Cycloadducts from Diazocumulenes and 1,2,3(λ^3)-Diazaphospholes: Thermolysis Generates Products Derived from 3-Alkenylidene-1,2,3(λ^5)-diazaphospholes

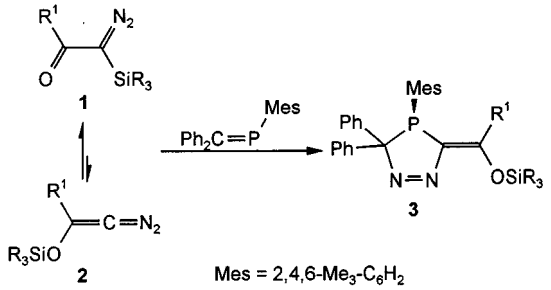
Jochen Kerth[a] and Gerhard Maas*[a]

Keywords: Diazo compounds / Cycloadditions / Phosphaalkenes / Phosphorus heterocycles / Phosphoranes

(1-Diazo-2-oxoalkyl)silanes **1** react with 2-acyl-1,2,3(λ^3)-diazaphospholes **4** to form [3+2] cycloaddition products **5**, which indicate that 1-diazo-2-silyloxy-1-alkenes **2**, coexisting with **1** as the minor equilibrium component, have been trapped. Thermal impact on cycloadducts **5** generates the tricyclic phosphorus heterocycles **9**; their formation can be rationalized by two competing processes, namely thermal [3+2] cycloreversion into **2** and **4**, and extrusion of molecular nitrogen. The latter process is likely to generate 3-alkenylidene-1,2,3(λ^5)-diazaphospholes **8**, which are trapped intermolecularly by diazaphospholes **4**. Intermediates **8** could not be intercepted with dimethyl acetylenedicarboxylate (DMAD); rather, **5i** reacts with DMAD to form the spiro-λ^5-phosphorane **11** in low yield.

Introduction

α-Diazo-α-silyl ketones [(1-diazo-2-oxoalkyl)silanes] **1** maintain an equilibrium with minor amounts of 1-diazo-2-silyloxy-1-alkenes **2**. Although the diazocumulenes **2** have not yet been observed directly, they could be trapped by 1,3-dipolar cycloaddition reactions with activated alkenes,[1][2] and kinetic evidence for their intermediacy in these reactions has been provided.[1] The diazocumulene can also be intercepted from the equilibrium **1/2** by [3+2] cycloaddition with phosphaalkenes, e.g. diphenylmethylene(mesityl)phosphane, to form 3-alkylidene-4,5-dihydro-1,2,4-diazaphospholes **3** (Scheme 1).[3] Thermally induced extrusion of molecular nitrogen from **3** gives access to short-lived methylene(vinylidene)phosphoranes, which are rapidly isomerized by cyclization and rearrangement reactions.[4]



Scheme 1. Trapping of diazocumulenes with a phosphaalkene

Along these lines, we wondered whether diazoalkenes **2** would also cycloadd to the P=C bond incorporated in heterophospholes. Although several classes of heterophospholes containing a $\sigma^2\lambda^3$-phosphorus atom are considered to have aromatic character according to various theoretical criteria,[5] the participation of their P=C bond in cycloaddition and polar 1,2-addition reactions is well established.[6][7] This is especially true for 1,2,3(λ^3)-2*H*-diazaphospholes, the best-studied class of heterophospholes so far.[7] Of particular importance for our project were the reports by Arbuzov and co-workers[8][9] that a variety of diazo compounds, including diazoalkanes, diazoacetates, and diazophosphonates, react smoothly with 1,2,3-2*H*-diazaphospholes to give an array of novel phosphorus-containing heterocycles after an initial 1,3-dipolar cycloaddition reaction.

Results and Discussion

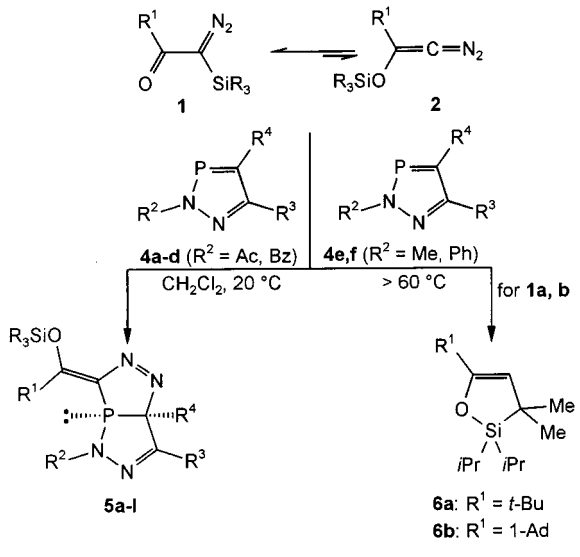
Synthesis of Cycloadducts 5

α-Diazo-α-silyl ketones **1a**−**c** react with the 2-acyl-1,2,3-diazaphospholes **4a**−**d** already at 20°C to form bicyclic compounds **5a**−**l**, which represent the products of an 1,3-dipolar cycloaddition reaction of diazoalkenes **2**, which are in equilibrium with diazo ketones **1**, at the P=C bond of **4** (Scheme 2 and Table 1). Although ^{31}P-NMR spectroscopy did not indicate significant amounts of other P-containing products besides **5**, the yields of isolated products were lower than expected in some cases. This may be attributed at least in part to the rather low tendency of some of these moisture-sensitive cycloadducts to crystallize. The 2-acyl substitution of diazaphospholes **4** is a prerequisite for the success of the cycloaddition, as 2-methyl and 2-phenyl derivatives (**4e**,**f**) fail to react with the same diazo ketones even at temperatures around 60°C, where thermal decomposition of the diazo compound becomes significant and leads to silaheterocycles such as **6a**,**b**. These products result from an intramolecular reaction of alkylidenecarbenes derived from diazoalkenes **2**.[10]

Cycloadducts **5a**−**l** have some characteristic spectroscopic features in common, such as a ^{31}P-NMR signal at $\delta = -4.9-11.5$, a deshielded bridgehead proton (if R^4 = H) [$\delta(^1H) = 5.61-6.44$, $^2J_{P,H} = 50\pm1$ Hz), and the ^{13}C-

[a] Abteilung Organische Chemie I, Universität Ulm, Albert-Einstein-Allee 11, D-89081 Ulm, Germany
Fax: (internat.) + 49-(0)731/502-2803
E-mail: gerhard.maas@chemie.uni-ulm.de

  1434−193X/99/1010−2633 $ 17.50+.50/0



1,2	R^1	SiR_3
a	*t*Bu	Si*i*Pr$_3$
b	1-Ad	Si*i*Pr$_3$
c	*t*Bu	SiMe$_2$*t*Bu

4	R^2	R^3	R^4
a	Ac	Me	H
b	Ac	Ph	H
c	Ac	-(CH$_2$)$_4$-	
d	Bz	Me	H
e	Me	Me	H
f	Ph	Ph	H

Scheme 2. See Table 1 for substituents and yields of **5**

Table 1. Cycloaddition products **5a**−**l** prepared[a]

Cmpd.	Precursors	R^1	R^2	R^3	R^4	SiR_3	Yield (%)
5a	**1a** + **4a**	*t*Bu	Ac	Me	H	Si*i*Pr$_3$	70
5b	**1a** + **4b**	*t*Bu	Ac	Ph	H	Si*i*Pr$_3$	66
5c	**1a** + **4c**	*t*Bu	Ac	−(CH$_2$)$_4$−		Si*i*Pr$_3$	51
5d	**1a** + **4d**	*t*Bu	Bz	Me	H	Si*i*Pr$_3$	65
5e	**1b** + **4a**	1-Ad	Ac	Me	H	Si*i*Pr$_3$	52
5f	**1b** + **4b**	1-Ad	Ac	Ph	H	Si*i*Pr$_3$	67
5g	**1b** + **4c**	1-Ad	Ac	−(CH$_2$)$_4$−		Si*i*Pr$_3$	73
5h	**1b** + **4d**	1-Ad	Bz	Me	H	Si*i*Pr$_3$	86
5i	**1c** + **4a**	*t*Bu	Ac	Me	H	SiMe$_2$*t*Bu	75
5j	**1c** + **4b**	*t*Bu	Ac	Ph	H	SiMe$_2$*t*Bu	66
5k	**1c** + **4c**	*t*Bu	Ac	−(CH$_2$)$_4$−		SiMe$_2$*t*Bu	80
5l	**1c** + **4d**	*t*Bu	Bz	Me	H	SiMe$_2$*t*Bu	74

[a] 1-Ad = 1-adamantyl.

NMR data of the molecular skeleton given in Table 2. By analogy to the monocyclic cycloadducts **3**,[3] the (*E*) configuration of the exocyclic C=C bond is concluded from the observation of a $^5J_{P,H}$ coupling (0.9−1.4 Hz) and of a rather large $^4J_{P,C}$ coupling (8.6−9.8 Hz) between the phosphorus nucleus and the nuclei of the =C-alkyl (*t*Bu, 1-Ad) groups. The IR spectra display only one carbonyl stretching vibration (1640−1670 cm^{-1} for the *N*-acetyl, and 1630−1640 cm^{-1} for the *N*-benzoyl derivatives), thus giving another indication of the incorporation of the diazoalkene rather than the diazo ketone dipole in these cycloaddition products.

Additional structural proof is provided by the single-crystal X-ray diffraction analysis of **5c** (Figure 1). The molecular structure of the two independent molecules in the unit cell is analogous to that of **3a**;[3] a detailed comparison of bond lengths and angles is inappropriate, however, due to the limited accuracy of the data in the present case.

The isolation of cycloaddition products **5a**−**l** is remarkable, since the reactions of diazo compounds $R^1R^2CN_2$ with 2*H*-1,2,3-diazaphospholes rarely stop at the stage of the initially formed bicyclic Δ^1-pyrazoline.[8] Only with 9-diazofluorene as 1,3-dipole could such a product be isolated and it was found to decompose when heated in petroleum ether at 70°C;[11] reactions with diazoalkanes R_2CN_2 (R_2C = H_2C, Me_2C, HPhC, MePhC, Ph_2C) at room temperature or below were accompanied by evolution of molecular nitrogen and afforded products that suggest the intermediacy of 3-alkylidene-2*H*-1,2,3-diazaphospholes.

Thermolysis of Cycloadducts 5

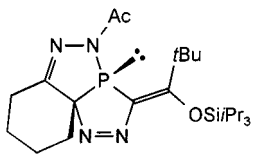
Cycloadducts **5** lose molecular nitrogen when heated at 80−100°C in solution. From the complex product mixtures obtained from **5b**,**e**,**i**,**j**, the tricyclic heterocycles **9b**,**e**,**i**,**j** could be isolated in low or moderate yield (Scheme 3). In mechanistic terms, it is assumed that thermal impact on **5** initiates two parallel reactions, namely [3+2] cycloreversion generating diazaphospholes **4** and 1-oxa-2-silacyclopentenes **6** (products derived from alkylidenecarbenes, see above) as well as extrusion of molecular nitrogen generating 3-alkenylidene-1,2,3(λ^5)-diazaphopholes **8** via 1,3-diradicals **7**. The semicyclic methylene(vinylidene)phosphoranes **8** are trapped by diazaphospholes **4** in a [$3_{4\pi}$+$2_{2\pi}$] cycloaddition reaction. Partial support for this mechanism is provided by the NMR-spectroscopic observation of signals attributed to **4** and **6** in the crude product mixtures [e.g. **4a**: δ(=CH) = 7.8, δ(P) = 238; **6b**:[10] δ(=CH) = 4.3]. In principle, products **9** could also result from an intermolecular trapping of 1,3-diradicals **7** rather than of phosphoranes **8**. If these diradicals were persistent enough to undergo a bimolecular reaction, we would expect them to undergo an intramolecular reaction even faster, namely the abstraction of two hydrogen atoms from an Si*i*Pr group. While this reaction mode is significant in the case of related acyclic methylene-(vinylidene)phosphoranes,[4] a corresponding product could not be observed in this study.

The proposed mechanism is completely analogous to the one for the reaction of diazaphospholes **4** with diazoalkanes,[8,11,12] except for the fact that the $R_2C(N_2)$ moiety in Arbuzov's cases is replaced by $R_2C{=}C(N_2)$ in ours. In contrast to some 3-alkylidene-1,2,3(λ^5)-diazaphospholes, however, the cumulenic analogues **8** do not seem to form bicyclic phosphiranes by a 4π-cyclization reaction. ^{31}P-NMR spectra of the crude product mixtures showed signals of some unidentified by-products, but not in the region of δ = −60 to −100, which is the typical range[9] of such bicyclic phosphiranes.

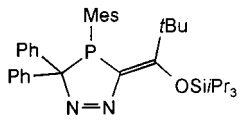
Thermolyses of cycloadducts **5f**,**h**,**l** were also carried out. NMR examination (^{1}H, ^{31}P) of the crude reaction mixture indicated again the presence of the expected heterotricyclic compounds **9**, but only as a minor component in an even

Table 2. ^{13}C- and ^{31}P-NMR data of cycloadducts **5a**−**l** ($CDCl_3$, δ values, *J* [Hz])

Cmpd.	P−*C*-R⁴	*C*=C−OSi	δ(¹³C) ($J_{P,C}$) C=*C*−OSi	C=N	C=O	Other Signals	δ(³¹P)
5a	100.8 (21.7)	147.8 (62.7)	185.9 (23.9)	151.8	173.3 (10.0)	14.8, 17.6, 17.8, 18.1, 22.3, 29.2 (d, $^4J_{P,C}$ = 9.4 Hz, C*Me*$_3$), 40.4 (d, $^3J_{P,C}$ = 2.8 Hz, *C*Me$_3$)	−4.0
5b	97.8 (21.7)	147.9 (62.0)	186.2 (24.3)	151.4	173.6 (9.6)	14.9, 17.8, 18.0, 22.4, 29.5 (d, $^4J_{P,C}$ = 9.4 Hz, C*Me*$_3$), 40.7 (d, $^3J_{P,C}$ = 2.8 Hz, *C*Me$_3$), 127.6, 128.8, 130.1, 132.7	−0.5
5c	109.2 (19.1)	146.3 (60.1)	186.1 (22.9)	156.5	173.8 (10.0)	15.0, 17.8, 18.0, 22.3, 22.4 (d, $^3J_{P,C}$ = 10.0 Hz), 26.1, 28.5, 29.3 (d, $^4J_{P,C}$ = 9.1 Hz, C*Me*$_3$), 33.4 (d, $^2J_{P,C}$ = 36.7 Hz, CH_2), 40.4 (d, $^3J_{P,C}$ = 2.9 Hz, *C*Me$_3$)	8.6
5d	100.0 (20.0)	147.7 (62.9)	186.3 (23.8)	152.7	170.9 (11.5)	14.9, 17.8, 18.0, 18.5, 29.4 (d, $^4J_{P,C}$ = 9.5 Hz, C*Me*$_3$), 40.6 (d, $^3J_{P,C}$ = 2.9 Hz, *C*Me$_3$), 127.6, 129.5, 130.9, 134.5	0.5
5e	100.7 (20.8)	147.7 (62.8)	185.6 (23.2)	151.8	173.3 (9.8)	14.8, 17.8, 18.0, 18.3, 22.4, 28.3, 36.5, 40.1 ($^4J_{P,C}$ = 10.0 Hz, Ad-C-2,-8,-9), 42.6 ($^3J_{P,C}$ = 3.1 Hz, Ad-C-1)	7.2
5f	97.6 (21.5)	147.7 (62.2)	185.8 (23.7)	151.3	173.8 (9.3)	14.8, 17.9, 18.1, 22.5, 28.4, 36.6, 40.3 ($^4J_{P,C}$ = 10.4 Hz, Ad-C-2,-8,-9), 42.9, 127.6, 128.8, 130.1, 132.8	11.5
5g	108.8 (19.6)	146.1 (60.1)	185.8 (22.5)	156.2	173.5 (9.6)	14.9, 17.9, 18.0, 22.3, 22.4, 26.0, 28.3, 28.5, 33.2 (d, $^2J_{P,C}$ = 37.1 Hz, CH_2), 36.5, 40.1 (d, $^4J_{P,C}$ = 9.6 Hz, Ad-C-2,-8,-9), 42.5 (d, $^3J_{P,C}$ = 2.8 Hz, Ad-C-1)	9.0
5h	99.7 (22.0)	147.5 (62.7)	185.7 (23.2)	152.3	170.7 (10.3)	14.8, 17.8, 18.0, 18.4, 28.2, 36.4, 40.0 (d, $^4J_{P,C}$ = 9.8 Hz, Ad-C-2,-8,-9), 42.6 (d, $^3J_{P,C}$ = 2.5 Hz, Ad-C-1), 127.4, 129.2, 130.5, 134.7	0.5
5i	101.2 (21.7)	148.2 (63.1)	185.2 (24.6)	152.0	173.7 (10.6)	−3.8, −2.6, 18.2, 19.5, 22.6, 26.2, 29.3 (d, $^4J_{P,C}$ = 9.5 Hz, CC*Me*$_3$), 40.2 (d, $^3J_{P,C}$ = 2.8 Hz, C*C*Me$_3$)	−4.9
5j	97.9 (21.6)	148.1 (62.6)	185.2 (24.9)	151.1	174.0 (10.1)	−3.9, −2.6, 19.5, 22.5, 26.1, 29.3 (d, $^4J_{P,C}$ = 9.7 Hz, CC*Me*$_3$), 40.2 (d, $^3J_{P,C}$ = 2.4 Hz, C*C*Me$_3$), 127.6, 128.8, 130.1, 132.8	2.5
5k	109.5 (19.3)	146.7 (60.4)	185.3 (23.7)	156.6	173.9 (10.5)	−3.9, −2.6, 19.6, 22.4, 22.5, 26.2 (SiC*Me*$_3$), 28.48, 28.49, 29.3 (d, $^4J_{P,C}$ = 9.1 Hz, CC*Me*$_3$), 33.6 (d, $^2J_{P,C}$ = 37.0 Hz, CH_2), 40.1 (d, $^3J_{P,C}$ = 2.7 Hz, C*C*Me$_3$)	7.5
5l	100.1 (21.9)	148.1 (62.9)	185.4 (24.8)	152.7	170.9 (11.0)	−3.9 (d, $^5J_{P,C}$ = 4.3 Hz, SiMe), −2.6 (s, SiMe), 18.3, 19.5, 26.2 (SiC*Me*$_3$), 29.3 (d, $^4J_{P,C}$ = 9.1 Hz, CC*Me*$_3$), 40.2 (d, $^3J_{P,C}$ = 2.4 Hz, C*C*Me$_3$), 127.5, 129.6, 130.9, 134.3	−0.4



5c



3a

more complex product mixture than in the previous cases. Therefore, no efforts to separate these mixtures were made.

Tricyclic **5k** behaved like the bicyclic analogues in Scheme 3 and afforded the pentacyclic compound **9k** on heating (Scheme 4). Since all compounds of type **9** were obtained at best as microcrystalline samples and escaped all our efforts to grow single crystals suited for X-ray structure analysis, we were happy to find that a sample of **9k**, when stored at 8°C for about two years, had hydrolyzed to an extent of about 50%, and that recrystallization of this mixture from dichloromethane gave well-formed crystals of hydrolysis product **10**. The X-ray crystal structure determi-

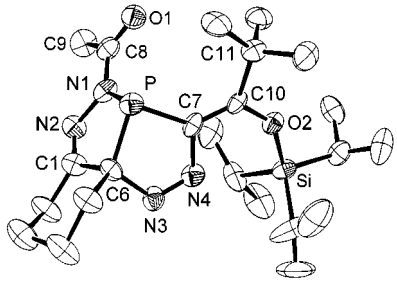
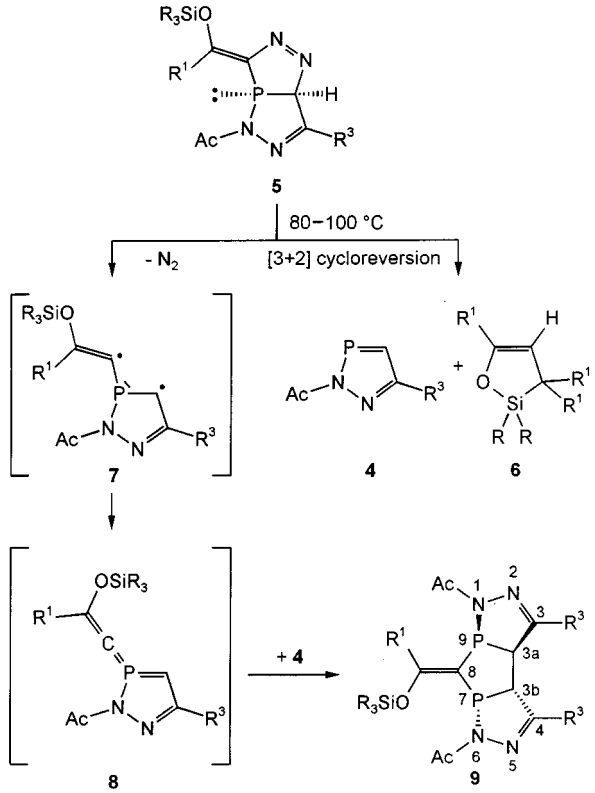


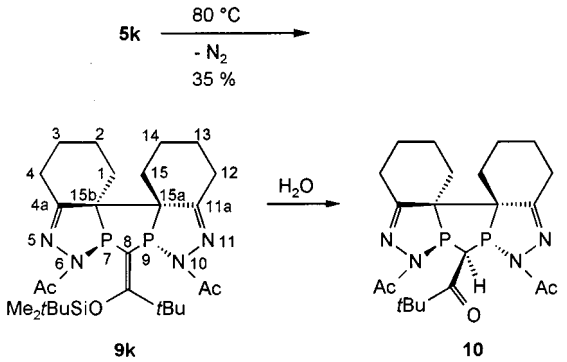
Figure 1. Structure of **5c** in the solid state (ORTEP plot); ellipsoids of thermal vibration are shown at the 20% probability level; only one of the two independent molecules in the unit cell is shown; selected bond lengths [Å] and bond angles [°]; values for the second molecule are given in brackets: P1−N1 1.814(7) [1.766(8)], P1−C6 1.856(9) [1.886(8)], P1−C7 1.813(9) [1.803(8)], N1−N2 1.431(11) [1.432(9)], C1−N2 1.246(11) [1.257(11)], N3−N4 1.266(9) [1.277(8)], C7−C10 1.364(11) [1.377(9)]; N1−P1−C7 102.1(3) [102.1(4)], N1−P1−C6 87.2(5) [87.4(4)], C6−P1−C7 87.6(5) [89.0(4)], C10−O2−Si1 141.3(6) [139.8(5)]



5,9	R^1	R^3	SiR_3	Yield [%]
b	*t*Bu	Ph	Si*i*Pr$_3$	27
e	1-Ad	Me	Si*i*Pr$_3$	17
i	*t*Bu	Me	SiMe$_2$*t*Bu	34
j	*t*Bu	Ph	SiMe$_2$*t*Bu	50

Scheme 3. Thermolysis of cycloadducts **5**

nation (Figure 2) revealed the *cis,anti,cis* configuration of the heterotricyclic core. This geometry, the nonplanarity of the diazaphospholine rings and the pyramidal configuration of the two P atoms are in agreement with similar structures determined by Arbuzov and co-workers.[13] The central diphospholane ring adopts an envelope conformation with C13 at the tip and a torsion angle of 6.6° for the P1−C6−C7−P2 fragment. An interesting detail of the structure is the elongation of the C6−C7 bond (1.614 Å), which is certainly a consequence of a conformation not far from eclipsed around this bond and the resulting buildup of steric strain.



Scheme 4. Formation and hydrolysis of **9k**

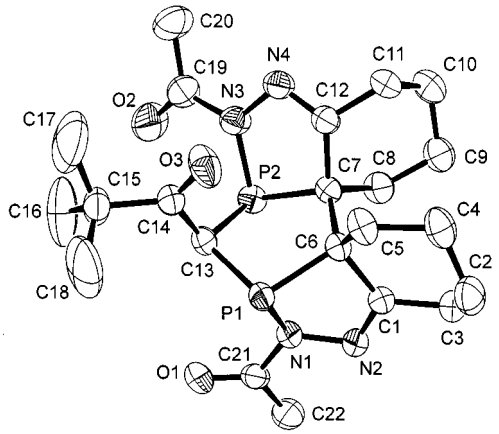


Figure 2. Structure of **10** in the solid state (ORTEP plot); ellipsoids of thermal vibration are shown at the 20% probability level; selected bond lengths [Å] and bond angles [°]: P1−N1 1.759(2), N1−N2 1.413(2), N2−C1 1.285(3), C1−C6 1.537(3), P1−C6 1.886(2), C6−C7 1.614(3), P1−C13 1.839(2), P2−C13 1.860(2), P2−N3 1.745(2), N3−N4 1.401(2), N4−C12 1.278(3), C7−C12 1.530(3), P2−C7 1.896(2); P1−C13−P2 104.5(1), C13−P1−C6 101.33(9), C13−P2−C7 99.63(8); selected torsion angles [°]: P1−C6−C7−P2 6.6(2), C1−C6−C7−C8 −20.6(2), C5−C6−C7−C12 −15.2(2), P1−N1−C21−O1 18.6(3), P2−N3−C19−O2 −1.7(3)

In the NMR spectra (^{1}H: Experimental Section; ^{13}C, ^{31}P: Table 3), corresponding atoms in the two diazaphospholine rings of **9** and **10** give rise to separate signals. With the exception of the two phosphorus atoms and the carbon atoms C-3a/C-3b (Table 3), the chemical shift differences are rather small. We assume that **9b**,**e**,**i**,**j** have the same configuration of the tricyclic skeleton as **9k** and **10**, i.e. *cis,anti,cis*. Evidence for this configuration is provided by the small values of the coupling constant ^3J(3a-H,3b-H), namely 2.1−2.4 Hz in the 3,4-diphenyl derivatives (**9b**,**j**) and ca. 0 Hz in the 3,4-dimethyl cases (**9e**,**i**), pointing to a *trans* relationship of these two protons at the diphospholane ring. The signals of the two protons are also split by geminal

coupling with one P atom (33.1−39.9 Hz) and ^3J (or ^4J) coupling with the other (12.4−16.5 Hz). Interestingly, line broadening for one or both proton signals is observed in the 500-MHz spectra (Figure 3), which is likely to be caused by rapid conformational changes of the central 1,3-diphospholane ring. Also worth mentioning are the long-range P,C and P,H couplings between the phosphorus atoms and the corresponding *cis* substituents at the exocyclic bond. In particular, the *Si*-attached alkyl groups are engaged in remarkably large and far-reaching long-range couplings. In the SiMe$_2$*t*Bu derivatives (**9i**,**j**,**k**), one finds ^5J(P,SiCH_3) = 16.4−19.4 Hz and ^6J(P,SiCH_3) = 3.6−4.0 Hz for one of the two methyl groups, while the other appears uncoupled, and ^6J[P,SiC(CH_3)$_3$] = 1.0−2.4 Hz is found for the Si*t*Bu group. In the Si*i*Pr$_3$ derivatives (**9b**,**e**), the ^5J(P,SiCH) coupling constants amount to 5.7−6.7 Hz. The unusually high values of these long-range couplings[14] suggest a coupling mechanism by through-space interaction between the lone pair at the phosphorus atom and the *Si*-alkyl group involved. On the other hand, the coupling constants $^4J_{P,C}$ (10−10.5 Hz) and $^5J_{P,H}$ (0−1.1 Hz) involving the C=C-*alkyl* (*t*Bu, 1-Ad) group have similar values as in the cycloadducts **5** (see above).

The change from silylenol ether **9k** to its hydrolysis product **10** entails a deshielding of the two ^{31}P nuclei by 35 and 56 ppm, while the ^{13}C chemical shifts of the ring carbon atoms (except C-8) do not change much. The observation that proton 8-H couples with only one of the two phosphorus atoms ($^2J_{P,H}$ = 24.9 Hz) points to different dihedral angles between the direction of the P lone-pair and the C−H bond[14] and is another indication of the *anti* configuration at the 1,3-diphospholane ring.

Table 3. ^{13}C- and ^{31}P-NMR data of heterocycles **9** and **10** (CDCl$_3$, δ values, *J* [Hz])

Compd.	δ(^{13}C) ($J_{C,P}$)[a]							δ(^{31}P) ($J_{P,P}$)[a]
	*Me*CO	Me*C*O	PCH(R)	PCP	PC=*C*	C=N	Other Signals	
9b	22.7, 22.9	172.2 (9.1), 173.4 (11.4)	47.9 (10.5), 55.5 (9.3, 2.6)	114.9 (60.1, 51.0)	184.5 (20.5, 16.7)	156.2, 156.6 (2.4)	14.3 (d, $^5J_{P,C}$ = 5.7 Hz, SiCH), 18.6 (SiCH*Me*$_2$), 30.0 (d, $^4J_{P,C}$ = 10.5 Hz, C*Me*$_3$), 42.9 (d, $^3J_{P,C}$ = 3.8 Hz, *C*Me$_3$), 127.49, 127.51, 128.9, 129.0, 130.2, 130.3, 131.3, 131.6	37.8, 55.3 (18.2)
9e	22.6 (br.), 23.0	171.8 (10.0), 173.0 (11.9)	48.7 (7.6), 57.3 (br.)	112.6 (60.1, 49.1)	184.6[b]	154.7, 155.8 (1.4)	14.1 (d, $^5J_{P,C}$ = 6.7 Hz, SiCH), 14.7 (Me), 15.3 (Me), 18.4 (SiCH*Me*$_2$), 28.4 (Ad-C-3,-5,-7), 36.3 (Ad-C-4,-6,-10), 40.2 (d, $^4J_{P,C}$ = 10.5 Hz, Ad-C-2,-8,-9), 44.8 (d, $^3J_{P,C}$ = 3.3 Hz, Ad-C-1)	32.6, 48.9 (18.4)
9i	22.6, 22.8	172.1 (10.0), 173.0 (11.5)	49.5 (7.6), 55.0 (6.2)	114.9 (59.9, 50.4)	183.4 (21.3, 17.0)	154.6, 156.3	−3.1 (SiMe), −2.1 (d, $^5J_{P,C}$ = 17.6 Hz, SiMe), 14.7 (Me), 14.9 (Me), 19.7 (Si*C*Me$_3$), 26.8 (d, $^6J_{P,C}$ = 2.4 Hz, SiC*Me*$_3$), 29.5 (d, $^4J_{P,C}$ = 10.0 Hz, CC*Me*$_3$), 42.1 (d, $^3J_{P,C}$ = 2.9 Hz, C*C*Me$_3$)	29.8, 42.1 (19.2)
9j	22.6, 22.7	172.3 (10.0), 173.2 (11.0)	48.1 (9.5), 53.2 (8.6)	116.7 (58.2, 51.5)	183.2 (21.7, 16.5)	155.9, 156.7	−3.0 (SiMe), −1.8 (d, $^5J_{P,C}$ = 16.4 Hz, SiMe), 19.6 (Si*C*Me$_3$), 26.7 (d, $^6J_{P,C}$ = 2.4 Hz, SiC*Me*$_3$), 29.6 (d, $^4J_{P,C}$ = 10.5 Hz, CC*Me*$_3$), 42.2 (d, $^3J_{P,C}$ = 3.3 Hz, C*C*Me$_3$),	34.9, 48.7 (17.0)
9k	22.30, 22.39	172.4 (8.6), 173.2 (9.1)	61.8[c], 63.9[d]	112.6 (47.2, 46.3)	182.3 (22.4, 13.4)	162.3, 163.5	−3.0 (SiMe), −1.1 (d, $^5J_{P,C}$ = 19.5 Hz, SiMe), 19.5 (Si*C*Me$_3$), 22.43 (CH$_2$), 22.47 (CH$_2$), 26.8 (d, $^6J_{P,C}$ = 1.0 Hz, SiC*Me*$_3$), 28.5 (br, 2 × CH$_2$), 29.75 (d, $^4J_{P,C}$ = 10.5 Hz, CC*Me*$_3$), 29.80 (CH$_2$), 30.0 (CH$_2$), 30.7 (dd, $^2J_{P,C}$ = 37.0 Hz, $^3J_{P,C}$ = 2.2 Hz, CH$_2$), 30.9 (dd, $^2J_{P,C}$ = 37.0 Hz, $^3J_{P,C}$ = 1.7 Hz, CH$_2$), 42.3 (d, $^3J_{P,C}$ = 3.3 Hz, C*C*Me$_3$), 127.3, 127.4, 128.9, 129.0, 130.1, 130.3, 131.0, 131.2	64.8, 77.3[e]
10	21.8, 22.2	173.6 (9.7), 174.4 (6.9)	64.8 (19.4, 4.6), 72.6 (15.6, 4.5)	46.6 (52.0, 36.1)		163.2, 163.5	22.9 (d, $J_{P,C}$ = 12.5 Hz, CH$_2$), 23.7 (d, $J_{P,C}$ = 15.3 Hz, CH$_2$), 26.2 (d $^4J_{P,C}$ = 4.9 Hz, C*Me*$_3$), 26.24 (CH$_2$), 28.7 (CH$_2$), 29.4 (CH$_2$), 31.6 (CH$_2$), 33.6 (dd, $J_{P,C}$ = 37.8 Hz, $J_{P,C}$ = 2.4 Hz, CH$_2$), 35.8 (d, $J_{P,C}$ = 42.3 Hz, CH$_2$), 45.6 (*C*Me$_3$), 212.5 (d, $^2J_{P,C}$ = 10.4 Hz, *t*Bu*C*O)	100.4, 133.2

[a] br. = Signal broadened due to a dynamic process. − [b] pt, $^2J(P^1,C) + {}^2J(P^2,C)$ = 35.8 Hz. − [c] pt, $^2J(P^1,C) + {}^2J(P^2,C)$ = 11.0 Hz. − [d] pt, $^2J(P^1,C) + {}^2J(P^2,C)$ = 10.0 Hz. − [e] Broadened signals, half-line width ca. 55 Hz, P,P coupling not resolved.

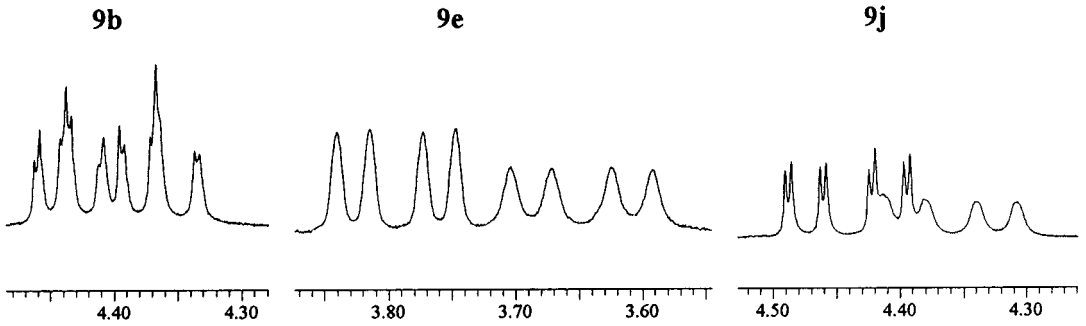
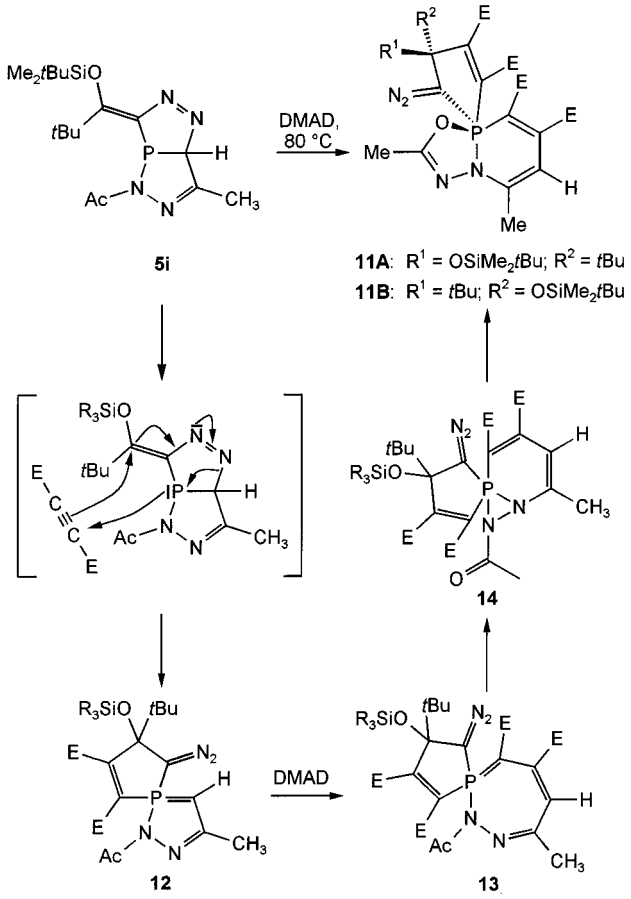


Figure 3. ^{1}H-NMR signals of protons 3a-H and 3b-H in **9b**,**e**,**j** (500 MHz, $CDCl_3$, δ values); signals of **9i** resemble corresponding ones of **9e**

Reaction of 5i with DMAD

According to the mechanism proposed in Scheme 3, short-lived 3-alkenylidene-1,2,3(λ^5)-diazaphospholes **8** can be trapped by an intermolecular [$3_{4\pi}+2_{2\pi}$] cycloadddition of their bis(methylene)phosphorane functionality to the P=C bond of diazaphospholes **4**. Therefore, we expected that electron-deficient 2π components other than **4** would also be suited to be cycloaddition partners. However, various experiments in which cycloadducts **5** were heated in the presence of activated alkenes or alkynes (ethyl propynoate, maleic anhydride, diethyl fumarate, norbornadiene) were unsuccessful, since either the usual thermolysis products **9** were formed or mostly unspecific decomposition (as indicated by many small and/or by broad ^{31}P-NMR signals) was observed. On the other hand, heating of **5i** in dimethyl acetylenedicarboxylate (DMAD) as solvent provided after chromatographic workup a small quantity of a yellow oil, which was a mixture of two diastereomers according to the NMR spectra (two very similar sets of signals). The major component could be crystallized and was identified as the spiro-λ^5-phosphorane **11A** by crystallographic structure determination (Scheme 5 and Figure 4). Obviously, this compound represents a 2:1 adduct from DMAD and **5i**, and no loss of N_2 from the latter has occurred. Although the combined yield of the two diastereomers of **11** was only 5%, they were the only major phosphorus-containing products in the reaction mixture according to the ^{31}P-NMR spectrum which also showed a multitude of minor signals in the range δ = 0−40 besides a broad bump in the baseline over the same δ range. Interestingly, the ^{31}P signal of the "normal" thermolysis product **9i** was not found in the crude product mixture. NMR control indicated the same result for the reaction of **5j** with DMAD, but because of the low yield of **11**, 5-Ph instead of 5-Me, no effort was made to isolate this product.

For the unexpected formation of phosphorane **11**, we propose a reaction cascade which starts by a cycloaddition reaction of DMAD with the 3-alkylidene-1,2,4-diazaphospholine moiety of **4i**, whereby the 5-diazo-4,5-dihydrophosphole ring incorporated in the final product is already formed (**12**). The subsequent 5→7 ring expansion (**12** → **13**) is reminescent of the insertion of DMAD into the P=C bond of simple (acylmethylene)phosphoranes.[15] The electrocyclic valence isomerization of diazaphosphepine **13** has its parallel in the azepine-to-azanorcaradiene valence equilibrium[16] and generates phosphorane **14**, which is transformed into **11** by a ring expansion of the 2-acetyldiazaphosphiridine moiety.



Scheme 5. DMAD = MeOOCC≡CCOOMe; E = COOMe

Characteristic spectroscopic features of **11** are the diazo stretching vibration in the IR spectrum [$\tilde{\nu}(CN_2)$ = 2076 cm^{-1}] and the ^{31}P-NMR signal at δ = −45.2, which falls in the general range of phosphoranes.[14] The crystal-structure determination (Figure 4) reveals a slightly distorted trig-

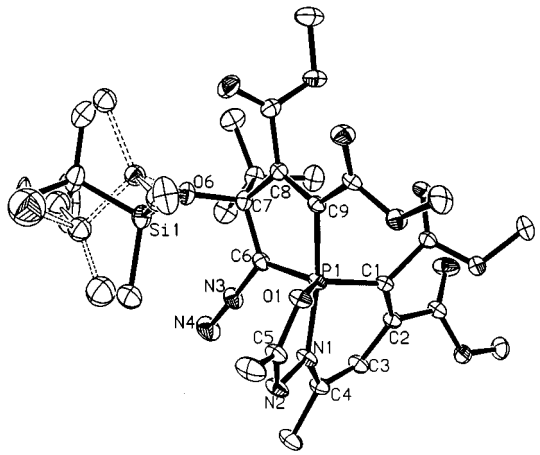


Figure 4. Structure of **11A** in the solid state (ORTEP plot); ellipsoids of thermal vibration are shown at the 20% probability level; the structure shows disorder for the $OSiMe_2tBu$ group; the second group site is indicated by dashed bonds; selected bond lengths [Å] and bond angles [°]: P1−O1 1.688(2), P1−C1 1.788(2), P1−C6 1.779(3), P1−C9 1.862(2), P1−N1 1.828(2), C6−N3 1.307(3), N3−N4 1.122(3); N1−P1−C9 167.22(9), O1−P1−C1 128.3(1), O1−P1−C6 116.5(1), C1−P1−C6 115.2(1), C6−N3−N4 177.9(3), C7−O6−Si1 132.9(2)

onal-pyramidal coordination around the phosphorus atom with the P−N bond and one of the P−C bonds of the dihydrophosphole ring in the axial positions and, as a consequence, with a facial (*e,a,e*) placement of the bicycle. The $N_{ax}-P-C_{ax}$ angle is 167.2°. The P−N bond is rather long (1.828 Å), but similar values have been found for axial P−N bonds in other tricyclic phosphoranes (e.g. ref.[17], where some factors influencing the length of axial P−O and P−N bonds are discussed).

Conclusion

The successful isolation of cycloadducts **5** demonstrates once more that the minor amounts of diazocumulenes **2** coexisting with diazo ketones **1** can be intercepted from the equilibrium by 1,3-dipolar cycloaddition reactions. The relative thermal stability of cycloadducts **5** is worth mentioning, since in related cases, i.e. with 1,2,3,4(λ^3)-triazaphospholes[18] as cycloaddition partners, extrusion of molecular nitrogen from the cycloadducts is faster than the cycloaddition itself. The formation of tricyclic phosphorus heterocycles **9** in the thermolysis of **5** suggests the intermediate formation of so far unreported 3-alkenylidene-1,2,3(λ^5)-diazaphospholes **8,** which represent the semicyclic analogues of methylene(vinylidene)phosphoranes postulated by us in a related study.[4]

Experimental Section

General Remarks: All reactions were carried out in rigorously dried glassware and under argon. Solvents were dried by standard procedures and kept under argon. The petroleum ether used had a boiling range of 30−60°C. − Column chromatography was performed under hydrostatic conditions (silica gel Si 60, Macherey−Nagel, 0.063−0.02 mm). − NMR: Bruker AMX 500 (^{1}H: 500.14 MHz; ^{13}C: 125.77 MHz; ^{31}P: 202.48 MHz) and Bruker AMX 400 (^{1}H: 400.1 MHz; ^{13}C: 100.61 MHz; ^{31}P: 161.98 MHz); $CDCl_3$ was used as solvent. The following references were applied: internal TMS for the proton spectra, the solvent signal for the ^{13}C-NMR spectra [$\delta(CDCl_3) = 77.0$], and external 85% H_3PO_4 for the ^{31}P spectra. − IR: Perkin−Elmer IR 1310 and IR 883 spectrometers. − MS: Varian MAT 711. − Microanalyses: Perkin−Elmer EA 240 and EA 2400. Melting points were determined in an apparatus according to Dr. Tottoli (Büchi) and are uncorrected. − The following compounds were prepared by literature methods: **1a**,**c**,[10] **1b**,[19] **4a**,[20] **4b**,**c**,[21] **4d**,[22] **4e**;[23] **4f**[24] was prepared by the route described in ref.[23]

Synthesis of 3-Alkylidene-5,7a-dihydro-3*H*-[1,2,4]diazaphospholo-[4,3-*c*][1,2,3]diazaphospholes 5. − General Procedure: A solution of equimolar amounts (2−15 mmol) of diazo ketone **1** and 2*H*-1,2,3-diazaphosphole **4** in dichloromethane (10−30 mL) was stirred at room temperature until **1** was consumed (4−17 h, IR control). The solvent was removed under reduced pressure. Cycloadducts **5d,h** were separated as colorless microcrystalline solids after addition of pentane and were isolated by filtration and washed with pentane. The other cycloadducts were obtained by crystallization from diethyl ether (**5a**−**c**,**e**−**g**,**j**,**k**) or pentane (**5i**,**l**) at −30°C.

5-Acetyl-3-[(*E*)-2,2-dimethyl-1-(triisopropylsilyloxy)propylidene]-7-methyl-5,7a-dihydro-3*H*-[1,2,4]diazaphospholo[4,3-*c*][1,2,3]diazaphosphole (5a): Prepared from **1a** and **4a**; yield: 70%; m.p. 79°C. − IR (KBr): $\tilde{\nu}$ = 1644, 1636, 1428, 1394 cm^{-1}. − ^{1}H NMR (400.1 MHz): δ = 0.89 and 0.91 (each d, $^3J_{H,H}$ = 7.4 Hz, 9 H, CHMe_2), 1.14 (sept, 3 H, CHMe$_2$), 1.49 (s, 9 H, CMe_3), 2.09 (s, 3 H, Me), 2.38 (s, 3 H, Me), 5.84 (d, $^2J_{P,H}$ = 50.8 Hz, 1 H, PCH). − $C_{20}H_{37}N_4O_2PSi$ (424.6): calcd. C 56.6, H 8.8, N 13.2; found C 56.7, H 8.8, N 13.2.

5-Acetyl-3-[(*E*)-2,2-dimethyl-1-(triisopropylsilyloxy)propylidene]-7-phenyl-5,7a-dihydro-3*H*-[1,2,4]diazaphospholo[4,3-*c*][1,2,3]-diazaphosphole (5b): Prepared from **1a** and **4b**; yield: 66%; m.p. 101°C. − IR (KBr): $\tilde{\nu}$ = 1670, 1376, 1288, 1262 cm^{-1}. − ^{1}H NMR (400.1 MHz): δ = 0.97 and 1.02 (each d, $^3J_{H,H}$ = 7.5 Hz, 9 H, CHMe_2), 1.25 (sept, 3 H, CHMe$_2$), 1.64 (s, 9 H, CMe_3), 2.32 (s, 3 H, Me), 6.44 (d, $^2J_{P,H}$ = 49.2 Hz, 1 H, PCH), 7.47−7.53 (m, 3 H, Ph), 8.24−8.26 (m, 2 H, Ph). − $C_{25}H_{39}N_4O_2PSi$ (486.7): calcd. C 61.7, H 8.1, N 11.5; found C 61.6, H 8.0, N 11.7.

5-Acetyl-3-[(*E*)-2,2-dimethyl-1-(triisopropylsilyloxy)propylidene]-7,8,9,10-tetrahydro-3*H*,5*H*-benzo[*d*][1,2,4]diazaphospholo[4,3-*c*]-[1,2,3]diazaphosphole (5c): Prepared from **1a** and **4c**; yield: 51%; m.p. 93°C. − IR (KBr): $\tilde{\nu}$ = 1666, 1540, 1464, 1382, 1301, 1216 cm^{-1}. − ^{1}H NMR (500.14 MHz): δ = 0.98 and 1.02 (each d, $^3J_{H,H}$ = 7.5 Hz, 9 H, CHMe_2), 1.25 (sept, 3 H, CHMe$_2$), 1.57 (d, $^5J_{P,H}$ = 0.9 Hz, 9 H, CMe_3), 1.68−2.77 [m, 8 H, $(CH_2)_4$], 2.21 (s, 3 H, MeCO). − $C_{23}H_{41}N_4O_2PSi$ (464.7): calcd. C 59.45, H 8.89, N 12.06; found C 59.43, H 8.86, N 12.00.

5-Benzoyl-3-[(*E*)-2,2-dimethyl-1-(triisopropylsilyloxy)propylidene]-7-methyl-5,7a-dihydro-3*H*-[1,2,4]diazaphospholo[4,3-*c*][1,2,3]-diazaphosphole (5d): Prepared from **1a** and **4d**; yield: 89%; m.p. 84°C. − IR (KBr): $\tilde{\nu}$ = 1636, 1543, 1392, 1355, 1304, 1218 cm^{-1}. − ^{1}H NMR (500.14 MHz): δ = 1.00 and 1.04 (each d, $^3J_{H,H}$ = 7.5 Hz, 9 H, CHMe_2), 1.27 (sept, 3 H, CHMe$_2$), 1.63 (s, 9 H, CMe_3), 2.48 (s, 3 H, Me), 5.90 (d, $^2J_{P,H}$ = 50.8 Hz, 1 H, PCH), 7.33−7.36 (m, 2 H, Ph), 7.39−7.42 (m, 1 H, Ph), 7.62−7.63 (m, 2 H, Ph). − $C_{25}H_{39}N_4O_2PSi$ (486.7): calcd. C 61.70, H 8.06, N 11.51; found C 61.43, H 8.17, N 11.38.

5-Acetyl-3-[(*E*)-1-(1-adamantyl)-1-(triisopropylsilyloxy)methylene]-7-methyl-5,7a-dihydro-3*H*-[1,2,4]diazaphospholo[4,3-*c*]-[1,2,3]diazaphosphole (5e): Prepared from **1b** and **4a**; yield: 52%; colorless crystals, m.p. 102°C. − IR (KBr): $\tilde{\nu}$ = 1668, 1542, 1286, 1258 cm^{-1}. − ^1H NMR (400.1 MHz): δ = 0.95 and 0.99 (each d, $^3J_{H,H}$ = 7.6 Hz, 9 H, CH*Me*$_2$), 1.21 (sept, 3 H, C*H*Me$_2$), 1.73−1.83 (m, 6 H, Ad), 2.12−2.15 (m, 6 H, Ad), 2.17 (s, 3 H, Me), 2.47−2.49 (m, 3 H, Ad), 2.45 (s, 3 H, Me), 5.85 (d, $^2J_{P,H}$ = 51.0 Hz, 1 H, PCH). − $C_{26}H_{43}N_4O_2PSi$ (502.7): calcd. C 62.12, H 8.62, N 11.14; found C 61.5, H 8.6, N 11.0.

5-Acetyl-3-[(*E*)-1-(1-adamantyl)-1-(triisopropylsilyloxy)methylene]-7-phenyl-5,7a-dihydro-3*H*-[1,2,4]diazaphospholo[4,3-*c*]-[1,2,3]diazaphosphole (5f): Prepared from **1b** and **4b**; yield: 67%; m.p. 120°C. − IR (KBr): $\tilde{\nu}$ = 1662, 1542, 1384, 1348 cm^{-1}. − ^1H NMR (400.1 MHz): δ = 0.97 and 1.02 (each d, $^3J_{H,H}$ = 7.4 Hz, 9 H, CH*Me*$_2$), 1.24 (sept, 3 H, C*H*Me$_2$), 1.79−1.88 (m, 6 H, Ad), 2.18−2.24 (m, 6 H, Ad), 2.32 (s, 3 H, Me), 2.54−2.57 (m, 3 H, Ad), 6.41 (d, $^2J_{P,H}$ = 49.4 Hz, 1 H, PCH), 7.47−7.53 (m, 3 H, Ph), 8.24−8.26 (m, 2 H, Ph). − $C_{31}H_{45}N_4O_2PSi$ (564.8): calcd. C 65.93, H 8.03, N 9.92; found C 65.5, H 8.0, N 9.9.

5-Acetyl-3-[(*E*)-1-(1-adamantyl)-1-(triisopropylsilyloxy)methylene]-7,8,9,10-tetrahydro-3*H*,5*H*-benzo[*d*][1,2,4]diazaphospholo[4,3-*c*][1,2,3]diazaphosphole (5g): Prepared from **1b** and **4c**; yield: 73%; m.p. 105°C. − IR (KBr): $\tilde{\nu}$ = 1656, 1546, 1462, 1393, 1281 cm^{-1}. − ^1H NMR (500.14 MHz): δ = 0.98 and 1.03 (each d, $^3J_{H,H}$ = 7.5 Hz, 9 H, CH*Me*$_2$), 1.24 (sept, 3 H, C*H*Me$_2$), 1.71−2.78 [m, 8 H, $(CH_2)_4$], 1.75−1.85 (m, 6 H, Ad), 2.14−2.16 (m, 6 H, Ad), 2.21 (s, 3 H, MeCO), 2.48−2.50 (m, 3 H, Ad). − $C_{29}H_{47}N_4O_2PSi$ (542.5): calcd. C 64.17, H 8.73, N 10.32; found C 63.41, H 8.66, N 10.22.

3-[(*E*)-1-(1-Adamantyl)-1-(triisopropylsilyloxy)methylene]-5-benzoyl-7-methyl-5,7a-dihydro-3*H*[1,2,4]diazaphospholo[4,3-*c*]-[1,2,3]diazaphosphole (5h): Prepared from **1b** and **4d**; yield: 86%; m.p. 92°C. − IR (KBr): $\tilde{\nu}$ = 1634, 1542, 1358, 1285 cm^{-1}. − ^1H NMR (500.14 MHz): δ = 1.01 and 1.05 (each d, $^3J_{H,H}$ = 7.5 Hz, 9 H, CH*Me*$_2$), 1.27 (sept, 3 H, C*H*Me$_2$), 1.78 (m, 3 H, Ad), 1.87 (m, 3 H, Ad), 2.16 (broadened s, 3 H, Ad), 2.22 (m, 3 H, Ad), 2.44 (s, 3 H, Me), 2.56 (m, 3 H, Ad), 5.85 (d, $^2J_{P,H}$ = 50.7 Hz, 1 H, PCH), 7.30−7.33 (m, 2 H, Ph), 7.36−7.39 (m, 1 H, Ph), 7.59−7.61 (m, 2 H, Ph). − $C_{31}H_{45}N_4O_2PSi$ (564.8): calcd. C 65.93, H 8.03, N 9.92; found C 65.83, H 7.89, N 9.89.

5-Acetyl-3-[(*E*)-1-(*tert*-butyldimethylsilyloxy)-2,2-dimethylpropylidene]-7-methyl-5,7a-dihydro-3*H*-[1,2,4]diazaphospholo-[4,3-*c*][1,2,3]diazaphosphole (5i): Prepared from **1c** and **4a**; yield: 75%; m.p. 82°C. − IR (KBr): $\tilde{\nu}$ = 1660, 1480, 1427, 1392, 1370, 1341 cm^{-1}. − ^1H NMR (500.14 MHz): δ = 0.08 (s, 3 H, SiMe), 0.33 (s, 3 H, SiMe), 0.99 (s, 9 H, SiCMe$_3$), 1.57 (d, $^5J_{P,H}$ = 1.4 Hz, 9 H, CCMe$_3$), 2.24 (s, 3 H, MeCO), 2.48 (d, $^4J_{P,H}$ = 0.4 Hz, 3 H, Me), 5.92 (d, $^2J_{P,H}$ = 51.0 Hz, 1 H, PCH). − $C_{17}H_{31}N_4O_2PSi$ (382.5): a correct elemental analysis could not be obtained, although the NMR spectra did not indicate significant amounts of an impurity.

5-Acetyl-3-[(*E*)-1-(*tert*-butyldimethylsilyloxy)-2,2-dimethylpropylidene]-7-phenyl-5,7a-dihydro-3*H*-[1,2,4]diazaphospholo-[4,3-*c*][1,2,3]diazaphosphole (5j): Prepared from **1c** and **4b**; yield: 66%; m.p. 172°C (dec.) − IR (KBr): $\tilde{\nu}$ = 1670, 1425, 1375, 1351 cm^{-1}. − ^1H NMR (400.1 MHz): δ = −0.02 (s, 3 H, SiMe), 0.27 (s, 3 H, SiMe), 0.92 (s, 9 H, SiCMe$_3$), 2.28 (s, 3 H, Me), 6.36 (d, $^2J_{P,H}$ = 49.5 Hz, 1 H, PCH), 7.47−7.53 (m, 3 H, Ph), 8.24−8.26 (m, 2 H, Ph). − $C_{22}H_{23}N_4O_2PSi$ (444.6): calcd. C 59.44, H 7.48, N 12.60; found C 59.1, H 7.3, N 12.6.

5-Acetyl-3-[(*E*)-1-(*tert*-butyldimethylsilyloxy)-2,2-dimethylpropylidene]-7,8,9,10-tetrahydro-3*H*,5*H*-benzo[*d*][1,2,4]diazaphospholo[4,3-*c*][1,2,3]diazaphosphole (5k): Prepared from **1c** and **4c**; yield 80%; m.p. 98°C. − IR (KBr): $\tilde{\nu}$ = 1663, 1551, 1387, 1290, 1254, 1204 cm^{-1}. − ^1H NMR (500.14 MHz): δ = 0.06 (s, 3 H, SiMe), 0.35 (s, 3 H, SiMe), 0.99 (s, 9 H, SiCMe$_3$), 1.54 (d, $^5J_{P,H}$ = 1.3 Hz, 9 H, CCMe$_3$), 1.70−2.78 [m, 8 H, $(CH_2)_4$], 2.25 (d, $^4J_{P,H}$ = 0.6 Hz, 3 H, MeCO). − $C_{20}H_{35}N_4O_2PSi$ (422.6): calcd. C 56.85, H 8.35, N 13.26; found C 56.87, H 8.32, N 13.33.

5-Benzoyl-3-[(*E*)-1-(*tert*-butyldimethylsilyloxy)-2,2-dimethylpropylidene]-7-methyl-5,7a-dihydro-3*H*-[1,2,4]diazaphospholo-[4,3-*c*][1,2,3]diazaphosphole (5l): Prepared from **1c** and **4d**; yield: 74%; light-yellow crystals, m.p. 83°C. − IR (KBr): $\tilde{\nu}$ = 1640, 1549, 1465, 1448, 1391, 1354, 1292, 1259 cm^{-1}. − ^1H NMR (500.14 MHz): δ = 0.10 (s, 3 H, SiMe), 0.38 (s, 3 H, SiMe), 1.00 (s, 9 H, SiCMe$_3$), 1.62 (d, $^5J_{P,H}$ = 1.2 Hz, 9 H, CCMe$_3$), 2.49 (s, 3 H, Me), 5.91 (d, $^2J_{P,H}$ = 50.7 Hz, 1 H, PCH), 7.35−7.42 (m, 3 H, Ph), 7.70−7.72 (m, 2 H, Ph). − $C_{22}H_{33}N_4O_2PSi$ (444.6): calcd. C 59.44, H 7.48, N 12.60; found C 58.43, H 7.41, N 12.37.

[1,2,3]Diazaphospholo[3′,4′:3,4][1,3]diphospholo[1,5-*c*][1,2,3]-diazaphospholes 9. − General Procedure: A solution of cycloadducts **5** (ca. 0.8−3.0 mmol) in dichloromethane (10 mL) was placed in a thick-walled Schlenk tube and heated at 80°C for 2 h (**5e**: benzene, 100°C, 3 h). For the isolation of **9b**, the solvent was evaporated, and the residue was triturated with pentane to afford a microcrystalline product, which was separated by centrifugation and washed with several portions of pentane. For the isolation of **9e**,**i**,**j**,**k** the solvent was evaporated, the residue was separated by column chromatography [silica gel (30 g), elution with diethyl ether], and the product was washed with pentane. Since recrystallization proved difficult due to the low tendency of these products to crystallize, complete purification was not always possible which may explain some unsatisfactory elemental analyses (especially the C values).

***cis,anti,cis*-1,6-Diacetyl-8-[2,2-dimethyl-1-(triisopropylsilyloxy)-propylidene]-3,4-diphenyl-1,3a,3b,6-tetrahydro[1,2,3]diaza-phospholo[3′,4′:3,4][1,3]diphospholo[1,5-*c*][1,2,3]diazaphosphole (9b):** Thermolysis of **5b** (0.41 g, 0.84 mmol) gave 0.075 g (27%) of colorless **9b**, m.p. 224°C. − IR (KBr): $\tilde{\nu}$ = 1677, 1669, 1373, 1346, 1274 cm^{-1}. − ^1H NMR (500.14 MHz): δ = 1.17 and 1.20 (each d, $^3J_{H,H}$ = 7.5 Hz, 9 H, CH*Me*$_2$), 1.41 (d, $^5J_{P,H}$ = 1.0 Hz, 9 H, CMe$_3$), 1.49 (sept, $^3J_{H,H}$ = 7.5 Hz, 3 H, C*H*Me$_2$), 2.23 and 2.28 (each s, 3 H, MeCO), 4.39 (ddd, $^2J_{P,H}$ = 37.5 Hz, $^3J_{P,H}$ = 15.0 Hz, $^3J_{H,H}$ = 2.1 Hz, 1 H, PCH),), 4.42 (ddd, $^2J_{P,H}$ = 33.3 Hz, $^3J_{P,H}$ = 12.4 Hz, $^3J_{H,H}$ = 2.1 Hz, 1 H, PCH), 7.49−7.53 (m, 6 H, Ph), 7.60−7.62 (m, 2 H, Ph), 7.68−7.70 (m, 2 H, Ph). − MS (EI, 70 eV); *m*/*z* (%) = 662 (50) [M^+], 619 (100) [M^+ − Ac], 605 (67), 506 (2), 458 (18), 416 (6). − $C_{35}H_{48}N_4O_3P_2Si$ (662.8): calcd. C 63.42, H 7.30, N 8.45; found C 62.73, H 7.11, N 8.50.

***cis,anti,cis*-1,6-Diacetyl-8-[(1-adamantyl)-1-(triisopropylsilyl-oxy)methylene]-3,4-dimethyl-1,3a,3b,6-tetrahydro[1,2,3]diazaphospholo[3′,4′:3,4][1,3]diphospholo[1,5-*c*][1,2,3]diazaphosphole (9e):** Thermolysis of **5e** (1.54 g, 3.07 mmol) gave 0.16 g (17%) of colorless **9e**, m.p. 152°C. − IR (KBr): $\tilde{\nu}$ = 1665, 1482, 1388, 1364, 1337, 1244 cm^{-1}. − ^1H NMR (500.14 MHz): δ = 1.14 and 1.18 (each d, $^3J_{H,H}$ = 7.5 Hz, 9 H, CH*Me*$_2$), 1.45 (sept, $^3J_{H,H}$ = 7.5 Hz, 3 H, C*H*Me$_2$), 1.64−1.79 (m, 6 H, Ad), 2.04 (s, br., 6 H, Ad), 2.09 (s, 3 H, CH_3), 2.14 (s, 3 H, Me), 2.21 (s, 6 H, 2 × MeCO), 2.24 (s, br., 3 H, Ad), 3.66 (dd, $^2J_{P,H}$ = 39.9 Hz, $^3J_{P,H}$ = 16.2 Hz, PCH), 3.80 (dd, $^2J_{P,H}$ = 33.5 Hz, $^3J_{P,H}$ = 13.0 Hz, PCH). − $C_{31}H_{50}N_4O_3P_2Si$ (616.80): calcd. C 60.37, H 8.17, N 9.08; found C 59.82, H 8.08, N 9.07.

***cis,anti,cis*-1,6-Diacetyl-8-[1-(*tert*-butyldimethylsilyloxy)-2,2-dimethylpropylidene]-3,4-dimethyl-1,3a,3b,6-tetrahydro[1,2,3]diazaphospholo[3′,4′:3,4][1,3]diphospholo[1,5-*c*][1,2,3]diazaphosphole (9i):** Thermolysis of **5i** (0.77 g, 2.01 mmol) afforded 0.17 g (34%) of **9i** as an off-white microcrystalline solid, m.p. 167°C. − IR (KBr): $\tilde{\nu}$ = 1677, 1656, 1496, 1391, 1366, 1339, 1248, 1172 cm^{-1}. − ^1H NMR (500.14 MHz): δ = 0.20 (s, 3 H, SiMe), 0.40 (d, $^6J_{P,H}$ = 3.6 Hz, 3 H, SiMe), 1.02 (s, 9 H, $SiCMe_3$), 1.30 (s, 9 H, $CCMe_3$), 2.12 (s, 3 H, Me), 2.14 (s, 3 H, Me), 2.22 (s, 3 H, MeCO), 2.23 (s, 3 H, MeCO), 3.66 (dd, $^2J_{P,H}$ = 38.3 Hz, $^3J_{P,H}$ = 16.3 Hz, PCH), 3.81 (dd, $^2J_{P,H}$ = 34.0 Hz, $^3J_{P,H}$ = 14.3 Hz, PCH). − $C_{22}H_{38}N_4O_3P_2Si$ (496.6): calcd. C 53.21, H 7.71, N 11.28; found C 52.62, H 7.62, N 10.97.

***cis,anti,cis*-1,6-Diacetyl-8-[1-(*tert*-butyldimethylsilyloxy)-2,2-dimethylpropylidene]-3,4-diphenyl-1,3a,3b,6-tetrahydro[1,2,3]diazaphospholo[3′,4′:3,4][1,3]diphospholo[1,5-*c*][1,2,3]diazaphosphole (9j):** Thermolysis of **5j** (0.49 g, 1.10 mmol) afforded 0.17 g (50%) of nearly colorless **9j**, m.p. 195°C. − IR (KBr): $\tilde{\nu}$ = 1672, 1591, 1373, 1346, 1274 cm^{-1}. − ^1H NMR (500.14 MHz): δ = 0.26 (s, 3 H, SiMe), 0.44 (d, $^6J_{P,H}$ = 3.7 Hz, 3 H, SiMe), 1.05 (s, 9 H, $SiCMe_3$), 1.36 (d, $^5J_{P,H}$ = 1.1 Hz, 9 H, $CCMe_3$), 2.26 (d, $^4J_{P,H}$ = 0.5 Hz, 3 H, MeCO), 2.27 (s, br., 3 H, MeCO), 4.36 (dd, br., $^2J_{P,H}$ = 36.5 Hz, $^3J_{P,H}$ = 16.5 Hz, PCH), 4.44 (ddd, $^2J_{P,H}$ = 33.1 Hz, $^3J_{P,H}$ = 13.7 Hz, $^3J_{H,H}$ = 2.4 Hz, PCH), 7.48−7.55 (m, 6 H, Ph), 7.65−7.70 (m, 4 H, Ph). − HR MS; $C_{32}H_{42}N_4O_3P_2Si$: calcd. 620.2501; found 620.2502.

(*rel*-7*S*,9*S*,15a*S*,15b*S*)-6,10-Diacetyl-8-[1-(*tert*-butyldimethylsilyloxy)-2,2-dimethylpropylidene]-2,3,4,6,12,13,14,15-octahydro-1*H*,10*H*-benzo[*d*]benzo[4′,5′][1,2,3]diazaphospholo[3′,4′:3,4][1,3]diphospholo[1,5-*c*][1,2,3]diazaphosphole (9k): Thermolysis of **5k** (0.63 g, 1.15 mmol) and recrystallization from ether after chromatographic workup afforded colorless **9k** (0.10 g, 31%), m.p. 148°C. − IR (KBr): $\tilde{\nu}$ = 1681, 1671, 1588, 1527, 1375, 1324 cm^{-1}. − ^1H NMR (500.14 MHz): δ = 0.13 (s, 3 H, SiMe), 0.45 (d, $^6J_{P,H}$ = 4.0 Hz, 3 H, SiMe), 1.00 (s, 9 H, $SiCMe_3$), 1.28 (s, 9 H, $CCMe_3$), 1.71−1.95 (m, 8 H, cyclohexyl), 2.20−2.25 (m, 2 H, CH_2), 2.22 (s, 3 H, MeCO), 2.25 (s, 3 H, MeCO), 2.49−2.54 (m, 2 H, CH_2), 2.64−2.73 (m, 4 H, CH_2). − $C_{28}H_{46}N_4O_3P_2Si$ (576.7): calcd. C 58.31, H 8.04; N 9.71; found C 57.46, H 7.96, N 9.53.

1-(6,10-Diacetyl-2,3,4,6,12,13,14,15-octahydro-1*H*,10*H*-benzo[*d*]-benzo[4′,5′][1,2,3]diazaphospholo[3′,4′:3,4][1,3]diphospholo[1,5-*c*]-[1,2,3]diazaphosphol-8-yl)-2,2-dimethyl-1-propanone (10): When **9k** was stored at 8°C for about 2 years, the sample consisted of **9k** and **10** in about equal amounts (NMR). Recrystallization from CH_2Cl_2 at −30°C provided colorless rhombohedric crystals of **10**, m.p. 143°C. − IR (KBr): $\tilde{\nu}$ = 1670, 1527, 1376, 132, 1138 cm^{-1}. − ^1H NMR ($CDCl_3$, 500.14 MHz): δ = 1.15 (s, 9 H, $CCMe_3$), 1.55−1.73 (m, 6 H, cyclohexyl), 1.84−1.89 (m, 1 H, CH-cyclohexyl), 2.02−2.13 (m, 3 H, cyclohexyl), 2.30 (d, $^4J_{P,H}$ = 1.1 Hz, 3 H, MeCO), 2.32 (s, 3 H, MeCO), 2.49−2.54 (m, 2 H, CH_2), 2.64−2.73 (m, 4 H, CH_2-cyclohexyl), 4.78 (d, $^2J_{P,H}$ = 24.9 Hz, 1 H, 8-H).

Tetramethyl *cis*-(1′-*TBPY*-5−24)-4′-*tert*-Butyl-4′-(*tert*-butyldimethylsilyloxy)-5′-diazo-2,5-dimethyl-4′,5′-dihydro-1′λ^5-spiro[[1,3,4,2]-oxadiazaphospholo-[3,2-*a*][1,2]azaphosphinine-9,1′-phosphole]-2′,3′,7,8-tetracarboxylate (11): A mixture of **5i** (1.73 g, 4.5 mmol) and dimethyl acetylenedicarboxylate (6.40 g, 45.1 mmol) was kept in a thick-walled Schlenk tube at 100°C for 1 h. Excess alkyne was distilled off (80°C/0.01 mbar), and the residue was subjected to column chromatography [silica gel (150 g), elution with ether.petroleum ether (2:1)] to afford a diastereomeric mixture of **11** (0.16 g, 5%) as a yellow oil. The major isomer **11A** was obtained by crystallization from diethyl ether at −30°C after 3 months; yellow crystals, m.p. 136°C. − IR (KBr): $\tilde{\nu}$ = 2076, 1732, 1449, 1432, 1412, 1251, 1133, 1062 cm^{-1}. − ^{31}P NMR: δ = −45.2. − ^1H NMR (500.14 MHz): δ = 0.07 (s, 3 H, SiMe), 0.20 (s, 3 H, SiMe), 0.93 (s, 9 H, $SiCMe_3$), 0.98 (s, 9 H, $CCMe_3$), 2.11 (d, $^4J_{P,H}$ = 1.0 Hz, 3 H, MeC=N), 2.25 (s, 3 H, MeC=C), 3.63, 3.75, 3.76, 3.78 (4 × s, each 3 H, COOMe), 5.76 (s, br., 1 H, C=CH). − ^{13}C NMR (125.77 MHz): δ = −3.9 (SiMe), −3.1 (SiMe), 15.3 (d, $^3J_{P,C}$ = 3.8 Hz, *Me*C=C), 18.73 ($SiCMe_3$), 19.3 (Me*C*=N), 25.9 ($CCMe_3$), 26.1 ($SiCMe_3$), 44.8 (d, $^3J_{P,C}$ = 5.2 Hz, $CCMe_3$), 51.9, 52.1, 52.2, 52.8 (4 COO*Me*), 52.3 (d, $^1J_{P,C}$ = 157.8 Hz, C=N_2), 84.9 (d, $^2J_{P,C}$ = 24.3 Hz, COSi), 99.3 (d, $^1J_{P,C}$ = 147.8 Hz, P*C*=C, 6-ring), 100.1 (d, $^3J_{P,C}$ = 9.1 Hz, C=*C*H), 143.1 (d, $^1J_{P,C}$ = 95.9 Hz, P*C*=C, 5-ring), 144.8 (d, $^2J_{P,C}$ = 6.2 Hz, C=C), 145.1 (d, $^2J_{P,C}$ = 18.6 Hz, C=C), 149.0 (d, $^2J_{P,C}$ = 2.9 Hz, Me*C*=N), 154.2 (Me*C*=C), 164.6 (d, $^3J_{P,C}$ = 8.1 Hz, C=O), 166.8 (d, $J_{P,C}$ = 18.6 Hz, C=O), 167.6 (d, $J_{P,C}$ = 19.1 Hz, C=O), 167.8 (d, $J_{P,C}$ = 18.1 Hz, C=O). − MS (EI, 70 eV); *m*/*z* (%) = 666 (4) [M^+], 635 (9) [M^+ − OCH_3], 609 (100) [M^+ − *t*Bu], 387 (10), 331 (8). − $C_{29}H_{43}N_4O_{10}PSi$ (666.7): calcd. C 52.24, H 6.50, N 8.40; found C 52.06, H 6.70, N 8.18. − Spectroscopic data of diastereomer **11B** (obtained from the mixture **11A/B**): ^{31}P NMR: δ = −48.8. − ^1H NMR (500.14 MHz): δ = 0.14 (s, 3 H, SiMe), 0.23 (s, 3 H, SiMe), 0.92 (s, 9 H, $SiCMe_3$), 0.97 (s, 9 H, $CCMe_3$), 2.21 (d, $^4J_{P,H}$ = 1.0 Hz, 3 H, MeC=N), 2.31 (s, 3 H, MeC=C), 3.60, 3.69, 3.74, 3.79 (4 s, each 3 H, COOMe) 5.47 (s, br., 1 H, C=CH). − ^{13}C NMR (125.77 MHz): δ = −4.5 (SiMe), −3.7 (SiMe), 15.4 (d, $^3J_{P,C}$ = 4.8 Hz, Me), 18.4 (*Me*C=C), 18.71 ($SiCMe_3$), 26.1 ($CCMe_3$ or $SiCMe_3$, 26.2 ($CCMe_3$ or $SiCMe_3$), 45.2 (br., $CCMe_3$), 52.02, 52.05, 52.3, 52.6 (4 COO*Me*), 84.5 (d, $^2J_{P,C}$ = 28.6 Hz, COSi), 96.2 (d, $^1J_{P,C}$ = 153.6 Hz, P*C*=C, 6-ring), 99.2 (d, $^3J_{P,C}$ = 8.6 Hz, C=*C*H), 143.7 (d, $J_{P,C}$ = 16.2 Hz), 145.4 (d, $J_{P,C}$ = 7.2 Hz), 145.7, 149.5 (d, $^2J_{P,C}$ = 3.8 Hz, Me*C*=N), 154.1 (Me*C*=C), 166.0 (d, $J_{P,C}$ = 8.6 Hz, C=O), 166.3 (d, $J_{P,C}$ = 17.7 Hz, C=O), 168.0 (s, C=O), 168.7 (d, $J_{P,C}$ = 24.3 Hz, C=O); signal for CN_2 hidden by other signals.

X-ray Crystallographic Study:[25] Single crystals were grown by conventional crystallization from an appropriate solvent. Data collection was carried out with a Stoe IPDS instrument. The structures were solved with direct methods and refined by a full-matrix least-squares method (G. M. Sheldrick, *SHELX-97*, University of Göttingen, **1997**). Molecule plots: *ORTEP-3 for Windows* (L. J. Farrugia, University of Glasgow, **1998**). The reflection data set obtained for **5c** indicated a triclinic lattice where most of the reflections with $l = 2n + 1$ were either very weak or absent, pointing to the presence of a second individual crystal. These reflections were eliminated from the data set and the length of the *c* axis was set to half of its original value. Due to the presence of an unusually high percentage of very weak reflections in the remaining data set, the refinement results are not very accurate. Crystals of **11A** were grown from diethyl ether and contained a substoichiometric amount of solvent molecules (ca. 0.5 equivalents according to ^1H NMR). In the crystal structure, the solvent molecule appears disordered around a crystallographic C_2 axis; this axis runs through the oxygen atom and (approximately) through the terminal carbon atoms. The displacement of the latter two atoms from the twofold axis could not be handled in the least-squares refinement, so that the average position on the twofold axis was refined. Furthermore, the $SiMe_2tBu$ group is disordered over two sites, with occupation factors fixed at 0.75 and 0.25. Several geometrical restraints were introduced for the two group sites, but the positions of the methyl groups on the minor site remained poorly determined. Crystallo-

Table 4. Details of the single-crystal X-ray structure analysis of compounds **5c**, **10**, and **11A**

	5c	**10**	**11A**
Empirical formula	$C_{23}H_{41}N_4O_2PSi$	$C_{22}H_{32}N_4O_3P_2$	$C_{29}H_{43}N_4O_{10}PSi \cdot 0.5\ (C_2H_5)_2O$
Formula mass [g/mol]	464.66	462.46	703.79
Temperature [K]	293(2)	293(2)	295(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal size [mm]	0.46 × 0.43 × 0.31	0.65 × 0.46 × 0.19	0.65 × 0.42 × 0.31
Crystal system	triclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	$P2_12_12$
a [Å]	17.327(3)	11.5986(9)	20.082(1)
b [Å]	19.173(4)	13.0028(14)	17.324(1)
c [Å]	10.251(2)	15.7816(12)	10.790(1)
α [°]	64.12(3)	90	90
β [°]	83.01(3)	95.74(1)	90
γ [°]	64.71(3)	90	90
Volume [Å^3]	2761.5(9)	2368.1(4)	3753.9(5)
Z	4	4	4
$D_{calcd.}$ [g·cm^{-3}]	1.118	1.297	1.245
μ(Mo-K_α) [cm^{-1}]	1.67	2.14	1.63
θ range [°]	2.21−22.50	2.03−26.03	2.22−25.98
Index ranges	$-18 \le h \le 18$ $-20 \le k \le 20$ $-11 \le l \le 11$	$-14 \le h \le 14$ $-15 \le k \le 15$ $-18 \le l \le 19$	$-24 \le h \le 24$ $-21 \le k \le 21$ $-13 \le l \le 13$
Collected reflections	16495	19826	29520
Independent reflections (R_{int})	6873 (0.225)	4590 (0.0463)	7290 (0.0484)
Completeness of data set (%)	95.2	98.4	99.1
Data/restraints/parameters	6873/0/579	4590/0/289	7290/14/478
Goodness-of-fit on F^2	0.575	0.902	0.911
Final R indices [$I > 2\sigma(I)$]; $R1$, $wR2$	0.0626, 0.1011	0.0407, 0.1049	0.0405, 0.0624[a]
R indices (all data); $R1$, $wR2$	0.2470, 0.1404	0.0601, 0.1125	0.0870, 0.0935[a]
Largest diff. peak and hole [e·Å^{-3}]	0.18, −0.18	0.35, −0.19	0.20, − 0.17

[a] The Flack parameter was −0.06(9), indicating the correct absolute structure.

graphic data and details of the refinement for the three structures are given in Table 4.

Acknowledgments

Financial support of this work by the Deutsche Forschungsgemeinschaft (Graduiertenkolleg: Phosphor als Bindeglied zwischen verschiedenen chemischen Disziplinen) and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Dr. R. Graf (University of Saarbrücken) for a HRMS spectrum.

[1] R. Munschauer, G. Maas, *Angew. Chem.* **1991**, *103*, 312−314; *Angew.Chem. Int. Ed. Engl.* **1991**, *30*, 306−308.
[2] R. Munschauer, G. Maas, *Chem. Ber.* **1992**, *125*, 1227−1234.
[3] B. Manz, G. Maas, *Tetrahedron* **1996**, *52*, 10053−10072.
[4] [4a] B. Manz, G. Maas, *J. Chem. Soc., Chem. Commun.* **1995**, 25−26. − [4b] B. Manz, U. Bergsträßer, J. Kerth, G. Maas, *Chem. Ber.* **1997**, *130*, 779−788.
[5] [5a] L. Nyulászi, T. Veszprémi, *J. Mol. Struct.* **1995**, *347*, 57−72. − [5b] L. Nyulászi, T. Veszprémi, J. Réffy, B. Burkhardt, M. Regitz, *J. Am. Chem. Soc.* **1992**, *114*, 9080−9084.
[6] A. Schmidpeter, K. Karaghiosoff in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**, pp. 258−286.
[7] A. Schmidpeter in *Comprehensive Heterocyclic Chemistry II* (Eds: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), vol. 4 (Ed.: R. C. Storr), Pergamon, Oxford, **1996**, chapter 4.22.
[8] B. A. Arbuzov, E. N Dianova, *Phosphorus Sulfur* **1986**, *26*, 203−251.
[9] B. A. Arbuzov, E. N. Dianova, R. T. Galiaskarova, A. Schmidpeter, *Chem. Ber.* **1987**, *120*, 597−599.
[10] R. Brückmann, G. Maas, *Chem. Ber.* **1987**, *120*, 635−641.
[11] B. A. Arbuzov, E. N. Dianova, S. M. Sharipova, *Izv. Akad. Nauk SSSR, Ser. Khim*. **1981**, 1113−1116; *Chem. Abstr.* **1981**, *95*, 97919d.
[12] [12a] B. A. Arbuzov, E. N. Dianova, L. Z. Galeeva, L. A. Litvinov, Y. T. Struchkov, A. N. Chernov, A. V. Ilyasov, *J. Gen. Chem. USSR* **1985**, *55*, 1−8. − [12b] B. A. Arbuzov, E. N. Dianova, E. Y. Zabotina, *J. Gen. Chem. USSR* **1985**, *55*, 1310−1312.
[13] I. A. Litvinov, Y. T. Struchkov, B. A. Arbuzov, E. N. Dianova, I. Z. Galeeva, *Izv. Akad. Nauk SSSR, Ser. Khim*. **1982**, 2718−2723; *Chem. Abstr.* **1983**, *98*, 160810r. − *cis,syn,cis* Isomer: I. A. Litvinov, Y. T. Struchkov, B. A. Arbuzov, E. N. Dianova, I. Z. Galeeva, *Izv. Akad. Nauk SSSR, Ser. Khim*. **1984**, 2023−2028; *Chem. Abstr.* **1985**, *102*, 78981q.
[14] S. Berger, S. Braun, H.-O. Kalinowski, *NMR-Spektroskopie von Nichtmetallen*, vol. 3 ("^{31}P-NMR-Spektroskopie"), Thieme, Stuttgart, **1993**.
[15] H. J. Bestmann, O. Rothe, *Angew. Chem.* **1964**, *76*, 569; *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 512. J. B. Hendrickson, C. Hall, R. Rees, J. F. Templeton, *J. Org. Chem.* **1965**, *30*, 3312−3316.
[16] L. A. Paquette, *Angew. Chem.* **1971**, *83*, 11−20; *Angew. Chem. Int. Ed. Engl.* **1971**, *10*, 11. H. Günther, J. B. Pawliczek, B. D. Tunggal, H. Prinzbach, R. H. Levin, *Chem. Ber.* **1973**, *106*, 984−995.
[17] W. S. Sheldrick, D. Schomburg, A. Schmidpeter, *Acta Crystallogr.* **1980**, *B36*, 2316−2323.
[18] J. Kerth, U. Werz, G. Maas, *Tetrahedron* **1999**, submitted.
[19] R. Brückmann, K. Schneider, G. Maas, *Tetrahedron* **1989**, *45*, 5517−5530.
[20] A. F. Vasil′ev, L. V. Vilkov, N. P. Ignatova, N. N. Mel′nikov, V. V. Negrebeckij, N. I. Svecov-Silovskij, L. S. Chajkin, *J. Prakt. Chem.* **1972**, *314*, 806−814.
[21] R. Chen, B. Cai, G. Li, *Synthesis* **1991**, 783−784.
[22] N. I. Svecov-Silovskij, N. P. Ignatova, R. G. Bobkova, V. Ya. Manyukhina, N. N. Mel′nikov, *J. Gen. Chem. USSR* **1972**, *42*, 1932−1934.

[23] J. H. Weinmaier, G. Brunnhuber, A. Schmidpeter, *Chem. Ber.* **1980**, *113*, 2278−2290.
[24] G. Märkl, C. Martin, *Tetrahedron Lett*. **1973**, *45*, 4503−4506.
[25] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-115861 (**4c**), -115862 (**10**), -116072 (**11A**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Received March 13, 1999
[O99167]