Thermal Reactions of 5-Alkylidene-4,5-dihydro-3*H*-1,2,4(λ^3)-diazaphospholes (4-Phosphapyrazolines) – A Route to Various P-Heterocycles and to 2-Phosphabutadienes☆

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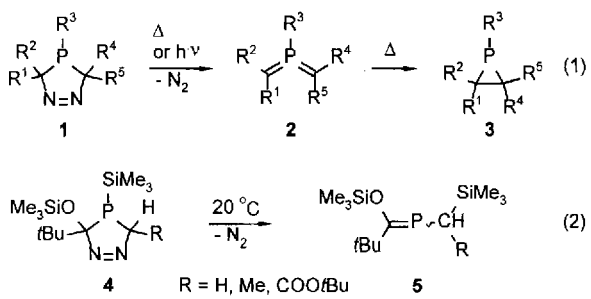
The 5-alkylidene-4,5-dihydro-3*H*-1,2,4(λ^3)-diazaphospholes (4-phosphapyrazolines) are thermally much more stable than related compounds without the exocyclic double bond. Thermolysis reactions typically occur in the range 110–150°C in toluene solution, and different, mostly competing, reaction pathways are observed. Thermal extrusion of nitrogen from **6a–g** gives rise to β-phosphanylsiloxyalkenes **10**, benzo[*c*]-phosphole derivatives **11**, **14**, and **15**, (β-siloxyalkylidene)-phosphiranes **12**, and dihydro-1,3-oxaphospholes **13**. The thermolysis of 5-alkylidene-4,5-dihydro-4-trimethylsilyl-3-trimethylsilyloxy-3*H*-1,2,4-diazaphospholes **17** afforded three products, including the highly substituted and stable 2-phosphabutadienes **18** formed by nitrogen extrusion and rearrangement. Finally, the 4-chloro-3-trimethylsilyloxy-substituted heterocycle **21** was transformed at 170°C into 4*H*-1,2,4-diazaphosphole **23**. The structures of **13c** and **18a** were determined by single-crystal X-ray diffraction.

A convenient route to bis(alkylidene)phosphoranes **2** and phosphiranes **3** is provided by the thermal or, less frequently, the photochemical, extrusion of dinitrogen from 4,5-dihydro-3*H*-1,2,4(λ^3)-diazaphospholes **1**[1]. So far, the heterocycles **1** have been prepared exclusively by [3 + 2] cycloaddition of diazo compounds to phosphaalkenes[1–5]; quite often, the nitrogen elimination already occurs during the cycloaddition procedure at or below room temperature[1c–f]. The resulting bis(alkylidene)phosphoranes **2** (as well as those prepared by other methods and which are substituted differently[5]) typically undergo a thermally induced, conrotatory 4π-electrocyclic isomerization to the thermodynamically more stable phosphiranes **3**. Depending on the substituent pattern, this rearrangement occurs in a temperature range between −80 and +120°C, i.e. compounds **2** can have a fleeting existence (e.g. **2**, R^3 = Cl[1e,f]) and can be detected spectroscopically at room temperature (e.g. $R^1 = R^2 = SiMe_3$, $R^3 = R^4 = R^5 = Ph$[1d]), or a stable enough to be isolated ($SiMe_3$ groups at one or both C atoms, NR_2 at P[1a,b,5]). Thermal reactions of **2** which do not lead to phosphiranes are rare[5].

Several 4,5-dihydro-3*H*-diazaphospholes do not lend themselves as precursors to **2** and **3**. As in other cases (see above), the dediazonation of *P*-trimethylsilyl-substituted derivatives **4** already occurs under the conditions of their synthesis by [3 + 2] cycloaddition, but phosphaalkenes **5** are obtained[4]. A „triotropic" reaction mechanism was suggested, in which 1,2-migration of the trimethylsilyl group attached to the phosphorus atom, and the extrusion of nitrogen, occur simultaneously.



In other cases, the extrusion of N_2 from **1** is prevented by faster elimination or isomerization reactions. Unassisted thermal 1,2-elimination of chlorotrimethylsilane[3a–c,e], or base-catalyzed 1,2-elimination of hexamethyldisiloxane[3d,4] accompanied by a 1,3(C→N) shift of H or $SiMe_3$, leads to aromatic 1*H*-1,2,4-diazaphospholes[3a–d,4]. For **1** ($R^1 = R^2 = SiMe_3$, R^3 = Cl, R^4 = *t*Bu or $SiMe_3$, R^5 = H), formation of a phosphirane **3** competes with a 1,3(C→N) $SiMe_3$ shift, leading to a 4,5-dihydro-1*H*-1,2,4-diazaphosphole[2f].

We have found recently that 5-alkylidene-4,5-dihydro-3*H*-1,2,4(λ^3)-diazaphospholes can be synthesized from phosphaalkenes, and 1-diazo-2-siloxyethenes generated in situ from α-diazo-α-silyl ketones[6,7]. These novel phoshole derivatives are thermally much more stable than their related compounds lacking the exocyclic C–C double bond, and can therefore be isolated and handled conveniently[7]. Nevertheless, we expected them to lose nitrogen at higher

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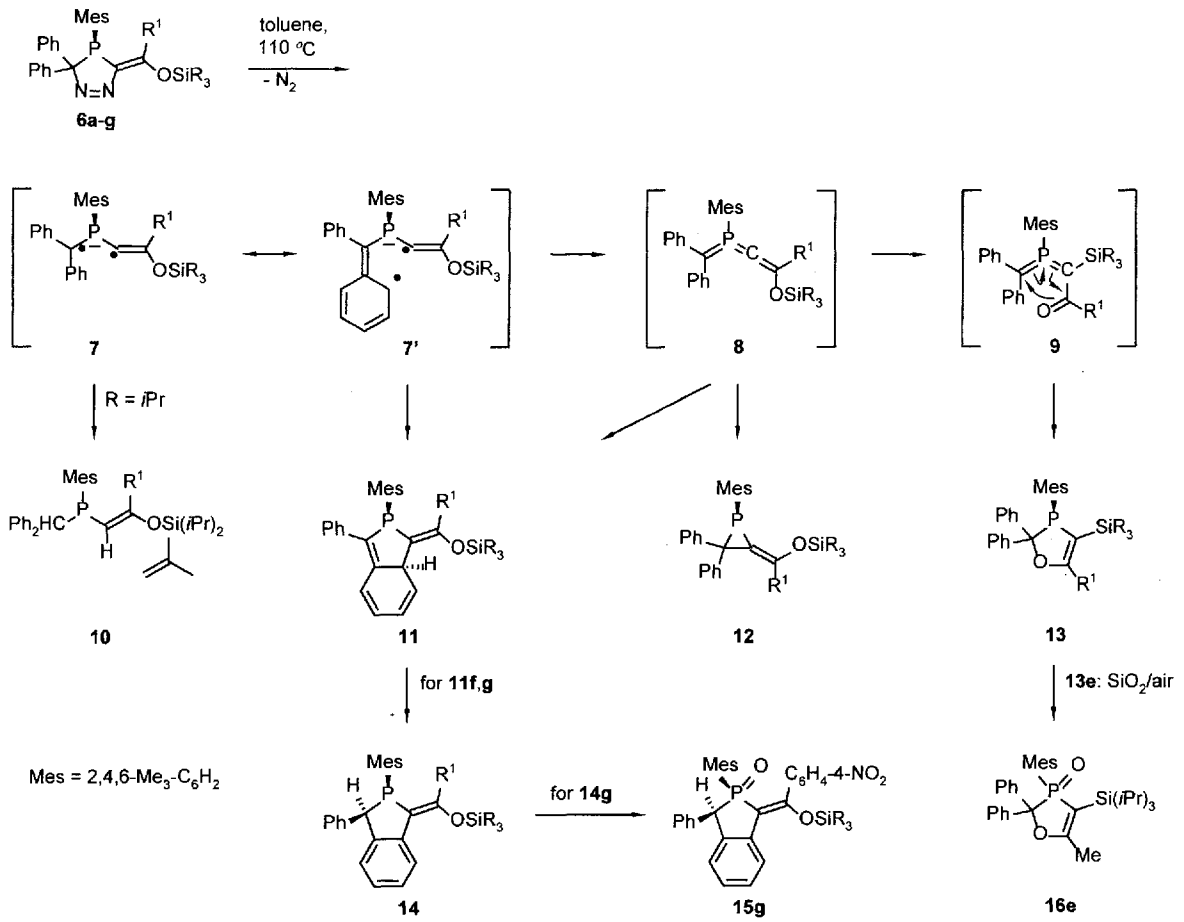
Scheme 1. Thermolysis of diazaphosphole derivatives **6**; see Table 1 for substituents and products



temperatures and, according to equations (1) and (2), to give access to the barely known 2-alkylidenephosphiranes[8] and to the novel 2-phosphabutadiene[9] derivatives. In this paper, we show that these goals could indeed be reached, but that the thermal decomposition of the 5-alkylidene-4,5-dihydro-3*H*-1,2,4(λ^3)-diazaphospholes (4-phosphapyrazolines) may also follow other pathways.

Results

Thermolysis of 5-Alkylidene-*P*-mesityl-3*H*-1,2,4-diazaphospholes 6a–g

We have already reported[6] that thermolysis of 5-alkylidene-4,5-dihydro-3*H*-1,2,4-diazaphospholes **6a**, **b** in boiling toluene provides not only the expected alkylidenephosphiranes **12a**, **b** as the main products (**12a**: 47%; **12b**: 48%), but also a considerable amount of (2-siloxy-1-alkenyl)phosphanes **10a**, **b** (**10a**: 32%; **10b**: 33%), as shown in Scheme 1. It should be noted that the configuration of the silyl enol double bond in **6** is retained in the alkenylphosphane, but inverted in the alkylidenephosphirane. These observations are in agreement with the generally accepted decomposition pathway of 4,5-dihydro-3*H*-1,2,4-diazaphospholes, i.e. initial formation of a 1,3-diradical after loss of N_2, followed by electron redistribution to give a bis(alkylidene)phosphirane[1a]. In our case, the 1,3-diradical **7** is considered to be the direct precursor of **10** by intramolecular hydrogen atom abstraction from an isopropyl group, whereas **12** results from the (methylene)vinylidenephosphorane **8** by a conrotatory electrocyclic ring closure. It should be noted that phosphiranes **12a**, **b**, in spite of their ring strain[10], are thermally very stable compounds. For example, **12a** survived intact a distillation at 190°C/0.005 mbar and heating in toluene (24 h at 150°C followed by 3 h at 190°C).

Further substituent variations at the silyl enol moiety of **6** opened the path to even more reaction channels during the thermolysis of these 4-phosphapyrazolines. The results, together with the suggested reaction pathways, are displayed in Scheme 1; reaction conditions and product yields are given in Table 1. In order to prevent the formation of vinylphosphanes **10** and to increase the yield of alkylidenephosphiranes **12**, we first replaced the triisopropylsilyl group in **6** by $SiPh_2tBu$ and $SiMe_2tBu$ substituents. Nitrogen elimination from **6c**, **d** occurred more rapidly than for **6a**, **b**, indicating that the remote silyl group had an unexpectedly high influence on either the ease of C–N bond dissociation or on the stability of the developing vinylic radical center in **7**. To our further surprise, alkylidenephosphiranes were obtained only in trace amounts (**12c**), or not at all (**12d**). In both cases the 2,3-dihydro-1,3-oxaphospholes **13** were the major products. We assume that the methylene-

(vinylidene)phosphorane **8**, instead of undergoing the 4π-cyclization to form **12**, isomerizes to the acylbis(methylene)-phosphorane **9** by a 1,3(O→C) silyl shift, and that 6π-cyclization of **9** then leads to **13**. It could be argued that the vanishing yield of **12** is due to rapid rearrangement into **13** by a thermal 1,3(O→C) silyl shift and subsequent ring expansion of the formed 2-acyl-2-silylphosphirane. However, **12c** proved to be completely stable even after 20 h at 109°C in [D_8]toluene. Furthermore, ^{31}P-NMR spectroscopic monitoring of the thermolysis of **6c** in toluene did not indicate any build-up of **12c**, with respect to **13c**, until **6c** had disappeared completely. On the contrary, we will show in a forthcoming paper that prolonged heating of dihydrooxaphospholes **13** results, inter alia, in the formation of methylenephosphiranes **12**!

Table 1. Thermolysis of diazaphosphole derivatives **6**; reaction conditions and products

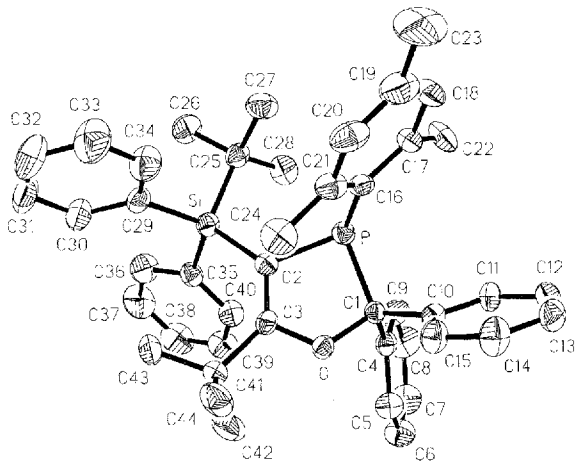
	R^1	SiR_3	Reaction time at 110 °C	Products and yields [%] 10	11	12	13	14	15
6a	*t*Bu	Si(*i*Pr)$_3$	16 h	32		47			
6b	1-Ad[a]	Si(*i*Pr)$_3$	16h	33		48			
6c	*t*Bu	$SiPh_2$*t*Bu	20 min			6	83		
6d	*t*Bu	$SiMe_2$*t*Bu	20 min		13		73		
6e	Me	Si(*i*Pr)$_3$	5 min[b]				4[c,d]		
6f	4-MeOC$_6$H$_4$	Si(*i*Pr)$_3$	15 min[b]				27	54	
6g	4-O$_2$NC$_6$H$_4$	Si(*i*Pr)$_3$	10 min[b]						25[d]

[a] 1-Ad = 1-adamantyl. – [b] Extrusion of nitrogen is significant already at 80°C, especially for **6e**, **g**. – [c] Compound **16e** (10%) was also obtained after chromatographic workup; some unidentified by-products could not be isolated. – [d] High loss of product during work-up.

The composition of **13c** was revealed by an X-ray crystal structure analysis. Figure 1 shows one of the two symmetry-independent molecules in the unit cell. The crystals also contain dichloromethane molecules; their partial disorder (see Experimental Section) limits the precision of the structure refinement. The heterocyclic ring has an envelope conformation with C-1 at the tip. The two independent molecules show appreciable differences in the torsion angles around the substituent/ring and the Si/phenyl bonds. the NMR data of **13c**, **d** do not reveal a great deal. The ^{31}P NMR (**13c**: δ = 14.3; **13d**: δ = 26.6) indicate the $\lambda^3\sigma^3$-phosphane. Due to the substituent effects, the ^{13}C-NMR chemical shifts of the ring atoms C-2 and C-4 are outside the „typical" ranges [C-2: δ = 94.0 (**13c**) and 91.7 (**13d**); C-4: δ = 89.5 (**13c**) and 92.0 (**13d**)]. The large $^1J_{P,C}$ coupling constants manifest the high s-character of the P–C bond[11]. The mesityl ring, which adopts an orthogonal position relative to the heterocycle (see Figure 1), is rotationally hindered and its *ortho*-methyl group, oriented towards the phosphorus lone pair, is distinguished by a large $^3J_{P,C}$ coupling constant (**13c**: J = 34.5 Hz; **13d**: J = 37.7 Hz).

Much more revealing are the NMR data of the by-product formed in the thermolysis of **6d**, allowing the unambiguous assignment to the 3,3a-dihydroisophosphindole **11d**. The ^{1}H-NMR spectrum shows not only 5 aromatic H atoms (besides those of the mesityl ring), but also 4H atoms

Figure 1. Structure of **13c** in the crystal; only one of the two symmetry-independent molecules in the unit cell is shown[a]



[a] Selected bond lengths [Å], bond angles [°] and torsion angles [°]; values given after the slash (/) refer to the second molecule: O–C1 1.451(7)/1.448(8), C1–P 1.872(6)/1.876(7), P–C2 1.821(7)/1.829(7), C2–C3 1.348(9)/1.350(9), C2–Si 1.897(7)/1.895(6), P–C16 1.856(7)/1.855(6); O–C1–P 104.5(4)/105.2(4), C1–P–C2 89.0(3)/89.0(3), P–C2–C3 109.1(5)/110.0(5), C2–C3–O 118.1(6)/117.3(6), O–C3–C41 108.3(5)/107.8(6), C2–C3–C41 133.6(6)/134.9(6), P–C2–Si 118.0(4)/119.0(4), C3–C2–Si 130.9(5)/128.6(5), C2–P–C16 110.6(3)/112.6(3), C16–P–C1 105.4(3)/106.2(3); Si–C2–C3–O 164.5(5)/–163.8(4), P–C2–C3–C41 177.7(6)/–179.8(6), C3–C2–P–C16 92.8(5)/96.4(5).

in the olefinic range with the expected[12] long-range coupling constants $J_{P,H}$ and $J_{H,H}$. The high value of $^3J_{P,H}$ (17.8 Hz) indicates the *syn* relationship between the phosphorus lone pair and the angular proton[11]. The *E* configuration of the exocyclic double bond is suggested by a $^4J_{P,C}$ = 8.0 Hz, which is similar to that found in (*E*)-**6**[7]. The formation of **11d** is readily explained by a 1,5-cyclization of diradical **7'** which is mesomeric with 1,3-diradical **7**, but it is also possible that the 6π-cyclization of **8** can occur. Although a thermal 1,3- or 1,7-H shift is not a process allowed by orbital symmetry, the stability of **11d** towards aromatization is surprising, especially since thermolysis of **6f**, **g** yielded directly the phosphindoles **14** and **15**, rather than compounds **11f**, **g** (see below).

Not only the silyl group but also the substituent R^1 affect the thermal stability and the decomposition pathway of 4-phosphapyrazolines **6**, as the comparison between the triisopropylsiloxy-substituted derivatives **6a**, **b** and **6e–g** shows. In the latter three cases, alkylidenephosphiranes **12** or vinylphosphanes **10** were eventually detected in the product mixtures in trace amounts by their ^{31}P-NMR signals, but they were never isolated; rather, derivatives of 1,3-oxaphospholes (**13**, **16**) and/or benzo[*c*]phospholes (**14**, **15**) were obtained. Compounds **6e–g** are the thermally most labile diazaphosphole derivatives reported here, already releasing nitrogen at an appreciable rate at 80°C. For the thermolysis of **6e**, the crude mixture of the diastereomers (*E* and *Z*) can be used, since an experiment with the pure *E* isomer, obtained only after repeated crystallization[7], does not lead to different results. While the ^{31}P-NMR spectrum

indicates **13e** as the main product, the sensitivity towards air and moisture impairs isolation and purification of this heterocycle. During chromatographic workup, the majority of **13e** is oxidized to form the cyclic phosphinoxide **16e**, but this compound seems to be easily consumed by desilylation, leading to an unknwon material of very low solubility. After the thermolysis of **6f**, 1,3-dioxaphosphole (**13f**) and benzo[*c*]phosphole (**14f**) derivatives were isolated in a 1:2 ratio in a combined yield of 81%; trace amounts of **10f** and **12f** were identified in the crude product mixture by their ^{31}P-NMR signals. Thermolysis of **6g** affords the dihydrobenzo[*c*]phosphole oxide **15g**; the low yield is partly due to the difficulty in separating this product from the polymeric material also formed. It seems likely that the formation of **14f** and **15g** has the same origin as discussed above for **11d**, this time followed by a spontaneous aromatization of **11f**, **g** to give **14f**, **g**. Isolation of **15g** instead of **14g** is likely to be caused by fast oxygen transfer from the nitro group to the λ^3,σ^3-P atom. Nitro as well as nitroso groups are well known as oxygen sources for the transformation of $\lambda^3\sigma^3$-phosphanes into phosphane oxides[13].

The composition of **13e**, **f** follows immediately from the close similarity of the NMR spectral data with that of **13c**, **d** (see above). The phosphane oxide function of **16e** is indicated by the IR spectrum [$\tilde{\nu}$ (P=O) = 1190 cm^{-1}], the expected effects on the ^{13}C chemical shifts, and also by the increased $^1J_{P,C}$ coupling constants as compared to those of **13c–f**.

The NMR data also leave no doubt about the structure of benzo[*c*]phosphole derivatives **14f** and **15g**. In both cases, the signals in the ^{1}H-NMR spectrum (400 MHz) show the presence of one aromatic proton less than in the starting material, and the ABCD spin system of the condensed aromatic ring is well resolved. For **14f**, the magnitude of $^2J_{P,3\text{-}H}$ (21.1 Hz) indicates the 2α,3α diastereomer[11]. The *E* configuration is suggested in the ^{13}C-NMR spectrum by large longe-range coupling constants from P to the anisyl substituent ($^3J_{P,C}$ = 3.9 Hz; $^4J_{P,C}$ = 5.5 Hz). In comparison with **14f**, the ^{31}P-NMR spectrum of dihydrobenzo[*c*]phosphole oxide **15g** shows the expected low-field shift for the $\lambda^5\sigma^4$-P atom (δ = 56.2). The oxidation is further indicated by markedly increased $^1J_{P,C}$ coupling constants, the elemental analysis, and a mass spectrum. The *syn* relationship between the oxygen atom and 3-H is suggested by the large $^2J_{P,H}$ coupling constant (25.0 Hz)[11]. For the silyl enol double bond, the *E* configuration may again be assumed, based on the similarity of chemical shifts and the observation of small $^3J_{P,C}$ coupling constants for the ^{13}C-NMR signals at δ = 140.7 (J = 2.9 Hz) and 143.0 (J = 1.9 Hz), one of which must be assigned to the *ipso*-C atom of the 4-nitrophenyl ring. Due to the $\lambda^5\sigma^4$ character of the P atom, a $^4J_{P,C}$ coupling to the 4-nitrophenyl ring can no longer be observed.

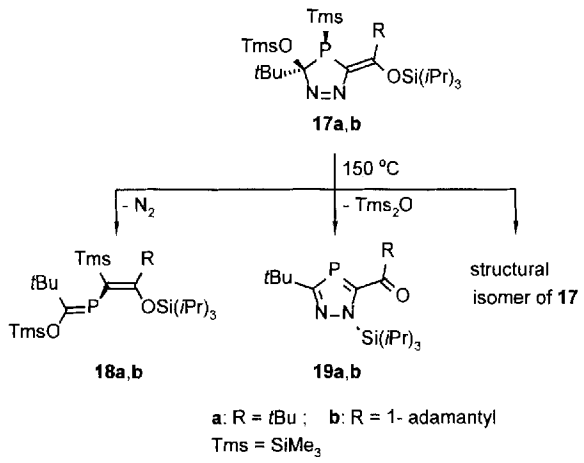
Thermolysis of 5-alkylidene-*P*-trimethylsilyl-3*H*-1,2,4-diazaphospholes 17

As mentioned in the introduction, *P*-trimethylsilyl-4,5-dihydro-3*H*-1,2,4-diazaphospholes **4** are readily transformed into phosphaalkenes **5** by loss of N_2 and 1,2-migration of the $SiMe_3$ group. We expected that application of this transformation to 5-akylidene-4,5-dihydro-3*H*-1,2,4-diazaphospholes **17**[7] would give access to new examples of the barely known 2-phosphabutadienes. While the transformation **4** → **5** occurs already at, or below, room temperature[4] (only 3*H*-4,5-dihydro-1,2,4-diazaphospholes, with bulky substituents at C-3 and C-5, are moderately stable and can be isolated[3d,4]), the thermal reaction of the 5-alkylidene-4,5-dihydro-1,2,4-diazaphospholes **17a**, **b** is complete only after heating at 150°C in toluene for 4 h (Scheme 2). The ^{31}P-NMR spectrum of the thermolysis mixture from **17a** showed three major signals at δ = 151.4, 109.2, and 63.2 in the ratio 51:11:38 (from **17b**: δ = 153.0, 109.1, 63.7, ratio 49:13:38). To our satisfaction, the low-field signals belonged to the 2-phosphabutadienes **18a**, **b**, which could be obtained as air-sensitive crystals after bulb-to-bulb distillation and crystallization from toluene in 26 and 30% yield, respectively. These phosphadienes are also very sensitive to the acid traces present in chloroform. The 1*H*-1,2,4-diazaphospholes **19a**, **b**, giving rise to ^{31}P-NMR signals at ca. δ = 109, were formed as minor by-products but were not isolated. Compound **19a** was identified by NMR by comparison with a sample prepared independently[7]. It is reasonable to assume that **19a** and **b** result from a thermally induced elimination of hexamethyldisiloxane, followed by a (formal) 1,7(O→N) silyl group migration (or from the reversed sequence of events). In both thermolyses, a so far unknown product, causing the ^{31}P-NMR signal at δ = 63, was formed in a significant quantity, but it could not be isolated in its pure form due to its high sensitivity to air and/or moisture. The ^{13}C-NMR spectra (see Experimental Section) and elemental analysis of (still impure) samples suggest that these compounds differ from the precursors **17** only in the position of the $SiMe_3$ and $OSiMe_3$ groups.

2-Phosphabutadienes represent a little known class of compounds in both their synthetic and structural aspects[9]. The parent compound[9f], and derivatives which are not heavily substituted, have a high tendency to polymerize even at low temperatures. With the exception of the *P*-pentacarbonyltungsten complex of a 2-phosphabutadiene **20**[9e], no experimental study on the structures of these hetero-1,3-dienes exists. The rotational energy surfaces of 2-phosphabutadienes and their equilibrium with 3,4-dihydrophosphetes via a conrotatory 4π-electrocyclic reaction were recently the subject of ab initio calculations[14]. It was pointed out that, for the parent system, the 3,4-dihydrophosphete isomer is energetically favored by 8.41 kcal/mol (MP2/6-31G*//6-31G*), and that the ring opening requires an activation barrier of 40.76 kcal/mol to be overcome[14b]. For the parent 2-phosphabutadiene, single-point energy calculations at the same level of theory using the optimized HF structures predict that the *gauche* isomer lies 2.06 kcal/mol above the *trans* isomer, with a rotational barrier of 3.59 kcal/mol (at φ = 94.06°) between them, and that the *cis* isomer is 4.88 kcal/mol less stable than the *trans* isomer[14a]. The energy gap between the 3,4-dihydrophosphete and the 2-phosphabutadiene (and its three conformers) is conse-

quently so narrow, that substituents should be able to change the energetic situation completely.

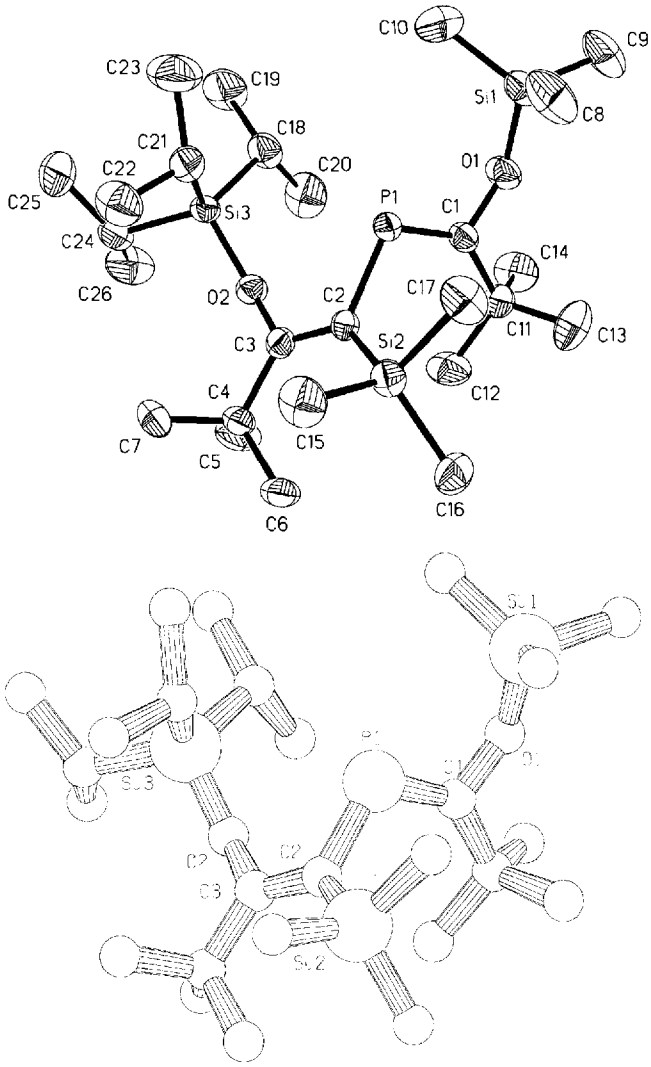
Scheme 2



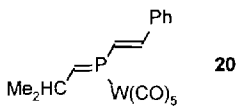
With crystals of **18a** to hand, we were able to determine, for the first time, the crystal structure of an uncomplexed 2-phosphabutadiene. Figure 2 shows that **18a** exists in the (1*E*,3*Z*) configuration, and that the phosphadiene unit adopts a *gauche* conformation (φ = 76.7°). The P=C bond length is in the typical range[9g], and the P–C bond length is typical for a single bond of this type (see HF/6-31G* calculations for representative examples[15]: 1.832–1.868 Å). Interestingly, the P–C bond in **18a** is longer by 0.046 Å than in Mathey's *P*-complexed phosphadiene **20**[9e], which has a planar *s-trans* conformation. The bond elongation in the gauche conformation with respect to the planar conformation is also predicted by theoretical calculations[13a]. Whether, or how much, this change reflects a loss of conjugation between the two π-systems of the phosphadiene, is not clear if one considers discussions in earlier papers[9e,f]. It is clear that the bulky substituents at all three carbon atoms of our phosphadiene enforce the *gauche* conformation, since both the *cis* and the *trans* planar arrangements would entail larger steric interactions. Even in the *gauche* conformation, unfavorable 1,2-*cis* interactions between the bulky substituents can only be partly relieved by a widening of the respective bond angles at C1, C2, and C3.

The ^{13}C-NMR spectra of **18a**, **b** display the signals of the heterodiene unit at expected values [δ(P=C) = 205.0/204.5; δ(C=C) = 108.3/108.1 and 172.7/173.1]. Furthermore, analysis of the P,C coupling constants confirms the configuration and conformation as found in the solid state. The small $^3J_{P,C}$ coupling constants of the *C*-attached trimethylsilyl group (**18a**: J = 5.7 Hz; **18b**: J = 5.9 Hz), in combination with the relatively large $^5J_{P,C}$ coupling constant to the *i*Pr groups (7.3 and 7.7 Hz), can only be understood if the 2-phosphabutadienes exist as *gauche* conformers with a *Z* configuration at the C=C bond. The *gauche* conformation is also suggested by the very small coupling between P and the triisopropylsiloxy-substituted olefinic carbon atom (3 Hz). While the corresponding $^2J_{P,C}$ values in 2-phosphabutadienes unsubstituted at C-3 are in the range of 15–30 Hz[9c], a similarly low value has also been reported for 1,3-di-*tert*-butyl-2-phosphabutadiene[9d], another phosphadiene that bears a bulky substituent at C-3. The configuration at the P=C bond can also be concluded from the P,C coupling constants. The comparatively large $^4J_{P,C}$ coupling to the $OSiMe_3$ substituent (4.9 Hz), and the rather small $^2J_{P,C}$ coupling to the *tert*-butyl group (13.8 and 13.6 Hz), suggest the *E* configuration for **18a** and **b**, since larger ^2J and zero ^4J values have been reported for a

Figure 2. Structure of **18a** in the crystal; top: molecule plot showing ellipsoids of thermal vibration; bottom: molecule plot illustrating the conformation of the phosphadiene unit[a]



[a] Selected bond lengths [Å], bond angles [°] and torsion angles [°]: P1–C1 1.702(3), P1–C2 1.846(3), C2–C3 1.356(4); C1–P1–C2 109.6(1), P1–C2–C3 116.7(2), P1–C2–Si2 111.5(1), C3–C2–Si2 129.6(2), C2–C3–C4 129.2(2), P1–C1–C11 136.6(2), P1–C1–O1 114.8(2), C1–O1–Si1 136.3(2), C3–O2–Si3 141.8(2); C1–P1–C2–C3 –103.3(2), C2–P1–C1–C11 6.6(3).



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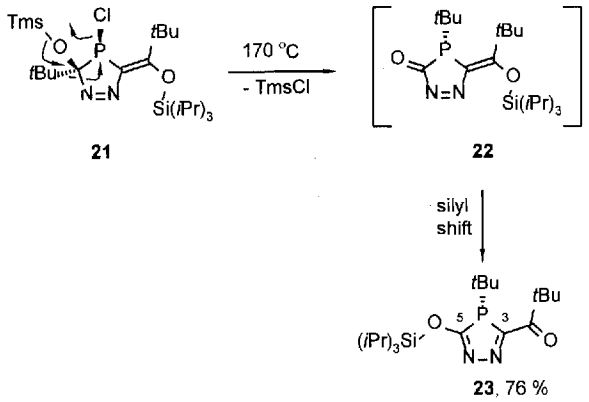
phosphaalkane that has the *t*Bu group *cis*, and the $OSiMe_3$ substituent *trans* to the lone electron pair at P[16].

It should not be concealed that the ^{31}P-NMR spectrum of "analytically pure" **18b** shows, besides the signal of the *gauche* isomer (δ = 153.0), a second signal at δ = 153.2 in a 10:1 ratio, indicating the presence of a second stereoisomer. A related observation was made when the progress of a thermolysis of **17a** at 110°C was monitored by ^{31}P-NMR spectroscopy. A weak signal at δ = 152.7, which decreased towards the end of the reaction, may again be assigned to a stereoisomer of *gauche*-**18a**. In both cases, the identity of the minor isomer could not be established due to the lack of ^{13}C-NMR data.

Thermolysis of 4-Chloro-4,5-dihydro-3-trimethylsiloxy-3*H*-1,2,4-diazaphosphole 21

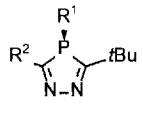
Compound **21** is, thermally, a surprisingly stable compound. Thermolysis in toluene was complete only after 8 h at 170°C. As the only product, 4*H*-1,2,4-diazaphosphole **23** was isolated in good yield (Scheme 3). Obviously, even at this high temperature, no extrusion of N_2 has taken place. We explain the formation of **23** by the elimination of chlorotrimethylsilane from **21**, in concert with, or followed by, a 1,2(C→P) *tert*-butyl group migration; the resulting intermediate **22** could then isomerize to **23** by a (probably bimolecular) O→O silyl group shift. It is remarkable that the thermal impact on **23** does not cause elimination of isobutene and formation of an aromatic 1*H*-1,2,4-diazaphosphole, since this was observed for another 4-*tert*-butyl-1,2,4-diazaphosphole[9d] and for 4-*tert*-butyl-4,5-dihydro-1*H*-1,2,4-diazaphospholes[7].

Scheme 3

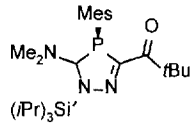


21 **22** **23**, 76 %

The structure of **23** was derived from the NMR data. While the ^{31}P-NMR signal at δ = −8.4 indicates a phosphane, it does not immediately point to a 4*H*-1,2,4-diazaphosphole. The wide range of ^{31}P chemicals shifts for such heterocycles is illustrated by the δ values of **24a**[17], **24b**[18], and **25**[7] (δ = 19, 56.9, and −52.2, respectively). More evidential are the ^{13}C chemical shifts of C-3 (δ = 160.6) and C-5 (δ = 192.5); the rather small $^1J_{P,C}$ coupling of these signals indicates again the high p character of the P−C bond. The δ(C-3) values, as well as the low IR wavenumber for ν(C=O) of 1645 cm^{-1}, are in reasonable agreement with the corresponding data for **25**, where full π-conjugation between C=N and C=O is suggested by an X-ray crystal structure analysis[7]. One of the two *t*Bu groups of **23** shows a rather large $^3J_{P,H}$ coupling (14.2 Hz), a clear indication that this substituent is connected to the phosphorus atom.



24a: $R^1 = R^2$ = Ph
24b: $R^1 = R^2$ = *t*Bu



25

Conclusion

5-Alkylidene-4,5-dihydro-3*H*-1,2,4-diazaphospholes have a much higher thermal stability than their counterparts lacking the exocyclic double bond. Typically, the extrusion of nitrogen from these compounds occurs at 110−150°C in toluene solution and, in most cases, P-containing heterocycles can be obtained that are difficult to obtain otherwise. A particularly interesting case, however, is the formation of highly substituted, stable 2-phosphabutadienes from **17**. A straightforward rationalization or prediction of the usually observed competing reaction pathways is not yet possible. It is obvious, however, that the large variety of phosphaalkenes, which can serve as precursors to the 5-alkylidene-4,5-dihydro-3*H*-1,2,4-diazaphospholes, offer opportunities for the synthesis of many more organophosphorus compounds of novel structural type or substituent pattern.

We thank the *Deutsche Forschungsgemeinschaft* (Graduiertenkolleg "Phosphor als Bindeglied verschiedener chemischer Disziplinen") for postgraduate grants to B. M. and J.K.

Experimental Section

All reactions were carried out under argon (purity <99.998%). Solvents were dried by standard procedures. All thermolyses in toluene that required temperatures above 110°C were done in thick-walled (2 mm) glass pressure tubes, fitted with a teflon ring and a screw cap behind a safety shield. Bulb-to-bulb distillations were carried out in a Büchi GKR 50 apparatus, the reported temperatures being oven temperatures. Column chromatography was performed on Lobar columns (Merck, LiChroprep Si 60) with anhydrous and distilled solvents but not under argon. − Microanalyses: Perkin-Elmer Model 2400 elemental analyzer. − Melting points were determined in a copper block and are not calibrated. − IR: Perkin-Elmer 1310 Infrared Spectrophotometer. − MS: Finnigan Mat 90. − NMR: Bruker AMX 400 (^{1}H: 400 MHz; ^{13}C: 101 MHz; ^{31}P: 162 MHz), for ^{1}H spectra taken in $CDCl_3$ solution, external $CHCl_3$ was used as standard, for other ^{1}H and ^{13}C spectra, the solvent signals served as internal standard. The chemical shifts for ^{31}P are relative to external 85% orthophosphoric acid. − The synthesis of **6a−g**, **17a**, **b**, and **21** has already been reported[7].

(Z)-2-[1-(tert-Butyldiphenylsilyloxy)-2,2-dimethylpropylidene]-3,3-diphenyl-1-(2,4,6-trimethylphenyl)phosphirane (**12c**) *and 5-tert-Butyl-4-(tert-butyldiphenylsilyl)-2,3-dihydro-2,2-diphenyl-3-(2,4,6-trimethylphenyl]-1,3-oxaphosphole* (**13c**): A solution of diazaphosphole **6c** (1.140 g, 1.67 mmol) in toluene (30 ml) was refluxed for 20 min. After cooling and removal of the solvent, crystallization from dichloromethane/acetonitrile (3:2) at −30°C gave colorless

crystals of **13c**. Lobar column chromatography of the residue [ether/pentane (1:200)] afforded **12c** [yield after crystallization from ether/pentane (1:1): 70 mg (6%); m.p. 137°C], followed by a small fraction of **13c** [combined yield: 910 mg (83%), m.p. 165°C (dec.)]. – Spectral and analytical data of **12c**: IR (KBr): $\tilde{\nu}$ = 3050, 3025, 2995, 2930, 2900, 2835, 1625, 1585, 1460, 1430, 1415, 1380, 1350, 1250, 1190, 1140, 1100, 1090, 1020, 890, 840, 820, 810, 760, 750, 730, 690, 655 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 0.96, 1.21 [2 s, 9H, $C(CH_3)_3$], 2.02, 2.20, 2.46 (3 s, 3H, CH_3), 6.27, 6.44 (2 s, 1H, *m*-H at Mes), 6.78–6.80 (m, 1H, Ph), 6.86 (t, $^3J_{H,H}$ = 7.5 Hz, 2H, Ph), 7.01–7.11 (m, 7H, Ph), 7.19 (t, $^3J_{H,H}$ = 7.2 Hz, 2H, Ph), 7.30–7.43 (m, 4H, Ph), 7.77 (d, $^3J_{H,H}$ = 7.9 Hz, 2H, Ph), 7.86 (d, $^3J_{H,H}$ = 7.9 Hz, 2H, Ph). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 20.3 (s, Si*C*Me$_3$), 20.8 (s, Me), 22.4 (d, $^3J_{P,C}$ = 26.7 Hz, *o*-Me), 22.6 (s, Me), 22.6 (s, Me), 27.8, 28.6 (2 s, C*Me*$_3$), 39.5 (s, C*C*Me$_3$), 51.1 (d, $^1J_{P,C}$ = 22.4 Hz, *C*Ph$_2$), 116.6 (d, $^1J_{P,C}$ = 48.3 Hz, P–C=), 124.9, 125.1, 126.5, 127.3, 127.4 (5 s, Ph), 127.8, 128.809 (2 s, *m*-C at Mes), 128.811 (d, $^3J_{P,C}$ = 13.2 Hz, Ph), 129.4, 129.5, 129.8 (3 s, Ph), 131.1 (d, $^1J_{P,C}$ = 55.5 Hz, *i*-C at Mes), 133.8, 134.5, 136.2 (3 s, Ph), 136.8 (s, *p*-C at Mes), 137.1 (d, $J_{P,C}$ = 2.2 Hz, Ph), 140.1, 141.9 (2 s, Ph), 143.7 (d, $^2J_{P,C}$ = 25.9 Hz, *o*-C at Mes), 146.0 (d, $^2J_{P,C}$ = 8.2 Hz, Ph), 163.9 (d, $^2J_{P,C}$ = 8.0 Hz, =C–O). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –131.5 (s). – $C_{44}H_{49}OPSi$ (652.9): calcd. C 80.94, H 7.56; found C 80.9, H 7.5. – Spectral and analytical data of **13c**: IR (KBr): $\tilde{\nu}$ = 3040, 3000, 2985, 2950, 2925, 2905, 2880, 2840, 1590, 1490, 1450, 1430, 1415, 1380, 1370, 1350, 1250, 1115, 1095, 1090, 1075, 1015, 1005, 995, 845, 810, 760, 735, 695. – ^{1}H NMR ($CDCl_3$): δ = 0.78, 0.86 (2 s, 9H, $C(CH_3)_3$), 2.13, 2.45 (2 s, 3H, CH_3), 2.83 (d, $^4J_{P,H}$ = 3.6 Hz, 3H, *o*-CH_3), 6.58 (s, 1H at Mes), 6.66 (d, $^4J_{P,H}$ = 4.9 Hz, 1H at Mes), 6.88 (t, $^3J_{H,H}$ = 7.3 Hz, 1H, Ph), 6.99 (t, $^3J_{H,H}$ = 7.8 Hz, 2H, Ph), 7.06 (t, $^3J_{H,H}$ = 7.6 Hz, 2H, Ph), 7.20–7.33 (m, 7H, Ph), 7.38 (t, $^3J_{H,H}$ = 7.5 Hz, 2H, Ph), 7.47 and 7.66 (2 d, $^3J_{H,H}$ = 7.2 Hz, 4H, Ph), 8.04–8.06 (m, 2H, Ph). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 19.9 (s, Si*C*Me$_3$), 21.0, 22.0 (2 s, Me), 24.4 (d, $^3J_{P,C}$ = 34.5 Hz, *o*-Me), 28.0 (d, $^4J_{P,C}$ = 8.0 Hz, SiC*Me*$_3$), 29.1 (s, CC*Me*$_3$), 38.0 (s, C*C*Me$_3$), 89.5 (d, $^1J_{P,C}$ = 46.7 Hz, Si–C=), 94.0 (d, $^1J_{P,C}$ = 27.6 Hz, *C*Ph$_2$), 125.0 (d, $J_{P,C}$ = 3.6 Hz, Ph), 125.6, 127.0, 127.4, 127.5, 127.8 (5 s, Ph), 127.9 (d, $J_{P,C}$ = 18.0 Hz, Ph), 128.2, 128.4 (2 s, Ph), 129.3 (d, $^3J_{P,C}$ = 7.1 Hz, *m*-C at Mes), 129.4 (d, $^1J_{P,C}$ = 45.2 Hz, *i*-C at Mes), 130.4 (s, *m*-C at Mes), 135.6, 136.3 (2 s, Ph), 137.9 (d, $J_{P,C}$ = 3.7 Hz, Ph), 138.6 (d, $J_{P,C}$ = 2.0 Hz, Ph), 139.4 (s, *p*-C at Mes), 142.9 (s, Ph), 145.5 (d, $^2J_{P,C}$ = 7.8 Hz, *o*-C at Mes), 145.7 (d, $^2J_{P,C}$ = 39.6 Hz, *o*-C at Mes), 146.1 (d, $J_{P,C}$ = 32.4 Hz, Ph), 179.1 (s, =C–O). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 14.3 (s). – $C_{44}H_{49}OPSi$ (652.9): calcd. C 80.94, H 7.56; found C 80.5, H 7.7.

(3E,2α,3aβ)-3-[1-(tert-Butyldimethylsilyloxy)-2,2-dimethylpropylidene]-3,3a-dihydro-1-phenyl-2-(2,4,6-trimethylphenyl)-1H-benzo[c]phosphole (**11d**) *and 5-tert-Butyl-4-(tert-butyldimethylsilyl)-2,3-dihydro-2,2-diphenyl-3-(2,4,6-trimethylphenyl)-1,3-oxaphosphole* (**13d**): A solution of **6d** (560 mg, 1.01 mmol) in toluene (30 ml) was refluxed for 20 min. After cooling and removal of the solvent, crystallization from dichloromethane/acetonitrile (1:1) at –30°C gave a mixture of two crystal types, namely colorless globular hard crystal lumps of **13d** on which fan-shaped ensembles of yellow needles of **11d** were sitting, which were separated manually under argon. Both products were recrystallized from dichloromethane/acetonitrile (1:1) at –30°C and washed with small portions of cold acetonitrile (–40°C). Yield of **13d**: 388 mg (73%); m.p. 101°C; yield of **11d**: 70 mg (13%); m.p. 161°C (dec.). – Spectral and analytical data of **11d**: IR (KBr): $\tilde{\nu}$ = 3010, 2940, 2910, 2880, 2840, 1580, 1560, 1455, 1440, 1250, 1150, 1130, 1090, 970, 830, 815, 805, 770, 750, 735, 695 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 0.27, 0.31 (2 s, 3H, $SiCH_3$), 1.03, 1.15 (2 s, 9H, $C(CH_3)_3$), 2.12, 2.26 (2 s, 3H, CH_3), 2.46 (d, $^4J_{P,H}$ = 2.4 Hz, 3H, *o*-CH_3), 4.83 (dd, $^3J_{P,H}$ = 17.8 Hz, $^3J_{H,H}$ = 3.0 Hz, 1H, H-3a), 5.95–6.01 (m, 2H, H-diene), 6.29–6.33 (m, 1H, H-diene), 6.36–6.39 (m, 1H, H-diene), 6.58 (s, 1H, *m*-H at Mes), 6.61 (d, $^4J_{P,H}$ = 4.8 Hz, 1H, *m*-H at Mes), 7.02–7.15 (m, 5H, Ph). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = –1.8, –1.4 (2 s, SiMe), 19.7 (s, Si*C*Me$_3$), 20.9 (s, *p*-Me), 21.9 (d, $^3J_{P,C}$ = 2.4 Hz, *o*-Me), 23.4 (d, $^3J_{P,C}$ = 31.9 Hz, *o*-Me), 27.0 (s, SiC*Me*$_3$), 29.7 (d, $^4J_{P,C}$ = 8.0 Hz, CC*Me*$_3$), 38.6 (d, $^3J_{P,C}$ = 1.6 Hz, C*C*Me$_3$), 54.4 (s, C-3a), 117.3 (d, $^1J_{P,C}$ = 20.5 Hz, C-3), 121.2 (s, C-diene), 123.1 (s, C-diene), 125.3 (d, $J_{P,C}$ = 3.2 Hz, C-diene), 126.5, 127.6 (2 s, Ph), 128.9 (d, $J_{P,C}$ = 4.1 Hz, Ph), 129.1 (d, $^3J_{P,C}$ = 7.2 Hz, *m*-C at Mes), 129.8 (s, *m*-C at Mes), 131.3 (d, $^1J_{P,C}$ = 40.9 Hz, *i*-C at Mes), 134.3 (s, diene-C), 137.1 (d, $^1J_{P,C}$ = 19.3 Hz, C-1), 138.6 (s, *p*-C at Mes), 139.3 (d, $^2J_{P,C}$ = 4.3 Hz, *o*-C at Mes), 140.6 (d, $^2J_{P,C}$ = 12.3 Hz, C-7a), 142.9 (d, $^2J_{P,C}$ = 34.8 Hz, *o*-C at Mes), 144.2 (d, $^2J_{P,C}$ = 5.7 Hz, *i*-C at Ph), 163.5 (d, $^2J_{P,C}$ = 33.8 Hz, =C–O). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –2.9 (s). – MS (EI, 120 eV); *m/z* (%): 528 (100) [M^+], 513 (29) [$M^+ - CH_3$], 471 (37) [$M^+ - t$Bu], 413 (4) [$M^+ - SiMe_2t$Bu], 397 (4) [$M^+ - OSiMe_2t$Bu], 371 (9), 342 (7), 328 (5) [$M^+ - (t$BuMe$_2$SiO)*t*BuC=], 209 (6), 73 (57), 57 (15) [*t*Bu$^+$]. – $C_{34}H_{45}OPSi$ (528.8): calcd. C 77.23, H 8.58; found C 77.2, H 8.4. – Spectral and analytical data of **13d**: IR (KBr): $\tilde{\nu}$ = 3035, 3000, 2940, 2900, 2835, 1585, 1520, 1450, 1430, 1390, 1350, 1250, 1130, 1110, 1070, 1020, 975, 830, 800, 775, 740, 695 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = –0.20, 0.24 (2 s, 3H, $SiCH_3$), 0.87, 1.29 [2 s, 9H, $C(CH_3)_3$], 2.06, 2.33 (2 s, 3H, CH_3), 2.66 (d, $^4J_{P,H}$ = 3.8 Hz, 3H, *o*-CH_3), 6.42 (s, 1H, *m*-H at Mes), 6.57 (d, $^4J_{P,H}$ = 5.0 Hz, 1H, *m*-H at Mes), 6.80–6.84 (m, 1H, Ph), 6.90–6.94, 7.08–7.11 (2 m, 2H, Ph), 7.18–7.22 (m, 1H, Ph), 7.27–7.31, 7.88–7.91 (2 m, 2H, Ph). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = –0.9 (d, $^3J_{P,C}$ = 17.3 Hz, SiMe), 1.2 (d, $^3J_{P,C}$ = 4.5 Hz, SiMe), 18.9 (s, Si*C*Me$_3$), 20.8, 22.3 (2 s, Me), 24.3 (d, $^3J_{P,C}$ = 37.7 Hz, *o*-Me), 28.2 (d, $^4J_{P,C}$ = 7.8 Hz, SiC*Me*$_3$), 29.8 (s, CC*Me*$_3$), 36.7 (s, C*C*Me$_3$), 91.7 (d, $^1J_{P,C}$ = 29.0 Hz, *C*Ph$_2$), 92.0 (d, $^1J_{P,C}$ = 46.6 Hz, Si–C=), 125.2 (d, $J_{P,C}$ = 3.6 Hz, Ph), 125.4, 127.0, 127.2, 127.6 (each s, Ph), 127.8 (d, $J_{P,C}$ = 17.8 Hz, Ph), 129.0 (d, $^3J_{P,C}$ = 6.4 Hz, *m*-C at Mes), 130.1 (s, *m*-C at Mes), 130.2 (d, $^1J_{P,C}$ = 45.5 Hz, *i*-C at Mes), 138.6 (s, *p*-C at Mes), 143.1 (s, Ph), 144.5 (d, $^2J_{P,C}$ = 34.9 Hz, *o*-C at Mes), 144.7 (d, $^2J_{P,C}$ = 7.3 Hz, *o*-C at Mes), 146.2 (d, $J_{P,C}$ = 32.9 Hz, Ph), 173.7 (s, =C–O). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 26.6 (s). – $C_{34}H_{45}OPSi$ (528.8): calcd. C 77.23, H 8.58; found C 76.8, H 8.4.

2,3-Dihydro-5-methyl-2,2-diphenyl-4-(triisopropylsilyl)-3-(2,4,6-trimethylphenyl)-1,3-oxaphosphole (**13e**) *and 2,3-Dihydro-5-methyl-2,2-diphenyl-4-(triisopropylsilyl)-3-(2,4,6-trimethylphenyl)-1,3-oxaphosphole 3-Oxide* (**16e**): Diazaphosphole **6e** was generated in situ by stirring a solution of diphenylmethylene(mesityl)phosphane[19] (1.175 g, 3.71 mmol) and 1-diazo-1-(triisopropylsilyl)-2-propanone[20] (893 mg, 3.71 mmol) in dichloromethane (5 ml) at 45°C for 2 d in a Schlenk pressure tube. The solvent was replaced by toluene (15 ml). This solution was heated at 110°C for 5 min, and after cooling the solvent was stripped off. The residue was twice subjected to Lobar column chromatography, eluating first with ether/pentane (1:200), then with ether/pentane (1:400). The two fractions obtained were each recrystallized from ether/pentane (1:1) at –78°C. Yield of **13e**: 75 mg [4% based on diphenylmethylene(mesityl)phosphane], m.p. 137°C; yield of **16e**: 208 mg (10%), m.p. 158°C. – Spectral and analytical data of **13e**: IR (KBr): $\tilde{\nu}$ = 3040, 3000, 2950, 2920, 2900, 2840, 2820, 2800, 1590, 1560, 1480, 1450, 1430, 1360, 1200, 1175, 1150, 1025, 1005, 985, 880, 865, 845, 750, 735, 695 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 0.70, 0.93 (2 d, $^3J_{H,H}$ = 7.4 Hz, 9H, $CHCH_3$), 1.13 (sept, $^3J_{H,H}$ = 7.4 Hz, 3H,

C*H*CH_3), 2.10, 2.13 (2 s, 3H, CH_3), 2.22 (d, $^4J_{P,H}$ = 1.6 Hz, 3H, OCCH_3), 2.82 (d, $^4J_{P,H}$ = 4.2 Hz, 3H, *o*-CH_3), 6.47 (s, 1H, *m*-H at Mes), 6.74 (d, $^4J_{P,H}$ = 4.9 Hz, 1H, *m*-H at Mes), 6.89–6.93 (m, 1H, Ph), 6.97–7.01, 7.06–7.09 (2 m, 2H, Ph), 7.11–7.15 (m, 1H, Ph), 7.22–7.26, 7.72–7.75 (2 m, 2H, Ph). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 13.2 (d, $^3J_{P,C}$ = 4.2 Hz, SiCH), 18.2 (s, SiCH*Me*), 18.78 (d, $^4J_{P,C}$ = 1.9 Hz, SiCH*Me*), 18.82 (d, $^3J_{P,C}$ = 6.0 Hz, OC*Me*), 20.7, 20.9 (2 s, Me), 24.5 (d, $^3J_{P,C}$ = 39.1 Hz, *o*-Me), 91.4 (d, $^1J_{P,C}$ = 42.5 Hz, Si–C=), 93.5 (d, $^1J_{P,C}$ = 32.0 Hz, CPh_2), 125.76 (d, $J_{P,C}$ = 4.5 Hz, Ph), 125.85 (s, Ph), 125.88 (d, $J_{P,C}$ = 19.6 Hz, Ph), 126.7 (d, $J_{P,C}$ = 2.4 Hz, Ph), 127.4, 127.6 (2 s, Ph), 129.0 (d, $^3J_{P,C}$ = 7.2 Hz, *m*-C at Mes), 129.8 (d, $^1J_{P,C}$ = 47.6 Hz, *i*-C at Mes), 130.3 (s, *m*-C at Mes), 139.3 (d, $^4J_{P,C}$ = 1.6 Hz, *p*-C at Mes), 142.6 (d, $J_{P,C}$ = 1.6 Hz, Ph), 145.0 (d, $^2J_{P,C}$ = 4.8 Hz, *o*-C at Mes), 145.6 (d, $^2J_{P,C}$ = 39.4 Hz, *o*-C at Mes), 147.5 (d, $J_{P,C}$ = 32.2 Hz, Ph), 166.1 (s, =C–O). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 23.2 (s). – $C_{34}H_{45}OPSi$ (528.8): calcd. C 77.23, H 8.58; found C 77.9, H 8.4. – Spectral and analytical data of **16e**: IR (KBr): $\tilde{\nu}$ = 3040, 2945, 2920, 2870, 2845, 1565, 1480, 1450, 1435, 1360, 1215, 1200, 1190 (P=O), 1155, 1060, 1040, 1025, 1000, 985, 890, 875, 745, 695 cm^{-1}. – ^1H NMR (400.1 MHz): δ = 0.83, 0.98 (2 d, $^3J_{H,H}$ = 7.5 Hz, 9H, SiCHCH_3), 1.33 (sept, $^3J_{H,H}$ = 7.5 Hz, 3H, SiC*H*CH_3), 1.90, 2.17, 2.37, 2.83 (4 s, 3H, CH_3), 6.48 (d, $^4J_{P,H}$ = 3.6 Hz, 1H, *m*-H at Mes), 6.87 (s, 1H, *m*-H at Mes), 7.01–7.10 (m, 4H, Ph), 7.17 (t, $^3J_{H,H}$ = 7.2 Hz, 1H, Ph), 7.25–7.37 (m, 5H, Ph). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 12.6 (d, $^3J_{P,C}$ = 1.1 Hz, SiCH), 18.5, 18.8 (2 s, SiCH*Me*), 20.3 (d, $^3J_{P,C}$ = 11.2 Hz, OC*Me*), 20.8 (s, Me), 21.4 (d, $^3J_{P,C}$ = 3.5 Hz, *o*-Me), 25.5 (s, Me), 89.2 (d, $^1J_{P,C}$ = 56.9 Hz, Si–C=), 96.0 (d, $^1J_{P,C}$ = 54.2 Hz, CPh_2), 126.0 (d, $^1J_{P,C}$ = 93.2 Hz, *i*-C at Mes), 126.3 (d, $J_{P,C}$ = 2.5 Hz, Ph), 126.5 (d, $J_{P,C}$ = 4.2 Hz, Ph), 127.0 (s, Ph), 127.1 (d, $J_{P,C}$ = 1.6 Hz, Ph), 127.2 (s, Ph), 127.7 (d, $J_{P,C}$ = 1.2 Hz, Ph), 130.7 (d, $^3J_{P,C}$ = 12.3 Hz, *m*-C at Mes), 132.0 (d, $^3J_{P,C}$ = 11.9 Hz, *m*-C at Mes), 139.2 (d, $^3J_{P,C}$ = 4.1 Hz, *p*-C at Mes), 139.8 (s, Ph), 141.4 (d, $^2J_{P,C}$ = 3.0 Hz, *o*-C at Mes), 142.3 (d, $J_{P,C}$ = 13.3 Hz, Ph), 146.4 (d, $^2J_{P,C}$ = 8.7 Hz, *o*-C at Mes), 174.2 (d, $^2J_{P,C}$ = 4.0 Hz, =C–O). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 72.1 (s). – MS (CI, 120 eV); *m/z* (%): 545 (70) [M^+], 544 (23) [M^+ – H], 501 (15) [M^+ – H/*i*Pr], 375 (13) [M^+ – (iPr)$_3$SiC], 332 (100) [M^+ – (iPr)$_3$SiC=C(O)CH_3], 297 (12), 255 (17). – $C_{34}H_{45}O_2PSi$ (544.8): calcd. C 74.96, H 8.33; found C 75.0, H 8.2.

2,3-Dihydro-5-(4-methoxyphenyl)-2,2-diphenyl-4-(triisopropylsilyl)-3-(2,4,6-trimethylphenyl)-1,3-oxaphoshole (**13f**) *and (1E,2α,3α)-2,3-Dihyro-1-[4-methoxy-α-(triisopropylsilyloxy)-benzylidene]-3-phenyl-2-(2,4,6-trimethylphenyl)-1H-benzo[c]phosphole* (**14f**): A solution of **6f** (686 mg, 1.06 mmol) in toluene was heated at reflux for 15 min. From the residue left after evaporation of the solvent, colorless crystals of **14f** were obtained by crystallization from dichloromethane/acetonitrile (2:1) at –30°C. Lobar column chromatography with ether/pentane (30:1) as the eluent yielded **13f** as the first fraction, followed by a small portion of **14f**. Yield of **13f**: 183 mg (27%), m.p. 143°C (from pentane); yield of **14f**: 359 mg (54%), m.p. 143°C. – Spectral and analytical data of **13f**: IR (KBr): $\tilde{\nu}$ = 3070, 3040, 3010, 2920, 2840, 1590, 1535, 1480, 1445, 1440, 1290, 1240, 1160, 1065, 1025, 1010, 990, 975, 875, 830, 810, 760, 735, 690 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.60, 0.86 (2 d, $^3J_{H,H}$ = 7.2 Hz, 9H, CHCH_3), 0.95 (sept, 3H, $^3J_{H,H}$ = 7.2 Hz, C*H*CH_3), 2.11, 2.36 (2 s, 3H, CH_3), 2.87 (d, $^4J_{P,H}$ = 4.1 Hz, 3H, *o*-CH_3), 3.85 (s, 3H, OCH_3), 6.48 (s, 1H, *m*-H at Mes), 6.73 (d, $^4J_{P,H}$ = 4.6 Hz, 1H, *m*-H at Mes), 6.85–6.97 (m, 5H, Ph), 7.17–7.24 (m, 3H, Ph), 7.31 (t, $^3J_{H,H}$ = 7.6 Hz, 2H, Ph), 7.51–7.54, 7.95–7.97 (2 m, 2H, Ph). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 13.2 (d, $^3J_{P,C}$ = 4.6 Hz, SiCH), 18.5, 19.0 (2 s, SiCH*Me*), 20.9, 21.4 (2 s, Me), 24.6 (d, $^3J_{P,C}$ = 38.6 Hz, *o*-Me), 55.2 (s, OMe), 94.1 (d, $^1J_{P,C}$ = 32.3 Hz, CPh_2), 94.8 (d, $^1J_{P,C}$ = 46.4 Hz, Si–C=), 113.1 (s, *m*-C at PhOMe), 125.5 (d, $J_{P,C}$ = 3.6 Hz, Ph), 125.6 (s, Ph), 126.6 (d, $J_{P,C}$ = 15.7 Hz, Ph), 127.0, 127.3, 127.8 (3 s, Ph), 128.1 (d, $^4J_{P,C}$ = 2.4 Hz, *i*-C at PhOMe), 129.0 (d, $^3J_{P,C}$ = 7.3 Hz, *m*-C at Mes), 129.6 (d, $^1J_{P,C}$ = 45.7 Hz, *i*-C at Mes), 130.3 (*m*-C at Mes), 130.5 (s, *o*-C at PhOMe), 139.4 (s, *p*-C at Mes), 142.7 (s, Ph), 145.2 (d, $^2J_{P,C}$ = 4.1 Hz, *o*-C at Mes), 145.7 (d, $^2J_{P,C}$ = 40.0 Hz, *o*-C at Mes), 147.4 (d, $J_{P,C}$ = 32.8 Hz, Ph), 160.4 (s, *p*-C at PhOMe), 166.6 (s, =C–O). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 22.2 (s). – $C_{40}H_{49}O_2PSi$ (620.9): calcd. C 77.38, H 7.95; found C 77.2, H 8.0. – Spectral and analytical data of **14f**: IR (KBr): $\tilde{\nu}$ = 3045, 3005, 2940, 2920, 2900, 2875, 2845, 2830, 1595, 1575, 1490, 1450, 1285, 1255, 1235, 1215, 1175, 1165, 1110, 1100, 1075, 1060, 1025, 1005, 875, 820, 755, 740, 720, 690 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 1.00–1.08 [m, 21H, SiC*H*(CH_3)$_2$], 1.84 (d, $^4J_{P,H}$ = 3.5 Hz, 3H, *o*-CH_3), 2.06, 2.11 (2 s, 3H, CH_3), 3.73 (s, 3H, OMe), 4.96 (d, $^2J_{P,H}$ = 21.1 Hz, 1H, H-3), 6.33 (d, $^4J_{P,H}$ = 4.1 Hz, 1H, *m*-H at Mes), 6.52 (s, 1H, *m*-H at Mes), 6.63 (d, $^3J_{H,H}$ = 8.7 Hz, 2H, *m*-H at PhOMe), 6.79–6.81 (m, 2H, Ph), 6.89–6.91 (m, 3H, Ph), 7.01 (d, $^3J_{H,H}$ = 7.7 Hz, 1H), 7.09 (t, $^3J_{H,H}$ = 7.3 Hz, 1H), 7.14 (d, $^3J_{H,H}$ = 8.7 Hz, 2H, *o*-H at PhOMe), 7.26 (t, $^3J_{H,H}$ = 7.3 Hz, 1H), 8.27 (d, $^3J_{H,H}$ = 7.7 Hz, 1H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 13.5 (s, SiCH), 17.9, 18.0 (2 s, SiCH*Me*), 20.7 (s, Me), 23.7 (d, $^4J_{P,C}$ = 36.2 Hz, *o*-Me), 23.7 (s, Me), 50.9 (d, $^1J_{P,C}$ = 15.3 Hz, C-3), 55.1 (s, OMe), 112.7 (s, *m*-C at PhOMe), 118.7 (d, $^1J_{P,C}$ = 11.7 Hz, C-1), 125.3, 125.9, 126.2, 126.3, 126.7, 127.2 (6 s, aryl), 128.5 (d, $^3J_{P,C}$ = 6.2 Hz, *m*-C at Mes), 128.8 (s, aryl), 129.8 (s, *m*-C at Mes), 130.2 (d, $^1J_{P,C}$ = 40.2, *i*-C at Mes), 130.3 (d, $^4J_{P,C}$ = 5.5 Hz, *o*-C at PhOMe), 133.3 (d, $^3J_{P,C}$ = 3.9 Hz, *i*-C at PhOMe), 137.7 (s, *p*-C at Mes), 139.8 (d, $J_{P,C}$ = 3.7 Hz, aryl), 142.6 (d, $^2J_{P,C}$ = 5.9 Hz, *o*-C at Mes), 143.4 (s, aryl), 144.4 (d, $^2J_{P,C}$ = 35.4 Hz, *o*-C at Mes), 146.9 (d, $J_{P,C}$ = 3.7 Hz, aryl), 154.3 (d, $^2J_{P,C}$ = 42.2 Hz, =C–O), 159.5 (s, *p*-C at PhOMe). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 2.6 (s). – MS: (EI, 35 eV); *m/z* (%): 620 (47) [M^+], 619 (64) [M^+ – H], 576 (8) [M^+ – *i*Pr], 358 (6), 331 (28) [M^+ – =C{O*Si*(*i*Pr)$_3$}PhOMe], 330 (100) [M^+ – H/=C{O*Si*(*i*Pr)$_3$}PhOMe], 280 (46), 265 (21), 237 (43), 167 (14), 131 (19), 103 (16), 57 (32), 43 (85) [*i*Pr$^+$]. – $C_{40}H_{49}O_2PSi$ (620.9): calcd. C 77.38, H 7.95; found C 77.6, H 8.0.

(1E,2α,3β)-2,3-Dihydro-1-[4-nitro-α-(triisopropylsilyloxy)-benzylidene]-3-phenyl-2-(2,4,6-trimethylphenyl)-1H-benzo[c]phosphole 2-Oxide (**15g**): A solution of **6g** (892 mg, 1.34 mmol) in toluene (30 ml) was heated at reflux for 10 min. After cooling and removal of the solvent, the residual dark-red viscous oil was dissolved in ether and placed in a centrifuge vial under argon. At –78°C, a suspension of a yellow powder formed to which pentane (50 ml) was added. After 1 h, this suspension was brought to 20°C and separated in an ultracentrifuge. The red solution was pipetted off, and the yellow solid, which was still contaminated with polymeric material, was recrystallized twice from ether at –78°C and washed with cold pentane (–78°C). After drying (70°C/0.005 mbar), analytically pure **15g** was obtained as a yellow powder; yield: 220 mg (25%); m.p. 204°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3080, 3040, 3000, 2920, 2850, 1590, 1555, 1505, 1450, 1330, 1295, 1255, 1215, 1190, 1160, 1130, 1095, 1075, 1055, 1005, 875, 860, 850, 775, 755, 730, 710, 695 cm^{-1}. – ^1H NMR ($CDCl_3$, 249 K): δ = 0.98–1.07 [m, 21H, SiC*H*(CH_3)$_2$], 1.73, 1.94, 2.26 (3 s, 3H, CH_3), 5.02 (d, $^2J_{P,H}$ = 25.0 Hz, 1H, 3-H), 6.24 (br. s, 1H, *m*-H at Mes), 6.32 (s, 1H, *m*-H at Mes), 6.95 (br. s, 5H, aryl), 7.26–7.33 (m, 2H, aryl), 7.40 (t, $^3J_{H,H}$ = 7.3 Hz, 1H, aryl), 7.60 and 7.86 (AA'BB' spin system, $PhNO_2$), 8.30 (d, $^3J_{H,H}$ = 7.9 Hz, 1H, aryl). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 249 K): δ = 13.1 (s, SiCH), 17.6 (s, SiCHMe_2), 20.6, 23.5 (2 s, Me), 24.2 (d, $^3J_{P,C}$ = 3.7 Hz, *o*-Me),

55.2 (d, $^1J_{P,C}$ = 66.3 Hz, C-3), 118.3 (d, $^1J_{P,C}$ = 96.6 Hz, C-1), 121.9 (s, *m*-C at $PhNO_2$), 122.3 (d, $^1J_{P,C}$ = 97.4 Hz, *i*-C at Mes), 126.1 (s, aryl), 126.5 (d, $J_{P,C}$ = 10.6 Hz, aryl), 127.5 (br. s, aryl), 128.5 (d, $J_{P,C}$ = 11.0 Hz, aryl), 129.3 (d, $^3J_{P,C}$ = 12.0 Hz, *m*-C at Mes), 129.7 (s, aryl), 130.4 (d, $^3J_{P,C}$ = 11.6 Hz, *m*-C at Mes), 135.8 (d, $J_{P,C}$ = 3.7 Hz, aryl), 136.8 (d, $^2J_{P,C}$ = 9.1 Hz, aryl), 137.6 (d, $J_{P,C}$ = 24.2 Hz, aryl), 139.1 (d, $^2J_{P,C}$ = 12.6 Hz, *o*-C at Mes), 140.7 (d, $J_{P,C}$ = 2.9 Hz, aryl), 143.0 (d, $J_{P,C}$ = 1.9 Hz, aryl), 145.4 (d, $^2J_{P,C}$ = 8.1 Hz, *o*-C at Mes), 147.0 (s, *p*-C at $PhNO_2$), 156.1 (d, $^2J_{P,C}$ = 18.9 Hz, =C–O). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 56.2 (s). – MS (EI, 70 eV); *m/z* (%): 652 (15) [M^+], 611 (21), 610 (74) [$M^+ - C_3H_6$], 609 (100) [$M^+ - i$Pr], 563 (8), 59 (10). – $C_{39}H_{46}NO_4PSi$ (651.9): calcd. C 71.86, H 7.11, N 2.15; found C 72.1, H 7.0, N 2.6.

Thermolysis of **17a**: A stirred solution of **17a** (855 mg, 1.57 mmol) in toluene (5 ml) was heated in a Schlenk pressure tube at 150°C for 4 h. After cooling, the volatile compounds were removed in vacuo (20°C/0.002 mbar and 80°C/0.002 mbar). The green-yellow residue consisted of a mixture of **18a**, **19a**[7], and an unknown compound in the ratio 51:11:38 (ratio determined by integration of the $^{31}P\{^1H\}$ NMR signals). *(3E,5Z)-2,2,7,7-Tetramethyl-6-(triisopropylsilyloxy)-5-(trimethylsilyl)-3-(trimethylsilyloxy)-4-phosphaocta-3,5-diene* (**18a**) was isolated by twofold bulb-to-bulb distillation at 120°C/0.002 mbar, followed by crystallization from a small portion of toluene at −78°C over a period of 4 months, and washing three times with small portions of cold toluene (−78°C). Yield: 210 mg (26%) of very air-sensitive crystals, m.p. 55°C. – ^1H NMR (C_6D_6): δ = 0.37 (d, $J_{P,H}$ = 1.2 Hz, 9H, $Si(CH_3)_3$), 0.44 [s, 9H, $Si(CH_3)_3$], 1.24, 1.260 (2 d, $^3J_{H,H}$ = 7.5 Hz, 9H, $CHCH_3$), 1.261, 1.32 [2 s, 9H, $C(CH_3)_3$], 1.66 (sept, 3H, $CHCH_3$). ^{13}C-NMR (C_6D_6): δ = 0.9 (d, $^3J_{P,C}$ = 5.7 Hz, 5-$SiMe_3$), 5.4 (d, $^4J_{P,C}$ = 4.9 Hz, $OSiMe_3$), 15.4 (d, $^5J_{P,C}$ = 7.3 Hz, SiCH), 19.0 (s, $SiCHMe_2$), 30.0 (d, $^3J_{P,C}$ = 4.0 Hz, P=CCMe_3), 30.5 (s, C=CCMe_3), 41.0 (s, C=C*C*Me_3), 45.8 (d, $^2J_{P,C}$ = 13.8 Hz, P=C*C*Me_3), 108.3 (d, $^1J_{P,C}$ = 60.2 Hz, P–C=), 172.7 (d, $^2J_{P,C}$ = 2.9 Hz, P–C=*C*), 205.0 (d, $^1J_{P,C}$ = 58.3 Hz, P=C). – $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 151.4 (s). – $C_{26}H_{57}O_2PSi_3$ (517.0): calcd. C 60.41, H 11.11; found C 60.74, H 10.94. – The unknown component of the thermolysis mixture could not be isolated in a pure form due to its high sensitivity towards air and/or moisture. – Spectral data: ^{13}C NMR ([D_8]toluene): δ = 2.1 (s, $SiMe_3$), 2.2 (d, $J_{P,C}$ = 4.6 Hz, $SiMe_3$), 14.8 (s, SiCH), 19.9, 20.0 (2 s, $SiCHMe$), 29.9 (s, CMe_3), 30.8 (d, $J_{P,C}$ = 4.1 Hz, CMe_3), 37.0 (d, $J_{P,C}$ = 17.7 Hz, *C*Me_3), 39.8 (d, $J_{P,C}$ = 2.4 Hz, *C*Me_3), 140.2 (d, $J_{P,C}$ = 27.2 Hz), 162.6 (d, $J_{P,C}$ = 38.5 Hz), 170.4 (d, $J_{P,C}$ = 37.4 Hz). – ^{31}P NMR (C_6D_6): δ = 63.2 (s).

Thermolysis of **17b**: A stirred solution of **17b** (482 mg, 0.77 mmol) in toluene (6 ml) was heated in a Schlenk pressure tube at 150°C for 4 h. The volatile compounds were removed at 20°C/0.005 mbar and 80°C/0.005 mbar. The residual yellow-green oil was a mixture of **18b**, **19b**, and an unknown compound in the ratio 49:13:38 (determined by $^{31}P\{^1H\}$-NMR integration). *(3E,5Z)-6-(1-Adamantyl)-2,2-dimethyl-6-(triisopropylsilyloxy)-5-(trimethylsilyl)-3-(trimethylsilyloxy)-4-phosphahexa-3,5-diene* (**18b**) was isolated by twofold bulb-to-bulb distillation at 140°C/0.005 mbar in nearly analytically pure form. The product was crystallized in a few days from a small portion of toluene first at −30°C and then at −78°C. The toluene was pipetted off, and the colorless crystals were dried for 2 h at 70°C/0.005 mbar. Yield: 138 mg (30%); m.p. 149°C. – ^1H NMR (C_6D_6): δ = 0.38 [d, $J_{P,H}$ = 0.8 Hz, 9H, $Si(CH_3)_3$], 0.49 [s, 9H, $Si(CH_3)_3$], 1.28, 1.29 (2 d, $^3J_{H,H}$ = 7.6 Hz, 9H, $CHCH_3$), 1.34 [s, 9H, $C(CH_3)_3$], 1.61–1.77 (m, 9H, 6H-Ad and $CHCH_3$), 1.98 (br. s, 3H, Ad), 2.07–2.08 (m, 6H, Ad). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 0.9 (d, $^3J_{P,C}$ = 5.9 Hz, 5-$SiMe_3$), 5.9 (d, $^4J_{P,C}$ = 4.9 Hz, $OSiMe_3$), 15.4 (d, $^5J_{P,C}$ = 7.7 Hz, SiCH), 19.1 (s, $SiCHMe_2$), 29.1 (s, C-3, -5, -7-Ad), 30.1 (d, $^3J_{P,C}$ = 4.0 Hz, CMe_3), 37.0 (s, C-4, -6, -10-Ad), 40.8 (s, C-2, -8, -9-Ad), 43.5 (s, C-1-Ad), 45.9 (d, $^2J_{P,C}$ = 13.6 Hz, *C*Me_3), 108.1 (d, $^1J_{P,C}$ = 60.0 Hz, P–C=), 173.1 (d, $^2J_{P,C}$ = 3.2 Hz, P–C=*C*), 204.5 (d, $^1J_{P,C}$ = 58.1 Hz, P=C). – $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 153.0 (s). – MS (EI, 70 eV); *m/z* (%): 595 (1) [M^+], 580 (4) [$M^+ - CH_3$], 552 (12) [$M^+ - i$Pr], 363 (100), 348 (7), 306 (16), 294 (9), 263 (8), 159 (18), 147 (7), 135 (8), 115 (7), 87 (8), 73 (47) [$SiMe_3^+$], 59 (13), 57 (8) [tBu$^+$]. – $C_{32}H_{63}O_2PSi_3$ (595.1): calcd. C 64.59, H 10.67; found C 64.4, H 10.6. – Compound **19b** was identified in the crude product mixture by its ^{31}P- and ^{13}C-NMR signals which show close similarity to those of **19a**[7]. The third, unknown constituent of the product mixture could not be obtained in pure form due to its high sensitivity towards air and/or moisture. It showed the following spectral data: ^{13}C NMR (C_6D_6): δ = 2.0 (s, $SiMe_3$), 2.4 (d, $J_{P,C}$ = 5.1 Hz, $SiMe_3$), 14.8 (s, SiCH), 19.8, 19.9 (2 s, $SiCHMe$), 28.9 (s, C-3, -5, -7-Ad), 30.7 (d, $J_{P,C}$ = 4.1 Hz, CMe_3), 36.8 (d, $J_{P,C}$ = 18.1 Hz, CMe_3), 37.1 (s, C-4, -6, -10-Ad), 40.6 (s, C-2, -8, -9-Ad), 42.2 (d, $J_{P,C}$ = 1.6 Hz, C-1-Ad), 140.5 (d, $J_{P,C}$ = 27.4 Hz), 162.5 (d, $J_{P,C}$ = 37.7 Hz), 170.0 (d, $J_{P,C}$ = 37.3 Hz). – $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 63.7 (s).

4-tert-Butyl-5-(2,2-dimethyl-1-propanoyl)-3-(triisopropylsilyloxy)-4H-1,2,4-diazaphosphole (**23**): A suspension of **21** (918 mg, 1.81 mmol) in toluene (15 ml) was heated to 170°C in a Schlenk pressure tube, whereby a homogeneous solution was formed. After 8 h, the solution was allowed to cool and the solvent was removed. Rapid bulb-to-bulb distillation of the residue at 150°C/0.002 mbar furnished **23** as a pale-green oil which solidified on storing at 0°C. Yield: 548 mg (76%); m.p. 42–50°C. – IR (oil): $\tilde{\nu}$ = 2920, 2845, 1645 (C=O), 1450, 1380, 1355, 1245, 1205, 1145, 1070, 1010, 895, 875 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 1.10 [d, $^3J_{H,H}$ = 7.5 Hz, 18H, $CH(CH_3)_2$], 1.25 [d, $^3J_{P,H}$ = 14.2 Hz, 9H, $PC(CH_3)_3$], 1.33 [s, 9H, $CC(CH_3)_3$], 1.61 (sept, $^3J_{H,H}$ = 7.5 Hz, 3H, $CHCH_3$). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.8 (s, SiCH), 17.8, 17.9 (2 s, $SiCHMe$), 27.1 (s, CCMe_3), 28.7 (d, $^2J_{P,C}$ = 12.0 Hz, PCMe_3), 37.1 (d, $^1J_{P,C}$ = 20.4 Hz, P*C*Me_3), 43.8 (s, *C*CMe_3), 160.6 (d, $^1J_{P,C}$ = 30.5 Hz, C-3), 192.5 (d, $^1J_{P,C}$ = 19.3 Hz, C-5), 202.1 (d, $^2J_{P,C}$ = 13.3 Hz, C=O). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −8.4 (s). – $C_{20}H_{39}N_2O_2PSi$ (398.6): calcd. C 60.27, H 9.86, N 7.03; found C 60.1, H 9.9, N 5.7.

X-Ray Crystal Structure Determination of **13c**[21]. – *Crystal Data:* $C_{44}H_{49}OPSi \cdot 0.25\ CH_2Cl_2$; M = 674.12 g/mol; triclinic space group $P\bar{1}$, a = 10.353(8), b = 19.040(1), c = 20.269(9) Å, α = 87.49(4), β = 78.16(4), γ = 87.79(4)°; V = 3905(3) Å^3; Z = 4; $d_{calcd.}$ = 1.147 Mg/m^3; μ(Mo-K_α) = 0.167 mm^{-1}. – *Data Collection:* T = 293 K, crystal size 0.4 × 0.2 × 0.7 mm, diffractometer Enraf-Nonius CAD4; radiation Mo-K_α; Θ range 2.01–21.01°, ω/2Θ scans; 8684 reflections measured (one hemisphere), 8375 unique reflections. – *Structure Solution and Refinement:* Structure solution by direct methods (program SHELXS-86), full-matrix least-squares refinement on F^2 (program SHELXL-93) with all unique data and 873 variables. Hydrogen atoms are in calculated positions and were treated as riding atoms. R = 0.1316 for all reflections [0.0749 for 5227 observed reflections, $I > 2\sigma(I)$], R_w = 0.2238 (0.1697), residual electron density between 1.06 and −0.20 eÅ^{-3}. The dichloromethane molecules in the crystal are disordered. Pairs of CH_2Cl_2 molecules (site occupation factor = 0.5) appear as a C_2Cl_2 four-membered ring in the electron density map, because their respective Cl positions nearly coincide under the action of a crystallographic inversion center; as a consequence, the calculated bond geometry was not considered to be reasonable and the ellipsoid of thermal vibration for chlorine was refined with considerable anisotropy. It was not possible to refine split positions for the individual Cl atoms.

X-Ray Crystal Structure Determination of **18a**[21]. – *Crystal Data:* $C_{26}H_{57}O_2PSi_3$; M = 516.96 g/mol; monoclinic space group $P2_1/n$, a = 10.199(1), b = 21.367(2), c = 16.066(2) Å, α = 90, β = 106.54(1), γ = 90°; V = 3356.3(6) Å^3; Z = 4; $d_{calcd.}$ = 1.023 Mg/m^3; μ(Mo-K_α) = 0.207 mm^{-1}. – *Data Collection:* T = 203 K, crystal size 0.5 × 0.4 × 0.25 mm, diffractometer Siemens P4; radiation Mo-K_α; Θ range 1.63–25.00°; 7372 reflections measured (one quadrant of reciprocal space) 5893 unique reflections. – *Structure Solution and Refinement:* Structure solution by direct methods (program SHELXS-86), full-matrix least-squares refinement on F^2 (program SHELXL-93) with all unique data and 301 variables. Hydrogen atoms are in calculated positions and were treated as riding atoms. R = 0.0865 for all reflections [0.0497 for 4060 observed reflections, $I > 2\sigma(I)$], R_w = 0.1281 (0.1055), residual electron density between 0.26 and −0.23 e Å^{-3}.

☆ Dedicated to Professor *M. Hanack* on the occasion of his 65th birthday.

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