Triphenylphosphonio-Substituted 1,2,3,4-Triazaphospholes and 1,2,4-Diazaphospholes

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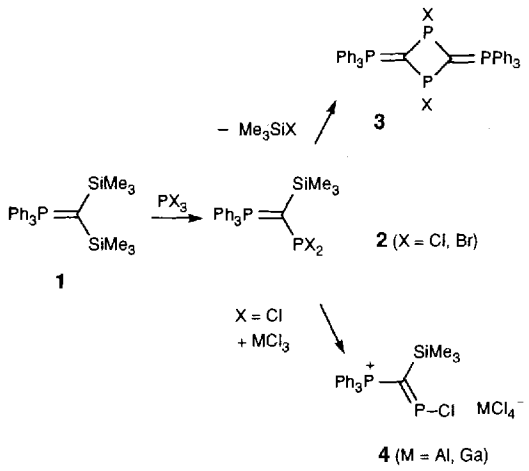
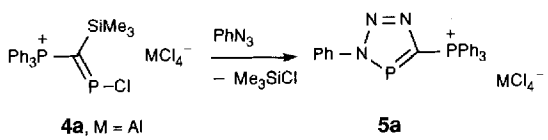
Several products resulting from the condensation of the bis(trimethylsilyl)ylide **1** with PCl_3 serve as synthetic equivalents of a phosphoniophosphaethyne. Cycloaddition reactions with azides lead to phosphonio-1,2,3,4-triazaphosphole cations **5**, **7** and to the zwitterionic phosphonio-1,2,3,4-triazaphospholide **6**. The latter readily undergoes a cycloreversion yielding a phosphoranediyl diazomethane **12** as intermediate. Its cycloaddition affords the diphosphonio-1,2,4-diazaphosholide chloride **9a** as the final product. **9a** is a remarkably stable and unreactive derivative of the two-coordinate phosphorus. By HCl it is protonated at a nitrogen atom to give a dication without any tendency to associate with the chloride counterions.

C-Phosphoniosubstituents at phospholides[1,2], diphospholides[3,4], and triphospholides[5] significantly affect the behavior of the two-coordinate phosphorus ring member(s) and promote its (their) incorporation into the heterocyclic system. The synthesis of phosphonio-substituted azaphospholes and azaphospholides with a π-system isoelectronic to that of phospholides was therefore of interest.

1,2,3,4-Triazaphospholes are known since 1984[6,7] and are accessible by different routes[8,9]. One of them is of interest as model for the intended synthesis. It involves the regiospecific 1,3-dipolar cycloaddition of azides to phosphaalkynes[6,7,10,11] or to certain phosphaalkenes[12,13] which can act as synthons in place of phosphaalkynes. Analogous syntheses of 5-phosphonio-1,2,3,4-triazaphospholes may be anticipated and in one case the cycloaddition of mesityl acide was successfully used for trapping a possible phosphoniophosphaethyne[14]. Although phosphoniophosphaalkynes as such are generally not available as dipolarophiles, some other compounds have recently become accessible that might serve as synthetic equivalents. Starting material is the bis(trimethylsilyl)methylenetriphenylphosphorane **1**[15,16]. Its condensation with phosphorus trichloride or tribromide yields the ylidyl dihalophosphines **2**[16] which undergo a self-condensation reaction to give the bis(triphenylphosphoranediyl)-1,3-diphosphetanes **3** (and other Ph_3PCPX-oligomers)[17]. Aluminum and gallium trichloride abstract a chloride ion from **2** (X = Cl) to give salts of the corresponding phosphenium ion **4**. As the charge of this cation is predominantly taken over by the ylide group, it is better addressed as 2-triphenylphosphonio-1-chlorophosphaethene[18].



and -gallate **4**, which may be prepared in situ from **2a**, with phenyl azide cleanly and regiospecifically yields the respective 3-phenyl-5-triphenylphosphonio-1,2,3,4-triazaphosphole salts **5**.



2-Alkyl- or 2-aryltriphenylphosphoniochlorophosphaalkene tetrachloroaluminates[18], i.e. compounds such as **4a**, but with an ethyl or a *p*-tolyl group in place of the trimethylsilyl group, react with phenyl azide with immediate loss of dinitrogen. From the resulting reaction mixture no product could be identified.

In contrast to phenyl azide trimethylsilyl azide does react with the dichlorophosphane **2a**. Elimination of two mol of

The Reaction of Triphenylphosphoniophosphaethyne Equivalents with Azides

No reaction was observed between phenyl azide and the dichlorophosphane **2a**. Reaction of tetrachloroaluminate

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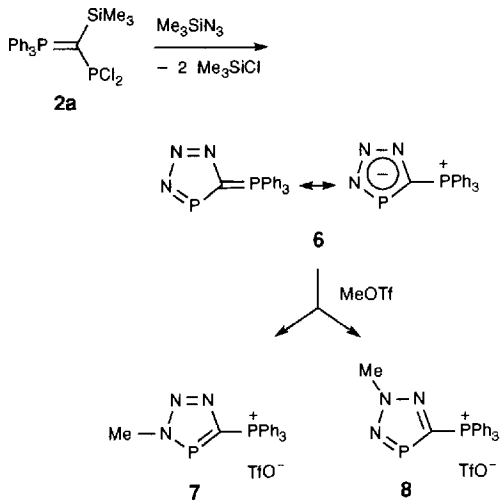
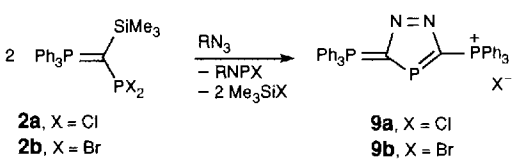
trimethyl chlorosilane leads to the 5-triphenylphosphoranediyl-1,2,3,4-triazaphosphole **6**. This is the first heteroatom-unsubstituted triazaphosphole derivative, and according to the second resonance formula it may also be viewed as triphenylphosphonio triazaphospholide.



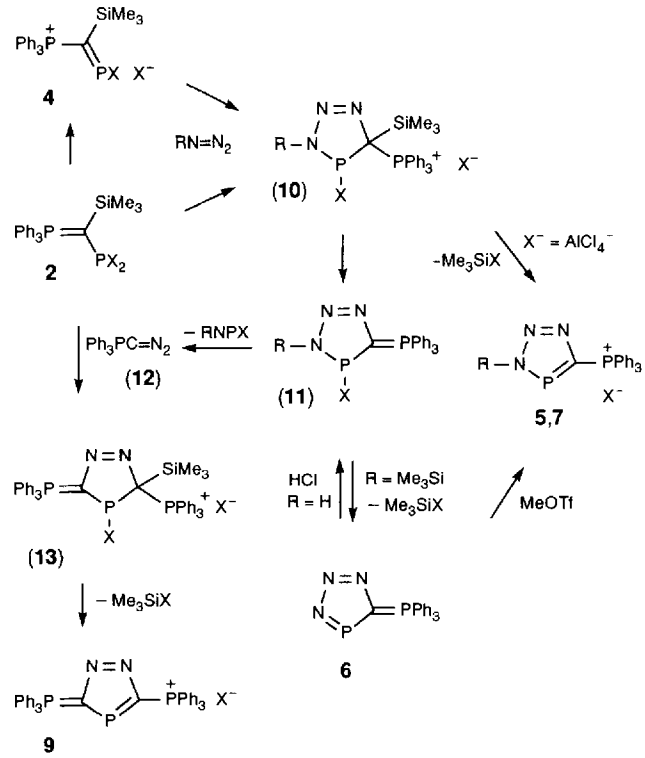
Methyl trifluoromethanesulfonate reacts with **6** to give the 3- and 2-methylphosphoniotriazaphosphole triflates **7** and **8** in almost equal amounts. The positions of the methyl group were elucidated by the NMR spectra of the two isomers (Table 1). For the methyl group of **7** coupling constants to phosphorus were observed similar to those of authentic 3-methyl-1,2,3,4-triazaphospholes[10,12,19]. For the methyl group of the isomer **8** no coupling with phosphorus was observed in accord with other 2-substituted 1,2,3,4-triazaphospholes[10]; 1-substituted isomers are unknown[8]. The bonding situation of **7** corresponds to that of **5**.

The synthesis of **6** is inevitably accompanied by a secondary reaction leading to the 3,5-bis(triphenylphosphonio)-1,2,4-diazaphospholide chloride **9a**. In this compound obviously two molecules of **2a**, each losing trimethylchlorosilane, are combined with the dinitrogen fragment of the azide while the imino fragment of the azide is lost together with the tervalent phosphorus atom of one moelcule of **2a**. If the trimethylsilyl azide is used in a 1:1 or lower molar ratio, **9a** becomes the only product. The same is true when triphenylsiyl azide, sodium azide or even tosyl azide are used for the reaction. From the dibromophosphane **2b** and trimethylsilyl azide the corresponding bromide **9b** is formed.



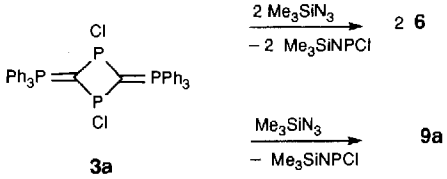
These results are best explained by the sequence of steps as they are shown in Scheme 1: In the first step the respective azide and **2** form the ionic adduct **10**; a predissociation of **2** facilitates this addition. The intermediate **10** then loses trimethylhalosilane to give either the covalent compounds **11** (X = Cl, Br) or the salts **5** ($X^- = AlCl_4^-$, $GaCl_4^-$). The latter are stable (as are the ionic methylation products **7**, **8** of **6** with triflate as the counterion).

Scheme 1. The numbers of the postulated but not observed intermediates are given in parentheses



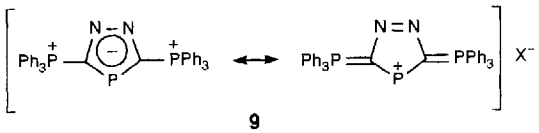
If R = Me_3Si, compound **11** may lose another molecule of trimethylhalosilane to give **6** which can be isolated, but which in solution readily adds again polar reagents such as HCl to the PN bond. A [2 + 3] cycloreversion of the intermediate **11** yields the phosphoranediyldiazomethane **12**. Its cycloaddition to a second molecule of **2** and the loss of another molecule of Me_3SiX finally give compound **9**. The formation of **9** and its explanation find a parallel in the formation of a 1,2,4-diazaphosphole by the reaction of the phosphaalkene $(Me_3Si)PhC{=}PCl$ with different azides[12]. The synthesis of 1,2,4-diazaphospholes from diazoalkanes and phosphaethynes or their equivalents is of course well-known[8,9,11,20].

The dichloro-1,3-diphosphetane **3a** reacts with trimethylsilyl azide, even at low temperature to give **6** as the minor and **9a** as the major product.



Reactions of the 3,5-Bis(triphenylphosphonio)-1,2,4-diazaphosphole Chloride

As compared to the isomeric diazaphospholes and in general to most other azaphospholes 1,2,4-diazaphospholes are rather unreactive[8,9]. They are not oxidized by atmospheric oxygen and they are stable to hydrolysis in acidic and basic media[22]. The cation of **9** may be understood as a diphosphonio-substituted 1,2,3-diazaphospholide as represented by the first resonance formula. The second resonance formula on the other hand suggests that the two-coordinate phosphorus participates in the overall charge and attains some phosphenium character which would make its susceptible to nucleophilic attack. In practice, neither a nucleophilic nor an electrophilic reactivity of the phosphorus ring member could be verified however.



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The chloride and bromide **9a**, **b** are ionic compounds. They are stable to water and alcohol and can be handled, e.g. in methanol solution. By metathesis with $Na^+BPh_4^-$, $Et_3NH^+BF_4^-$, and $MeNH_3^+SbCl_6^-$ the chloride **9a** can be converted to the salts **9c** (X = BPh_4), **9d** (X = BF_4), and **9e** (X = $SbCl_6$). Combination of the methanol solutions causes the pure salts to precipitate immediately. Their ^{31}P-NMR data are identical with those of the chloride **9a** and the bromide **9b** and this documents again the ionic nature of the halides (Table 1). X-ray structure investigations of a single crystal of the chloride **9a** · 2 CH_3OH[23] as well as of the hexachloroantimonate **9e** show the compounds to be ionic also in the crystal and to contain identical cations. No reaction of **9a** was observed with elemental sulfur and selenium or with $(CO)_5Cr$ · THF. This excludes even a low equilibrium concentration of the covalent form of **9a** in which the chloride ion would be associated to the ring phosphorus atom. This isomer should display normal chlorophosphane reactivity and would certainly undergo reactions with the above reagents. Furthermore, **9a** does not react with nucleophiles such as NaH, $NaBH_4$, MeMgBr, or $LiNPh_2$.

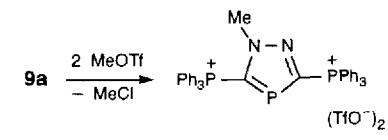
Reaction of **9a** with two equivalents of methyl trifluoromethanesulfonate affords 1-methyl-diphosphonio-1,2,4-diazaphosphole **14**. The dication was identified unambiguously by its ^{31}P-NMR spectrum that shows three different phosphorus nuclei (Table 1). No sign of a *P*-methylation could be detected.

The addition of hydrogen chloride also results solely in the protonation of a nitrogen ring atom. In solution the proton migrates rapidly enough between the two nitrogen atoms so as to maintain an AB_2 symmetry of the dication. The low-field ^{31}P chemical shift indicates an unchanged dicoordination of the phosphorus atom. This shift is not sensitive to solvent polarity and remains the same in chloroform and in mixtures of chloroform/benzene up to a ratio of 4:3. This experiment excludes an equilibrium participation of the covalent form **16**, which seemed quite feasible in regard of the doubly charged cation of **15**.

Table 1. ^{31}P-NMR data (in $CDCl_3$ or CD_2Cl_2) of 5-triphenylphosphonio-1,2,3,4-triazaphosphole derivatives **5**–**8** (AB spin systems) and of 3,5-bis(triphenylphosphonio)-1,2,4-diazaphosphole derivatives **9**, **15** (AB_2), and **14** (ABC spin system). 3,5-P refers to the Ph_3P substituents in position 3 and 5

	$\delta^{31}P$ (P-4)	$\delta^{31}P$ (3,5-P)	$^2J_{PP}$ [Hz]
6	245.4	14.5	50.3
5a	215.4[a]	11.5	58.0
5b	214.7	12.2	59.0
7	223.1[b]	11.7	59.5
8	240.5	14.2	35.1
9a	178.5	13.6	76.3
9b	178.8	13.8	76.9
9c	178.5	13.8	77.8
9d	178.6	13.8	76.3
9e	178.8	13.8	76.9
14	200.2	13.4[c]	59.5
		15.8	64.9
15	188.8	14.3	62.6

[a] $^2J_{PC}$ = 9.2 Hz (from ^{13}C NMR). – [b] $^3J_{PH}$ = 7.82 Hz, $^2J_{PC}$ = 14.5 Hz (from ^1H and ^{13}C NMR). – [c] $^4J_{PP}$ = 1.5 Hz.



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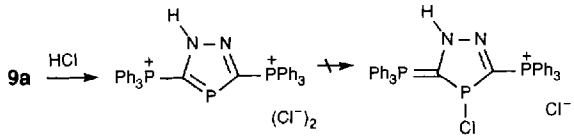

15 **16**

We thank Dr. *Dietrich Gudat*, Universität Bonn, for recording a ^{15}N-INEPT NMR spectrum, Dr. *Rita Fröde*, Universität München, for recording a FAB mass spectrum, and Prof. Dr. *Heinrich Nöth* and *Holger Schwenk*, Universität München, for performing X-ray structure analyses of **9a** and **9e**.

Experimental Section

Where necessary, operations were carried out in flame-dried glassware under dry argon by using Schlenk techniques. Tetrahydrofuran was dried by refluxing it with sodium/benzophenone and distillation. Pentane was dried over molecular sieve (4 Å). Dry chloroform, dichloromethane and benzene were used as obtained (Fluka). Melting points were measured in sealed capillaries and are uncorrected. – NMR: JEOL GSX 270 (^{31}P), JEOL EX 400 (^1H, ^{13}C) with Me_4Si (int.) and 85% H_3PO_4 (ext.) as standards. ^{31}P-NMR data are given in Table 1. The atoms of Ph_3P groups are identified as *o,m,p*-H and *i,o,m,p*-C, the atoms of other phenyl groups as 2,3,4-H and C-1,2,3,4.

3-Phenyl-5-triphenylphosphonio-1,2,3,4-triazaphosphole Tetrachloroaluminate (**5a**): To a suspension of 0.93 g (6.93 mmol) of $AlCl_3$ in 15 ml of dichloromethane at 0 °C, a solution of 2.08 g (4.62

mmol) of **2a** in 10 ml of dichloromethane was added dropwise. A recorded $^{31}P\{^1H\}$-NMR spectrum shows the signals of **4a**[18]. After 15 min a solution of 0.83 g (6.93 mmol) of PhN_3 in 10 ml of dichloromethane was added dropwise. The color of the solution turned from pale yellow to dark green. After 2 h the reaction mixture was warmed up to room temp. and a small amount of a precipitate was filtered off. Afterwards all volatile components were removed in vacuo from the dichloromethane solution. The residue could not be recrystallized. – ^1H-NMR (CD_2Cl_2): δ = 7.97 (m, 2H, 3-H), 7.83 (m, 1H, 4-H) and (m, 15H, *o,m,p*-H), 7.60 (m, 2H, 2-H), 5.33 (s, 3H, CH_2Cl_2), 0.18 (s, 1H, Me_3Si). – $^{13}C\{^1H\}$-NMR (CD_2Cl_2): δ = 117.7 (d, $^1J_{PC}$ = 91.5 H, *i*-C), 131.0 (d, $^3J_{PC}$ = 13.7 Hz, *m*-C), 134.4 (d, $^2J_{PC}$ = 10.7 Hz, *o*-C), 136.4 (d, $^4J_{PC}$ = 3.0 Hz, *p*-C), 123.2 (d, $^3J_{PC}$ = 7.6 Hz, C-2), 130.4 (s, C-3), 138.8 (s, C-4), 139.1 (d, $^2J_{PC}$ = 9.2 Hz, C-1).

The corresponding tetrachlorogallate **5b** was obtained by addition of 10 mg (0.09 mmol) of PhN_3 to a solution of 57 mg (0.59 mmol) of **4b**[18] in 0.6 ml of [D$_2$]dichloromethane.

5-Triphenylphosphorandiyl-1,2,3,4-triazaphosphole (**6**): To a solution of 5.61 g (12.48 mmol) of **2a** in 100 ml of benzene, a solution of 2.16 g (18.72 mmol) of Me_3SiN_3 in 3 ml of benzene was added dropwise at room temp. After stirring for 1 h the precipitate formed was separated and identified by its $^{31}P\{^1H\}$-NMR spectrum as a mixture of about equal amounts of **6** and **9a**. The mixture was then agitated with 30 ml of dichloromethane and the white residue was filtered off after 1 h, washed with dichloromethane and dried in vacuo. Yield 1.21 g (28%) of **6**, colorless powder, decomp. >105°C. – ^1H NMR ($CDCl_3$): δ = 7.68 (9H, *o,p*-H) 7.55 (6H, *m*-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 122.4 (d, $^1J_{PC}$ = 91.6 Hz, *i*-C), 129.6 (d, $^3J_{PC}$ = 13.7 Hz, *m*-C), 134.0 (d, $^2J_{PC}$ = 10.7 Hz, *o*-C), 134.2 (d, $^4J_{PC}$ = 3.0 Hz, *p*-C), 150.4 (dd, $^1J_{PC}$ = 78.7 Hz, $^1J_{PC}$ = 103.6 Hz, C-5). – $C_{19}H_{15}N_3P_2$ (347.3): calcd. C 65.71, H 4.35, N 12.10; found C 65.40, H 4.20, N 11.76.

3- and 2-Methyl-5-triphenylphosphonio-1,2,3,4-triazaphosphole Triflates (**7**, **8**): In an NMR tube to a solution of 25 mg (0.08 mmol) of **6** in 0.6 ml of [D$_1$]trichloromethane, 12 mg (0.08 mmol) of methyl trifluoromethanesulfonate was added by means of a syringe. – ^1H NMR ($CDCl_3$): δ = 7.84 (m, 6H, *p*-H, **7**, **8**), 7.68 (m, 24H, *o,m*-H, **7**, **8**), 4.72 (s, 3H, Mc **8**), 4.47 (d, $^3J_{PC}$ = 7.82 Hz, 3H, Me **7**), 4.18 (s, MeOTf). – $^{13}C\{^1H\}$ NMR ($CDCl_3$) (**7**): δ = 122.8 (d, $^1J_{PC}$ = 127.4 Hz, *i*-C), 130.7 (d, $^3J_{PC}$ = 13.7 Hz, *m*-C), 134.1 (d, $^2J_{PC}$ = 9.9 Hz, *o*-C), 136.0 (d, $^4J_{PC}$ = 3.0 Hz, *p*-C), 39.6 (d, $^2J_{PC}$ = 14.5 Hz, Me); (**8**): δ = 122.8 (d, $^1J_{PC}$ = 127.4 Hz, *i*-C), 130.7 (d, $^3J_{PC}$ = 13.7 Hz, *m*-C), 134.1 (d, $^2J_{PC}$ = 10.0 Hz, *o*-C), 135.8 (d, $^4J_{PC}$ = 2.3 Hz, *p*-C), 61.6 (s, MeOTf), 48.6 (s, Me).

3,5-Bis(triphenylphosphonio)-1,2,4-diazaphospholide Chloride (**9a**): To a suspension of 6.07 g (13.53 mmol) of **2a** in 80 ml of benzene, 0.92 g (8.0 mmol) of Me_3SiN_3 was added dropwise at 5°C. After stirring for 15 h at room temp., the yellow precipitate formed was filtered off, washed with 20 ml of benzene and dried in vacuo. The product was recrystallized from methanol. Yield 3.24 g (68%) of colorless crystals of **2a** · 2 CH_3OH, m.p. 137°C (decomp.). – FAB MS (3-nitrobenzyl alcohol), *m/z* (%): 623 (10) [M^+ + 16], 608 (40) [M^+ + 1], 607 (100) [M^+]. – $C_{38}H_{30}ClN_2P_3$ · 2 CH_3OH = $C_{40}H_{38}ClN_2O_2P_3$ (701.13): calcd. C 67.94 H 5.42 N 3.96 Cl 5.01, found C 68.02, H 5.54 N 4.16 Cl 5.03.

3,5-Bis(triphenylphosphonio)-1,2,4-diazaphospholide Bromide (**9b**): To a suspension of 0.98 g (1.80 mmol) of **2b** in 25 ml of benzene, a solution of 0.27 g (2.30 mmol) of Me_3SiN_3 in 2 ml of benzene was added dropwise at 5°C. After stirring for 5 h at room temp. the white precipitate formed was filtered off, washed with 10 ml of benzene and dried in vacuo.

3,5-Bis(triphenylphosphonio)-1,2,4-diazaphospholide Tetraphenyloborate (**9c**): To a solution of 1.57 g (2.44 mmol) of **9a** in 10 ml of methanol, a saturated solution of $NaBPh_4$ in methanol was added as long as a precipitate formed. The precipitate was filtered off, washed three times with methanol and dried in vacuo. Yield 1.68 g (74%) of **9a**. – ^1H NMR (CD_2Cl_2): δ = 7.81 (m, 6H, *p*-H), 7.73 (m, 12H, *o*-H), 7.64 (m, 12H, *m*-H), 7.33 (br, 8H, 2-H), 7.00 (m, 8H, 3-H), 6.85 (m, 4H, 4-H).

3,5-Bis(triphenylphosphonio)-1,2,4-diazaphospholide Tetrafluoroborate (**9d**): Prepared as described above from 1.22 g (1.89 mmol) of **9a** and a saturated solution of $[Et_3NH]BF_4$ in methanol. Yield 0.77 g (59%) of **9d**. ^1H NMR (CD_2Cl_2): δ = 7.84 (m, 6H, *p*-H), 7.72 (m, 24H, *o,m*-H). – $C_{38}H_{30}BF_4N_2P_3$ (942.1): calcd. C 65.74, H 4.35, N 4.03; found C 65.60, H 4.47, N 4.47.

3,5-Bis(triphenylphosphonio)-1,2,4-diazaphospholide Hexachloroantimonate (**9e**): Prepared as described above from 1.38 (2.14 mmol) of **9a** and a saturated solution of $[MeNH_3]SbCl_6$ in methanol. Yield 1.65 g (82%) of **9e**, m.p. 215°C (decomp.). – ^1H NMR (CD_2Cl_2): δ = 7.82 (m, 6H, *p*-H), 7.70 (m, 24H, *o,m*-H). – $C_{38}H_{30}Cl_6N_2P_3Sb$ (942.06): calcd. C 48.45, H 3.21, N 2.97, Cl 22.58; found C 48.61, H 3.27, N 2.91, Cl 22.50.

3,5-Bis(triphenylphosphonio)-1 H-1,2,4-diazaphosphole Dichloride (**14**): To a solution of 436 mg (0.86 mmol) of **9a** in 3 ml of dichloromethane, 1.4 ml of a 1 M solution of HCl in diethyl ether was added at room temp. by means of a syringe. After 2 h the white precipitate formed was filtered off and dried in vacuo. Yield 3.28 mg (71%), m.p. 141°C (decomp.). – ^1H NMR ($CDCl_3$): δ = 7.7 (m, 6H, *p*-H), 7.72 (m, 12H, *o*-H), 7.66 (m, 12H, *m*-H), 5.37 (s, 1H, CH_2Cl_2). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 118.5 (d, $^1J_{PC}$ = 91.6 Hz, *i*-C), 130.6 (d, $^3J_{PC}$ = 13.7 Hz, *m*-C), 134.4 (d, $^2J_{PC}$ = 10.7 Hz, *o*-C), 135.5 (s, *p*-C). – $C_{38}H_{31}Cl_2N_2P_3$ · 0.5 CH_2Cl_2 (721.97): calcd. C 64.05, H 4.48, N 3.88; found C 64.01, H 4.77, N 4.99.

3,5-Bis(triphenylphosphonio)-1-methyl-1,2,4-diazaphosphole Bistriflate (**15**): In an NMR tube to a solution of 39 mg (0.06 mmol) of **9a** in 0.6 [D$_1$]trichloromethane, 14 µl (0.12 mmol) of MeOTf was added and **15** was identified by its ^{31}P-NMR spectrum. Only addition of a second equivalent of MeOTf resulted in *N*-methylation and a change in the spectrum.

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[23] Crystal Data: **9a**: $C_{38}H_{30}N_2P_3Cl \cdot 2\ CH_3OH$, $M = 707.13$, monoclinic colorless plate, space group C2/c, $Z = 4$, $a = 27.01(1)$, $b = 7.629(3)$, $c = 17.717(6)$ Å, $\beta = 96.31(3)°$, $V = 3640(2)$ Å^3, $d_{calcd.} = 1.290$ Mg/m^3, $\mu = 0.274$ mm^{-1}. 2958 reflection collected, 2886 unique reflections of which 1995 were considered as observed structure solution with direct methods (SHELXTL), refinement converged at $R = 0.061$ [$F > 4\sigma(F_o)$] and $wR_2 = 0.139$. The PC_2N_2 ring is positionally disordered due to a "center of inversion" of two equally populated five membered rings. Typical bond lengths within the five membered rings are: P–C(av.), 1671(5), C–N(av.), 1.47(1), N–N 1.376(9), P–C_{exo} 1.778(4) Å. – Studies by H. Nöth and H. Schwenk. [96173]