Photochemical Isomerizations of 5-Alkylidene-4,5-dihydro-3*H*-1,2,4(λ^3)-diazaphospholes (4-Phosphapyrazolines): (5 → 4) Ring Contraction Generates Azomethineimine Dipoles

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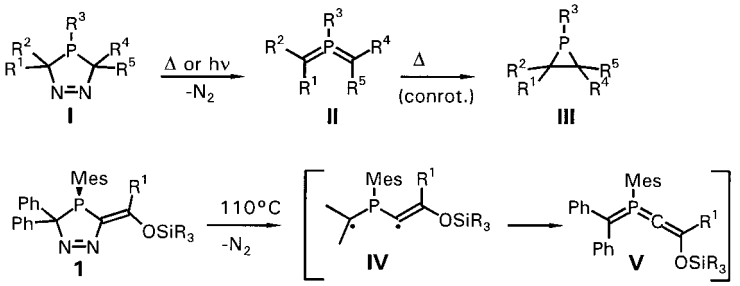
Abstract: UV irradiation of the title compounds **1a–d** results not in extrusion of molecular nitrogen, but in a skeletal rearrangement generating amino(imidoyl)-phosphanes **2a–c** from **1a–c** and 2-hydrazinobenzo[*b*]phosphole **4** from **1d**. The first step in these isomerizations is an unprecedented (5 → 4) ring contraction of **1** to form the semicyclic azomethineimine dipoles **10** incorporating a 1,2,3-diazaphosphetidine ring. Dipoles **10a–c**, but not **10d**, can be observed by NMR spectroscopy after brief irradiation of the precursors. Furthermore, they could be trapped by [3+2] cycloaddition reaction with dimethyl acetylenedicarboxylate to give the bicyclic 1,2,3-diazaphosphetidines **12a–c**, and, in the case of **10a** and **10c**, also the dihydrophospholes **13a**,**c** resulting from a second [3+2] cycloaddition.

Keywords: azomethineimines · 1,2,4-diazaphospholes · phosphorus · phosphorus heterocycles · photolysis · rearrangements

Introduction

The thermally or photochemically induced extrusion of molecular nitrogen is an effective reaction for many 1-pyrazolines[1] and constitutes an approved strategy in cyclopropane synthesis.[2] The analogous elimination of N_2 from 4-phosphapyrazolines **I** has recently been introduced as a convenient route to bis(alkylidene)-phosphoranes **II** or phosphiranes **III**. Typically, these transformations of **I** have been performed under thermal conditions (elevated temperature[3] or at $\leq 20\,^{\circ}C$ during the synthesis of **I** from a phosphaalkene and a diazo compound[3b,3c,4]), and there seems to be only one reported example of a photochemically induced extrusion of N_2 from **I**[5] ($R^1 = R^4 = H$; $R^2 = R^5 = SiMe_3$, $R^3 = N(SiMe_3)_2$). Evidently, the remarkably low thermal stability of various 4-phosphapyrazolines **I** prevents a systematic comparison of thermal and photochemical nitrogen-elimination reactions.



Scheme 1. Mes = 2,4,6-$Me_3C_6H_2$.

We have recently found that 4-alkylidene-4,5-dihydro-3*H*-1,2,4(λ^3)-diazaphospholes **1**, easily obtained by [3+2] cycloaddition of 1-diazo-2-siloxyethenes to phosphaalkenes,[6] are distinctly more thermally stable than similar 4-phosphapyrazolines **I** lacking the exocyclic double bond. Nevertheless, extrusion of molecular nitrogen from **1** (R^1 = *t*Bu, 1-adamantyl, Me, 4-anisyl, 4-nitrophenyl) can be achieved in boiling toluene.[7,8] Depending on the substituents, vinylphosphanes, benzo[*c*]phosphole derivatives, alkylidenephosphiranes, or 1,3-oxaphospholes are formed, and we have proposed that the products are derived from intermediate 1,3-diradicals **IV** and methylene(vinylidene)phosphoranes **V.**

We now report that none of the products formed upon thermolysis of 4-phosphapyrazolines **1** is found under photochemical conditions. Surprisingly, UV irradiation of **1** did not lead to N_2 elimination but rather to skeletal rearrangements, with a (5 → 4) ring contraction as the initial product-forming step.

Results

The UV spectrum of **1a** in dichloromethane shows absorption maxima at $\lambda = 337$ nm (log $\varepsilon = 3.58$) and 254 nm (4.34); in pentane $\lambda_{max} = 326$ nm (3.49). When solutions of 4-alkylidene-

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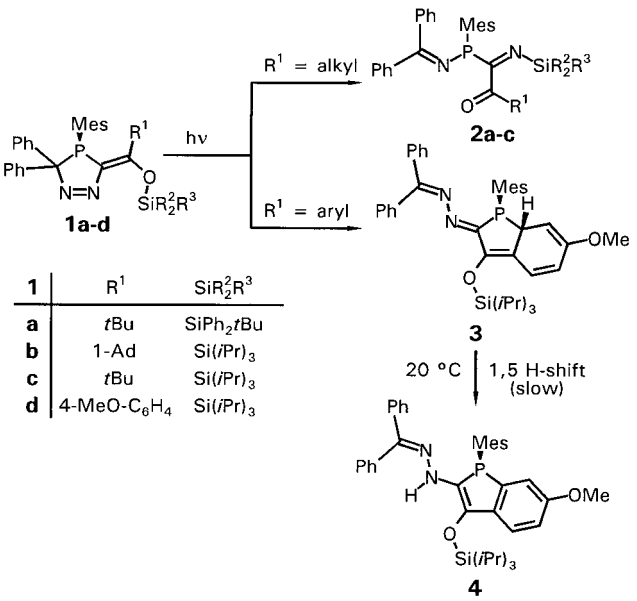
4,5-dihydro-3*H*-1,2,4(λ^3)-diazaphospholes **1a–d** in pentane or ether were irradiated with a high-pressure mercury lamp ($\lambda \geq$ 300 nm) at temperatures between -40 and 0 °C, no evolution of molecular nitrogen was observed. Nevertheless, ^{31}P NMR spectra indicated a rather clean transformation in all cases. In the case of **1a–c**, a transient red color was observed during irradiation, and the amino(imidoyl)phosphanes **2a–c** were isolated in good yields after workup. A different result was



1	R^1	$SiR^2_2R^3$
a	*t*Bu	$SiPh_2$*t*Bu
b	1-Ad	Si(*i*Pr)$_3$
c	*t*Bu	Si(*i*Pr)$_3$
d	4-MeO-C$_6$H$_4$	Si(*i*Pr)$_3$

Scheme 2.

obtained with **1d**, which bears an aryl ring at the exocyclic double bond. When the reaction mixture was worked up at 20 °C immediately after complete conversion of **1d**, a mixture of 2-hydrazinobenzo[*b*]phosphole **4** and its nonaromatic isomer **3** (vide infra) was obtained; however, after leaving the reaction mixture alone for 24 h, complete isomerization **3**→**4** had occurred. Thus, **3** is the direct photoisomerization product from **1d**, while **4** results from a subsequent thermal isomerization by a formal 1,5 hydrogen shift. This latter reaction presumably proceeds in a bimolecular fashion rather than as an intramolecular pericyclic process due to the difficulty in adopting the cyclic transition state of a 1,5-sigmatropic shift.

The constitution of the amino(imidoyl)phosphanes was established by single crystal X-ray structure analysis of **2a**. In this structure (Figure 1; see Table 2), the phosphorus atom has a pyramidal coordination; the C=O and the two C–N double bonds show no sign of bond elongation, and the P1–N1 and P1–C23 bond lengths correspond to typical single bonds. Thus, there is no indication of π conjugation in the C1–N1–P1–C23–N2 chain (the C=O/C=N π system is also electronically decoupled judging by the torsion angle), although the torsion angles around the N1–P1 and P1–C23 bonds (Figure 2) suggest a certain degree of overlap of the nonbonding sp^3 orbital at phosphorus with the two adjacent π systems.

The ^{31}P NMR chemical shifts of compounds **2a–c** are in the expected range for aminophosphanes ($\delta = 44.8–45.7$), but

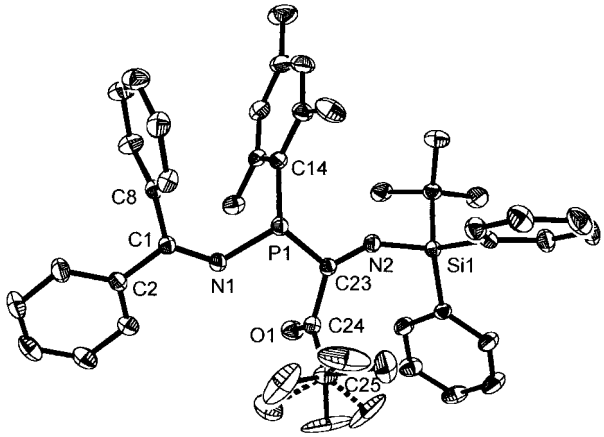


Figure 1. Molecular structure of **2a**; the disorder of the *tert*-butyl group attached to C24 is shown. Selected bond lengths [Å] and angles [°]: C1–C2 1.474(4), C1–C8 1.478(4), C1–N1 1.261(4), N1–P1 1.691(3), P1–C14 1.822(3), P1–C23 1.838(3), C23–N2 1.241(3), N2–Si1 1.702(3), C24–O1 1.187(4), C24–C25 1.522(5); C1-N1-P1 124.6(2), N1-P1-C14 108.6(1), N1-P1-C23 99.0(1), C14-P1-C23 100.3(1), C23-N2-Si1 147.4(2).

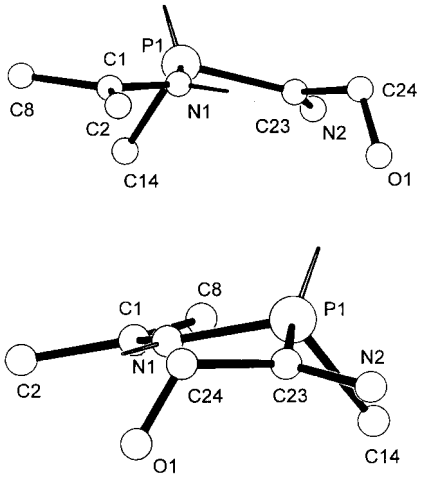


Figure 2. Torsion angles at the N1–P1 (top), C23–P1 and C23–C24 (bottom) bonds of **2a**. The direction of the lone pairs of electrons at P1(lp_P) and N1 (lp_N) is represented by narrow, open rods; for calculation of torsion angles, lp_P and lp_N were mimicked by dummy hydrogen atoms placed in calculated positions. Torsion angles [°]: P1-N1-C1-C2 –179.8(2), C14-P1-N1-C1 –63.1(3), lp_N-N1-P1-lp_P –111, C1-N1-P1-lp_P 69, N1-P1-C23-N2 159.8(2), lp_P-P1-C23-N2 –76, lp_P-P1-C23-C24 101, N2-C23-C24-O1 –83.3(4).

some noteworthy spectroscopic features are seen in the ^{13}C NMR spectra. The two imine-C resonances ($\delta(CPh_2) =$ 169.8–170.2; δ(P*C*=N) = 192.3–197.7) appear at rather low field. The observation of only one set of signals for the two phenyl groups of the diphenylmethyleneamino moiety at 298 K indicates a fast stereomutation at the C–N double bond. The lowering of the inversion barrier at the N atom of imines by less electronegative second and higher row main group elements attached to the nitrogen is well known. Although the phenomenon seems not to have been studied for *N*-phosphinoimines, it was investigated for related *N*-[alkyl(or aryl)thio]imines, and it was suggested that the effect is caused by a stabilizing interaction in the linear transition state between the occupied nonbonding *p* orbital at N and empty *d*

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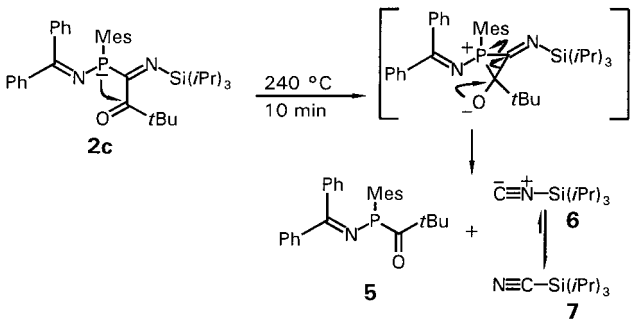
and/or σ^* orbitals at the heteroatom.[9] While we did not try to render the imine inversion observable by lowering the temperature, two other dynamic processes were apparent from the temperature-dependent ^{13}C NMR spectra. Some signals of the mesityl group (*o*-C, *m*-C, *o*-CH_3) are in coalescence at 298 K (101 MHz spectrum), while the averaged (but in most cases still broadened) signals could be seen at 328 K. We attribute this phenomenon to a hindered rotation of the mesityl ring around the P–C bond, while the averaging of signals for diastereotopic substituents in the silyl group (i.e. the *o*- and *m*-C signals of the two Si-attached phenyl groups in **2a** and of the isopropyl-Me groups in **2b**) in the same temperature range indicates the occurrence of pyramidal inversion at the phosphorus atom.

The amino(imidoyl)phosphanes **2a–c** are very moisture-sensitive, but can be isolated from the reaction mixture and purified by crystallization. An attempt to purify **2c** by bulb-to-bulb vacuum distillation resulted in fragmentation into acylphosphane **5** and triisopropylsilyl cyanide (**7**). This transformation starts above 150 °C and is rapid at 240 °C. We propose (Scheme 3) that the initial step of the fragmentation reaction is nucleophilic attack by the phosphorus atom at the carbonyl group, followed by elimination of triisopropylsilyl isocyanide (**6**). The latter compound rapidly equilibrates with



Scheme 3.

its thermodynamically more stable isomer **7**, which was identified by its IR spectrum.[10] The constitution of phosphane **5** was determined unambiguously by NMR spectroscopy. The ^{31}P signal ($\delta = 41.2$) and the ^{13}C NMR resonance for C=N [$\delta = 171.9$, $^2J(P,C) = 7.8$ Hz] as well as the magnetic equivalence of the two phenyl groups indicate the relationship with the aminophosphane moiety in **2**. The ^{13}C NMR data for the acylphosphane part of the molecule also correspond to expectations[11] [CMe_3: $\delta = 48.1$, $^2J(P,C) = 31.5$ Hz; C=O: $\delta = 227.5$, $^2J(P,C) = 49.8$ Hz].

The constitution of benzo[*b*]phosphole **4** was also determined by X-ray diffraction. The molecular structure of **4** (Figure 3; see Table 2) features close similarities with those of other phosphindoles containing a λ^3,σ^3 phosphorus atom.[12,13] The phosphole ring adopts an envelope conformation with P 0.30 Å from the C1-C2-C3-C8 plane and the mesityl ring in the equatorial position. Also typical are the pyramidal coordination at the P atom, a rather small endocyclic bond angle at P, and endocyclic P–C bond lengths somewhat shorter than the sum of the single-bond covalent radii

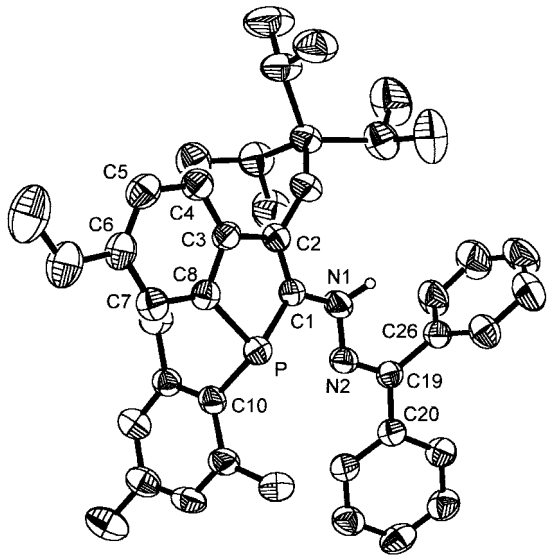
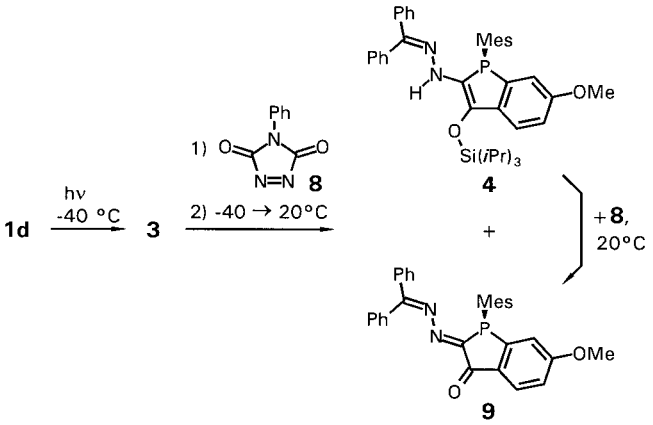


Figure 3. Molecular structure of **4**; ellipsoids of thermal vibration are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: P–C1 1.807(4), P–C8 1.798(4), P–C10 1.821(4), C1–C2 1.338(5), C2–C3 1.449(5), C3–C8 1.401(5); C8-P-C1 89.2(2), C8-P-C10 107.3(2), C1-P-C10 112.2(2).

(1.84 Å). Characteristic features of the structure are confirmed by the IR (3290 cm^{-1}, NH), ^{31}P NMR ($\delta = -32.8$), and ^{13}C NMR spectra of **4**. The ^{31}P resonance at much higher field than in typical phosphanes and low ^{31}P-^{13}C coupling constants (^1J and ^2J) in the phosphole ring meet the expectations.[14] In contrast to the imine stereomutation of (diphenylmethyleneamino)phosphanes **2** (vide supra), the two phenyl rings of the diphenylimine moiety in **4** are magnetically nonequivalent.

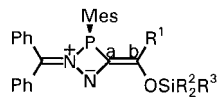
It was mentioned above that benzo[*b*]phosphole derivative **3** is the direct photoisomerization product resulting from **1d**, and **4** is a product of subsequent thermal isomerization. In fact, **3** could be obtained in nearly quantitative yield when the irradiation of **1d** was carried out at -40 °C in pentane followed by evaporation of the solvent at this temperature. The absence of significant amounts of by-products allowed a complete characterization by NMR spectroscopy that left no doubt about the constitution of **3**. A close similarity with published ^1H[15a] and ^{13}C[15b] NMR chemical shifts of 2-methoxycyclohexa-1,3-diene indicates the presence of this substructure in **3**. The ^{31}P chemical shift ($\delta = -23.1$) is in accord with the phospholene structure, but the magnitudes of the coupling constants ^2J(P,C-3) and ^1J(P,C-7a) (26.1 and ca. 0 Hz, respectively) are unusual. The ^2J value is larger than in 3-phospholenes without a 3-substituent for which a value of 3–5 Hz seems typical.[14b] The absence of ^1J(P,C-7a) coupling has precedence in another, partially saturated phosphindole, namely 1-methyl-2,3,4,5,6,7-hexahydrobenzo[*b*]phosphole (0 Hz, C-7a being sp^2-hybridized),[16a] while a value of 15 Hz has been reported for the structurally more closely related 1-methyl-2,4,5,6,7,7a-hexahydro-benzo[*b*]phosphole.[16b] In the proton-coupled ^{31}P NMR spectrum, only a singlet can be seen, that is no ^2J(P,7a-H) coupling is resolved. This points to an *anti* relationship between the C–H bond and the nonbonding pair of electrons at P,[17] or in other words to the *syn* arrangement of H-7 and the mesityl ring.

Our effort to characterize compound **3** either by a Diels–Alder or by an ene reaction with triazolinedione **8** failed. Instead, reaction of **3** with a slightly greater than stoichiometric amount of **8** at $-40\,^{\circ}C$ produced a mixture of **4** and **9** (Scheme 4). A control experiment showed that **9** is also formed when **4** is allowed to react with **8**. In the absence of kinetic data, it is not clear whether the isomerization **3** → **4** under the given conditions is merely a thermal process (see above) or is assisted by **8**; furthermore, it cannot be determined whether the dehydrosilylation reaction leading to **9** applies exclusively to **4** or also to **3**. We mention, however, that we have previously observed an oxidative desilylation of a 1,4-bis(siloxy)-1,3-butadiene by the highly electrophilic **8**.[18] As in this former study, the reaction details are a matter of speculation, especially since no reaction products derived from **8** could be identified.

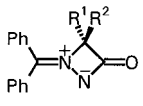


Scheme 4.

While it was surprising enough that UV irradiation of 4-phosphapyrazolines **1** did not lead to extrusion of molecular nitrogen, it was even more remarkable that the N–N double bond in **1a–c** was cleaved completely in the course of the isomerization, leading to **2**. A reasonable mechanism was proposed after an intermediate of the photoisomerization had been observed (Scheme 5): When solutions of **1a–c** were irradiated for a few minutes at $-40\,^{\circ}C$, they turned deep red, and the ^{31}P NMR spectrum indicated the presence of a new product [$\delta(^{31}P) = 160.0 - 161.9$], together with unconverted **1** and the corresponding amino(imidoyl)phosphane **2**. This reaction mixture was thermally stable even at room temperature for at least one day, and conversion of the new product into **2** was achieved only when the irradiation was continued (color change from red to yellow). The structures of the transient products were assigned as the photolabile azomethineiminedipoles **10a–c**, embedded in a 1,2,3-phosphadiazetidine. Since the dipoles could not be isolated by column chromatography, this proposal is based on NMR data recorded on the aforementioned reaction mixture (Table 1) and on the subsequent identification of cycloaddition products **12** (vide infra). The ^{31}P NMR resonance for **10a–c** is shifted downfield by about 46 ppm with respect to the bicyclic 1,2,3-diazaphosphetidines **12**, an effect likely caused by the electron-deficient iminium function attached to P. (An isomeric dipolar structure, with no P–N bond and a $\lambda^2\sigma^2$ phosphenium center, can be ruled out because phosphenium ions are known to react readily with Lewis bases;[19] i.e., P–N bond formation would immediately lead back to structure **10**).



10	R^1	$SiR^2_2R^3$
a	*t*Bu	$SiPh_2$*t*Bu
b	1-Ad	$Si(iPr)_3$
c	*t*Bu	$Si(iPr)_3$



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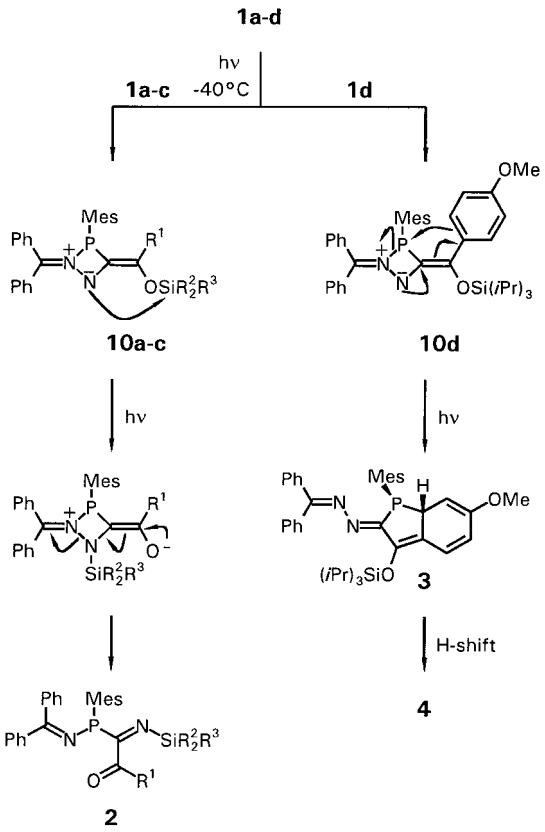

Scheme 5.

Table 1. Selected ^{31}P and ^{13}C NMR data of 1,2,3-diazaphosphetidines **10** and **12**.[a]

Compound	^{31}P NMR	^{13}C NMR		
		C^a[b]	C^b[b]	$Ph_2C{=}N$
10a	160.0		136.6–136.9[c]	
10b	161.6	121.4 (12.0)	142.1 (17.2)	145.5 (1.5)
10c[d]	161.9	121.9 (12.0)	141.7 (17.9)	146.1 (0)
12a	116.0	125.4 (3.8)	151.2 (8.6)	
12b	115.0	123.5 (5.7)	151.4 (9.1)	
12c	115.7	123.3 (6.6)	151.2 (9.3)	

[a] The solvent was $CDCl_3$ unless noted otherwise; δ values [ppm] are given. ^{31}P-^{13}C coupling constants [Hz] are given in parentheses. For definition of C^a and C^b, see formula. [b] Signals were assigned based on a gradient-selected HMBC experiment (cross-peak for C^b/CMe_3, but not for C^a/CMe_3)]. [c] Signal coincides with one of two signals of **2a**; the other ^{13}C signals of **10a** could not be assigned unambiguously due to their low intensity. [d] In C_6D_6.

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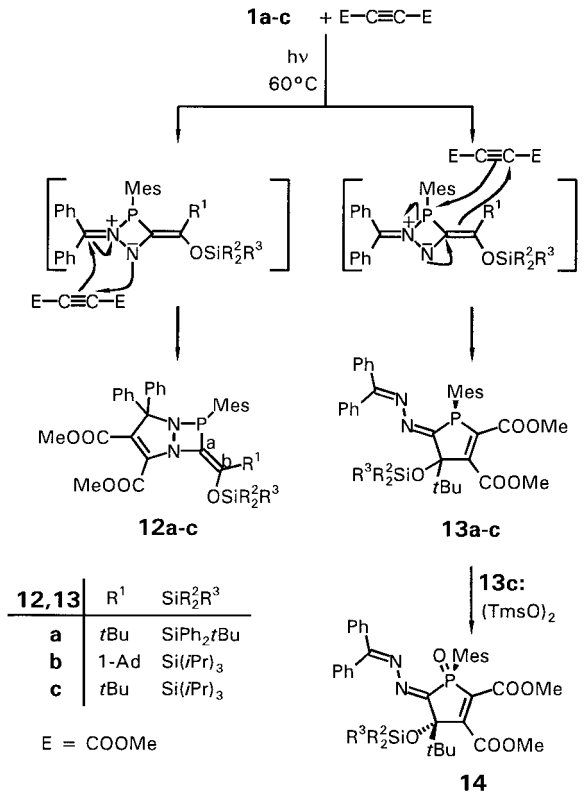
In the ^{13}C NMR spectra, the chemical shifts for the carbon atoms of the exocyclic double bond show significant changes with respect to those in **12**, corresponding to slight shielding of the ring carbon C-4 and significant shielding of the exocyclic carbon, in agreement with charge delocalization in the azaallyl anion moiety of the dipole.[20] The stereochemistry at the exocyclic double bond is the same as in the starting materials **1** (*E* configuration), as suggested by the observation of ^3J(P,C) and ^4J(P,C) couplings.[7] Dipoles **10a–c** are structurally similar to 1,2-diazetidinium ylides **11**, which represent another example of isolable, ring-strained cyclic azomethineimine dipoles.[21] The ^{13}C chemical shift of $Ph_2C{=}N$ in **10** is quite similar to the values found for these as well as other azomethineimines.[22]

In order to furnish chemical proof for betaines **10**, we tried to trap them by [3+2] cycloaddition reaction with a suitable dipolarophile. In fact, this transformation was successful with dimethyl acetylenedicarboxylate (DMAD), but not with methyl propiolate, dimethyl fumarate, dimethyl maleate, maleic anhydride, or norbornadiene. Irradiation of **1a–c** in excess DMAD at 60 °C furnished the cycloaddition products **12a–c** as yellow, air-stable crystals with isolated yields of 45–72 % (Scheme 6). The constitution of these bicyclic 1,2,3-diazaphosphetidines was established by an X-ray crystal structure determination of **12b** (Figure 4; see Table 2). The results also revealed that the bicyclic system has a *cis* fusion



12,13	R^1	$SiR^2_2R^3$
a	*t*Bu	$SiPh_2$*t*Bu
b	1-Ad	$Si(i-Pr)_3$
c	*t*Bu	$Si(i-Pr)_3$

E = COOMe

Scheme 6.

Table 2. Crystallographic data for compounds **2a, 4, 12b,** and **14**.[a]

	2a[b]	**4**[c]	**12b**[d]	**14**[e]
empirical formula	$C_{44}H_{49}N_2OPSi$	$C_{40}H_{49}N_2O_2PSi$	$C_{49}H_{63}N_2O_5PSi$	$C_{43}H_{57}N_2O_6PSi$
formula weight	680.91	648.87	819.07	756.97
temperature [K]	293(2)	293(2)	293(2)	293(2)
crystal size [mm]	0.60 × 0.35 × 0.30	0.55 × 0.50 × 0.25	0.80 × 0.30 × 0.30	0.30 × 0.30 × 0.20
crystal system	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a [Å]	9.653(4)	10.536(1)	9.682(3)	9.824(2)
b [Å]	11.781(4)	27.196(2)	11.371(3)	22.122(3)
c [Å]	19.117(7)	13.179(2)	20.732(6)	19.655(4)
α [°]	80.87(1)	90	84.45(3)	90
β [°]	88.71(1)	91.77(1)	81.33(3)	98.97(2)
γ [°]	66.37(2)	90	82.03(3)	90
V [Å^3]	1964.5(13)	3774.5(7)	2227.9(11)	4219.3(13)
Z	2	4	2	4
ρ_{calcd} [g cm^{-3}]	1.151	1.142	1.221	1.192
$\mu(Mo_{K\alpha})$ [cm^{-1}]	1.35	1.39	1.37	1.41
F (000)	728	1392	880	1624
θ range [°]	1.91–24.06	1.72–23.99	1.81–24.12	1.84–24.15
index ranges	$-1 \le h \le 10$	$-12 \le h \le 12$	$-10 \le h \le \le 11$	$-11 \le h \le 10$
	$-12 \le k \le 13$	$-29 \le k \le 30$	$-12 \le k \le 13$	$-25 \le k \le 25$
	$-21 \le l \le 21$	$-15 \le l \le 15$	$0 \le l \le 23$	$-22 \le l \le 22$
reflections collected	7404	24000	17182	27050
independent reflections	6161	5894	6606	6636
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	6150/12/477	5865/0/415	6606/0/534	6636/0/492
goodness-of-fit on F^2	1.075	0.910	0.964	0.931
final R indices $[I > 2\sigma(I)]$[f]	$R1 = 0.0547$, $wR2 = 0.1358$	$R1 = 0.0644$, $wR2 = 0.1664$	$R1 = 0.0506$, $wR2 = 0.1303$	$R1 = 0.0449$, $wR2 = 0.1080$
R indices (all data)	$R1 = 0.0911$, $wR2 = 0.1629$	$R1 = 0.1374$, $wR2 = 0.2063$	$R1 = 0.0743$, $wR2 = 0.1413$	$R1 = 0.0732$, $wR2 = 0.1174$
largest diff. peak and hole [e Å^{-3}]	0.26, −0.20	0.46, −0.20	0.58, −0.42	0.28, −0.19

[a] The data of **2a** were collected on a Siemens P4 diffractometer (ω scans), the other three data sets were obtained on a Stoe IPDS instrument (completeness of data sets: **4**, 99.1 %; **12b**: 93.9 %; **14**, 94.5 %. Graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) was used in all cases. [b] The *tert*-butyl group is disordered. [c] Only crystals of rather bad quality were available. [d] There is dynamic and/or static disorder in all three isopropyl groups, which could not be resolved. [e] Very anisotropic ellipsoids of thermal vibration are found for one ester group (O2, O3, C15) and one isopropyl group (C26, C27); treatment by introducing disorder models was unsuccesful. [f] $R1 = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$; $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$.

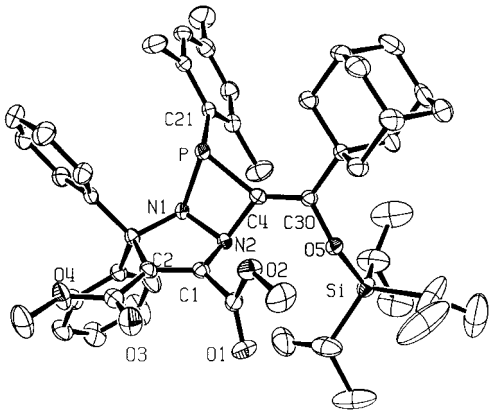


Figure 4. Molecular structure of **12b**; ellipsoids of thermal vibration are shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: P–N1 1.785(2), N1–N2 1.490(3), N2–C4 1.466(3), N2–C1 1.410(3), P–C4 1.824(3), P–C21 1.833(3); N1-P-C4 75.3(1), P-N1-N2 92.1(1), N1-N2-C4 96.5(2), N2–C4–P 91.3(2). Torsion angles [°]: P-N1-N2-C4 –18.4(2), N1-N2-C4-P 18.0(2), N1-P-C4-N2 –15.3(1), C4-P-N1-N2 15.1(1).

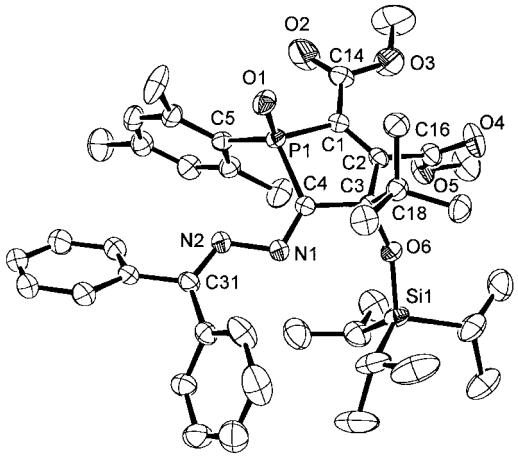


Figure 5. Molecular structure of **14**; ellipsoids of thermal vibration are shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: P1–C1 1.805(2), P1–C4 1.841(2), C1–C2 1.335(3), C4–N1 1.273(3), N1–N2 1.408(3), N2–C31 1.290(3); C1-P1-C4 89.0(1), C4-N1-N2 110.7(2), N1-N2-C31 116.2(2). Torsion angles [°]: N2-N1-C4-P1 3.5(3), C4-N1-N2-C31 –168.8(2), C2-C1-C14-O2 165.4(3), C1-C2-C16-O4 107.7(3).

and bears the mesityl ring in the *exo* position, that the four-membered heterocyclic ring is nonplanar, and that the exocyclic double bond is in the *E* configuration as in the precursor **1b**. The NMR data are in agreement with the solid-state structure: the ^{31}P NMR chemical shifts of **12a–c** ($\delta =$ 115.0–116.0) fall in the range considered typical for four-membered P,N heterocycles,[23] and the low values of the $^{1}J(P,C_{ring})$ coupling constants (3.8–6.6 Hz) and the high values of ^{1}J(P,C-mesityl) (45–47 Hz) also seem to be typical for phosphetane systems.[24] Long-range P,C coupling constants (^{3}J and ^{4}J) observed for the alkyl substituents are in accord with the *E* configuration of the exocyclic double bond. The differences in the ^{13}C chemical shifts of C^{a} and C^{b} with respect to the dipoles **10** (Table 1) have already been discussed (see above). A detailed assignment of ^{1}H and ^{13}C signals based on C,H correlation and heteronuclear multiple bond correlation (HMBC) spectra was carried out for **12c** (see Experimental Section); this revealed a remarkable difference in the chemical shift for the two *ipso* carbon atoms of the two phenyl rings ($\Delta\delta = 9.3$ ppm), evidently a manifestation of a γ-effect between the phosphorus atom and the *i*-C of the *cis*-oriented phenyl ring.[25]

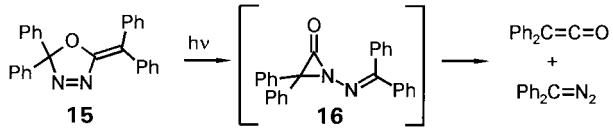
2-(Diphenylmethylene)hydrazono-2,3-dihydrophospholes **13** were formed as by-products upon irradiation of phosphapyrazolines **1a–c** in DMAD. While **13a**, **c** could be isolated in significant amounts (18 and 21%), each as a mixture of two diastereomers, only traces of **13b** were formed, which were detected by ^{31}P NMR spectroscopy ($\delta = -22.0$) but not isolated. The constitution of these products was confirmed by an X-ray crystal structure determination of 2,3-dihydrophosphole-1-oxide **14** (Figure 5; see Table 2), which was obtained from **13c** by oxidation with bis(trimethylsilyl)peroxide.

2,3-Dihydrophospholes **13** clearly represent the products of a second [3+2] cycloaddition mode between DMAD and betaines **10**. In this mode, the P–C=C fragment, rather than the azomethineimine dipole, constitutes the three-atom cycloaddition partner. We suggest that this transformation is the result of a Michael addition/ring-closure sequence.

In contrast to betaines **10a–c**, the analogous dipole **10d** could be neither observed by spectroscopy as a photochemical intermediate nor trapped chemically upon irradiation of **1d** in excess DMAD. In all cases, phosphindole derivatives **3** and **4** were the only products detected.

Discussion

The central result of this study is the observation that irradiation of the title compounds at $\lambda \geq 300$ nm leads not to extrusion of molecular nitrogen, but to a (5→4) ring contraction caused by a 1,2(C→N) shift of the phosphorus atom. This behavior contrasts with the smooth elimination of N_2 under thermal conditions[8] and is the more remarkable as most Δ^1-pyrazolines efficiently lose molecular nitrogen under both thermal *and* photochemical conditions.[1] 5,5-Diphenyl-2-diphenylmethylene-1,3,4-oxadiazoline (**15**), structurally closely related to the title compounds, is a notable exception, since it is cleaved photochemically into diphenylketene and diphenyldiazomethane.[26] There is evidence that this is not simply a [3+2] cycloreversion reaction,[27] but a stepwise process that begins with a (5→3) ring contraction of **15** to form aziridinone **16** (Scheme 7).[28] Sulfur and selenium



Scheme 7.

analogues of **15** are also known (i.e. 3-alkylidene-2,5-dihydro-1,3,4-thiadiazoles[29] and -selenadiazoles[30]), but their photochemistry seems not to have been reported. It is however known that 2,2-di-*tert*-butyl-5-(2,2-dimethylpropylidene)-2,5-dihydro-1,2,4-selenadiazole can be prepared by irradiation of

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a 1,2,3-selenadiazole in the presence of (di-*tert*-butyl)diazomethane, indicating a certain degree of photostability of the pyrazoline product.[30]

In a series of detailed investigations, Quast and co-workers have studied the thermal and photochemical behavior of Δ^1-pyrazolines with π bonds at the C-4 position of the ring but lacking 3-(or 5-)alkylidene substitution. While N_2 elimination was the major pathway in most cases, some photochemical side reactions were also observed, such as the cleavage of 3,3,5,5-tetramethyl-1-pyrazolin-4-one into acetone azine and carbon monoxide,[31] and the photoreduction of the azo group of 3,3,5,5-tetramethyl-4-methylene-1-pyrazoline[32] and 4-imino-3,3,5,5-tetraalkyl-1-pyrazolines[33] in hydrogen-donating solvents. Upon irradiation of 3,3,5,5-tetramethyl-1-pyrazolin-4-one azine, cleavage of the N–N bond of the azino group is the major reaction.[34] The temperature dependence of the efficiency of N_2 elimination indicates a significant activation barrier to photochemical N_2 elimination in some cases,[1,31,33] and other modes of deactivation of the photochemically exited state[35] may become competitive due to this barrier. In the case of 4-phosphapyrazolines **1**, it should be noted that products of the thermal decomposition mode by N_2 elimination[8] were observed either not at all (**1c**) or only in trace amounts (**1a**) even when the irradiation was performed at 60 °C (see the experiments designed to trap the azomethineimine dipoles, see Scheme 6). Quast et al. have pointed out that a parallel between the barriers to photochemical and thermal loss of molecular nitrogen may exist not only for the so-called reluctant cyclic azoalkanes of the 2,3-diazabicyclo[2.2.2]oct-2-ene type, as suggested by Engel et al.,[36] but also for 4-methylene-, 4-oxo-, and 4-imino-1-pyrazolines.[33,37] In line with these suggestions, we observe that 5-alkylidene-4-phosphapyrazolines **1** require a higher temperature for thermal N_2 extrusion than simple phosphapyrazolines lacking the exocyclic double bond (see Introduction) as well as certain bicyclic analogues of **1**,[38] both of which lose N_2 upon irradiation but do not undergo skeletal rearrangement.

Our current results do not yet give insight into the driving force or mechanistic details of the photochemically induced (5→4) ring contraction **1**→**10**. We hope that our ongoing studies on the scope of this novel photorearrangement will soon provide us with a clearer picture.

Conclusion

In this paper we have shown that 5-alkylidene-4,5-dihydro-3*H*-1,2,4(λ^3)-diazaphospholes **1** undergo unusual photochemical reactions. Instead of the expected elimination of molecular nitrogen, rearrangement to amino(imidoyl)phosphanes **2** or 2-hydrazinobenzo[*b*]phosphole **4** takes place, depending on whether the exocyclic double bond bears an alkyl or an aryl substituent. The key step in these isomerization reactions is an unprecedented **5**→**4** ring contraction of **1** to form the semicyclic azomethineimine dipoles **10**, which could be observed by spectroscopy and trapped in the case of **10a–c**. While the novel photochemical rearrangement is remarkable enough, the products resulting from the photochemical isomerization of **1** are of interest in their own right: amino(imidoyl)phosphanes **2** are a new type of phosphane with an unusual combination of various functional groups, and compounds **10** and **12** are the first 1,2,3-diazaphosphetidines. Finally, the effective synthesis of 2-hydrazinobenzo[*b*]phosphole **4** is notable in view of the emerging interest in phosphole systems as ligands in catalytically active metal complexes.[13, 14d, 39]

Experimental Section

Part of the experimental work was carried out at the University of Kaiserslautern (B. Manz, Ph.D. thesis, Kaiserslautern, **1995**); therefore, the instrumentation used both at Kaiserslautern and at Ulm is described below. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AMX 400 and AMX 500 spectrometers. All spectra were recorded from $CDCl_3$ solutions at 30 °C, unless stated otherwise. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. The ^{31}P NMR spectra were recorded by using 85 % H_3PO_4 as external standard. In the presentation of the ^{13}C NMR data, the indicated multiplicities refer to P,C couplings; the value of the corresponding coupling constants is given without sign. Assignments of ^{1}H and ^{13}C signals were based on ^{13}C, ^{1}H correlation spectra and gradient-selected HMBC spectra when necessary. Infrared spectra were recorded on Perkin-Elmer 1310, Perkin-Elmer FT-IR 16 PC, and Perkin-Elmer FT-IR Spectrum 1000 instruments; peaks are given in wavenumbers [cm^{-1}]. Ultraviolet spectra were taken with a Varian Cary 17 spectrophotometer. Mass spectra were acquired with Finnigan MAT 90 and Varian MAT 711 instruments. Elemental analyses were performed by using Perkin-Elmer EA 2400 and Heraeus CHN-O-Rapid instruments. Melting points are uncorrected. All experiments were carried out in rigorously dried glassware under an atmosphere of dry argon. Solvents were dried according to standard methods and stored under an argon atmosphere. Photochemical reactions were performed by using a Philips HPK 125 high-pressure mercury lamp and conventional Pyrex glassware. Liquid chromatography was performed with silica gel (Macherey & Nagel, $\mu = 0.063$–0.2 mm). The 5-alkylidene-4,5-dihydro-3*H*-1,2,4(λ^3)-diazaphospholes **1a–d** were prepared as reported.[6]

1-[(*tert*-Butyldiphenylsilyl)imino]-3,3-dimethyl-1-[diphenylmethyleneamino-(2,4,6-trimethylphenyl)phosphino]-butan-2-one (2a): A vigorously stirred solution of **1a** (642 mg, 1.20 mmol) in diethyl ether (50 mL) was cooled to 0 °C and irradiated for about 1 h; irradiation of a solution in pentane at −40 °C was also tested and gave the same results. The solution was allowed to warm to room temperature, and the solvent was removed at 0.002 mbar. The product was crystallized from pentane at −78 °C, followed by recrystallization from dichloromethane/acetonitrile (1:1) at −30 °C. Yellow crystals of **2a** were obtained; yield: 417 mg (65 %); m.p. 169 °C; ^{1}H NMR (400 MHz, 328 K): $\delta = 0.80, 0.94$ (both s, both 9H; $C(CH_3)_3$), 2.12 (s, 3H; *p*-CH_3), 2.22 (s, 6H; *o*-CH_3), 6.55 (s, 2H; *m*-H at Mes), 7.08-7.13 (m, 8H; Ph), 7.17–7.25 (m, 6H; Ph), 7.30–7.50 (m, 6H; Ph); ^{13}C{^{1}H} NMR (101 MHz, 328 K): $\delta = 19.3$ (s, Si*C*Me$_3$), 20.9 (s, *p*-Me), 23.8[40] (at 298 K: 23.0 (br) and 24.5 (br); *o*-Me), 27.0 (d, ^4J(P,C) = 2.5, CC*Me*$_3$), 27.1 (s, SiC*Me*$_3$), 41.7 (s, C*C*Me$_3$), 127.22 (at 298 K: 127.14 (s) and 127.21(s); *m*-C at Si–Ph), 127.8 (2 x), 127.9 (each s, Ph), 128.5 (*m*-C at Mes),[40] 129.1 (s, Ph), 132.1 (d, ^1J(P,C) = 21.8 Hz, *i*-C at Mes), 134.3 (s, *i*-C of Si–Ph), 136.2 (at 298 K: 136.00 (s) and 136.15 (s); *o*-C of Si–Ph), 139.5 (d, ^4J(P,C) = 1.4 Hz, *p*-C at Mes), 139.9 (d, ^3J(P,C) = 6.3 Hz, *i*-C at C–Ph), 143.8[40] (at 298 K: 143.0 (br) and 144.7 (br); *o*-C at Mes), 170.2 (d, ^2J(P,C) = 7.0 Hz, P–N=C), 197.7 (d, ^1J(P,C) = 21.4 Hz, P–C=), 212.7 (d, ^2J(P,C) = 25.7 Hz, C=O); ^{31}P{^{1}H} NMR (162 MHz): $\delta = 45.7$; IR (KBr): $\tilde{\nu} = 1670$ cm^{-1} (C=O); $C_{44}H_{49}N_2OPSi$ (680.94): calcd C 77.61, H 7.25, N 4.11; found C 77.3, H 7.3, N 4.0.

1-(1-Adamantyl)-2-[diphenylmethyleneamino-(2,4,6-trimethylphenyl)-phosphino]-2-[(triisopropylsilyl)imino]-ethan-1-one (2b): A solution of **1b** (690 mg, 1.02 mmol) in pentane (50 mL) was irradiated and worked up as described above for **1a**. Yellow crystals of **2b** were obtained; yield: 455 mg (66 %); m.p. 137 °C; ^{1}H NMR (400 MHz, 328 K): $\delta = 0.89$–0.90 (s, 21H; C*H*(C*H*$_3$)$_2$), 1.70 (br s, 6H; Ad), 2.00 (br s, 3H; Ad), 2.06 (br s, 6H; Ad), 2.09 (s, 3H; *p*-CH_3), 2.20 (s, 6H; *o*-CH_3), 6.51 (s, 2H; *m*-H at Mes), 7.15–7.24 (m, 10H; Ph); ^{13}C{^{1}H} NMR (101 MHz, 328 K): $\delta = 13.3$ (s, SiCH), 18.5 (s; at 298 K: 18.37 (s) and 18.49 (s); SiCH*Me*$_2$), 20.8 (s, *p*-Me), 23.5 (d,

^3J(P,C) = 14.5, *o*-Me), 28.4 (s, C-3, -5, -7-Ad), 36.8 (s, C-4, -6, -10-Ad), 38.9 (d, ^4J(P,C) = 2.4, C-2, -8, -9-Ad), 44.2 (s, C-1-Ad), 127.8 (s, *m*-C at Ph), 127.9 (s, *o*-C at Ph), 128.4 (s; at 298 K: 128.4 (br); *m*-C at Mes), 129.0 (s, *p*-C at Ph), 132.1 (d, ^1J(P,C) = 24.7 Hz, *i*-C at Mes), 139.5 (d, ^4J(P,C) = 1.2 Hz, *p*-C at Mes), 140.2 (d, ^3J(P,C) = 5.9 Hz, *i*-C at Ph), 144.0 (*o*-C at Mes),[40] 169.8 (d, ^2J(P,C) = 5.5 Hz, P-N=C), 192.4 (d, ^1J(P,C) = 23.6 Hz, P−C=), 213.2 (d, ^2J(P,C) = 28.0 Hz, C=O); ^{31}P{^{1}H} NMR (162 MHz): δ = 44.8; IR (KBr): $\tilde{\nu}$ = 1635 cm^{-1} (C=O); $C_{43}H_{57}N_2OPSi$ (677.00): calcd C 76.29, H 8.49, N 4.14; found C 76.5, H 8.3, N 4.1.

3,3-Dimethyl-1-[diphenylmethyleneamino-(2,4,6-trimethylphenyl)phosphino]-1-[(triisopropylsilyl)imino]-butan-2-one (2c): A vigorously stirred solution of **1c** (720 mg, 1.20 mmol) in diethyl ether (50 mL) was cooled to 0 °C (alternatively: pentane, −40 °C) and irradiated for 2 h. The solution was allowed to warm to room temperature, and concentrated at 0.002 mbar to a volume of 2.5 mL. After the mixture had been left to stand for several weeks at −78 °C, **2c** (446 mg, 62 %) was obtained as a yellow microcrystalline solid, m.p. 58 °C; ^{1}H NMR (400 MHz, 328 K): δ = 0.89 (s, 3H; C*H*CH$_3$), 0.90 (s, 18H; CH(C*H*$_3$)$_2$), 1.30 (s, 9H; C(CH$_3$)$_3$), 2.09 (s, 3H; *p*-CH$_3$), 2.20 (s, 6H; *o*-CH$_3$), 6.52 (s, 2H; *m*-H at Mes), 7.15–7.24 (m, 10H; Ph); ^{13}C{^{1}H} NMR (101 MHz, 328 K): δ = 13.3 (d, ^4J(P,C) = 1.6 Hz, SiCH), 18.5 (s, SiCH*Me*$_2$), 20.8 (s, *p*-Me), 23.5 (d, ^3J(P,C) = 14.2 Hz, *o*-Me), 27.7 (d, $^4J_{(P,C)}$ = 2.4 Hz, C*Me*$_3$), 41.7 (s, *C*Me$_3$), 127.8 (s, *m*-C at Ph), 127.9 (s, *o*-C at Ph), 128.4 (d, ^3J(P,C) = 4.4 Hz, *m*-C at Mes), 129.1 (s, *p*-C at Ph), 131.9 (d, ^1J(P,C) = 23.8 Hz, *i*-C at Mes), 139.6 (d, ^4J(P,C) = 1.7 Hz, *p*-C at Mes), 140.2 (d, ^3J(P,C) = 5.9 Hz, *i*-C at Ph), 143.9 (*o*-C at Mes),[40] 170.1 (d, $^2J_{(P,C)}$ = 6.2 Hz, P−N=C), 192.3 (d, ^1J(P,C) = 25.3 Hz, P−C=), 213.9 (d, ^2J(P,C) = 28.5 Hz, C=O); ^{31}P{^{1}H} NMR (162.0 MHz): δ = 44.8; IR (KBr): $\tilde{\nu}$ = 1660 cm^{-1} (C=O); $C_{37}H_{51}N_2OPSi$ (598.88): calcd C 74.21, H 8.58, N 4.68; found C 74.3, H 8.5, N 4.5.

[(1α,7aα)-2,7a-Dihydro-6-methoxy-2-[(diphenylmethylene)hydrazono]-3-[(triisopropylsilyl)oxy]-1-(2,4,6-trimethylphenyl)-1*H*-phosphindole (3): A vigorously stirred solution of **1d** (640 mg, 0.99 mmol) in pentane (75 mL) was cooled to −40 °C and irradiated for 3 h. The residue obtained after removal of solvent at −40 °C/0.002 mbar consisted nearly exclusively of **3**. The compound can be stored at −40 °C in the dark. ^{1}H NMR (400 MHz, 233 K): δ = 0.77 (m, 3H; SiCH), 0.86 (pseudo-t, ^3J(H,H) = 7.5 Hz, 18H; CH(C*H*$_3$)$_2$), 1.95, 2.23, 2.92 (each s, 3H; CH$_3$), 3.54 (s, 3H; OCH$_3$), 4.37–4.39 (m, 1H; H-7a), 5.05–5.07 (m, 1H; H-7), 5.89 (dt, ^3J(H,H) = 9.8 Hz, *J* = 2.1 Hz, 1H; H-4), 6.79 (s, 1H; *m*-H at Mes), 6.84 (d, ^3J(H,H) = 9.8 Hz, 1H; H-5), 6.96–6.98 (m, 2H; Ph), 7.02 (d, ^4J(P,H) = 4.4 Hz, *m*-H at Mes), 7.05–7.12 (m, 4H; Ph), 7.23–7.26 (m, 1H; Ph), 7.36–7.42 (m, 3H; Ph); ^{13}C{^{1}H} NMR (101 MHz, 233 K): δ = 13.5 (s, SiCH), 18.1 (s, SiCH*Me*$_2$), 21.1, 21.4 (both s, Me + *o*-Me), 24.5 (d, ^3J(P,C) = 33.2 Hz, *o*-Me), 40.5 (s, C-7a), 54.5 (s, OMe), 98.3 (d, ^2J(P,C) = 18.0 Hz, C-7), 124.0, 124.5, 127.5, 127.7, 127.76, 127.83 (each s), 128.6 (d, ^1J(P,C) = 30.1 Hz, *i*-C at Mes), 128.7, 129.5, 129.6, 134.8, 137.1, 137.4 (each s), 139.9 (s, *p*-C at Mes), 142.9 (d, ^2J(P,C) = 5.6 Hz, *o*-C at Mes), 144.0 (d, ^2J(P,C) = 36.9 Hz, *o*-C at Mes), 146.3 (d, ^2J(P,C) = 22.7 Hz, C-3), 153.0 (d, ^3J(P,C) = 11.6 Hz, C-6), 163.2 (s, C=N), 176.7 (d, ^1J(P,C) = 26.1 Hz, C-2); ^{31}P{^{1}H} NMR (162 MHz, 233 K): δ = −23.1.

2-[(Diphenylmethylene)hydrazino]-6-methoxy-3-[(triisopropylsilyl)oxy]-1-(2,4,6-trimethylphenyl)-1*H*-phosphindole (4): A solution of **1d** (799 mg, 1.23 mmol) in pentane (75 mL) was irradiated at −40 °C for 3 h. The solution was allowed to warm to room temperature, left for 24 h, and concentrated. Crystallization at −78 °C and recrystallization from dichloromethane/acetonitrile (1:1) at −30 °C furnished **4** as yellow crystals; yield 599 mg (75 %); m.p. 144 °C; ^{1}H NMR (400 MHz): δ = 0.88 (sept, ^3J(H,H) = 6.7 Hz, 3H; SiCH), 0.94 (d, ^3J(H,H) = 6.7 Hz, 9H; CHC*H*$_3$), 0.97 (d, ^3J(H,H) = 6.7 Hz, 9H; CHC*H*$_3$), 1.73, 2.31 (both s, 3H; CH$_3$), 2.97 (d, ^4J(P,H) = 1.3 Hz, 3H; *o*-CH$_3$), 3.74 (s, 3H; OCH$_3$), 6.74 (s, 1 H), 6.82 (ddd, ^3J(H,H) = 8.4, ^4J(H,H) = 2.4, ^5J(P,H) = 1.0 Hz, 1H; H-5), 6.86–6.88 (m, 2 H), 6.91 (dd, ^3J(P,H) = 5.1 Hz, ^4J(H,H) = 2.4 Hz, 1H; H-7), 7.05–7.15 (m, 4 H), 7.18 (dd, ^3J(H,H) = 8.4 Hz, ^4J(P,H) = 1.6 Hz, 1H; H-4), 7.24–7.26 (m, 2H; Ph), 7.46–7.55 (m, 4 H); ^{13}C{^{1}H} NMR (101 MHz): δ = 13.7 (s, SiCH), 17.8 (s, SiCH*Me*$_2$), 19.4, 21.1 (both s, Me), 24.6 (d, ^3J(P,C) = 34.4 Hz, *o*-Me), 55.4 (s, OMe), 113.3 (d, ^2J(P,C) = 20.7 Hz, C-7), 113.5 (s, C-5), 118.8, 126.0 (both s), 126.7 (d, ^1J(P,C) = 19.3 Hz, *i*-C at Mes), 127.2, 127.6 (both s), 128.8 (d, *J*(P,C) = 6.9 Hz), 128.9, 129.1, 129.6 (each s), 129.7 (s, *m*-C at Mes), 129.8 (d, ^3J(P,C) = 5.6 Hz, *m*-C at Mes), 131.1 (d, *J*(P,C) = 16.8 Hz), 133.0 (s), 135.1 (d, *J*(P,C) = 5.4 Hz), 136.2 (s), 138.3 (s), 139.7 (s, *p*-C at Mes), 142.6 (s), 145.4 (d, ^2J(P,C) = 5.8 Hz, *o*-C at Mes), 146.7 (d, ^2J(P,C) = 39.1 Hz, *o*-C at Mes), 156.5 (d, ^3J(P,C) = 9.2 Hz, C-6); ^{31}P{^{1}H} NMR (162 MHz): δ = −32.8; IR (KBr): $\tilde{\nu}$ = 3290 cm^{-1} (N−H), 1585; $C_{40}H_{49}N_2O_2PSi$ (648.90): calcd C 74.04, H 7.61, N 4.32; found C 73.7, H 7.5, N 4.3.

1-[(Diphenylmethylene)amino]-(2,4,6-trimethylphenyl)phosphino]-2,2-dimethyl-propan-1-one (5): A vigorously stirred solution of **1c** (961 mg, 1.60 mmol) in pentane (75 mL) was cooled to −40 °C and irradiated for 2 h. The solvent was removed at 20 °C/0.005 mbar, and the crude product was heated in a Kugelrohr distillation unit at 240 °C for 10 min. An orange-colored oil distilled over, from which colorless triisopropylsilyl cyanide (**7**) was removed by repeated bulb-to-bulb distillation at 50 °C/0.005 mbar. The residue was crystallized from pentane at −78 °C; yield: 466 mg (70 %); m.p. 88 °C; ^{1}H NMR (400 MHz, 328 K): δ = 1.12 (d, ^4J(P,H) = 0.8 Hz, 9H; C(CH$_3$)$_3$), 2.17 (s, 3H; *p*-CH$_3$), 2.22 (s, 6H; *o*-CH$_3$), 6.65 (d, ^4J(P,H) = 2.3 Hz, 2H; *m*-H at Mes), 7.19-7.29 (m, 6H; Ph), 7.32–7.35 (m, 4H; Ph); ^{13}C{^{1}H} NMR (101 MHz, 328 K): δ = 20.8 (s, *p*-Me), 22.7 (d, ^3J(P,C) = 14.7 Hz, *o*-Me), 27.1 (d, ^3J(P,C) = 4.3 Hz, C*Me*$_3$), 48.1 (d, ^2J(P,C) = 31.5 Hz, *C*Me$_3$), 127.7 (d, ^4J(P,C) = 1.6 Hz, *o*-C at Ph), 127.8 (s, *m*-C at Ph), 128.9 (d, ^3J(P,C) = 5.0 Hz, *m*-C at Mes), 129.1 (s, *p*-C at Ph), 130.7 (d, ^1J(P,C) = 17.1 Hz, *i*-C at Mes), 139.9 (d, ^4J(P,C) = 1.4 Hz, *p*-C at Mes), 140.2 (d, ^3J(P,C) = 7.2 Hz, *i*-C at Ph), 143.7 (d, ^2J(P,C) = 15.9 Hz, *o*-C at Mes), 171.9 (d, ^2J(P,C) = 7.8 Hz, N=C), 227.5 (d, ^1J(P,C) = 49.8 Hz, C=O); ^{31}P{^{1}H} NMR (162 MHz): δ = 41.2; IR (KBr): $\tilde{\nu}$ = 1630 cm^{-1} (C=O), 1575, 1545, 1430, 1272; MS (EI, 70 eV): *m/z* (%): 415 (1) [*M*$^+$], 330 (100) [*M*$^+$ − *t*Bu-CO], 210 (10), 165 (4), 149 (31), 57 (7); $C_{27}H_{30}NOP$ (415.51): calcd C 78.05, H 7.28, N 3.37; found C 78.0, H 7.3, N 3.5.

2-[(Diphenylmethylene)hydrazono]-6-methoxy-1-(2,4,6-trimethylphenyl)-2,3-dihydro-1*H*-phosphindol-3-one (9): A vigorously stirred solution of **1b** (762 mg, 1.17 mmol) in pentane (60 mL) was cooled to −40 °C and irradiated for 3 h. 4-Phenyl-1,2,4-triazoline-3,5-dione (**8**)[41] (205 mg, 1.17 mmol) in dichloromethane (15 mL) was then added dropwise to the cold solution. After 20 min at −40 °C, the mixture was brought to room temperature over the course of 1.5 h, and the solvent was removed at 20 °C/0.002 mbar. Medium-pressure column chromatography (Merck Lobar column) with ether/petroleum ether (4:1) as eluent yielded **4** (250 mg, 33 %) as the first component and **9** (190 mg) as the second. Compound **9** was purified further by crystallization from dichloromethane at −78 °C, yielding 160 mg (28 %) of yellow powder; m.p. 144 °C; ^{1}H NMR (400 MHz, 330 K): δ = 2.13 (6H; *o*-CH$_3$)[40] 2.18 (s, 3H; *p*-CH$_3$), 3.80 (s, 3H; OCH$_3$), 6.69 (d, ^4J(P,H) = 2.3 Hz, 2H; *m*-H at Mes), 6.83 (dd, ^3J(P,H) = 5.6 Hz, ^4J(H,H) = 2.4 Hz, 1H; H-7), 6.90 (ddd, ^3J(H,H) = 8.6 Hz, ^4J(H,H) = 2.4 Hz, ^5J(P,H) = 1.6 Hz, 1H; H-5), 6.98 (d, ^3J(H,H) = 7.1 Hz, 2H; Ph), 7.23–7.36 (m, 8H; Ph), 7.93 (dd, ^3J(H,H) = 8.6 Hz, ^4J(P,H) = 2.0 Hz, 1H; H-4); ^{13}C{^{1}H} NMR (101 MHz, 330 K): δ = 20.8 (s, *p*-Me), 22.8 (*o*-Me),[40] 55.6 (s, OMe), 113.9 (d, ^2J(P,C) = 21.1 Hz, C-7), 115.8 (s, C-5), 125.0 (d, ^1J(P,C) = 24.1 Hz, *i*-C at Mes), 127.7, 127.8, 128.5, 129.0, 129.19, 129.23 (all s), 129.7 (d, ^3J(P,C) = 4.2 Hz, *m*-C at Mes), 130.2 (s), 132.6 (d, *J*(P,C) = 4.1 Hz), 134.1, 137.1 (both s), 140.6 (d, ^4J(P,C) = 1.2 Hz, *p*-C at Mes), 145.3 (*o*-C at Mes),[40] 149.7 (d, *J*(P,C) = 8.7 Hz), 159.8 (d, *J*(P,C) = 2.3 Hz), 165.50 (d, ^1J(P,C) = 30.7 Hz, C-2), 165.54 (d, *J*(P,C) = 7.1 Hz), 186.5 (d, ^2J(P,C) = 9.5 Hz, C-3). ^{31}P{^{1}H} NMR (162 MHz): δ = −48.6; IR (KBr): $\tilde{\nu}$ = 1665 cm^{-1} (C=O), 1570, 1245; MS (EI, 70 eV): *m/z* (%): 490 (39) [*M*$^+$], 475 (17) [*M*$^+$ − CH$_3$], 371 (100) [*M*$^+$ − Mes], 283 (22) [*M*$^+$ − H/Ph$_2$C=N−N=C], 269 (11), 267 (20), 180 (12), 77 (8); $C_{31}H_{27}N_2O_2P$ (490.54): calcd C 75.90, H 5.55, N 5.71; found C 75.8, H 5.7, N 5.7.

Observation of betaines 10a–c: *General procedure*: The betaines were generated photochemically from **1a–c** (0.80 mmol) under the same reaction conditions as described for the synthesis of **2a–c**, but irradiation was stopped after 6–7 min. The solution was allowed to warm to room temperature, and the solvent was removed in vacuo (0.003 mbar). The dark red oil was identified as a mixture of **1**, **2**, and **10**. The latter compounds did not survive attempts to isolate them by column chromatography.

4-{(*E*)-1-[(*tert*-Butyldiphenylsilyl)oxy]-2,2-dimethylpropylidene}-2-diphenylmethylene-3-(2,4,6-trimethylphenyl)-1,2,3-diazaphosphetidin-2-ium-1-ylide (10a): Obtained as a mixture of **1a**/**2a**/**10a** in 2.2:1.9:1 ratio (^{31}P NMR). Spectral data of **10a**: see Table 1.

4-{(*E*)-(1-Adamantyl)-[(triisopropylsilyl)oxy]methylene}-2-diphenylmethylene-3-(2,4,6-trimethylphenyl)-1,2,3-diazaphosphetidin-2-ium-1-ylide (10b): Obtained as a mixture of **1b**/**2b**/**10b** in 1:1:3 ratio (^{31}P NMR). Spectral data of **10b**: ^{13}C{^{1}H} NMR (101 MHz): δ = 15.0 (s, SiCH), 18.6 (s, SiCH*Me*$_2$), 19.0, 21.1 (both s, Me), 22.1 (d, ^3J(P,C) = 32.4 Hz, *o*-Me), 28.4 (s,

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C-3, -5, -7-Ad), 36.8 (s, C-4, -6, -10-Ad), 39.6 (d, ^3J(P,C) = 0.6 Hz, C-1-Ad), 40.3 (d, ^4J(P,C) = 6.8 Hz; C-2, -8, -9-Ad), 121.4 (d, ^1J(P,C) = 12.0 Hz, PC=), 125.0 (s, Ph), 126.0 (d, ^1J(P,C) = 45.9 Hz, *i*-C at Mes), 126.3, 127.7, 128.0, 128.2, 129.1, 130.3, 131.0, 133.9 (all s), 134.7 (d, ^3J(P,C) = 2.8 Hz, *i*-C at Ph), 139.4 (s, *p*-C at Mes), 142.1 (d, ^2J(P,C) = 17.2 Hz, =COSi), 142.4 (s, *o*-C at Mes), 145.4 (d, ^2J(P,C) = 38.4 Hz, *o*-C at Mes), 145.6 (d, ^2J(P,C) = 1.5 Hz, *C*Ph$_2$) (due to signal overlap in this spectrum, coupling constants of the latter two signals were taken from a 50 MHz spectrum); ^{31}P{^{1}H} NMR (162 MHz): δ = 161.6.

4-{(*E*)-[2,2-Dimethyl-1-[(triisopropylsilyl)oxy]propylidene]-2-diphenylmethylene-3-(2,4,6-trimethylphenyl)-1,2,3-diazaphosphetidin-2-ium-1-ylide (**10c**): Obtained as a mixture of **1c**/**2c**/**10c** in 15:5:4 ratio (^{31}P NMR). The following ^{13}C{^{1}H}NMR (101 MHz, C_6D_6) signals were assigned to **10c**: δ = 15.6 (s, SiCH), 18.8, 18.9 (both s, SiCH*Me*), 19.3, 21.2 (both s, Me), 22.5 (d, ^3J(P,C) = 33.2 Hz, *o*-Me), 28.8 (d, ^4J(P,C) = 6.3 Hz, C*Me*$_3$), 38.0 (s, *C*Me$_3$), 121.9 (d, ^1J(P,C) = 12.0 Hz, PC=), 126.4 (d, ^1J(P,C) = 47.1 Hz, *i*-C at Mes), 134.4 (s, *i*-C at Ph), 135.2 (*i*-C at Ph), 139.6 (s, *p*-C at Mes), 141.7 (d, ^2J(P,C) = 17.1 Hz, =COSi), 142.9 (s, *o*-C at Mes), 146.0 (d, ^2J(P,C) = 38.6 Hz, *o*-C at Mes), 146.1 (s, *C*Ph$_2$); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ = 161.9 (s).

Dimethyl 2-{(*E*)-1-[(*tert*-butyldiphenylsilyl)oxy]-2,2-dimethylpropylidene}-6,6-diphenyl-1-(2,4,6-trimethylphenyl)-1,2-dihydro-6*H*-[1,2,3]diazaphospheto[1,2-*a*]pyrazole-4,5-dicarboxylate (**12a**) **and dimethyl 3-*tert*-butyl-3-[(*tert*-butyldiphenylsilyl)oxy]-2-[(diphenylmethylene)hydrazono]-1-(2,4,6-trimethylphenyl)-2,3-dihydro-1*H*-phosphole-4,5-dicarboxylate** (**13a**): A suspension of **1a** (1.09 g, 1.60 mmol) in dimethyl acetylenedicarboxylate (DMAD) (5.31 g, 37.36 mmol), heated in a water bath at 60 °C, was irradiated for 8 h with an externally placed water-cooled high-pressure mercury lamp. Excess DMAD was removed by bulb-to-bulb distillation (60 °C/0.005 mbar), and the residue was passed through a silica gel column (13 × 1 cm) with diethyl ether/petroleum ether (1:1) as eluent. The yellow-brown fraction was collected and concentrated to 10 mL. Yellow crystals of **12a** were obtained upon cooling to −30 °C. The mother liquor was subjected to column chromatography (silica gel, column 52 × 2 cm, diethyl ether/petroleum ether (1:4) as eluent), which furnished first **13a** and then another crop of **12a**. Compound **13a** was purified by repeated crystallization from pentane at −78 °C and obtained as a yellow solid. **12a**: Combined yield: 697 mg (53 %); m.p. 208 °C; ^{1}H NMR (500 MHz): δ = 0.54, 1.19 (both s, 9H; C(CH$_3$)$_3$), 1.78 (d, ^4J(P,H) = 2.9 Hz, 3H; *o*-CH$_3$), 2.16, 2.97 (both s, 3H; CH$_3$), 3.66, 3.86 (both s, 3H; OCH$_3$), 6.52 (d, ^4J(P,H) = 4.8 Hz, 1H; *m*-H at Mes), 6.74 (s, 1H; *m*-H at Mes), 6.97 (d, 2H; Ph), 7.12 (t, 2H; Ph), 7.16–7.27 (m, 4H; Ph), 7.35–7.45 (m, 6H; Ph), 7.64 (d, 2H; Ph), 7.79 (d, 2H; Ph), 7.87 (d, 2H; at Ph); ^{13}C{^{1}H} NMR (126 MHz): δ = 20.3 (s, SiC*Me*$_3$), 21.1 (s, Me), 22.2 (d, ^3J(P,C) = 34.3 Hz, *o*-Me), 22.8 (s, Me), 27.7 (s, SiC*Me*$_3$), 28.9 (d, ^4J(P,C) = 4.8 Hz, CC*Me*$_3$), 36.5 (s, =C*C*Me$_3$), 51.4, 52.7 (both s, OMe), 78.2 (d, ^2J(P,C) = 13.8 Hz, *C*Ph$_2$), 111.9 (s), 125.4 (d, ^1J(P,C) = 3.8 Hz, PC=), 126.7, 127.3, 127.5, 127.6 (all s), 128.2 (d, ^1J(P,C) = 45.3 Hz, *i*-C at Mes), 128.4 (s), 128.8 (d, ^3J(P,C) = 6.2 Hz, *m*-C at Mes), 129.6, 129.9 (both s), 130.2 (d, *J*(P,C) = 1.9 Hz, Ph), 130.3, 134.19, 134.23, 136.3 (all s, Ph), 136.5 (d, ^3J(P,C) = 9.5 Hz, *i*-C at Ph), 136.8 (s, Ph), 141.7 (s, *p*-C at Mes), 145.8 (d, ^2J(P,C) = 41.0 Hz, *o*-C at Mes), 146.1, 146.3 (both s, *i*-C at Ph and *o*-C at Mes), 151.2 (d, ^2J(P,C) = 8.6 Hz, =CO), 154.5 (s, N−C=), 162.2, 163.7 (both s, C=O); ^{31}P{^{1}H} NMR (203 MHz): δ = 116.0; IR (KBr): $\tilde{\nu}$ = 1748 cm^{-1} (CO), 1705 (C=O), 1650, 1602, 1306, 1274; $C_{50}H_{55}N_2O_5PSi$ (823.05): calcd C 72.97, H 6.74, N 3.40; found C 73.2, H 6.7, N 3.3. **13a**: Yield: 232 mg (18 %); mixture of two diastereomers (7:2 ratio by ^{1}H NMR integration); m.p. 79–90 °C; ^{1}H NMR (500 MHz): Major isomer: δ = 0.66 (s, 9H; C(CH$_3$)$_3$), 0.86 (s, 9H; SiC(CH$_3$)$_3$), 1.93 (s, 3H; *o*-CH$_3$ at Mes), 2.22 (s, 3H; *p*-CH$_3$ at Mes), 2.40 (s, 3H; *o*-CH$_3$ at Mes), 3.37 (s, 3H; OCH$_3$), 3.50 (s, 3H; OCH$_3$), 6.58–6.59 (d, 2H; Ph), 6.70-6.71 (m, 2H; *m*-H at Mes), 6.91–6.94 (m, 3H; Ph), 7.12–7.30 (m, 11H; Ph), 7.64–7.66 (d, 2H; *o*-H at SiPh), 7.72–7.74 (d, 2H; *o*-H at SiPh); minor isomer: δ = 1.95, 2.11 (each s, CH$_3$), 3.28 (s, OCH$_3$), 3.72 (s, OCH$_3$), remaining signals overlap with those of major isomer; ^{13}C{^{1}H} NMR of major isomer (125.8 MHz): δ = 20.9 (s, Si*C*(CH$_3$)$_3$), 21.1(s, p-CH$_3$ at Mes), 23.4 (s, *o*-CH$_3$ at Mes), 23.9 (d, ^3J(P,C) = 35.2 Hz, *o*-CH$_3$ at Mes), 26.1 (d, ^4J(P,C) = 5.2 Hz, C(*C*H$_3$)$_3$), 27.9 (s, SiC(*C*H$_3$)$_3$), 42.3 (s, *C*(CH$_3$)$_3$), 51.7 (s, OCH$_3$), 52.2 (s, OCH$_3$), 93.6 (d, ^2J(P,C) = 3.1 Hz, C-3), 122.3 (d, ^1J(P,C) = 26.4 Hz, *i*-C at Mes), 126.4, 126.6, 127.5, 128.1, 128.3 128.4, 128.5, 128.7, 129.2, 129.7 (all s), 135.7 (2 s), 136.3, 136.9, 137.0, 137.2 (all s), 140.3 (*p*-C at Mes), 144.0 (d, ^1J(P,C) = 11.9 Hz, C-5), 145.1 (d, ^2J(P,C) = 5.2 Hz, *o*-C at Mes), 145.4 (d, ^2J(P,C) = 12.8 Hz, C-4), 146.0 (d, ^2J(P,C) = 40.8 Hz, *o*-C at Mes), 159.5 (d, ^4J(P,C) = 2.4 Hz, Ph$_2$*C*=N), 165.3 (s, C=O), 165.6 (d, ^2J(P,C) = 15.0 Hz, C=O), 174.9 (d, ^1J(P,C) = 42.9 Hz, C-2); ^{31}P{^{1}H} NMR (203 MHz): δ = −22.14 / −22.07 (major/minor isomer); IR (KBr): $\tilde{\nu}$ = 1736 cm^{-1} (C=O), 1598, 1429, 1246; $C_{50}H_{55}N_2O_5PSi$ (823.05): calcd C 72.97, H 6.74, N 3.40; found C 73.0, H 6.7, N 3.1.

Dimethyl 2-{(*E*)-(1-adamantyl)-[(triisopropylsilyl)oxy]methylene}-6,6-diphenyl-1-(2,4,6-trimethylphenyl)-1,2-dihydro-6*H*-[1,2,3]diazaphospheto[1,2-*a*]pyrazole-4,5-dicarboxylate (**12b**): The synthesis and work-up of **12b** from **1b** (1.13 g, 1.66 mmol) and DMAD (5.41 g, 38.06 mmol) was analogous to the procedure described above for **12a**, but crystallization was achieved from dichloromethane/acetonitrile (1:1) at −30 °C. After removal of the solvent, the yellow crystals were washed with cold acetonitrile (−30 °C) and dried at 80 °C/0.005 mbar. At this stage, the crystals contained 0.5 equivalents of dichloromethane, which could be removed by dissolving the crystals in pentane, evaporating the solvent, and drying the crystals at 80 °C/0.005 mbar; yield 983 mg (72 %); m.p. 199 °C; ^{1}H NMR (500 MHz): δ = 1.25 (d, ^3J(H,H) = 7.5 Hz, 9H; CHC*H*$_3$), 1.30 (d, ^3J(H,H) = 7.5 Hz, 9H; CHC*H*$_3$), 1.42–1.51 (m, 6H; SiC*H* and Ad), 1.58–1.67 (m, 9H; Ad), 1.85 (br, s, 3H; Ad), 1.88 (d, ^4J(P,H) = 2.9 Hz, 3H; *o*-CH$_3$), 2.22, 3.12 (both s, 3H; CH$_3$), 3.68, 3.95 (both s, 3H; OCH$_3$), 6.59 (d, ^4J(P,H) = 4.5 Hz, 1H; *m*-H at Mes), 6.81 (s, 1H; *m*-H at Mes), 7.00 (d, 2H; Ph), 7.13 (t, 2H; Ph), 7.20 (d, 1H; Ph), 7.23 (d, 1H; Ph), 7.27 (t, 2H; Ph), 7.70 (d, 2H; Ph); ^{13}C{^{1}H} NMR (126 MHz): δ = 14.3 (s, SiCH), 18.7, 19.0 (both s, SiCH*Me*), 21.1 (s, Me), 22.0 (d, ^3J(P,C) = 34.3 Hz, *o*-Me), 22.9 (s, Me), 28.2 (s; C-3, -5, -7-Ad), 36.4 (s; C-4, -6, -10-Ad), 39.3 (d, ^3J(P,C) = 3.1 Hz, C-1-Ad), 39.8 (d, ^4J(P,C) = 7.0 Hz; C-2, -8, -9-Ad), 51.2, 52.8 (both s, OMe), 78.1 (d, ^2J(P,C) = 14.2 Hz, *C*Ph$_2$), 111.2 (s), 123.5 (d, ^1J(P,C) = 5.7 Hz, PC=), 126.5, 127.2, 127.3, 127.5, 128.3 (all s), 128.7 (d, ^3J(P,C) = 7.2 Hz, *m*-C at Mes), 129.1 (d, ^1J(P,C) = 46.4 Hz, *i*-C at Mes), 130.18, 130.21 (both s), 136.6 (d, ^3J(P,C) = 9.5 Hz, *i*-C at Ph), 141.4 (s, *p*-C at Mes), 145.55 (d, ^2J(P,C) = 40.4 Hz, *o*-C at Mes), 145.56 (d, *J*(P,C) = 2.4 Hz, *i*-C at Ph or *o*-C at Mes), 145.9 (d, *J*(P,C) = 2.9 Hz, *i*-C at Ph or *o*-C at Mes), 151.4 (d, ^2J(P,C) = 9.1 Hz, =CO), 154.9 (s, N-C=), 162.2, 163.6 (both s, C=O); ^{31}P{^{1}H} NMR (203 MHz): δ = 115.0; IR (KBr): $\tilde{\nu}$ = 1730 cm^{-1} (C=O), 1692 (C=O), 1582, 1435, 1420, 1302, 1265, 1210; $C_{49}H_{63}N_2O_5PSi$ (819.57): calcd C 71.85, H 7.75, N 3.42; found C 71.9, H 8.0, N 3.3.

Dimethyl 2-{(*E*)-1-[(triisopropylsilyl)oxy]-2,2-dimethylpropylidene}-6,6-diphenyl-1-(2,4,6-trimethylphenyl)-1,2-dihydro-6*H*-[1,2,3]diazaphospheto[1,2-*a*]pyrazole-4,5-dicarboxylate (**12c**) **and dimethyl 3-*tert*-butyl-3-[(triisopropylsilyl)oxy]-2-[(diphenylmethylene)hydrazono]-1-(2,4,6-trimethylphenyl)-2,3-dihydro-1*H*-phosphole-4,5-dicarboxylate** (**13c**): Compounds **12c** and **13c** were prepared from **1c** (921 mg, 1.54 mmol) and DMAD (5.55 g, 39.01 mmol) as described above for **12a**/**13a**. Compound **12c** (only 1 diastereomer): Combined yield: 517 mg (45 %); m. p. 183 °C; ^{1}H NMR (500 MHz): δ = 0.92 (s, 9H; C(CH$_3$)$_3$), 1.20 (d, ^3J = 7.4 Hz, 9H; CHC*H*$_3$), 1.24 (d, ^3J = 7.4 Hz, 9H; CHC*H*$_3$), 1.41 (sept, ^3J = 7.4 Hz, 3H; C*H*CH$_3$), 1.79 (d, ^4J(P,H) = 2.2 Hz, 3H; *o*-CH$_3$ at Mes), 2.17 (s, 3H; *p*-CH$_3$ at Mes), 3.07 (s, 3H; *o*-CH$_3$ at Mes), 3.63 (s, 3H; OCH$_3$), 3.89 (s, 3H; OCH$_3$), 6.54 (d, ^4J(P,H) = 4.4 Hz, 1H; *m*-H at Mes), 6.76 (s, 1H; *m*-H at Mes), 6.94 (m$_c$, 2H; *o*-H at Ph-1), 7.08 (m$_c$, 2H; *m*-H at Ph-1), 7.14–7.18 (m, 2H; *p*-H), 7.21–7.24 (m, 2H; *m*-H at Ph-2), 7.64 (m$_c$, 2H; *o*-H at Ph-2); ^{13}C{^{1}H} NMR (126 MHz): δ = ^{31}P{^{1}H} NMR (203 MHz): δ = 14.3 (s, SiCH), 18.6 and 18.9 (both s, SiCH*C*H$_3$), 21.1 (s, *p*-CH$_3$ at Mes), 22.1 (d, ^3J(P,C) = 35.0 Hz, *o*-CH$_3$ at Mes), 22.8 (s, *o*-CH$_3$ at Mes), 28.7 (d, ^4J(P,C) = 6.7 Hz, C(*C*H$_3$)$_3$), 37.2 (s, *C*(CH$_3$)$_3$), 51.2 and 52.8 (both s, OCH$_3$), 78.1 (d, ^2J(P,C) = 14.1 Hz, *C*Ph$_2$), 111.4 (s), 123.3 (d, ^1J(P,C) = 6.6 Hz, PC=), 126.6 (s, *p*-C, Ph-2), 127.2 (s, *m*-C, Ph-2), 127.4 (s, *m*-C, Ph-1), 127.5 (s, *p*-C, Ph-1), 128.3 (s, *o*-C, Ph-2), 128.8 (d, ^3J(P,C) = 7.1 Hz, *m*-C at Mes), 129.0 (d, ^1J(P,C) = 47.4 Hz, *i*-C at Mes), 130.2 (s, *m*-C at Mes), 130.3 (s, *o*-C, Ph-1), 136.6 (d, ^3J(P,C) = 9.6 Hz, *i*-C at Ph-1), 141.6 (s, *p*-C at Mes), 145.8 (d, ^2J(P,C) = 41.0 Hz, *o*-C at Mes), 145.9 (d, ^2J(P,C) = 3.3 Hz, *o*-C at Mes), 151.2 (d, ^2J(P,C) = 9.3 Hz, =COSi), 154.9 (s), 162.2 (s, C=O), 163.6 (s, C=O); ^{31}P{^{1}H} NMR (203 MHz): δ = 115.7; IR (KBr): $\tilde{\nu}$ = 1753 cm^{-1} (C=O), 1711 (C=O), 1600, 1274, 1172; $C_{43}H_{57}N_2O_5PSi$ (740.99): calcd C 69.70, H 7.75, N 3.78; found C 69.71, H 7.98, N 3.81. **13c**: 238 mg (21 %), yellow oil; ^{1}H NMR (500 MHz): δ = 0.94 (s, 9H; C(CH$_3$)$_3$), 0.98 (d, ^3J = 7.4 Hz, 9H; CHC*H*$_3$), 0.99 (d, ^3J = 7.4 Hz, 9H; CHC*H*$_3$), 1.10 (sept, ^3J = 7.4 Hz, 3H; C*H*CH$_3$), 2.33 and 2.34 (both s, both 3H; *o*-CH$_3$ at Mes and p-CH$_3$ at Mes), 2.55 (s, 3H; *o*-CH$_3$ at Mes), 3.56 (s, 3H; OCH$_3$), 3.72 (s, 3H; OCH$_3$), 6.70 (d, 1H; Ph), 6.71 (d, 1H; Ph), 6.86–6.88 (m, 2H; m-H at Mes), 7.00–7.04 (m, 2H; Ph), 7.16–7.18 (m, 2H; Ph), 7.22–7.24 (m, 1H; Ph), 7.36–7.37 (m, 3H; Ph); ^{13}C{^{1}H} NMR

(126 MHz): $\delta = 14.5$ (s, SiCH), 18.9 and 19.0 (both s, SiCHCH_3), 21.0 and 23.7 (both s, CH_3 at Mes), 23.9 (d, ^3J(P,C) = 35.7 Hz, *o*-CH_3 at Mes), 26.4 (s, C(CH_3)$_3$), 42.8 (s, $C(CH_3)_3$), 51.8 and 52.0 (both s, OCH_3), 92.8 (d, ^2J(P,C) = 3.9 Hz, C–3), 123.7 (d, ^1J(P,C) = 27.4 Hz, *i*-C at Mes), 127.5, 127.9, 128.5, 128.6, 128.7 (all s), 129.1 (d, ^3J(P,C) = 16.6 Hz, *m*-C at Mes), 129.2, 129.9 135.9, 137.1 (all s), 140.0 (s, *p*-C at Mes), 142.8 (d, *J*(P,C) = 11.2 Hz), 144.0 (d, ^2J(P,C) = 5.4 Hz, *o*-C at Mes), 146.1 (d, ^2J(P,C) = 40.9 Hz, *o*-C at Mes), 146.2 (d, ^2J(P,C) = 11.5 Hz), 162.3 (s, Ph_2C=N), 165.3 (d, ^2J(P,C) = 14.9 Hz, C=O), 165.7 (s, C=O), 179.6 (d, ^1J(P,C) = 46.6 Hz, C-2); $^{31}P\{^1H\}$ NMR (203 MHz): $\delta = -22.1$; IR (KBr): $\tilde{\nu} = 1725$ cm^{-1} (C=O), 1599, 1434, 1241, 1167; $C_{43}H_{57}N_2O_5PSi$ (740.99): calcd C 69.70, H 7.75, N 3.78; found C 69.11, H 8.10, N 3.74.

Dimethyl 1*α*,3*α*-3-*tert*-butyl-3-[(triisopropylsilyl)oxy]-2-[(diphenylmethylene)hydrazono]-1-oxo-1-(2,4,6-trimethylphenyl)-2,3-dihydro-1*H*-phosphole-4,5-dicarboxylate (14): A solution of **13c** (300 mg, 0.41 mmol) and bis(trimethylsilyl)peroxide (278 mg, 1.56 mmol) was stirred for three days. After evaporation of solvent in vacuo, **14** was obtained as a yellow solid by crystallization of the residue from ether (–30 °C); yield: 251 mg (82 %); m.p. 129 °C; ^1H NMR (500 MHz): $\delta = 0.88$ (d, $^3J = 7.1$ Hz, 9H; CHCH_3), 0.93 (d, $^3J = 7.0$ Hz, 9H; CHCH_3), 0.98 (sept, $^3J = 6.8$ Hz, 3H; C*H*CH$_3$), 1.13 (s, 9H; C(CH_3)$_3$), 2.29 (s, 3H; *o*-CH_3 at Mes), 2.39 (s, 3H; *p*-CH_3 at Mes), 2.57 (s, 3H; *o*-CH_3 at Mes), 3.60 (s, 3H; OCH_3), 3.83 (s, 3H; OCH_3), 6.77–6.79 (m, 2H; Ph), 6.89–6.91 (m, 2H; *m*-H at Mes), 7.06–7.09 (m, 2H; Ph), 7.24–7.26 (m, 2H; Ph), 7.30–7.40 (m, 4H; Ph); $^{13}C\{^1H\}$ NMR (126 MHz): $\delta = 14.4$ (s, SiCH), 18.7 and 18.9 (both s, SiCHCH_3), 21.1 and 23.8 (both s, CH_3 at Mes), 24.4 (d, ^3J(P,C) = 7.0 Hz, *o*-CH_3 at Mes), 28.1 (s, C(CH_3)$_3$), 42.7 (s, $C(CH_3)_3$), 52.48 and 52.53 (both s, OCH_3), 89.8 (d, ^2J(P,C) = 37.0 Hz, C-3), 122.8 (d, ^1J(P,C) = 110.6 Hz, *i*-C at Mes), 127.6, 127.9, 129.0, 129.1, 129.3 (all s), 130.2 (d, ^3J(P,C) = 12.8 Hz, *m*-C at Mes), 130.6 (s), 132.1 (d, ^3J(P,C) = 13.4 Hz, *m*-C at Mes), 134.4 (d, ^1J(P,C) = 83.9 Hz, C-5), 135.4 (s), 136.8 (s), 139.5 (d, ^2J(P,C) = 14.1 Hz, *o*-C at Mes), 141.5 (d, ^4J(P,C) = 2.9 Hz, *p*-C at Mes), 147.6 (d, ^2J(P,C) = 9.9 Hz, *o*-C at Mes), 162.3 (d, ^2J(P,C) = 11.2 Hz, C-4), 162.9 (d, *J*(P,C) = 8.9 Hz, C=O), 165.7 (d, *J*(P,C) = 15.0 Hz, C=O) 166.4 (s, Ph_2C=N), 169.8 (d, ^1J(P,C) = 72.1 Hz, C-2); $^{31}P\{^1H\}$ NMR (203 MHz): $\delta = 22.7$; IR (KBr): $\tilde{\nu} = 1742$ cm^{-1} (C=O), 1726 (C=O), 1250, 1194, 1185, 1163; $C_{43}H_{57}N_2O_6PSi$ (756.99): calcd C 68.14, H 7.58, N 3.70; found C 68.15, H 7.58, N 3.78.

Single-crystal X-ray structure determinations: Data collection was performed on a four-circle diffractometer (P4, Siemens AG, Analytical Systems, Karlsruhe) for **2a** and on an imaging plate diffractometer (IPDS, STOE & CIE, Darmstadt) for **4**, **12b**, and **14**. Crystal structure analyses were performed with SHELXS-86,[42a] SHELXL-93,[42b] and SHELXTL [Siemens AG, Analytical Systems, Karlsruhe]. Molecule plots were obtained using the programs SHELXTL and PLUTON-92.[43] Details of the data collection and structure analyses are given in Table 2. 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-100703. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, (UK) (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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