Analogous α,α'-Bis-Carbenoid Triply Bonded Species: Synthesis of a Stable λ^3-Phosphinocarbene–λ^5-Phosphaacetylene

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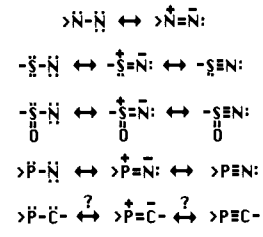
Abstract: Depending on the nature of the substituents and the experimental conditions used, transient or stable phosphinocarbenes are generated from the corresponding α-diazophosphines. Of particular interest thermolysis of (trimethylsilyl)[bis(diisopropylamino)phosphino]diazomethane (**1**), at 250 °C under vacuum, leads to the corresponding stable phosphinocarbene **2** (bp 75–80 °C/10^{-2} mmHg). According to NMR data (^{1}H, ^{13}C, ^{31}P, ^{29}Si), **2** possesses a phosphorus–vinyl ylide or a λ^5-phosphaacetylene structure. A [2 + 3] cycloaddition, typical for multiple-bond behavior, is observed when **2** is treated with trimethylsilyl azide, but pyrolysis of **2** leads to five-membered rings **22** probably through carbene insertion into a CH bond of a phosphorus substituent.

In the fifties, the possibility of synthesizing a low coordinated heavier main group element was questionable.[1] However, in the last few years, molecules featuring p_π–p_π double bonds, involving silicon, germanium, phosphorus, arsenic, and sulfur have been reported.[2] The next challenge was to prepare triply-bonded derivatives, and, up to now, only thiazyltrifluoride (F_3S–N)[3] and a few phospha[4] and arsaalkynes[5] are known to be stable at room temperature. It is well established that aminonitrene,[6] sulfenylnitrene,[3] sulfinylnitrene,[7] and phosphinonitrene[8] can be regarded as diazene, thiazyne, oxathyazyne, and phosphonitrile, respectively, due to delocalization of the lone pair. We wanted to find out if the generation of a carbenoid species next to a heteroatom, bearing both a lone pair and a vacant p or d orbital, is a general method for obtaining "triple-bonded-like" derivatives. Here we want to report that λ^3-phosphinocarbenes can behave either as "usual" carbenes or as polarized λ^5-phosphaacetylenes (Scheme I).

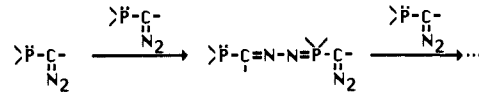
Results and Discussion

Diazo compounds are classical precursors of carbenes. Although diazo-λ^5-phosphorus derivatives are well documented,[9] as far as we know, no examples of molecules possessing a diazo group bonded to a λ^3-phosphorus atom have been reported before this work.[10,11] This class of compounds, like phosphine azides, should be very unstable due to possible intermolecular reactions of the diazo moiety with the phosphorus lone pair[12] (Scheme II).

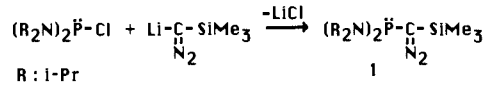
Scheme I



Scheme II



Scheme III



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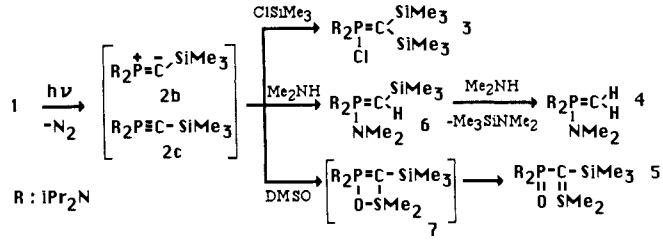
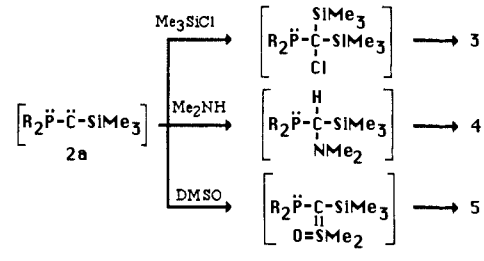


Scheme V



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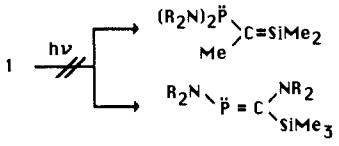
Scheme VI



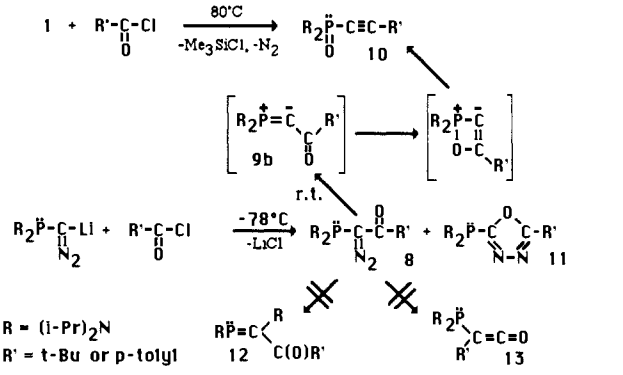
Taking into account the observed stability of phosphine azides,[8,13] we chose to prepare (trimethylsilyl)[bis(diisopropylamino)phosphino]diazomethane (**1**). Treatment of the lithium salt of (trimethylsilyl)diazomethane[14] with a stoichiometric amount of bis(diisopropylamino)chlorophosphine[13d] led to the desired product **1** in 85% isolated yield (Scheme III). The red oily diazo derivative **1** was stable enough to be purified by distillation at 85–90 °C (10^{-2} mmHg) without noticeable decomposition.

Having in hand the precursor, we first chose to generate the carbene by photolysis. When a benzene solution of **1** was irradiated, at λ = 300 nm, for 8 h, in the presence of an excess of trimethylchlorosilane, dimethylamine, or dimethyl sulfoxide, release of nitrogen was observed and products **3**, **4**, or **5** were obtained in near quantitative yield. To rationalize the formation of λ^5-phosphorus compound **3**, it is reasonable to postulate a 1,2-addition of the trapping agent to the phosphorus–carbon multiple bond of a "phosphorus vinyl ylide–phosphaacetylene" intermediate **2b,c**. In the case of dimethylamine, a similar mechanism followed by aminolysis of the carbon–silicon bond of **6** could explain the formation of **4**. The subsequent cleavage of the C–Si bond of **6** was confirmed by the action of dimethylamine on $(R_2N)_2P(Cl)$=$CHSiMe_3$[15] which also led to **4**. The formation of sulfur ylide **5** could result from a 2 + 2 cycloaddition giving rise to a four-membered cyclic phosphorus ylide **7** followed by ring opening[16] (Scheme IV).

However, one can argue that [1 − 1] addition of Me_3SiCl or dimethylamine and [1 + 1] addition of DMSO, on the carbene form **2a**, followed by subsequent rearrangements, might also explain the nature of products **3**, **4**, and **5**; chloromethylenephosphine–chlorophosphorus ylide rearrangement has already been exemplified[17] (Scheme V).

In order to choose between the two mechanistic possibilities further studies were performed. The carbene type reactivity of **2** seems unlikely since (i) no trapping reactions occurred when the photolysis was carried out in the presence of cyclohexene, dimethylbutadiene, or dimethylsulfur which are well known to react with carbenes;[18] (ii) although α-silyl and α-phosphoryl diazo derivatives rearrange into reactive silaethylenes[19] and tricoordinated pentavalent phosphorus intermediates,[9] respectively, diazo phosphine **1** does not undergo 1,2-migration of a substituent from silicon or phosphorus to the carbene center (Scheme VI). On the other hand, although no trapping reactions occurred when **1** was irradiated in the presence of ketones, heating of **1** with a stoichiometric amount of acylchloride led to phosphorylated acetylenic derivatives **10** in good yield along with a quantitative amount of Me_3SiCl. **10** probably came from the decomposition of diazo derivatives **8**, followed by an intramolecular Wittig-like reaction involving the phosphorus vinyl ylide intermediate **9b**. This hypothesis was partly confirmed by the synthesis of diazoketones **8** by action of the lithium salt of [bis(diisopropylamino)]phosphinodiazomethane on the acyl chloride. Derivative **8** (R′ = *t*-Bu) was characterized in solution, at 0 °C, along with 1,3,4-oxadiazoles **11** in a 75/25 ratio (according to ^{31}P NMR spectroscopy). At room temperature, evolution of nitrogen was observed, and the acetylenics **10** were isolated in 70% yield. It is noteworthy, that no 1-2 shift, which would have led to phosphaalkenes **12** or phosphinoketenes **13**, was observed confirming the atypical behavior of phosphinocarbenes **9** (Scheme VII).

Scheme VII



Scheme VIII

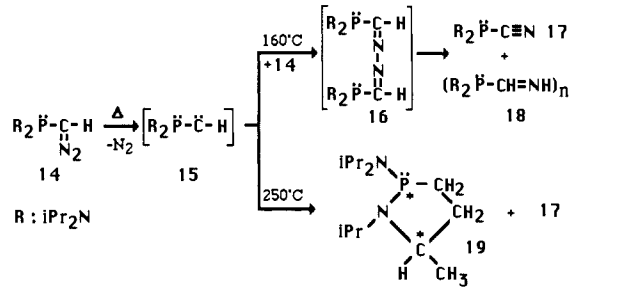


Table I. NMR Data for **1**, **2**, and P≡$CSiMe_3$[a,21]

		2	1	:P≡$CSiMe_3$[21]
^{31}P		−40	+56	+96
^{13}C	$SiCH_3$	3.95 (10.56)	−0.80 (5.28)	
	$CHCH_3$	22.65	23.80, 23.88, 25.01, 25.12	
	$CHCH_3$	48.57 (2.26)	48.00 (12.07)	
	C	142.75 (159.3)	28.34 (90.94)	201.4 (13.9)
^{29}Si		−19.67 (59.34)	+1.68 (43.10)	
^{1}H	$SiCH_3$	+0.46 (1.14)	−0.23	
	$CHCH_3$	1.22	1.17, 1.20	
	$CHCH_3$	3.38 (18.3)	3.32 (12.2)	

[a] ^{1}H (300.1 MHz), ^{13}C (75.5 MHz), ^{31}P (121.5 MHz), and ^{29}Si (59.6 MHz) spectra measured in benzene-d_6 at room temperature. Chemical shifts are reported in ppm relative to external TMS or H_3PO_4. Coupling constants with phosphorus, reported in hertz, are in parentheses.

These results, as a whole, strongly argue for the phosphorus–carbon multiple-bond character of **2** and **9**. In marked contrast, the formation of phosphinonitrile **17** (30% yield), in the attempted distillation (90 °C/10^{-2} mmHg) of bis(diisopropylamino)phosphinodiazomethane (**14**), probably involved the carbene-like behavior of intermediate **15**. Indeed, the reaction of carbene **15** with the starting diazo **14** could give acetaldazine **16**[20] which would rearrange into the observed nitrile **17** and the corresponding imine, polymerizing under the experimental conditions used. Moreover, pyrolysis of **14** at 250 °C under vacuum led to five-membered rings **19** as a 70/30 mixture of diastereoisomers (60% yield) along

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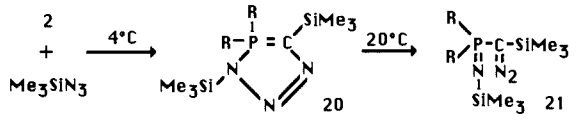
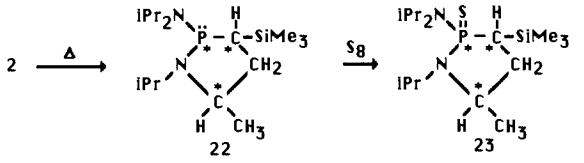
Scheme IX



Scheme X



with **17** (20% yield). Formally, these heterocycles **19** result from a carbene insertion into a carbon–hydrogen bond of a phosphorus substituent (Scheme VIII).

Taking into account the complexity of all of these results, it was of particular interest to try to spectroscopically characterize one of the postulated intermediates **2**, **9**, or **15**. We have been able to isolate compound **2**, in pure form. In the preliminary communication,[10] we mentioned that according to ^{31}P NMR, besides numerous products, a major species (δ^{31}P:–40 ppm) was formed when the photolysis of **1** was performed in the absence of trapping agents. Interestingly, flash thermolysis of **1**, at 250 °C, under vacuum, produced the same species in 80% yield as a red oily material identified as the desired phosphinocarbene **2**:bp 75–80 °C (10^{-2} mmHg); UVλ_{max} = 300.4 nm. This compound is stable for several weeks at room temperature, in benzene solution, but is readily decomposed in chlorinated solvents. The high field chemical shift in ^{31}P NMR and the large ^1J(PC) and ^2J(PSi) coupling constants observed for **2**, compared with those of **1** or trimethylsilyl λ^3-phosphaalkyne[21] (Table I), suggest an increase of the number of valence bonds of the phosphorus atom. The low field signal in ^{13}C NMR is in the range expected for a multiply bonded carbon. In marked contrast with ^{1}H and ^{13}C NMR data available for other bis(diisopropylamino)phosphines, the four isopropyl groups are equivalent in the case of **2**, arguing for an increase of the N–P–N angle (allowing free rotation of the substituents) and perhaps for a symmetrical molecule.[22] Theoretical calculations performed on H_2PCH predicted[23] that, in **2a** the phosphorus atom would be pyramidal, **2b** would be a planar molecule but bent at the carbon, while **2c** would be planar and linear. Thus, based on NMR spectroscopy, it is clear that **2** possesses a multiple-bond character and is most probably a λ^5-phosphaacetylene **2c**.[22]

Although **2** is thermally stable, it is quite reactive. Addition of trimethylchlorosilane or dimethyl sulfoxide led to products **3** (85% yield) and **5** (95% yield), respectively, already formed in the trapping of photochemically generated **2**. However, as noted before, these reactions do not allow differentiation between carbene and multiple-bond reactivity. A typical example of the multiple-bond behavior of **2** was found with trimethylsilylazide. Diazo derivative **21** was isolated in 92% yield, but the first formed [2 + 3] cycloadduct **20** was characterized by NMR spectroscopy, at 4 °C (Scheme IX). This reaction is strictly analogous to that often reported between azides and alkynes.[24] On the other hand, pyrolysis of **2**, at 300 °C under vacuum, afforded the four five-membered ring diastereoisomers **22** in 90% total yield; the two major isomers were isolated in pure form after treatment with elemental sulfur (Scheme X). This result can be explained in terms of insertion of singlet carbene **2a** into a carbon–hydrogen bond of an isopropyl substituent, although the total regioselectivity of this ring closure—no trace of four-membered ring—is surprising.

Conclusions

These results, as a whole, (i) demonstrate that λ^3-phosphinocarbenes possess a strong multiple-bond character, which probably explains their surprising stability, but nonetheless they can also react as carbene species; (ii) support theoretical calculations[23] that predicted, for the parent compound H_2PCH, a phosphinocarbene–phosphorus vinyl ylide separation of only 4 Kcal/mol (in favor of the ylide). Note that the "sulfur–carbon triple-bonded compound" (F_3CC–SF_3), characterized at –130 °C by Seppelt et al.,[25] underwent 1,2-addition of HF at low temperature but dimerized at –30 °C giving the carbene dimer [$(CF_3)(SF_3)C{=}C(SF_3)(CF_3)$]. Thus, we can probably conclude that this ambiguity—α,α'-bis-carbenoid; triple bond—is a characteristic feature of the heavier main group elements and illustrates their reluctance to give multiply bonded species.

Experimental Section

All experiments were performed in an atmosphere of dry argon or nitrogen. Melting points are uncorrected. ^{1}H, ^{31}P, ^{13}C, ^{29}Si, and ^{15}N NMR spectra were recorded on Bruker AC80, WM250, or AM300 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 shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. ^{15}N NMR chemical shifts are given in ppm relative to nitromethane as external standard. Infared spectra were recorded on a Beckman IR10 and a Perkin-Elmer lattice spectrometer (Mol 598), by using a polystyrene film for calibration. Mass spectra were obtained on a Ribermag R10 10E instrument. Photochemical reactions were performed in quartz tubes with a Rayonnet photochemical reactor. Conventional glassware was used. Liquid chromatography was done on silica gel.

Synthesis of (Trimethylsilyl)[bis(diisopropylamino)phosphino]diazomethane (1). To a THF solution (90 mL) of bis(diisopropylamino)chlorophosphine (6.8 g, 26 mmol), at –78 °C was added dropwise the lithium salt of (trimethylsilyl)diazomethane[14] (26 mmol). After evaporation of the solvent, treatment with pentane, and filtration, distillation gave **1** (7.6 g, 85% yield) as a red oil: bp 85–90 °C (10^{-2} mmHg); ^{31}P NMR (C_6D_6) +56 ppm; ^{1}H NMR (C_6D_6) 0.2 (s, 9 H, $SiMe_3$), 1.17 (d, J(HH) = 7 Hz, 12 H, CH_3C), 1.20 (d, J(HH) = 7 Hz, 12 H, CH_3C), 3.3 (sept d, J(HH) = 7 Hz, J(PH) = 12 Hz, 4 H, CH); ^{13}C NMR ($CDCl_3$) –0.80 (d, J(PC) = 5.28 Hz, CH_3Si), 23.80, 23.88, 25.01, 25.12 (s, CH_3C), 28.34 (d, J(PC) = 90.94 Hz, CN_2), 48.00 (d, J(PC) = 12.07 Hz, CH); IR (C_6H_6) 2010 cm^{-1} (CN_2); mass spectrum, m/e 344 (M^+), 273 (M^+ – iPr – N_2). Anal. Calcd for $C_{16}H_{37}N_4PSi$: C, 55.77; H, 10.82; N, 16.26. Found: C, 55.83; H, 10.80; N, 16.30.

Irradiation of 1 in the Presence of Me_3SiCl, Me_2NH, and Me_2SO. A benzene solution of **1** (344 mg, 1 mmol) was irradiated, at λ = 300 nm, in the presence of an excess of trapping agent (2 mmol), for 8 h. After evaporation of the solvent and of the excess of trapping agent, product **3** was characterized without further purification, while **4** was recrystallized from hexane/benzene, and **5** was isolated by column chromatography. **3**: ^{31}P NMR (C_6D_6) +72 ppm; ^{1}H NMR (C_6D_6) 0.35 (s-like, 18 H, $SiMe_3$), 1.2 (d, J(HH) = 7 Hz, 24 H, CCH_3), 4.3 (m, 4 H, CH); mass spectrum, m/e 424 (M^+). **4**: ^{31}P NMR (C_6D_6) +59 ppm; ^{1}H NMR (C_6D_6) 1.15 (d, J(HH) = 7 Hz, 24 H, CCH_3), 2.15 (d, J(PH) = 13 Hz, 2 H, CH_2), 2.65 (d, J(PH) = 12 Hz, 6 H, NCH_3), 3.50 (m, 4 H, CH); mass spectrum, m/e 289 (M^+). Anal. Calcd for $C_{15}H_{36}N_3P$: C, 62.24; H, 12.54; N, 14.52. Found C, 62.40; H, 12.58, N, 12.48. **5**: mp 143–145 °C; ^{31}P NMR (C_6D_6) +44 ppm; ^{1}H NMR ($CDCl_3$) 0.1 (s, 9 H, $SiMe_3$), 1.20 (d, J(HH) = 7 Hz, 12 H, CCH_3), 1.25 (d, J(HH) = 7 Hz, 12 H, CCH_3), 2.6 (s, 6 H, CH_3S), 3.8 (m, 4 H, CH); IR (KBr) 1200 cm^{-1} (P=O); mass spectrum, m/e 394 (M^+). Anal. Calcd for $C_{18}H_{43}N_2POSSi$: C, 54.78; H, 10.98; N, 7.10. Found: C, 54.55; H, 10.98; N, 7.12.

Reaction of 1 with Acyl Chlorides. A benzene solution of **1** (344 mg, 1 mmol) and acyl chloride (1 mmol) was stirred under reflux for 24 h, whereupon the ^{1}H NMR signal of the Me_3Si group of the starting material was totally transformed into the signal of Me_3SiCl. After evaporation of the solvents, **10** was isolated by column chromatography (pentane/ether 70/30). **10** (R′ = *p*-tolyl): 85% yield; mp 102–104 °C; ^{31}P NMR ($CDCl_3$) +0.17 ppm; ^{1}H NMR ($CDCl_3$) 1.25 (d, J(HH) = 7 H,

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24 H, CHCH_3), 2.35 (s, 3 H, ArCH_3), 3.35 (m, 4 H, CH), 7.15 and 7.45 (AB system, J_{AB} = 8 Hz, 4 H, H_{ar}); IR (KBr) 2180 (C≡C), 1220 (P=O) cm^{-1}; mass spectrum, *m/e* 362 (M^+). Anal. Calcd for $C_{21}H_{35}N_2OP$: C, 69.57; H, 9.73; P, 8.55. Found: C, 69.68; H, 9.68; N, 7.68; P, 8.43. **10** (R′ = *t*-Bu): 85% yield; mp 102–103 °C; ^{31}P NMR (C_6D_6) −0.6 ppm; ^1H NMR (C_6D_6) 1.18 (s, 9 H, *t*-Bu), 1.38 (d, *J*(HH) = 7 Hz, 12 H, CHCH_3), 1.42 (d, *J*(HH) = 7 Hz, 12 H, CHCH_3), 3.50 (sept d, *J*(HH) = 7 Hz, *J*(PH) = 17 Hz, 4 H, CH); ^{13}C NMR (C_6D_6) 22.11, 22.21, 23.34, 23.45 (CHCH_3), 27.88 (d, *J*(PC) = 3.02 Hz, CCH_3), 29.79 (d, *J*(PC) = 1.81 Hz, CCH_3), 45.68, 45.95 (s, CH), 80.11 (d, *J*(PC) = 220.61 Hz, P–C–), 107.44 (d, *J*(PC) = 36.03 Hz, P–C–*C*–); IR (KBr) 2210, 2180 (C≡C), 1220 (P=O) cm^{-1}; mass spectrum, *m/e* 328 (M^+). Anal. Calcd for $C_{18}H_{35}N_2OP$: C, 65.81; H, 11.35; N, 8.53; P, 9.43. Found: C, 65.66; H, 11.39; N, 8.56; P, 9.35.

Synthesis of Bis(diisopropylamino)phosphinodiazomethane (14). A THF solution of **1** (3.44 g, 10 mmol) and methanol (0.64 g, 20 mmol) was stirred, at room temperature, for 3 **h**. After evaporation of the solvent, the residue was treated with pentane. Removal of the pentane gave crude **14** (2.31 g, 85%) as a red oil which can be used without further purification: ^{31}P NMR (C_6D_6) +48 ppm; ^1H NMR (C_6D_6) 0.95 (d, *J*(HH) = 7 Hz, 12 H, CCH_3), 1.05 (d, *J*(HH) = 7 Hz, 12 H, CCH_3), 2.7 (d, *J*(PH) = 20 Hz, 1 H, CHN_2), 3.2 (sept d, *J*(HH) = 7 Hz, *J*(PH) = 11 Hz, 4 H, CH); ^{13}C NMR ($CDCl_3$) 24.07, 24.14, 24.16, 24.24 (s, CH_3), 31.00 (d, *J*(PC) = 8.83 Hz, C=N_2); IR (C_6H_6) 2030 cm^{-1} (N_2); mass spectrum, *m/e* 272 (M^+), 244 ($M^+ - N_2$).

Reaction of the Lithium Salt of Bis(diisopropylamino)phosphinodiazomethane with Acyl Chlorides. To a THF solution (30 mL) of the lithium salt of bis(diisopropylamino)phosphinodiazomethane [prepared by adding dropwise, at −78 °C, 4.6 mL of a hexane solution of BuLi (7 mmol) to **14** (2 g, 7 mmol)], was added, at −78 °C, a THF solution (15 mL) of acyl chloride (7 mmol). After stirring for 1 h, **8** (R = *t*-Bu) was characterized in solution at 0 °C: ^{31}P NMR (THF) +70.6 ppm; IR (THF) 2045 (CN_2), 1640 (CO) cm^{-1}. After 1 h at room temperature, solvent was removed under vacuum, and products **10** and **11** were isolated by column chromatography (pentane/ether 70/30). **10** (R = *t*-Bu) 70% yield; **10** (R = *p*-tolyl) 70% yield; **11** (R = *t*-Bu) 25% yield; bp 90–95 °C/0.5 mmHg; ^{31}P NMR (C_6D_6) +38.3 ppm; ^1H NMR ($CDCl_3$) 1.23 (t-like, *J*(HH) = 7 Hz, 24 H, CHCH_3), 1.40 (s, 9 H, CCH_3), 3.45 (sept d, *J*(HH) = 7 Hz, *J*(PH) = 14 Hz, 4 H, CH); ^{13}C NMR ($CDCl_3$) 23.75, 23.84, 24.07, 24.16 (s, CH_3-CH), 28.29 (s, CH_3-C), 32.28 (s, CH_3-*C*), 48.91, 49.07 (s, CH), 171.42 (d, *J*(PC) = 18.6 Hz, P-C), 174.12 (d, *J*(PC) = 2 Hz, *t*-Bu-*C*); ^{15}N NMR ($CDCl_3$, $MeNO_2$) −304.30 (d, *J*(PN) = 67.7 Hz, N-P), −84.14 (s, *t*-Bu-CN), −65.30 (d, *J*(PN) = 7.5 Hz, P–C–N); IR (neat) 1560 (C=N) cm^{-1}, mass spectrum, *m/e* 356 (M^+). Anal. Calcd for $C_{18}H_{37}N_4OP$: C, 60.64; H, 10.46; N, 15.72; P, 8.69. Found: C, 60.50; H, 10.49; N, 15.63; P, 8.57. **11** (R = *p*-tolyl) 25% yield; mp 118 °C; ^{31}P NMR ($CDCl_3$) +38.22 ppm; ^1H NMR ($CDCl_3$), 1.30 (d, *J*(HH) = 7 Hz, 24 H, CHCH_3), 2.40 (s, 3 H, $C_{ar}CH_3$), 3.45 (sept d, *J*(HH) = 7 Hz, *J*(PH) = 14 Hz, 4 H, CH), 7.25 and 7.95 (AB system, J_{AB} = 7 Hz, 4 H, H_{ar}); ^{13}C NMR ($CDCl_3$) 21.66 (s, CH_3C_{ar}) 23.09, 23.77, 24.12, 24.44 (s, CH_3-CH), 48.95, 49.56 (s, CH), 122.01, 126.87, 129.81, 141.80 (s, C_{ar}), 165.73 (s, Ar–*C*–O), 171.50 (d, *J*(PC) = 21.36 Hz, P–C); IR (KBr) 1615 (C=N) cm^{-1}; mass spectrum, *m/e* 390 (M^+). Anal. Calcd for $C_{21}H_{35}N_4OP$: C, 64.59; H, 9.01; N, 14.35; P, 7.93. Found: C, 64.45; H, 8.96; N, 14.28; P, 7.85.

Attempted Distillation of Bis(diisopropylamino)phosphinodiazomethane (14). Distillation of **14** (542 mg, 2 mmol), under vacuum (10^{-2} mmHg), in a claisen with an oil bath at 160 °C, led to phosphinonitrile **17** (154 mg, 30%) as the only distilable product. **17**: bp 80–85 °C (10^{-2} mmHg); mp 105 °C; ^{31}P NMR (C_6H_6) +29 ppm; ^1H NMR (C_6D_6) 1.00 (d, *J*(HH) = 7 Hz, 12 H, CCH_3), 1.15 (d, *J*(HH) = 7 Hz, 12 H, CCH_3), 3.4 (sept d, *J*(HH) = 7 Hz, *J*(PH) = 14 Hz, 4H, CH); mass spectrum, *m/e* 257 (M^+). Anal. Calcd for $C_{13}H_{28}N_3PC$: 60.67; H, 10.97; N, 16.33. Found: C, 60.52; H, 10.88; N, 16.40.

Thermolysis of 14. **14** (500 mg, 1.84 mmol), vaporized under vacuum (10^{-2} mmHg) through a 25-cm high column heated at 250 °C, led to **19** as a 70/30 mixture of diastereoisomers (60% total yield) along with **17** (20% yield). The isomeric mixture **19** was characterized by ^{31}P NMR spectroscopy ($\delta^{31}P$ +64.09/+74.00), and then the mixture of diastereoisomers was isolated by column chromatography (pentane/ether, 90/10), after treatment with elemental sulfur: ^{31}P NMR ($CDCl_3$) +73.10/+82.35; ^{13}C NMR ($CDCl_3$) 19.43 (s)/20.93 (d, *J*(PC) = 4.6 Hz), CH_3CH ring; 22.61, 22.63, 22.65, 22.67, 24.33 (s)/22.60, 23.65, 23.67, 23.68, 23.69 (s), CH_3CH; 30.30 (s)/30.04 (d, *J*(PC) = 2.0 Hz), CCH_2C; 33.13 (d, *J*(PC) = 82.2 Hz)/31.84 (d, *J*(PC) = 82.3 Hz), PCH_2; 43.67 (d, *J*(PC) = 5.6 Hz)/44.68 (d, *J*(PC) = 5.4 Hz), CH; 46.81 (d, *J*(PC) = 5.2 Hz)/46.55 (d, *J*(PC) = 5.2 Hz), CH; 50.97 (d, *J*(PC) = 20.9 Hz)/49.10 (d, *J*(PC) = 20.9 Hz), CH ring; mass spectrum, *m/e* 276 (M^+). Anal. Calcd for $C_{13}H_{29}N_2PS$: C, 56.46; H, 10.57; N, 10.13. Found: C, 56.32; H, 10.45; N, 10.05.

Thermolysis of 1. **1** (688 mg, 2 mmol) was pyrolyzed by using the same procedure as described for **14**. Compound **2** (505 mg, 80% yield) was obtained as a red oil. Anal. Calcd for $C_{16}H_{37}N_2PSi$: C, 60.71; H, 11.78; N, 8.84. Found: C, 60.99; H, 11.95; N, 8.60.

Reaction of 2 with Trimethylsilyl Azide. To a toluene solution of 2 (300 mg, 0.95 mmol) was added, at −78 °C, trimethylsilyl azide (115 mg, 1 mmol). The reaction was followed by NMR spectroscopy, and **20** was characterized at 4 °C: ^{31}P NMR (C_6D_6) +76.2 ppm; ^{13}C NMR (C_6D_6) −0.64 (s, CH_3SiC), +1.61 (s, CH_3SiN), 22.63, 23.43 (s, CH_3C), 47.09 (d, *J*(PC) = 4.53 Hz, CH); ^{29}Si NMR (C_6D_6) −8.25 (d, *J*(PSi) = 33.5 Hz, SiN), +12.95 (d, *J*(PSi) = 12.56 Hz, SiC). After 3 h, at room temperature, the solvent was removed, and **21** was obtained as a yellow oil in near quantitative yield. **21**: ^{31}P NMR (C_6D_6) +3.9 ppm; ^{13}C NMR (C_6D_6) −0.30 (s, CH_3SiC), +4.83 (s, CH_3SiN), 24.11, 24.16, 24.68, 24.69 (s, CH_3C), 31.93 (d, *J*(PC) = 150.04 Hz, C=N_2), 46.64 (d, *J*(PC) = 6.04 Hz, CH); ^{29}Si NMR (C_6D_6) −19.25 (d, *J*(PSi) = 34.34 Hz, SiN), +0.27 (d, *J*(PSi) = 8.58 Hz, SiC); IR (pentane) 2060 cm^{-1}; mass spectrum, *m/e* 431 (M^+). Anal. Calcd for $C_{19}H_{46}N_5PSi_2$: C, 52.85; H, 10.74; N, 16.22. Found: C, 52.50; H, 10.51; N, 16.09.

Pyrolysis of 2. **2** (600 mg, 1.9 mmol) was pyrolyzed by using the same procedure as described for **14**, but the column was heated at 300 °C. **22** was obtained as a mixture of four diastereoisomers (90% total yield) which were characterized by ^{31}P NMR spectroscopy: **22a–d**: $\delta^{31}P$ (C_6D_6) +73.25, +74.41, +74.63, +86.27 ppm. After treatment with elemental sulfur and column chromatography, the two major isomers, **23a** and **23b**, were isolated in pure form, while the minor ones were characterized as a mixture by NMR spectroscopy. **23a**: white crystals (45%, mp 129 °C); ^{31}P NMR +82.78 ppm; ^{13}C NMR (C_6D_6) −1.28 (s, $SiCH_3$), 19.63 (d, *J*(PC) = 4.45 Hz, $CHCH_3$ ring), 23.74 24.79, 24.89, 25.15, 25.20 (s, $CH(CH_3)_2$), 28.15 (d, *J*(PC) = 71.6 Hz, $CHSiMe_3$), 32.97 (s, CH_2), 42.86 (d, *J*(PC) = 6.0 Hz, $CH(CH_3)_2$), 46.85 (d, *J*(PC) = 5.6 Hz, $CH(CH_3)_2$), 52.40 (d, *J*(PC) = 21.7 Hz, $CHCH_3$ ring); mass spectrum, *m/e* 348 (M^+). **23b**: white crystals (30%, mp 113 °C); ^{31}P NMR (C_6D_6) +77.74 ppm; ^{13}C NMR (C_6D_6) −0.32 (s, $SiCH_3$), 21.45 (d, *J*(PC) = 4.45, $CHCH_3$ ring), 24.59, 24.76, 25.00 (s, $CH(CH_3)_2$), 33.81 (s, CH_2), 36.35 (d, *J*(PC) = 74.4 $CHSiMe_3$), 44.00 (d, *J*(PC) = 5.7 Hz, $CH(CH_3)_2$), 48.44 (d, *J*(PC) = 5.35 Hz, $CH(CH_3)_2$), 51.26 (d, *J*(PC) = 16.70 Hz, $CHCH_3$ ring). Anal. Calcd for $C_{16}H_{37}N_2PSSi$: C, 55.12; H, 10.70; N, 8.04. Found: 55.20; H, 10.72; N, 7.99. **23c**: ^{31}P NMR +86.80 ppm; ^{13}C NMR (C_6D_6) −0.73 (s, $SiCH_3$), 19.73 (s, $CHCH_3$ ring), 24.07, 24.64, 24.72, 25.10, 25.20 (s, $CH(CH_3)_2$), 25.62 (d, *J*(PC) = 64.2 Hz, $CHSiMe_3$), 32.77 (d, *J*(PC) = 4.07 Hz, CH_2), 44.28 (d, *J*(PC) = 5.36 Hz, $CH(CH_3)_2$), 47.15 (d, *J*(PC) = 5.8 Hz, $CH(CH_3)_2$), 47.68 (d, *J*(PC) = 20.1 Hz, $CHCH_3$ ring). **23d**: ^{31}P NMR (C_6D_6) +86.40.

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