The Stable (Phosphino)(silyl)carbene as a Useful Building Block: Synthesis and Reactivity of 2-Phosphorus-Substituted 2*H*-Azirines

Valérie Piquet, Antoine Baceiredo, Heinz Gornitzka, Françoise Dahan, and Guy Bertrand*

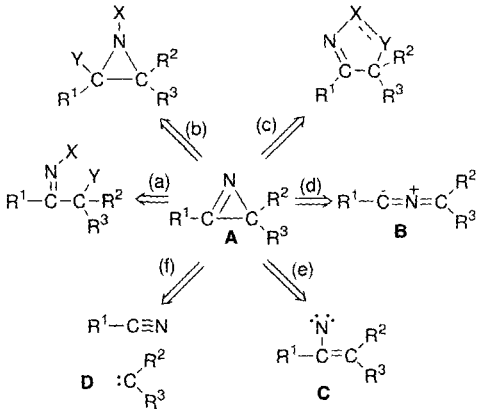
Abstract: [Bis(dicyclohexylamino)phosphino]trimethylsilylcarbene (**1**) reacts with benzonitrile leading to the corresponding 2-phosphino-2*H*-azirine **3** in 85% yield. Treatment of **3** with trifluoromethanesulfonic acid, methyl trifluoromethanesulfonate, or elemental sulfur leads to the *P*-hydrogeno-2-phosphonio-, *P*-methyl-2-phosphonio-, or 2-thioxophosphoranyl-2*H*-azirine (**4**, **5**, and **7**) in 77, 87, and 91% yields, respectively. Irradiation of **3** gives rise to the 1,2λ^5-azaphosphete **8** (98% yield). Treatment of **3** with $BF_3 \cdot OEt_2$, $BH_3 \cdot SMe_2$, Lawesson's reagent, or methyl isothiocyanate gives heterocycles **9** (90% yield), **10** (76% yield), **12** (83% yield), or **13** (80% yield), while under the same experimental conditions, heterocycle **8** reacts with the same reagents to give **9** (82% yield), **11** (83% yield), **12** (86% yield), and **15** (56% yield), respectively. Thermolysis of the *P*-hydrogeno-2-phosphonio-2*H*-azirine **4** at 55 °C leads to the cationic, four-membered heterocycle **17** (96% yield), while photolysis of the *P*-methylazirine analogue **5** in the presence of dimethyl acetylenedicarboxylate affords pyrrole **19** (64% yield). Irradiation of the thioxophosphoranyl azirine **7** gives the 1,3,5λ^5-thiazaphosphole **20** in 79% yield. The influence of the coordination state of phosphorus on the reactivity of 2-phosphorus-substituted 2*H*-azirines is studied.

Keywords
nitrogen heterocycles · phosphinocarbenes · ring expansions · ylides

Introduction

The chemistry of 2*H*-azirines **A**, the smallest of the nitrogen-unsaturated heterocycles, has been extensively explored because of the high reactivity of this ring system towards nucleophilic and electrophilic reagents, as well as for their versatile photochemical and thermal behavior.[1] A retrosynthetic analysis of **A** is given in Scheme 1. Routes (a) and (b) can be considered as modified Neber reactions,[2] route (c) refers to the thermolysis of isoxazoles[3] or oxazaphospholines,[4] route (d) to the ring closure of nitrile ylides,[5] and route (e) to the thermolysis or photolysis of vinyl azides.[6] Surprisingly, one of the most obvious routes to 2*H*-azirines **A**, namely the cycloaddition of a carbene to a nitrile [route (f)], has not been used before this work[7] (Scheme 1).

Interestingly, all three bonds of the azirine ring can be cleaved, depending on the experimental conditions used. In the absence of other reagents and under photolytic or thermolytic conditions, heterocycle **A** can undergo ring-opening reactions involving either C–C bond cleavage leading to transient nitrile ylides **B**,[1] or a C–N bond cleavage with formation of transient vinyl nitrenes **C**,[1] or even cheletropic fragmentation to nitriles and carbenes **D**[8] (Scheme 1).



Scheme 1. Retrosynthetic analysis of **A**.

Here we report the synthesis of the 2-phosphino-2*H*-azirine **3** by means of the unprecedented cycloaddition reaction of a carbene to a nitrile and its transformation into new 2*H*-azirines **4**–**7** that contain a phosphorus substituent in various coordination states. The photochemical, thermal, and chemical behavior of heterocycles **3**–**7** is also presented.

Results

The phosphinocarbene **1**[9c] reacts with a large excess of benzonitrile in toluene at room temperature to afford 2-phosphino-2*H*-azirine **3** in 85% isolated yield. Azirine **3** can also be directly

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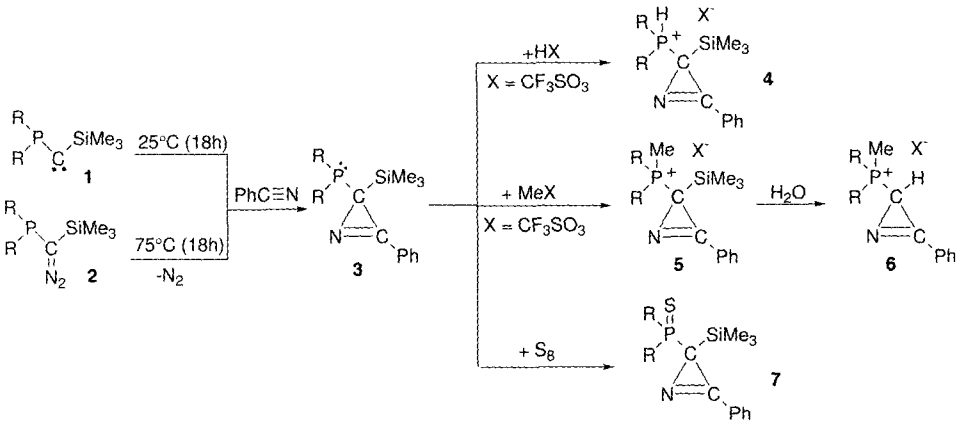
obtained in 78% yield by heating a toluene solution of [bis(dicyclohexylamino)phosphino](trimethylsilyl)diazomethane (**2**)[10] at 75 °C with excess benzonitrile (Scheme 2). Compound **3** has been characterized in solution and by a single-crystal X-ray diffraction study.[7]



Scheme 2. Synthesis and some reactions of azirine **3**. R = *c*-Hex$_2$N.

The azirine **3** reacts at −78 °C with a stoichiometric amount of trifluoromethanesulfonic acid to afford the *P*-hydrogenophosphonioazirine **4**, which was isolated as a white powder in 77% yield. Derivative **4** is hardly soluble in nonpolar solvents, which highlights the ionic structure. The presence of a proton directly bound to the phosphorus atom is revealed by the ^{31}P NMR spectrum, which showed a doublet of quintets at $\delta = +26.6$ (^1J(P,H) = 562.8 Hz and ^3J(P,H) = 15.1 Hz). The ^{13}C NMR signal of the imino carbon appears as a doublet at $\delta = 156.6$ (J(P,C) = 6.0 Hz). The *P*-methyl-2-phosphonio-2*H*-azirine **5** was prepared in 87% yield by adding a stoichiometric amount of methyl trifluoromethanesulfonate to a toluene solution of **3**. The presence of the methyl group bound to the phosphorus is revealed by NMR spectroscopy [^{1}H: $\delta = 2.52$, ^2J(P,H) = 10.8 Hz; ^{13}C: $\delta = 15.9$, ^1J(P,C) = 84.0 Hz], while the presence of the azirine ring can be deduced from the IR spectrum ($\tilde{\nu} = 1753$ cm^{-1}) and the ^{13}C NMR signal at $\delta = 163.6$ (CN, d, J(P,C) = 3.3 Hz). The carbon–silicon bond can be easily cleaved: washing compound **5** with wet THF is sufficient. The 2-phosphonio-2*H*-azirine **6** was isolated as a colorless powder in 78% yield (Scheme 2).

Compound **3** also reacts cleanly with excess elemental sulfur to afford the 2-thioxophosphoranyl-2*H*-azirine **7** in 91% yield. The structure of **7** was clearly established by a single-crystal X-ray diffraction analysis (Table 1). The solid-state structure of the molecule is illustrated in Figure 1. As in the starting azirine **3**,[7] the C1–N1 bond in **7** is very long [**3**: 1.629(4), **7**: 1.623(3) Å].

We now turn to the photochemical, thermal and chemical behavior of these synthesized phosphorus-substituted azirines.

Abstract in French: *Le [bis(dicyclohexylamino)phosphino]-triméthylsilylcarbène (**1**) réagit avec le benzonitrile pour donner, avec un rendement de 85%, la 2-phosphino-2 H-azirine **3**. Le composé **3** réagit avec l'acide trifluorométhanesulfonique, le trifluorométhanesulfonate de méthyle et le soufre pour conduire respectivement aux P-hydrogéno-2-phosphonio-, P-méthyl-2-phosphonio et 2-thioxophosphoranyl-2H-azirines **4**, **5** et **7** avec des rendements respectifs de 77, 87 et 91%. Le 1,2λ^5-azaphosphète **8** (98% yield) est obtenu par irradiation de **3**. La réaction de **3** avec $BF_3.OEt_2$, $BH_3\cdot SMe_2$, le réactif de Lawesson et l'isothiocyanate de méthyle permet la synthèse des hétérocyles **9** (90%), **10** (76%), **12** (83%) et **13** (80%), alors que dans les mêmes conditions expérimentales l'hétérocycle **8** réagit avec les mêmes réactifs en donnant, respectivement, **9** (82%), **11** (83%), **12** (86%) et **15** (56%). La thermolyse à 55 °C de la P-hydrogéno-2-phosphonio-2 H-azirine **4** conduit à l'hétérocycle à quatre chaînons cationique **17** (96%), alors que la photolyse de la P-méthylazirine **5**, en présence d' acétylènedicarboxylate de diméthyle, donne le pyrrole **19** (64%). L'irradiation de la thioxophosphoranylazirine **7** permet la synthèse, avec un rendement de 79%, du 1,3,5λ^5-thiazaphosphole **20**. L'influence de la coordinance de l'atome de phosphore sur la réactivité des 2H-azirines substituées en position 2 par des groupements phosphorés sera présentée.*

Table 1. Crystal structure data of **7**, **10**, **14** and **19**.

	7	**10**	**14**	**19**
formula	$C_{35}H_{58}N_3PSSi$	$C_{35}H_{61}FBN_3SiP$	$C_{34}H_{53}N_4PS$	$C_{44}H_{69}F_3N_3O_8PS$
M_r	611.96	593.74	580.83	888.05
T [K]	293(2)	293(2)	193(2)	173(2)
crystal system	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	19.495(3)	16.811(2)	10.549(7)	10.258(2)
b [Å]	10.157(1)	10.385(1)	11.979(9)	14.506(2)
c [Å]	20.309(3)	20.778(3)	15.481(14)	16.632(3)
α [°]	90	90	111.85(3)	103.43(2)
β [°]	116.64(2)	99.91(2)	91.16(4)	103.68(2)
γ [°]	90	90	111.91(3)	92.88(2)
V [Å^3]	3594.5(8)	3573.3(9)	1656(2)	2324.3(6)
Z	4	4	2	2
$\rho_{(calcd)}$ [Mg m^{-3}]	1.131	1.104	1.165	1.269
$F(000)$	1336	1304	632	952
cryst. size [mm]	0.5, 0.3, 0.15	0.5, 0.4, 0.3	0.4, 0.4, 0.2	0.7, 0.5, 0.4
$2\theta_{max}$ [°]	47	47	42	48
reflns collected	5306	5271	8675	13519
independent reflections	5306	5271	3462	6876
absorption correction	empirical	empirical	–	–
T_{min}, T_{max}	0.911, 0.999	0.985, 0.999		
parameters	340	346	362	604
R ($I > 2\sigma(I)$)	0.0364	0.0360	0.0654	0.0398
$wR2$ [a] (all data)	0.0915	0.1123	0.1341	0.1105
$(\Delta/\rho)_{min}$ [e Å^{-3}]	−0.183	−0.177	−0.304	−0.325
$(\Delta/\rho)_{max}$ [e Å^{-3}]	0.206	0.206	0.215	0.283

[a] $wR2 = \{[\sum w(F_c^2 - F_o^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$.

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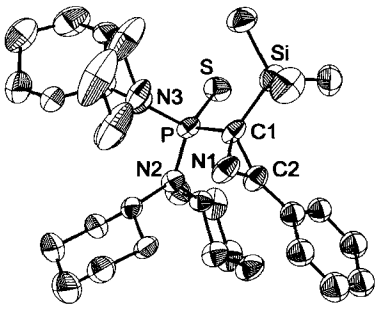


Figure 1. Crystal structure of **7**; anisotropic displacement parameters depicting 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–C2, 1.466(4); C1–N1, 1.623(3); C2–N1, 1.268(3); C1–Si, 1.913(3); C1–P, 1.805(3); N1-C1-C2, 48.2(2); C1-C2-N1, 72.4(2); C1-N1-C2, 59.4(2); N1-C1-P, 117.7(2); C2-C1-P, 118.5(2); N1-C1-Si, 115.4(2); C2-C1-Si, 115.9(2); P-C1-Si, 120.6(2).

Irradiation at 254 nm of a pentane solution of the phosphinoazirine **3** led to the 1,2λ^5-azaphosphete **8**, which was isolated in 98% yield.[7] Addition of a catalytic amount of transition-metal complexes, such as dichloro(*p*-cymene)ruthenium(II), $[Mo(CO)_4(HNC_5H_{10})_2]$ or $[CpFe(CO)_2]_2$, to a dichloromethane solution of **3** also afforded compound **8** in 95, 95, or 96% yield respectively (Scheme 3). The four-π-electron, four-membered heterocycle **8** has been fully characterized, and the NMR data compared very well with those of the recently reported 1,2λ^5-azaphosphete **E**[11] [^{31}P: δ = + 52.3 (**8**), +52.6 (**E**); ^{13}C α and β: δ = + 84.9 and +192.4 (**8**), +92.4 and 181.7 (**E**)].

A stoichiometric amount of $BF_3 \cdot OEt_2$ reacted with **3** to give the four-membered heterocycle–borane complex **9** (90% yield), which can also be obtained in 82% yield by adding $BF_3 \cdot OEt_2$ to **8** (Scheme 3). As already shown for similar compounds,[11,12] NMR data for **9** indicated that the four-π-electron, four-membered ring structure is only slightly disturbed by complexation of the ring nitrogen. The presence of boron was confirmed by a broad singlet at δ = −1.0 in the ^{11}B NMR spectrum.

Completely different behavior was observed with $BH_3 \cdot SMe_2$. Indeed, one equivalent of borane reacted at room temperature with a toluene solution of azirine **3** to afford the five-membered heterocycle **10** in 76% yield. The broad signal observed by ^{31}P NMR (δ = +108.8) is in agreement with boron directly bound to a phosphorus atom.[13] Doublets at δ = 80.0 (J(P,C) = 40.3 Hz) and 177.8 (J(P,C) = 35.2 Hz) in the ^{13}C NMR spectrum are consistent with a PC=C sequence. In the IR spectrum, a band around $\tilde{\nu}$ = 2400 cm^{-1} indicates the presence of the BH_2 group, while absorption at $\tilde{\nu}$ = 3411 cm^{-1} confirms the NH fragment. The structure of **10** was unequivocally determined by an X-ray diffraction study (Table 1, Figure 2). The five-membered ring system features a P-B-N linkage and is nearly planar, as shown by the maximum deviation from the best plane [0.0739(2) Å]. The bond lengths in the ring are consistent with single bonds for P–C [1.779(2) Å], P–B [1.982(2) Å], B–N [1.522(3) Å], and C–N [1.336(3) Å], and with a double bond for C–C [1.404(3) Å]. Note that azaphosphete **8** reacted cleanly with borane, affording the four-membered ring adduct **11** (Scheme 3).

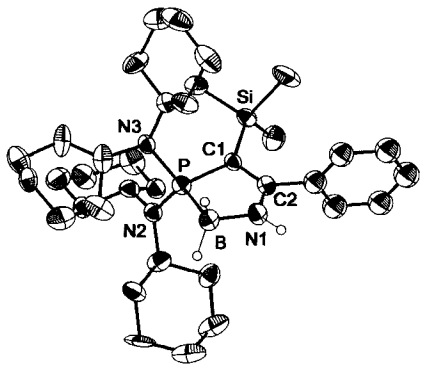
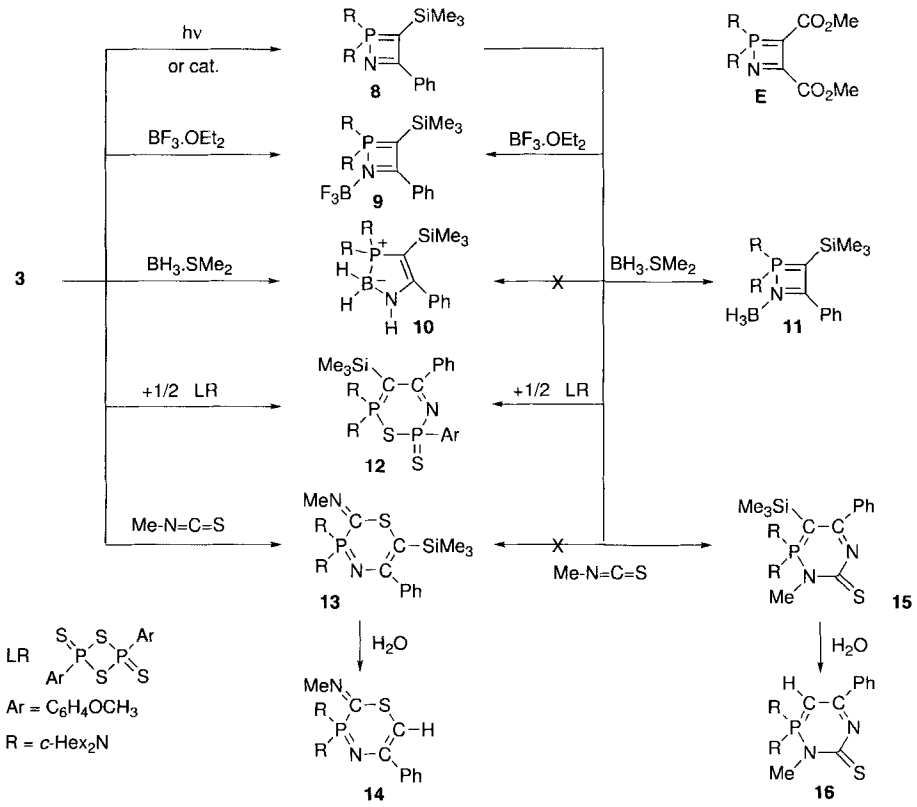


Figure 2. Crystal structure of **10**; anisotropic displacement parameters depicting 50% probability. Most of the hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–C2, 1.404(3); C2–N1, 1.336(3); N1–B, 1.522(3); B–P, 1.982(2); P–C1, 1.779(2); P-C1-C2, 105.1(2); C1-C2-N1, 122.0(2); C2-N1-B, 118.1(2); N1-B-P, 97.2(1); B-P-C1, 96.1(1).

Addition of 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (Lawesson's reagent) to **3** resulted in the formation of the six-membered heterocycle **12** (83% yield). The structure of this compound was established by NMR. The presence of two different phosphorus atoms was indicated by an AX system in the ^{31}P NMR spectrum at δ = 79.2 and



Scheme 3. Photochemical, thermal, and chemical reactions of azirine **3**.

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56.7 (^2J(P,P) = 13.9 Hz). The ylidic and imino carbons appeared, in the ^{13}C NMR spectrum, as doublets of doublets at δ = 57.2 (J(P,C) = 86.7 and 26.6 Hz) and 176.3 (J(P,C) = 28.1 and 4.4 Hz), respectively. Interestingly, the same heterocycle **12** was obtained, in good yield, by reacting half an equivalent of Lawesson's reagent with azaphosphete **8** (Scheme 3).

Methyl isothiocyanate reacted with azirine **3** leading to 2-imino-1,2-dihydro-1,4,3λ^5-thiazaphosphinine **13** in 80% yield. The carbon–silicon bond appeared to be very sensitive towards moisture, and attempts to recrystallize **13** led to **14**, which was isolated as colorless crystals. Heterocycle **14** was fully characterized, including determination of the molecular structure by X-ray diffraction (Table 1, Figure 3). Addition of methyl isothiocyanate to the azaphosphete **8** gave the isomeric 2-thioxo-2,3-dihydro-1,3,4λ^5-diazaphosphinine **15**, which was isolated as a brown powder in 56% yield. The ^{31}P NMR signal at δ = 61.5 suggested an ylidic structure.[14] This was confirmed by the ^{13}C NMR spectrum, which exhibited a resonance at δ = 106.1 [^1J(P,C) = 82.7 Hz], consistent with a carbon atom in this type of environment. Similarly to **13**, the C–Si bond of **15** was easily cleaved by hydrolysis to produce the six-membered ring **16** (Scheme 3).

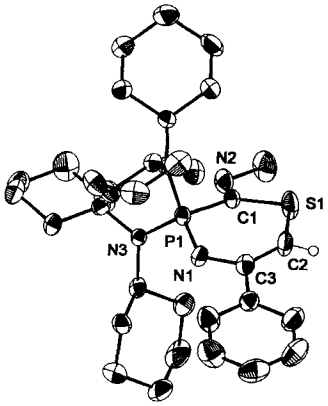
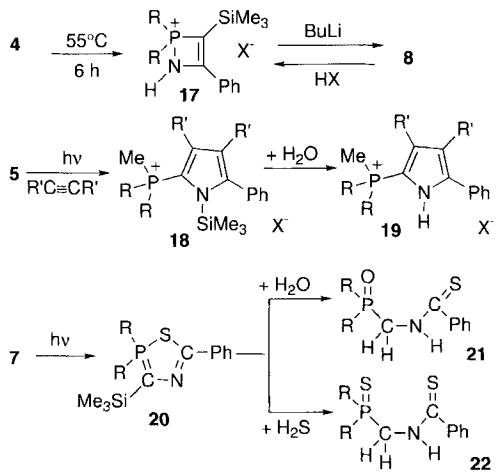


Figure 3. Crystal structure of **14**; anisotropic displacement parameters depicting 50% probability. Most of the hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–S1, 1.767(5); S1–C2, 1.744(5); C2–C3, 1.348(6); C3–N1, 1.389(5); N1–P1, 1.567(4); P1–C1, 1.835(4); C1-S1-C2, 106.4(2); S1-C2-C3, 128.7(4); C2-C3-N1, 124.8(4); C3-N1-P1, 127.2(3); N1-P1-C1, 109.6(2); P1-C1-S1, 116.4(3).

A chloroform solution of phosphonioazirine **4** heated at 55 °C for 6 h afforded the *N*-protonated azaphosphete **17**, which was isolated in 96% yield (Scheme 4). Heterocycle **17** can also be obtained by addition of trifluoromethanesulfonic acid to azaphosphete **8**. Addition of one equivalent of BuLi to **17** regenerated the four-membered ring **8** in nearly quantitative yield (99%). Photolysis of the *P*-methylphosphonioazirine **5** at 254 nm led to a number of products which could not be identified. However, when the irradiation of **5** was carried out in the presence of a slight excess of dimethyl acetylenedicarboxylate, pyrrole **19** was isolated in 64% yield; it was fully characterized, by single-crystal X-ray diffraction amongst other techniques (Table 1, Figure 4).

Irradiation of 2-[bis(dicyclohexylamino)thioxophosphoranyl]-3-phenyl-2-trimethylsilyl-2*H*-azirine (**7**) in pentane at 254 nm led to the formation of heterocycle **20**, which was isolated in 79% yield. The disappearance of the azirine ring was observed in the infrared spectrum, while mass spectrometry supported the formation of an isomer of **7**. The ring expansion to the five-membered heterocycle was corroborated by the ^{13}C NMR spectrum: a doublet was observed at δ = 86.4 (J(P,C) = 43.9 Hz) for the ylide fragment, and a singlet at δ = 170.5 for the imino carbon. The structure of **20** was confirmed by hydrolysis on silica gel and by addition of H_2S, which led to (phosphoranyl) thioamide **21** (99% yield) and (thioxophosphoranyl)thioamide **22** (48% yield), respectively (Scheme 4).



Scheme 4. Thermal or photochemical reactions of phosphonio-2*H*-azirines **4**, **5**, and **7**. R = *c*-Hex$_2$N, N = CF_3SO_3.

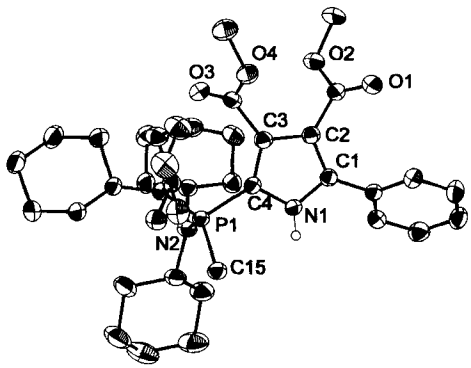


Figure 4. Crystal structure of **19**; anisotropic displacement parameters depicting 50% probability. The hydrogen atoms, the uncoordinated lattice diethyl ether molecule, and the CF_3SO_3 anion have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–C2, 1.388(3); C2–C3, 1.419(3); C3–C4, 1.385(2); C4–N1, 1.383(2); N1–C1, 1.364(2); C1-C2-C3, 107.8(2); C2-C3-C4, 107.9(2); C3-C4-N1, 106.2(2); C4-N1-C1, 111.5(2); N1-C1-C2, 106.6(2).

Discussion

Electrophilic carbenes are known to react with nitriles to give transient[5] or even stable nitrile ylides.[15] However, phosphinocarbenes have not yet demonstrated any electrophilic character, and thus nitrile ylide **23** is probably not the intermediate leading to **3**. A stepwise mechanism, involving the initial nucleophilic attack of the carbene at the carbon atom of the nitrile, would lead to the 1,3-dipole **24**, which can also be regarded as the azabetaine **24′**, or the vinyl nitrene **24″**. The ring closure of vinyl nitrenes to produce azirines is known,[16] but Padwa et

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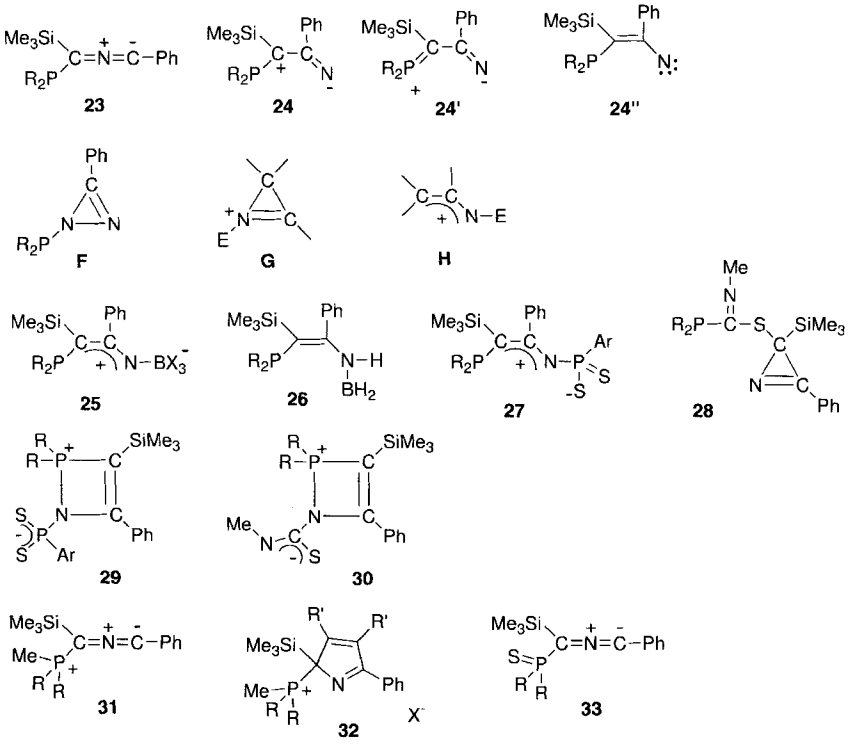
al.[16a] and Nishiwaki et al.[16b,c] showed that vinyl nitrenes, generated by thermolysis of azirines, are efficiently trapped by phosphanes to give phosphazene adducts; therefore, in the case of the vinyl nitrene **24''** an intramolecular reaction of this type should lead to the azaphosphete **8**. However, since **24** can also be the intermediate in the ring expansion reaction of azirine **3** to **8**, it can be postulated that azirine **3** is the kinetic product of the stepwise reaction of the stable carbene **1** with benzonitrile, while azaphosphete **8** is the thermodynamic product. On the other hand, the formation of **3** by a concerted [1 + 2] cycloaddition of the carbene **1** to the nitrile cannot be excluded, nor can the formation of **8** from a concerted ring expansion reaction, as postulated in the case of 2-phosphino-2*H*-diazirine **F**.[17]



R = *c*-Hex$_2$N

It is well known that azirines undergo selective electrophile-induced ring-opening reactions via the transient formation of azirinium ions **G** or azaallyl cations **H**.[18] Although the formation of **8** (metal catalysis) or **9** could be explained by the formation of an azirine complex, which could undergo a ring expansion reaction by the nucleophilic attack of the phosphorus atom, the formation of the five-membered heterocycle **10** strongly suggests the transient formation of the azaallyl–borane adduct **25**.[18] Indeed, it seems quite reasonable that at this stage a hydride transfer occurs from the tetracoordinated boron atom to nitrogen, leading to the γ-phosphinoborane **26**; the observed product **10** results from the interaction of the phosphine with the borane. The superior migratory ability of H^- compared to F^- easily accounts for the difference in the results observed between BH_3 and BF_3. This hypothesis is reinforced by the formation of the four-π-electron, four-membered-ring complexes **9** and **11** by direct addition of $BF_3 \cdot OEt_2$ and $BH_3 \cdot SMe_2$ to **8**.

In the same way, the formation of the heterocycle **12** probably involved the zwitterionic intermediate **27**, resulting from the electrophilic attack of Lawesson's reagent on the nitrogen atom of the azirine **3** followed by a ring closure. With methyl isothiocyanate, a different reaction must take place, since heterocycle **13** is obtained instead of **15**. In this case, the first step is the insertion of Me–N=C=S into the P–C bond of **3** to afford thioazirine **28**, with a subsequent ring-expansion reaction.[19] Note that **12** and **15** are obtained starting from azaphosphete **8**, via adducts **29** and **30**.

The reactivity of **3** towards Brönsted acids and alkylating agents such as trifluoromethanesulfonic acid and methyl trifluoromethanesulfonate is also of great interest. Here, the presence of the phosphino center primarily prevents the protonation or the alkylation of the nitrogen atom, and thus ring opening. However, formation of the cationic, four-membered ring **17** by heating *P*-hydrogenophosphonioazirine **4** probably results from a deprotonation at the phosphorus site and reprotonation at nitrogen to give an azirinium **G** and then an azaallyl cation **H**. Of course, the methyl group of *P*-methylphosphonioazirine **5** does not migrate, and under irradiation, this compound appeared to be a precursor of the transient *C*-phosphonio nitrile ylide **31**, which was trapped by dimethyl acetylenedicarboxylate, leading to 1*H*-pyrrole **19**; the initially formed 2*H*-pyrrole **32** could not be directly detected,[1b] while the highly moisture-sensitive **18** was characterized solely by ^{31}P NMR.

Lastly, the photochemical behavior of thioxophosphoranylazirine **7**, which leads to five-membered heterocycle **20**, can easily be rationalized by the transient formation of the *C*-thioxophosphoranyl nitrile ylide **33**, which is trapped intramolecularly by the P=S moiety.[20]

Conclusion

The synthesis of 2*H*-azirine **3** provides new evidence for the carbene nature of **1**. The extension of this synthetic method to transient carbenes is currently under investigation.

The *P*-methyl-2-phosphonio- and 2-thioxophosphoranyl-2*H*-azirines **5** and **7** behave as classical 2*H*-azirines: on irradiation the C–C bond is cleaved to produce the corresponding transient nitrile ylide. In contrast, the 2-phosphino- and *P*-methyl-2-phosphonio-2*H*-azirine **3** and **4** undergo ring-expansion reactions in which the C–N bond is broken. If the lability of the C–N bond and the presence of the tricoordinated phosphorus center are employed, a variety of novel heterocycles can be prepared.

Experimental Section

All experiments were performed under an atmosphere of dry Ar or N_2. Melting points were obtained on an electrothermal capillary apparatus and were not corrected. ^1H, ^{31}P, ^{13}C, ^{11}B, and ^{29}Si NMR spectra were recorded on Bruker AC 80, AC 200, WM 250, or AMX 400 spectrometers. ^1H and ^{13}C

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chemical shifts are reported in ppm relative to Me_4Si as the external standard. ^{31}P and ^{11}B downfield shifts are expressed with a positive sign relative to external 85% H_3PO_4 and $BF_3 \cdot OEt_2$, respectively. For the ^{13}C NMR data of cyclohexylamino groups the following labeling has been used: N–CH (C_1), N–$CHCH_2$ (C_2), N–$CHCH_2CH_2$ (C_3), N–$CHCH_2CH_2CH_2$ (C_4). Infrared spectra were recorded on a Perkin–Elmer 1725X. Mass spectra were obtained on a Ribermag R1010E instrument. Conventional glassware was used.

2-[Bis(dicyclohexylamino)phosphino]-3-phenyl-2-trimethylsilyl-2*H*-azirine (3): A large excess of freshly distilled benzonitrile (25 mL, 245.15 mmol) was added to a toluene solution (80 mL) of [bis(dicyclohexylamino)phosphino]-(trimethylsilyl)diazomethane (**2**, 6.0 g, 11.90 mmol). The mixture was heated at 75 °C for 18 h. After evaporation of the solvents, the orange oil obtained was washed several times with pentane. Crystallization at −20 °C in pentane gave **3** as yellow crystals (5.38 g, 78%). M.p. 104–105 °C; ^{31}P NMR (32 MHz, $CDCl_3$): $\delta = 69.3$; ^{29}Si NMR (16 MHz, $CDCl_3$): $\delta = 4.26$ [d, J(P,Si) = 51.7 Hz]; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.91$–7.46 (m, 5H; C_6H_5), 2.89–2.53 (m, 4H; NCH), 1.85–0.83 (m, 40H; CH_2), 0.06 (s, 9H; $SiCH_3$); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 165.5$ (C=N), 131.9 (*p*-C_6H_5), 129.4, 128.4 (*o*-,*m*-C_6H_5), 126.8 (*ipso*-C_6H_5), 57.7 [d, ^2J(P,C) = 7.9 Hz; C_1], 35.3, 34.6 (C_2), 26.8, 26.6, 25.7, 25.6 (C_3 and C_4), −0.6 [d, ^3J(P,C) = 3.5 Hz; $SiCH_3$], PC was not observed; IR (CH_2Cl_2): $\tilde{\nu} = 2019$, 1726 cm^{-1} (C=N); MS (NH_3, CI): *m/z* 580 [*M*+1]; $C_{35}H_{58}N_3PSi$: calcd C 72.49, H 10.08, N 7.25; found C 72.23, H 9.97, N 7.26.

The 2*H*-azirine **3** was also obtained in 85% yield (0.41 g) by the reaction of excess benzonitrile (257 μL, 2.52 mmol) with phosphino(silyl)carbene **1** (0.40 g, 0.84 mmol) for 18 h at RT in toluene solution (10 mL).

2-[Bis(dicyclohexylamino)phosphonio]-3-phenyl-2-trimethylsilyl-2*H*-azirine (4): A stoichiometric amount of trifluoromethanesulfonic acid (95 μL, 0.11 mmol) was added to a CH_2Cl_2 solution (15 mL) of **3** (0.62 g, 0.11 mmol) at −78 °C. The mixture was stirred for 2 h at RT, and the solvent evaporated. The residue was washed several times with ether to give **4** as a white powder (0.60 g, 77%). M.p. 77–78 °C; ^{31}P NMR (32 MHz, $CDCl_3$): $\delta = 26.6$ [dq, ^3J(P,H) = 15.1 and ^1J(P,H) = 562.8 Hz]; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 8.02$–7.63 (m, 5H; C_6H_5), 7.98 [d, ^1J(P,H) = 562.8 Hz, 1H; PH], 3.26–2.92 (m, 4H; NCH), 2.06–0.91 (m, 40H; CH_2), 0.25 (s, 9H; $SiCH_3$); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 156.6$ [d, J(P,C) = 6.0 Hz; C=N], 135.6 (*p*-C_6H_5), 130.4, 130.1 (*o*-,*m*-C_6H_5), 121.4 (*ipso*-C_6H_5), 120.3 [q, ^1J(C,F) = 319.7 Hz; CF_3], 58.2, 57.3 (C_1), 34.2 (C_2), 26.4, 24.7, 24.6, 24.5 (C_3 and C_4), −1.5 ($SiCH_3$), PC was not observed; IR (THF): $\tilde{\nu} = 1753$ cm^{-1} (C=N); $C_{36}H_{59}F_3N_3O_3PSSi$: calcd C 59.23, H 8.15, N 5.76; found C 58.94, H 8.08, N 5.68.

2-[Bis(dicyclohexylamino)methylphosphonio]-3-phenyl-2-trimethylsilyl-2*H*-azirine (5): A stoichiometric amount of methyl trifluoromethanesulfonate (49 μL, 0.43 mmol) was added to a toluene solution (5 mL) of **3** (0.25 g, 0.43 mmol). After stirring for 15 min at RT, the addition of pentane (10 mL) precipitated **5** as a pale yellow powder (0.26 g, 87%). M.p. 139 °C (decomp.); ^{31}P NMR (81 MHz, C_6D_6): $\delta = 72.4$; ^1H NMR (200 MHz, C_6D_6): $\delta = 8.35$–7.42 (m, 5H; C_6H_5), 3.42–2.97 (m, 4H; NCH), 2.52 [d, ^2J(P,H) = 10.8 Hz, 3H; PCH_3], 2.00–0.86 (m, 40H; CH_2), 0.23 (s, 9H; $SiCH_3$); ^{13}C NMR (50 MHz, C_6D_6): $\delta = 163.6$ [d, J(P,C) = 3.3 Hz; C=N], 135.2 (*p*-C_6H_5), 131.9, 130.7 (*o*-,*m*-C_6H_5), 122.4 (*ipso*-C_6H_5), 120.1 [q, ^1J(C,F) = 320.8 Hz; CF_3], 59.7 [d, ^2J(P,C) = 2.8 Hz; C_1], 56.9 [d, ^2J(P,C) = 4.6 Hz; C_1], 36.3, 35.9 (C_2), 27.5, 27.3, 26.9, 26.5, 25.7, 25.5 (C_3 and C_4), 15.9 [d, ^1J(P,C) = 84.0 Hz; PCH_3], −0.7 ($SiCH_3$), PC was not observed; IR (CH_2Cl_2): $\tilde{\nu} = 1753$ cm^{-1} (C=N); MS (FAB): *m/z* 594 [M^+]; $C_{37}H_{61}F_3N_3O_3PSSi$: calcd C 59.73, H 8.26, N 5.65; found C 60.14, H 8.32, N 5.93.

2-[Bis(dicyclohexylamino)methylphosphonio]-3-phenyl-2*H*-azirine (6): A wet THF solution (10 mL) of **5** (0.20 g, 0.27 mmol) was stirred for 2 h at RT. Cleavage of the carbon–silicon bond was monitored by ^{31}P NMR spectroscopy. Addition of pentane (10 mL) precipitated **6** as a white powder (0.14 g, 78%). M.p. 112 °C (decomp.); ^{31}P NMR (32 MHz, $CDCl_3$): $\delta = 57.0$; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 8.01$–7.63 (m, 5H; C_6H_5), 3.93 [d, J(P,H) = 13.0 Hz, 1H; PCH], 3.36–3.12 (m, 4H; NCH), 2.13 [d, ^2J(P,H) = 12.4 Hz, 3H; PCH_3], 2.09–0.98 (m, 40H; CH_2); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 160.3$ (C=N), 135.4 (*p*-C_6H_5), 130.6, 130.1 (*o*-,*m*-C_6H_5), 121.3 (*ipso*-C_6H_5), 120.6 [q, ^1J(C,F) = 320.7 Hz; CF_3], 58.4 [d, ^2J(P,C) = 3.4 Hz; C_1], 57.8 [d, ^2J(P,C) = 3.5 Hz; C_1], 34.2, 34.1, 34.0, 33.8 (C_2), 28.5, 26.7, 26.5, 25.0, 24.9, 24.6 (C_3 and C_4), 15.7 [d, ^1J(P,C) = 55.3 Hz; PCH_3], PC was not observed; IR (CH_2Cl_2): $\tilde{\nu} = 1749$ cm^{-1} (C=N); $C_{34}H_{53}F_3N_3O_3PSi$: calcd C 60.78, H 7.95, N 6.25; found C 60.52, H 7.87, N 6.07.

2-[Bis(dicyclohexylamino)thioxophosphoranyl]-3-phenyl-2-trimethylsilyl-2*H*-azirine (7): Excess elemental sulfur (0.4 g, 12.50 mmol) was added to a THF solution (40 mL) of **3** (1.0 g, 1.73 mmol). The mixture was sonicated for 1 h at RT. After evaporation of the solvent the excess sulfur was precipitated by adding pentane. After filtration and evaporation of pentane the residue was purified by flash chromatography on silica gel (pentane/ether 98:2) to give **7** as a pale yellow powder (0.96 g, 91%). M.p. 191 °C (decomp.); ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 86.7$ (br); ^{29}Si NMR (16 MHz, $CDCl_3$): $\delta = 4.83$ [d, J(P,Si) = 26.9 Hz]; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 8.08$–7.48 (m, 5H; C_6H_5), 3.76–3.44 (m, 4H; NCH), 2.15–0.86 (m, 40H; CH_2), 0.21 (s, 9H; $SiCH_3$); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 164.9$ [d, J(P,C) = 4.1 Hz; C=N], 133.0 (*p*-C_6H_5), 130.9, 129.0 (*o*-,*m*-C_6H_5), 125.3 (*ipso*-C_6H_5), 58.2 [d, ^2J(P,C) = 4.9 Hz; C_1], 57.0 [d, ^2J(P,C) = 4.7 Hz; C_1], 36.1, 34.8 (C_2), 27.7, 27.6, 27.4, 26.9, 26.0, 25.8 (C_3 and C_4), 0.2 ($SiCH_3$), PC was not observed; IR ($CDCl_3$) $\tilde{\nu} = 2047$, 1741 cm^{-1} (C=N); MS (CH_4, CI): *m/z* 612 [*M*+1]; $C_{35}H_{58}N_3PSSi$: calcd C 68.69, H 9.55, N 6.87; found C 68.70, H 9.51, N 6.91.

[2-Bis(dicyclohexylamino)-4-phenyl-3-trimethylsilyl]-2λ^5-azaphosphete (8):

Method a: A catalytic amount of $[(p\text{-Cym})RuCl_2]_2$ (< 5 mg) was added to a CH_2Cl_2 solution (10 mL) of **3** (0.50 g, 0.86 mmol) at RT. After stirring for 5 min and evaporation of the solvent, the four-membered ring **8** was obtained as a brown-yellow oil (0.47 g, 95% yield): ^{31}P NMR (32 MHz, C_6D_6): $\delta = 52.3$; ^1H NMR (200 MHz, C_6D_6): $\delta = 8.36$ [d, $J = 7.1$ Hz, 2H; *o*-C_6H_5], 7.28–7.13 (m, 3H; *m*-,*p*-C_6H_5), 3.49–3.30 (m, 4H; NCH), 2.11–0.96 (m, 40H; CH_2), 0.45 (s, 9H; $SiCH_3$); ^{13}C NMR (50 MHz, C_6D_6): $\delta = 192.4$ [d, ^2J(P,C) = 46.7 Hz; PCC], 139.0 [d, ^3J(P,C) = 55.7 Hz; *ipso*-C_6H_5], 130.7 (*p*-C_6H_5), 128.8, 128.7 (*o*-,*m*-C_6H_5), 84.9 [d, J(P,C) = 42.8 Hz; PC], 58.3 [d, ^2J(P,C) = 4.9 Hz; C_1], 34.3, 34.1 (C_2), 27.8, 27.6, 26.4 (C_3 and C_4), 3.5 [d, J(P,C) = 3.9 Hz; $SiCH_3$]; MS (NH_3, CI): *m/z* 580 [*M*+1].

The four-membered ring **8** was also obtained under the same experimental conditions using a catalytic amount of $Mo(CO)_4(HNC_5H_{10})_2$ after 20 h or $[CpFe(CO)_2]_2$ after 96 h (yields: 95 and 96% respectively).

Method b: A freshly distilled pentane solution (5 mL) of **3** (0.14 g, 0.24 mmol) was irradiated at 254 nm. The reaction was monitored by ^{31}P NMR spectroscopy and was complete after 19 h. The solvent was removed under vacuum and the four-membered ring **8** was obtained as a brown-yellow oil (0.14 g, 98%).

Method c: Butyllithium in hexanes (1.6 M, 28 μL, 0.04 mmol) was added to a THF solution (3 mL) of compound **17** (0.03 g, 0.04 mmol) at −78 °C. After the solution was stirred for 15 min at RT, the solvent was removed under vacuum, and pentane (10 mL) was added to the residue. Elimination of the lithium salts by filtration, followed by evaporation of pentane afforded the four-membered ring **8** as a brown-yellow oil (0.03 g, 99%).

BF_3 complex 9: A stoichiometric amount of $BF_3 \cdot OEt_2$ (8.5 μL, 0.07 mmol) was added to a toluene solution (3 mL) of **3** (0.04 g, 0.07 mmol) at −78 °C. The solution was stirred for 2 h at RT. After evaporation of the solvent the residue was washed several times with pentane to give derivative **9** as a pale yellow powder (0.04 g, 90%). M.p. 85–87 °C; ^{31}P NMR (81 MHz, C_6D_6): $\delta = 48.9$; ^{11}B NMR (26 MHz, C_6D_6): $\delta = -1.0$; ^1H NMR (250 MHz, C_6D_6): $\delta = 7.83$–7.08 (m, 5H; C_6H_5), 3.22–2.96 (m, 4H; NCH), 2.09–0.88 (m, 40H; CH_2), 0.07 (s, 9H; $SiCH_3$); ^{13}C NMR (62 MHz, C_6D_6): $\delta = 181.6$ [d, ^2J(P,C) = 33.2 Hz; PCC], 134.6 [d, ^3J(P,C) = 40.1 Hz; *ipso*-C_6H_5], 130.5 (*p*-C_6H_5), 129.2, 128.1 (*o*-,*m*-C_6H_5), 102.2 [d, J(P,C) = 62.8 Hz; PC], 59.3 [d, ^2J(P,C) = 4.9 Hz; C_1], 33.8, 33.7 (C_2), 27.1, 27.0, 26.0, 25.7 (C_3 and C_4), 1.9 ($SiCH_3$); $C_{35}H_{58}BF_3N_3PSi$: calcd C 64.90, H 9.02, N 6.49; found C 64.34, H 9.02, N 6.40.

The complex **9** was also obtained in 82% yield (0.04 g), under the same experimental conditions, starting from **8** (0.04 g, 0.07 mmol) and $BF_3 \cdot OEt_2$ (8.5 μL, 0.07 mmol).

Five-membered ring 10: A stoichiometric amount of $BH_3 \cdot SMe_2$ (88 μL, 0.93 mmol) was added to a toluene solution (10 mL) of **3** (0.54 g, 0.93 mmol) at RT. The solution was stirred for 2 h at RT. After the solvent was removed under vacuum, the residue was purified by crystallization from pentane at

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−20 °C to give five-membered ring **10** as colorless crystals (0.42 g, 76%): M.p. 150–151 °C; ^{31}P NMR (32 MHz, C_6D_6): δ = 108.8 (br); ^{11}B NMR (26 MHz, C_6D_6): δ = −15.0 (br); ^{1}H NMR (200 MHz, C_6D_6): δ = 7.21–7.00 (m, 5H; C_6H_5), 3.56–3.38 (m, 4H; NCH), 2.11–1.11 (m, 40H; CH_2), 0.27 (s, 9H; $SiCH_3$), NH and BH_2 are not observed; ^{13}C NMR (50 MHz, C_6D_6): δ = 177.8 [d, J(P,C) = 35.2 Hz; PCC], 143.4 [d, J(P,C) = 16.7 Hz; *ipso*-C_6H_5], 129.2, 128.8 (*o*-,*m*-C_6H_5), 127.3 (*p*-C_6H_5), 80.0 [d, J(P,C) = 40.3 Hz; PC], 58.6 [d, ^2J(P,C) = 5.6 Hz; C_1], 36.2 [d, ^3J(P,C) = 2.3 Hz; C_2], 35.5 [d, ^3J(P,C) = 2.1 Hz; C_2], 28.7, 28.4, 27.8, 27.2 (C_3 and C_4), 4.7 ($SiCH_3$); IR (C_6D_6): $\tilde{\nu}$ = 3411 (N–H), 2400 cm^{-1} (B–H); $C_{35}H_{61}BN_3PSi$: calcd C 70.80, H 10.36, N 7.08; found C 70.38, H 10.24, N 6.88.

BH_3 complex 11: To a CH_2Cl_2 solution (5 mL) of **8** (0.13 g, 0.22 mmol) was added at −78 °C a stoichiometric amount of $BH_3 \cdot SMe_2$ (21 µL, 0.22 mmol). After stirring the solution for 10 min at RT, the solvent was removed under vacuum and the final product was precipitated by adding pentane (10 mL). Compound **11** was obtained as a pale yellow powder by filtration (0.11 g, 83%). M.p. 132 °C (decomp.); ^{31}P NMR (32 MHz, C_6D_6): δ = 53.2; ^{11}B NMR (26 MHz, C_6D_6): δ = −21.2; ^{1}H NMR (200 MHz, C_6D_6): δ = 8.06–7.13 (m, 5H; C_6H_5), 3.62–3.20 (m, 4H; NCH), 2.19–1.01 (m, 40H; CH_2), 0.18 (s, 9H; $SiCH_3$), BH_3 was not observed; ^{13}C NMR (50 MHz, C_6D_6): δ = 186.7 (d, ^2J(P,C) = 31.9 Hz; PCC], 135.0 [d, ^3J(P,C) = 44.7 Hz; *ipso*-C_6H_5], 130.8 (*p*-C_6H_5), 129.3, 128.7 (*o*-,*m*-C_6H_5), 95.9 [d, J(P,C) = 60.6 Hz; PC], 59.0 [d, ^2J(P,C) = 4.2 Hz; C_1], 34.1, 34.0 (C_2), 27.8, 27.5, 26.6, 26.1 (C_3 and C_4), 2.8 [d, J(P,C) = 4.1 Hz; $SiCH_3$]; $C_{35}H_{61}BN_3PSi$: calcd C 70.80, H 10.35, N 7.08; found: C 70.52, H 10.28, N 6.98.

6-Bis(dicyclohexylamino)-2-(*p*-methoxyphenyl)thioxo-4-phenyl-5-trimethylsilyl-1,2-dihydro-1,3-thiaza-2λ^5,6λ^5-diphosphinine (12): A suspension of Lawesson's reagent (0.09 g, 0.22 mmol) in toluene (10 mL) was added to a toluene solution (5 mL) of **3** (0.25 g, 0.43 mmol). After stirring for 30 min at RT, the solvent was removed under vacuum and the residue was recrystallized from pentane/toluene (3:1) at −20 °C to give **12** as a white powder (0.28 g, 83%). M.p. 112 °C (decomp.); ^{31}P NMR (32 MHz, $CDCl_3$): δ = 79.2 [d, J(P,P) = 13.9 Hz], 56.7 [d, J(P,P) = 13.9 Hz]; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.71 [dd, ^3J(P,H) = 14.3 Hz, ^3J(H,H) = 8.7 Hz, 2H; *o*-$C_6H_4OCH_3$], 7.22 [t, ^3J(H,H) = 7.4 Hz, 1H; *p*-C_6H_5], 7.07 [dd, ^3J(H,H) = 7.4 and 7.3 Hz, 2H; *m*-C_6H_5], 6.88 [d, ^3J(H,H) = 7.3 Hz, 2H; *o*-C_6H_5], 6.42 [dd, ^3J(H,H) = 8.7 Hz, ^4J(P,H) = 2.3 Hz, 2H; *m*-$C_6H_4OCH_3$], 4.16–4.01 (m, 4H; NCH), 3.70 (s, 3H; OCH_3), 2.14–1.13 (m, 40H; CH_2), −0.09 (s, 9H; $SiCH_3$); ^{13}C NMR (62 MHz, $CDCl_3$): δ = 176.3 [dd, J(P,C) = 28.1 and 4.4 Hz; C=N], 160.3 [d, ^4J(P,C) = 2.9 Hz; *p*-$C_6H_4OCH_3$], 133.4 [d, ^3J(P,C) = 14.2 Hz; *m*-$C_6H_4OCH_3$], 131.3 [d, ^3J(P,C) = 35.9 Hz; *ipso*-C_6H_5], 128.9 (*p*-C_6H_5), 128.0, 126.9 (*o*-,*m*-C_6H_5), 113.2 [dd, J(P,C) = 65.7 and 3.8 Hz; *ipso*-$C_6H_4OCH_3$], 111.6 [d, ^2J = 15.0 Hz; *o*-$C_6H_4OCH_3$), 60.7 [d, ^2J(P,C) = 5.0 Hz; C_1], 57.2 [dd, J(P,C) = 86.7 and 26.6 Hz; P=C], 55.1 (OCH_3), 35.4, 35.3 (C_2), 27.0, 26.8, 25.5, 24.8 (C_3 and C_4), 0.8 [d, J(P,C) = 3.3 Hz; $SiCH_3$]; $C_{42}H_{65}N_3OP_2S_2Si$: calcd C 64.50, H 8.38, N 5.37; found C 64.35, H 8.32, N 5.41.

Diphosphinine **12** was also obtained under the same experimental conditions by using 0.25 g (0.43 mmol) of **8** (yield: 0.29 g, 86%).

3-Bis(dicyclohexylamino)-2-imino-5-phenyl-6-trimethylsilyl-1,2-dihydro-1,4,3λ^5-thiazaphosphinine (13): A stoichiometric amount of methyl isothiocyanate (0.04 g, 0.55 mmol) was added to a toluene solution (10 mL) of **3** (0.32 g, 0.55 mmol). The mixture was heated at 80 °C for 5 h. After evaporation of the solvent, the residue was washed several times with acetonitrile to give heterocycle **13** as an orange-yellow oil (0.29 g, 80%). ^{31}P NMR (32 MHz, C_6D_6): δ = 0.2; ^{1}H NMR (250 MHz, C_6D_6): δ = 7.67–7.16 (m, 5H; C_6H_5), 3.40–3.27 (m, 4H; NCH), 3.35 [d, J(P,H) = 3.2 Hz, 3H; NCH_3], 1.91–0.99 (m, 40H; CH_2), 0.12 (s, 9H; $SiCH_3$); ^{13}C NMR (62 MHz, C_6D_6): δ = 159.6 [d, J(P,C) = 141.1 Hz; PC], 156.8 (CC_6H_5), 147.6 [d, J(P,C) = 19.5 Hz; *ipso*-C_6H_5], 129.3, 128.2 (*o*-,*m*-C_6H_5), 127.7 (*p*-C_6H_5), 95.0 [d, ^3J(P,C) = 17.4 Hz; PCSC], 57.3 [d, ^2J(P,C) = 4.6 Hz; C_1], 41.1 [d, J(P,C) = 20.9 Hz; NCH_3], 34.8, 34.1 (C_2), 27.9, 27.8, 27.7, 26.6 (C_3 and C_4), 2.1 ($SiCH_3$); MS (EI) *m*/*z* 652 [M^+].

3-Bis(dicyclohexylamino)-2-imino-5-phenyl-1,2-dihydro-1,4,3λ^5-thiazaphosphinine (14): Attempts to recrystallize compound **13** from acetonitrile gave heterocycle **14** as colorless crystals in a quantitative yield. M.p. 87–89 °C; ^{31}P NMR (81 MHz, $CDCl_3$): δ = 4.4; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.80–7.16 (m, 5H; C_6H_5), 5.66 [d, J(P,H) = 3.1 Hz, 1H; SCH], 3.24 [d, J(P,H) = 3.2 Hz, 3H; NCH_3], 3.18–2.76 (m, 4H; NCH), 1.98–0.80 (m, 40H; CH_2); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 144.8 (CC_6H_5), 141.6 (*ipso*-C_6H_5), 127.5, 125.3 (*o*-,*m*-C_6H_5), 126.4 (*p*-C_6H_5), 84.2 [d, ^3J(P,C) = 20.7 Hz; SCH], 56.4 [d, ^2J(P,C) = 4.3 Hz; C_1], 41.0 (NCH_3), 34.0, 33.1 (C_2), 27.0, 26.9, 26.6, 25.7 (C_3 and C_4), PC was not observed; $C_{34}H_{53}N_4PS$: calcd C 70.31, H 9.20, N 9.64; found C 69.98, H 9.16, N 9.58.

4-Bis(dicyclohexylamino)-2-thioxo-5-trimethylsilyl-6-phenyl-2,3-dihydro-1,3,4λ^5-diazaphosphinine (15): A stoichiometric amount of methyl isothiocyanate (0.04 g, 0.55 mmol) was added to a toluene solution (10 mL) of **8** (0.32 g, 0.55 mmol). The mixture was heated at 50 °C for 60 h. After evaporation of the solvent, the residue was washed several times with pentane (25 mL) to afford heterocycle **15** as a brown-yellow powder (0.20 g, 56% yield). M.p. 147 °C (decomp.); ^{31}P NMR (32 MHz, $CDCl_3$): δ = 61.5; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.43–7.31 (m, 5H; C_6H_5), 3.20 (d, J(P,H) = 9.7 Hz, 3H; NCH_3), 3.22–3.07 (m, 4H; NCH), 1.88–0.86 (m, 40H; CH_2), 0.08 (s, 9H; $SiCH_3$); ^{13}C NMR (62 MHz, $CDCl_3$): δ = 167.5 [d, J(P,C) = 6.1 Hz; C=S], 155.0 (C=N), 144.5 [d, J(P,C) = 18.1 Hz; *ipso*-C_6H_5], 128.3, 127.6 (*o*-,*m*-C_6H_5), 127.5 (*p*-C_6H_5), 106.1 [d, J(P,C) = 82.7 Hz; P=C], 58.1 [d, ^2J(P,C) = 4.5 Hz; C_1], 36.5 [d, J(P,C) = 4.6 Hz; NCH_3], 34.3, 34.2 (C_2), 27.4, 27.3, 26.9, 26.8 (C_3 and C_4), 2.3 [d, J(P,C) = 2.1 Hz; $SiCH_3$].

4-Bis(dicyclohexylamino)-2-thioxo-6-phenyl-2,3-dihydro-1,3,4λ^5-diazaphosphinine (16): Attempts to recrystallize compound **15** in pentane/ether (5:1), at −20 °C, yielded heterocycle **16** as pale yellow crystals. M.p. 113 °C (decomp.); ^{31}P NMR (32 MHz, $CDCl_3$): δ = 38.1; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.91–7.31 (m, 5H; C_6H_5), 5.14 [d, J(P,H) = 14.9 Hz, 1H; P=CH], 3.43 [d, J(P,H) = 6.2 Hz, 3H; NCH_3], 3.24–3.05 (m, 4H; NCH), 2.13–0.97 (m, 40H; CH_2); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 183.2 [d, J(P,C) = 3.8 Hz; C=S], 159.1 [d, J(P,C) = 3.8 Hz; C=N], 140.0 [d, J(P,C) = 17.4 Hz; *ipso*-C_6H_5], 129.3 (*p*-C_6H_5), 127.8, 127.1 (*o*-,*m*-C_6H_5), 78.7 [d, J(P,C) = 167.9 Hz; P=C], 58.1 [d, ^2J(P,C) = 4.0 Hz; C_1], 38.7 [d, J(P,C) = 4.2 Hz; NCH_3], 34.1, 32.9 (C_2), 26.7, 26.6, 25.5, 25.1 (C_3 and C_4); MS (CH_4, CI): *m*/*z* 581 [M+1]; $C_{34}H_{53}N_4PS$: calcd C 70.31, H 9.20, N 9.64; found C 70.62, H 9.25, N 9.60.

Cationic, four-membered heterocycle 17: A stoichiometric amount of trifluoromethanesulfonic acid (76 µL, 0.86 mmol) was added to a CH_2Cl_2 solution (10 mL) of **8** (0.50 g, 0.86 mmol) at −78 °C. After the solution was stirred for 15 min at RT, the solvent was evaporated and the residue washed with pentane several times to give **17** as a pale yellow powder (0.54 g, 86%). M.p. 80–82 °C; ^{31}P NMR (32 MHz, $CDCl_3$): δ = 48.1; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.43 (m, 1H; NH), 7.83–7.51 (m, 5H; C_6H_5), 3.46–3.18 (m, 4H; NCH), 2.07–1.08 (m, 40H; CH_2), 0.29 (s, 9H; $SiCH_3$); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 172.5 [d, J(P,C) = 29.1 Hz; PCC], 132.9 (*p*-C_6H_5), 129.6 [d, J(P,C) = 30.7 Hz; *ipso*-C_6H_5], 129.0, 128.5 (*o*-,*m*-C_6H_5), 120.3 (q, ^1J(C,F) = 320.4 Hz; CF_3], 104.5 [d, J(P,C) = 61.8 Hz; PC], 58.8 [d, ^2J(P,C) = 4.3 Hz; C_1], 32.9 (C_2), 28.4, 26.3, 24.8, 24.4 (C_3 and C_4), 1.1 [d, J(P,C) = 3.1 Hz; $SiCH_3$); IR ($CDCl_3$): $\tilde{\nu}$ = 3066 cm^{-1} (N–H); $C_{36}H_{59}F_3N_3O_3PSSi$: calcd C 59.23, H 8.15, N 5.76; found C 59.45, H 8.19, N 5.70.

Derivative **17** was also obtained in 96% yield (0.20 g) by heating, for 6 h at 55 °C, a chloroform solution (5 mL) of azirine **4** (0.21 g, 0.29 mmol).

Photolysis of azirine 5: A mixture of freshly distilled THF solution (8 mL) of azirine **5** (0.25 g, 0.37 mmol) and a stoichiometric amount of dimethyl acetylenedicarboxylate (46 µL, 0.37 mmol) was irradiated at 254 nm. According to ^{31}P NMR spectroscopy, **5** completely disappeared after 1 h and two new compounds were formed: **18** (δ = 51.2, 44%) and **19** (δ = 44.5, 56%). After evaporation of the solvent, the residue was washed several times with acetonitrile. Only derivative **19** was obtained as a yellow powder. Recrystallization from a dichloromethane/ether (5:1) solution, at −20 °C, gave **19** as white crystals (0.17 g, 64% yield). M.p. 218–219 °C (decomp.); ^{31}P NMR (81 MHz, $CDCl_3$): δ = 44.8; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 10.20 (m, 1H; NH), 7.57–7.40 (m, 5H; C_6H_5), 3.85 (s, 3H; OCH_3), 3.71 (s, 3H; OCH_3), 3.69–3.39 (m, 4H; NCH), 2.54 [d, ^2J(P,H) = 12.9 Hz, 3H; PCH_3), 1.86–1.04 (m, 40H; CH_2); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 164.6, 164.1 (C=O), 142.9 [d, J(P,C) = 10.3 Hz; PCNC], 129.5 (*p*-C_6H_5), 129.2, 128.2 (*o*-,*m*-C_6H_5), 128.1 (*ipso*-C_6H_5), 126.8 [d, J(P,C) = 13.2 Hz; PCCC], 120.2 (q, J(P,C) = 319.5 Hz; CF_3], 116.2 (PCC), 115.1 [d, ^1J(P,C) = 146.7 Hz; PC],

58.8 [d, ^2J(P,C) = 5.7 Hz; C_1], 52.6, 51.9 (OCH_3), 34.8, 34.3 (C_2), 26.8, 26.6, 25.1 (C_3 and C_4), 17.6 [d, ^1J(P,C) = 80.0 Hz; PCH_3]; IR ($CDCl_3$): $\tilde{\nu}$ = 3425 (N–H), 1726 cm^{-1} (C=O); $C_{40}H_{59}F_3N_3O_7PS$: calcd C 59.03, H 7.31, N 5.16; found C 58.87, H 7.28, N 4.96.

1,3,5λ^5-Thiazaphosphole (20): A freshly distilled pentane solution (80 mL) of azirine **7** (1.42 g, 2.32 mmol) was irradiated at 254 nm. According to ^{31}P NMR spectroscopy, the transformation of **7** into **20** was complete after 14 h. Evaporation of the solvent gave **20** as an orange oil (1.12 g, 79%): ^{31}P NMR (81 MHz, $CDCl_3$): δ = 97.9; ^1H NMR (250 MHz, $CDCl_3$): δ = 7.61–7.43 (m, 5H; C_6H_5), 3.45–3.25 (m, 4H; NCH), 1.87–0.85 (m, 40H; CH_2), 0.26 (s, 9H; $SiCH_3$); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 170.5 (C=N), 138.7 (*ipso*-C_6H_5), 132.5 (*p*-C_6H_5), 128.9, 127.4 (*o*-,*m*-C_6H_5), 86.4 [d, J(P,C) = 43.9 Hz; P=C], 58.5 [d, ^2J(P,C) = 3.0 Hz; C_1], 33.9 [d, ^3J(P,C) = 2.9 Hz; C_2], 33.5 [d, ^3J(P,C) = 2.4 Hz; C_2], 27.4, 26.9, 26.8, 25.4 (C_3 and C_4), 1.6 ($SiCH_3$); MS (NH_3, CI): *m*/*z* 612 [*M*+1].

(Phosphoranyl)thioamide (21): A $CDCl_3$ solution (3 mL) of **20** (0.12 g, 0.20 mmol) was filtered through silica gel with ether as eluent. Evaporation of the solvent under vacuum led to **21** as an orange powder (0.11 g, 99%). M.p. 151–153 °C (decomp.); ^{31}P NMR (81 MHz, $CDCl_3$): δ = 29.1; ^1H NMR (250 MHz, $CDCl_3$): δ = 8.70 [d, ^3J(H,H) = 4.5 Hz, 1H; NH], 7.84–7.28 (m, 5H; C_6H_5), 4.18 [dd, ^2J(P,H) = 9.7 and ^3J(H,H] = 4.5 Hz, 2H; PCH_2), 3.08–2.87 (m, 4H; NCH), 1.96–0.80 (m, 40H; CH_2); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 198.0 [d, ^3J(P,C) = 10.6 Hz; C=S], 140.7 (*ipso*-C_6H_5), 131.9 (*p*-C_6H_5), 128.2, 126.8 (*o*-,*m*-C_6H_5), 55.8 [d, ^2J(P,C) = 4.5 Hz; C_1]. 46.3 [d, ^1J(P,C) = 115.2 Hz; PCH_2], 33.8, 33.5 (C_2), 27.3, 26.8, 26.7, 26.6, 25.7, 25.3 (C_3 and C_4); IR ($CDCl_3$): $\tilde{\nu}$ = 1265 cm^{-1} (P=O); $C_{32}H_{52}N_3OPS$: calcd C 68.90, H 9.40, N 7.53; found C 68.69, H 9.48, N 7.43.

(Thioxophosphoranyl)thioamide (22): A pentane solution (30 mL) of azirine **7** (0.48 g, 0.79 mmol) and excess elemental sulfur was irradiated at 254 nm for 14 h. After removal of unreacted sulfur by filtration and evaporation of the solvent, the residue was purified by flash chromatography on silica gel (hexane/ether: 98/2) to yield **22** as an orange powder (0.22 g, 48%). M.p. 254–256 °C (decomp.); ^{31}P NMR (81 MHz, $CDCl_3$): δ = 69.2; ^1H NMR (200 MHz, $CDCl_3$): δ = 9.17 (m, 1H; NH), 7.91–7.23 (m, 5H; C_6H_5), 4.23 [dd, ^2J(P,H) = 8.1 and ^3J(H,H) = 4.7 Hz, 2H; PCH_2], 3.30–2.96 (m, 4H; NCH), 1.97–0.85 (m, 40H; CH_2); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 196.9 [d, ^3J(P,C) = 11.6 Hz; C=S], 140.4 (*ipso*-C_6H_5), 131.2 (*p*-C_6H_5), 128.4, 126.7 (*o*-,*m*-C_6H_5), 56.8 [d, ^2J(P,C) = 4.2 Hz; C_1], 48.9 [d, ^1J(P,C) = 91.4 Hz; PCH_2], 34.0, 33.4 (C_2), 27.0, 26.8, 25.7, 25.4 (C_3 and C_4); $C_{32}H_{52}N_3PS_2$: calcd C 66.97, H 9.13, N 7.32; found C 67.15, H 9.18, N 7.28.

Solution and refinement of structures 7, 10, 14 and 19: Crystal data for all structures are presented in Table 1. The data for **7** and **10** were measured on an Enraf–Nonius CAD4 diffractometer with $Mo_{K\alpha}$ (λ = 0.71073 Å) radiation and ω–2θ scans. A Huber Stoe–Siemens AED diffractometer with a CCD detector was used to collect data for **14**, and a STOE-IPDS diffractometer for **19** with $Mo_{K\alpha}$ (λ = 0.71073 Å) radiation and φ-scans. A semiempirical absorption correction was employed for **7** and **10**. All structures were solved by direct methods using SHELXS-86[21] (structures **7** and **10**) and SHELXS-90[21] (structures **14** and **19**) and refined with all data on F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (g1 \times P)^2 + (g2 \times P)$ with $P = (F_o^2 + 2F_c^2)/3$ in SHELXL-93[22a] (structures **7** and **10**) and SHELXL-96[22b] (structures **14** and **19**). All non-hydrogen atoms were treated anisotropically except those of the phenyl rings in **7** and **10**, which were refined isotropically. For the atoms C40, F1, F2, and F3 in structure **19** a disorder in two positions was found and refined with an occupancy of 0.55/0.45, for the atoms C41 and C42 in structure **19** a disorder in two positions was found and refined with an occupancy of 0.6/0.4. All hydrogen atoms were located by difference Fourier maps and were refined with a riding model, except for H atoms bonded to the B atom in **10**, which were refined with constraint bond lengths, and H1 in **19**, which was refined free. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100358. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code +(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

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