Pergamon

Tetrahedron 56 (2000) 35–42

TETRAHEDRON

Reactions of (1-Diazo-2-oxoalkyl)silanes with 3*H*-1,2,3,4-Triazaphospholes: a Route to Short-Lived 4-Imino-1,2,4(λ^5)-diazaphospholes

Jochen Kerth, Udo Werz and Gerhard Maas*

Abteilung Organische Chemie I, Universität Ulm, Albert-Einstein-Allee 11, D-89081 Ulm, Germany

Received 5 February 1999; accepted 28 May 1999

Abstract—(1-Diazo-2-oxoalkyl)silanes **1** react with a 3-phenyl-3*H*-1,2,3,4-triazaphosphole (**3**) to form dispiroannulated 1,3-diaza-2,4-diphosphetidines **4**. With 3-alkoxycarbonyl-3*H*-1,2,3,4-triazaphospholes **5**, 4-alkoxy-4-isocyanato-1,2,4(λ^5)-diazaphospholes **6** are obtained. The structures of **4a** and **6c** were established by X-ray crystal structure analysis. It is proposed that 4-imino-1,2,4(λ^5)-diazaphospholes are the immediate precursors of both types of products.

Introduction

The first syntheses of 3*H*-1,2,3,4-triazaphospholes were reported in 1984 by Carrié[1] and Regitz[2] independently. It is astonishing that the chemistry of these heterocycles has been left largely unexplored, although they are readily accessible by 1,3-dipolar cycloaddition of organic azides with phosphaalkynes[1a,2] and phosphaalkenes[1b] (followed by a 1,2-elimination step), respectively. It appears that, except for a study of the pyrolytic N_2 extrusion from 3-aryl-3*H*-1,2,3,4-triazaphospholes,[3] this class of heterophospholes has not received much attention.

In continuation of our studies on [3+2] cycloaddition reactions of α-silyl-α-diazoketones [(1-diazo-2-oxoalkyl)-silanes] and acyclic phosphaalkenes,[4] we became interested in heterophospholes containing a ($\sigma^2\lambda^3$)P=C moiety which would be able to act as a dipolarophile towards the diazo function. Although 1,3-dipolar cycloaddition reactions have been reported for various azaphospholes (e.g. 2*H*-1,2,3-diazaphospholes,[5] 1,3,4-thiazaphospholes,[6] 1,2,4-oxazaphospholes[1a,7]), it was not clear a priori whether 3*H*-1,2,3,4-triaza-phospholes would be reactive enough to undergo this type of addition reaction. Ab-initio quantum-chemical calculations for various azaphospholes containing a $\sigma^2\lambda^3$ phosphorus atom have revealed bond length averaging that is typical for a delocalized bond structure, and have suggested that the aromaticity, as measured by the heats of formation of bond separation and ring fragmentation reactions, increases with the number of nitrogen atoms in these ring systems.[8]

We report in this paper that α-silyl-α-diazoketones react with 3*H*-1,2,3,4-triazaphospholes under surprisingly mild conditions, and that instead of the expected bicyclic 1,3-dipolar cycloaddition products, 1,2,4(λ^5)-diazaphospholes are obtained via 4-imino-1,2,4(λ^5)-diazaphospholes resulting from the cycloaddition products by spontaneous N_2 extrusion.

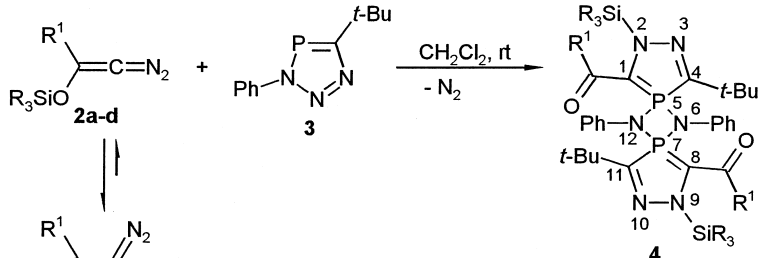
Results and Discussion

α-Silyl-α-diazoketones **1** are in equilibrium with minor amounts of 1-diazo-2-siloxy-1-alkenes **2** which are likely to be the more reactive components for 1,3-dipolar cycloaddition reactions.[9] The reaction of equimolar amounts of **1a**–**d** with the 3-phenyl-1,2,3,4-triazaphosphole **3** in dichloromethane was accompanied by slow gas evolution (Scheme 1). After 2–3 days, the reaction was complete, and a yellow precipitate was obtained for which the elemental analysis suggested the composition of a 1:1 adduct minus N_2. The true nature of the products, which are dispiroannulated 1,3-diaza-2,4-diphosphetidines **4a**–**d**, could be established only by an X-ray single crystal structure determination of **4a** (see below). Interestingly, no molecule ion peak was found in the mass spectra of these symmetrical dimers: In the CI mass spectra of **4a**,**b**, no peaks were observed above *m*/*z*=473 and 552, respectively, corresponding to the monomeric unit. It is likely that thermal fragmentation of **4a**–**d** occurred prior to ionization, since the thermally induced [2+2] cycloreversion of diazadiphosphetidines leading to phosphine imines has been observed before.[10] In dispiroannulated

Keywords: diazo compounds; phosphine imines; phosphorus heterocycles; cycloadditions.

* Corresponding author. Tel.: +49-731-502-2790; fax: +49-731-502-2803; e-mail: gerhard.maas@chemie.uni-ulm.de

0040–4020/00/$ - see front matter
PII: S0040-4020(99)00770-X



1,2,4	R^1	SiR_3	Yield [%]
a	*t*-Bu	Si*i*-Pr_3	55
b	1-Ad[a]	Si*i*-Pr_3	45
c	*t*-Bu	$SiMe_2$*t*-Bu	66
d	*t*-Bu	$SiPh_2$*t*-Bu	53

[a] 1-Adamantyl.

Scheme 1.

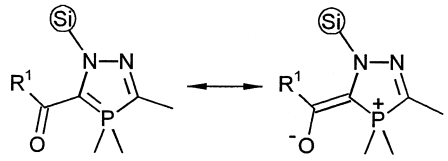


Figure 1. Resonance structures for the moiety O=C(R^1)–C=PR_3 in **4** and **6**.

1,3-diaza-2,4-diphosphetidines structurally related to **4** (e.g. **7**[11]), both the M^+ and the $M^+/2$ peak were observed in the mass spectra (EI mode), and the intensity of the molecular ion peak varied from low to high depending on the substituent pattern.[11] It can be excluded that the monomer and its cyclodimer coexist in solution since **4a**–**d** show only one set of signals in the ^1H and ^{13}C NMR spectra and one ^{31}P NMR signal (δ 4.7–6.6 ppm). As expected for the cyclodimer, the ^{13}C NMR spectra of **4a**–**d** contain several subspectra of the ABX and AA′X spin systems which are indicative of coupling with two P atoms (see below).

An interesting detail is the contribution of a 1,4-dipolar resonance structure to the bond structure of the O=C(R^1)–C=PR_3 moiety in **4a**–**d** (Fig. 1). The participation of a phosphonium enolate structure is suggested mainly by the IR absorption at 1567–1602 cm^{-1}, some 30–50 cm^{-1} lower than the usual values for pivaloyl groups. The observed bond lengths in **4a** (see below) also support this interpretation.

As was mentioned above, spin coupling between the two P atoms and ^{13}C nuclei gives rise to several ABX and AA′X spin systems (with A, B corresponding to P^1,P^2). ABX systems (with six lines in the X part) are observed for the carbon atoms C-1(8) and C-4(11) in the diazaphosphole ring, and AA′X systems (with five lines in the X part, the two outer lines of which were too weak to be observed) are found for carbon atoms R_3C–C=O, R_3C–*C*=O, and 4(11)-*C*Me_3. The coupling constants for these spin systems were calculated for **4a**–**d** by known methods[12] with the assumption that $\nu_A-\nu_B=0$ Hz (neglecting the $^{12}C/^{13}C$ isotope shift on the ^{31}P resonance). The values so obtained are given in Table 1, and a comparison between the experimental and computer-simulated[13] spectra of **4a** is shown in Fig. 2. The best fit was obtained when the computer-simulated spectra were calculated with $\nu_A-\nu_B=3$ Hz.

The reactions of the diazoketone/diazoalkene systems **1a**,**b**/**2a**,**b** with 3-alkoxycarbonyl-3*H*-1,2,3,4-triazaphospholes **5a**–**c** differ from those with the 3-phenyl derivative **3** in two points: They are faster (complete reaction at 20°C within one day), and they lead to different products, namely to 1,2,4-diazaphospholes **6a**–**d** which feature a unique geminal alkoxy/isocyanato substitution at the $\sigma^4\lambda^5$ phosphorus atom (Scheme 2). Definite structural proof was furnished by a crystal structure determination of **6c** (Fig. 3). Although the ^{31}P and ^1H NMR spectra at the end of the reaction suggested the clean formation of only one P-containing product, purification by crystallization led to reduced isolated yields. These compounds have a rather low tendency to crystallize, are decomposed during attempted chromatography over silica gel or alumina, and show signs of unspecific decomposition after one day in $CDCl_3$

Table 1. Calculated P,P and P,C coupling constants [Hz] in **4a**–**d**

	4a	**4b**	**4c**	**4d**		**4a**	**4b**	**4c**	**4d**
^2J(P,P)[a]	42.2	45.3	42.0	44.8	^3J(P,COCR_3)	7.1	7.4	7.3	7.3
^1J(P,C-1)	170.9	169.0	167.7	173.4	^5J(P,COCR_3)	−1.4	−1.7	−1.1	−1.6
^3J(P,C-1)	4.6	5.6	4.5	5.4	^2J(P,*C*Me_3)	13.8	14.1	13.8	13.8
^1J(P,C-4)	85.0	85.3	84.7	83.7	^4J(P,*C*Me_3)	5.3	5.0	5.3	4.8
^3J(P,C-4)	2.7	2.9	2.6	4.0	^2J(P,*C*=O)	12.1	11.9	11.6	11.7
					^4J(P,*C*=O)	3.6	2.9	3.2	2.6

[a] Average values; values obtained from analysis of the two spin systems P^1,P^2,C-1 and P^1,P^2,C-4 differ by ±0.6 Hz or less.

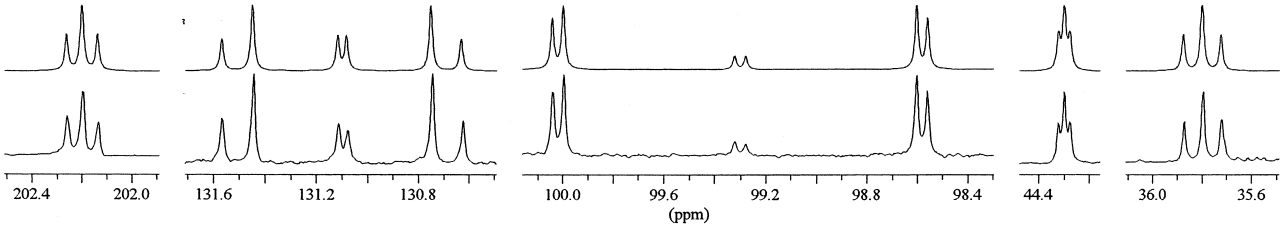
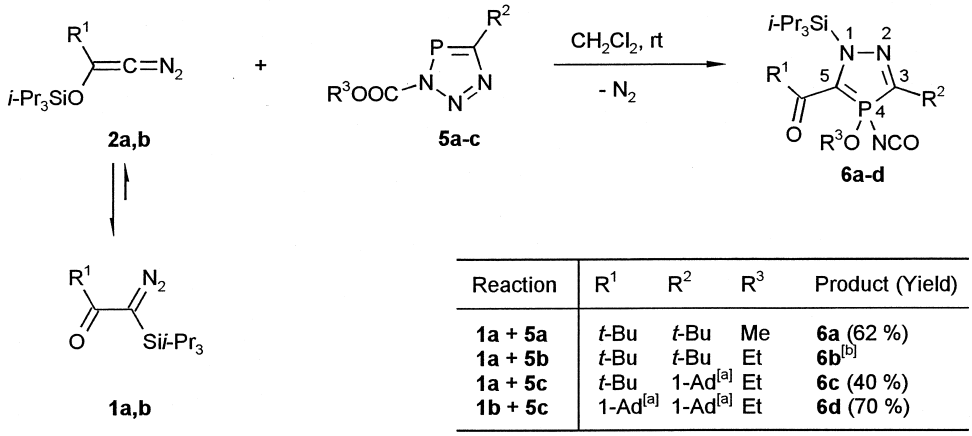


Figure 2. Experimental (125.77 MHz) and computer-simulated (upper part) ^{13}C-NMR spectra of **4a**; simulations are based on values given in Table 1.



Reaction	R^1	R^2	R^3	Product (Yield)
1a + 5a	*t*-Bu	*t*-Bu	Me	**6a** (62 %)
1a + 5b	*t*-Bu	*t*-Bu	Et	**6b**[b]
1a + 5c	*t*-Bu	1-Ad[a]	Et	**6c** (40 %)
1b + 5c	1-Ad[a]	1-Ad[a]	Et	**6d** (70 %)

[a] 1-Adamantyl. - [b] Not determined.

Scheme 2.

solution. In the solid state, they appear to be completely stable when stored under an atmosphere of argon.

Spectroscopically, **6a**–**d** are characterized by an IR absorption at 2253–2264 cm^{-1} [ν(N=C=O)] and a ^{31}P NMR signal at δ 20.7–23.9 ppm. The large ^1J(P,C) coupling constants [^1J(P,C-3)=110.9±0.7 Hz, ^1J(P,C-5)=194.8±0.7 ppm] are in agreement with the presence of a pentavalent phosphorus atom. The contribution of a phosphonium enolate resonance structure to the bond state of the O=C(R^1)–C=P moiety appears to be more pronounced than in **4** (see above) according to IR [ν(C=O)=1554±7 cm^{-1}] and ^{13}C NMR data [δ(*C*=O) 194.4±0.1,[14] δ(*C*=P) 100.2–100.7 ppm; values in **4a**–**d**: δ(*C*=O) 202.2–203.5, δ(*C*=P) 98.0–99.3 ppm]. The presence of a stereogenic center at the phosphorus atom

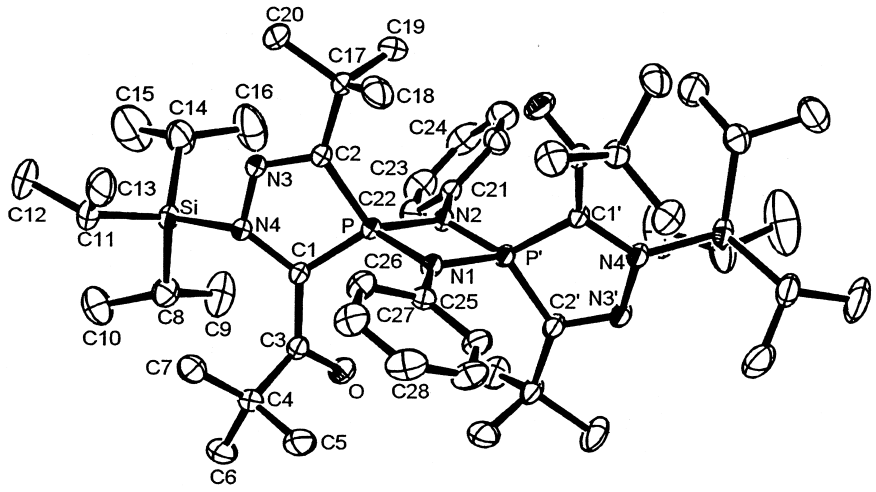


Figure 3. Structure of **4a** in the crystal (ORTEP plot). Thermal ellipsoids are shown at the 20% probability level. The molecule has crystallographic C_2 symmetry; atoms N1, N2, C21, C24, C25, and C28 occupy positions on a C_2 axis. Selected bond lengths (Å): P–N1 1.716(2); P–N2 1.702(2); P–C1 1.706(2); P–C2 1.761(2); C1–N4 1.418(3); C1–C3 1.460(3); C3–O 1.229(3); C2–N3 1.318(3); N3–N4 1.349(3). Bond angles (deg): N1–P–N2 79.95(10); P–N1–P′ 99.47(15); P–N1–C25 130.26(7); P–N2–P′ 100.63(14); P–N2–C21 129.69(7); C1–P–C2 91.36(11); C1–P–N1 119.02(9); C2–P–N2 120.91(10). Torsion angles (deg): P–N1–C25–C26 −16.1(1); P–N2–C21–C22 −54.8(1); C1–P–C2–N3 −6.1(2); C2–N3–N4–C1 0.1(3); N3–N4–C1–P −4.7(3); C2–P–C1–N4 5.9(2); P–C1–C3–O −48.2(3).

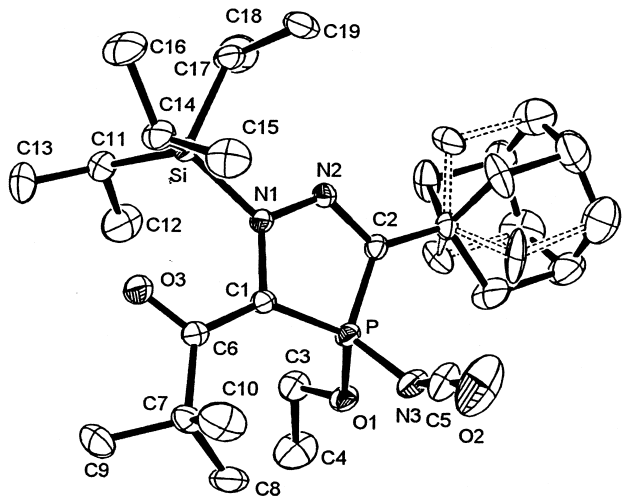


Figure 4. Structure of **6c** in the crystal (ORTEP plot). Thermal ellipsoids are shown at the 20% probability level. The adamantyl group is disordered around the C2–C_{Ad} axis (see Experimental part). Selected bond lengths (Å): P–C1 1.698(3); C1–N1 1.429(4); N1–N2 1.341(3); N2–C2 1.326(4); P–C2 1.726(3); P–O1 1.593(2); P–N3 1.673(3); N3–C5 1.168(4); C5–O2 1.146(4); C1–C6 1.431(4); C6–O3 1.230(4). Bond angles (deg): C1–P–C2 93.32(14); C1–P–O1 119.74(13); C1–P–N3 119.30(15); C2–P–O1 117.39(13); C2–P–N3 116.19(14); P–N3–C5 139.8(3); N3–C5–O2 175.1(4). Torsion angles (deg): C1–N1–N2–C2 0.2(3); N1–N2–C2–P 0.4(3); N2–N1–C1–P −0.7(3); P–C1–C6–O3 −171.3(2).

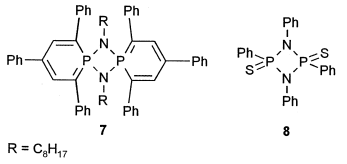
causes the isopropyl-CH_3 groups to be diastereotopic, which can be observed in both the ^{1}H and ^{13}C NMR spectra.

Molecular structures of 4a and 6c

The structures of **4a** and **6c** were determined by single-crystal X-ray diffraction. Molecule plots are shown in Figs. 3 and 4, respectively. Both compounds contain the 1,2,4(λ^5)-diazaphosphole ring system. This ring is completely planar in **6c**, but a little bit puckered in **4a**, where the phosphorus atom is displaced by 0.13 Å from the plane defined by the other four ring atoms. Furthermore, the silyl-substituted nitrogen atom in the ring is weakly pyramidalized in **4a** but has a planar configuration in **6c** (sum of valence angles: 352° in **4a** and 359.9° in **6c**). The differences between corresponding ring bonds in the two structures are only marginal, except for the P–C single bond (P–C2: 1.761 Å in **4a** and 1.726 Å in **6c**). In both cases, the bond lengths in the diazaphosphole ring indicate a certain degree of bond delocalization. The overall picture of bond lengths and ring geometry suggests that the cyclic π conjugation is somewhat higher in the completely planar ring system of **6c**. It should also be noted that the bond distances in **4a** agree remarkably well—except for the C–N(SiR_3) bond—with those calculated for 1*H*-1,2,4(σ^{2}λ^3)-diazaphosphole by ab initio methods.[8] Thus, 1,2,4-diazaphospholes are similar to the λ^3- and λ^5-phosphinines[15] in that the bond lengths in the ring do not respond significantly to a change of coordination number at the phosphorus atom.

For the above mentioned contribution of a phosphonium enolate resonance structure to the bond state of the O=C(R^1)–C=P moiety, the C=O bond length (1.23 Å in both structures) and the C11–C(=O) bond length (**4a**: 1.460 Å; **6c**: 1.431 Å) must be compared with expected average values[16] for a C=C–C=O unit [1.222(10) Å for C=O; 1.464(18) Å for conjugated =C–C= and 1.484(17) Å for unconjugated =C–C=). The comparison suggests a significant additional bond delocalization in the case of **6c**, where the O=C(R^1)–C=P moiety is nearly planar. In **4a**, on the other hand, the reduced π orbital overlap (torsion angle P–C1–C3–O: −48.2°, see Fig. 4) allows only a weak contribution from the dipolar resonance structure.

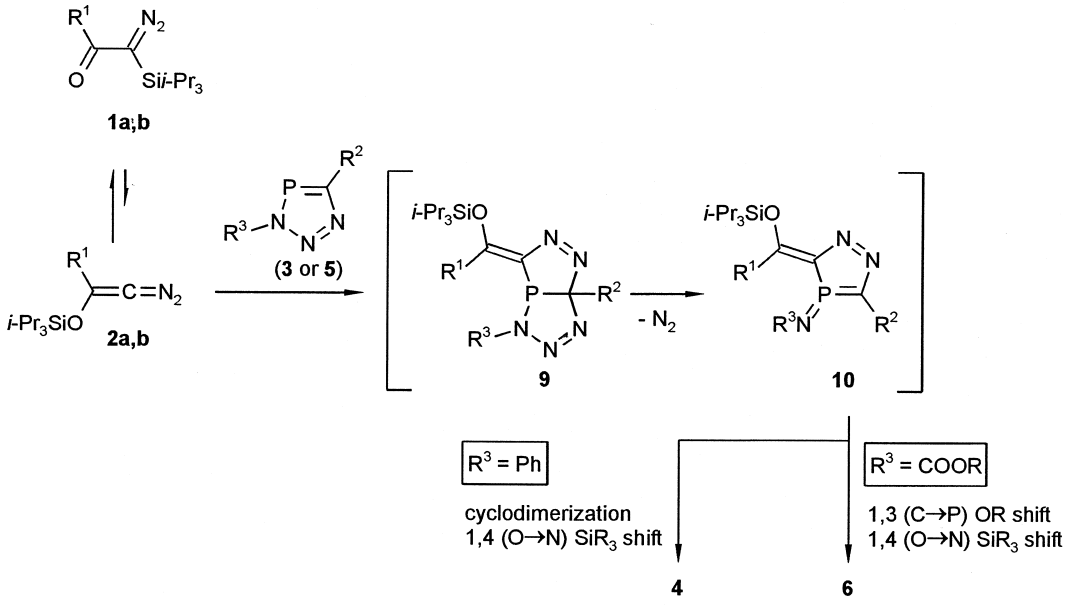
The diazadiphosphetidine ring in **4a** is planar and has C_2 symmetry with slightly different P–N bond lengths [1.716(2) and 1.702(2) Å] and endocyclic angles of 80.0° at P and of 99.5° at N. An analogous P–N bond length difference (1.706 vs. 1692 Å) has been found in the structurally related dispiroannulated diazadiphosphetidine **7**,[11] while all P–N distances are equal in the monocyclic system **8**.[17]



Mechanistic considerations

Based on earlier investigations, we assume that the reaction of α-silyl-α-diazoketones **1** with 3*H*-1,2,3,4-triazaphospholes **3** and **5** leads initially to the cycloadducts **9**. They represent the products of a [3+2] cycloaddition reaction between **3** or **5** and 1-diazo-1-alkenes **2**, which exist as the minor component in an equilibrium with diazoketones **1**.[9] Cycloadducts of this type have been isolated with activated alkenes,[9] acyclic phosphaalkenes,[4] and 1,2,3(λ^3)-diazaphospholes[18] as dipolarophiles. In the present case, however, spontaneous N_2 elimination from the bicyclic 4,5-dihydro-3*H*-1,2,3,4-triazaphospholes **9** occurs, and 4-imino-1,2,4(λ^5)-diazaphospholes **10** are formed which can be considered as semicyclic imino(methylene)phosphoranes. In fact, the same reaction type—N_2 elimination from the [3+2] cycloaddition product obtained from an iminophosphine and a diazoalkane[10]—has allowed the preparation of an acyclic imino(methylene)phosphorane. In other cases, such phosphoranes were obtained from iminophosphines and diazoalkanes directly.[19] Depending on the substituents, the kinetic stability of imino(methylene)phosphoranes ranges from high to low.[20] Kinetically labile representatives can undergo cyclization to form phosphaaziridines,[10] or cyclodimerization across the P=N[10] or P=C[19b] double bond. A semicyclic imino(methylene)phosphorane structurally related to **10**, namely a 4-phenylimino-2*H*-1,2,3(λ^5)-diazaphosphole, underwent a spontaneous cyclotrimerization reaction.[21]

In our case, the further fate of **10** depends on the imine substituent. For R=Ph, cyclodimerization across the P=N bond leads to dispiroannulated 1,3-diaza-2,4-diphosphetidines **4**. For R=alkoxycarbonyl, a 1,3(C→P) OR migration generates diazaphosphole **6** with the unusual geminal alkoxy/isocyanato substitution at the phosphorus atom (Scheme 3).



Scheme 3.

In summary, we have shown that α-silyl-α-diazoketones react with 3*H*-1,2,3,4-triazaphospholes under surprisingly mild conditions. Instead of 4,5-dihydro-3*H*-1,2,3,4-triazaphospholes, which are the products expected for a 1,3-dipolar cycloaddition at the P=C function in the azaphosphole, 1,2,4(λ^5)-diazaphospholes are obtained. Their formation is readily explained with the intermediacy of 4-imino-1,2,4(λ^5)-diazaphospholes resulting from the expected cycloaddition products by spontaneous elimination of N_2. It is to be expected that other cycloaddition or addition reactions at the P=C bond of readily available 3*H*-1,2,3,4-triazaphospholes[22] will allow to enter a similar reaction channel and will give access to related, highly reactive semicyclic imino(methylene)phosphoranes.

Experimental

General information. All reactions were carried out in rigorously dried glassware and under an argon atmosphere. Solvents were dried by standard procedures and kept under argon. NMR spectra: Bruker AC 200 (^{13}C: 50.32 MHz) and Bruker AMX 500 (^{1}H: 500.14 MHz; ^{13}C: 125.77 MHz; ^{31}P: 202.48 MHz). All spectra were recorded in $CDCl_3$ solution, if not stated otherwise. As internal standard, TMS was used for ^{1}H spectra, and the solvent signal for the ^{13}C spectra [$\delta(CDCl_3)$=77.0]. The ^{31}P-NMR spectra were recorded using 85% H_3PO_4 as external standard. IR spectra: Perkin–Elmer IR-883 Spectrometer; wavenumbers [cm^{-1}] are given. Elemental analyses: Perkin–Elmer EA 2400 and EA 240. Melting points were determined in an apparatus after Dr Tottoli (Büchi) and are uncorrected.

Starting materials. α-Silyl-α-diazoketones **1a**,**c**,[23] **1b**,[24] **1d**[25] were prepared according to literature methods. Yields were higher than the reported ones when the purification by column chromatography was carried out at −4°C (silica gel, 0.063–0.2 mm, mixtures of ether–petroleum ether). Triazaphospholes **3** and **5a** were prepared as described.[3] The following new triazaphospholes were synthesized analogously.

Ethyl 5-(*tert*-butyl)-3*H*-1,2,3,4-triazaphosphole-3-carboxylate (5b). The synthesis from (*tert*-butylmethylidyne)phosphine[26] (2.037 g, 20.35 mmol) and ethoxycarbonylazide (2.341 g, 20.35 mmol) gave **5b** (3.90 g, 89%) as a colorless oil. IR (neat): ν=1786 (vs), 1757 (vs), 1479 (s), 1396 (s), 1372 (s), 1301 (s), 1249 (s), 1224 (s), 1156 (s), 1126 (s), 1049 (s) cm^{-1}. ^{1}H NMR: δ=1.48 (d, $^4J_{P,H}$=1.7 Hz, 9 H, CMe_3), 1.50 (t, $^3J_{H,H}$=7.1 Hz, 3 H, OCH_2CH_3), 4.60 (q, $^3J_{H,H}$=7.1 Hz, 2 H, OCH_2CH_3). ^{13}C NMR (50.32 MHz): δ=14.0 (s, OCH_2CH_3), 30.9 (d, $^3J_{P,C}$=8.3 Hz, CMe_3), 35.4 (d, $^2J_{P,C}$=14.8 Hz, CMe_3), 65.3 (s, OCH_2CH_3), 150.9 (d, $^2J_{P,C}$=11.4 Hz, *C*OOEt), 200.9 (d, $^1J_{P,C}$=56.1 Hz, C-5). ^{31}P NMR: δ=177.4.

Ethyl 5-(1-adamantyl)-3*H*-1,2,3,4-triazaphosphole-3-carboxylate (5c). (Adamant-1-ylmethylidyne)phosphine[26] (1.887 g, 10.59 mmol) and ethoxycarbonylazide (1.219 g, 10.59 mmol) were allowed to react for 22 h; yield of **5c**: 2.32 g (75%); colorless crystals, mp 96°C. IR (KBr): ν=1730 (s), 1451 (s), 1297 (s), 1239 (s) cm^{-1}. ^{1}H NMR: δ=1.50 (t, $^3J_{H,H}$=7.2 Hz, 3 H, OCH_2CH_3), 1.81 (m, 6 H, Ad), 2.08 (m, 6 H, Ad), 2.12 (m, 3 H, Ad), 4.60 (q, $^3J_{H,H}$=7.2 Hz, 2 H, OCH_2CH_3). ^{13}C NMR (125.77 MHz): δ=14.1 (s, OCH_2CH_3), 28.4 (s, C-3/C-5/C-7-Ad), 36.4 (s, C-4/C-6/C-10-Ad), 37.4 (d, $^2J_{P,C}$=13.8 Hz, C-1-Ad), 43.5 (d, $^3J_{P,C}$=8.6 Hz, C-2/C-8/C-9-Ad), 65.3 (s, OCH_2CH_3), 151.0 (d, $^2J_{P,C}$=11.3 Hz, *C*OOEt), 200.9 (d, $^1J_{P,C}$= 55.5 Hz, C-5). ^{31}P NMR: δ=178.5.

Synthesis of diazadiphosphetidines 4a–d; general procedure. A solution of 5-(*tert*-butyl)-3-phenyl-3*H*-1,2,3,4-triazaphosphole (**3**) and diazoketone **1** in dichloromethane (5 mL) was stirred at room temperature for 3 days. The

solvent was removed under reduced pressure. After the addition of pentane, the diazadiphosphetidines **4** separated as yellow microcrystalline solids which were washed with pentane.

4,11-Di(*tert*-butyl)-1,8-di(2,2-dimethylpropanoyl)-6,12-diphenyl-2,9-di(triisopropylsilyl)-2,3,6,9,10,12-hexaaza-5λ^5,7λ^5-diphosphadispiro[4.1.4.1]dodeca-1(5),3,7,10-tetraene (4a). Reaction of **3** (1.189 g, 5.42 mmol) and **1a** (1.532 g, 5.42 mmol) gave **4a** (1.41 g, 55%), mp 143 °C. IR (KBr): ν=1599 (s), 1498 (m), 1479 (m), 1466 (m), 1392 (m), 1364 (m), 1303 (m), 1256 (s), 1085 (s) cm^{-1}. ^{1}H NMR: δ=0.83 (s, 18 H, CMe_3CO), 1.08 (d, $^3J_{H,H}$=7.8 Hz, 36 H, CH*Me*), 1.40 (sept, $^3J_{H,H}$=7.8 Hz, 6 H, C*H*Me), 1.41 (s, 18 H, CMe_3), 6.92–6.96 (m, 6 H, *o*- and *p*-H at Ph), 7.05–7.08 (m, 4 H, *m*-H at Ph). ^{13}C NMR (125.77 MHz): δ=14.6 (s, SiCH), 19.0 (s, SiCH*Me*), 28.8 (d, $^4J_{P,C}$=5.7 Hz, COC*Me*$_3$), 31.3 (s, C*Me*$_3$), 35.8 (pt, $^2J_{P,C}$=13.8 Hz, $^4J_{P,C}$=5.3 Hz, C*C*Me$_3$), 44.3 (pt, $^3J_{P,C}$=7.1 Hz, $^5J_{P,C}$=−1.4 Hz, Me$_3$*C*CO), 99.3 (m$_c$, $^1J_{P,C}$=170.9 Hz, $^3J_{P,C}$=4.6 Hz, C-1 and C-8), 123.7 (t, $^3J_{P,C}$=6.2 Hz, *o*-C at Ph), 124.0 (s, *p*-C at Ph), 128.3 (s, *m*-C at Ph), 131.1 (m$_c$, $^1J_{P,C}$=85.0, $^3J_{P,C}$=2.7, C-4 and C-11), 136.7 (s, *i*-C at Ph), 202.2 (pt, $^2J_{P,C}$=12.1 Hz, $^4J_{P,C}$=3.6 Hz, C=O). ^{31}P NMR: δ=4.7. MS (CI, 100 eV): *m/z* (%): 474 (100) [M$^+$H/2], 458 (8) [M$^+$/2−CH$_3$], 430 (30) [M$^+$/2−*i*Pr], 411 (9), 383 (33), 367 (10), 339 (67). MS (EI, 70 eV): *m/z* (%)=473 (37) [M$^+$/2], 458 (6), 430 (12) [M$^+$-*i*Pr], 381 (4), 347 (3), 339 (100). Anal. calcd. for $C_{52}H_{88}N_6O_2P_2Si_2$ (947.4): C, 65.92; H, 9.36; N, 8.87. Found: C, 65.72; H, 9.32; N, 8.77.

1,8-Di(1-adamantanoyl)-4,11-di(*tert*-butyl)-6,12-diphenyl-2,9-di(triisopropylsilyl)-2,3,6,9,10,12-hexaaza-5λ^5,7λ^5-diphosphadispiro[4.1.4.1]dodeca-1(5),3,7,10-tetraene (4b): Reaction of **3** (0.760 g, 3.47 mmol) and **1b** (1.250 g, 3.47 mmol) gave **4b** (0.79 g, 45%), mp 138°C. IR (KBr): ν=1597 (s), 1499 (m), 1464 (m), 1453 (m), 1391 (m), 1323 (m), 1296 (s), 1253 (s), 1081 (s) cm^{-1}. ^{1}H NMR: δ=1.07 (d, $^3J_{H,H}$=7.5 Hz, 36 H, CH*Me*), 1.38 (m, 6 H, Ad), 1.41 (s, 18 H, CMe_3), 1.42 (sept, $^3J_{H,H}$=7.5 Hz, 6 H, C*H*Me), 1.49 (m, 18 H, Ad), 1.69 (m, 6 H, Ad), 6.92–6.95 (m, 2 H, *p*-H at Ph), 7.00–7.02 (m, 4 H, *o*-H at Ph), 7.06–7.09 (m, 4 H, *m*-H at Ph). ^{13}C NMR (125.77 MHz): δ=14.5 (s, SiCH), 19.0 (s, SiCH*Me*), 28.4 (s, C-3, -5, -7-Ad), 31.4 (s, CC*Me*$_3$), 35.7 (pt, $^2J_{P,C}$=14.1 Hz, $^4J_{P,C}$=5.0 Hz, C*C*Me$_3$), 36.4 (s, C-4, -6, -10-Ad), 39.2 (s, C-2, -8, -9-Ad), 47.1 (pt, $^3J_{P,C}$=7.4 Hz, $^5J_{P,C}$=−1.7 Hz, C-1-Ad), 98.5 (m$_c$, $^1J_{P,C}$=169.0 Hz, $^3J_{P,C}$=5.6 Hz, C-1 and C-8), 124.0 (s, *p*-C at Ph), 124.5 (s, broad, *o*-C at Ph), 128.3 (s, *m*-C at Ph), 131.2 (m$_c$, $^1J_{P,C}$=85.3 Hz, $^3J_{P,C}$=2.9, C-4 and C-11), 136.7 (s, *i*-C at Ph), 202.6 (pt, $^2J_{P,C}$=11.9 Hz, $^4J_{P,C}$=2.9 Hz, C=O). ^{31}P NMR: δ=6.1. MS (CI, 100 eV): *m/z* (%)=552 (100) [M$^+$/2], 469 (3), 461 (9), 417 (24). Anal. calcd. for $C_{64}H_{100}N_6O_2P_2Si_2$ (1103.7): C, 69.65; H, 9.13; N, 7.61. Found: C, 69.14; H, 9.09; N, 7.44.

4,11-Di(*tert*-butyl)-2,9-di[*tert*-butyl(dimethyl)silyl]-1,8-di(2,2-dimethylpropanoyl)-6,12-diphenyl-2,3,6,9,10,12-hexaaza-5λ^5,7λ^5-diphosphadispiro[4.1.4.1]dodeca-1(5),3,7,10-tetraene (4c). Reaction of **3** (0.520 g, 2.37 mmol) and **1c** (0.570 g, 2.37 mmol) gave **4c** (0.67 g, 66%), mp 146°C. IR (KBr): ν=1602 (s), 1499 (m), 1484 (s), 1462 (m), 1390 (s), 1362 (m), 1309 (s), 1258 (vs), 1082 (vs) cm^{-1}. ^{1}H NMR: δ=0.14 (s, 12 H, SiMe), 0.85 (s, 18 H, CMe_3CO), 1.02 (s, 18 H, $SiCMe_3$), 1.39 (s, 18 H, CMe_3), 6.96–7.00 (m, 6 H, *o*- and *p*-H at Ph), 7.09–7.12 (m, 4 H, *m*-H at Ph). ^{13}C NMR ($CDCl_3$, 125.77 MHz): δ=−3.5 (s, SiMe), 19.7 (s, Si*C*Me$_3$), 27.6 (s, SiC*Me*$_3$), 28.7 (d, $^4J_{P,C}$=4.8 Hz, *Me*$_3$CCO), 31.3 (s, CC*Me*$_3$), 35.8 (pt, $^2J_{P,C}$=13.8 Hz, $^4J_{P,C}$=5.3 Hz, C*C*Me$_3$), 44.8 (pt, $^3J_{P,C}$=7.3 Hz, $^5J_{P,C}$=−1.1 Hz, Me$_3$*C*CO), 98.0 (m$_c$, $^1J_{P,C}$=167.7 Hz, $^3J_{P,C}$=4.5 Hz, C-1 and C-8), 123.3 (t, $^3J_{P,C}$=6.0 Hz, *o*-C at Ph), 124.1 (s, *p*-C at Ph), 128.5 (s, *m*-C at Ph), 133.3 (m$_c$, $^1J_{P,C}$=84.7, $^3J_{P,C}$=2.6, C-4 and C-11), 136.6 (s, *i*-C at Ph), 203.5 (pt, $^2J_{P,C}$=11.6 Hz, $^4J_{P,C}$=3.2 Hz, C=O). ^{31}P NMR: δ=6.6. Anal. calcd. for $C_{46}H_{76}N_6O_2P_2Si_2$ (863.3): C, 64.00; H, 8.87; N, 9.74. Found: C, 63.91; H, 8.98; N, 9.61.

4,11-Di(*tert*-butyl)-2,9-di[*tert*-butyl(diphenyl)silyl]-1,8-di(2,2-dimethylpropanoyl)-6,12-diphenyl-2,3,6,9,10,12-hexaaza-5λ^5,7λ^5-diphosphadispiro[4.1.4.1]dodeca-1(5),3,7,10-tetraene (4d). Reaction of **3** (0.517 g, 2.36 mmol) and **1d** (0.860 g, 2.36 mmol) gave **4d** (0.69 g, 53%), mp 174°C. IR (KBr): ν=1599 (s), 1499 (s), 1484 (s), 1462 (m), 1428 (s), 1417 (m), 1390 (s), 1363 (m), 1306 (s), 1255 (s), 1192 (m), 1164 (w), 1136 (m), 1111 (s), 1083 (vs) cm^{-1}. ^{1}H NMR: δ=0.13 (s, 18 H, $SiCMe_3$), 0.78 (s, 18 H, CMe_3CO), 1.51 (s, 18 H, CMe_3), 6.96–6.98 (m, 2 H, *p*-H at Ph), 7.13–7.14 (m, 8 H, *o*- and *m*-H at Ph), 7.42–7.43 (m, 12 H, *m*- and *p*-H at SiPh), 7.83–7.84 (m, 8 H, *o*-H at SiPh). ^{13}C NMR (125.77 MHz): δ=23.0 (s, Si*C*Me$_3$), 27.8 (s, SiC*Me*$_3$), 28.2 (s, *Me*$_3$CCO), 31.4 (s, CC*Me*$_3$), 36.0 (pt, $^2J_{P,C}$=13.8 Hz, $^4J_{P,C}$=4.8 Hz, C*C*Me$_3$), 44.2 (pt, $^3J_{P,C}$=7.3 Hz, $^5J_{P,C}$=−1.6 Hz, Me$_3$*C*CO), 99.0 (m$_c$, $^1J_{P,C}$=173.4 Hz, $^3J_{P,C}$=5.4 Hz, C-1 and C-8), 123.4 (t, $^3J_{P,C}$=6.2 Hz, *o*-C at Ph), 124.0 (s, *p*-C at Ph), 127.9 (s, *m*-C at SiPh), 128.5 (s, *m*-C at Ph), 130.0 (s, *p*-C at SiPh), 132.0 (s, *i*-C at SiPh), 132.9 (m$_c$, $^1J_{P,C}$=83.7 Hz, $^3J_{P,C}$=4.0 Hz, C-4 and C-11), 136.4 (s, *o*-C at SiPh), 136.8 (s, *i*-C at Ph), 202.0 (pt, $^2J_{P,C}$=11.7 Hz, $^4J_{P,C}$=2.6 Hz, C=O). ^{31}P NMR: δ=5.6. Anal. calcd. for $C_{66}H_{84}N_6O_2P_2Si_2$ (1111.6): C, 71.32; H, 7.62; N, 7.56. Found: C, 70.72; H, 7.61; N, 7.46.

Synthesis of 1,2,4(λ^5)-diazaphospholes 6a–d; general procedure. A solution of 3-alkoxycarbonyl-3*H*-1,2,3,4-triazaphosphole **5** and diazoketone **1** in dichloromethane (20 mL) was stirred at room temperature for 24 h. The solvent was removed under reduced pressure. The diazaphospholes **6** were obtained by crystallization from diethyl ether at −30°C.

3-(*tert*-Butyl)-5-(2,2-dimethylpropanoyl)-4-isocyanato-4-methoxy-1-(triisopropylsilyl)-1*H*-1,2,4λ^5-diazaphosphole (6a). Reaction of **5a** (0.351 g, 1.75 mmol) and **1a** (0.493 g, 1.75 mmol) gave **6a** (0.49 g, 62%) as colorless crystals, mp 98 °C. IR (KBr): ν=1579 (s), 1453 (s), 1407 (s), 1388 (s), 1356 (s), 1309 (s), 1274 (s), 1259 (s), 1208 (s), 1185 (m), 1157 (m), 1104 (s), 1025 (s) cm^{-1}. ^{1}H NMR: δ=1.05 (d, $^3J_{H,H}$=7.4 Hz, 9 H, CH*Me*), 1.06 (d, $^3J_{H,H}$=7.5 Hz, 9 H, CH*Me*), 1.29 (s, 9 H, CMe_3CO), 1.37 (s, 9 H, CMe_3), 1.48 (sept, $^3J_{H,H}$=7.4 Hz, 3 H, C*H*Me), 3.37 (d, $^3J_{P,H}$=16.7 Hz, 3 H, OMe). ^{13}C NMR (125.77 MHz): δ=15.6 (s, SiCH), 18.6 (s, both SiCH*Me*), 27.8 (s, C*Me*$_3$CO), 30.8 (s, C*Me*$_3$), 34.1 (d, $^2J_{P,C}$=18.8 Hz, *C*Me$_3$),

41.3 (s, *C*Me$_3$CO), 52.0 (s, OMe), 100.2 (d, $^1J_{P,C}$=195.5 Hz, C-5), 124.4 (d, $^1J_{P,C}$=111.6 Hz, C-3), 127.8 (d, $^2J_{P,C}$=17.6 Hz, NCO), 194.5 (d, $^2J_{P,C}$=24.6 Hz, C=O). ^{31}P NMR: δ=23.9. Anal. calcd. for $C_{22}H_{42}N_3O_3PSi$ (455.7): C, 57.99; H, 9.29; N, 9.22. Found: C, 57.94; H, 8.94; N, 9.14.

3-(*tert*-Butyl)-5-(2,2-dimethylpropanoyl)-4-ethoxy-4-isocyanato-1-(triisopropylsilyl)-1*H*-1,2,4λ^5-diazaphosphole (6b). Reaction of **5b** (0.305 g, 1.42 mmol) and **1a** (0.400 g, 1.42 mmol) gave **6b** as an oil which could not be purified further by crystallization. IR (KBr): ν=1587 (s), 1479 (s), 1463 (s), 1389 (s), 1362 (s), 1274 (s), 1255 (s), 1197 (s), 1104 (s), 1032 (s) cm^{-1}. ^{1}H NMR: δ=1.05 (d, $^3J_{H,H}$=7.4 Hz, 9 H, CH*Me*), 1.07 (d, $^3J_{H,H}$=7.5 Hz, 9 H, CH*Me*), 1.30 (d, $^5J_{P,H}$=0.8 Hz, 9 H, CMe$_3$CO), 1.31 (t, $^3J_{H,H}$=7.2 Hz, 3 H, OCH$_2$C*H*$_3$), 1.38 (s, 9 H, CMe$_3$), 1.49 (sept, $^3J_{H,H}$=7.4 Hz, 3 H, C*H*Me), 3.63 (m, 2 H, OC*H*$_2$CH$_3$). ^{13}C NMR (50.32 MHz): δ=15.3 (d, $^3J_{P,C}$=11.8 Hz, OCH$_2$*C*H$_3$), 15.6 (s, SiCH), 18.53 (s, SiCH*Me*), 18.56 (s, SiCH*Me*), 27.8 (s, C*Me*$_3$CO), 30.8 (d, $^3J_{P,C}$=3.1 Hz, C*Me*$_3$), 34.0 (d, $^2J_{P,C}$=18.9 Hz, *C*Me$_3$), 41.2 (d, $^3J_{P,C}$=2.6 Hz, *C*Me$_3$CO), 62.1 (d, $^2J_{P,C}$=3.2 Hz, OC*H*$_2$CH$_3$), 100.6 (d, $^1J_{P,C}$=195.2 Hz, C-5), 124.7 (d, $^1J_{P,C}$=111.6 Hz, C-3), 127.7 (d, $^2J_{P,C}$=18.0 Hz, NCO), 194.3 (d, $^2J_{P,C}$=24.5 Hz, C=O). ^{31}P NMR: δ=20.7. MS (FD, 8 kV): *m/z* (%)=469 [M$^+$].

3-(1-Adamantyl)-5-(2,2-dimethylpropanoyl)-4-ethoxy-4-isocyanato-1-triisopropylsilyl-1*H*-1,2,4λ^5-diazaphosphole (6c). Reaction of **5c** (0.401 g, 1.42 mmol) and **1a** (0.401 g, 1.42 mmol) gave **6c** (0.31 g, 40%) as colorless crystals, mp 108°C. IR (KBr): ν=1581 (s), 1479 (m), 1452 (m), 1396 (m), 1363 (m), 1351 (m), 1250 (m), 1210 (s), 1189 (m), 1165 (m), 1031 (s) cm^{-1}. ^{1}H NMR (500.14 MHz): δ=1.04 (d, $^3J_{H,H}$=7.5 Hz, 9 H, CH*Me*), 1.05 (d, $^3J_{H,H}$=7.5 Hz, 9 H, CH*Me*), 1.29 (s, 9 H, CMe$_3$), 1.31 (t, $^3J_{H,H}$=7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 1.47 (sept, $^3J_{H,H}$=7.4 Hz, 3 H, C*H*Me), 1.78 (s, broad, 6 H, Ad), 1.98–2.08 (m, 9 H, Ad), 3.62 (m, 2 H, OC*H*$_2$CH$_3$). ^{13}C NMR (125.77 MHz): δ=15.3 (d, $^3J_{P,C}$=11.9 Hz, OCH$_2$*C*H$_3$), 15.6 (s, SiCH), 18.6 (s, SiCH*Me*), 18.7 (s, SiCH*Me*), 27.9 (s, C*Me*$_3$), 28.7 (s, C-3, -5, -7-Ad), 36.4 (d, $^3J_{P,C}$=18.1 Hz, C-1-Ad), 36.8 (s, C-4, -6, -10-Ad), 41.2 (d, $^3J_{P,C}$=2.4 Hz, *C*Me$_3$), 43.1 (d, $^4J_{P,C}$=3.3 Hz, C-2, -8, -9-Ad), 62.2 (d, $^2J_{P,C}$=3.3 Hz, OC*H*$_2$CH$_3$), 100.7 (d, $^1J_{P,C}$=194.5 Hz, C-5), 125.8 (d, $^1J_{P,C}$=110.2 Hz, C-3), 127.8 (d, $^2J_{P,C}$=17.2 Hz, NCO), 194.3 (d, $^2J_{P,C}$=24.8 Hz, C=O). ^{31}P NMR: δ=21.0. Anal. calcd. for $C_{29}H_{53}O_3PSi$ (547.8): C, 63.59; H, 9.20; N, 7.67. Found: C, 63.33; H, 8.98; N, 7.26.

3-(1-Adamantyl)-5-[(1-adamantyl)carbonyl]-4-ethoxy-4-isocyanato-1-triisopropylsilyl-1*H*-1,2,4λ^5-diazaphosphole (6d). Reaction of **5c** (1.389 g, 4.74 mmol) and **1b** (1.708 g, 4.74 mmol) gave **6d** (2.06 g, 70%) as colorless crystals, mp 134°C. IR (KBr): ν=1741 (m), 1720 (m), 1567 (m), 1452 (m), 1402 (m), 1369 (m), 1310 (m), 1231 (m), 1194 (m), 1166 (m), 1125 (m), 1101 (m), 1032 (s) cm^{-1}. ^{1}H NMR: δ=1.035 (d, $^3J_{H,H}$=7.4 Hz, 9 H, CH*Me*), 1.04 (d, $^3J_{H,H}$=7.4 Hz, 9 H, CH*Me*), 1.33 (d, $^3J_{H,H}$=7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 1.45 (sept, $^3J_{H,H}$=7.4 Hz, 3 H, C*H*Me), 1.76–1.78 (m, 12 H, Ad), 1.98–2.07 (m, 18 H, Ad), 3.62 (m, 2 H, OC*H*$_2$CH$_3$). ^{13}C NMR (125.77 MHz): δ=15.5 (d, $^3J_{P,C}$=11.9 Hz, OCH$_2$*C*H$_3$), 15.7 (s, SiCH), 18.67 (s, SiCH*Me*), 18.70 (s, SiCH*Me*), 28.5 (s, C-3, -5, -7-AdCO), 28.8 (s, C-3, -5, -7-Ad), 36.4 (d, $^3J_{P,C}$=18.1 Hz, C-1-Ad), 36.77 (s, C-4, -6, -10-Ad), 36.79 (s, C-4, -6, -10-Ad), 39.2 (s, C-2, -8, -9-AdCO), 43.1 (d, $^4J_{P,C}$=3.3 Hz, C-2, -8, -9-Ad), 43.6 (d, $^3J_{P,C}$=2.9 Hz, C-1-AdCO), 62.2 (d, $^2J_{P,C}$=3.3 Hz, OC*H*$_2$CH$_3$), 100.7 (d, $^1J_{P,C}$=194.1 Hz, C-5), 125.8 (d, $^1J_{P,C}$=110.6 Hz, C-3), 127.8 (d, $^2J_{P,C}$=17.2 Hz, NCO), 194.3 (d, $^2J_{P,C}$=23.8 Hz, C=O). ^{31}P NMR: δ=20.9. Anal. calcd. for $C_{35}H_{56}O_3PSi$ (625.9): C, 67.16; H, 9.02; N, 6.71. Found: C, 66.85; H, 9.12; N, 6.65.

X-Ray crystal structure analysis of 4a[27,28]

Suitable crystals were obtained from toluene solution at −30°C. *Crystal data:* $C_{52}H_{88}N_6O_2P_2Si_2$, f. w. 947.4, orthorhombic, space group *Pbcn*; a=15.823(1), b=30.377(3), c=11.941(1) Å; $\alpha=\beta=\gamma$=90°; V=5739.4(7) Å^3, Z=4, D_x=1.096 g cm^{-3}; μ(Mo-K$_\alpha$)=1.59 cm^{-1}, crystal size 0.5×0.4×0.1 mm. *Data collection*: T=293 K, diffractometer Stoe IPDS, monochromatized Mo-K$_\alpha$ radiation, phi scans; 40 644 reflections measured in the range 2.24≤θ≤24.09°, 4547 unique reflections (R_{int}=0.072); completeness of data set 99.6%. *Structure solution and refinement*: The structure was solved by direct methods and refined by a full-matrix least-squares method based on F^2 values. Hydrogen atoms were included at calculated positions and were treated by a riding model. Refinement with all unique reflections and 304 parameters converged at R1=0.0731, wR2=0.1189 [for 2899 reflections with $I>2\sigma(I)$: R1=0.0454; wR2=0.1120]; the residual electron density was between 0.42 and −0.20 e Å^{-3}.

X-Ray crystal structure analysis of 6c[27,28]

Crystal data: $C_{29}H_{30}N_3O_3PSi$, f. w. 527.6, triclinic, space group P$\bar{1}$; a=10.680(1), b=11.541(2), c=14.686(2) Å; α=107.68(2), β=94.86(2), γ=110.21(1)°; V=1581.6(4) Å^3, Z=2, D_x=1.108 g cm^{-3}; μ(Mo-K$_\alpha$)= 1.55 cm^{-1}, crystal size 0.6×0.5×0.3 mm. *Data collection*: T=293 K, diffractometer Stoe IPDS, monochromatized Mo-K$_\alpha$ radiation, phi scans; 15 966 reflections measured in the range 2.01≤θ≤26.03 deg, 5708 unique reflections (R_{int}=0.063), completeness of data set 91.4%. *Structure solution and refinement*: The structure was solved by direct methods and refined by a full-matrix least-squares method based on F^2 values. The adamantyl group is disordered over two sites (occupancy factors 0.65 and 0.35) which differ from each other by a 60° rotation around the C2–C20(adamantyl) bond (see Fig. 4). The disorder could be resolved for the adjacent CH$_2$ groups (C21, C22, C23) (refinement was done with restraints on the bond distances between these atoms and C20 and on the non-bonding distances between these atoms), but not for the cyclohexane ring formed by atoms C24–C29 which therefore appear in averaged positions. Hydrogen atom positions were included in calculated positions and were treated by a riding model; because of the disorder, no hydrogen atoms attached to C24 through C29 were included. Refinement with all unique reflections and 369 parameters (plus 15 restraints) converged at R1=0.0977, wR2=0.1752 [for 3444 reflections with $I>2\sigma(I)$: R1=0.0591; wR2=0.1576];

the residual electron density was between 0.44 and -0.13 e $Å^{-3}$.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (Graduiertenkolleg 'Phosphor als Bindeglied zwischen verschiedenen chemischen Disziplinen') and the Fonds der Chemischen Industrie.

References

1. (a) Yeung Lam Ko, Y. Y. C.; Carrié, R.; Muench, A.; Becker, G. *J. Chem. Soc., Chem. Commun.* **1984**, 1634–1635. (b) Yeung Lam Ko, Y. Y. C.; Carrié, R. *J. Chem. Soc., Chem. Commun.* **1984**, 1640–1641.
2. Rösch, W.; Regitz, M. *Angew. Chem.* **1984**, *96*, 898–899; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 900–901.
3. Rösch, W.; Facklam, T.; Regitz, M. *Tetrahedron* **1987**, *43*, 3247–3256.
4. Manz, B.; Maas, G. *Tetrahedron* **1996**, *52*, 10053–10072.
5. Arbuzov, B. A.; Dianova, E. N. *Phosphorus, Sulfur* **1986**, *26*, 203–251.
6. Arbuzov, B. A.; Dianova, E. N.; Galiaskarova, R. T.; Schmidpeter, A. *Chem. Ber.* **1987**, *120*, 597–599.
7. Rösch, W.; Regitz, M. *Synthesis* **1987**, 689–693.
8. Nyulászi, L.; Veszprémi, T.; Réffy, J.; Burkhardt, B.; Regitz, M. *J. Am. Chem. Soc.* **1992**, *114*, 9080–9084.
9. Munschauer, R.; Maas, G. *Angew. Chem.* **1991**, *103*, 312–314; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 306–308.
10. Niecke, E.; Seyer, A.; Wildbredt, D. A. *Angew. Chem.* **1981**, *93*, 687–688; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 675–676.
11. Märkl, G.; Sommer, H.; Nöth, H. *Tetrahedron Lett.* **1993**, *34*, 3107–3110.
12. Sørensen, S.; Jakobsen, H. *J. Org. Magn. Reson.* **1977**, *9*, 101–104.
13. Computer simulations of the NMR spectra were performed using the software Win-Daisy, BRUKER-Franzen Analytik, Bremen, 1998.
14. This value is very similar to δ(C=O) 193.5 ppm found in the (acylmethylene)phosphorane Ph_3P=C(Pr)–CO*t*-Bu: Aitken, A.; Atherton, J. I. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1281–1284.
15. Nyulászi, L.; Veszprémi, T. *J. Phys. Chem.* **1996**, *100*, 6456–6462.
16. Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. J. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1–S19.
17. Peterson, M. B.; Wagner, A. J. *J. Chem. Soc., Dalton Trans.* **1973**, 106–111.
18. Kerth, J.; Maas, G. Unpublished results.
19. (a) Niecke, E.; Wildbredt, D. A. *Angew. Chem.* **1978**, *90*, 209–210; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 199–200. (b) Niecke, E.; Wildbredt, D. A. *Chem. Ber.* **1980**, *113*, 1549–1565.
20. Review: Heydt, H. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J. Eds.; Thieme: Stuttgart, 1990, pp 375–391.
21. Arbuzov, B. A.; Dianova, E. N.; Sharipova, S. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 1600–1602; *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1981**, 1293–1295.
22. Schmidpeter, A.; Karaghiosoff, K. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme: Stuttgart, 1990, pp 274–275.
23. Brückmann, R.; Maas, G. *Chem. Ber.* **1987**, *120*, 635–641.
24. Brückmann, R.; Schneider, K.; Maas, G. *Tetrahedron* **1989**, *45*, 5517–5530.
25. Brückmann, R.; Maas, G. *J. Chem. Soc., Chem. Commun.* **1986**, 1782–1783.
26. Rösch, W.; Allspach, T.; Bergsträßer, U.; Regitz, M. In *Synthetic Methods of Organometallic and Inorganic Chemistry*; Herrmann, W. A., Karsch, H. H., Eds.; Thieme: Stuttgart, 1996; Vol. 3, pp 11–16.
27. The crystal structures were solved and refined with the program package SHELX-97 (Sheldrick, G. M., University of Göttingen, 1997). Molecule plots were made with ORTEP-3 for Windows (Farrugia, L. J., University of Glasgow, 1998).
28. Crystallographic data (excluding structure factors) for the X-ray crystal structure analyses reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033, e-mail: deposit@ccdc.cam.ac.uk).