From 2-Phosphino-2*H*-Phosphirene to 1-Phosphino-1*H*-Phosphirene, 1λ^5,2λ^3-Diphosphete, and 1,2-Dihydro-1λ^3,2λ^3-Diphosphete: an Experimental and Theoretical Study

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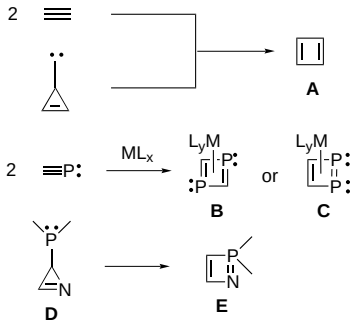
Abstract: The [bis(diisopropylamino)-phosphino](trimethylsilyl)carbene **4** reacts cleanly with *tert*-butylphosphaalkyne **2** to give 2-phosphino-2*H*-phosphirene **5**, which was spectroscopically characterized. Heterocycle **5** is thermally unstable and quantitatively rearranges after 3 h at room temperature into the 1λ^5,2λ^3-diphosphete **3**. Irradiation of **5** at room temperature ($\lambda = 254$ nm) with a Rayonnet photochemical reactor produces 1-phosphino-1*H*-phosphirene **6** (10%), 1,2-dihydrodiphosphete **7** (3%), and diphosphete **3** (87%). Irradiation of **3** with a high pressure mercury lamp at $\lambda = 254$ nm affords the dihydrodiphosphete **7**, which was isolated in 69% yield. Calculations carried out on heterocycles **3** and **5**–**7** emphasize the crucial effect the amino substituents have on the stability of λ^5-phosphacyclobutadiene derivatives, and show that the intrinsic difference in the thermodynamic stability between 1*H* and 2*H*-phosphirenes is rather small (68 kJ mol^{-1}).

Keywords: carbenes · diazo compounds · phosphaalkynes · phosphorus heterocycles · rearrangements

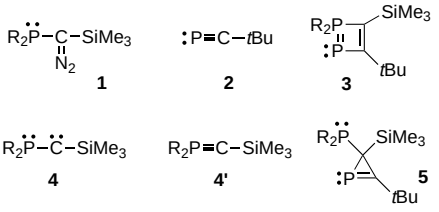
Introduction

[2+2] Dimerization of alkynes and ring-expansion reactions involving transient cyclopropenyl carbenes are well-known methods for the synthesis of cyclobutadienes **A**, the archetype of four-π-electron four-membered ring systems.[1] Similarly, in the phosphorus series, transition metal-coordinated 1λ^3,3λ^3- and 1λ^3,2λ^3-diphosphetes **B** and **C**[2] have been prepared by inner-sphere dimerization of λ^3-phosphaalkynes, while it has been shown that 2-phosphino-2*H*-azirines **D** rearrange into 1,2λ^5-azaphosphetes **E**[3] (Scheme 1).



Scheme 1. Synthesis of unsaturated four-membered ring systems.

We have already reported that the photolysis of [bis(diisopropylamino)phosphino](trimethylsilyl)diazomethane (**1**) in the presence of *tert*-butylphosphaalkyne **2** afforded the 1λ^5,2λ^3-diphosphete **3** as the major product (90% yield).[4] Since under photolysis conditions, derivative **1** is a precursor of the λ^3-phosphinocarbene **4**, which can also be regarded as the λ^5-phosphaalkyne **4′**,[5] two mechanisms can account for the formation of the non-antiaromatic four-π-electron four-membered heterocycle **3**:[6] the head-to-tail codimerization (governed by steric factors) of the λ^5-phosphaalkyne **4′** with the λ^3-phosphaalkyne **2**, or the [1+2] cycloaddition of the λ^3-phosphinocarbene **4** with **2**, followed by a ring-expansion reaction of the initially formed 2-phosphino-2*H*-phosphirene



R = *i*Pr$_2$N

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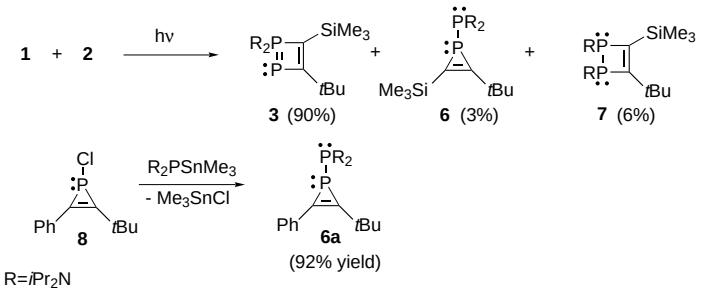
5. Here we report a detailed experimental study of the reaction leading to **3**, as well as ab initio calculations on different cyclic isomers of **3**.

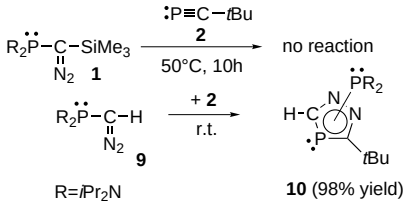
Results and Discussion

A careful examination of the ^{31}P NMR spectrum of the crude reaction mixture obtained by photolysis of the diazo derivative **1** with the phosphaalkyne **2** showed the presence of two minor products **6** (3%) and **7** (6%), along with diphosphete **3** (90%). The 1-phosphino-1*H*-phosphirene structure of **6** was established by comparison of its ^{31}P NMR spectrum [$\delta = -171.5$ (PC_2), 85.4 (PN_2) (J(P,P) = 291.2 Hz)] with that of the analogous compound **6a** [$\delta = -164.6$ (PC_2), 83.3 (PN_2) (J(P,P) = 290.1 Hz)], prepared by addition of the bis(diisopropylamino)trimethylstannylphosphine to the chlorophosphirene **8** (Scheme 2). The 1,2-dihydro-1λ^3,2λ^3-diphosphete structure of **7** was established by comparison of its spectroscopic data with those of an authentic sample prepared by another route described below.



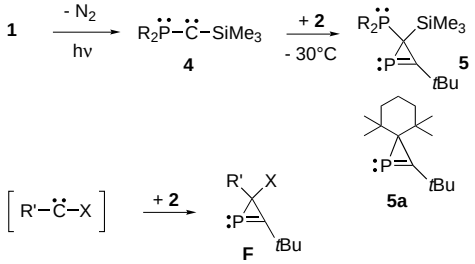
Scheme 2. Reaction scheme for the preparation of **3**, **6**, **6a**, and **7**.

In order to prove whether λ^3-phosphinocarbene **4** or λ^5-phosphaalkyne **4′** was the precursor of products **3**, **6**, and/or **7**, we first checked that the diazo derivative **1** did not react with **2** in the absence of UV light, even on heating a toluene solution at 50 °C for 10 h. Note, that in marked contrast, the corresponding nonsilylated diazophosphine **9** reacted with **2** at room temperature to afford the diazaphosphole **10** in quantitative yield. All attempts to remove dinitrogen from **10**, by photolysis or thermolysis, failed (Scheme 3).



Scheme 3. Reaction of diazo derivatives **1** and **9** in the absence of UV light.

We then prepared the stable phosphinosilylcarbene **4**/**4′** by photolysis of **1**. The reaction of **4**/**4′** with a slight excess of **2** was monitored by multinuclear NMR spectroscopy at −30 °C. After a few minutes the signals corresponding to both starting materials disappeared, and new signals corresponding to only one new compound, the 2-phosphino-2*H*-phosphirene **5**, were observed. The absence of a direct P–P bond was indicated by the small P–P coupling constant [J(P,P) = 26.6 Hz], while the presence of a phosphaalkene moiety was apparent from a low field doublet in the ^{13}C NMR spectrum [$\delta = 195.6$ (J(P,C) = 38.6 Hz)]. The spectroscopic data for **5**, as a whole, compared well with those reported for the only other known stable 2*H*-phosphirene **5a** [^{13}C NMR: $\delta = 215.4$ (J(P,C) = 50.9 Hz)].[7] Therefore, the λ^3-phosphinocarbene **4** had reacted with the phosphaalkyne **2** by a [1+2]-cycloaddition process and not by a [2+2]-cycloaddition mechanism, as expected for the λ^5-phosphaalkyne structure **4′**. Indeed, the formation of **5** is strictly analogous to that of 2*H*-phosphirene **F**, obtained by reacting transient halogenocarbenes with **2**[8] (Scheme 4).

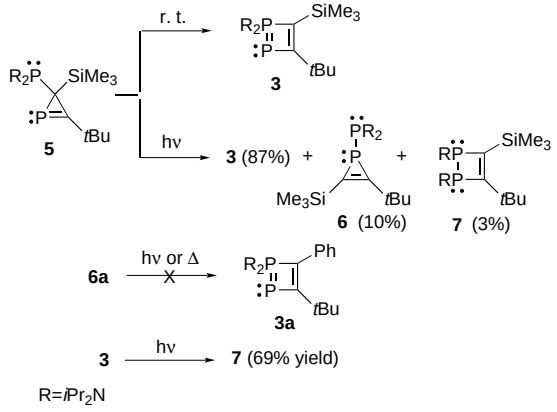


Scheme 4. Reaction scheme for the formation of **5**.

The 2-phosphino-2*H*-phosphirene **5** appeared to be rather unstable and quantitatively rearranged after 3 h at room temperature into the 1λ^5,2λ^3-diphosphete **3**; no trace of the 1*H*-phosphirene **6** and dihydrodiphosphete **7** was detected. Interestingly, irradiation ($\lambda = 254$ nm) at room temperature of a toluene solution of the 2*H*-phosphirene **5** afforded diphosphete **3** (87%), in addition to small amounts of the 1*H*-phosphirene **6** (10%) and 1,2-dihydrodiphosphete **7** (3%) (according to ^{31}P NMR spectroscopy). Therefore, in contrast to most of 2*H*-phosphirenes, which isomerize thermally into

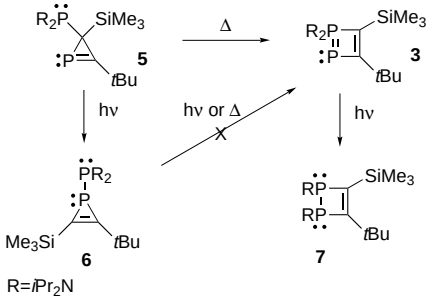
Abstract in French: *Le [bis(diisopropylamino)phosphino]-(triméthylsilyl)carbène (**4**) réagit avec le tert-butylphosphaacétylène (**2**) en donnant le 2-phosphino-2H-phosphirène **5** qui a été caractérisé par les méthodes spectroscopiques usuelles. L'hétérocycle **5** est instable thermiquement et se réarrange quantitativement après 3 h à température ambiante en 1λ^5,2λ^3-diphosphète **3**. L'irradiation de **5** à température ambiante avec un réacteur photochimique Rayonnet ($\lambda = 254$ nm) conduit aux 1-phosphino-1H-phosphirène **6** (10%), 1,2-dihydrodiphosphète **7** (3%) et diphosphète **3** (87%). L'irradiation de **3** avec une lampe à mercure à haute pression à $\lambda = 254$ nm donne le dihydrodiphosphète **7** qui a été isolé avec un rendement de 69%. Des calculs menés sur les hétérocycles **3** et **5**–**7** mettent en évidence le rôle déterminant joué par les substituants amino sur la stabilité des dérivés λ^5-phosphacyclobutadiéniques et montrent que la différence intrinsèque de stabilité thermodynamique entre les 1H- et 2H-phosphirènes est relativement faible (68 kJ mol^{-1}).*

1*H*-phosphirenes,[8, 9] **5** only rearranges into **6** under UV irradiation. In order to confirm that the 1*H*-phosphirene **6** was not an intermediate in the rearrangement of **5** to diphosphete **3**, 1*H*-phosphirene **6a** was heated and photolyzed under various conditions; however, no trace of the ring-expansion product, namely the $1\lambda^5,2\lambda^3$-diphosphete **3a**, was detected. Lastly, it was of interest to explain the formation of 1,2-dihydrodiphosphete **7** in the photolysis of **5**. We found that irradiation of the $1\lambda^5,2\lambda^3$-diphosphete **3** with a high-pressure mercury lamp at $\lambda = 254$ nm afforded the dihydrodiphosphete **7**, which was isolated in 69% yield (Scheme 5).



Scheme 5. Reaction scheme for the formation of **7**.

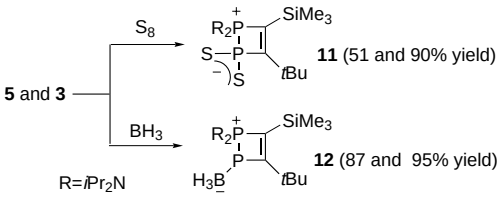
To summarize, it is clear that 2-phosphino-2*H*-phosphirene **5** is a rather unstable species, which thermally rearranges into $1\lambda^5,2\lambda^3$-diphosphete **3**, and photochemically into the 1-phosphino-1*H*-phosphirene **6**. Compound **6** does not undergo a thermal or photochemical ring-expansion reaction to give **3**. Finally, irradiation of diphosphete **3** gives rise to the isomeric 1,2-dihydrodiphosphete **7** (Scheme 6).



Scheme 6. Rearrangement of **5**.

Since, as mentioned above, there is only one known example of a stable 2*H*-phosphirene,[7] we attempted to isolate **5** as a thiophosphoranyl derivative or a BH_3 adduct; instead, new diphosphete derivatives **11** and **12**, were isolated in 51 and 87% yield, respectively. The same adducts **11** (90% yield) and **12** (95% yield) were also prepared directly from the diphosphete **3** (Scheme 7).

In order to gain more insight into the rearrangement processes of Scheme 6, theoretical calculations were carried out on model derivatives. The optimized geometry at the SCF/



Scheme 7. Reaction scheme for the formation of **11** and **12**.

DZP level of derivatives **3b**, **5b**, **6b**, and **7b** (where $R = H_2N$ instead of iPr_2N used in the experimental work) is shown in Figure 1,[10] and the relative energies (kJ mol^{-1}) at the B3LYP/DZP level of these isomers, as well as those of the parent

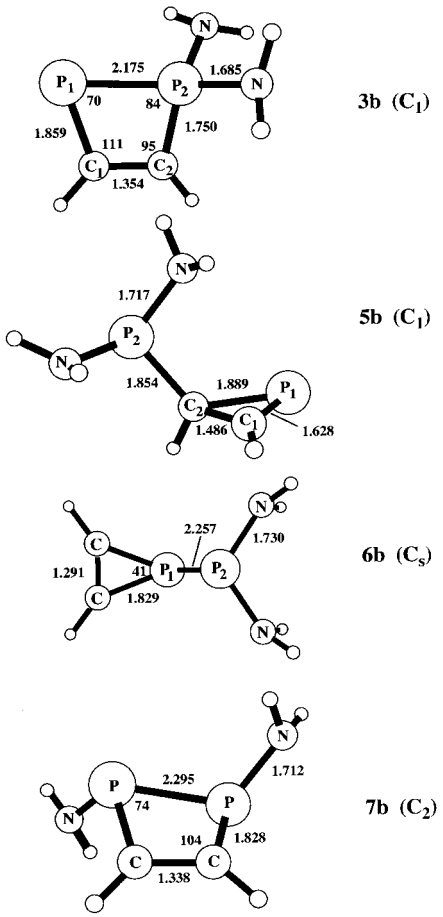


Figure 1. Optimized geometry at the SCF/DZP level for derivatives **3b**, **5b**, **6b**, and **7b** with selected bond lengths [Å] and angles [°].

compounds **3c**, **5c**, **6c**, and **7c** (R = H), are given in Scheme 8. Not surprisingly, in both series, dihydrodiphosphetes **7b** and **7c** are by far the most stable isomers. However the order of stability of the three other isomers is dependent on the nature of the substituents. The NH_2 substituents dramatically stabilized the diphosphete **3b**, which is in agreement with the postulated structure of four-π-electron four-membered ring systems containing a λ^5-phosphorus and where a positive charge is located on the phosphorus.[6] Because derivatives **7** are substantially more stable than **3**, it might appear surprising that **3** can be prepared and that it is kinetically stable. A

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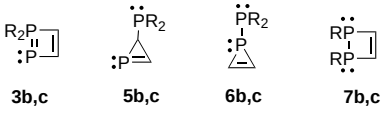

	3	5	6	7
b: R = NH_2	85	113	127	0
c: R = H	122	105	95	0

	5	6
d: X = Cl	68	0
e: X = H	0	36

Scheme 8. The relative energies (kJ mol^{-1}) at the B3LYP/DZP level of derivatives **3b**, **5b**, **6b**, and **7b** (where R = H_2N instead of *i*Pr_2N used in the experimental work) as well as those of the parent compounds **3c**, **5c**, **6c**, and **7c** (R = H).

search for the transition state linking **3c** and **7c** showed that it lies 85 kJ mol^{-1} above **3c** at the B3LYP/DZP level of theory. While this value should not, of course, be taken as accurate to within 1 kJ mol^{-1}, we are confident that it is sufficiently large to show that kinetic stability for **3** is to be expected. The geometries of **3c**, **7c**, and the intermediate transition state (TS) are shown in Figure 2. Interestingly, although the 2*H*-phosphirene **5c** appears to be higher in energy by 10 kJ mol^{-1} than the isomeric 1*H*-phosphirene **6c**, the P-amino analogues

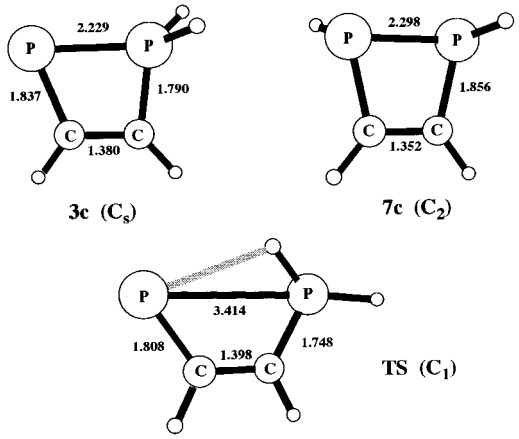

Figure 2. Optimized geometry and selected bond lengths [Å] at the B3LYP/DZP level of theory for **3c**, **7c**, and the transition state (TS) **7c**.

present an inverse order of stability: **5b** is lower in energy by 14 kJ mol^{-1} than **6b**. As the instability of 2*H*-phosphirenes towards their isomerization into 1*H*-phosphirene was believed to be the result of to the disappearance of the P=C double bond in favor of the more thermodynamically stable C=C double bond,[9] the later result was rather surprising. We therefore investigated the relative energy of simple 1*H*- and 2*H*-phosphirenes **5d**, **5e, 6d**, and **6e**. The C–Cl and P–Cl bond energies are almost identical (326 kJ mol^{-1} and 331 kJ mol^{-1}, respectively), so that the relative stability of the two isomers **5d** and **6d** indicates the intrinsic stabilities of the respective ring systems. Because the 1*H*-phosphirene **6d** is only some 68 kJ mol^{-1} more stable than the 2*H*-isomer **5d**, it is evident that if the C–X bond energy is stronger than the corresponding P–X bond by at least this amount, 2*H*-phosphirenes will be stable towards isomerization. Indeed, for the parent compound, **5e** is more stable than **6e** by 36 kJ mol^{-1} [D(C–H) = 414 kJ mol^{-1}; D(P–H) = 326 kJ mol^{-1}). Therefore, with regard to the difference in the order of stability of **5b** and **6b** versus **5c** and **6c**, it can be concluded that amino substituents on the P atom strongly increase the stability of the P–C bond compared with a P–P bond.

Conclusion

The formation of the 2-phosphino-2*H*-phosphirene **5** demonstrates that the phosphinosilylcarbene **4** reacts as a normal transient singlet carbene, although it is known that it features a P–C multiple bond. The rearrangement of **5** into diphosphete **3** illustrates the broad range of application of the ring-expansion reaction method for the preparation of four-π-electron four-membered heterocyles. The calculations emphasize the crucial role played by the amino substituents on the stability of λ^5-phosphacyclobutadiene derivatives. Moreover, they show that the intrinsic difference in the thermodynamic stability between 1*H*- and 2*H*-phosphirenes is rather small (68 kJ mol^{-1}) and can be overcome by the appropriate choice of substituents.

Experimental Section

All experiments were performed under an atmosphere of dry argon. Melting points are uncorrected. ^{1}H, ^{13}C, ^{11}B, and ^{31}P NMR spectra were recorded on Brucker AC80, AC200, WM250, or AMX400 spectrometers. ^{1}H and ^{13}C chemical shifts are reported relative to Me_4Si as an external standard. ^{11}B and ^{31}P NMR downfield chemical shifts are expressed relative to external BF_3, Et_2O, and 85 % H_3PO_4, respectively. Infrared spectra were recorded on a Perkin–Elmer FT-IR Spectrometer 1725X. Mass spectra were obtained on a Ribermag R10 10E instrument. Conventional glassware was used.

Photolysis of diazophosphine 1 with phosphaalkyne 2: A solution of [bis(diisopropylamino)phosphino](trimethylsilyl)diazomethane (**1**,[5a] 1.09 g, 3.15 mmol) in ether (30 mL) and *tert*-butylphosphaalkyne (**2**,[11] 0.35 g, 3.47 mmol) was irradiated at λ = 254 nm for 5 h at room temperature. According to the ^{31}P NMR spectrum of the resulting mixture, two other products **6** (3 %) and **7** (6 %) were present in addition to the 1λ^5,2λ^3-diphosphete **3** (90 %). The major product **3** was isolated and characterized as already reported.[4, 12] The 1*H*-phosphirene **6** and 1,2-dihydrodiphosphete **7** were identified by ^{31}P NMR.

1*H*-Phosphirene 6: ^{31}P NMR ($CDCl_3$, 81.015 MHz): δ = −171.5 (d, J(P,P) = 291.2 Hz, PC_2), 85.4 (d, J(P,P) = 291.2 Hz, PN_2).

Dihydrodiphosphete 7: ^{31}P NMR ($CDCl_3$, 81.015 MHz): δ = 3.0 (d, J(P,P) = 144.1 Hz, J(P,H) = 13.6 Hz), 11.2 (d, J(P,P) = 144.1 Hz).

1-Phosphino-1*H*-phosphirene (6a): A solution of [bis(diisopropylamino)](trimethylstannyl)phosphine[13] (0.94 g, 2.37 mmol) in ether (3 mL) was added, at −78 °C, to a solution of 1-chloro-1*H*-phosphirene (**8**,[14] 0.53 g, 2.37 mmol) in ether(2 mL). The solution was allowed to warm to room temperature then the solvent and Me_3SnCl were removed under vacuum at 40 °C. Derivative **6a** was obtained as a very viscous pale yellow oil. Yield: 0.92 g (92 %); ^{31}P NMR (C_6D_6, 162.000 MHz): δ = −164.6 (d, J(P,P) = 290.1 Hz, PC_2), 83.3 (d, J(P,P) = 290.1 Hz, PN_2); ^{1}H NMR (C_6D_6, 400 MHz): δ = 1.09 (d, J(H,H) = 6.6 Hz, 6H, CH_3CHN), 1.23 (d, J(H,H) = 6.6 Hz, 6H, CH_3CHN), 1.31 (d, J(H,H) = 6.8 Hz, 6H, CH_3CHN), 1.43 (s, 9H, CH_3C), 1.47 (d, J(H,H) = 6.8 Hz, 6H, CH_3CHN), 3.55 (sept d, J(H,H) = 6.8 Hz, J(P,H) = 8.8 Hz, 2H, CH_3CHN), 3.94 (sept d, J(H,H) = 6.6 Hz, J(P,H) = 7.7 Hz, 2H, CH_3CHN), 7.14 (t, J(H,H) = 7.2 Hz, 1H, $CH_{arom.}$), 7.27 (dd, J(H,H) = 7.2, 8.1 Hz, 2H, $CH_{arom.}$), 7.75 (d, J(H,H) = 8.1 Hz, 2H, $CH_{arom.}$); ^{13}C NMR (C_6D_6, 100.630 MHz): δ = 24.80 (d, J(P,C) = 5.7 Hz, CH_3CHN), 24.85 (d, J(P,C) = 5.7 Hz, CH_3CHN), 25.87 (d,

J(P,C) = 9.7 Hz, CH_3CHN), 25.95 (d, J(P,C) = 10.2 Hz, CH_3CHN), 30.20 (d, J(P,C) = 1.5 Hz, CH_3C), 34.53 (dd, J(P,C) = 1.0, 8.9 Hz, CH_3C), 49.34 (dd, J(P,C) = 1.0, 8.2 Hz, CH_3CHN), 51.93 (dd, J(P,C) = 6.5, 9.9 Hz, CH_3CHN), 116.17 (dd, J(P,C) = 10.1, 47.0 Hz, PhC), 128.35 (s, $C_{arom.}$), 128.78 (s, $CH_{arom.}$), 130.82 (d, J(P,C) = 1.5 Hz, $CH_{arom.}$), 131.24 (dd, J(P,C) = 2.4, 7.1 Hz, $CH_{arom.}$), 134.56 (dd, J(P,C) = 15.3, 50.7 Hz, C-*t*Bu); $C_{24}H_{42}N_2P_2$ (420.56): C 68.54, H 10.06, N 6.66; found: C 69.10, H 10.34, N 6.90.

(Phosphino)diazaphosphole (**10**): Neat *tert*-butylphosphaalkyne (**2**, 0,18 g, 2.00 mmol) was added at room temperature to a solution of bis(diisopropylamino)phosphinodiazomethane (**9**,[5a] 0.54 g, 2.00 mmol) in ether (30 mL). The solution was allowed to stand for 1 h at room temperature and then the solvent was removed under vacuum. Derivative **10** was obtained as an orange oil. Yield: 0.73 g (98 %); ^{31}P NMR ($CDCl_3$, 81.015 MHz): δ = 76.5 (d, J(P,H) = 42.0 Hz, PC), 93.7 (br s, PN); ^{1}H NMR ($CDCl_3$, 200.133 MHz): δ = 1.05 (d, J(H,H) = 6.7 Hz, 12 H, CH_3CHN), 1.24 (d, J(H,H) = 6.7 Hz, 12 H, CH_3CHN), 1.39 (s, 9 H, CH_3C), 3.36 (sept d, J(H,H) = 6.7 Hz, J(P,H) = 12.8 Hz, 4 H, CH_3C*H*N), 8.73 (dd, J(P,H) = 42.0 Hz, J(P,H) = 5.9 Hz, 1 H, NH); ^{13}C NMR ($CDCl_3$, 20.149 MHz): δ = 23.16 (d, J(P,C) = 8.8, CH_3CHN), 23.94 (d, J(P,C) = 6.9, CH_3CHN), 32.03 (d, J(P,C) = 6.6 Hz, CH_3C), 36.20 (d, J(P,C) = 17.3 Hz, CH_3C), 47.16 (d, J(P,C) = 13.7 Hz, CH_3CHN), 159.05 (dd, J(P,C) = 51.2, 21.7 Hz, PCH), 192.06 (d, J(P,C) = 63.7 Hz, PC-*t*Bu); $C_{18}H_{38}N_4P_2$ (372.47): C 58.04, H 10.28, N 15.04; found: C 57.85, H 10.14, N 15.27.

2-Phosphino-2*H*-phosphirene (**5**): A solution of [bis(diisopropylamino)]-(trimethylsilyl)diazomethane (**1**, 0.25 g, 0.73 mmol) in ether (30 mL) was irradiated at λ = 254 nm for 3 h at room temperature. The solvent was removed under vacuum, and the residue then dissolved in [D_8]toluene (0.5 mL). This solution was transferred to a NMR tube, and neat *tert*-butylphosphaalkyne (**2**, 0.115 mL, 0.81 mmol) was added dropwise at −30 °C. Derivative **5** was characterized in solution. ^{31}P NMR ([D_8]toluene, 162.003 MHz, 243 K): δ = 48.1 (d, J(P,P) = 26.6 Hz, σ^2-P), 94.4 (d, J(P,P) = 26.6 Hz, σ^3-P); ^{13}C NMR ([D_8]toluene, 50.323 MHz, 243 K): δ = 1.68 (d, J(P,C) = 5.9 Hz, CH_3Si), 27.53 (m, CH_3CHN), 29.01 (m, CH_3CHN), 31.00 (d, J(P,C) = 1.0 Hz, CH_3C), 38.96 (s, CH_3C), 45.90 (m, CH_3CHN), 195.56 (d, J(P,C) = 38.6 Hz, PC-*t*Bu), the PCSi carbon atom was not observed.

Thermal rearrangement of 5: A solution of **5** in [D_8]toluene, prepared as indicated above, was allowed to warm to room temperature. After 3 h, the diphosphete **3** was the only product formed, according to ^{31}P NMR spectroscopy. After work up, **3** was isolated in 70 % yield.

Photochemical rearrangement of 5: A solution of **5** in [D_8]toluene, prepared as indicated above, was irradiated at λ = 254 nm at room temperature for 3 h. According to ^{31}P NMR spectroscopy, diphosphete **3** (87 %), 1*H*-phosphirene **6** (3 %), and 1,2-dihydrodiphosphete **7** (10 %) were formed.

1,2-Dihydro-1λ^3,2λ^3-diphosphete (**7**): A solution of 1λ^5,2λ^3-diphosphete (**3**; 0.75 g, 1.80 mmol) in ether (50 mL) was irradiated with a mercury vapor lamp for 4 h at room temperature. The solvent was removed under vacuum and the 1,2-dihydro-1λ^3,2λ^3-diphosphete **7** was isolated by column chromatography. Yield: 0.52 g (69 %), colorless crystals; m.p. 121 °C; ^{31}P NMR ($CDCl_3$, 81.015 MHz): δ = 3.0 (d, J(P,P) = 144.1 Hz, J(P,H) = 13.6 Hz), 11.2 (d, J(P,P) = 144.1 Hz); ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.51 (s, 9 H, CH_3Si), 1.05 (d, J(H,H) = 6.7 Hz, 6 H, CH_3CHN), 1.23 (d, J(H,H) = 6.5 Hz, 6 H, CH_3CHN), 1.43 (d, J(H,H) = 6.8 Hz, 6 H, CH_3CHN), 1.46 (d, J(H,H) = 6.7 Hz, 6 H, CH_3CHN), 1.49 (s, 9 H, CH_3C), 2.90 – 3.15 (m, 4 H, CH_3C*H*N); ^{13}C NMR ($CDCl_3$, 50.323 MHz): δ = 2.25 (d, J(P,C) = 2.8 Hz, CH_3Si), 18.94 – 26.38 (m, CH_3CHN), 31.20 (s, CH_3C), 38.21 (t-like, J(P,C) = 13.0 and 13.0 Hz, CH_3C), 44.19 – 53.87 (m, CH_3CHN), 142.09 (dd, J(P,C) = 38.1, 34.3 Hz, PCSi), 171.75 (dd, J(P,C) = 36.6, 26.7 Hz, PC-*t*Bu); $C_{21}H_{46}N_2P_2Si$ (416.64): C 60.54, H 11.13, N 6.72; found: C 59.80, H 10.90, N 6.80.

1λ^5,2λ^5-Diphosphete (**11**): A suspension of elemental sulfur (0.16 g, 0.63 mmol) in ether was added at −78 °C to a solution of **5** (0.26 g, 0.63 mmol) in ether (1 mL). The solution was allowed to warm to room temperature, the solvent was removed under vacuum, and the residue treated with ether (3 × 5 mL). Derivative **11** was isolated as a pale yellow powder (0.15 g, 51 % yield). By means of the same experimental procedure but starting from **3**, derivative **11** was obtained in 90 % yield. M.p. 54 °C (decomp); ^{31}P NMR ($CDCl_3$, 101.256 MHz): δ = 87.3 (q d, J(P,H) = 10.2 Hz, J(P,P) = 23.9 Hz, N_2P), 127.3 (d, J(P,P) = 23.9 Hz, PS_2); ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.42 (s, 9 H, CH_3Si), 1.40 (d, J(H,H) = 6.8 Hz, 12 H, CH_3CHN), 1.47 (d, J(H,H) = 6.8 Hz, 12 H, CH_3CHN), 1.56 (s, 9 H, CH_3C), 4.11 (sept d, J(H,H) = 6.8 Hz, J(P,H) = 10.2 Hz, 4 H, CH_3C*H*N); ^{13}C NMR ($CDCl_3$, 62.896 MHz): δ = 3.85 (s, CH_3Si), 24.70 (d, J(P,C) = 4.3 Hz, CH_3CHN), 25.34 (d, J(P,C) = 3.8 Hz, CH_3CHN), 31.54 (d, J(P,C) = 4.1 Hz, CH_3C), 41.47 (dd, J(P,C) = 12.9, 48.1 Hz, CH_3C), 50.00 (d, J(P,C) = 3.5 Hz, CH_3CHN), 136.31 (dd, J(P,C) = 21.6, 24.5 Hz, PCSi), 200.31 (dd, J(P,C) = 37.6, 64.8 Hz, PC-*t*Bu); CIMS(CH_4): m/e = 481 [M^+]; $C_{21}H_{46}N_2P_2S_2Si$ (480.77): C 52.46, H 9.64, N 5.83; found: C 52.54, H 9.77, N 5.79.

Diphosphete · BH_3 adduct 12: A solution of $BH_3 \cdot SMe_2$ (0.08 mL, 1.70 mmol) in THF (2.0 M) was added dropwise, at −78 °C, to a solution of **5** (0.71 g, 1.70 mmol) in ether (1 mL). The solution was allowed to warm to room temperature, then it was filtered, the solvent removed under vacuum, and the residue was washed with pentane (3 × 5 mL). Derivative **12**, along with another unidentified product (< 5 % according to ^{31}P NMR spectroscopy), was isolated as a light brown powder from a CH_2Cl_2/pentane solution at −30 °C. Yield: 0.62 g, (87 %). By means of the same experimental procedure, but starting from **3**, derivative **12** along with the same unidentified product observed previously was obtained in 95 % yield. ^{31}P NMR ($CDCl_3$, 162.000 MHz): δ = 61.8 (d q, J(P,P) = 17.6 Hz, J(P,H) = 11.2 Hz, N_2P), 123.7 (br d, J(P,P) = 17.6 Hz, PBH_3); ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.41 (s, 9 H, CH_3Si), 1.39 (s, 9 H, CH_3C), 1.44 (d, J(H,H) = 6.4 Hz, 12 H, CH_3CHN), 1.45 (d, J(H,H) = 6.4 Hz, 12 H, CH_3CHN), 4.09 (sept d, J(H,H) = 6.4 Hz, J(P,H) = 11.2 Hz, 4 H, CH_3C*H*N), BH_3 was not observed; ^{13}C NMR ($CDCl_3$, 50.323 MHz): δ = 3.69 (d, J(P,C) = 2.4 Hz, CH_3Si), 24.68 (d, J(P,C) = 3.8 Hz, CH_3CHN), 25.20 (d, J(P,C) = 3.8 Hz, CH_3CHN), 30.94 (dd, J(P,C) = 3.3, 2.6 Hz, CH_3C), 42.24 (dd, J(P,C) = 13.0, 47.2 Hz, CH_3C), 49.78 (d, J(P,C) = 5.5 Hz, CH_3CHN), 143.07 (dd, J(P,C) = 3.2, 37.4 Hz, PCSi), 199.42 (dd, J(P,C) = 8.6, 13.7 Hz, PC-*t*Bu); ^{11}B NMR ($CDCl_3$, 128.379 MHz): δ = −30.6 (br s).

Computational details: We have used standard, well-calibrated computational methods incorporated into the Gaussian 92 program.[15] In view of the size of the molecules concerned, typical approximations were made so that the computations were actually performed on model compounds in which the $SiMe_3$, *t*Bu, and *i*Pr substituents were all replaced by hydrogen atoms. While these substituents are, no doubt, very important in a practical, kinetic sense, we do not think that their electronic role is crucial for the bonding or thermodynamic stabilities of the various isomers. Geometries were optimized at the SCF level, initially with the compact 3-21G* basis set[16] and subsequently with a more complete DZP basis.[17] Vibrational frequencies were calculated for the various stationary points located, to check that these are indeed true minima. Better estimates of relative energies were then obtained by the use of a hybrid form of DFT theory, usually known as B3LYP,[18] with the DZP basis in order to optimize the geometries of those conformers of **3**, **5**, **6**, and **7** which are most stable at the SCF level. This method is generally thought to incorporate dynamic correlation effects very effectively, and any nondynamic effects are at least partially included, so that the relative energies will certainly be more reliable than those obtained at the SCF level of theory.

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