Polycyclic Isophosphindole Derivatives by Intramolecular Trapping of 2-Phospha-1,3-diyls or Isomeric Bis(methylene)phosphoranes

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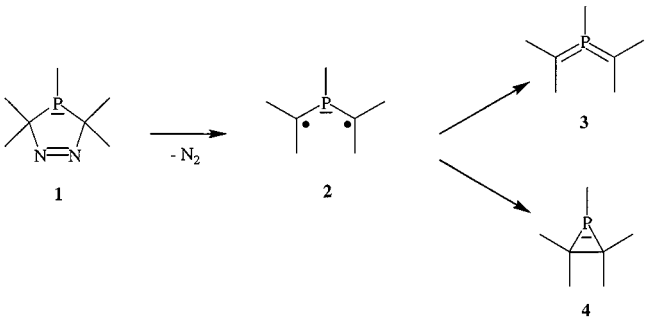
5-Alkylidene-5,7a-dihydro-3*H*-[1,2,4]diazaphospholo[4,3-*c*][1,2,3]diazaphospholes **10a–c** were obtained from (1-diazo-2-oxoalkyl)silane **8** and 2-acetyl-2*H*-1,2,3-diazaphospholes **9a–c**. Thermally induced elimination of molecular nitrogen from **10** generated polycyclic isophosphindole (benzo[*c*]phosphole) derivatives **13** by means of intramolecular [3+2] cycloaddition of an intermediate 2-phospha-1,3-diradical or an isomeric bis(methylene)phosphorane onto a benzene ring.

Introduction

Bis(methylene)phosphoranes **3** contain a phosphorus atom in an unusual bonding state ($\lambda^5\sigma^3$) and therefore belong to the active research objectives of contemporary organophosphorus chemistry.[1] Their most typical transformation is the thermally induced valence isomerization leading to phosphiranes **4** (Scheme 1). This process occurs stereospecifically as a conrotatory 4π-electrocyclic reaction[2] and can occur at temperatures between −80 and +150 °C, depending on the substituents.[2,3] Full substitution of the carbon atoms of **3** can suppress the isomerization completely.[4]



Scheme 1. N_2 extrusion pathways for 4-phosphapyrazolines **1**

Bis(methylene)phosphoranes or phosphiranes can be generated by thermal[2b,3,5] or photochemical[2a] extrusion of molecular nitrogen from 3,5-dihydro-1,2,4(λ^3)-diazaphospholes **1**, which are readily prepared by means of 1,3-dipolar cycloaddition of diazoalkanes to the P=C bond of phosphaalkenes. Cycloadducts obtained with heterophospholes as dipolarophiles react analogously.[6] The mechanistic details of the conversion **1**→**3**,**4** have not been investigated experimentally. It is usually supposed, without proof, that elimination of N_2 from **1** generates a 2-phospha-1,3-diradical (2-phospha-1,3-diyl) **2**, which is transformed into phosphacumulene **3** by interaction of the lone electron pair at phosphorus with the adjacent radical centers, or directly into phosphirane **4** by 1,3-cyclization. A semiempirical study for the system **2/3/4** has been carried out.[5a] However, a heterolytic course of the N_2 elimination reaction, resulting in a 1,3-dipole rather than a 1,3-diradical, has also been suggested.[5b] The possibility that **3** results from **1** through a concerted $_\sigma2+_\sigma2+_\omega2$ cycloreversion reaction[7] seems not to have been considered so far, although the extremely mild conditions for the N_2 elimination reaction of some compounds **1** suggest this idea.

We have recently reported that thermal extrusion of N_2 from 5-alkylidene-4-phosphapyrazolines **5** does not only produce 2-alkylidenephosphiranes **7**, but also vinylphosphanes **6** (Scheme 2).[8] On the basis of the observation that the configuration at the C=C bond of **5** is retained in **6** but inverted in **7**, we have argued that vinylphosphane **6** is derived from an intermediate 2-phospha-1,3-diradical by means of double intramolecular hydrogen abstraction, while phosphirane **7** is formed from a bis(alkylidene)phosphorane through a conrotatory electrocyclic reaction. The formation of **6** can be taken as an experimental proof for the intermediate formation of a 2-phospha-1,3-diyl moiety and, furthermore, it indicates that such a reactive intermediate is sufficiently long lived to be trapped intramolecularly. We now wish to report a novel finding that either a 2-phospha-1,3-diradical or a bis(methylene)phosphorane can be trapped in an intramolecular [3+2] cycloaddition reaction.

Results and Discussion

Similarly to other α-silyl-α-diazo ketones,[9] *tert*-butyldiphenylsilyl-substituted diazo ketone **8** reacts with 2-acetyl-1,2,3-diazaphospholes **9a−c** even at 20 °C to form bicyclic compounds **10**, which represent the products of a 1,3-dipolar cycloaddition reaction of a 1-diazo-2-siloxyalkene, existing in equilibrium with diazo ketone **8**,[10] at the P=C bond of **9** (Scheme 3). As expected, the NMR spectroscopic data are closely analogous to similar cycloadducts bearing other silyl groups.[9] The ^{31}P NMR signal appears at δ = −5.4 to 6.9, the bridgehead proton in **10a** and **10b** is

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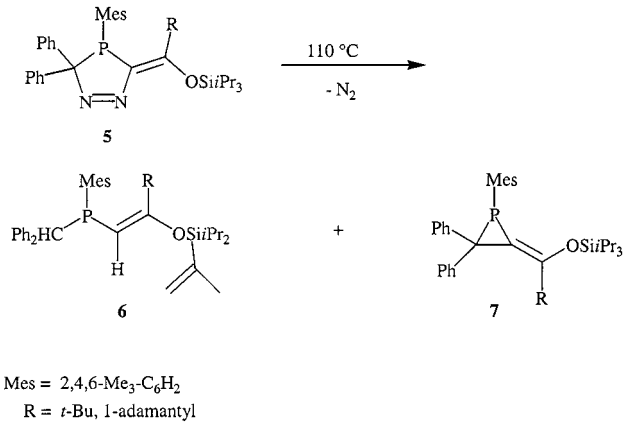
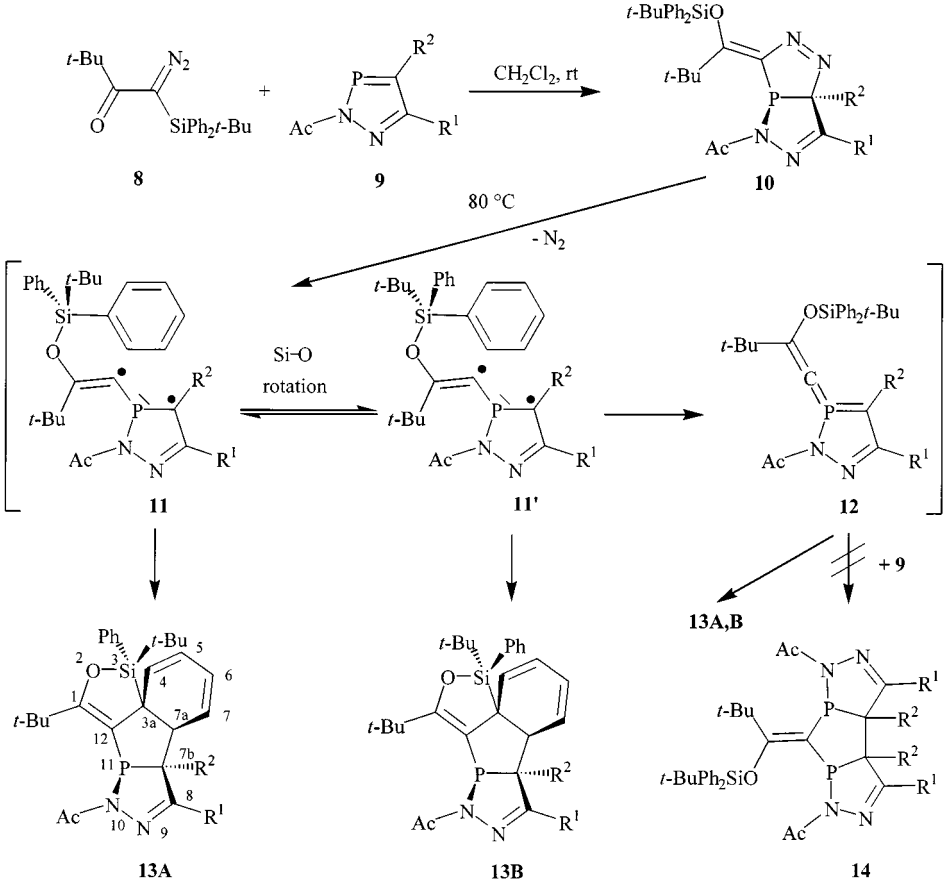


Scheme 2. N_2 extrusion in 5-alkylidene-3,3-diphenyl-3,5-dihydro-1,2,4-diazaphospholes **5**

strongly deshielded [δ(^{1}H) = 5.61 and 6.10, $^2J_{P,H}$ = 50±1 Hz], and the ^{13}C signals of the exocyclic enol ether double bond are found at δ(OC=*C*) = 146.6−148.2 ($^1J_{P,C}$ = 61.0−64.4 Hz) and δ(O*C*=C) = 182.5−182.8 ($^2J_{P,C}$ = 22.9−23.8 Hz). The (*E*) configuration of this double bond is indicated by a $^5J_{P,H}$ coupling in **10a** and **10c** (0.9−1.2 Hz) and a $^4J_{P,C}$ coupling in **10a**−**c** (9.1−9.5 Hz) between phosphorus and the nuclei of the *t*Bu methyl groups; these comparatively large long-range coupling constants point to a close proximity of the coupling nuclei.[11]

Cycloadducts **10a**−**c** lose molecular nitrogen when heated at 80 °C in solution. In all three cases, isophosphindole (benzo[*c*]phosphole) derivatives **13** were obtained as a mixture of two diastereomers, **A** and **B**, that could not be fractionated by conventional column chromatography. However, **13bA** and **13cA** could be partially separated from the mixture by crystallization. Although the ^{31}P NMR spectrum showed only one pair of significant signals (δ = 57.6−76.5) at the end of the thermolysis, the yields of isolated products **13** were surprisingly low (35−36%). This is probably due to partial loss of material during chromatographic workup, as verified in an independent experiment. The constitution of the tetracyclic (**13a** and **13b**) and pentacyclic (**13c**) isophosphindole derivatives was readily suggested by the ^{1}H NMR spectra which, in comparison with those of the precursor compounds, showed the appearance of four olefinic signals and one aliphatic signal (δ = 1.94−2.94) at the expense of five phenyl protons. The aliphatic proton is assigned to the bridgehead proton 7a-H, which couples with two neighbors in **13a** and **13b** and with only one other proton (7-H) in **13c**. The second bridgehead proton (7b-H) in the two diastereomers of **13a** and **13b** appears at δ = 3.26/3.51 and 4.04/4.29, respectively; the high-



9–14	R^1	R^2	Yield of **10**, %
a	Me	H	80
b	Ph	H	49
c	-$(CH_2)_4$-		77

13	R^1	R^2	A : B
a	Me	H	1 : 0.8
b	Ph	H	1 : 0.7
c	-$(CH_2)_4$-		1 : 0.7

Scheme 3. Synthesis and thermolysis of 5-alkylidene-5,7a-dihydro-3*H*-[1,2,4]diazaphospholo[4,3-*c*][1,2,3]diazaphospholes **10**. The position numbers are shown for **13a** and **13b**; for those of **13c**, see Figure 1

field shift as compared to **10a** and **10b** is clearly attributable to the disappearance of the deshielding azo function. The $^2J_{P,H}$ coupling constant for this proton amounts to 35.5−35.8 Hz; although smaller by some 14 Hz than in the precursors, there can be no doubt that the *cis* relationship between the proton and the lone pair at phosphorus is retained. In the ^{13}C NMR spectra, the transformation of a phenyl into a cyclohexadiene ring is confirmed by the appearance of signals at δ = 51.5−55.3 ($J_{P,C}$ = 5.2−5.7 Hz) and δ = 42.1−52.2 ($J_{P,C}$ = 2.9−4.3 Hz), assigned to C-3a and C-7a, respectively. Similarly to that of the corresponding proton, the signal of bridgehead carbon atom C-7b is shifted to higher field as compared to that of cycloadduct **10**, and is found at δ = 57.4−72.6 ($J_{P,C}$ = 9.5−11.9 Hz). The *cis* relationship of phosphorus and the *t*Bu group at the enol ether double bond is indicated, as in **10**, by the $^5J_{P,H}$ and $^4J_{P,C}$ coupling constants, the latter again being distinctly larger (8.6−8.7 Hz) than the $^3J_{P,C}$ coupling constants (1.9−2.4 Hz).

A crystal structure analysis was carried out for the pentacyclic compound **13cA**, which had been obtained as a pure diastereoisomer by crystallization. Although it could not be refined satisfactorily because of crystal twinning,[12] there is no doubt that the constitution proposed by the preceding spectroscopic arguments is correct. Furthermore, Figure 1 reveals the *cis,syn,cis* connectivity of the condensed tricyclic dihydrodiazaphosphole/phospholane/cyclohexadiene system and also the *syn* relationship between the cyclohexadiene ring and the silicon-bound *t*Bu group.

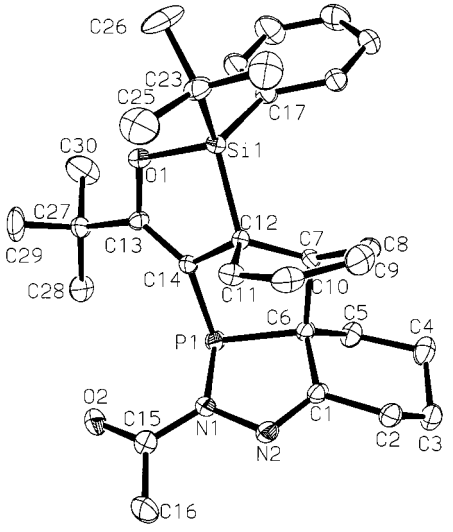


Figure 1. ORTEP plot of one independent molecule of **13cA**; ellipsoids of thermal vibration represent a 20% probability. Selected bond lengths [Å]: C10−C11 1.32(1), C9−C10 1.45(2), C8−C9 1.33(2), C7−C12 1.53(1), C13−C14 1.35(1), C1−N2 1.27(1), N1−N2 1.40(1), P1−N1 1.786(8)

A comparison of the ^1H NMR spectroscopic data of **13a−c** (Table 1) suggests that in all three cases the prevailing diastereomers **A** have the same relative stereochemistry at the five stereogenic centers and that diastereomers **B** have a different common stereochemistry. While no significant differences in the *P,H* and *H,H* coupling constants are observed, the major differences in chemical shifts are found for protons 4-H and 7a-H; taken together, these findings indicate an inversion of configuration at the silicon atom. Thus, the high-field shift of δ(4-H) and the simultaneous low-field shift of δ(7a-H) by about 0.7 ppm in epimer **B** appear as a consequence of magnetic shielding, by the phenyl ring attached to silicon, of 7a-H in epimer **13A** and of 4-H in **13B**. Furthermore, the result of a NOE NMR experiment, depicted in Figure 2, is in full agreement with the interchange of a *t*Bu and a Ph substituent at silicon in epimers **A** and **B**. Unfortunately, these spectroscopic arguments are not sufficient to establish the configuration of epimer **B**, since they would also hold if the configuration at silicon were retained and the cyclohexadiene ring were to become *anti* to the dihydrodiazaphosphole ring. However, the following NMR spectroscopic arguments speak in favor of the *cis,syn,cis* fusion of the tricyclic core in both epimers of **13a−c**:

a) We find ^3J(7a-H, 7b-H) coupling constants of 8.7−9.0 Hz for both epimers of **13a** and **13b**, a clear indication of a *cis* relationship; note that the torsion angle C5−C6−C7−H7 in the crystal structure of **13cA** is indeed −34.9°. For comparison, in *cis,anti,cis*-fused tricyclic systems **14**, the vicinal coupling constant of the protons at the central ring (R^2 = H) has values of 0−2.4 Hz.[9]

b) The preceding argument does not apply to **13c** because of the absence of a proton at C-7b. However, it can be predicted that δ(C-8) would be shifted upfield by a few ppm if **13cB** was *cis,anti,cis*-fused, due to the action of a γ-effect operating between atom C-7 (cyclohexadiene ring) and C-8 (cyclohexane ring). The absence of such an effect [δ(C-8) = 39.9 (**31cA**) and 40.5 (**31cB**)] once again indicates *cis,syn,cis* fusion.

c) It can be helpful to consider the dependency of $^3J_{P,C}$ and $^3J_{P,H}$ coupling constants on the dihedral angle.[11] The absence of a ^3J(P,C,C,7a-H) coupling constant indicates a *syn* relationship between the dihydrodiazaphosphole and cyclohexadiene rings for both diastereoisomers of **13a−c**. According to the crystal structure of **13cA**, the corresponding torsion angle is 88.2° (Figure 1: P1−C6−C7−H7) and, thus, a coupling constant not far from 0 Hz is expected. If the configuration at C-3a and C-7a in, for example, **13cB** was reversed with respect to **13cA** − i.e., if the cyclohexadiene ring were to become *anti* to the dihydrodiazaphosphole ring − the P−C−C−7a-H dihedral angle would be similar to the torsion angle P1−C6−C7−C8 (153°) found in the crystal structure of **13cA**, and the ^3J(P,H) value should be around 10 Hz. The change of ^3J(P,C,C,C-4) accompanying this change of configuration is probably not diagnostic, since similarly small values are expected for dihedral angles of 84.7° (in **13cA**) and ca. 110−120° (in the *anti* configuration according to a molecular model).

The formation of isophosphindole derivatives **13** was surprising, since we had originally expected that thermolysis of **10** would afford tricyclic compounds **14**, similar to the transformation of bicyclic precursors with the same molecular framework as in **10**, but with Si*i*Pr$_3$ and SiMe$_2$*t*Bu substituents.[9] Compounds **14** would result from an intermolecular [$3_{4\pi}+2_{2\pi}$] cycloaddition reaction of semicyclic

Table 1. Selected ^{1}H NMR spectroscopic data for polycyclic compounds **13a−c** (500.14 MHz, $CDCl_3$, δ/ppm, coupling constants given in parentheses)

position	13aA	13aB	13bA	13bB	13cA	13cB
Si-*t*Bu	0.97	0.96	0.945	0.952	0.96	0.99
1-*t*Bu	1.55 (1.3)	1.56 (1.3)	1.58 (1.2)	1.59 (1.3)	1.54 (1.3)	1.55 (0.9)
4-H	5.69 (9.3)	4.98 (9.2)	5.67 (9.7)	4.96 (9.3)	5.69 (9.3)	4.99 (9.3)
5-H	5.63 (9.4, 5.1)	5.32 (9.4, 5.1)	5.50 (9.3, 5.3)	5.20 (9.3, 5.3)	5.59 (9.3, 5.3)	5.28 (9.3, 5.0, 0.9)
6-H	6.25 (9.5, 5.1)	6.20 (9.3, 4.9)	5.63 (9.3, 5.0)	5.57 (9.3, 5.3)	6.21 (9.3, 5.0)	6.15−
7-H	5.99 (9.4, 6.2)	6.15 (9.3, 6.2)	5.53 (9.3, 6.2)	5.70 (9.3, 6.2)	6.01 (9.3, 6.5)	6.20 (m)
7a-H	2.13 (8.8, 6.4, 0.4)	2.84 (8.7, 6.1, 1.2)	2.23 (9.0, 6.2)	2.94 (9.0, 6.2)	1.94 (6.5)	2.73 (5.9)
7b-H	3.26 (36.5, 8.7)	3.51 (36.8, 8.7)	4.04 (35.5, 8.7)	4.29 (35.8, 9.0)	−	−

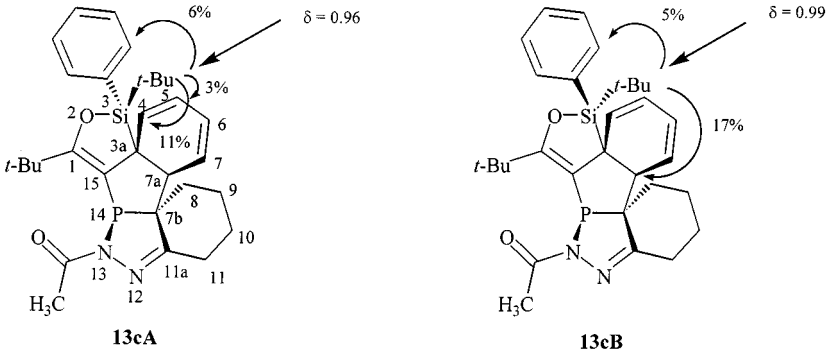


Figure 2. Nuclear Overhauser effects for **13cA** and **13cB**: Signal enhancements on irradiation at the proton resonance of *t*Bu

methylene(vinylidene)phosphoranes such as **12** with diazaphospholes **9** arising from **10** through a [3+2] cycloreversion process (Scheme 3). Isophosphindole derivatives **13A** and **13B** are obviously formed by an *intra*molecular [3+2] cycloaddition of a C−P−C unit onto an aromatic C=C bond of either the *pro-R* or the *pro-S* phenyl ring bound at silicon. No decision can be made as to the phosphorus-containing species undergoing the cycloaddition: the 2-phospha-1,3-diradicals **11** and **11′**, which are the first intermediates after thermal N_2 extrusion from **10**, may be trapped directly by addition to one of the phenyl rings or may first undergo bond reorganization to form bis(alkylidene)phosphoranes **12** which then undergo the intramolecular [$3_{4\pi}+2_{2\pi}$] cycloaddition. It should be recalled that thermal 4π+2π cycloaddition reactions in which a benzene ring plays the role of the dienophile are extremely rare. They require either a 4π system with exceptionally low LUMO energy (1,4-bis(trifluoromethyl)-1,2,4,5-tetrazine,[13] tetracyano carbonylylide[14]) or, in the intramolecular case,[15] rather favorable rigid geometries that tend to compensate for the entropy contribution to the activation energy. The 1,3-diradical pathway, on the other hand, has some similarity with the reactivity of 1,3-diradicals of the trimethylenemethane type, generated from bicyclic diazenes, which can be trapped intramolecularly even by a non-activated olefinic C=C bond.[16]

Conclusion

We have shown that the thermal elimination of N_2 from appropriately substituted bicyclic 5-alkylidene-4-phosphapyrazolines **10** leads in one step to tetracyclic or pentacyclic isophosphindole (benzo[*c*]phosphole) derivatives **13**. The key step in the construction of the polycyclic framework is an intramolecular [3+2] cycloaddition of a C−P−C unit to the C=C bond of a benzene ring. While the available results do not permit distinction of whether a 2-phospha-1,3-diradical or an isomeric bis(alkylidene)phosphorane was trapped, it can be stated that no such reaction mode has previously been reported for either one of the two intermediates under discussion.

Experimental Section

General Remarks: All reactions were carried out in rigorously dried glassware and under an argon atmosphere. Solvents were dried by standard procedures and kept under argon. The petroleum ether used had a boiling point range of 30−60 °C. − Column chromatography was performed under hydrostatic conditions (Si 60 silica gel, Macherey−Nagel, 0.063−0.02 mm). − NMR: Bruker AMX 500 (^{1}H: 500.14 MHz; ^{13}C: 125.77 MHz; ^{31}P: 202.48 MHz); $CDCl_3$ was used as solvent. The following references were applied: internal TMS for the proton spectra, the solvent signal for the ^{13}C NMR

spectra [δ($CDCl_3$) = 77.0], and external 85% H_3PO_4 for the ^{31}P spectra. − IR: Perkin−Elmer IR 883 spectrometer. − MS: Varian MAT 711. − Microanalyses: Perkin−Elmer EA 240 and EA 2400. Melting points: Büchi apparatus (′Dr. Tottoli′), uncorrected values. − The following compounds were prepared by literature methods: diazo ketone **8**,[17] 1,2,3-diazaphospholes **9a**,[18] **9b**,[19] **9c**.[19]

Synthesis of 5-Alkylidene-5,7a-dihydro-3*H*-[1,2,4]diazaphospholo-[4,3-*c*][1,2,3]diazaphospholes 10a−c. − General Procedure: A solution of equimolar amounts (2.6−4.5 mmol) of diazo ketone **8** and 2*H*-1,2,3-diazaphosphole **9** in dichloromethane (20 mL) was stirred at room temperature until **8** had been consumed (14 h, IR control). The solvent was removed under reduced pressure. Upon addition of pentane (10 mL) to the residue, a colorless, microcrystalline solid was formed; it was isolated by filtration under an argon atmosphere and washed with pentane.

5-Acetyl-3-[(*E*)-1-(*tert*-butyldiphenylsilyloxy)-2,2-dimethylpropylidene]-7-methyl-5,7a-dihydro-3*H*-... (10a): Prepared from **8** (0.97 g, 2.66 mmol) and **9a** (0.38 g, 2.66 mmol); yield 1.08 g (80%); m.p. 98 °C (recryst. from dry ether). − IR (KBr): ṽ = 1661, 1428, 1393, 1344, 1050, 705 cm^{-1} (all s). − ^1H NMR ($CDCl_3$): δ = 1.02 (s, 9 H, $SiCMe_3$), 1.73 (d, $^5J_{P,H}$ = 0.9 Hz, 9 H, $CCMe_3$), 2.01 (s, 3 H, 7-Me), 2.20 (s, 3 H, MeCO), 5.61 (d, $^2J_{P,H}$ = 50.8 Hz, 1 H, PCH), 7.15−7.21 (m, 3 H, *m*- and *p*-H-Ph), 7.33−7.37 (m, 3 H, *m*- and *p*-H-Ph), 7.49−7.51 (m, 2 H, *o*-H-Ph), 7.65−7.67 (m, 2 H, *o*-H-Ph). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 17.6 (s, 7-Me), 20.5 (s, Si*C*Me_3), 22.6 (s, *Me*CO), 26.9 (s, SiC*Me*$_3$), 29.2 (d, $^4J_{P,C}$ = 9.5 Hz, CC*Me*$_3$), 40.0 (d, $^3J_{P,C}$ = 2.9 Hz, C*C*Me_3), 100.8 (d, $^1J_{P,C}$ = 21.9 Hz, C-7a), 127.1 (s, *m*-C of SiPh), 127.3 (s, *m*-C of SiPh), 128.9 (s, *p*-C of SiPh), 129.0 (s, *p*-C of SiPh), 133.5 (s, *o*-C of SiPh), 133.9 (s, *o*-C of SiPh), 134.0 (s, *i*-C of SiPh), 134.6 (s, *i*-C of SiPh), 148.0 (d, $^1J_{P,C}$ = 64.4 Hz, C-3), 151.9 (s, C-7), 173.3 (d, $^2J_{P,C}$ = 10.5 Hz, Me*C*O), 182.7 (d, $^2J_{P,C}$ = 23.4 Hz, =COSi). − ^{31}P NMR ($CDCl_3$): δ = −5.4. − $C_{27}H_{35}N_4O_2PSi$ (506.76): calcd. C 64.01, H 6.96, N 11.06; found C 64.08, H 6.98, N 10.51.

5-Acetyl-3-[(*E*)-1-(*tert*-butyldiphenylsilyloxy)-2,2-dimethylpropylidene]-7-phenyl-5,7a-dihydro-3*H*-... (10b): Prepared from **8** (1.66 g, 4.54 mmol) and **9b** (0.93 g, 4.54 mmol), obtained as the monohydrate; yield 1.27 g (49%); m.p. 64 °C. − IR (KBr): ṽ = 3550−3100 (very broad, OH), 1668, 1428, 1380, 1352, 1285, 1114, 701 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 1.02 (s, 9 H, $SiCMe_3$), 1.76 (s, 9 H, $CCMe_3$), 2.29 (s, 3 H, MeCO), 6.10 (d, $^2J_{P,H}$ = 49.2 Hz, 1 H, PCH), 6.99−7.02 (m, 2 H, *m*-H-Ph), 7.04−7.06 (m, 1 H, *p*-H-Ph), 7.27−7.37 (m, 6 H, *m*- and *p*-H-Ph), 7.45−7.46 (m, 2 H, *o*-H of SiPh), 7.62−7.63 (m, 2 H, *o*-H of SiPh), 7.88−7.90 (m, 2 H, *o*-H-Ph). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 20.6 (s, Si*C*Me_3), 22.6 (s, *Me*CO), 27.1 (s, SiC*Me*$_3$), 29.3 (d, $^4J_{P,C}$ = 9.5 Hz, CC*Me*$_3$), 40.2 (d, $^3J_{P,C}$ = 2.9 Hz, C*C*Me_3), 97.7 (d, $^1J_{P,C}$ = 21.9 Hz, C-7a), 127.0 (s, *m*-C of SiPh), 127.3 (s, *m*-C of SiPh), 127.6 (s, *o*- or *m*-C of Ph), 128.4 (s, *o*- or *m*-C of Ph), 128.9 (s, *p*-C of SiPh), 129.8 (s, *p*-C of Ph), 132.3 (s, *i*-C of Ph), 133.6 (s, *i*-C of SiPh), 133.8 (s, *o*-C of SiPh), 134.2 (s, *o*-C of SiPh), 134.5 (s, *i*-C of SiPh), 148.2 (d, $^1J_{P,C}$ = 62.9 Hz, C-3), 151.4 (s, C-7), 173.7 (d, $^2J_{P,C}$ = 10.0 Hz, Me*C*O), 182.8 (d, $^2J_{P,C}$ = 23.8 Hz, =COSi). − ^{31}P NMR ($CDCl_3$): δ = 1.8. − $C_{32}H_{37}N_4O_2PSi{\cdot}H_2O$ (586.7): calcd. C 65.51, H 6.70, N 9.55; found C 65.45, H 6.83, N 9.21.

5-Acetyl-3-[(*E*)-1-(*tert*-butyldiphenylsilyloxy)-2,2-dimethylpropylidene]-7,8,9,10-tetrahydro-3*H*,5*H*-benzo[*d*][1,2,4]diazaphospholo[4,3-*c*][1,2,3]diazaphosphole (10c): Prepared from **8** (1.13 g, 3.09 mmol) and **9c** (0.56 g, 3.09 mmol); yield 1.31 g (77%), m.p. 95 °C. − IR (KBr): ṽ = 1657, 1555, 1391, 1290, 1203, 1119, 1053, 698 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 1.02 (s, 9 H, $SiCMe_3$), 1.54−2.43 [m, 8 H, $(CH_2)_4$], 1.70 (d, $^5J_{P,H}$ = 1.2 Hz, 9 H, $CCMe_3$), 2.22 (s, 3 H, MeCO), 7.16−7.21 (m, 3 H, *m*- and *p*-H-Ph), 7.31−7.38 (m, 3 H, *m*- and *p*-H-Ph), 7.49−7.51 (m, 2 H, *o*-H-Ph), 7.65−7.67 (m, 2 H, *o*-H-Ph). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 20.6 (s, Si*C*Me_3), 22.1 (d, $^3J_{P,C}$ = 10.0 Hz, CH_2), 22.6 (s, *Me*CO), 26.1 (s, CH_2), 27.1 (s, SiC*Me*$_3$), 27.9 (s, CH_2), 29.2 (d, $^4J_{P,C}$ = 9.1 Hz, CC*Me*$_3$), 33.3 (d, $^2J_{P,C}$ = 36.2 Hz, CH_2), 40.0 (d, $^3J_{P,C}$ = 2.9 Hz, C*C*Me_3), 109.6 (d, $^1J_{P,C}$ = 19.1 Hz, C-10a), 127.1 (s, *m*-C of SiPh), 127.3 (s, *m*-C of SiPh), 128.80 (s, *p*-C of SiPh), 128.84 (s, *p*-C of SiPh), 133.6 (s, *o*-C of SiPh), 134.1 (s, *o*-C of SiPh), 134.3 (s, *i*-C of SiPh), 134.7 (s, *i*-C of SiPh), 146.6 (d, $^1J_{P,C}$ = 61.0 Hz, C-3), 156.7 (s, C-6a), 173.6 (d, $^2J_{P,C}$ = 10.5 Hz, Me*C*O), 182.5 (d, $^2J_{P,C}$ = 22.9 Hz, =COSi). − ^{31}P NMR ($CDCl_3$): δ = 6.9. − $C_{30}H_{39}N_4O_2PSi$ (546.7): calcd. C 65.91, H 7.19, N 10.25; found C 65.69, H 7.17, N 9.80.

Preparation of [1,2]Oxasilolo[3′,4′:7a,1]isophosphindolo[2,3-*c*]-[1,2,3]diazaphospholes 13

***rel*-(3*S*,3a*R*,7a*R*,7b*S*,11*R*)-10-Acetyl-1,3-di(*tert*-butyl)-8-methyl-3-phenyl-7b,10-dihydro-7a*H*-[1,2]oxasilolo[3′,4′:7a,1]isophosphindolo-[2,3-*c*][1,2,3]diazaphosphole (13aA) and *rel*-(3*R*,3a*R*,7a*R*,7b*S*,11*R*)-... (13aB):** A solution of **10a** (0.40 g, 0.78 mmol) in toluene (20 mL) was placed in a thick-walled Schlenk tube and heated at 110 °C for 30 min. After cooling to room temp., the solvent was evaporated at 0.01 mbar. The brown-violet, foam-like residue was purified by column chromatography over silica gel with diethyl ether−petroleum ether (1:1) as eluent. The second fraction afforded **51a** as a mixture of diastereomers (**A/B** = 1:0.8); yield 0.28 g (35%). The foam-like solid thus obtained seemed to contain small amounts of oligomeric impurities (^1H NMR and elemental analysis) which could not be removed. − IR (KBr): (**13aA/B**): ṽ = 1686, 1657, 1583, 1428, 1392, 1365, 1142, 1111 cm^{-1}. − MS (FD, 8 kV), *m*/*z* = 478 [M^+]. − $C_{27}H_{35}N_2O_2PSi$ (478.7): calcd. C 67.75; H 7.37; N 5.85; found C 67.46, H 7.91, N 4.77.

NMR Spectroscopic Data of 13aA (mixture with **13aB):** ^1H NMR ($CDCl_3$): δ = 0.97 (s, 9 H, $SiCMe_3$), 1.55 (d, $^5J_{P,H}$ = 1.3 Hz, 9 H, $CCMe_3$), 1.97 (s, 3 H, 8-Me), 2.13 (ddd, $^3J_{H,H}$ = 8.8 Hz, $^3J_{H,H}$ = 6.4 Hz, $^3J_{P,H}$ = 0.4 Hz, 1 H, 7a-H), 2.18 (s, 3 H, MeCO), 3.26 (dd, $^2J_{P,H}$ = 36.5 Hz, $^3J_{H,H}$ = 8.7 Hz, 1 H, 7b-H), 5.63 (dd, $^3J_{H,H}$ = 9.4, 5.1 Hz, 1 H, 5- or 6-H), 5.69 (d, $^3J_{H,H}$ = 9.3 Hz, 1 H, 4-H), 5.99 (dd, $^3J_{H,H}$ = 9.4, 6.2 Hz, 1 H, 7-H), 6.25 (dd, $^3J_{H,H}$ = 9.5, 5.1 Hz, 1 H, 6- or 5-H), 7.34−7.43 (m, 3 H, *m*- or *p*-H-Ph), 7.53−7.55 (m, 2 H, *o*-H-Ph). −$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 19.2 (s, Si*C*Me_3), 20.3 (d, $^3J_{P,C}$ = 1.9 Hz, 8-Me), 22.4 (s, *Me*CO), 26.1 (d, $^5J_{P,C}$ = 5.2 Hz, SiC*Me*$_3$), 29.33 (d, $^4J_{P,C}$ = 8.6 Hz, CC*Me*$_3$), 38.10 (d, $^3J_{P,C}$ = 2.4 Hz, C*C*Me_3), 43.6 (d, $^2J_{P,C}$ = 2.9 Hz, C-7a), 51.6 (d, $^2J_{P,C}$ = 5.3 Hz, C-3a), 62.7 (d, $^1J_{P,C}$ = 11.9 Hz, C-7b), 118.4 (d, $^1J_{P,C}$ = 38.6 Hz, C-12), 119.9 (s, C-5 or C-6), 124.4 (s, C-7), 127.0 (s, C-6 or C-5), 127.8 (s, *m*-C of SiPh), 130.1 (s, *p*-C of SiPh), 130.69 (s, *i*-C of SiPh), 130.9 (s, C-4), 133.9 (s, *o*-C of SiPh), 160.6 (s, C-8), 173.9 (d, $^2J_{P,C}$ = 8.6 Hz, Me*C*O), 175.7 (d, $^2J_{P,C}$ = 33.9 Hz, C-1). − ^{31}P NMR ($CDCl_3$): δ = 57.8.

NMR Spectroscopic Data of 13aB (mixture with **13aA):** ^1H NMR ($CDCl_3$): δ = 0.96 (s, 9 H, $SiCMe_3$), 1.56 (d, $^5J_{P,H}$ = 1.3 Hz, 9 H, $CCMe_3$), 2.02 (s, 3 H, 8-Me), 2.09 (s, 3 H, MeCO), 2.84 (ddd, $^3J_{H,H}$ = 8.7, 6.1 Hz, $^3J_{P,H}$ = 1.2 Hz, 1 H, 7a-H), 3.51 (dd, $^2J_{P,H}$ = 36.8 Hz, $^3J_{H,H}$ = 8.7 Hz, 1 H, 7b-H), 4.98 (d, $^3J_{H,H}$ = 9.2 Hz, 1 H, 4-H), 5.32 (ddd, $^3J_{H,H}$ = 9.4, 5.1 Hz, $^4J_{H,H}$ = 1.1 Hz, 1 H, 5- or 6-H), 6.15 (dd, $^3J_{H,H}$ = 9.3, 6.2 Hz, 1 H, 7-H), 6.20 (dd, $^3J_{H,H}$ = 9.3, 4.9 Hz, 1 H, 6- or 5-H), 7.28−7.31 (m, 2 H, *m*-H-Ph), 7.34−7.43 (m, 3 H, *o*- and *p*-H-Ph). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 19.8 (s, Si*C*Me_3), 20.4 (d, $^3J_{P,C}$ = 1.9 Hz, 8-Me), 22.3 (s, *Me*CO), 26.4 (d,

$^5J_{P,C}$ = 5.7 Hz, SiC*Me*$_3$), 29.27 (d, $^4J_{P,C}$ = 7.6 Hz, CC*Me*$_3$), 38.13 (d, $^3J_{P,C}$ = 2.4 Hz, C*C*Me$_3$), 42.1 (d, $^2J_{P,C}$ = 3.8 Hz, C-7a), 51.5 (d, $^2J_{P,C}$ = 5.7 Hz, C-3a), 63.4 (d, $^1J_{P,C}$ = 11.5 Hz, C-7b), 119.25 (s, C-5 or C-6), 119.32 (d, $^1J_{P,C}$ = 38.6 Hz, C-12), 123.7 (s, C-7), 127.1 (s, C-6 or C-5), 127.5 (s, *m*-C of SiPh), 129.8 (s, *p*-C of SiPh), 130.67 (s, *i*-C of SiPh), 132.0 (s, C-4), 134.3 (s, *o*-C of SiPh), 160.3 (s, C-8), 173.7 (d, $^2J_{P,C}$ = 8.6 Hz, Me*C*O), 175.8 (d, $^2J_{P,C}$ = 33.4 Hz, C-1). − ^{31}P NMR (CDCl$_3$): δ = 57.6.

***rel*-(3*S*,3a*R*,7a*R*,7b*S*,11*R*)-10-Acetyl-1,3-di(*tert*-butyl)-3,8-diphenyl-7b,10-dihydro-7a*H*-[1,2]oxasilolo[3′,4′:7a,1]isophosphindolo[2,3-*c*]-[1,2,3]diazaphosphole (13bA) and *rel*-(3*R*,3a*R*,7a*R*,7b*S*,11*R*)-... (13bB):** Prepared from **10c** (0.83 g, 1.45 mmol) as described above for **10a→13a**; yield 0.28 g (35%) as a mixture of diastereomers (**A/B** = 1:0.7). Recrystallization from diethyl ether afforded pure **13bA** as colorless crystals, m.p. 180 °C.

Spectral and Analytical Data for 13bA: IR (KBr): ṽ = 1666, 1564, 1381, 1353, 1318, 1267, 1135, 1109, 1024, 837, 816, 738, 720, 698, 655 cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 0.945 (s, 9 H, SiCMe$_3$), 1.58 (d, $^5J_{P,H}$ = 1.2 Hz, 9 H, CCMe$_3$), 2.23 (dd, $^3J_{H,H}$ = 9.0 Hz, $^3J_{H,H}$ = 6.2 Hz, 1 H, 7a-H), 2.31 (s, 3 H, MeCO), 4.04 (dd, $^2J_{P,H}$ = 35.5 Hz, $^3J_{H,H}$ = 8.7 Hz, 1 H, 7b-H), 5.50 (dd, $^3J_{H,H}$ = 9.3, 5.3 Hz, 1 H, 5- or 6-H), 5.53 (dd, $^3J_{H,H}$ = 9.3, 6.2 Hz, 1 H, 7-H), 5.63 (dd, $^3J_{H,H}$ = 9.3, 5.0 Hz, 1 H, 6- or 5-H), 5.67 (d, $^3J_{H,H}$ = 9.7 Hz, 1 H, 4-H), 7.25−7.43 (m, 6 H, *m*- and *p*-H-Ph), 7.52−7.55 (m, 4 H, *o*-H-Ph). − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 19.2 (s, Si*C*Me$_3$), 22.4 (s, *Me*CO), 26.1 (s, SiC*Me*$_3$), 29.4 (d, $^4J_{P,C}$ = 8.6 Hz, CC*Me*$_3$), 38.16 (d, $^3J_{P,C}$ = 2.4 Hz, C*C*Me$_3$), 43.7 (d, $^2J_{P,C}$ = 2.9 Hz, C-7a), 51.8 (d, $^2J_{P,C}$ = 5.7 Hz, C-3a), 57.4 (d, $^1J_{P,C}$ = 11.4 Hz, C-7b), 118.4 (d, $^1J_{P,C}$ = 38.6 Hz, C-12), 120.2 (s, C-5 or C-6), 124.3 (s, C-7), 126.0 (s, C-6 or C-5), 127.00 (s, *o*-C of Ph), 127.9 (s, *m*-C of SiPh), 127.98 (s, *m*-C of Ph), 128.8 (s, *p*-C of Ph), 130.1 (s, *p*-C of SiPh), 130.4 (s, C-4), 130.8 (s, *i*-C of SiPh), 133.9 (s, *o*-C of SiPh), 135.2 (d, $^3J_{P,C}$ = 1.9 Hz, *i*-C of Ph), 159.7 (s, C-8), 174.5 (d, $^2J_{P,C}$ = 8.1 Hz, Me*C*O), 175.99 (d, $^2J_{P,C}$ = 34.3 Hz, C-1). − ^{31}P NMR (CDCl$_3$): δ = 60.6. − $C_{32}H_{37}N_2O_2PSi$ (540.7): calcd. C 71.08, H 6.90, N 5.18; found C 70.63, H 7.04, N 5.13.

NMR Spectroscopic Data of 13bB (mixture with **13bA**)**:** ^{1}H NMR (CDCl$_3$): δ = 0.952 (s, 9 H, SiCMe$_3$), 1.59 (d, $^5J_{P,H}$ = 1.3 Hz, 9 H, CCMe$_3$), 2.21 (s, 3 H, MeCO), 2.94 (dd, $^3J_{H,H}$ = 9.0, 6.2 Hz, 1 H, 7a-H), 4.29 (dd, $^2J_{P,H}$ = 35.8 Hz, $^3J_{H,H}$ = 9.0 Hz, 1 H, 7b-H), 4.96 (d, $^3J_{H,H}$ = 9.3 Hz, 1 H, 4-H), 5.20 (dd, $^3J_{H,H}$ = 9.3, 5.3 Hz, 1 H, 5- or 6-H), 5.57 (dd, $^3J_{H,H}$ = 9.3, 5.3 Hz, 1 H, 6- or 5-H), 5.70 (dd, $^3J_{H,H}$ = 9.3 Hz, 1 H, 7-H), 7.25−7.43 (m, 6 H, *m*- and *p*-H of Ph), 7.52−7.55 (m, 2 H, *o*-H of Ph), 7.59−7.61 (m, 2 H, *o*-H of Ph). − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 19.9 (s, Si*C*Me$_3$), 22.3 (s, *Me*CO), 26.4 (s, SiC*Me*$_3$), 29.3 (d, $^4J_{P,C}$ = 8.6 Hz, CC*Me*$_3$), 38.20 (d, $^3J_{P,C}$ = 2.4 Hz, C*C*Me$_3$), 42.2 (d, $^2J_{P,C}$ = 3.8 Hz, C-7a), 51.7 (d, $^2J_{P,C}$ = 5.7 Hz, C-3a), 58.1 (d, $^1J_{P,C}$ = 11.4 Hz, C-7b), 119.4 (d, $^1J_{P,C}$ = 37.7 Hz, C-12), 119.5 (s, C-5 or C-6), 123.7 (s, C-7), 126.1 (s, C-6 or C-5), 127.03 (s, *o*-C of Ph), 127.4 (s, *m*-C of SiPh), 128.01 (s, *m*-C of Ph), 128.9 (s, *p*-C of Ph), 129.8 (s, *p*-C of SiPh), 130.7 (s, *i*-C of SiPh), 131.5 (s, C-4), 134.3 (s, *o*-C of SiPh), 135.3 (d, $^3J_{P,C}$ = 1.9 Hz, *i*-C of Ph), 159.6 (s, C-8), 174.3 (d, $^2J_{P,C}$ = 8.6 Hz, Me*C*O), 176.01 (d, $^2J_{P,C}$ = 36.2 Hz, C-1). − ^{31}P NMR (CDCl$_3$): δ = 60.5.

***rel*-(3*S*,3a*R*,7a*R*,7b*S*,14*R*)-13-Acetyl-1,3-di(*tert*-butyl)-3-phenyl-9,10,11,13-tetrahydro-7aH,8H-benzo[*d*][1,2]oxasilolo[3′,4′:7a,1]-isophosphindolo[2,3-*c*][1,2,3]diazaphosphole (13cA) and *rel*-(3*R*,3a*R*,7a*R*,7b*S*,14*R*)-... (13cB):** Prepared from **10c** (0.98 g, 1.79 mmol) as described above for **10a→13a**; yield 0.33 g (36%) as a mixture of diastereomers (**A/B** = 1:0.7). Recrystallization from diethyl ether afforded pure **13cA** as colorless crystals.

Physical and Spectral Data of 13cA: M.p. 174 °C. − IR (KBr): ṽ = 1661, 1573, 1389, 1329, 1311, 1143, 1110, 835, 812, 735, 700, 649 cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 0.96 (s, 9 H, SiCMe$_3$), 1.38−1.43 (m, 2 H, CH$_2$), 1.54 (d, $^5J_{P,H}$ = 1.3 Hz, 9 H, CCMe$_3$), 1.57−1.58 (m, 1 H, cyclohexyl), 1.65−1.68 (m, 1 H, cyclohexyl), 1.93−2.00 (m, 2 H, CH$_2$), 1.94 (d, $^3J_{H,H}$ = 6.5 Hz, 1 H, 7a-H), 2.20 (s, 3 H, MeCO), 2.43−2.45 (m, 1 H, cyclohexyl), 2.56−2.62 (m, 1 H, cyclohexyl), 5.59 (dd, $^3J_{H,H}$ = 9.3 Hz, 5.3 Hz, 1 H, 5-H), 5.69 (d, $^3J_{H,H}$ = 9.3 Hz, 1 H, 4-H), 6.01 (dd, $^3J_{H,H}$ = 9.3, 6.5 Hz, 1 H, 7-H), 6.21 (dd, $^3J_{H,H}$ = 9.3, 5.0 Hz, 1 H, 6-H), 7.35−7.38 (m, 2 H, *m*-H of Ph), 7.40−7.43 (m, 1 H, *p*-H of Ph), 7.55−7.57 (m, 2 H, *o*-H of Ph). − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 19.2 (s, Si*C*Me$_3$), 22.2 (s, *Me*CO), 23.9 (d, $^3J_{P,C}$ = 14.3 Hz, C-9), 26.2 (s, SiC*Me*$_3$), 27.0 (s, C-10 or C-11), 29.3 (s, C-10 or C-11), 29.4 (d, $^4J_{P,C}$ = 8.6 Hz, CC*Me*$_3$), 38.1 (d, $^3J_{P,C}$ = 1.9 Hz, C*C*Me$_3$), 39.9 (d, $^2J_{P,C}$ = 39.1 Hz, C-8), 52.3 (d, $^2J_{P,C}$ = 3.3 Hz, C-7a), 55.3 (d, $^2J_{P,C}$ = 5.2 Hz, C-3a), 71.4 (d, $^1J_{P,C}$ = 9.5 Hz, C-7b), 116.5 (d, $^1J_{P,C}$ = 36.2 Hz, C-15), 119.5 (s, C-5 or C-6), 126.2 (s, C-7), 126.5 (s, C-6 or C-5), 127.8 (s, *m*-C of SiPh), 130.1 (s, *p*-C of SiPh), 130.7 (s, *i*-C of SiPh), 131.3 (s, C-4), 133.8 (s, *o*-C of SiPh), 164.7 (s, C-11a), 173.7 (d, $^2J_{P,C}$ = 7.6 Hz, CH$_3$*C*O), 175.9 (d, $^2J_{P,C}$ = 32.9 Hz, C-1). − ^{31}P NMR (CDCl$_3$ MHz): δ = 76.1. − $C_{30}H_{39}N_2O_2PSi$ (518.7): calcd. C 69.47, H 7.58, N 5.40; found C 69.11, H 7.56, N 5.33.

NMR Spectroscopic Data of 13cB (mixture with **13cA**)**:** ^{1}H NMR (CDCl$_3$, 500.14 MHz): δ = 0.99 [s, 9 H, SiC(CH$_3$)$_3$], 1.55 [d, $^5J_{P,H}$ = 0.9 Hz, 9 H, CC(CH$_3$)$_3$], 1.74−1.79 (m, 1 H, cyclohexyl), 1.93−2.07 (m, 5 H, cyclohexyl), 2.10 (s, 3 H, CH$_3$CO), 2.46 (m, 1 H, cyclohexyl), 2.58−2.63 (m, 1 H, cyclohexyl), 2.73 (d, $^3J_{H,H}$ = 5.9 Hz, 1 H, 7a-H), 4.99 (d, $^3J_{H,H}$ = 9.3 Hz, 1 H, 4-H), 5.28 (ddd, $^3J_{H,H}$ = 9.3 Hz, 5.0 Hz, $^4J_{H,H}$ = 0.9 Hz, 1 H, 5- or 6-H), 6.15−6.20 (m, 2 H, 6- or 5-H, 7-H), 7.27−7.30 (m, 2 H, *m*-H-Ph), 7.34−7.44 (m, 3 H, *p*- and *o*-H-Ph). − ^{13}C{^{1}H} NMR (CDCl$_3$, 125.77 MHz): δ = 20.1 (s, Si*C*Me$_3$), 22.1 (s, *Me*CO), 24.0 (d, $^3J_{P,C}$ = 13.4 Hz, C-9), 26.2 (s, C-10 or C-11), 26.4 (s, SiC*Me*$_3$), 29.2 (d, $^4J_{P,C}$ = 9.5 Hz, C*Me*$_3$), 29.3 (s, C-10 or C-11), 38.1 (d, $^3J_{P,C}$ = 1.9 Hz, C*C*Me$_3$), 40.5 (d, $^2J_{P,C}$ = 39.6 Hz, C-8), 50.8 (d, $^2J_{P,C}$ = 4.3 Hz, C-7a), 54.9 (d, $^2J_{P,C}$ = 5.2 Hz, C-3a), 72.6 (d, $^1J_{P,C}$ = 9.5 Hz, C-7b), 117.5 (d, $^1J_{P,C}$ = 36.7 Hz, C-15), 118.8 (s, C-5 or C-6), 125.3 (s, C-7), 126.6 (s, C-6 or C-5), 127.4 (s, *m*-C of SiPh), 129.8 (s, *p*-C of SiPh), 130.5 (s, *i*-C of SiPh), 132.1 (s, C-4), 134.2 (s, *o*-C of SiPh), 164.4 (s, C-11a), 173.5 (d, $^2J_{P,C}$ = 7.6 Hz, Me*C*O), 175.8 (d, $^2J_{P,C}$ = 31.9 Hz, C-1). − ^{31}P NMR (CDCl$_3$, 202.48 MHz): δ = 76.5.

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[7] See, for example, the elimination of N_2 from 3,4-diazabicyclo[4.1.0]hept-3-ene and 3,4-diazabicyclo[4.2.0]oct-3-ene systems by a $_{\sigma}2+_{\sigma}2+_{\sigma}2$ cycloreversion reaction: [7a] J. A. Berson, S. S. Olin, *J. Am. Chem. Soc.* **1969**, *91*, 777−778. − [7b] J. A. Berson, E. W. Petrillo Jr., P. Bickart, *J. Am. Chem. Soc.* **1974**, *96*, 636−637. − [7c] E. L. Allred, J. C. Hinshaw, A. L. Johnson, *J. Am. Chem. Soc.* **1969**, *91*, 3382−3383.

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[12] There are indications that the X-ray single crystal diffraction analysis was carried out on a nonmerohedral twin. Since the twinning could not be handled computationally and also because of some disorder of the ether molecules in the crystal, no satisfactory level of refinement was achieved. Data were collected for a crystal of **13cA**·0.5 Et_2O on an imaging-plate instrument (IPDS, Stoe & Cie); 33568 reflections were measured which, after averaging, gave 9777 unique reflections (R_{int} = 0.0880). The structure was solved and refined in the monoclinic space group *P*2/*c* with a = 30.275(2), b = 10.948(1), c = 20.459(3) Å, β = 108.72(1)°, Z = 8. Least-squares refinement against F^2 values (hydrogen atoms in calculated positions) resulted in the following R values: $R1$ = 0.112 for reflections with $I > 2\sigma(I)$; $R1$ = 0.155, $wR2$ = 0.353 for all unique reflections. The goodness-of-fit was 1.12, and the residual electron density was between 0.56 and −0.40 Å. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-153575. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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