Pergamon

Tetrahedron, Vol. 52, No. 30, pp. 10053-10072, 1996

0040-4020/96 $15.00 + 0.00

PII: S0040-4020(96)00541-8

Synthesis of 5-Alkylidene-4,5-dihydro-3*H*-1,2,4(λ^3)-diazaphospholes from α-Silyl-α-diazoketones and Phosphaalkenes

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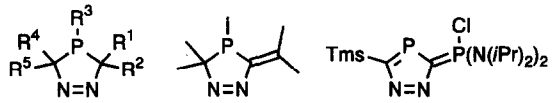
Abstract: 5-Alkylidene-4,5-dihydro-3*H*-1,2,4(λ^3)-diazaphospholes (**II**) arise from a [3+2] cycloaddition reaction between various, differently substituted phosphaalkenes and 2-siloxy-1-diazoalkenes that are present to a minor extent in a thermal equilibrium with α-silyl-α-diazoketones. The cycloaddition products **4a-g**,**6a**,**b**,**e**,**f**, and **8** are sufficiently thermally stable to be isolated. In other cases, silyl group migration (ring-C → N or O →N) leads to isomeric N-silyl-1,2,4-diazaphospholes.

Stable 4,5-dihydro-3*H*-1,2,4-diazaphospholes I were first reported in the year 1981.[1,2] Until now, the [3+2] cycloaddition of diazo compounds to P=C double bonds has constituted the sole access to these heterocycles. In contrast, the aromatic 1*H*-1,2,4-diazaphospholes are accessible by a wide array of methods.[3] While the aromatic ring system is well investigated, not much is known about 4,5-dihydro-3*H*-1,2,4-diazaphospholes. This is partly due to the fact, that many of these compounds are thermally rather unstable; quite often, they lose nitrogen already under the cycloaddition conditions at room temperature, and phosphiranes are isolated.[1b,4,6] Formation of a phosphaalkene by spontaneous loss of nitrogen and subsequent rearrangement (I, R^1 = H, R^2 = H, Me, COOR, R^3 = $SiMe_3$, R^4 = $OSiMe_3$, R^5 = *t*Bu)[5] and isomerization by 1,3-silyl migration (I, R^1 = R^2 = $SiMe_3$, R^3 = Cl)[6] can also occur. Furthermore, the interaction between diazo compounds and phosphaalkenes does not always lead to a 4,5-dihydro-3*H*-1,2,4-diazaphosphole as the primary product. Formation of bis(alkylidene)phosphoranes by Staudinger reaction[7] and of a 1,2,3-diazaphosphole[8,9] have also been reported.



When we started our investigations, 5-alkylidene-4,5-dihydro-3*H*-1,2,4(λ^3)-diazaphospholes II were unknown, except for a 2-isopropylidene-3,4-diaza-1-phosphabicyclo[3.1.0]hexane.[10] We expected, however, that heterocycles **II** would be accessible from phosphaalkenes and 1-diazoalkenes by a [3+2] cycloaddition reaction. Our expectation was based on the successful cycloaddition between phosphaalkenes and diazo compounds and on the formation of III from a diazomethylenephosphorane and bis(trimethylsilyl)-methylenechlorophosphine[11] (1,3-dipolar cycloaddition followed by elimination of Me_3SiCl. 1-Diazoalkenes are cumulenic diazo compounds which cannot be isolated in substance, but they can be generated in situ and trapped. A convenient entry to diazoalkene chemistry starts from silyl-diazoketones **1** that maintain a thermal

equilibrium with minor (< 1%) amounts of 2-silyloxy-1-diazoalkenes **2** via a 1,3-silyl migration[12] (Scheme 1), and we have shown that these diazoalkenes can be intercepted with dipolarophiles such as norbornene, norbornadiene, and electron-deficient alkenes.

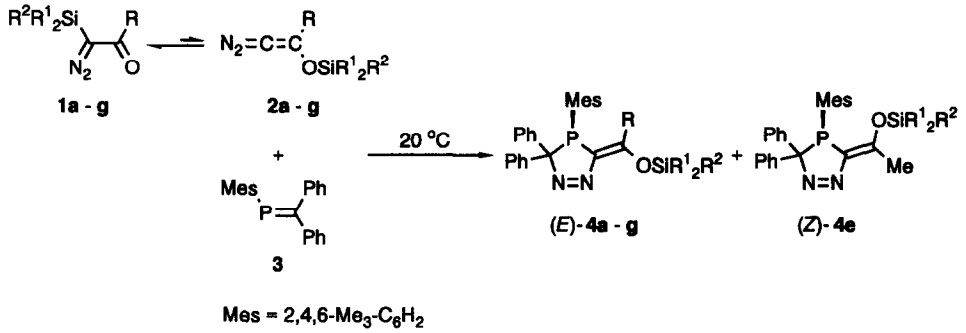
We report in this paper that the [3+2] cycloaddition of 2-silyloxy-1-diazoalkenes with phosphaalkenes offers indeed a practicable access to heterocycles II. Our interest in the last-mentioned compounds was given by the perspective to transform them, by nitrogen extrusion, into various other phosphaheterocycles, e. g. alkylidenephosphiranes.[13]

RESULTS

Diphenylmethylene(mesityl)phosphine (**3**), an all carbon substituted and by steric protection merely kinetically stabilized phosphaalkene, is electronically very close to the unsubstituted methylenephosphine.[14] The only known reaction of **3** with a diazo compound (diazodiphenylmethane, 80 °C, 24 h) yielded, unexpectedly, a 4,5-dihydro-3*H*-1,2,3-diazaphosphole rather than the 1,2,4-isomer.[8] In contrast, the interaction between phosphaalkene **3** and diazo compounds **1/2** at room temperature provides 5-alkylidene-3*H*-1,2,4-diazaphospholes **4** in good yields (Scheme 1 and Table 1). The reaction time depends on the substituent R of the diazo compound, whereby electron-donating substituents enhance the reaction rate. Thus, the reaction lasts 16 hours for generating **1/2f**, but 4 days for **1/2g**, and for alkyl substituents, the reaction becomes faster in the series methyl, 1-adamantyl, *tert*-butyl. This reactivity order is remarkable also because it reveals that the reaction becomes faster in spite of increasing steric bulk of substituent R. Obviously, the products represent the [3+2] cycloaddition products of the 2-siloxy-1-diazoalkenes **2**, and the dipole orientation is opposite to the case of diazodiphenylmethane. In principle, heterocycles **4** could also result from a reversed order of events, i.e. diazoketones **1** undergo the 1,3-dipolar cycloaddition, and silyl group migration is the final step. We recall here, however, that there is kinetic evidence that diazoalkenes **2** are the reacting species in cycloaddition reactions with electron-poor alkenes.[12]

In contrast to most of the known 4,5-dihydro-3*H*-1,2,4-diazaphospholes,[1b,4,6] the 5-alkylidene derivatives **4** are thermally rather stable. Compounds **4a-d, f** lose nitrogen at a significant rate only above ca. 100 °C, and solely **4g** decomposes slowly at room temperature. In the solid state, these compounds are inert towards oxygen and atmospheric moisture, but unspecific decomposition occurs in solution. The constitution of these heterocycles is established by their ^{31}P and ^{13}C NMR spectra (Table 1). The dihydro-1,2,4-diazaphosphole structure is indicated by the high-field[4b] ^{31}P chemical shifts; the signal of the 1,2,3-diazaphosphole derivatives would be expected at much lower field.[8] In the ^{13}C NMR spectrum, the low-field shifts of the olefinic carbon atoms are in good agreement with earlier observations on similar cycloadducts.[12,15] In the cases of **4a-d,f,g**, only one diastereomer is found. The large long-range $^4J_{(P,C)}$ coupling constants to the alkyl (J = 9.2 - 9.4 Hz) or aryl substituent (J = 7.4 - 7.7 Hz), as well as the splitting of the CMe_3 ^1H NMR signal in **4a,c,d** by $^5J_{(P,H)}$ coupling (0.3-0.5 Hz), point to a *cis*-relationship between the respective carbon atom and the lone electron pair at phosphorus,[16] and therefore, to the *E*-configuration of the exocyclic double bond. Again, this is in line with related cycloadducts,[12,15] and it is confirmed by an X-ray crystal structure analysis of **4a** (vide infra). Product **4e** is formed as a diastereomeric mixture (^1H NMR: *E*:*Z* = 56:44), but workup by repeated crystallization yielded only *E*-**4e** in analytically pure form and in low yield, while the *Z*-isomer was lost. In this case, the stereochemical assignment of the *E*-isomer is based on the observation of similar values of the ^{31}P chemical shift as compared with *E*-**4a-d**, and on the larger $^2J_{(P,C(O))}$ coupling constant and, by analogy with related cases

on the lower δ(=C(O)) value.[17] Due to the stereogenic center at the P atom, the methyl groups in the silyl substituent of **4a,b,d-g** are diastereotopic, and separate ^{1}H and ^{13}C NMR signals are observed indeed. For steric reasons, the mesityl ring adopts an orthogonal orientation with respect to the heterocycle, and its rotation around the P-C bond is hindered on the NMR time scale. This geometry causes a remarkably high $J_{(P,C)}$ coupling (36.7 - 37.6 Hz) for the *ortho*-methyl group which is oriented towards the lone pair at phosphorus, whereas the second *ortho*-methyl carbon atom does not couple.



Scheme 1

Table 1. 5-Alkylidene-4,5-dihydro-3*H*-1,2,4(λ^3)-diazophospholes **4** prepared from diazo compounds **1/2** and phosphaalkene **3**; yields and characteristic ^{31}P and ^{13}C NMR data.

1,2,4	R	$SiR^1{}_2R^2$	Yield	^{31}P NMR	^{13}C NMR (δ, ppm / $J_{(P,C)}$, Hz)		
			(%)	(δ, ppm)	C(Ph)$_2$	P-C=	=C-O
a	*t*Bu	Si(*i*Pr)$_3$	78	-55.0	105.0/27.3	139.6/36.1	176.9/25.4
b	1-Ad[a]	Si(*i*Pr)$_3$	77	-52.4	104.7/27.6	139.5/36.2	176.9/24.1
c	*t*Bu	SiPh$_2$*t*Bu	85	-54.5	104.9/27.8	139.6/38.5	174.5/24.2
d	*t*Bu	SiMe$_2$*t*Bu	74	-55.4	105.1/27.5	139.5/36.6	176.6/25.4
e	CH_3	Si(*i*Pr)$_3$	14[b]	-54.1[c]	104.5/28.2[c]	142.9/26.0[c]	162.6/32.4[c]
				-58.0[d]	104.7/29.1[d]		167.6/19.5[d]
f	4-MeO-C_6H_4	Si(*i*Pr)$_3$	79	-47.6	105.0/27.1	141.3/32.2	163.0/30.4
g	4-O_2N-C_6H_4	Si(*i*Pr)$_3$	79	-48.6	106.0/28.0	145.2/35.0	160.1/29.7

[a] 1-Ad = 1-Adamantyl. - [b] The low yield is a consequence of workup, by which *Z*-**4e** is lost; see text. - [c] Values for *E*-**4e**. - [d] Values for *Z*-**4e**.

The X-ray crystal structure analysis of *E*-**4a** (Figure 1) confirms the stereochemical assignments derived from NMR data and provides, as far as we know, the first structural data of a 4,5-dihydro-3*H*-1,2,4-diazaphosphole. The unit cell contains two symmetry-unrelated molecules, which differ slightly in the torsion angles involving ring atoms and substituents. The five-membered ring adopts a half-chair conformation. The bond lengths of the 1,2-azadiene moiety show small but significant deviations from the values expected for the isolated bonds, indicative of a conjugative interaction between the C=C and N=N bond. Steric interactions between the mesityl group and the neighboring substituents (phenyl and *tert*-butyl) are minimized by widening

of the bond angles at C1, C2, and C3, as well as by a small deviation of the P-C2 bond vector from the plane of the exocyclic double bond.

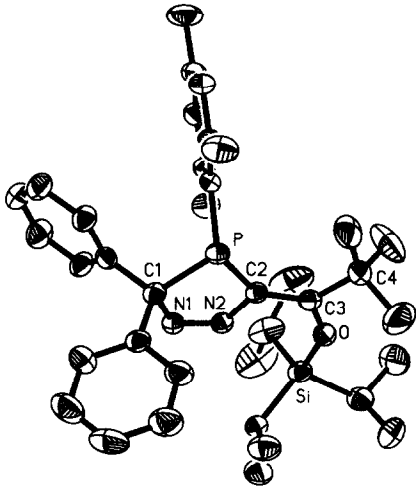


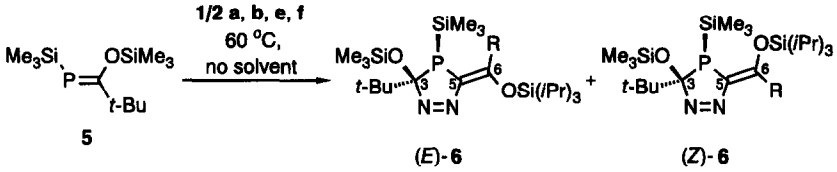
Figure 1. Solid-state structure of 5-alkylidene-4,5-dihydro-3*H*-1,2,4-diazaphosphole **4a**. Only one of the two symmetry-independent molecules in the unit cell is shown. Selected bond distances and angles (esd's are given in parentheses): Bond distances [Å]: P-C1 1.899(5), P-C2 1.829(5), C1-N1 1.514(5), N1-N2 1.251(5), N2-C2 1.413(6), C2-C3 1.356(6), C3-O 1.359(5). Bond angles [deg]: C1-P-C2 86.8(2), P-C2-C3 133.7(4), N2-C2-C3 114.0(4), P-C2-N2 112.0(3), C2-C3-C4 128.2(5), C2-C3-O 120.8(4), C3-O-Si 141.8(3). Torsion angles [deg]: P-C2-C3-C4 7.7(9), P-C2-C3-O 172.7(4), N2-C2-C3-O -0.6(7), N2-C2-C3-C4 178.9(5).

The successful cycloaddition of diazoalkenes **2** with phosphaalkene **3** induced us to use some representative heteroatom-substituted phosphaalkenes as dipolarophiles in order to explore the scope of this synthesis. As will be seen, regiospecific cycloaddition with formation of the 1,2,4-diazaphosphole skeleton takes place in all cases, and 1,2,3-diazaphosphole derivatives or products of a Staudinger reactions are never observed.

In terms of frontier-orbital theory, the smooth 1,3-dipolar cycloaddition reactions of **1/2** with phosphaalkene **3** as well as with electron-poor alkenes indicates a HOMO(dipole) - LUMO(dipolarophile) controlled reaction. The donor-substituted phosphaalkenes **5** and **7**, however, have a LUMO that is higher in energy than in **3**,[18] and therefore, they are expected to react less readily. Nevertheless, they do react with diazo compounds **1/2** at 60 °C to form the thermally stable (vide infra) but very moisture-sensitive 5-alkylidene-4,5-dihydro-3*H*-1,2,4-diazaphospholes **6** and **8**, respectively (Scheme 2). The thermal decomposition of the diazoalkenes **2** at the given reaction temperature[19] can be avoided by heating equimolar amounts of the two reactants in the absence of solvent. As in the case of cycloadducts **4**, only the *E*-configuration of the exocyclic double bond is observed for **6a,b**, **8**, where R is a bulky substituent, but **6e** and **6f** are formed as *E/Z* mixtures. In the latter two cases, the presence of the two stereoisomers renders purification by crystallization difficult (**6f**) if not impossible (**6e**).

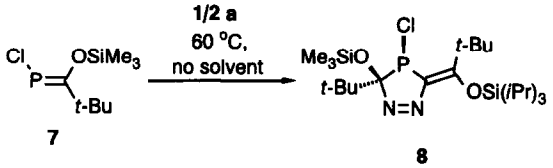
The ^{31}P NMR chemical shifts of heterocycles **6** (δ -104.6 - -96.7 ppm) are similar to the values found in other 4,5-dihydro-3*H*-1,2,4-diazaphospholes derived from the same phosphaalkene[5,20]; on the other hand, the ^{13}C chemical shifts and P,C coupling constants of the olefinic carbon atoms are in close agreement with the values given in Table 1. Replacement of the $SiMe_3$ substituent at phosphorus by chlorine leads to the expected low-field shift of the ^{31}P signal (**8**; δ = 47.0 ppm) and causes deshielding of the carbon atoms C-5 and C-6, but a slight shielding of C-3 with respect to heterocycles **6**. The *E*-configuration at the enol ether double bond is again suggested by large $^4J_{(P,C)}$ coupling constants; moreover, the *Z*-isomers display a high-field shift of the ^{31}P resonance and a low-field shift of both olefinic carbon atoms as compared to the *E*-isomers. The relative configuration at the stereogenic centers C-3 and P is also established by NMR data: The large P,C coupling

constant observed for the *tert*-butyl group at C-3 [$^2J_{(P,C)}$ = 27.2 - 28.2 Hz] indicates a *syn*-relationship between this substituent and the phosphorus lone pair. This implies that the original configuration of the phosphaalkenes **5** and **7** has been preserved in the cycloaddition product.



1/2, 6	R	Yield [%]	Ratio *E*
a	*t*-Bu	88	only *E*
b	1-adamantyl	85	only *E*
e	Me	[a]	5 : 1
f	4-MeO-C_6H_4	61[b]	10 : 1

[a] Not isolated in pure form. - [b] Yield of pure (*E*)-isomer.



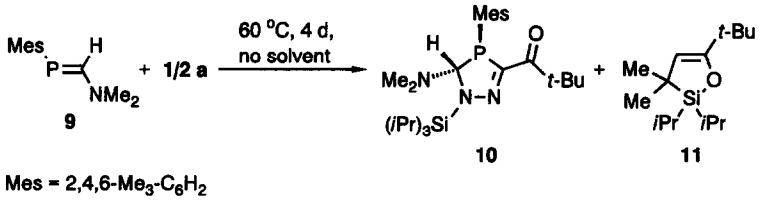
Scheme 2. 5-Alkylidene-4,5-dihydro-3*H*-1,2,4-diazaphospholes from phosphaalkenes **5**,**7** and the diazoketone / diazoalkene system **1/2**

The 1,2,4-diazaphosphole derivatives **6** and **8** are thermally even more stable than their relatives **4**. Thus, thermally induced reactions of **6**, with and without loss of N_2, require a temperature of 150 °C, and **8** is even stable up to 170 °C. The products of these reactions will be reported in a forthcoming publication.

The amino-substituted phosphaalkene **9** was a priori expected to be a critical case for a successful 1,3-dipolar cycloaddition, since it is even more electron-rich than phosphaalkenes **5** and **7**, which have already shown a lower reactivity than **3**. Furthermore, calculations on the model compound (*E*)-P=CH(NMe_2) suggested a strong polarization of the P=C bond, in line with an enamine-type conjugation.[14c] In fact, Carrié et al.[7] could not observe [3+2] cycloaddition between similar amino-substituted phosphaalkenes and diazomalonates or diazodiphenylmethane, but rather hydrazonophosphine derivatives that suggest a Staudinger reaction involving the phosphorus lone pair. This remarkable result is in conflict with calculations[14c, 18] that identify the $\pi_{(P=C)}$ and not the $\sigma_{(P)}$ orbital as the HOMO.

The reaction between equimolar amounts of **9** and **1/2a** at 60 °C proceeded indeed more slowly than in the case of phosphaalkenes **5** and **7**. It provided the cycloaddition product **10**, but also the (only NMR spectroscopically detected) oxasilacyclopentene derivative **11** which results from the partial thermal decomposition of **2a** under the reaction conditions.[19] We do not know whether **10** results from the [3+2] cycloaddition of dia-

zoketone **1a** to **9**, followed by a 1,3(C→N) silyl shift, or, as in the other cases described above, from the diazoalkene (**2a**) cycloaddition, followed by a 1,5(O→N) silyl shift. In the related case of 3-(siloxyalkylidene)-pyrazolines, we could show that the 1,5(O→N) silyl shift can indeed occur, probably as a bimolecular reaction.[12, 17] The low degree of substitution at the 5-position of the ring may permit migration of the bulky triisopropylsilyl group to the adjacent nitrogen atom, in contrast to the situation in the cycloadducts **4**, **6** and **8**, where the corresponding position is heavily substituted.



Mes = 2,4,6-Me_3-C_6H_2

Scheme 3

The structure of the 4,5-dihydro-1*H*-1,2,4-diazaphosphole **10** was established by a single-crystal X-ray diffraction analysis (Fig. 2), since the spectroscopic data did not allow an unequivocal assignment. Thus, the ^{31}P chemical shift (δ -52.2 ppm) is in the range of the value found for **4** (Table 1) and the ^{13}C NMR signal of C=N (δ 146.8 ppm) is observed at relatively high field. Furthermore, the C=O stretching vibration in the IR spectrum (ν 1630 cm^{-1}) has an unusually low intensity.

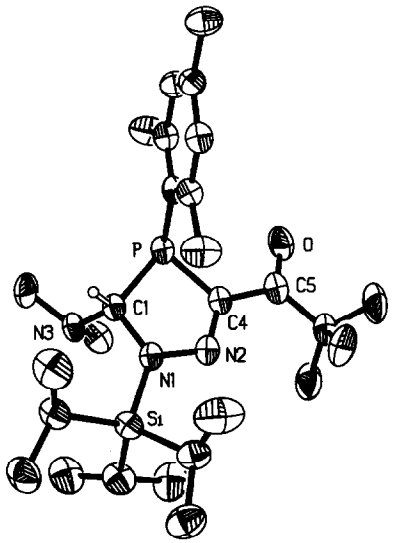
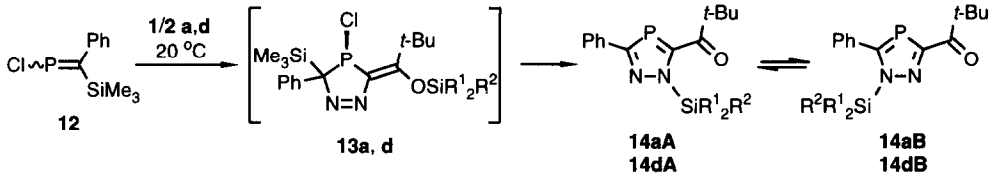


Figure 2. Solid-state structure of 4,5-dihydro-1*H*-1,2,4-diazaphosphole **10**. Selected bond distances and angles esd's are in parentheses): Bond distances [Å]: P-C1 1.893(4), P-C4 1.813(5), C1-N1 1.473(5), N1-N2 1.359(5), N2-C4 1.300(5), C4-C5 1.474(6), C5-O1 1.212(6). Bond angles [deg]: C1-P-C4 86.3(2), C1-P-C10 110.1(2), C4-P-C10 107.3(2), P-C4-C5 121.4(4); sum of angles at N1 359.6. Torsion angles [deg]: P-C4-C5-O 2.2(6), C1-N1-N2-C4 8.1(5).

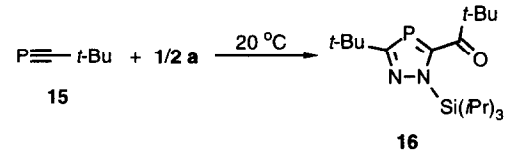
Chloro[bis(trimethylsilyl)methylene]phosphine and the related chloro(α-trimethylbenzylidene)-phosphine (**12**), as important building blocks in the chemistry of low-coordinate phosphorus compounds, have been employed as the 2π component in many [3+2] and [4+2] cycloaddition reactions; their reactivity towards diazo dipoles has been studied especially by the groups of Carrié[21], Märkl[4d, 22] and Regitz.[6,23] Reactions of **12**

with diazomethane or monosubstituted diazo compounds leads to 1*H*-1,2,4-diazaphospholes by cycloaddition and subsequent elimination of chlorotrimethylsilane.[22] With disubstituted diazo compounds (R_2CN_2, R = alkyl, aryl), 1-chlorophosphiranes are formed.[4d]

Reactions of our diazo compounds **1/2** with **12** at room temperature follow the first-mentioned pathway, since a mixture of the isomeric 1*H*-1,2,4-diazaphospholes **14A** and **14B** is obtained (Scheme 4). Monitoring of the reaction progress at 10 °C by ^{31}P NMR spectroscopy showed the transient appearance of a signal at δ 62.3 ppm which is assigned to the primarily formed cycloaddition product **13a**. A similar observation has been described.[6]



1/2, 13, 14	a	d
$SiR^1{}_2R^2$	$Si(iPr)_3$	$SiMe_2tBu$



Scheme 4

Table 2. Characteristic NMR data for 1*H*-1,2,4-diazaphospholes **14** and **16**

Com-pound	Ratio **A** : **B**[a]	Isomer	^{31}P NMR[b] (δ, ppm)	^{13}C NMR[b] (δ, ppm / $J_{(P,C)}$, Hz) C=O	C-C=O[c]	OCCMe$_3$	OCCMe$_3$
14a	74 : 26	**A**	110.9	201.4 / 20.2	172.4 / 59.4	44.1 / 2.7	29.1 / 9.6
		B	118.4	203.3 / 17.8	178.6 / 56.4	43.9	27.2
14d	42 : 58	**A**	104.5	203.2 / 18.2	175.2 / 60.5	44.2	28.1 / 8.5
		B	116.7	203.2 / 18.2	178.2 / 54.6	43.9	27.3
16			111.1	201.4 / 20.2	172.0 / 59.0	44.2 / 2.8	29.4 / 9.6

[a] In $CDCl_3$ solution at 293 K. - [b] In $CDCl_3$ (**14a,d**) or C_6D_6 (**16**). - [c] This signal is distinguished from the P-C-Ph signal,which has a similar δ value, by the triplet structure ($^3J_{(C,H)}$) of the latter.

In solution, a dynamic equilibrium exists between the positional isomers **14A** and **14B** which is detected by NMR spectroscopy. For example, temperature-dependent NMR spectra are observed for **14dA/14dB** above 318 K ([D_8]-toluene, 400.1 MHz) and the coalescence temperature is probably close to 368 K, the highest tem-

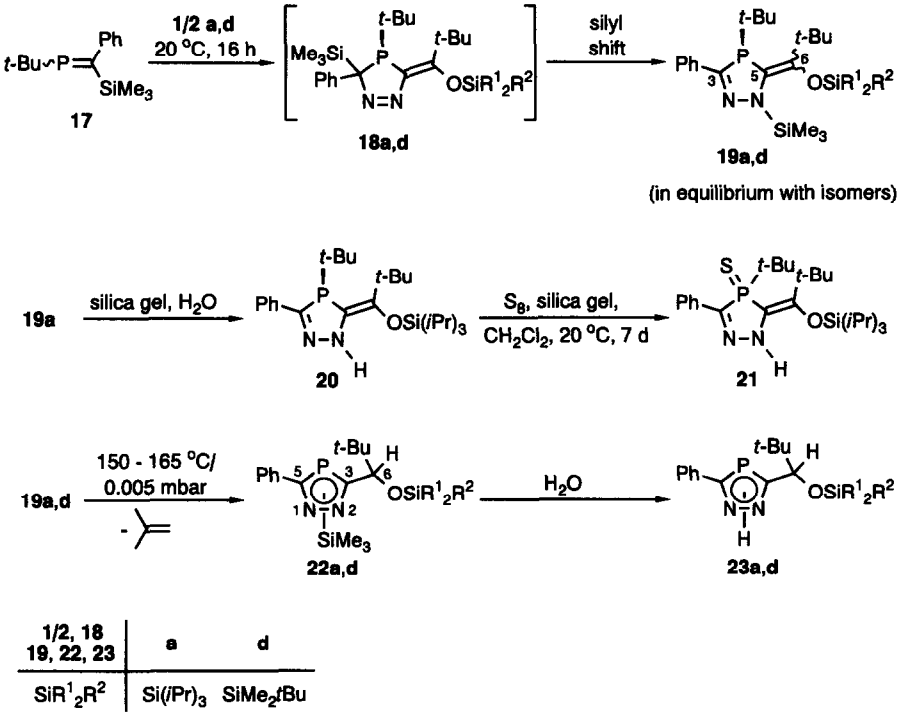
perature investigated. The occurrence of positional isomers has already been described for a N-trimethylsilyl- and some acyl-substituted 1,2,4-diazaphospholes[24]; in one study[24a] the two isomers could be separated and did not equilibrate upon subsequent heating.

Due to the similarity of structures **14A** and **14B**, assignment of the NMR data is not straightforward. However, simple molecular models suggest that the steric interaction of the triisopropylsilyl group with the adjacent substituent is smaller in **14aA** than in **14aB**; on the other hand, the equilibrium should be more balanced in **14d** where the less space-demanding $SiMe_2tBu$ group is present. These considerations agree with the experimental findings, and the NMR assignments can be made based on the different signal intensities of the two isomers (Table 2). Our argumentation was further corroborated, when phosphaalkyne **15** was treated with **1/2a**. Only one product was formed to which the structure **16** was assigned based on the close similarity of the relevant NMR data with those of **14aA**. Obviously, severe steric repulsion between the $Si(iPr)_3$ and the adjacent *t*Bu group does not permit formation of **14B** (*t*-Bu instead of Ph).

The reaction of phosphaalkene **17**[25] with α-diazotoluene was accompanied by loss of nitrogen and furnished directly a 1-*tert*-butylphosphirane.[4d] In contrast, interaction of **17** with **1/2a** or **d** leads first to the expected 5-alkylidene-3*H*-1,2,4-diazaphospholes **18**, to which the transient ^{31}P NMR signals (**18a**: δ -25.0; **18b** δ -24.7 ppm) are assigned. A rapid 1,3-$SiMe_3$ shift transforms them into the 5-alkylidene-4,5-dihydro-1*H*-1,2,4-diazaphospholes **19** which can be isolated in quantitative yield as very moisture-sensitive oils (Scheme 5). These results underscore once more the stabilizing influence of the exocyclic double bond on the thermal stability of the [3+2] cycloaddition products.

The identity of **19a** is established by the NMR data. The ^{31}P signal (δ = -8.0 ppm) is in the expected range, and the presence of three olefinic ^{13}C signals indicates the migration of the trimethylsilyl group. The carbon atoms of the exocyclic double bond are shielded with respect to those in (*E*)-**4** [δ(C-5) = 127.4 ppm, $^1J_{(P,C)}$ = 25.0 Hz; δ(C-6) = 156.3 ppm, $^2J_{(P,C)}$ = 26.2 Hz] as a consequence of the missing azo function. The magnitude of the P,C coupling constants for these two signals together with the ^4J coupling between P and the *tert*-butyl group at C-6 (8.5 Hz) are indicative of the *E*-configuration. The observation of slight line broadening in the ^{13}C NMR spectrum at room temperature and of distinctly sharper lines at both 238 and 328 K suggests a dynamic equilibrium of **19a** with one or more isomers that are present in very small quantity. In the case of **19d**, the equilibria are much more pronounced. The ^{13}C NMR spectrum (100 MHz) at 298 K shows the closely spaced signals of two major species in unequal amounts and suggests a coalescence situation for some other species. In fact, two additional sets of signals, in unequal amounts and with low intensity, are registered in the low-temperature spectrum at 238 K. At 328 K, the time-averaged spectrum of the latter two sets of signals can be observed, and the major isomers approach a 1 : 1 ratio. The ^{31}P NMR spectrum shows only one signal (T = 298 - 323 K, 80.8 MHz) at δ = 35.2 ppm. The large low-field shift as compared to **19a** suggests a time-averaged signal position. While a straightforward assignment of the isomers that are present in small amounts was not possible, the NMR data of the two major species could be assigned unequivocally to *Z*- and *E*-**19d** with the former one prevailing. The configuration of *Z*-**19d** is indicated by $^5J_{(P,C)}$ and $^6J_{(P,H)}$ coupling between the phosphorus nucleus and the Si-$\underline{Me}_3$ group, while *E*-**19d** exhibits $^3J_{(P,C)}$ and $^4J_{(P,C)}$ coupling between phosphorus and the Si-$\underline{t}Bu$ group. We attribute the dynamic phenomena described to fast positional changes of the $SiMe_3$ group between N-1, C-3, and C-6. In the latter case, C-6 becomes the second stereogenic center of the molecule, and diastereomers can be expected; furthermore the reversibility of the migration to C-6 can entail an *E/Z* isomerization at the exocyclic double bond.

The pronounced moisture-sensitivity of **19a,d** was already mentioned. Deliberate hydrolysis of **19a** produced **20a** by cleavage of the N-$SiMe_3$ bond. This compound, which displays in solution a strong greenish fluorescence is readily decomposed in the presence of atmospheric oxygen, but the phosphorus atom could be oxidized in a controlled manner with sulfur in the presence of silica gel. The formation of the $\lambda^5\sigma^4$-phosphinesulfide **21**, a non-fluorescent compound, was confirmed by the elemental analysis and the NMR and IR spectra.



Scheme 5

Attempted bulb-to-bulb vacuum distillation of **19a,d** resulted in a fragmentation into isobutene and 1,2,4-diazaphospholes **22a,d** which are readily transformed into **23a,d** by desilylation in contact with atmospheric moisture. The thermally induced extrusion of isobutene from 4-*tert*-butyl-4*H*-1,2,4-diazaphospholes has been observed before.[10] ^{31}P NMR (**22**: δ = 100.1 and 99.9 ppm; **23**: 79.1 and 76.2 ppm) and ^{13}C NMR spectra [δ(C-3, C-5) = 177.1 - 183.5 ppm] leave no doubt about the structure of the new 1*H*-1,2,4-diazaphospholes. Only one set of signals is observed in the NMR spectra of **22a,d**, and a fast positional change of the $SiMe_3$ group is not expected.[6] Steric reasons suggest that the $SiMe_3$ group is attached to N-1. In contrast, NMR specta of **23a,d** are temperature-dependent which may be attributed to rapid exchange between the isomers.

In conclusion, we have presented evidence that 1-diazoalkenes **2**, which coexist in solution with diazoketones **1**, undergo regiospecific [3+2] cycloaddition to phosphaalkenes with different electron demand.

The 5-alkylidene-4,5-dihydro-3*H*-1,2,4-diazaphospholes so obtained (**4**, **6**, **8**, and **19**) are much more resistant to thermal extrusion of nitrogen than their relatives lacking the exocyclic double bond.

EXPERIMENTAL

General Information. NMR spectra: Bruker WP 200 (^{1}H NMR: 200.1 MHz; ^{13}C NMR: 50.2 MHz; ^{31}P NMR: 80.1 MHz) and Bruker AMX 400 (^{1}H NMR: ^{1}H 400.1 MHz; ^{13}C NMR: 100.6 MHz; ^{31}P NMR: 162.0 MHz). All spectra were recorded in $CDCl_3$ solution, if not stated otherwise. The solvent signal was used as the internal standard (^{1}H NMR: δ = 7.24 ppm; ^{13}C NMR: δ = 77.0 ppm). The ^{31}P NMR spectra were recorded using 85 % H_3PO_4 as external standard. In the presentation of the ^{13}C NMR data, the multiplicities reported for the ^{13}C and ^{31}P spectra refer to the proton-decoupled spectra; no sign is given for the P,C coupling constants. IR spectra: Perkin-Elmer 1310 Infrared Spectrophotometer; wavenumbers [cm^{-1}] are given. Elemental analyses: Perkin-Elmer EA 2400.

Starting Materials. α-Silyl-α-diazoketones **1a,c-e**[19], **1b**[26], **1f,g**[27] were prepared according to literature methods. The synthesis was improved by the use of an excess (20 %) of ethyldiisopropylamine and chromatographic workup (silica gel Macherey & Nagel, 0.063 - 0.2 mm) at -40 °C, with ether / petroleum ether mixtures as eluent. Phosphaalkenes **3**[14b], **5**[28], **7**[29], **9**[14b], **12**[30], **17**[25] and phosphaalkyne **15**[31] were prepared according to published procedures. All reactions were carried out in rigorously dried glassware under an argon atmosphere. Solvents were dried according to standard methods and stored under an argon atmosphere.

(*E*)-4,5-Dihydro-5-[2,2-dimethyl-1-(triisopropylsilyloxy)propylidene]-3,3-diphenyl-4-(2,4,6-trimethylphenyl)-3*H*-1,2,4-diazaphosphole (4a): To a stirred solution of diphenylmethylene(mesityl)-phosphine (**3**), (1.582 g, 5.00 mmol) in dichloromethane (50 mL) was added dropwise at 0 °C a solution of diazoketone **1a** (1.412 g, 5.00 mmol) in dichloromethane (20 mL). The reaction mixture was exposed to room temperature and stirred for 30 min. After removal of the solvent at 20 °C / 0.005 mbar, the product was crystallized from dichloromethane / acetonitrile (1 : 1) at -30 °C and washed with cold acetonitrile (-30 °C). The pale-yellow crystals were dried at 60 °C / 0.005 mbar; yield: 2.336 g (78 %); mp. 112 °C (dec.). - ^{1}H NMR δ 0.88, 1.04 (d, $^3J_{(H,H)}$ = 7.5 Hz, 9H, CHC$\underline{H}_3$), 1.24 (sept, $^3J_{(H,H)}$ = 7.5 Hz, 3H, C$\underline{H}$CH$_3$), 1.58 (s, 9H, C(CH$_3$)$_3$), 1.89, 1.95 (s, 3H, CH$_3$), 2.53 (d, $^4J_{(P,H)}$ = 3.6 Hz, 3H, *o*-CH$_3$), 6.36 (s, 1H, *m*-H at Mes), 6.46 (d, $^4J_{(P,H)}$ = 4.6 Hz, 1H, *m*-H at Mes), 6.77 - 6.87, 7.04 - 7.10 (m, 2H, Ph), 7.13 - 7.17 (m, 4H, Ph), 7.51 - 7.53 (m, 2H, Ph). - ^{13}C-NMR δ 14.8 (s, SiCH), 17.9, 18.2 (s, SiCH$\underline{Me}$), 20.7, 22.2 (s, Me), 24.0 (d, $^3J_{(P,C)}$ = 37.3 Hz, *o*-Me), 29.0 (d, $^4J_{(P,C)}$ = 9.4 Hz, C$\underline{Me}_3$), 39.1 (d, $^3J_{(P,C)}$ = 1.6 Hz, $\underline{C}$Me$_3$), 105.0 (d, $^1J_{(P,C)}$ = 27.3 Hz, $\underline{C}$Ph$_2$), 125.9, 126.9 (s), 127.0 (d, $J_{(P,C)}$ = 2.5 Hz), 127.2 (d, $J_{(P,C)}$ = 2.5 Hz), 127.9 (d, $J_{(P,C)}$ = 1.6 Hz), 128.3 (d, $J_{(P,C)}$ = 19.0 Hz), 128.6 (d, $^1J_{(P,C)}$ = 37.8 Hz, *i*-C at Mes), 129.0 (d, $^3J_{(P,C)}$ = 7.3 Hz, *m*-C at Mes), 130.0 (s), 138.6 (s), 139.6 (d, $^1J_{(P,C)}$ = 36.1 Hz, P-C=), 141.5 (s), 142.6 (d, $^2J_{(P,C)}$ = 4.7 Hz, *o*-C at Mes), 142.9 (d, $J_{(P,C)}$ = 29.8 Hz), 144.3 (d, $^2J_{(P,C)}$ = 38.1 Hz, *o*-C at Mes), 176.9 (d, $^2J_{(P,C)}$ = 25.4 Hz, =C-O). - Anal. Calcd. for $C_{37}H_{51}N_2OPSi$: C, 74.21; H, 8.58; N, 4.68. Found: C, 74.1; H, 8.5; N, 4.6.

(*E*)-5-[1-(1-Adamantyl)-1-(triisopropylsilyloxy)methylene]-4,5-dihydro-3,3-diphenyl-4-(2,4,6-trimethylphenyl)-3*H*-1,2,4-diazaphosphole (4b): The solution of **3** (4.743 g, 14.99 mmol) and of diazoketone **1b** (5.406 g, 14.99 mmol) in dichloromethane (120 mL) was stirred for 16 h. The solvent was removed at 0.005 mbar, and **4b** was isolated by crystallization from a mixture of dichloromethane / acetonitrile (1 : 1) at -30 °C. The yellow crystals were washed with cold acetonitrile (-30 °C) and dried at 60 °C / 0.005 mbar; yield: 7.815 g (77 %); mp. 111 °C (dec.). - ^{1}H NMR δ 0.90, 1.05 (d, $^3J_{(H,H)}$ = 7.5 Hz, 9H, CHC$\underline{H}_3$), 1.25 (sept, $^3J_{(H,H)}$

= 7.5 Hz, 3H, C<u>H</u>CH$_3$), 1.59 - 1.67 (m, 6H, Ad), 1.84 (s, 3H, CH$_3$), 1.94 - 2.09 (m, 12H, Ad and CH$_3$), 2.58 (d, $^4J_{(P,H)}$ = 4.0 Hz, 3H, *o*-CH$_3$), 6.39 (s, 1H, *m*-H at Mes), 6.53 (d, $^4J_{(P,H)}$ = 4.7 Hz, 1H, *m*-H at Mes), 6.87 - 6.96 (m, 3H, Ph), 7.07 - 7.10 (m, 2H, Ph), 7.15 - 7.24 (m, 3H, Ph), 7.44 - 7.47 (m, 2H, Ph). - ^{13}C NMR δ 14.8 (s, SiCH), 18.0, 18.2 (s, SiCH<u>Me</u>), 20.8, 22.3 (s, Me), 24.1 (d, $^3J_{(P,C)}$ = 37.2 Hz, *o*-Me), 28.3 (s, C-3, -5, -7-Ad), 36.6 (s, C-4, -6, -10-Ad), 39.9 (d, $^4J_{(P,C)}$ = 9.3 Hz, C-2, -8, -9-Ad), 41.2 (d, $^3J_{(P,C)}$ = 2.4 Hz, C-1-Ad), 104.7 (d, $^1J_{(P,C)}$ = 27.6 Hz, <u>C</u>Ph$_2$), 125.9, 127.0 (s), 127.2 (d, $J_{(P,C)}$ = 2.0 Hz), 127.2 (d, $J_{(P,C)}$ = 2.1 Hz), 128.0 (s), 128.2 (d, $J_{(P,C)}$ = 18.2 Hz), 128.9 (d, $^1J_{(P,C)}$ = 37.9 Hz, *i*-C at Mes), 129.0 (d, $^3J_{(P,C)}$ = 7.2 Hz, *m*-C at Mes), 130.0 (s), 138.7 (s), 139.5 (d, $^1J_{(P,C)}$ = 36.2 Hz, P-C=), 141.4 (s), 142.9 (d, $^2J_{(P,C)}$ = 4.7 Hz, *o*-C at Mes), 143.2 (d, $^2J_{(P,C)}$ = 30.2 Hz), 144.3 (d, $^2J_{(P,C)}$ = 38.1 Hz, *o*-C at Mes), 176.9 (d, $^2J_{(P,C)}$ = 24.1 Hz, =C-O). - Anal. Calcd. for $C_{43}H_{57}N_2OPSi$: C, 76.29; H, 8.49; N, 4.14. Found: C, 75.8; H, 8.4; N, 4.1.

(*E*)-4,5-Dihydro-5-{2,2-dimethyl-1-[(1,1-dimethylethyl)diphenylsilyloxy]propylidene}-3,3-diphenyl-4-(2,4,6-trimethylphenyl)-3*H*-1,2,4-diazaphosphole (4c): Synthesis and workup were analogous to **4b**. From phosphaalkene **3** (3.905 g, 12.34 mmol) and diazoketone **1c** (4.500 g, 12.34 mmol), **4c** (7.145 g, 85 %) was obtained as yellow crystals; mp. 110 °C (dec.). - ^{1}H NMR δ 1.00 (s, 9H, SiC(CH$_3$)$_3$), 1.18 (s, 3H, CH$_3$), 1.42 (d, $^5J_{(P,H)}$ = 0.3 Hz, 9H, CC(CH$_3$)$_3$), 2.01 (s, 3H, CH$_3$), 2.51 (d, $^4J_{(P,H)}$ = 3.8 Hz, 3H, *o*-CH$_3$), 6.26 (s, 1H, *m*-H at Mes), 6.50 (d, $^4J_{(P,H)}$ = 4.5 Hz, 1H, *m*-H at Mes), 6.71 - 6.78 (m, 5H, Ph), 6.91 - 7.14 (m, 8H, Ph), 7.32 - 7.38 (m, 3H, Ph), 7.44 - 7.47, 7.89 - 7.92 (m, 2H, Ph). - ^{13}C NMR δ 20.7 (s, Si<u>C</u>Me$_3$ and Me), 21.8 (s, Me), 24.1 (d, $^3J_{(P,C)}$ = 37.3 Hz, *o*-Me), 27.2 (s, SiC<u>Me</u>$_3$), 29.0 (d, $^4J_{(P,C)}$ = 9.2 Hz, CC<u>Me</u>$_3$), 38.9 (d, $^3J_{(P,C)}$ = 2.2 Hz, C<u>C</u>Me$_3$), 104.9 (d, $^1J_{(P,C)}$ = 27.8 Hz, <u>C</u>Ph$_2$), 125.7 (s), 126.7 (d, $J_{(P,C)}$ = 2.1 Hz), 126.7 (s), 127.0 (d, $J_{(P,C)}$ = 2.1 Hz), 127.2 (2 s), 127.8 (d, $J_{(P,C)}$ = 16.3 Hz), 128.0 (s), 128.2 (s), 128.7 (d, $^1J_{(P,C)}$ = 38.4 Hz, *i*-C at Mes), 128.8 (s), 128.9 (d, $^4J_{(P,C)}$ = 8.6 Hz, *m*-C at Mes), 129.9, 133.3, 134.4, 134.5, 135.7, 138.8 (all s), 139.6 (d, $^1J_{(P,C)}$ = 38.5 Hz, P-C=), 140.8 (s), 142.7 (d, $J_{(P,C)}$ = 29.9 Hz), 143.0 (d, $^2J_{(P,C)}$ = 5.0 Hz, *o*-C at Mes), 144.4 (d, $^2J_{(P,C)}$= 38.7 Hz, *o*-C at Mes), 174.5 (d, $^2J_{(P,C)}$ = 24.2 Hz, =C-O). - Anal. Calcd. for $C_{44}H_{49}N_2OPSi$: C, 77.61; H, 7.25; N, 4.11. Found: C, 77.5; H, 7.5; N, 4.2.

(*E*)-4,5-Dihydro-5-{2,2-dimethyl-1-[(1,1-dimethylethyl)dimethylsilyloxy]propylidene}-3,3-diphenyl-4-(2,4,6-trimethylphenyl)-3*H*-1,2,4-diazaphosphole (4d): The synthesis was analogous to **4b**, from **3** (947 mg, 2.99 mmol) and **1d** (720 mg, 2.99 mmol) in dichloromethane (30 mL). After crystallization from dichloromethane / acetonitrile (1 : 2) at -30 °C, followed by washing with cold acetonitrile (-30 °C) and drying of the yellow crystals at 60 °C / 0.005 mbar, diazaphosphole **4d** was obtained in a yield of 1.232 g (74 %); mp. 108 °C (dec.). - ^{1}H NMR δ -0.01, 0.40 (s, 3H, SiCH$_3$), 0.97 (s, 9H, SiC(CH$_3$)$_3$), 1.26 (d, $^5J_{(P,H)}$ = 0.4 Hz, 9H, CC(CH$_3$)$_3$), 1.79, 2.05 (s, 3H, CH$_3$), 2.58 (d, $^4J_{(P,H)}$ = 3.8 Hz, 3H, *o*-CH$_3$), 6.40 (s, 1H, *m*-H at Mes), 6.56 (d, $^4J_{(P,H)}$ = 4.7 Hz, 1H, *m*-H at Mes), 6.91 - 6.98 (m, 3H, Ph), 7.10 - 7.13 (m, 2H, Ph), 7.17 - 7.27 (m, 3H, Ph), 7.42 - 7.45 (m, 2H, Ph). - ^{13}C NMR δ -3.4, -1.9 (s, SiMe), 19.7 (s, Si<u>C</u>Me$_3$), 20.8, 21.9 (s, Me), 24.1 (d, $^3J_{(P,C)}$ = 36.9 Hz, *o*-Me), 26.3 (s, SiC<u>Me</u>$_3$), 28.9 (d, $^4J_{(P,C)}$ = 9.4 Hz, CC<u>Me</u>$_3$), 38.8 (d, $^3J_{(P,C)}$ = 1.6 Hz, C<u>C</u>Me$_3$), 105.1 (d, $^1J_{(P,C)}$ = 27.5 Hz, CPh$_2$), 126.0 (s), 127.1 (s), 127.2 (2 s), 127.9 (d, $J_{(P,C)}$ = 17.1 Hz), 128.2 (s), 128.9 (d, $^1J_{(P,C)}$ = 38.7 Hz, *i*-C at Mes), 129.1 (d, $^3J_{(P,C)}$ = 7.5 Hz, *m*-C at Mes), 130.3 (s), 138.9 (s), 139.5 (d, $^1J_{(P,C)}$ = 36.6 Hz, P-C=), 141.2 (s), 142.8 (d, $^2J_{(P,C)}$ = 5.0 Hz, *o*-C at Mes), 143.4 (d, $J_{(P,C)}$ = 30.2 Hz), 144.6 (d, $^2J_{(P,C)}$ = 38.3 Hz, *o*-C at Mes), 176.6 (d, $^2J_{(P,C)}$ = 25.4 Hz, =C-O). - Anal. Calcd. for $C_{34}H_{55}N_2OPSi$: C, 73.34; H, 8.14; N, 5.03. Found: C, 73.3; H, 8.1; N, 5.0.

(*E*)- and (*Z*)-4,5-Dihydro-3,3-diphenyl-5-[1-(triisopropylsilyloxy)ethylidene]-4-(2,4,6-trimethylphenyl)-3*H*-1,2,4-diazaphosphole (4e): A solution of **3** (1.090 g, 3.45 mmol) and of **1e** (0.828 g, 3.45 mmol) in dichloromethane (30 mL) was stirred during 3 weeks at room temperature and the volatile components were

removed in vacuo. After crystallization from pentane at -78 °C, the product was obtained as a mixture of diastereomers (^{1}H NMR: E:Z = 56:44), which was not analytically pure. Recrystallization from dichloromethane / acetonitrile (1 : 1) at -30 °C yielded (*E*)-**4e**. The crystals were washed with cold acetonitrile and dried at 45 °C / 0.005 mbar; yield: 272 mg (14 %); mp. 92 °C (dec.). (*E*)-**4e**: ^{1}H NMR δ 1.01, 1.08 (d, $^3J_{(H,H)}$ = 7.5 Hz, 9H, CHC$\underline{H}_3$), 1.33 (sept, $^3J_{(H,H)}$ = 7.5 Hz, 3H, C$\underline{H}$CH$_3$), 1.74, 2.09 (s, 3H, CH$_3$), 2.18 (d, $^4J_{(P,H)}$ = 1.8 Hz, 3H, =CCH$_3$), 2.64 (d, $^4J_{(P,H)}$ = 3.6 Hz, 3H, *o*-CH$_3$), 6.45 (s, 1H, *m*-H at Mes), 6.64 (d, $^4J_{(P,H)}$ = 4.5 Hz, 1H, *m*-H at Mes), 6.94 - 7.02 (m, 3H, Ph), 7.16 - 7.26 (m, 5H, Ph), 7.35 - 7.38 (m, 2H, Ph). - ^{13}C NMR δ 13.4 (s, SiCH), 17.9, 18.0 (s, SiCH$\underline{Me}$), 20.8, 22.2 (s, Me), 24.2 (d, $^3J_{(P,C)}$ = 37.6 Hz, *o*-Me), 25.1 (d, $^3J_{(P,C)}$ = 10.3 Hz, OC$\underline{Me}$), 104.5 (d, $^1J_{(P,C)}$ = 28.2 Hz, $\underline{C}$Ph$_2$), 126.2 (s), 127.2 (d, $J_{(P,C)}$ = 2.1 Hz), 127.2 (s), 127.6 (d, $J_{(P,C)}$ = 3.0 Hz), 127.6 (d, $^1J_{(P,C)}$ = 39.5 Hz, *i*-C at Mes), 127.8 (d, $J_{(P,C)}$ = 15.8 Hz), 128.1 (s), 129.0 (d, $^3J_{(P,C)}$ = 7.2 Hz, *m*-C at Mes), 130.2 (s), 139.2 (s), 141.0 (s), 142.9 (d, $^1J_{(P,C)}$ = 26.0 Hz, P-C=), 142.9 (d, $^2J_{(P,C)}$ = 4.6 Hz, *o*-C at Mes), 143.4 (d, $J_{(P,C)}$ = 29.0 Hz), 145.4 (d, $^2J_{(P,C)}$ = 38.4 Hz, *o*-C at Mes), 162.6 (d, $^2J_{(P,C)}$ = 32.4 Hz, =C-O). - Anal. Calcd. for $C_{34}H_{45}N_2OPSi$: C, 73.34; H, 8.14; N, 5.03. Found: C, 73.2; H, 8.1; N, 5.1. Spectral data of (*Z*)-**4e**: ^{13}C NMR δ 13.0 (s, SiCH), 17.5, 17.9 (s, SiCH$\underline{Me}$), 20.7, 21.7 (s, Me), 24.0 (d, $^3J_{(P,C)}$ = 37.4 Hz, *o*-Me), 24.3 (d, $^3J_{(P,C)}$ = 11.2 Hz, OC$\underline{Me}$), 104.7 (d, $^1J_{(P,C)}$ = 29.1 Hz, $\underline{C}$Ph$_2$), 125.7 - 129.7 (Ph and aryl), 137.7 - 147.7 (Ph, Mes and P-C=), 167.6 (d, $^2J_{(P,C)}$ = 19.5 Hz, =C-O).

(*E*)-4,5-Dihydro-3,3-diphenyl-5-(α-triisopropylsilyloxy-4-methoxybenzylidene)-4-(2,4,6-trimethylphenyl)-3*H*-1,2,4-diazaphosphole (4f): Synthesis and workup were analogous to **4b**, but from **3** (1.455 g, 4.60 mmol) and **1f** (1.529 g, 4.60 mmol) in dichloromethane (30 mL). Product **4f** was obtained as yellow needles; yield: 2.358 g (79 %); mp. 109 °C (dec.). - ^{1}H NMR δ 0.98, 1.07 (d, $^3J_{(H,H)}$ = 7.5 Hz, 9H, CHC$\underline{H}_3$), 1.33 (sept, $^3J_{(H,H)}$ = 7.5 Hz, 3H, C$\underline{H}$CH$_3$), 1.98, 2.09 (s, 3H, CH$_3$), 2.52 (d, $^4J_{(P,H)}$ = 3.7 Hz, 3H, *o*-CH$_3$), 3.78 (s, 3H, OCH$_3$), 6.47 (s, 1H, *m*-H at Mes), 6.58 (d, $^4J_{(P,H)}$ = 4.7 Hz, 1H, *m*-H at Mes), 6.78 (d, $^3J_{(H,H)}$ = 8.9 Hz, 2H, *m*-H at anisyl), 6.90 - 6.97 (m, 3H, Ph), 7.10 -7.22 (m, 5H, Ph), 7.46 - 7.49 (m, 2H, Ph), 7.64 (d, $^3J_{(H,H)}$ = 8.9 Hz, 2H, *o*-H at anisyl). - ^{13}C NMR δ 14.3 (s, SiCH), 18.0, 18.2 (s, SiCH$\underline{Me}$), 20.8, 22.3 (s, Me), 24.2 (d, $^3J_{(P,C)}$ = 37.1 Hz, *o*-Me), 55.2 (d, $^8J_{(P,C)}$ = 2.4 Hz, OMe), 105.0 (d, $^1J_{(P,C)}$ = 27.1 Hz, $\underline{C}$Ph$_2$), 113.4 (s, *m*-C at anisyl), 126.1 (s), 127.0 (s), 127.3 (d, $J_{(P,C)}$ = 1.6 Hz), 127.3 (d, $J_{(P,C)}$ = 2.2 Hz) 128.0 (s), 128.2 (d, $J_{(P,C)}$ = 18.1 Hz), 129.0 (d, $^1J_{(P,C)}$ = 36.3 Hz, *i*-C at Mes), 129.2 (d, $^3J_{(P,C)}$ = 7.0 Hz, *m*-C at Mes), 130.0 (d, $^4J_{(P,C)}$ = 7.7 Hz, *o*-C at anisyl), 130.1 (s), 130.3 (s), 139.0 (s), 141.3 (d, $^1J_{(P,C)}$ = 32.2 Hz, P-C=), 141.4 (s), 142.7 (d, $J_{(P,C)}$ = 28.8 Hz), 142.9 (d, $^2J_{(P,C)}$ = 4.3 Hz, *o*-C at Mes), 144.5 (d, $^2J_{(P,C)}$ = 37.5 Hz, *o*-C at Mes), 161.4 (s, *p*-C at anisyl), 163.0 (d, $^2J_{(P,C)}$ = 30.4 Hz, =C-O). - Anal. Calcd. for $C_{40}H_{49}N_2O_2PSi$: C, 74.04; H, 7.61; N, 4.32. Found: C, 74.1; H, 7.6; N, 4.2.

(*E*)-4,5-Dihydro-3,3-diphenyl-5-(α-triisopropylsilyloxy-4-nitrobenzylidene)-4-(2,4,6-trimethylphenyl)-3*H*-1,2,4-diazaphosphole (4g): A solution of **3** (1.074 g, 3.40 mmol) and of **1g** (1.180 g, 3.40 mmol) in dichloromethane (30 mL) was stirred during 4 days. After removing of the volatile components in vacuo, red-colored crystals were isolated by crystallization from dichloromethane at -78 °C. Another crystallization, followed by washing with small portions of cold acetonitrile (-40 °C) and drying in vacuo at 20 °C yielded 1.780 g (79 %) of **4g**; mp. 79 °C (decomp.). - ^{1}H NMR δ 1.00, 1.09 (d, $^3J_{(H,H)}$ = 7.5 Hz, 9H, CHC$\underline{H}_3$), 1.38 (sept, $^3J_{(H,H)}$ = 7.5 Hz, 3H, C$\underline{H}$CH$_3$), 1.90, 2.10 (s, 3H, CH$_3$), 2.51 (d, $^4J_{(P,H)}$ = 3.6 Hz, 3H, *o*-CH$_3$), 6.48 (s, 1H, *m*-H at Mes), 6.64 (d, $^4J_{(P,H)}$ = 5.0 Hz, 1H, *m*-H at Mes), 6.96 - 7.01 (m, 3H, Ph), 7.14 - 7.24 (m, 5H, Ph), 7.40 - 7.42 (m, 2H, Ph), 7.78 (d, $^3J_{(H,H)}$ = 8.8 Hz, 2H, *o*-H at aryl), 8.11 (d, $^3J_{(H,H)}$ = 8.8 Hz, 2H, *m*-H at aryl). - ^{13}C NMR δ 14.1 (s, SiCH), 18.0, 18.1 (s, SiCH$\underline{Me}$), 20.8, 22.5 (s, Me), 24.2 (d, $^3J_{(P,C)}$ = 36.7 Hz, *o*-Me), 106.0 (d, $^1J_{(P,C)}$ = 28.0 Hz, $\underline{C}$Ph$_2$), 123.2 (s), 126.4 (s), 127.2 (d, $J_{(P,C)}$ = 2.3 Hz), 127.3 (s), 127.5 (d, $J_{(P,C)}$ = 2.7 Hz),

128.0 (d, $J_{(P,C)}$ = 17.4 Hz), 128.0 (d, $^1J_{(P,C)}$ = 37.0 Hz, *i*-C at Mes), 128.2 (s), 129.0 (d, $^4J_{(P,C)}$ = 7.4 Hz, *o*-C at aryl), 129.5 (d, $^3J_{(P,C)}$ = 7.4 Hz, *m*-C at Mes), 130.3 (s), 139.8 (s), 140.7 (s), 142.3 (d, $J_{(P,C)}$ = 36.7 Hz), 142.5 (d, $^2J_{(P,C)}$ = 4.3 Hz, *o*-C at Mes), 144.2 (s), 144.9 (d, $^2J_{(P,C)}$ = 38.5 Hz, *o*-C at Mes), 145.2 (d, $^2J_{(P,C)}$ = 35.0 Hz, P-C=), 148.3 (s), 160.1 (d, $^2J_{(P,C)}$ = 29.7 Hz, =C-O). - Anal. Calcd. for $C_{39}H_{46}N_3O_3PSi$: C, 70.56; H, 6.98; N, 6.33. Found: C, 69.9; H, 6.7; N, 5.5.

Synthesis of 3-(1,1-Dimethylethyl)-4,5-dihydro-4-trimethylsilyl-3-(trimethylsilyloxy)-3H-1,2,4-diazaphospholes (6); General Procedure: Phosphaalkene **5** was placed in a 25 mL flask and the diazo compound **1** was added. After stirring for 4 h at 60 °C (in the case of **1e** 20 h at 45 °C) diazaphosphole **6** was obtained by crystallization.

(3α,4α,5*E*)-3-(1,1-Dimethylethyl)-4,5-dihydro-4-trimethylsilyl-3-trimethylsilyloxy-5-(1-triisopropylsilyloxy-2,2-dimethylpropylidene)-3*H*-1,2,4-diazaphosphole (6a): From **5** (1.190 g, 4.53 mmol) and **1a** (1.281 g, 4.53 mmol). Crystallization from dichloromethane at -78 °C yielded **6a** (2.178 g, 88 %) as a yellow powder; mp. 74 °C. - ^{1}H NMR δ 0.18 (d, $^3J_{(P,H)}$ = 4.2 Hz, 9H, PSi(CH$_3$)$_3$), 0.26 (s, 9H, OSi(CH$_3$)$_3$), 0.99 (s, 9H, PCC(CH$_3$)$_3$), 1.05, 1.07 (d, $^3J_{(H,H)}$ = 7.4 Hz, 9H, CHC<u>H</u>$_3$), 1.28 (sept, $^3J_{(H,H)}$ = 7.4 Hz, 3H, C<u>H</u>CH$_3$), 1.31 (s, 9H, =CC(CH$_3$)$_3$). - ^{13}C NMR δ 1.3 (d, $^2J_{(P,C)}$ = 10.5 Hz, PSi<u>Me</u>$_3$), 4.3 (s, OSi<u>Me</u>$_3$), 14.9 (s, SiCH), 18.3, 18.5 (s, SiCH<u>Me</u>), 26.1 (d, $^3J_{(P,C)}$ = 9.8 Hz, PCC<u>Me</u>$_3$), 29.6 (d, $^4J_{(P,C)}$ = 8.5 Hz, =CC<u>Me</u>$_3$), 38.4 (d, $^3J_{(P,C)}$ = 2.1 Hz, =C<u>C</u>Me$_3$), 42.5 (d, $^2J_{(P,C)}$ = 27.2 Hz, PC<u>C</u>Me$_3$), 132.4 (d, $^1J_{(P,C)}$ = 28.5 Hz, PCO), 137.8 (d, $^1J_{(P,C)}$ = 39.1 Hz, PC=), 172.8 (d, $^2J_{(P,C)}$ = 18.4 Hz, =CO). - ^{31}P NMR δ -96.7. - Anal. Calcd. for $C_{26}H_{57}N_2O_2PSi_3$: C, 57.30; H, 10.54; N, 5.14. Found: C, 57.2; H, 10.4; N, 5.0.

(3α,4α,5*E*)-5-[1-Adamantyl-(triisopropylsilyloxy)methylene]-3-(1,1-dimethylethyl)-4,5-dihydro-4-trimethylsilyl-3-trimethylsilyloxy-3*H*-1,2,4-diazaphosphole (6b): From **5** (696 mg, 2.65 mmol) and **1b** (956 mg, 2.65 mmol). Crystallization from dichloromethane at -78 °C yielded **6b** (1.400 g, 85 %) as a yellow powder, mp. 117 °C (dec.). - ^{1}H NMR δ 0.19 (d, $^3J_{(P,H)}$ = 4.1 Hz, 9H, PSi(CH$_3$)$_3$), 0.25 (s, 9H, OSi(CH$_3$)$_3$), 0.99 (s, 9H, C(CH$_3$)$_3$), 1.05, 1.07 (d, $^3J_{(H,H)}$ = 7.5 Hz, 9H, CHC<u>H</u>$_3$), 1.27 (sept, $^3J_{(H,H)}$ = 7.5 Hz, 3H, C<u>H</u>CH$_3$), 1.70 (br, s, 6H, Ad), 1.97 - 2.05 (m, 9H, Ad). - ^{13}C NMR δ 1.4 (d, $^2J_{(P,C)}$ = 10.4 Hz, PSi<u>Me</u>$_3$), 4.2 (s, OSi<u>Me</u>$_3$), 14.8 (s, SiCH), 18.4, 18.5 (s, SiCH<u>Me</u>), 26.0 (d, $^3J_{(P,C)}$ = 9.9 Hz, C<u>Me</u>$_3$), 28.3 (s, C-3, -5, -7-Ad), 36.7 (s, C-4, -6, -10-Ad), 40.4 (d, $^3J_{(P,C)}$ = 2.1 Hz, C-1-Ad), 40.5 (d, $^4J_{(P,C)}$ = 8.6 Hz, C-2, -8, -9-Ad), 42.5 (d, $^2J_{(P,C)}$ = 27.2 Hz, <u>C</u>Me$_3$), 132.1 (d, $^1J_{(P,C)}$ = 28.8 Hz, PCO), 137.7 (d, $^1J_{(P,C)}$ = 39.3 Hz, PC=), 172.7 (d, $^2J_{(P,C)}$= 17.7 Hz, =CO). - ^{31}P NMR δ -97.3. - Anal. Calcd. for $C_{32}H_{63}N_2O_2PSi_3$: C, 61.68; H, 10.19; N, 4.50. Found: C, 61.7; H, 10.2; N, 4.4.

(3α,4α)-3-(1,1-Dimethylethyl)-4,5-dihydro-4-trimethylsilyl-3-trimethylsilyloxy-5-[1-(triisopropylsilyloxy)ethylidene]-3*H*-1,2,4-diazaphosphole (6e): From **5** (1.300 g, 4.95 mmol) and **1e** (1.191 g, 4.95 mmol), a mixture of (*E*)- and (*Z*)-**6e** was obtained (5 : 1 ratio according to the ^{31}P NMR spectrum) observed. The crude product contained several impurities and did not crystallize. The spectroscopic data were, therefore, taken from the crude product. The full data set could be determined only for the main isomer: - (*E*)-**6e**: ^{1}H NMR δ 0.18 (s, 9H, OSi(CH$_3$)$_3$), 0.18 (d, $^3J_{(P,H)}$ = 5.2 Hz, 9H, PSi(CH$_3$)$_3$), 1.00 (s, C(CH$_3$)$_3$), 1.03, 1.07 (d, $^3J_{(H,H)}$ = 7.5 Hz, 9H, CHC<u>H</u>$_3$), 1.30 (sept, $^3J_{(H,H)}$ = 7.5 Hz, 3H, C<u>H</u>CH$_3$), 2.13 (d, $^4J_{(P,H)}$ = 0.8 Hz, 3H, =CCH$_3$). - ^{13}C NMR δ 0.6 (d, $^2J_{(P,C)}$ = 11.9 Hz, PSi<u>Me</u>$_3$), 4.0 (s, OSi<u>Me</u>$_3$), 13.6 (s, SiCH), 18.0, 18.1 (s, SiCH<u>Me</u>), 25.7 (d, $^3J_{(P,C)}$ = 6.7 Hz, =C<u>Me</u>), 26.3 (d, $^3J_{(P,C)}$ = 10.3 Hz, C<u>Me</u>$_3$), 41.2 (d, $^2J_{(P,C)}$ = 27.2 Hz, <u>C</u>Me$_3$), 132.3 (d, $^1J_{(P,C)}$ = 28.0 Hz, PCO), 140.7 (d, $^1J_{(P,C)}$ = 26.8 Hz, PC=), 158.7 (d, $^2J_{(P,C)}$ = 25.7 Hz, =<u>C</u>Me). - ^{31}P NMR δ -99.1. Selected ^{13}C NMR data for (*Z*)-**6e**: δ 132.2 (d, $^1J_{(P,C)}$ = 28.2 Hz, PCO), 147.0 (d, $^1J_{(P,C)}$ = 29.6 Hz, PC=), 164.5 (d, $^2J_{(P,C)}$ = 14.5 Hz, =<u>C</u>Me). - ^{31}P NMR δ -104.6.

(3α,4α)-3-(1,1-Dimethylethyl)-4,5-dihydro-4-trimethylsilyl-3-trimethylsilyloxy-5-[α-triisopropylsilyloxy-4-methoxybenzylidene]-3*H*-1,2,4-diazaphosphole (6f): Reaction of **5** (688 mg, 2.62 mmol) and **1f** (871 mg, 2.62 mmol) provided a mixture of (*E*)- and (*Z*)-**6f** (10 : 1 ratio according to ^{31}P NMR). Crystallization from a dichloromethane / acetonitrile mixture (1 : 2) at -30 °C yielded (*E*)-**6f** (945 mg, 61 %) as a bright yellow powder; mp. 69 °C. - (*E*)-**6f**: ^{1}H NMR δ -0.16 (d, $^{3}J_{(P,H)}$ = 4.6 Hz, 9H, PSi(CH$_3$)$_3$), 0.18 (s, 9H, OSi(CH$_3$)$_3$), 1.02 (d, $^{3}J_{(H,H)}$ = 7.5 Hz, 9H, CHC<u>H</u>$_3$), 1.07 (s, 9H, C(CH$_3$)$_3$), 1.09 (d, $^{3}J_{(H,H)}$ = 7.5 Hz, 9H, CHC<u>H</u>$_3$), 1.33 (sept, $^{3}J_{(H,H)}$ = 7.5 Hz, 3H, C<u>H</u>CH$_3$), 3.82 (s, 3H, OCH$_3$), 6.89 (d, $^{3}J_{(H,H)}$ = 8.9 Hz, 2H, *m*-H), 7.91 (dd, $^{3}J_{(H,H)}$ = 8.9 Hz, $^{5}J_{(P,H)}$ = 0.9 Hz, 2H, *o*-H). - ^{13}C NMR δ 0.2 (d, $^{2}J_{(P,C)}$ = 11.2 Hz, PSiMe$_3$), 4.0 (s, OSiMe$_3$), 14.1 (s, SiCH), 18.1, 18.3 (s, SiCH<u>Me</u>), 26.3 (d, $^{3}J_{(P,C)}$ = 10.5 Hz, C<u>Me</u>$_3$), 41.5 (d, $^{2}J_{(P,C)}$ = 28.2 Hz, <u>C</u>Me$_3$), 55.3 (d, $^{8}J_{(P,C)}$ = 2.4 Hz, OMe), 113.5 (s, *m*-C), 130.6 (d, $^{4}J_{(P,C)}$ = 8.7 Hz, *o*-C), 131.1 (d, $^{3}J_{(P,C)}$ = 2.2 Hz, *i*-C), 132.0 (d, $^{1}J_{(P,C)}$ = 30.6 Hz, PCO), 141.0 (d, $^{1}J_{(P,C)}$ = 33.1 Hz, PC=), 159.2 (d, $^{2}J_{(P,C)}$ = 18.6 Hz, =CO), 160.6 (s, *p*-C). - ^{31}P NMR δ -99.7. - Anal. Calcd. for $C_{29}H_{55}N_2O_3PSi_3$: C, 58.54; H, 9.32; N, 4.71. Found: C, 58.2; H, 9.0; N, 4.8. - (*Z*)-**10f**; ^{31}P NMR δ -102.7.

(3α,4α,5*E*)-4-Chloro-3-(1,1-dimethylethyl)-4,5-dihydro-5-[2,2-dimethyl-1-(triisopropylsilyloxy)-propylidene]-3-trimethylsilyloxy-3*H*-1,2,4-diazaphosphole (8): Phosphaalkene **7** (1.108 g, 4.93 mmol) was placed in a 25 mL flask, and **1a** (1.393 g, 4.93 mmol) was added. After stirring for 4h at 60 °C, a solid mass had formed. Crystallization from dichloromethane at -78 °C yielded **8** (2.03 g, 81 %) as a pale-yellow powder; mp. 104 °C. - ^{1}H NMR δ 0.18 (s, 9H Si(CH$_3$)$_3$), 0.95 (s, 9H, PCC(CH$_3$)$_3$), 1.03, 1.05 (d, $^{3}J_{(H,H)}$ = 7.5 Hz, 9H, CHC<u>H</u>$_3$), 1.30 (sept, $^{3}J_{(H,H)}$ = 7.5 Hz, 3H, C<u>H</u>CH$_3$), 1.45 (d, $^{5}J_{(P,H)}$ = 0.7 Hz, 9H, =CC(CH$_3$)$_3$).- ^{13}C NMR δ 2.3 (s, SiMe$_3$), 15.0 (s, SiCH), 18.09, 18.11 (s, SiCH<u>Me</u>), 25.7 (d, $^{3}J_{(P,C)}$ = 10.5 Hz, PCC<u>Me</u>$_3$), 29.7 (d, $^{4}J_{(P,C)}$ = 9.6 Hz, =CC<u>Me</u>$_3$), 40.3 (d, $^{3}J_{(P,C)}$ = 3.3 Hz, =C<u>C</u>Me$_3$), 41.2 (d, $^{2}J_{(P,C)}$ = 33.9 Hz, PC<u>C</u>Me$_3$), 130.7 (d, $^{1}J_{(P,C)}$ = 41.7 Hz, PCO), 143.8 (d, $^{1}J_{(P,C)}$ = 61.2 Hz, P<u>C</u>=C), 181.9 (d, $^{2}J_{(P,C)}$ = 22.9 Hz, =CO). - ^{31}P NMR δ 47.0. - Anal. Calcd. for $C_{23}H_{48}ClN_2O_2PSi_2$: C, 54.46; H, 9.54; N, 5.52. Found: C, 54.2; H, 9.4; N, 5.5.

(4α,5β)-4,5-Dihydro-3-(2,2-dimethyl-1-oxopropyl)-5-dimethylamino-1-triisopropylsilyl-4-(2,4,6-trimethylphenyl)-1*H*-1,2,4-diazaphosphole (10): The mixture of phosphaalkene **9** (588 mg, 2.84 mmol) and **1a** (802 mg, 2.84 mmol) was stirred for 2 d at 60 °C. The volatile components (including **11**, which was identified by its NMR signals[19]) were removed by bulb-to-bulb distillation at 120 °C / 0.005 mbar, and the residue was crystallized from pentane at -78 °C affording **10** (616 mg, 44 %) as yellow crystals; mp. 117 °C. - ^{1}H NMR δ 1.14, 1.16 (d, $^{3}J_{(H,H)}$ = 7.5 Hz, 9H, CHC<u>H</u>$_3$), 1.30 (s, 9H, C(CH$_3$)$_3$), 1.48 (sept, $^{3}J_{(H,H)}$ = 7.5 Hz, 3H, C<u>H</u>CH$_3$), 2.13 (s, 6H, *o*-CH$_3$), 2.21 (s, 3H, *p*-CH$_3$), 2.45 (s, 6H, CH$_3$), 5.26 (s, 1H, PCH), 6.80 (d, $^{4}J_{(P,H)}$ = 2.2 Hz, 2H, *m*-H). - ^{13}C NMR δ 12.6 (s, SiCH), 18.2, 18.6 (s, SiCH<u>Me</u>), 20.9 (s, *p*-Me), 22.5 (d, $^{3}J_{(P,C)}$ = 18.3 Hz, *o*-Me), 27.5 (s, C<u>Me</u>$_3$), 40.0 (br, s, NMe$_2$), 43.7 (d, $^{3}J_{(P,C)}$ = 1.1 Hz, <u>C</u>Me$_3$), 92.3 (d, $^{1}J_{(P,C)}$ = 20.7 Hz, PCH), 128.8 (d, $^{1}J_{(P,C)}$ = 34.7 Hz, *i*-C), 129.6 (d, $^{3}J_{(P,C)}$ = 4.3 Hz, *m*-C), 139.4 (d, $^{4}J_{(P,C)}$ = 1.2 Hz, *p*-C), 144.3 (d, $^{2}J_{(P,C)}$ = 16.3 Hz, *o*-C), 146.8 (d, $^{1}J_{(P,C)}$ = 25.1 Hz, C=N), 202.2 (d, $^{2}J_{(P,C)}$ = 16.9 Hz, C=O). - ^{31}P NMR δ -52.2. - IR (KBr): 1630 (C=O). - Anal. Calcd. for $C_{27}H_{48}N_3OPSi_2$: C, 66.22; H, 9.88; N, 8.58. Found: C, 66.3; H, 9.7; N, 8.6.

5-(2,2-Dimethyl-1-oxopropyl)-3-phenyl-1-triisopropylsilyl-1*H*-1,2,4-diazaphosphole (14aA) and **3-(2,2-Dimethyl-1-oxopropyl)-5-phenyl-1-triisopropylsilyl-1*H*-1,2,4-diazaphosphole (14aB):** To a stirred solution of **12** (755 mg, 3.30 mmol) in pentane (10 mL) was added **1a** (932 mg, 3.30 mmol). The reaction mixture was stirred further for 5 h, before the solvent was removed at 20 °C / 0.005 mbar. Bulb-to-bulb distillation at 130 °C / 0.005 mbar yielded a mixture of **14aA** and **14aB** (951 mg, 72%) in a ratio of 74 : 26 at

20 °C (ratio of isomers was determined from the ^{1}H NMR spectrum by integration of the methyl protons of the isopropyl groups). Crystallization from pentane at -78 °C yielded only **14a** (462 mg, 35 %) as colorless crystals; mp. 56 °C. When these crystals were dissolved, the above described mixture of **14aA** and **14aB** was obtained again. - **14aA**: ^{1}H NMR δ 1.12 (d, $^3J_{(H,H)}$ = 7.5 Hz, 18H, CH(C<u>H</u>$_3$)$_2$), 1.48 (s, 9H, C(CH$_3$)$_3$), 1.69 (sept, $^3J_{(H,H)}$ = 7.5 Hz, 3H, C<u>H</u>(CH$_3$)$_2$), 7.32 - 7.43 (m, 3H, Ph; and 5H, Ph of the isomer **14aB**), 7.99 - 8.01 (m, 2H, Ph). - ^{13}C NMR δ 14.2 (s, SiCH), 18.4 (s, SiCH<u>Me</u>$_2$), 29.1 (d, $^4J_{(P,C)}$ = 9.6 Hz, C<u>Me</u>$_3$), 44.1 (d, $^3J_{(P,C)}$ = 2.7 Hz, <u>C</u>Me$_3$), 126.2 (d, $^3J_{(P,C)}$ = 10.1 Hz, *o*-C), 128.4 (s), 128.7 (s), 136.1 (d, $^2J_{(P,C)}$ = 20.3 Hz, *i*-C), 172.4 (d, $^1J_{(P,C)}$ = 59.4 Hz, <u>C</u>-C=O), 178.0 (d, $^1J_{(P,C)}$ = 54.9 Hz, <u>C</u>-Ph), 201.4 (d, $^2J_{(P,C)}$ = 20.2 Hz, C=O). - ^{31}P NMR δ 110.9. - **14aB**: ^{1}H NMR δ 0.99 (d, $^3J_{(H,H)}$ = 7.5 Hz, 18H, CH(C<u>H</u>$_3$)$_2$), 1.28 (sept, $^3J_{(H,H)}$ = 7.5 Hz, 3H, C<u>H</u>(CH$_3$)$_2$), 1.44 (s, 9H, C(CH$_3$)$_3$), 7.32 - 7.43 (m, 5H, Ph; and 3H, Ph of **14aA**). - ^{13}C NMR δ 13.3 (s, SiCH), 18.1 (s, SiCH<u>Me</u>$_2$), 27.2 (s, C<u>Me</u>$_3$), 43.9 (s, <u>C</u>Me$_3$), 127.5 (s), 129.0 (s), 129.8 (d, $^3J_{(P,C)}$ = 5.7 Hz, *o*-C), 133.7 (d, $^2J_{(P,C)}$ = 19.7 Hz, *i*-C), 178.6 (d, $^1J_{(P,C)}$ = 56.4 Hz, <u>C</u>-C=O), 185.4 (d, $^1J_{(P,C)}$ = 49.5 Hz, <u>C</u>-Ph), 203.3 (d, $^2J_{(P,C)}$ = 17.8 Hz, C=O). - Spectral and analytical data of the yellow powder of **14a**: IR (KBr): 1645 (C=O). - Anal. Calcd. for $C_{22}H_{35}N_2OPSi$: C, 65.64; H, 8.76; N, 6.96. Found: C, 65.4; H, 8.6; N, 6.6.

1-[(1,1-Dimethylethyl)dimethylsilyl]-5-(2,2-dimethyl-1-oxopropyl)-3-phenyl-1*H*-1,2,4-diazaphosphole (14dA) and **1-[(1,1-Dimethylethyl)dimethylsilyl]-3-(2,2-dimethyl-1-oxopropyl)-5-phenyl-1*H*-1,2,4-diazaphosphole (14dB):** A solution of phosphaalkene **12** (584 mg, 2.55 mmol) and diazoketone **1d** (614 mg, 2.55 mmol) in pentane (10 mL) was stirred for 3 h at room temperature, and the solvent was removed at 20 °C / 0.005 mbar. Bulb-to-bulb distillation at 120 °C / 0.005 mbar yielded a isomer mixture of **14dA** and **14dB** (709 mg, 74 %) as a light-green oil in a ratio of 42 : 58 at 20 °C (^{1}H NMR). - Spectral data of **14dA**: ^{1}H NMR δ 0.48 (s, 6H, Si(CH$_3$)$_2$), 1.11 (d, $^6J_{(P,H)}$ = 0.6 Hz, 9H, SiC(CH$_3$)$_3$), 1.44 (s, 9H, C(CH$_3$)$_3$), 7.27 - 7.42 (m, 3H, Ph; and 5H, Ph of **14dB**), 7.95 - 7.99 (m, 2H, Ph). - ^{13}C NMR δ -2.3 (s, Si<u>Me</u>$_2$), 19.8 (s, Si<u>C</u>Me$_3$), 27.0 (s, SiC<u>Me</u>$_3$), 28.1 (d, $^4J_{(P,C)}$ = 8.5 Hz, CC<u>Me</u>$_3$), 44.2 (s, C<u>C</u>Me$_3$), 126.4 (d, $^3J_{(P,C)}$ = 9.9 Hz, *o*-C), 128.4 (s), 128.6 (s), 135.9 (d, $^2J_{(P,C)}$ = 20.5 Hz, *i*-C), 175.2 (d, $^1J_{(P,C)}$ = 60.5 Hz, <u>C</u>-C=O), 177.6 (d, $^1J_{(P,C)}$ = 54.6 Hz, <u>C</u>-Ph), 203.2 (d, $^2J_{(P,C)}$ = 18.2 Hz, C=O, signal overlap with C=O resonance of **14dB**). - **14dB**: ^{1}H NMR δ 0.14 (s, 6H, Si(CH$_3$)$_2$), 0.93 (s, 9H, SiC(CH$_3$)$_3$), 1.48 (s, 9H, CC(CH$_3$)$_3$), 7.27 - 7.42 (m, 5H, Ph; and 3H, Ph of **14dA**). - ^{13}C NMR δ -3.0 (s, Si<u>Me</u>$_2$), 19.0 (s, Si<u>C</u>Me$_3$), 26.6 (s, SiC<u>Me</u>$_3$), 27.3 (s, CC<u>Me</u>$_3$), 43.9 (s, C<u>C</u>Me$_3$), 127.6 (s), 128.8 (s), 130.0 (d, $^3J_{(P,C)}$ = 5.4 Hz, *o*-C), 133.7 (d, $^2J_{(P,C)}$ = 19.3 Hz, *i*-C), 178.2 (d, $^1J_{(P,C)}$ = 54.6 Hz, <u>C</u>-C=O), 185.2 (d, $^1J_{(P,C)}$ = 50.2 Hz, <u>C</u>-Ph), 203.2 (d, $^2J_{(P,C)}$ = 18.2 Hz, C=O, signal overlap with C=O resonance of **14dA**). - Isomer mixture of **14d**: IR (neat): 1655 (vs, C=O). - Anal. Calcd. for $C_{19}H_{29}N_2OPSi$: C, 63.30; H, 8.11; N, 7.77. Found: C, 62.5; H, 7.9; N, 7.9.

3-(1,1-Dimethylethyl)-5-(2,2-dimethyl-1-oxopropyl)-1-triisopropylsilyl-1*H*-1,2,4-diazaphosphole (16): Phosphaalkyne **15** (421 mg, 4.21 mmol) was dissolved in pentane (10 mL), and diazoketone **1a** (1.130 g, 4.00 mmol) was added. After stirring during 3.5 h at room temperature, the solvent was removed at 0.002 mbar. Bulb-to-bulb distillation at 95 °C / 0.002 mbar yielded **16** (1.515 g, 99 % based on **1a**) as a nearly colorless oil. - ^{1}H NMR (C_6D_6): δ 1.17 (d, $^3J_{(H,H)}$ = 7.5 Hz, 18H, CH(C<u>H</u>$_3$)$_2$), 1.40 (s, 9H, C(CH$_3$)$_3$), 1.47 (d, $J_{(P,H)}$ = 0.6 Hz, 9H, C(CH$_3$)$_3$), 1.73 (sept, $^3J_{(H,H)}$ = 7.5 Hz, 3H, C<u>H</u>(CH$_3$)$_2$).- ^{13}C NMR (C_6D_6) δ 14.6 (s, SiCH), 18.8 (s, SiCH<u>Me</u>$_2$), 29.4 (d, $J_{(P,C)}$ = 9.6 Hz, OCC<u>Me</u>$_3$), 32.3 (d, $^3J_{(P,C)}$ = 6.7 Hz, PCC<u>Me</u>$_3$), 36.4 (d, $^2J_{(P,C)}$ = 16.9 Hz, PC<u>C</u>Me$_3$), 44.2 (d, $^3J_{(P,C)}$ = 2.8 Hz, OC<u>C</u>Me$_3$), 172.0 (d, $^1J_{(P,C)}$ = 59.0 Hz, <u>C</u>-C=O), 191.7 (d, $^1J_{(P,C)}$ = 61.6 Hz, P<u>C</u>CMe$_3$), 201.4 (d, $^2J_{(P,C)}$ = 20.2 Hz, C=O). - IR (neat): 1645 (C=O). - Anal. Calcd. for $C_{20}H_{39}N_2OPSi$: C, 62.79; H, 10.27; N, 7.32. Found: C, 62.2; H, 10.2; N, 7.9.

(*E*)-4-(1,1-Dimethylethyl)-4,5-dihydro-5-[2,2-dimethyl-1-(triisopropylsilyloxy)propylidene]-3-phenyl-1-trimethylsilyl-1*H*-1,2,4-diazaphosphole (19a): Phosphaalkene **17** (605 mg, 2.42 mmol) was dissolved in pentane (10 mL), followed by addition of **1a** (683 mg, 2.42 mmol). The solution was stirred for 16 h, and the solvent was removed at 20 °C / 0.005 mbar. The remaining weakly fluorescent yellow oil was very moisture-sensitive and consisted of **19a** which in solution is in a dynamic equilibrium with other isomers present in low concentration (see text). - ^{1}H NMR δ 0.39 (s, 9H, Si(CH$_3$)$_3$), 1.02 (d, $^3J_{(P,H)}$ = 10.7 Hz, 9H, PC(CH$_3$)$_3$), 1.07, 1.11 (d, $^3J_{(H,H)}$ = 7.5 Hz, 9H, CHC<u>H</u>$_3$), 1.39 (sept, $^3J_{(H,H)}$ = 7.5 Hz, 3H, C<u>H</u>CH$_3$), 1.44 (s, 9H, =CC(CH$_3$)$_3$), 7.23 (t, $^3J_{(H,H)}$ = 7.3 Hz, 1H, *p*-H), 7.33 (t, $^3J_{(H,H)}$ = 7.5 Hz, 2H, *m*-H), 7.81 (d, $^3J_{(H,H)}$ = 8.0 Hz, 2H, *o*-H). - ^{13}C NMR (238 K) δ 1.1 (s, SiMe$_3$), 15.2 (s, SiCH), 18.5, 18.7 (s, SiCH<u>Me</u>), 31.1 (d, $^4J_{(P,C)}$ = 8.5 Hz, =CC<u>Me</u>$_3$), 31.2 (d, $^2J_{(P,C)}$ = 12.0 Hz, PC<u>Me</u>$_3$), 34.2 (d, $^1J_{(P,C)}$ = 34.9 Hz, P<u>C</u>Me$_3$), 38.3 (s, =C<u>C</u>Me$_3$), 127.2 (s, *p*-C), 127.40 (d, $^1J_{(P,C)}$ = 25.0 Hz, P<u>C</u>=C), 127.42 (d, $^3J_{(P,C)}$ = 7.2 Hz, *o*-C), 128.2 (s, *m*-C), 137.9 (d, $^2J_{(P,C)}$ = 19.6 Hz, *i*-C), 156.3 (d, $^2J_{(P,C)}$ = 26.2 Hz, =C-O), 160.6 (d, $^1J_{(P,C)}$ = 47.3 Hz, C=N). - ^{31}P NMR (298 K) δ 35.2 - Anal. Calcd. for $C_{29}H_{53}N_2OPSi_2$: C, 65.36; H, 10.02; N, 5.26. Found: C, 64.7; H, 9.7; N, 5.1.

4-(1,1-Dimethylethyl)-4,5-dihydro-5-{2,2-dimethyl-1-[dimethyl-(1,1-dimethylethyl)silyloxy]propylidene}-3-phenyl-1-trimethylsilyl-1*H*-1,2,4-diazaphosphole (19d): To a solution of **17** (630 mg, 2.52 mmol) in pentane (10 mL) was added **1d** (605 mg, 2.52 mmol). The mixture was stirred at room temperature for 16 h. Concentration under reduced pressure furnished a mixture of *E*- and *Z*-**19d** and small amounts of at least two other isomers; according to temperature-dependent NMR spectra, all isomers are in a dynamic equilibrium (see text); yield: 1.225 g (100 %). NMR data of *E*- and *Z*-**19d**: - ^{1}H NMR (328 K), *Z*-**19d** (major isomer): δ 0.25 (s, 3H, SiCH$_3$), 0.28 (s, 9H, Si(CH$_3$)$_3$), 0.48 (d, $^6J_{(P,H)}$ = 2.5 Hz, 3H, SiCH$_3$), 1.02 (s, 9H, C(CH$_3$)$_3$), 1.04 (d, ^3J = 11.7 Hz, 9H, PC(CH$_3$)$_3$), 1.32 (s, 9H, C(CH$_3$)$_3$), 7.20 - 7.24 (m, 1H, Ph, and 1H, Ph of minor isomer), 7.27 - 7.33 (m, 2H, Ph; and 2H, Ph of minor isomer), 7.70 - 7.72 (m, 2H, Ph). - *E*-**19d** (minor isomer): δ 0.16 (s, 3H, SiCH$_3$)), 0.19 (s, broadened by coalescence, 3H, SiCH$_3$), 0.33 (s, 9H, Si(CH$_3$)$_3$), 0.97 (d, $^3J_{(P,H)}$ = 11.3 Hz, 9H, P(CH$_3$)$_3$), 1.01 (s, 9H, C(CH$_3$)$_3$), 1.37 (s, 9H, C(CH$_3$)$_3$), 7.20 - 7.24 (m, 1H, Ph, and 1H of major isomer), 7.27 - 7.33 (m, 2H, Ph, and 2H, Ph major isomer), 7.79 - 7.82 (m, 2H, Ph). - ^{13}C NMR (328 K), *Z*-**19d** (major isomer): δ -2.5 (s, SiMe), -0.2 (d, $^5J_{(P,C)}$ = 18.3 Hz, SiMe), 1.4 (s, SiMe$_3$), 19.3 (s, Si<u>C</u>Me$_3$), 27.0 (s, C<u>Me</u>$_3$), 29.5 (d, $^2J_{(P,C)}$ = 12.2 Hz, PC<u>Me</u>$_3$), 30.4 (s, C<u>Me</u>$_3$), 39.2 (d, $^1J_{(P,C)}$ = 29.5 Hz, P<u>C</u>Me$_3$), 39.8 (s, =C<u>C</u>Me$_3$), 126.8 (d, $^3J_{(P,C)}$ = 7.0 Hz, *o*-C), 127.7 (s, *p*-C), 128.2 (s, *m*-C), 137.8 (d, $^2J_{(P,C)}$ = 20.6 Hz, *i*-C), 137.9 (d, $^1J_{(P,C)}$ = 28.6 Hz, P<u>C</u>-C), 148.5 (d, $^2J_{(P,C)}$ = 19.0 Hz, =C-O), 158.4 (d, $^1J_{(P,C)}$ = 28.2 Hz, C-N). - *E*-**19d** (minor isomer): δ -1.3 (s, SiMe), -1.1 (s, broadened by coalescence, SiMe), 1.5 (s, SiMe$_3$), 19.5 (s, Si<u>C</u>Me$_3$), 27.4 (s, C<u>Me</u>$_3$), 29.9 (d, $^2J_{(P,C)}$ = 11.9 Hz, PC<u>Me</u>$_3$), 31.5 (d, $^4J_{(P,C)}$ = 9.3 Hz, =CC<u>Me</u>$_3$), 35.6 (d, $^1J_{(P,C)}$ = 32.7 Hz, P<u>C</u>Me$_3$), 38.4 (d, $^3J_{(P,C)}$ = 1.5 Hz, =C<u>C</u>Me$_3$), 127.5 (s, *p*-C), 127.6 (d, $^3J_{(P,C)}$ = 7.5 Hz, *o*-C), 128.3 (s, *m*-C), 137.9 (d, $^1J_{(P,C)}$ = 28.6 Hz, P<u>C</u>=C), 138.1 (d, $^1J_{(P,C)}$ = 21.2 Hz, *i*-C), 148.5 (d, $^2J_{(P,C)}$ = 19.0 Hz, =C-O), 156.3 (d, $^1J_{((P,C)}$ = 27.2 Hz, C=N). - ^{31}P NMR (298 - 323 K): δ 35.2. - Anal. Calcd. for $C_{26}H_{47}N_2OPSi$: C, 63.63; H, 9.65; N, 5.71. Found: C, 63.4; H,10.0; N, 5.3.

(*E*)-4-(1,1-Dimethylethyl)-4,5-dihydro-5-[2,2-dimethyl-1-(triisopropylsilyloxy)propylidene]-3-phenyl-1*H*-1,2,4-diazaphosphole (20): Silica gel (10 g, Macherey & Nagel, 0.063 - 0.2 mm) was dissolved in water (2 mL, 0.111 mol). A solution of **19a** (1.239 g, 2.33 mmol) in pentane (20 mL) was added, and the solution was stirred for 3.5 h. The silica gel was filtered off and washed several times with diethyl ether. The volatile components were removed at 20 °C / 0.003 mbar, and the diazaphosphole **20** was obtained by crystallization from pentane at -78 °C as a yellow powder that shows a strong greenish fluorescence; yield 857 mg (80 %); mp. 82 °C. - ^{1}H NMR δ 0.96 (d, $^3J_{(P,H)}$ = 12.0 Hz, 9H, PC(CH$_3$)$_3$), 1.18 (d, $^3J_{(H,H)}$ = 7.4 Hz, 18H,

$CH(C\underline{H}_3)_2$), 1.30 (d, $^5J_{(P,H)}$ = 1.1 Hz, 9H, $=CC(CH_3)_3$), 1.40 (sept, $^3J_{(H,H)}$ = 7.4 Hz, 3H, $C\underline{H}CH_3$), 7.24 (t, $^3J_{(H,H)}$ = 7.3 Hz, 1H, *p*-H), 7.32 (t, $^3J_{(H,H)}$ = 7.5 Hz, 2H, *m*-H), 7.71(d, $^3J_{(P,H)}$ = 1.1 Hz, 1H, NH), 7.77 - 7.80 (m, 2H, *o*-H). - ^{13}C NMR δ 14.3 (s, SiCH), 18.4, 18.5 (s, $SiCH\underline{Me}$), 28.4 (d, $^2J_{(P,C)}$ = 13.0 Hz, $PC\underline{Me}_3$), 30.9 (d, $^4J_{(P,C)}$ = 9.8 Hz, $=CC\underline{Me}_3$), 35.4 (d, $^1J_{(P,C)}$ = 26.7 Hz, $P\underline{C}Me_3$), 37.6 (d, $^3J_{(P,C)}$ = 2.4 Hz, $=C\underline{C}Me_3$), 124.9 (d, $^1J_{(P,C)}$ = 26.5 Hz, $P\underline{C}$=C), 127.0 (d, $^3J_{(P,C)}$ = 7.7 Hz, *o*-C), 127.8 (s), 128.4 (s), 137.0 (d, $^2J_{(P,C)}$ = 20.9 Hz, *i*-C), 149.5 (d, $^1J_{(P,C)}$ = 25.0 Hz), 153.0 (d, $^2J_{(P,C)}$ = 29.5 Hz). ^{31}P NMR δ -10.0. - IR (KBr) 3370 (NH). - Anal. Calcd. for $C_{26}H_{45}N_2OPSi$: C, 67.78; H, 9.84; N, 6.08. Found: C, 67.7; H, 9.9; N, 6.1.

(*E*)-4-(1,1-Dimethylethyl)-4,5-dihydro-5-(2,2-dimethyl-1-(triisopropylsilyloxy)propylidene)-3-phenyl-1*H*-1,2,4-diazaphosphole-4-sulfide (21): To a solution of **20** (450 mg, 0.98 mmol) in dichloromethane (5 mL) was added silica gel (2 g, Macherey & Nagel, 0.063 - 0.2 mm) and sulfur (32 mg, 1.00 mmol). The suspension was stirred for 7 d at room temperature. The silica gel was filtered off and washed several times with diethyl ether. Evaporation of the solvent at 20 °C / 0.005 mbar and crystallization of the residue from pentane at -78 °C yielded **21** (350 mg, 73 % based on **20**) as a yellow powder; mp. 157 °C. ^{1}H NMR δ 1.12 (d, $^3J_{(P,H)}$ = 18.5 Hz, 9H, $PC(CH_3)_3$), 1.18 (d, $^3J_{(H,H)}$ = 7.5 Hz, 18H, $CH(C\underline{H}_3)_2$), 1.40 (sept, $^3J_{(H,H)}$ = 7.5 Hz, 3H, $C\underline{H}CH_3$), 1.43 (s, 9H, $=CC(CH_3)_3$), 7.28 - 7.34 (m, 3H, *m*- und *p*-H), 7.72 (d, $^3J_{(P,H)}$ = 9.7 Hz, 1H, NH), 8.18 - 8.20 (m, 2H, *o*-H). - ^{13}C NMR δ 14.1 (s, SiCH), 18.2 (s, $SiCH\underline{Me}_2$), 25.4 (d, $^2J_{(P,C)}$ = 2.8 Hz, $PC\underline{Me}_3$), 30.7 (s, $=CC\underline{Me}_3$), 38.6 (s, $=C\underline{C}Me_3$), 40.0 (d, $^1J_{(P,C)}$ = 51.6 Hz, $P\underline{C}Me_3$), 120.2 (d, $^1J_{(P,C)}$ = 91.3 Hz, $P\underline{C}$=C), 126.4 (d, $^3J_{(P,C)}$ = 2.7 Hz, *o*-C), 128.0 (s, *m*-C), 128.2 (s, *p*-C), 135.2 (d, $^2J_{(P,C)}$ = 19.2 Hz, *i*-C), 141.5 (d, $^1J_{(P,C)}$ = 54.8 Hz, C=N), 159.1 (d, $^2J_{(P,C)}$ = 19.2 Hz, =C-O). - ^{31}P-NMR ($CDCl_3$, 162.0 MHz): δ 55.0. - IR (KBr) 3370 (s, N-H). - Anal. Calcd. for $C_{26}H_{45}N_2OPSSi$: C, 63.37; H, 9.20; N, 5.68. Found: C, 63.6; H, 9.1; N, 5.7.

5-Phenyl-3-(1-triisopropylsilyloxy-2,2-dimethylpropyl)-1-trimethylsilyl-1*H*-1,2,4-diazaphosphole (22a): Diazaphosphole **19a** (580 mg, 1.09 mmol) was heated in a bulb-to-bulb distillation apparatus at 165 °C / 0.005 mbar. An orange oil started to distill which was collected and purified by fractionating bulb-to-bulb distillation at 140 °C / 0.004 mbar to give **22a** as a yellow oil; yield: 430 mg (83 %). - ^{1}H NMR δ 0.18 (s, 9H, $Si(CH_3)_3$), 0.97 - 1.02 (m_c, 30H, $C\underline{H}(C\underline{H}_3)_2$ and $C(CH_3)_3$), 4.80 (d, $^3J_{(P,H)}$ = 8.5 Hz, 1H, O-CH), 7.32 - 7.37 (m_c, 5H, Ph). - ^{13}C NMR δ 1.0 (s, $SiMe_3$), 13.0 (s, SiCH), 18.2 (s, $SiCH\underline{Me}_2$), 26.4 (d, $^4J_{(P,C)}$ = 3.9 Hz, $C\underline{Me}_3$), 36.0 (s, $\underline{C}Me_3$), 81.5 (d, $^2J_{(P,C)}$ = 15.0 Hz, CO), 127.8 (s), 128.5 (s), 129.7 (d, $^3J_{(P,C)}$ = 5.6 Hz, *o*-C), 135.0 (d, $^2J_{(P,C)}$ = 19.6 Hz, *i*-C), 182.6 (d, $^1J_{(P,C)}$ = 48.8 Hz), 182.8 (d, $^1J_{(P,C)}$ = 63.8 Hz). - ^{31}P-NMR δ 100.1. - Anal. Calcd. for $C_{25}H_{45}N_2OPSi_2$: C, 62.98; H, 9.51; N, 5.88. Found: C, 62.6; H, 9.3; N, 5.9.

3-{1-[(1,1-Dimethylethyl)dimethylsilyloxy]-2,2-dimethylpropyl}-5-phenyl-1-trimethylsilyl-1*H*-1,2,4-diazaphosphole (22d): 19d (600 mg, 1.22 mmol) was subjected to bulb-to-bulb distillation at 150 °C / 0.005 mbar to give a light-green oil. Purification by another fractionating bulb-to-bulb distillation (110 °C / 0.005 mbar) afforded **22d** as a yellow oil; yield: 404 mg (76 %). - ^{1}H NMR δ -0.15, 0.10 (s, 3H, $SiCH_3$), 0.26 (s, 9H, $Si(CH_3)_3$), 0.94, 1.01 (s, 9H, $C(CH_3)_3$), 4.64 (d, $^3J_{(P,H)}$ = 7.8 Hz, 1H, O-CH), 7.41 (br, s, 5H, Ph). - ^{13}C NMR δ -5.0 (s, SiMe), -4.4 (d, $^5J_{(P,C)}$ = 2.3 Hz, SiMe), 1.1 (s, $SiMe_3$), 18.1 (s, $Si\underline{C}Me_3$), 26.0 (s, $SiC\underline{Me}_3$), 26.2 (d, $^4J_{(P,C)}$ = 3.0 Hz, $CC\underline{Me}_3$), 35.6 (s, $C\underline{C}Me_3$), 80.9 (d, $^2J_{(P,C)}$ = 14.4 Hz, CO), 127.8 (s), 128.5 (s), 129.6 (d, $^3J_{(P,C)}$ = 5.5 Hz, *o*-C), 135.1 (d, $^2J_{(P,C)}$ = 19.9 Hz, *i*-C), 182.9 (d, $^1J_{(P,C)}$ = 48.9 Hz), 183.5 (d, $^1J_{(P,C)}$ = 62.6 Hz). - ^{31}P-NMR δ 99.9 (s). - Anal. Calcd. for $C_{22}H_{39}N_2OPSi_2$: C, 60.79; H, 9.04; N, 6.44. Found: C, 60.9; H, 9.0; N, 6.5.

5-Phenyl-3-(1-triisopropylsilyloxy-2,2-dimethylpropyl)-1*H*-1,2,4-diazaphosphole (23a): Diazaphosphole **22a** (396 mg, 0.83 mmol) was dissolved in moist pentane (30 mL), and the reaction mixture was allowed to stand for 6 h in contact with air. After evaporation of the solvent at 20 °C / 0.003 mbar and crystallization from dichloromethane at -78 °C, **23a** was obtained as a colorless powder; yield: 295 mg (88 %); mp. 79 °C. - ^{1}H NMR δ 0.99 - 1.04 (m, 30H, C<u>H</u>(C<u>H</u>$_3$)$_2$ and C(CH$_3$)$_3$), 4.97 (d, $^3J_{(P,H)}$ = 4.3 Hz, 1H, O-CH), 7.33 (t, $^3J_{(H,H)}$ = 7.2 Hz, 1H, *p*-H), 7.39 (t, $^3J_{(H,H)}$ = 7.3 Hz, 2H, *m*-H), 7.87 (d, $^3J_{(H,H)}$ = 7.9 Hz, 2H, *o*-H), 11.01 (br, s, 1H, NH). - ^{13}C NMR δ 12.7 (s, SiCH), 18.1 (s, SiCH<u>Me</u>$_2$), 26.2 (d, $^4J_{(P,C)}$ = 2.4 Hz, C<u>Me</u>$_3$), 36.4 (d, $^3J_{(P,C)}$ = 2.5 Hz, C<u>Me</u>$_3$), 79.2 (d, $^2J_{(P,C)}$ = 16.4 Hz, CO), 126.2 (d, $^3J_{(P,C)}$ = 9.7 Hz, *o*-C), 128.6 (s), 128.7 (s), 135.1 (d, $^2J_{(P,C)}$ = 18.9 Hz, *i*-C), 177.1 (d, $^1J_{(P,C)}$ = 58.4 Hz, P<u>C</u>), 178.1 (d, $^1J_{(P,C)}$ = 57.9 Hz, P<u>C</u>). - ^{31}P NMR δ = 79.1 (s). - IR (KBr) 3170 (N-H). - Anal. Calcd. for $C_{22}H_{37}N_2OPSi$: C, 65.31; H, 9.22; N, 6.92. Found: C, 64.6; H, 9.1; N, 6.7.

3-{1-[(1,1-Dimethylethyl)dimethylsilyloxy]-2,2-dimethylpropyl}-5-phenyl-1*H*-1,2,4-diazaphosphole (23d): Diazaphosphole **22d** (400 mg, 0.92 mmol) was dissolved in moist pentane (30 mL), and the reaction mixture was allowed to stand for 6 h in contact with air. After evaporation of the solvent at 20 °C / 0.003 mbar and crystallization from pentane at -78 °C, **23d** was obtained as colorless crystals; yield: 304 mg (91 %); mp. 97 °C. - ^{1}H NMR (330 K): δ -0.13, 0.11 (s, 3H, SiCH$_3$), 0.94, 0.99 (s, 9H, C(CH$_3$)$_3$), 4.78 (d, $^3J_{(P,H)}$ = 4.6 Hz, 1H, O-CH), 7.32 (t, $^3J_{(H,H)}$ = 7.3 Hz, 1H, *p*-H), 7.39 (t, $^3J_{(H,H)}$ = 7.3 Hz, 2H, *m*-H), 7.88 (d, $^3J_{(H,H)}$ = 7.7 Hz, 2H, *o*-H), 10.99 (br, s, 1H, NH). - ^{13}C NMR (330 K) δ -5.1, -4.8 (s, SiMe), 18.2 (s, Si<u>C</u>Me$_3$), 25.9 (s, SiC<u>Me</u>$_3$), 26.1 (d, $^4J_{(P,C)}$ = 2.7 Hz, CC<u>Me</u>$_3$), 36.1 (d, $^3J_{(P,C)}$ = 1.7 Hz, C<u>C</u>Me$_3$), 78.9 (d, $^2J_{(P,C)}$ = 17.0 Hz, CO), 126.3 (d, $^3J_{(P,C)}$ = 9.7 Hz, *o*-C), 128.6 (s), 128.8 (s), 135.7 (d, $^2J_{(P,C)}$ = 19.3 Hz, *i*-C), 177.6 (d, $^1J_{(P,C)}$ = 58.3 Hz, P<u>C</u>), 177.8 (d, $^1J_{(P,C)}$ = 59.3 Hz, P<u>C</u>). ^{31}P NMR δ 76.2. - IR (KBr) 3210 (N-H). - Anal. Calcd. for $C_{19}H_{31}N_2OPSi$: C, 62.95; H, 8.62; N, 7.73. Found: C, 63.2; H, 8.7; N, 7.8.

***X-Ray Crystal Structure Analysis of 4a*[32]**

Crystal Data: $C_{37}H_{51}N_2OPSi$, f. w. 598.86, triclinic, space group $P\bar{1}$; a = 10.461(2), b = 18.225(4), c = 20.409(4) Å; α = 67.68(3), β = 85.92(3), γ = 81.50(3) °; V = 3559.5(12) Å^3, Z = 4, D_x = 1.118 g·cm^{-3}; μ(Mo-K$_\alpha$) = 0.140 mm^{-1}, crystal size 0.4 x 0.2 x 0.5 mm. - *Data collection*: T = 293 K, diffractometer Siemens P4, monochromatized Mo-K$_\alpha$ radiation, ω-scans, 7335 independent reflections in the range 1.91 ≤ θ ≤ 21.00°; no absorption correction. - *Structure solution and refinement*: Structure solution by *SHELXS-86*, full-matrix least-squares refinement on F^2 (program SHELXLS-93[33]) with 781 variables. Hydrogen atoms are in calculated positions and and were treated as riding atoms. R1 = 0.1126 for all reflections (0.0578 for 4438 observed reflections, I > 2σ(I)), wR2 = 0.1457 (0.1193), residual electron density between 0.21 and -0.19 e Å^{-3}.

***X-Ray Crystal Structure Analysis of 10a*[32, 34]**

Crystal Data: $C_{27}H_{48}N_3OPSi$, f. w. 489.74, monoclinic, space group $P2_1/n$; a = 8.761(7), b = 15.503(5), c = 22.461(12) Å; α = γ = 90 °, β = 99.39(3) °; V = 3010(3) Å^3, Z = 4, D_x = 1.081 g·cm^{-3}; μ(Mo-K$_\alpha$) = 0.153 mm^{-1}; crystal size 0.35 x 0.25 x 0.6 mm. - *Data collection*: T = 293 K; diffractometer Enraf-Nonius CAD4, monochromatized Mo-K$_\alpha$ radiation; ω/2θ-scans, scan width (0.90 + 0.35 tan θ) °; 4392 independent reflections in the range 2.26 ≤ θ ≤ 23.47°; no absorption correction. - *Structure solution and refinement*: Structure solution by *MULTAN*, full-matrix least-squares refinement on F^2 (program SHELXLS-93[33]) with 312 variables. Hydrogen atoms are in calculated positions and and were treated as riding atoms. R1 = 0.1219

for all reflections (0.0639 for 2644 observed reflections, $I > 2\sigma(I)$), wR2 = 0.1578 (0.1165), residual electron density between 0.21 and -0.21 e $Å^{-3}$.

ACKNOWLEDGEMENT

We are grateful to the Deutsche Forschungsgemeinschaft for financial support.

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(*Received in Germany* 25 *April* 1996; *accepted* 5 *June* 1996)