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Phosphonitriles: Versatile Intermediates

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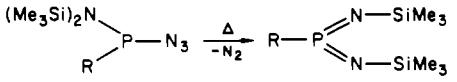
The photochemical and thermal behavior of five new azides $RR'PN_3$ (**2a–e**) is reported. Evidence for the primary formation of transient phosphonitriles RR'P≡N (**5a–e**) is given for all the azides by trapping with Me_3SiCl or/and structures: a In the absence of trapping agents, depending on the nature of the phosphorus substituents, the phosphonitriles dimerized, giving nonisolated cyclodiphosphazenes **3b,c** (R = $(i\text{-Pr})_2N$, R′ = Me_2N or *t*-Bu), trimerized, affording isolated cyclotriphosphazene **3a** (R = R″ = *t*-Bu), polymerized (R = $(i\text{-Pr})_2N$, R′ = Me_2N or *t*-Bu; R = R′ = *t*-Bu), or even rearranged via 1 → 3 trimethylsilyl migration (R = $(Me_3Si)_2N$, R′ = $(Me_3Si)_2CH$ or 2,2,6,6-tetramethylpiperidino), leading to stable or unstable tricoordinated pentavalent phosphorus derivatives ((methylene)(imino)phosphoranes **8d** and **11e** or bis(imino)phosphorane **10e**). The first spectroscopically characterized 1,3-diaza-2λ⁵,4λ⁵-diphosphetene **13e** resulting from a [2 + 2] cycloaddition of the phosphonitrile **5e** on a bis(imino)phosphorane, **10e**, is reported. No Staudinger reactions involving the azido group of phosphines **2** were observed.

The Curtius type rearrangement and the Staudinger reaction appeared to be very general features for organic[1] and heavier main-group-element[2] azides. However, phosphine azides present an entirely different behavior. Depending on the nature of the substituents, three types of reaction have been reported.

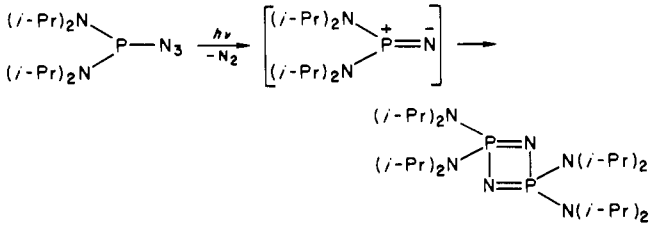
(i) Formation of phosphorus–nitrogen containing polymers have been observed with alkyl or aryl substituted phosphine azides.[3]

$$R_2P{-}N_3 \xrightarrow{-N_2} (R_2P{=}N{-})_{3,n} \qquad R = Ph, CF_3$$

(ii) The use of bulky silylated-amino substituents has provided a new route to tricoordinated pentavalent phosphorus derivatives by 1→3 silyl migration.[4]



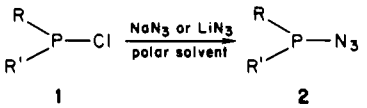
(iii) Bis(diisopropylamino)azidophosphine led to a transient phosphonitrile[5] that dimerized into the corresponding cyclodiphosphazene.[6]



Here we wish to demonstrate that a phosphonitrile is, in fact, always involved in all of these reactions, and we will discuss the particular behavior of phosphine azides and, specially, the absence of Staudinger reaction.

Results and Discussion

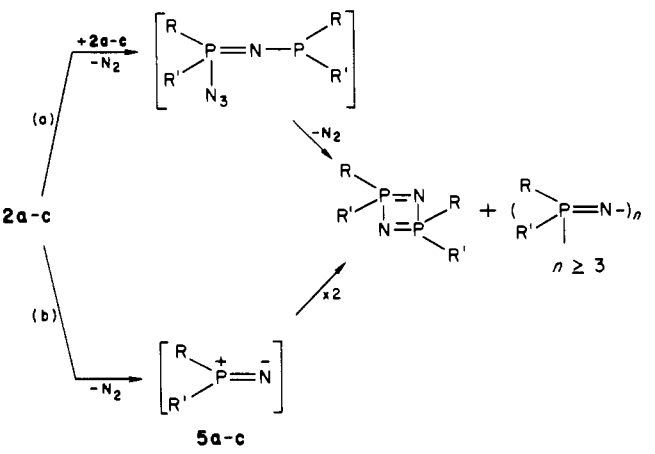
Phosphine azides **2** have been prepared by action of an alkali-metal azide on the corresponding chlorophosphine **1**, in a polar solvent, either at −25 °C (**2a–c**) or at room temperature (**2d,e**).[7]



1 **2**

a: R = *t*-Bu, R′ = *t*-Bu
b: R = *t*-Bu, R′ = $N(i\text{-Pr})_2$
c: R = NMe_2, R′ = $N(i\text{-Pr})_2$
d: R = $(Me_3Si)_2CH$, R′ = 2,2,6,6-tetramethylpiperidino
e: R = $(Me_3Si)_2CH$, R′ = $(Me_3Si)_2N$

Scheme I



Among these azides, **2a** appears to be the least thermally stable with respect to loss of nitrogen. It slowly decomposed even at −20

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(1) See for example: (a) Patai, S. *The Chemistry of the Azido Group*; Wiley-Interscience: New York, 1971. (b) Lwowski, W. *Nitrenes*; Wiley-Interscience: New York, 1970. (c) Scriven, E. F. V. *Azides and Nitrenes: Reactivity and Utility*; Academic: New York, 1984. (d) Gololobov, Yu. G.; Zhmurova, I. N.; Kasukhin, L. F. *Tetrahedron* **1981**, *37*, 937.
(2) See for example: (a) Bertrand, G.; Majoral, J. P.; Baceiredo, A. *Acc. Chem. Res.* **1986**, *19*, 17. (b) Thayer, J. S. *Organomet. Chem. Rev.* **1966**, *1*, 157. (c) Meier, H. U.; Paetzold, P.; Schröder, E. *Chem. Ber.* **1984**, *117*, 1954. (d) Parker, D. R.; Sommer, L. H. *J. Am. Chem. Soc.* **1976**, *98*, 618. (e) Baceiredo, A.; Bertrand, G.; Majoral, J. P.; Mazerolles, P. *Nouv. J. Chim.* **1983**, *7*, 645. (f) Baceiredo, A.; Bertrand, G.; Mazerolles, P. *Tetrahedron Lett.* **1981**, *22*, 2553. (g) Baceiredo, A.; Bertrand, G.; Majoral, J. P.; Vermuth, V.; Schmutzler, R. *J. Am. Chem. Soc.* **1984**, *106*, 7065. (h) Mulliez, M.; Majoral, J. P.; Bertrand, G. *J. Chem. Soc., Chem. Commun.* **1984**, 284.
(3) (a) Paciorek, K. L.; Kratzer, R. *Inorg. Chem.* **1964**, *3*, 594. (b) Tesi, G.; Haber, C. P.; Douglas, C. H. *Proc. Chem. Soc., London* **1960**, 219. (c) Herring, D. L. *Chem. Ind. (London)* **1960**, 717. (d) Tesi, G.; Douglas, C. M.; Haber, C. P. U.S. Patent 3087937, 1963. (e) Herring, D. L.; Douglas, C. M. *Inorg. Chem.* **1965**, *4*, 1012. (f) Kratzer, R. H.; Paciorek, K. L. *Inorg. Chem.* **1965**, *4*, 1767. (g) Paciorek, K. L.; Kratzer, R. H. U.S. Patent 3297751, 1966.
(4) (a) Schäfer, H. G. Dissertation, Universität Bielefeld, 1981. (b) Wildbredt, D. A. Dissertation, Universität Bielefeld, 1981. (c) Min Xie, Z.; Neilson, R. H. *Organometallics* **1983**, *2*, 921. (d) Neilson, R. H. *Inorg. Chem.* **1981**, *20*, 1679.
(5) (a) Sicard, G.; Baceiredo, A.; Bertrand, G.; Majoral, J. P. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 459. (b) Baceiredo, A.; Bertrand, G.; Majoral, J. P.; El Anba, F.; Manuel, G. *J. Am. Chem. Soc.* **1985**, *107*, 3945. (c) Majoral, J. P.; Bertrand, G.; Baceiredo, A.; Ocando, E. *Phosphorus Sulfur*, in press.
(6) Baceiredo, A.; Bertrand, G.; Majoral, J. P.; Sicard, G.; Jaud, J.; Galy, J. *J. Am. Chem. Soc.* **1984**, *106*, 1984.
(7) Although, up to now, no explosions occurred with compound **2**, maximum care must be taken. For example, $(CF_3)_2P{-}N_3$ is a violent detonator even at −196 °C.[3b]

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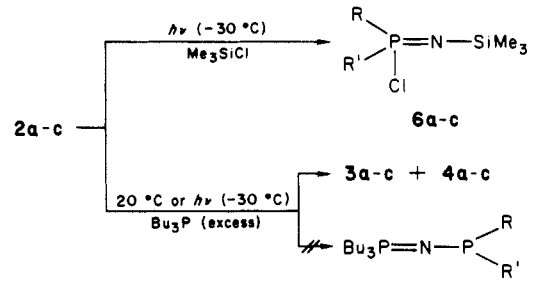
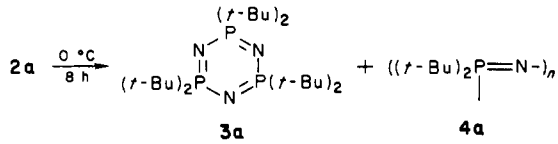
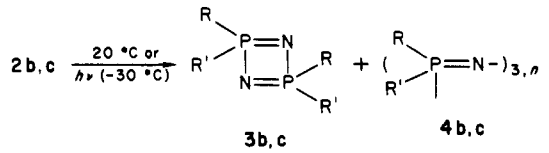
Scheme II



°C and the decomposition is complete, at 0 °C, within 8 h, leading mainly to the hexa-*tert*-butylcyclotriphosphazene **3a** along with cyclopolyphosphazenes **4a**.[8]



2b and **2c**, stable up to 0 °C, lead to a mixture of polyphosphazenes in the same way at 20 °C or by photolysis at −30 °C. According to the ^{31}P NMR spectrum, it is quite likely that cyclodiphosphazenes **3b** and **3c** are formed. However, because of their high instability, all attempts to isolate these products failed.



Two mechanisms could be postulated to rationalize the formation of cyclopolyphosphazenes **3** and **4**: (a) the Staudinger reaction or (b) polymerization of transient phosphonitrile **5** (Scheme I).

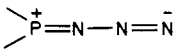
However, the photolysis of **2a–c**, at −20 °C, in the presence of a stoichiometric amount of trimethylchlorosilane leads to the chlorophosphazenes **6a–c**, which clearly result from a 1–2 addition of the trapping agent on transient phosphonitriles **5a–c**. Moreover, pathway a can be ruled out since the formation of cyclopolyphosphazenes **3** and **4** is not inhibited when phosphine azides **2a–c** are heated or irradiated in the presence of a large excess of tributylphosphine (Scheme II).

Azidophosphine **2d** is perfectly stable at room temperature; it melts without decomposition at 59–63 °C. In a first approach, its thermal and photochemical behavior is quite different from that observed for azides **2a–c**. Thermolysis at 70 °C quantitatively leads to stable (2,2,6,6-tetramethylpiperidino)((trimethylsilyl)imino)((trimethylsilyl)methylene)phosphorane (**8d**), while photolysis at −60 °C gives rise to the same product **8d**, along with another species, **9d** (5% yield) (Scheme III).

The structural assignment of the byproduct **9d** is mainly based on ^{31}P NMR spectroscopy. Its chemical shift (+319 ppm; $^3J_{PH}$ = 17.9 Hz) could be in agreement with the phosphonitrile structure of **5d** since the only characterized λ^5-phosphorus–nitrogen triple-bonded-like[5b] species has a ^{31}P chemical shift of +246 ppm. However, the ^{31}P signal at +319 ppm remains unchanged after addition of Me_3SiCl, excluding the phosphonitrile possibility. Therefore, dicoordinated species **9** or **10** is the most suitable candidate. **9** results from a 1→2 alkyl migration while **10** arises from amino migration followed by subsequent 1→3 hydrogen shift.[9]

A concerted 1→3 and 1→2 migration–nitrogen-loss mechanism could explain the formation of **8d** and **9d** or **10d**, respectively. However, photolysis or thermolysis of phosphine azide **2d**, in the presence of trimethylchlorosilane or dimethyldichlorosilane, demonstrate that the phosphonitrile **5d** is the common intermediate since the chlorophosphazenes **6d** and **7d** are obtained in quantitative yield (obviously, if **6d** could result from 1→2 chlorotrimethylsilyl addition on the phosphorus–carbon double bond of **8d**, obtention of **7d** can only be explained by the transient formation of **5d** (Scheme III)). Further evidence for phosphonitrile–bis(imino)phosphorane or (methylene)phosphorane–(imino)phosphorane rearrangements was found by starting from (bis(trimethylsilyl)amino)(bis(trimethylsilyl)methyl)azidophosphine (**2e**). Indeed, when photolysis is carried out in pure trimethylchlorosilane at 0 °C for 4 h, the chlorophosphazene **6e** is obtained in high yield, strongly supporting the transient formation of the phosphonitrile **5d**. Thermolysis at 80 °C or photolysis at room temperature leads to the diazadiphosphetidine **12e**, which apparently results from head to tail dimerization of the phosphorus–nitrogen double bond of the bis(imino)phosphorane intermediate **10e** (Scheme IV) However, when the photolysis is performed at −70 °C, new species are formed. The major product (60% yield) appears to be the diazadiphosphetene **13e**—which is the first example of a new class of P_2N_2 ring—arising from [2 + 2] cycloaddition of the phosphonitrile **5e** on the transient bis(imino)phosphorane **10e** (note that such [2 + 2] cycloadditions involving a phosphonitrile have already been observed with dimethyl sulfoxide[5b,c]). Not surprisingly, the diazadiphosphetene **13e** is thermally unstable and isomerizes into the diazadiphosphetidine **12e** via 1→3 trimethylsilyl migration at −10 °C. One of the minor products (5%) has been identified as the (imino)(methylene)phosphorane **11e** coming from the migration of a trimethylsilyl group from the carbon atom (Scheme IV).

An examination of these results as well as those previously reported[3-6] reveals (i) low thermal stability of phosphine azides, (ii) formation of a phosphonitrile-type intermediate that dimerizes, trimerizes, polymerizes, or alternatively leads to tricoordinated pentavalent phosphoranes, depending on the nature of the phosphorus substituents, (iii) no Staudinger reaction with phosphine, and (iv) quasi-absence of a Curtius-type rearrangement. This instability and anomalous reactivity may be easily explained by the delocalization of the nonbonded electron pair of the phosphorus atom strongly favoring the resonance form



Experimental Section

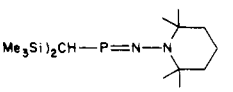
All experiments were performed in an atmosphere of dry argon or nitrogen. Melting points are uncorrected. ^1H NMR spectra were recorded on a Bruker WM 250 or a Bruker WP 80 spectrometer. ^1H chemical shifts are reported in ppm relative to Me_4Si as internal standard. ^{31}P NMR spectra were obtained on a Bruker AC 80 at 32.43 MHz and a Varian FT 80A at 32.203 MHz, respectively. Downfield shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. ^{13}C NMR spectra were recorded on a Bruker AC 80 at 20.15 MHz or a Varian FT 80A at 20.00 MHz. Infrared spectra were recorded on a Beckman IR 10 and a Perkin-Elmer lattice spectrometer (Model 598), respectively, by using polystyrene film for calibration. Mass spectra were obtained on a Ribermag R 10-10 E instrument or a Varian MAT 311 A.

Photochemical reactions were performed in quartz tubes with a Rayonnet photochemical reactor.

Synthesis of *tert*-Butyl(diisopropylamino)chlorophosphine (1b). To a solution of (diisopropylaminodichlorophosphine (1 g, 4.95 mmol) in 10

(8) For reviews concerning polyphosphazenes see: (a) Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic: New York, 1972. (b) Allcock, H. R. *Chem. Eng. News* **1985**, *63*, 22.

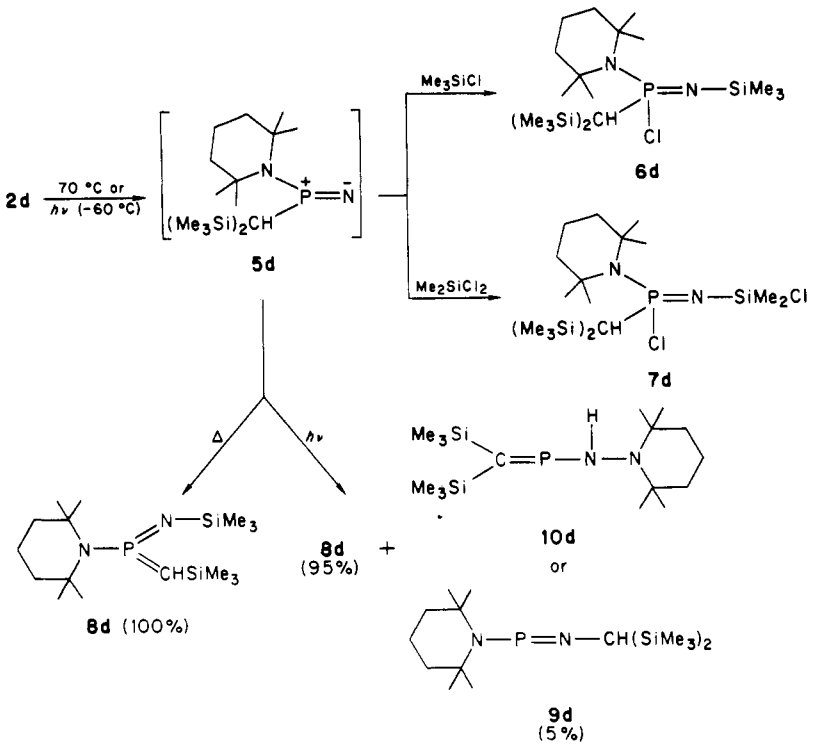
(9) The (imino)phosphane form



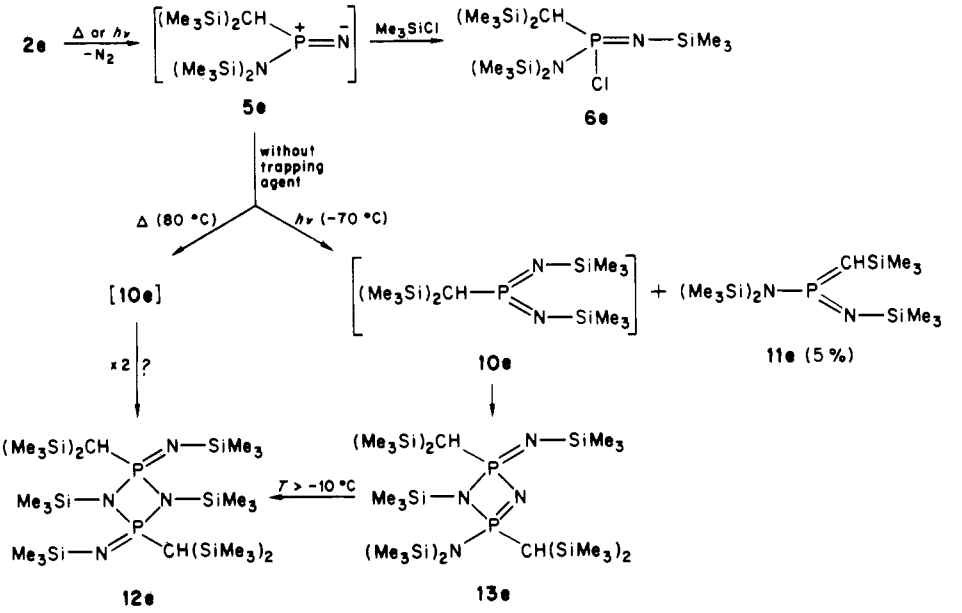
can be ruled out since it has been shown[10] that the compounds of type $(Me_3Si)_2CH—P{=}N—R$ spontaneously rearrange to phosphaalkenes $(Me_3Si)_2C{=}P—NHR$.

(10) Niecke, E.; Symalla, E., unpublished results.

Scheme III



Scheme IV



mL of ether maintained at −70 °C was added dropwise a solution of *tert*-butyllithium in hexane (4.95 mmol). The mixture was stirred at room temperature for 2 h. After filtration and evaporation of the solvent the residue was extracted with a hexane acetonitrile (4/1) solution. Removal of the solvent afforded 1.1 g (75% yield) of **1b** as a yellow liquid, which was used without further purification. ^{31}P NMR (C_6D_6): 151. ^1H NMR (C_6D_6): 1.05 (d, J_{HH} = 7 Hz, 6 H, $CHCH_3$), 1.10 (d, $^3J_{HP}$ = 16 Hz, 9 H, $C(CH_3)_3$), 1.15 (d, J_{HH} = 7 Hz, 6 H, $CHCH_3$), 3.50 (m, 2 H, $CHCH_3$).

Synthesis of (Dimethylamino)(diisopropylamino)chlorophosphine (1c). Diisopropylamine (15.7 g, 155 mmol) was added dropwise to an ethereal solution (50 mL) maintained at −70 °C of (dimethylamino)dichlorophosphine (11 g, 75 mmol). The resulting mixture was stirred 4 h at room temperature. Pentane (50 mL) was added, and the chlorohydrate was eliminated by filtration on Celite. After evaporation of the solvent, the residue was dissolved in 20 mL of hexane and washed with acetonitrile (5 mL). After evaporation of hexane and acetonitrile, **1c** (9.6 g, 76% yield) was obtained as an oil. ^{31}P NMR (C_6D_6): 150. ^1H NMR (C_6D_6): 0.97 (d, J_{HH} = 7 Hz, 6 H, CCH_3), 1.12 (d, J_{HH} = 7 Hz, 6 H, CCH_3), 2.38 (d, J_{HP} = 14 Hz, 6 H, NCH_3), 3.50 (m, 2 H, $CHCH_3$).

Synthesis of (Bis(trimethylsilyl)methyl)(2,2,6,6-tetramethylpiperidino)chlorophosphine (1d). A 16.6-g (113-mmol) sample of the lithium salt of 2,2,6,6-tetramethylpiperidine was dissolved in 100 mL of ether, and this mixture was added dropwise to a stirred solution of 29.6 g (113 mmol) of (bis(trimethylsilyl)methyl)dichlorophosphine in 100 mL of ether. The mixture was cooled to 0 °C for a further 4 h and then allowed to warm up to room temperature overnight. After filtration and evaporation of the solvent the byproduct of the reaction ($EtO-P(Cl)-CHR_2$) could be separated in vacuo at 60 °C for several hours. The remaining pure **1d** is a red viscous liquid, 20.5 g (49.5% yield). ^{31}P NMR ($CDCl_3$): 162.6. ^1H NMR ($CDCl_3$): 0.24 (d, $^4J_{HP}$ = 0.6 Hz, 9 H, $SiCH_3$), 0.28 (d, $^4J_{HP}$ = 1.0 Hz, 9 H, $SiCH_3$), 1.50 (s, 12 H, CCH_3), 1.63 (s, 6 H, CH_2), 2.36 (d, $^2J_{HP}$ = 19.5 Hz, 1 H, $CHSi_2$). ^{13}C NMR ($CDCl_3$): 2.3 (d, $^3J_{CP}$ = 4.5 Hz, SiC_3), 3.1 (d, $^3J_{CP}$ = 6.3 Hz, SiC_3), 16.4 (s, CH_2), 29.5 (d, $^1J_{CP}$ = 93.4 Hz, PCH), 29.4 (d, $^3J_{CP}$ = 9.2 Hz, CCH_3), 29.5 (d, $^3J_{CP}$ = 6.5 Hz, CCH_3), 33.8 (s, CCH_3), 36.0 (d, $^3J_{CP}$ = 41.4 Hz, CCH_3), 39.7 (d, $^3J_{CP}$ = 22.2 Hz, CH_2), 39.8 (d, $^3J_{CP}$ = 16.6 Hz, CH_2), 60.1 (d, $^2J_{CP}$ = 29.8 Hz, NC), 62.1 (d, $^2J_{CP}$ = 11.9 Hz, NC). Mass spectrum *m/e*: 365 (M^+).

Synthesis of (Bis(trimethylsilyl)methyl)(bis(trimethylsilyl)amino)-

chlorophosphine (1e). A solution of lithium bis(trimethylsilyl)amide (5.9 g, 35 mmol) in 30 mL of hexane was added to (bis(trimethylsilyl)-methyl)dichlorophosphine (9.2 g, 35 mmol) in 20 mL of hexane. The mixture was heated to reflux for 2 h, and LiCl was separated from it. After evaporation of the solvent, **1e** was distilled: bp 108–112 °C (0.1 mmHg); 8.3 g (61% yield). ^{31}P NMR (C_6D_6): 177.6. ^{1}H NMR (CH_2Cl_2): 0.15 (d, $^4J_{HP}$ = 0.8 Hz, 9 H, $NSiCH_3$), 0.21 (d, $^4J_{HP}$ = 0.8 Hz, 9 H, $NSiCH_3$), 0.30 (d, $^4J_{HP}$ = 1.6 Hz, 18 H, $CSiCH_3$), 1.98 (d, $^2J_{HP}$ = 15.1 Hz, 1 H, PCH). ^{13}C NMR (C_6D_6): 2.1 (d, $^3J_{CP}$ = 5.3 Hz, $CSiC_3$), 2.9 (d, $^3J_{CP}$ = 4.8 Hz, $CSiC_3$), 4.4 (d, $^3J_{CP}$ = 3.1 Hz, $NSiC_3$), 4.8 (d, $^3J_{CP}$ = 1.2 Hz, $NSiC_3$), 28.6 (d, $^1J_{CP}$ = 90.2 Hz, PCH). Mass spectrum *m/e*: 385 (M^+).

Synthesis of Di-*tert*-butylazidophosphine (2a). Sodium azide (0.20 g, 3 mmol) was added to a solution of di-*tert*-butylchlorophosphine (0.50 g, 2.8 mmol) in 10 mL of acetonitrile–toluene (1/2) solution at −18 °C. After the mixture was stirred for 4 h at −18 °C, the precipitate was eliminated by filtration at low temperature and **2a** was kept in solution at −60 °C. Removal of the solvent caused decomposition of the product. ^{31}P NMR (C_6D_6): 133. ^{1}H NMR (C_6D_6): 1.10 (d, $^3J_{HP}$ = 16.5 Hz, 18 H, CH_3). IR (C_6D_6): 2110 cm^{-1} (P–N_3).

Synthesis of *tert*-Butyl(diisopropylamino)azidophosphine (2b). To a solution of *tert*-butyl(diisopropylamino)chlorophosphine (**1b**) (0.50 g, 2.2 mmol) in 1 mL of acetonitrile and 2 mL of benzene cooled at 0 °C was added sodium azide (0.17 g, 2.6 mmol). After the mixture was stirred for 2 h at 0 °C, 20 mL of hexane was added and the resulting mixture was filtered on Celite. Impurities were extracted with 5 mL of acetonitrile; after evaporation of the hexane 0.4 g of **2b** (83% yield) was obtained as a yellow liquid and used without further purification. ^{31}P NMR (C_6D_6): 121. ^{1}H NMR (C_6D_6): 1.10 (d, J_{HP} = 16 Hz, 9 H, CCH_3), 1.11 (d, J_{HH} = 7 Hz, 6 H, $CHCH_3$), 1.20 (d, J_{HH} = 7 Hz, 6 H, $CHCH_3$), 3.45 (m, 2 H, $CHCH_3$). IR (neat): 2160 cm^{-1} (P–N_3).

Synthesis of (Dimethylamino)(diisopropylamino)azidophosphine (2c). Sodium azide (0.40 g, 5.97 mmol) was added to a solution of (dimethylamino)(diisopropylamino)chlorophosphine (**1c**) (1 g, 5.97 mmol) in 20 mL of acetonitrile–toluene (1/1) solution at −18 °C. After the mixture was stirred for 4 h at −18 °C, the precipitate was eliminated by filtration at −10 °C and the solvent removed at low pressure. Crude **2c** (1.20 g) was obtained as a yellow liquid and used without further purification. ^{31}P NMR (C_6D_6): 112. ^{1}H NMR (C_6D_6): 1.00 (d, J_{HH} = 7 Hz, 6 H, $CHCH_3$), 1.10 (d, J_{HH} = 7 Hz, 6 H, $CHCH_3$), 2.40 (d, J_{HP} = 11 Hz, 6 H, NCH_3), 3.30 (m, 2 H, $CHCH_3$). IR (neat): 2115 cm^{-1} (P–N_3).

Synthesis of (Bis(trimethylsilyl)methyl)(2,2,6,6-tetramethylpiperidino)azidophosphine (2d). (Bis(trimethylsilyl)methyl)(2,2,6,6-tetramethylpiperidino)chlorophosphine (**1d**) (20.5 g, 56 mmol) and lithium azide (2.8 g, 57 mmol) in 20 mL of pyridine were stirred at room temperature for 3 days. After filtration and evaporation of pyridine the crude product, **2d**, was dissolved in 25 mL of hexane and recrystallized at −30 °C: mp 59–63 °C; 13.0 g (62% yield). ^{31}P NMR ($CDCl_3$): 132.7. ^{1}H NMR ($CDCl_3$): 0.21 (s, 18 H, $SiCH_3$), 1.45 (m, 12 H, CCH_3), 1.59 (m, 6 H, CH_2), 1.80 (d, $^2J_{HP}$ = 11.2 Hz, 1 H, PCH). ^{13}C NMR ($CDCl_3$; −40 °C): 2.1 (s, SiC_3), 2.2 (d, $^3J_{CP}$ = 11.1 Hz, SiC_3), 17.2 (s, CH_2), 24.9 nd, $^1J_{CP}$ = 67.7 Hz, PCH), 28.5 (d, $^3J_{CP}$ = 2.6 Hz, CCH_3), 31.6 (d, $^3J_{CP}$ = 5.5 Hz, CCH_3), 34.0 (d, $^3J_{CP}$ = 0.8 Hz, CCH_3), 36.0 (d, $^3J_{CP}$ = 42.5 Hz, CCH_3), 40.0 (d, $^3J_{CP}$ = 4.7 Hz, CH_2), 41.1 (s, CH_2), 56.9 (d, $^2J_{CP}$ = 31.5 Hz, NC), 60.4 (d, $^2J_{CP}$ = 10.2 Hz, NC). IR (Nujol): 2095 cm^{-1} (P–N_3). Mass spectrum *m/e*: 372 (M^+).

Syntbesis of (Bis(trimethylsilyl)methyl)(bis(trimethylsilyl)amino)-azidophosphine (2e). A solution of (bis(trimethylsilyl)methyl)(bis(trimethylsilyl)amino)chlorophosphine (**1e**) (5.9 g, 15 mmol) and lithium azide (0.75 g, 15 mmol) in 15 mL of pyridine was stirred at room temperature for 1 day. After filtration and evaporation of the solvent the product, **2e**, is obtained almost quantitatively as pale yellow crystals: mp 27–31 °C; 5.7 g (95% yield). ^{31}P NMR (C_6D_6): 143.6. ^{1}H NMR (C_6D_6): 0.16 (d, $^4J_{HP}$ = 0.7 Hz, 9 H, $CSiCH_3$), 0.24 (d, $^4J_{HP}$ = 0.9 Hz, 9 H, $CSiCH_3$), 0.30 (d, $^4J_{HP}$ = 1.3 Hz, 18 H, $NSiCH_3$), 1.52 (d, $^2J_{HP}$ = 8.7 Hz, 1 H, PCH). ^{13}C NMR (C_6D_6): 2.0 (d, $^3J_{CP}$ = 5.2 Hz, $CSiC_3$), 2.5 (d, $^3J_{CP}$ = 5.2 Hz, $CSiC_3$), 4.5 (s, $NSiC_3$), 4.9 (s, $NSiC_3$), 23.4 (d, $^1J_{CP}$ = 66.9 Hz, PCH). IR (neat): 2100 cm^{-1} (P–N_3).

Synthesis of Hexa-*tert*-butylcyclotriphosphazene (3a). To a solution of di-*tert*-butylchlorophosphine (2.6 g, 14 mmol) in 30 mL of toluene–acetonitrile (2/1) maintained at −18 °C was added sodium azide (1 g, 15 mmol). The mixture was stirred at −18 °C for 4 h and then allowed to warm to 0 °C. After filtration and evaporation of the solvents, the residue was washed with 10 mL of hexane. Evaporation of hexane afforded a yellow liquid, which slowly crystallized. Recrystallization from hexane–acetonitrile (1/1) led to **3a** as a yellow powder: mp 248–251 °C; 1.33 g (60% yield). ^{31}P NMR (C_6D_6): 40. ^{1}H NMR (C_6D_6): 1.1 (m, 54 H, CH_3). Mass spectrum *m/e*: 420 (M^+ − *t*-Bu), 363 (M^+ − 2*t*-Bu), 306 (M^+ − 3*t*-Bu), 249 (M^+ − 4*t*-Bu).

Photolysis of Di-*tert*-butylazidophosphine (2a) in the Presence of Trimethylchlorosilane. A solution of di-*tert*-butylazidophosphine (**2a**) (0.075 g, 4 mmol) in deuterated toluene acetonitrile (2/1) solution (2 mL) was irradiated in the presence of trimethylchlorosilane (0.5 g, 5 mmol) at 254 nm for 2 h at −40 °C. After removal of the solvent at reduced pressure (15 mmHg) **6a** was distilled: bp 42 °C (1 mmHg); 0.85 g (80% yield). ^{31}P NMR (C_6D_6): 52. All the other spectroscopic data are in agreement with those of the literature.[11]

Photolysis of *tert*-Butyl(diisopropylamino)azidophosphine (2b) in the Presence of Trimethylchlorosilane. A solution of **2b** (0.1 g, 0.4 mmol) in deuterated toluene–acetonitrile (2/1) (2 mL) was irradiated in the presence of trimethylchlorosilane (0.54 g, 5 mmol) at 254 nm for 2 h at room temperature. According to NMR spectroscopy **6b** was formed in quantitative yield. ^{31}P NMR (C_6D_6): 27. ^{1}H NMR (C_6D_6): 0.35 (s, 9 H, $SiCH_3$), 1.30 (d, J_{HH} = 7 Hz, 6 H, $CHCH_3$), 1.35 (d, J_{HH} = 7 Hz, 6 H, $CHCH_3$), 1.40 (d, J_{HH} = 7 Hz, 6 H, $CHCH_3$), 3.40 (septet of d, J_{HH} = 7 Hz, J_{HP} = 7 Hz, $CHCH_3$). IR (neat): 1330 cm^{-1} (P=N). Mass spectrum *m/e*: 310, 275 (M^+ − Cl).

Photolysis of (Dimethylamino)(diisopropylamino)azidophosphine (2c) in the Presence of Trimethylchlorosilane. (Dimethylamino)(diisopropylamino)azidophosphine (**2c**) (0.22 g, 1 mmol) in deuterated toluene–acetonitrile (2/1) (2 mL) and trimethylchlorosilane (0.13 g, 1.2 mmol) were irradiated at room temperature for 2 h. According to NMR spectroscopy **6c** was formed quantitatively. ^{31}P NMR (CD_3CN): 4.78. ^{1}H NMR (toluene-d_8): 0.15 (s, 9 H, $SiCH_3$), 1.30 (d, J_{HH} = 7 Hz, 6 H, $CHCH_3$), 1.35 (d, J_{HH} = 7 Hz, 6 H, $CHCH_3$), 2.75 (d, $^3J_{HP}$ = 14 Hz, 6 H, NCH_3), 3.60 (m, 2 H, $CHCH_3$). IR (neat): 1345 cm^{-1} (P=N). Mass spectrum *m/e*: 297.

Photolysis of (Bis(trimethylsilyl)methyl)(2,2,6,6-tetramethylpiperidino)azidophosphine (2d) in the Presence of Trimethylchlorosilane. Azidophosphine **2d** (0.37 g, 1 mmol) in 2.5 mL of hexane and trimethylchlorosilane (0.13 g, 1.2 mmol) were irradiated at room temperature for 12 h. According to ^{31}P NMR spectroscopy **6d** was formed almost quantitatively. After evaporation of the solvent **6d** remained as a white crystalline solid. ^{31}P NMR (C_6D_6): 12.5. ^{1}H NMR ($CDCl_3$): 0.09 (s, 9 H, $NSiCH_3$), 0.27 (s, 9 H, $CSiCH_3$), 0.30 (s, 9 H, $CSiCH_3$), 1.41/1.51 (m, 12 H, CCH_3), 1.58/1.66 (m, 6 H, CH_2), 1.92 (d, $^2J_{HP}$ = 21.6 Hz, 1 H, PCH). ^{13}C NMR (C_6D_6): 3.23 (s, $CSiC_3$), 3.43 (d, $^3J_{CP}$ = 1.2 Hz, $CSiC_3$), 4.31 (d, $^3J_{CP}$ = 4.4 Hz, $NSiC_3$), 14.96 (d, $^4J_{CP}$ = 1.1 Hz, CH_2), 34.14 (d, $^1J_{CP}$ = 99.0 Hz, PCH), 39.17 (d, $^3J_{CP}$ = 5.6 Hz, $(CH_2)_2$), 31.09 (d, $^3J_{CP}$ = 4.4 Hz, CCH_3), 31.95 (d, $^3J_{CP}$ = 5.6 Hz, CCH_3), 34.13 (d, $^3J_{CP}$ = 2.9 Hz, $C(CH_3)_2$), 58.58 (d, $^2J_{CP}$ = 13.4 Hz, NC), 58.96 (s, broad, NC). IR (Nujol): 1250 cm^{-1} (P=N). Mass spectrum *m/e*: 452 (M^+).

Synthesis of (Bis(trimethylsilyl)methyl)((chlorodimethylsilyl)imino)(2,2,6,6-tetramethylpiperidino)chlorophosphorane (7d). A solution of **2d** in toluene was heated to 90 °C for 3 h in the presence of dimethyldichlorosilane (20% excess). According to ^{31}P NMR spectroscopy, compound **7d** was the only product of the reaction. ^{31}P NMR ($C_6H_5CH_3$): 17.8. ^{1}H NMR (CH_2Cl_2): 0.27 (s, 18 H, $CSiCH_3$), 0.41 (s, 6 H, $NSiCH_3$), 1.50 (m, 12 H, CCH_3), 1.62/1.67 (m/m, 6 H, CH_2), 1.95 (d, $^2J_{HP}$ = 22 Hz, 1 H, PCH).

Thermolysis of (Bis(trimethylsilyl)methyl)(2,2,6,6-tetramethylpiperidino)azidophosphine (2d). A solution of **2d** in deuterated benzene was heated to 70 °C for 15 h. According to ^{31}P NMR spectroscopy the formation of **8d** was quantitative and was only spectroscopically characterized. ^{31}P NMR (C_6D_6): 100.6. ^{1}H NMR (C_6D_6): 0.35 (s, 9 H, $NSiCH_3$), 0.41 (s, 9 H, $CSiCH_3$), 1.35 (m, 18 H, CCH_3 and CH_2), 2.82 (d, $^2J_{HP}$ = 7.6 Hz, 1 H, P=CH). ^{13}C NMR (C_6D_6): 0.86 (d, $^3J_{CP}$ = 6.8 Hz, $CSiC_3$), 3.14 (d, $^3J_{CP}$ = 3.7 Hz, $NSiC_3$), 17.39 (s, CH_2), 30.56 (d, $^3J_{CP}$ = 1.5 Hz, $C(CH_3)_4$), 39.45 (d, $^3J_{CP}$ = 5.8 Hz, $(CH_2)_2$), 54.36 (s, $(NC)_2$), 68.3 (d, $^1J_{CP}$ = 147.3 Hz, P=CH).

Photolysis of (Bis(trimethylsilyl)methyl)(bis(trimethylsilyl)amino)-azidophosphine (2e) in the Presence of Trimethylchlorosilane. Azidophosphine **2e** (0.4 g, 1 mmol) in 2.5 mL of pentane and trimethylchlorosilane (0.12 g, 1.1 mmol) were irradiated (254 nm) at 0 °C for 4 h. According to ^{31}P NMR spectroscopy the main product was **12e** (70%) whereas **6e** was formed only in a yield of 15%. By irradiation of **2e** in pure trimethylchlorosilane (10-fold excess) **6e** was formed as a main product (65%). All attempts to isolate **6e** in pure form failed. ^{31}P NMR ($CDCl_3$): 15.6 ($^2J_{PH}$ = 24.2 Hz).

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