s, CH_3C), 21.9 (s, CH_3C), 2.1 ppm (d, $^3J_{\text{PC}} = 5.8$ Hz, CH_3Si).

Ketenimine 7c: Yellow oil (91% yield); $^3\text{P}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 53.1$ ppm; ^1H NMR (C_6D_6): $\delta = 3.60$ (sept d, $^3J_{\text{HH}} = 6.8$ Hz, $^3J_{\text{PH}} = 11.0$ Hz, 4H; CHN), 3.27 (d, $^2J_{\text{PH}} = 10.2$ Hz, 1H; PCH), 1.43 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H; CH_3CH), 1.42 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H; CH_3CH), 1.31 ppm (m, 21H; CH_3CHSi); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 175.7$ (d, $^2J_{\text{PC}} = 36.6$ Hz, $\text{PC}=\text{C}$), 47.4 (d, $^2J_{\text{PC}} = 11.0$ Hz, CHN), 27.4 (d, $^1J_{\text{PC}} = 8.8$ Hz, PC), 24.7 (d, $^2J_{\text{PC}} = 5.8$ Hz, CH_3C), 24.5 (d, $^2J_{\text{PC}} = 9.2$ Hz, CH_3C), 18.3 (s, CH_3CSi), 12.7 ppm (s, CHSi); IR (C_6D_6): $\tilde{\nu} = 2044\text{ cm}^{-1}$ ($\text{C}=\text{C}=\text{N}$).

Ketenimine 7d: Yellow oil (69% yield); $^3\text{P}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 61.4$ ppm; ^1H NMR (C_6D_6): $\delta = 3.46$ (sept d, $^3J_{\text{HH}} = 6.6$ Hz, $^3J_{\text{PH}} = 11.0$ Hz, 4H; CHN), 1.86 (d, $^2J_{\text{PH}} = 9.4$ Hz, 3H; PCCH_3), 1.27 (d, $^3J_{\text{HH}} = 6.6$ Hz, 12H; CH_3CH), 1.25 (d, $^3J_{\text{HH}} = 6.6$ Hz, 12H; CH_3CH), 1.11 (s, 18H; CH_3CHSi), 1.04 ppm (s, 3H; CHSi); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 184.7$ (d, $^2J_{\text{PC}} = 11.1$ Hz, $\text{PC}=\text{C}$), 48.7 (d, $^2J_{\text{PC}} = 11.8$ Hz, CHN), 40.9 (d, $^1J_{\text{PC}} = 4.7$ Hz, PC), 25.8 (d, $^2J_{\text{PC}} = 8.0$ Hz, CH_3C), 25.3 (d, $^2J_{\text{PC}} = 7.0$ Hz, CH_3C), 20.1 (d, $^2J_{\text{PC}} = 6.4$ Hz, PCCH_3), 17.1 (s, CH_3CSi), 13.5 ppm (s, CHSi); IR (C_6D_6): $\tilde{\nu} = 2026\text{ cm}^{-1}$ ($\text{C}=\text{C}=\text{N}$).

1,4-Azaphosphabutadiene 8b: Yellow oil (58% yield); $^3\text{P}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 113.1$ ppm; ^1H NMR (C_6D_6): $\delta = 4.30$ (sept, $^3J_{\text{HH}} = 6.6$ Hz, 2H; CHN), 3.28 (sept, $^3J_{\text{HH}} = 6.6$ Hz, 2H; CHN), 2.66 (s, 6H; CH_3N), 1.36

(d, $^3J_{\text{PH}} = 6.6$ Hz, 12H; CH_3CH), 1.33 (d, $^3J_{\text{HH}} = 6.6$ Hz, 12H; CH_3CH), 1.18 (s, 3H; CH_3CHSi), 1.15 ppm (s, 18H; CH_3CHSi); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 180.5$ (d, $^1J_{\text{PC}} = 97.5$ Hz, $\text{P}=\text{C}$), 153.5 (d, $^2J_{\text{PC}} = 35.2$ Hz, $\text{C}=\text{N}$), 51.2 (d, $^2J_{\text{PC}} = 5.7$ Hz, CHN), 47.2 (s, CHN), 46.0 (s, CHN), 41.4 (s, CH_3N), 24.9 (d, $^2J_{\text{PC}} = 6.5$ Hz, CH_3CHNP), 24.7 (d, $^2J_{\text{PC}} = 6.3$ Hz, CH_3CHNP), 19.6 (s, CH_3CHN), 19.3 (s, CH_3CHN), 18.5 (s, CH_3CSi), 14.4 ppm (s, CHSi); $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = -28.7$ ppm.

Crystal structure determination for 4a and 9a: Crystal data for both structures are presented in Table 1. All data were collected at low temperatures by using an oil-coated shock-cooled crystal on a STOE-IPDS diffractometer. The structures were solved by direct methods (SHELXS-97)^[21] and refined by using the least-squares method on F^2 .^[22] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the molecules were geometrically idealized and refined using a riding model. A numerical absorption correction was employed for structure **9a**; the min/max transmissions were 0.8338/0.9375. Two positions for a disordered cyclohexyl group in **9a** were refined anisotropically by using 197 ADP and distance restraints.

CCDC-185685 and CCDC-185686 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union road, Cambridge CB21EZ, UK; (fax: (+44)1223–336–033; or e-mail: deposit@ccdc.cam.ac.uk).

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