Organophosphorus Compounds, Part 135[+]

# The 1-Silyl-1*H*-phosphirene/1,2-Dihydrophosphasilete Rearrangement and Its Preparative Significance

**Steffen Haber, Marion Schmitz, Uwe Bergsträßer, Jürgen Hoffmann, and Manfred Regitz*[a]**

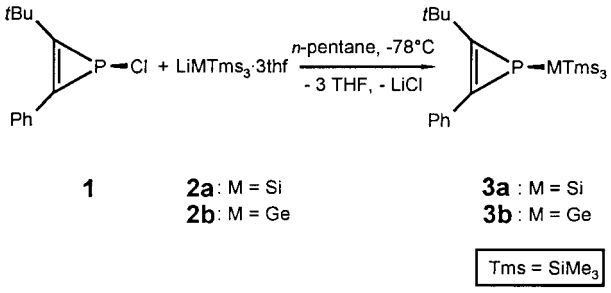
*Dedicated to Professor Edgar Niecke on the occasion of his 60th birthday*

**Abstract:** Photolysis of the silyl-substituted 1*H*-phosphirene **3a** proceeds selectively with cleavage of a silicon–silicon bond and ring expansion to furnish the 1,2-dihydro-1,2-phosphasilete **4a**. The corresponding heterocyclic germanium product, **4b**, is prepared analogously from **3b**. The preparative significance of **4a** is reflected not only in its numerous addition reactions to multiple-bond systems, such as alkynes **8** and **12** and ketene **10**, but also in its substitution reactions with the chloro compounds **15**, **18**, and **21**. The latter reactions proceed through the formation of chlorotrimethylsilane and the novel 1,2-dihydro-1,2-phosphasiletes (**16**, **19**, and **22**) which, depending on the substitution pattern at the phosphorus atom, undergo various isomerization reactions (**16** → **17**, **19** → **20**). The hydrolysis of **4a** to **23** by mere traces of water in carefully purified tetrahydrofuran demonstrates the extreme sensitivity of this compound towards moisture.

**Keywords:** electrophilic additions · phosphorus heterocycles · photolysis · ring enlargement · silicon

## Introduction

We accomplished the synthesis of 1-chloro-1*H*-phosphirenes, such as **1**, by the addition of chlorocarbenes, generated in situ, to $\lambda^3\sigma^1$-phosphaalkynes in 1989.[1, 2] In these reactions the corresponding 2*H*-phosphirenes must be considered as intermediates that undergo a rapid 1,3-chlorine shift to afford the thermodynamically more favorable 1*H*-phosphirenes.[3] In the meantime, the enormous synthetic potential of the 1-chloro-1*H*-phosphirenes has been investigated intensively and has been the subject of several review articles.[4–6] In particular, the substitution of the chlorine atom on the phosphorus by nucleophiles leads to a whole series of novelly substituted 1*H*-phosphirenes.[7] In this way, for example, the syntheses of cyano-, azido-, imido-, and phosphaalkene-substituted 1*H*-phosphirenes became possible.[1, 2, 7, 8] Reactions with organometallic compounds, such as **2a** and **2b**, proceed under formation of lithium chloride to afford the 1-silyl- and 1-germyl-1*H*-phosphirenes **3a** and **3b**, respectively (Scheme 1).[8, 9]




Scheme 1. Synthesis of the 1-silyl- and 1-germyl-1*H*-phosphirenes **3a** and **3b**.

While the 1-chloro-1*H*-phosphirenes preferentially take part in substitution reactions and only exhibit ring opening[10, 11] or ring expansion[5] behavior in isolated cases, we now report the first ring expansion reactions of the 1-silyl- and 1-germyl-1*H*-phosphirenes **3a** and **3b**.[9]

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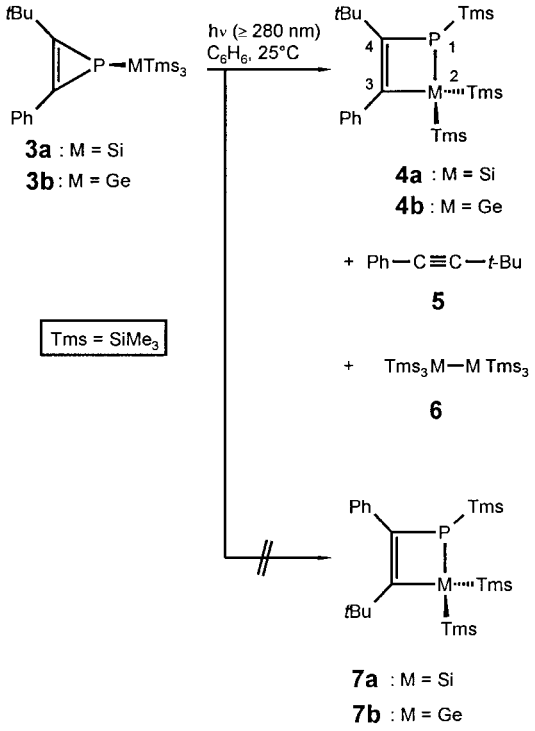
## Results and Discussion

**The rearrangement 3 → 4**: When the 1*H*-phosphirenes **3a,b** are irradiated in benzene they undergo isomerization to furnish the 1,2-dihydro-1,2-phosphasilete **4a** and the 1,2-dihydro-1,2-phosphagermete **4b**, respectively, within 40 hours (Scheme 2). Ring opening occurs specifically at the phenyl-substituted carbon–phosphorus bonds of **3**. The isomers **7**,




Scheme 2. Irradiation and ring opening of the 1*H*-phosphirenes **3a**,**b** to give the 1,2-dihydro-1,2-phosphasiletes **4a**,**b.**

which would arise through the opening of the *tert*-butyl-substituted carbon–phosphorus bonds in **3**, could not be detected. The alkyne **5** and the disilane **6** are formed as further photolysis products. This photolysis is extremely dependent on the solvent: if the reaction is performed in *n*-pentane the molecule undergoes fragmentation so that only the alkyne **5** can be detected. Benzene presumably functions as a UV filter for light with wavelengths shorter than 280 nm[12] and thus prevents further decomposition of **3**.

The NMR spectroscopic data of **4a**,**b** differ distinctly from those of the isomeric starting materials **3a**,**b** and are discussed below for the example of product **4a**. The shift of a silyl group from silicon to phosphorus is apparent in the $^1$H NMR spectrum from the splitting of a signal in the characteristic region for trimethylsilyl protons with a $^3J$(H,P) coupling constant of 4.0 Hz; this is a typical value for silylphosphanes.[13] The two silyl groups on the heterocyclic silicon do not show separate signals at room temperature, while in the low-temperature $^1$H NMR spectrum there are two singlets for these now magnetically nonequivalent groups. When the sample is warmed up again, these two signals become broader and migrate towards a central position; coalescence occurs at 314 K. At temperatures above 363 K only a sharp singlet is observed for the two groups on account of a rapid inversion at the phosphorus atom. The inversion barrier for the phosphorus atom in **4a** can thus be determined as 67.7 kJ mol$^{-1}$ (16.2 kcal mol$^{-1}$).[14] This value clearly shows the influence of two effects in **4a**: the substitution of carbon by silicon at the phosphorus atom generally lowers the inversion barrier,[15–17] while the incorporation of the inversion center in a small ring tends to increase the barrier.[18] In the case of the heterocyclic germanium compound **4b**, two separate signals are observed for the protons of the silyl groups on germanium even at room temperature. This is indicative of a higher barrier to inversion at phosphorus. The ring expansion in **4a** is apparent from the marked shift of the $^{31}$P NMR signal to low field: from $\delta = -205$ in **3a**[7] to $\delta = -131$ in **4a**. The $^{13}$C NMR data provide further evidence for the constitution of the products: the signals of the sp$^2$ skeletal carbon atoms C3 and C4 are shifted by more than 30 ppm to lower field in comparison with those of **3a**.[7] Additionally, the $J$(C,P) coupling constant for the signal of C4 is only 22.1 Hz. Small coupling constants of this type are a general feature of diphospha- and phosphacyclobutenes with $\lambda^3\sigma^3$ phosphorus atoms.[19, 20] The X-ray crystallographic analysis of **4a** has already been described in a short communication.[9]

The ring expansion **3** → **4** can be considered to be a diotropic rearrangement which may be followed by a radical fragmentation (**3a** → alkyne **5** + disilane **6**).

The dihydrophosphasilete **4a** represents the starting point for numerous transformations, for example, insertions into a P/Si bond or substitutions at the silylated phosphorus atom with subsequent reactions, as described below.

**Addition to electron-poor multiple bond systems**: The reactions of the dihydrophosphasilete **4a** with the electron-poor alkynes **8a–d** are exothermic (Scheme 3). The 1-alkenyl-1,2-dihydro-1,2-phosphasiletes **9a–d** are isolated in very good yields (≈90%) after workup by distillation. Products **9a–c** are colorless crystalline solids and **9d** is a yellow oil. Compounds **9** proved to be very stable: isomerization or subsequent reactions did not occur, even after heating at 200 °C for several days.

**Abstract in German:** *Die Photolyse des silylsubstituierten 1H-Phosphirens **3a** verläuft selektiv unter Spaltung einer Silicium-Silicium-Bindung und Ringerweiterung zum 1,2-Dihydro-1,2-phosphasilet **4a**. Der entsprechende Germaniumheterocyclus **4b** wird analog aus **3b** erhalten. Die präparative Bedeutung von **4a** spiegelt sich nicht nur in den zahlreichen Additionsreaktionen an Mehrfachbindungssysteme wie etwa Alkine **8** und **12** sowie Ketene **10** wider sondern auch in Substitutionsreaktionen mit den Chlorverbindungen **15**, **18** und **21**. Die letztgenannte Reaktion verläuft unter Bildung von Chlortrimethylsilan und der neuartigen 1,2-Dihydro-1,2-phosphasilete (**16**, **19**, **22**), die in Abhängigkeit vom Substitutionsmuster am Phosphoratom verschiedene Isomerisierungsreaktionen eingehen (**16** → **17**, **19** → **20**). Die Hydrolyse von **4a** zu **23** durch Spuren von Wasser selbst in sorgfältig gereinigtem Tetrahydrofuran demonstriert die extreme Empfindlichkeit dieser Verbindung gegenüber Feuchtigkeit.*



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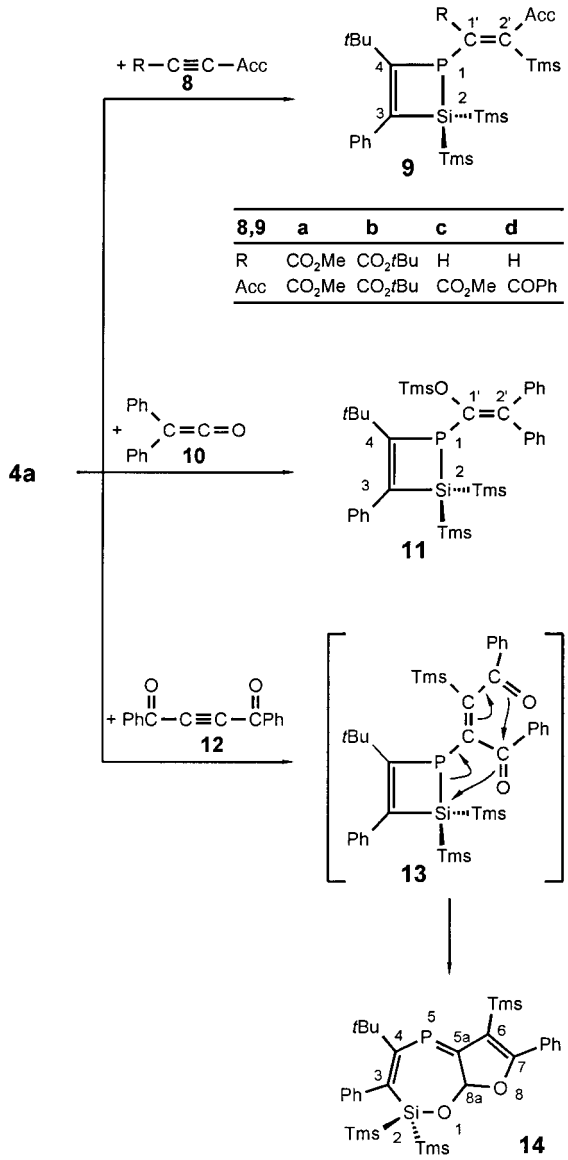



Scheme 3. Addition reactions of the dihydrophosphasilete **4a** to electron-poor multiple bond systems.

The composition of the 1:1 addition products **9** was confirmed by elemental analysis. The absence of $^3J$(H,P) couplings in the $^1$H NMR spectra of **9** demonstrates the cleavage of the exocyclic phosphorus–silicon bond (cf. **4a**); only singlet signals are observed in the expected region. The integration ratios also reveal the construction from one molecule of alkyne and one molecule of dihydrophosphete.

The $^{13}$C NMR spectra clearly show the characteristic signals of the skeletal carbon atoms, C3 and C4, in the olefinic region at $\delta = 151.3 - 169.9$, with the corresponding coupling constants [$^2J$(C,P) = 19.0–20.1 Hz, $^1J$(C,P) = 14.7–23.2 Hz] (cf. **4a**). Furthermore, the carbonyl carbon atoms of the ester groups give rise to signals at $\delta \simeq 165$. By comparison of the $^3J$(C,P) coupling constants of C2′ in **9a–d** [$^3J$(C,P) = 14.6–16.7 Hz] with the corresponding values for phosphane-substituted maleates and fumarates,[21] the formation of the *Z* isomers may be deduced. The carbon atoms of the exocyclic alkene unit, C1′ and C2′, give rise to signals between $\delta = 142.9$ and 164.6. The occurrence of $^1J$(C,P) couplings of ≈46 Hz for the hydrogen-substituted carbons C1′ in **9c** and **9d** confirm the direction of addition. The formation of a 1-allenyl-substituted dihydrophosphasilete (the product of a 1,4-addition) is excluded by the signal for the carbonyl carbon atom in the benzoyl group of **9d** at $\delta = 199.1$ [$^3J$(C,P) = 16.2 Hz].[22] The $^{31}$P NMR signals are shifted to lower field on account of the alkenyl substitution by ≈70 ppm for **9a**,**b** and by ≈50 ppm for **9c**,**d** as compared to the signals of the starting material **4a**.

The reaction of diphenylketene (**10**) with **4a** also proceeds through 1,2-addition. After the dropwise addition of the ketene to a solution of the dihydrophosphasilete at −78 °C, the pure 1-alkenyl-1,2-dihydro-1,2-phosphasilete **11** was isolated upon workup by distillation. Addition to the carbonyl function of **10** is demonstrated by the absence of CO bands in the IR spectrum of **11**.

The remaining spectroscopic data of **11** are very similar to those of the 1-alkenyl-1,2-dihydro-1,2-phosphasiletes **9** and therefore do not need to be discussed in detail. Even so, a characteristic effect for enol ethers was observed in the $^{13}$C NMR spectrum of **11**: in comparison with the signals of the other doubly bonded carbon atoms (C3, C4, and C1′) the signal for C2′ ($\delta = 134.1$) is shifted to higher field; this can be attributed to the shielding effect of the oxygen atom in the $\beta$-position to C4.[23] Also, the heterocyclic product **11** does not undergo any further isomerization under thermal conditions.

When the 1,2-dihydro-1,2-phosphasilete **4a** is cooled to −78 °C with dibenzoylacetylene (**12**) and the mixture subsequently allowed to warm up, a reaction occurs and the bicyclic compound **14** is obtained after crystallization from *n*-pentane at −20 °C; the novel product possesses the structural unit of a cyclic 3-phosphahexa-1,3,5-triene that also contains a 1-phospha-1,3-diene unit. Open-chain 1-phosphabutadienes are extremely reactive and can behave not only as dienes but also as dienophiles. However, systems of this type have been stabilized by the introduction of sterically demanding substituents.[24] This and the incorporation of the reactive moiety in a bicyclic system are apparently sufficient to prevent further reaction of **14**.

The first information on the structure of **14** was provided by the $^{31}$P NMR spectrum in which the conversion of a $\lambda^3\sigma^3$- to a $\lambda^3\sigma^2$-phosphorus atom is indicated by the shift of the signal ($\delta = 214$) to lower field. Additionally, there are no CO absorptions shown in the IR spectrum.

The expansion of the four-membered ring is also revealed by the $^{13}$C NMR spectrum: the carbon–phosphorus couplings of the C atoms originating from the double bond of the four-membered ring are clearly changed. While C4 ($\delta = 165.8$) in **14** has a $^1J$(C,P) coupling constant of 53.9 Hz, that is, almost twice as large as the corresponding coupling constant in **4a** [$^1J$(C,P) = 22.1 Hz], the splitting pattern at C3 ($\delta = 153.3$) breaks down completely. The acetal carbon C8a gives a signal at $\delta = 111.6$ [$^2J$(C,P) = 13.2 Hz]. The signals for the carbon atoms of the second alkene unit, C6 and C7, are seen at $\delta =$ 115.6 (C6) and $\delta = 168.6$ (C7). The $^2J$(C,P) coupling constant of 31.7 Hz for C6 is appreciably larger than those for C8a and C3; this is due to the effect of the free electron pair on phosphorus. In fixed bonds it increases the $^2J$(C,P) coupling if the carbon atom involved is in a *cis* position.[25–27] Finally, the

signal of the skeletal phosphaalkene carbon atom C5 appears at $\delta = 193.5$ with the typical doublet structure for a phosphaalkene [$^1J$(P,C) = 51.3 Hz].

The crystals of **14**, obtained from a cold *n*-pentane solution, were analyzed by X-ray crystallography (Figure 1). This confirmed the proposed constitutional assignments. Within

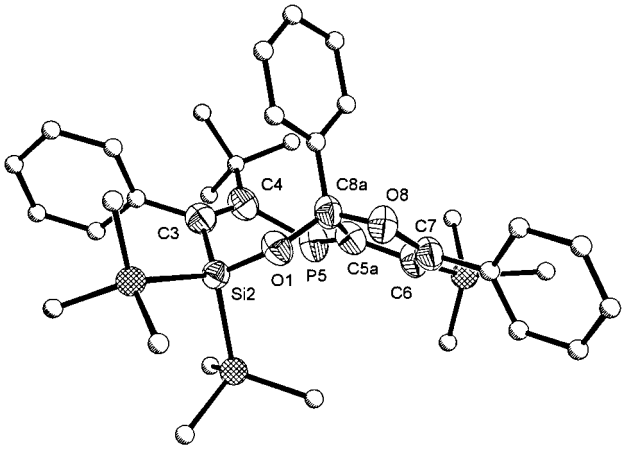
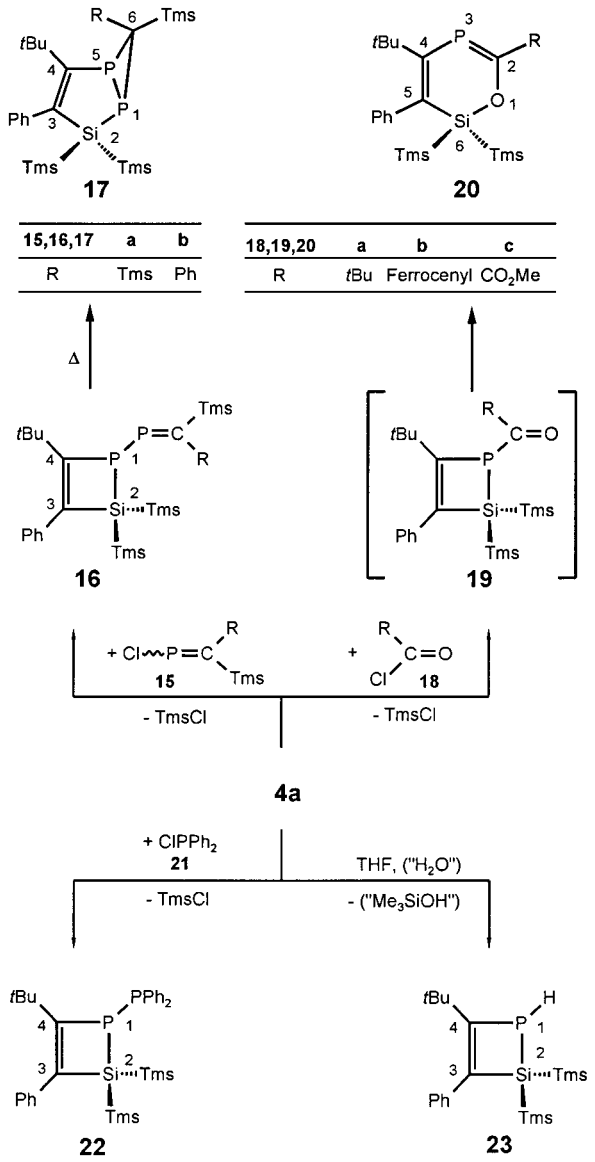



Figure 1. Molecular structure of **14** in the solid state. Selected bond lengths [Å] and angles [°]: Si2 – C3 1.890(5), C3 – C4 1.338(7), C4 – P5 1.841(6), P5 – C5a 1.675(5), C5a – C8a 1.527(7), C5a – C6 1.449(7), C6 – C7 1.349(7), C7 – O8 1.356(6), O8 – O8a 1.455(6), C8a – O1 1.390(6), O1 – Si2 1.670(3); O1-Si2-C3 108.9(2), Si2-C3-C4 121.8(4), C3-C4-P5 120.5(4), C4-P5-C5a 108.9(3), P5-C5a-C8a 128.9(4), P-C5a-C6 124.2(4), C5a-C8a-O1 111.6(4), C5a-C8a-O8 104.3(4), C5a-C6-C7 106.2(4), C6-C7-O8 115.3(4), C7-O8-C8a 108.1(4), O8-C8a-O1 104.3.

the limits of the standard deviations, the five-membered ring is planar and the phosphorus atom also lies in the same plane, thus providing the prerequisites for the interaction of the $\pi$ system with the 1-phosphabutadiene unit. This is, however, not the case for the second phosphabutadiene increment (C5a-P5-C4-C3) since C3 does not lie in the plane defined by C4-P5-C5a; the dihedral angle C5a-P5-C4-C3 = 58.4°. The C7 – O8 bond [135.6(6) pm] is significantly shorter than the C8a – O8 bond [145.5(6) pm; average: 143.6 pm].[28] The C6 – C7 bond length of 134.9(7) pm is in the typical range (average: 135.4 pm) for enol ethers.[28] The significantly shorter C6 – C5a bond length of 144.9(7) pm is in accord with its position in a conjugated 1-phosphabutadiene system (C7-C6-C5a-P5).

The formation of **14** can only be explained by the formation of the intermediate **13** through the insertion of the triple bond of **12** into the P – Si bond of **4a**; insertions of this sort are known in principle.[29] The further reaction in the direction of the arrows (see Scheme 3) requires a *cis* configuration of the two benzoyl groups at the alkene unit of **13**. The driving force for this process is most certainly the formation of the silicon – oxygen bond.

**Reactions with cleavage of the exocyclic *P*-silyl group**: Reactions of the *P*-chlorophosphaalkenes **15a**,**b** with the dihydrophosphasilete **4a** proceed with the formation of chlorotrimethylsilane to yield the phosphaalkene-substituted heterocyclic compounds **16a**,**b** as yellow oils in quantitative yields (Scheme 4). These products cannot be distilled; however, they can be stored for several weeks at −20 °C without decomposition.




Scheme 4. Hydrolysis and cleavage reactions of the 1,2-dihydro-1,2-phosphasilete **4a**.

Compounds **16** are unequivocally characterized by their spectral data which, as far as the four-membered ring is concerned, correspond closely to the data for the products **4a**, **9**, and **11**. However, the presence of a second phosphorus atom does give rise to some special features. Two doublet signals are observed in the $^{31}$P NMR spectra: the signal for each skeletal phosphorus atom experiences a paramagnetic shift of ≈80 ppm compared to that of the starting material **4a** (**16a**: $\delta = -38$; **16b**: $\delta = -66$), while the signals of the $\lambda^3\sigma^2$-phosphorus atoms at $\delta = +459.0$ (**16a**) and $\delta = +352.9$ (**16b**) are in the region typical for phosphane-substituted phosphaalkenes.[30] The presence of the P – P bond is clearly documented by the occurrence of $^1J$(P,P) couplings of ≈271 Hz. Since the $^{31}$P NMR spectrum of **16b** contains only one set of signals, it may be assumed that only one isomer, presumably the *E* isomer, has been formed.[31]

The $^{13}$C NMR signals for the ring carbon atoms, C3 and C4, are similar to those of the starting material **4a** except for the



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splitting to a double doublet structure on account of the presence of a further phosphorus atom. The $sp^2$ carbon atoms of the phosphaalkene unit give rise to doublet signals at significantly low field (**16a**: $\delta = 211$; **16b**: $\delta = 207.6$). The typically large phosphaalkene P,C-coupling constants amount to 96.5 (**16a**) and 83.3 Hz (**16b**). Surprisingly, no other couplings with the $\lambda^3\sigma^3$-phosphorus atom were observed.

In contrast to the alkenyl-substituted heterocyclic compounds **9** and **11**, the products **16a**,**b** do undergo thermal isomerization: when heated for 2 hours at 180 °C, they transform into the bicyclic diphosphiranes **17a**,**b** which were isolated in 80 and 95 % yields by distillation.

This rather unexpected transformation of the phosphane-substituted phosphaalkenes **16a**,**b** to the diphosphiranes **17a**,**b** is reflected in a dramatic shift to high field of the $^{31}$P NMR signal of the original $\lambda^3\sigma^2$-phosphorus atom by more than 600 ppm.[32] The signal at higher field (**17a**: $\delta = -261.5$; **17b**: $\delta = -283.5$) is assigned to P1 on account of the silicon substitution. The P–P coupling of $\approx 185$ Hz is of the magnitude expected for a $^1J$(P,P) coupling in a diphosphirane.[33, 34]

The final configurational elucidation of the bicyclic products **17a**,**b** was based on the $^1$H and $^{13}$C NMR data. In the $^1$H NMR spectrum of the bicyclic compound **17a** signals for the four trimethylsilyl groups appear at $\delta = 0.20$, 0.35, 0.45, and 0.50. The signal at $\delta = 0.35$ is split by 1.8 Hz into a pseudotriplet. A similar situation is observed in the spectrum of **17b** where the trimethylsilyl signal at $\delta = 0.30$ is split by 1.2 Hz into a pseudotriplet. Since in phosphiranes only those trimethylsilyl groups in a *cis* orientation to the free electron pair on phosphorus exhibit a P,H coupling, in contrast to *trans*-trimethylsilyl groups that do not experience any coupling,[35, 36] the *cis* orientation of one of the trimethylsilyl groups to both free electron pairs on the phosphorus may safely be assumed.

The $^{13}$C NMR spectral data are similar: the signals for the *cis*-trimethylsilyl group have a pseudotriplet structure [**17a**: $^3J$(C,P) = 8.1; **17b**: $^3J$(C,P) = 4.8 Hz], whereas that for the *trans*-trimethysilyl group in **17a** does not exhibit any coupling. The proposed bicyclic structure of **17** is further supported by the values for the ring carbon atoms: the signals for C3 and C4 appear in the olefinic region; those for C3 (**17a**: $\delta = 151.4$; **17b**: $\delta = 148.4$) are not split by any carbon–phosphorus couplings and are diamagnetically shifted compared to the signals of C4 (**17a**: $\delta = 165.5$; **17b**: $\delta = 160.4$).[36] The signals for C4 are each split into doublets by $^1J$(C,P) couplings of $\approx 70$ Hz. The signal for the carbon atom of the three-membered ring, C6, appears, as expected, at high field.[37] As a result of the two neighboring phosphorus atoms, the signal at $\delta = 16.4$ (**17a**) is split into a pseudotriplet by a $^1J$(C,P) coupling of 88 Hz [**17b**: $\delta = 30.6$, $^1J$(C,P) = 67.7 Hz].

The formation of **17** from **16** can formally be explained in terms of a 1,2-shift of the ring silyl fragment in **16** with subsequent ring closure to afford the bicyclic species **17**. This process requires the attack of the phosphaalkene phosphorus atom at the silicon. The different reactivity of the phosphaalkenyl-substituted heterocyclic system **16** in comparison to the alkenyl-substituted compounds **9** and **11** is thus caused by the heteroatom in the vinyl unit.

Another example for the influence exerted on the 1-vinyl-1,2-dihydro-1,2-phosphasilete isomerization by heteroatoms in the double bond moiety is provided by the reactions of **4a** with the acyl chlorides **18a–c**: the *P*-acyldihydrophosphasiletes **19a–c**, most certainly formed initially along with chlorotrimethylsilane, are not detectable, in contrast to the situation with **16a**,**b**. Instead spontaneous isomerization with 1,3-migration of the $Si(Tms)_2$ moiety from phosphorus to the carbonyl oxygen atom in **19a–c** takes place to furnish the dihydrooxaphosphasilines **20a–c**, heterocyclic species containing a 2-phospha-1,3-butadiene unit which have already been reported.[38]

Spectral and analytical data for **20a–c** strongly support the proposed structures. The transition from a $\lambda^3\sigma^3$ phosphorus to a $\lambda^3\sigma^2$ phosphorus is reflected in a pronounced downfield shift of the $^{31}$P NMR signal to $\delta = 91.0$ and 92.0 for **20a** and **20b**, respectively. This is a typical region for phosphaalkenes with oxygen substitution on the $sp^2$ carbon atom.[24, 28] The exceptionally low-field position of the $^{31}$P NMR signal for the acceptor-substituted derivative **20c** ($\delta = 172.0$) may be attributed to a considerable participation of conceivable mesomeric forms with negative partial charge on the oxygen atom.[39] This assumption is also supported by the diamagnetic shift of the $^{13}$C NMR signal of C2 in **20c** in comparison to the corresponding signals for **20a**,**b** as well as the shift to low field of the signal for C5. The positions of the signals for the olefinic carbon atom C4 in **20a–c** are almost identical.

The expansion from a four- to a six-membered ring becomes apparent on consideration of the C,P coupling constants: while the signal for the *tert*-butyl-substituted C4 in **4a** exhibits only a small coupling ($^1J$(C,P) = 22.1 Hz), those of C4 in **20** have $^1J$(C,P) coupling constants in the range 54.8–58.2 Hz. On the other hand, the $^2J$(C,P) couplings of 6.2–7.8 Hz are conspicuously small. Final confirmation of the constitutions of products **20** was provided by the single-crystal X-ray crystallographic analysis of **20b** (Figure 2).

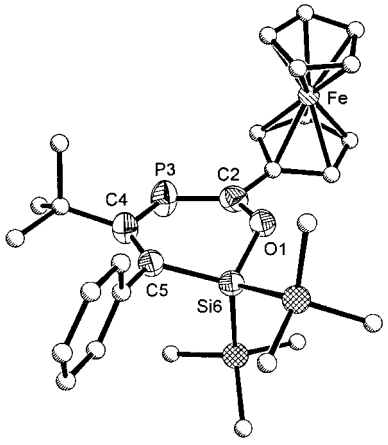


Figure 2. Molecular structure of **20b** in the solid state. Selected bond lengths [Å] and angles [°]: P3–C2 1.678(4), C2–O1 1.339(3), O1–Si6 1.692(2), Si6–C5 1.866(4), C5–C4 1.336(4), C4–P3 1.845(2); C4-P3-C2 105.5(1), P3-C2-O1 129.1(2), C2-O1-Si6 117.5(2), O1-Si6-C5 105.0(1), Si6-C5-C4 119.4(2), C5-C4-P3 123.0(3).

The phosphorus–carbon bond lengths agree very well with the average values of 167 pm for P–C double bonds and 185 pm for P–C single bonds.[40] The ring skeleton is not planar but has a slight boat conformation.

As a consequence of the strong oxophilicity of silicon, the formation of **20** from **19** can be explained by the migration of 1,3-Si(Tms)$_2$ from phosphorus to oxygen and ring closure. The same driving force is responsible for the reaction of acyl chlorides with silylphosphanes where the acylphosphane primary products, which are difficult to detect, undergo isomerization to phosphaalkenes by 1,3-silyl migration.[38]

When an equimolar amount of chloro(diphenyl)phosphane (**21**) is added to **4a**, the silyl group at phosphorus is again replaced by the phosphane substituent to furnish product **22**. Ring opening (cleavage of the endocyclic P–Si bond), however, does not take place, as is clearly apparent from the spectral data of **22**. The $^1$H NMR spectrum no longer shows any $^3J$(H,P) coupling and contains signals for only two trimethylsilyl groups at $\delta = 0.20$ and $\delta = 0.50$. A $^1J$(P,P) coupling of 186 Hz in the $^{31}$P NMR spectrum unequivocally confirms the exchange of a silyl fragment on the ring phosphorus atom for a phosphorus group ($\delta = -10.8$ and $-79.6$). Retention of the dihydrophosphasilete skeleton is demonstrated by a comparison of the $^{13}$C NMR data for the ring carbon atoms with the corresponding values for **4a**. Although the former have double doublet structures on account of the presence of two phosphorus atoms, the signals occur in the same regions and reveal the characteristically small $^2J$(C,P) coupling constants.

**Hydrolysis of the 1,2-dihydro-1,2-phosphasilete 4a**: The four-membered heterocyclic product **4a** proved to be extremely sensitive to hydrolysis. Cleavage of the *P*-silyl group occurred even in absolute tetrahydrofuran on moderate heating for a few hours. The resultant hydrogen-substituted 1,2-dihydro-1,2-phosphasilete **23** is obtained as a colorless, extremely moisture-sensitive oil. For this reason only NMR data were available for the elucidation of its structure and these exhibited the already sufficiently discussed characteristic features of a 1,2-dihydro-1,2-phosphasilete (see the Experimental Section). The presence of the PH function results in a splitting of the signal in the proton-coupled $^{31}$P NMR spectrum by a $^1J$(P,H) coupling of 160 Hz ($\delta = -173.0$), which is also seen in the $^1$H NMR signal at $\delta = 3.40$.

## Experimental Section

**General**: All experiments were carried out under argon (purity > 99.998 %) in previously evacuated and baked Schlenk vessels. The solvents were anhydrous and stored under argon until used. Melting points were determined on a Mettler FP61 apparatus (heating rate 2 °C min$^{-1}$) and are uncorrected. NMR spectra were recorded on Varian EM360, Varian EM390, Bruker WP200, and Bruker AM400 instruments. Chemical shifts for $^1$H and $^{13}$C are reported in ppm relative to tetramethylsilane as the internal standard; the chemical shifts for $^{31}$P are expressed relative to external 85 % orthophosphoric acid. Elemental analyses were performed on Perkin–Elmer analysers EA240 and 2400 CHN. Bulb-to-bulb distillations were carried out in a Büchi GKR50 apparatus (temperatures given refer to the heating mantle). IR spectra were determined on Perkin–Elmer 710B or Perkin–Elmer IR394 spectrophotometers. Mass spectra were recorded on a Finnigan MAT90 spectrometer. Compounds **3a,b**[7] were prepared by published methods. All other starting materials were purchased from commercial sources.

**General procedure for the photolytic isomerization of 3a,b**: A solution of 1-silyl-1*H*-phosphirene **1** in benzene (5 mL) in an NMR tube was irradiated with an Hg lamp (TQ150, Heraeus) for 40 h. The reaction was monitored by $^{31}$P NMR. The solvent was removed at 20 °C ($10^{-2}$ mbar) and the red-brown oily residue was purified by bulb-to-bulb distillation. Recrystallization from *n*-pentane at −78 °C yielded colorless crystals.

**4-*tert*-Butyl-3-phenyl-1,2,2-tris(trimethylsilyl)-1,2-dihydro-1,2-phosphasilete (4a)**: From **3a** (1.5 g, 3.4 mmol); to furnish **4a** (0.5 g, 34 %) as colorless crystals. M.p. 75 °C; b.p. 150 °C ($10^{-3}$ mbar); $^1$H NMR ($CD_2Cl_2$): $\delta = 0.2$–0.4 [br, 18H, Si(CH$_3$)$_3$], 0.45 [d, $^3J$(H,P) = 4.0 Hz, 9H, P-Si(CH$_3$)$_3$], 1.10 (s, 9H, *t*Bu), 7.0–7.2 (m, 5H, phenyl-H); $^{13}$C NMR ($CD_2Cl_2$): $\delta = 0.1$, 1.2 [each br, Si-Si(CH$_3$)$_3$], 2.0 [d, $^2J$(C,P) = 10.3 Hz, P-Si(CH$_3$)$_3$], 31.5 [d, $^3J$(C,P) = 5.0 Hz, C(*C*H$_3$)$_3$], 40.9 [d, $^2J$(C,P) = 13.7 Hz, *C*(CH$_3$)$_3$], 124.6, 126.5, 127.5 (each s, phenyl-C), 145.2 [d, $^3J$(C,P) = 4.5 Hz, *ipso*-C], 149.3 [d, $^2J$(C,P) = 13.3 Hz, C3], 166.2 [d, $J$(P,C) = 22.1 Hz, C4]; $^{31}$P NMR ($C_6D_6$): $\delta = -130.7$ (s); IR (film): $\tilde{\nu} = 3050$ (w), 2950 (vs), 2900 (s), 1600 (m), 1480 (m), 1360 (m), 1250 (vs), 1190 (w), 1050 (s), 850 (vs), 760 (s), 690 (s), 620 (s) cm$^{-1}$; inversion barrier at phosphorus (toluene): $T_c = 314$ K, $\Delta G^{\neq}(T_c) = 67.7$ kJ mol$^{-1}$; $C_{21}H_{41}PSi_4$ (436.9): calcd C 57.73, H 9.46; found C 57.4, H 9.4.

**4-*tert*-Butyl-3-phenyl-1,2,2-tris(trimethylsilyl)-1,2-dihydro-1,2-phosphagermete (4b)**: From **3b** (1.1 g, 2.3 mmol); to furnish **4b** (50 mg, 5 %) as colorless crystals. M.p. 90 °C; b.p. 180 °C ($10^{-3}$ mbar); $^1$H NMR ($C_6D_6$): $\delta =$ 0.25, 0.37 [each s, 9H, Si(CH$_3$)$_3$], 0.5 [d, $^3J$(H,P) = 4.0 Hz, 9H, P-Si(CH$_3$)$_3$], 1.2 (s, 9H, *t*Bu), 7.0–7.2 (m, 5H, phenyl-H); $^{13}$C NMR ($C_6D_6$): $\delta = 0.3$ [s, Ge-Si(CH$_3$)$_3$], 0.6 [d, $^3J$(C,P) = 2.6 Hz, Ge-Si(CH$_3$)$_3$], 1.9 [d, $^2J$(C,P) = 7.0 Hz, P-Si(CH$_3$)$_3$], 31.7 [d, $^3J$(C,P) = 6.2 Hz, C(*C*H$_3$)$_3$], 40.8 [d, $^2J$(C,P) = 13.3 Hz, *C*(CH$_3$)$_3$], 125.1–128.2 (phenyl-C), 146.9 [d, $^3J$(C,P) = 4.8 Hz, *ipso*-C], 151.3 [d, $^2J$(C,P) = 14.1 Hz, C3], 163.7 [d, $^1J$(C,P) = 23.4 Hz, C4]; $^{31}$P NMR ($C_6D_6$): $\delta = -92$ (s).

**General procedure for the reaction of 1,2-dihydro-1,2-phosphasilete 4a with acceptor-substituted alkynes 8a–d**: A solution of alkyne **8** in diethyl ether was added to a solution of **4a** in diethyl ether at −78 °C. The mixture was allowed to warm to room temperature and was then stirred for 4 h. The reaction was exothermic and the color of the solution became darker. The solvent was removed at 20 °C ($10^{-2}$ mbar) and the oily residue then purified by bulb-to-bulb distillation.

**Dimethyl 1-[4-*tert*-butyl-3-phenyl-2,2-bis(trimethylsilyl)-1,2-dihydro-1,2-phosphasilet-1-yl]-2-trimethylsilylmaleate (9a)**: From **8a** (66 mg, 0.46 mmol) and **4a** (200 mg, 0.46 mmol). Crystallization from *n*-pentane at −20 °C yielded **9a** (240 mg, 90 %) as colorless crystals. M.p. 116.0 °C; b.p. 200 °C ($10^{-3}$ mbar); $^1$H NMR ($C_6D_6$): $\delta = 0.4$, 0.5, 0.55 [each s, 9H, Si(CH$_3$)$_3$], 1.2 (s, 9H, *t*Bu), 3.55, 3.6 (each s, 3H, $CO_2$Me), 7.0–7.3 (m, 5H, phenyl-H); $^{13}$C NMR ($C_6D_6$): $\delta = 0.14$ [d, $J$(C,P) = 2.7 Hz, Si(CH$_3$)$_3$], 0.4 [d, $J$(C,P) = 10.9 Hz, Si(CH$_3$)$_3$], 1.2 [s, Si(CH$_3$)$_3$], 31.0 [d, $^3J$(C,P) = 4.7 Hz, C(*C*H$_3$)$_3$], 40.6 [d, $^2J$(C,P) = 13.1 Hz, *C*(CH$_3$)$_3$], 51.1, 51.3 (each s, $CO_2CH_3$), 125.5, 126.2, 127.7 (each s, phenyl-C), 144.7 [d, $^3J$(C,P) = 5.3 Hz, *ipso*-C], 150.5 [d, $^2J$(C,P) = 43.3 Hz, C2′], 152.8 [d, $^1J$(C,P) = 60.9 Hz, C1′], 157.5 [d, $^2J$(C,P) = 19.7 Hz, C3], 163.7 [d, $^3J$(C,P) = 15.9 Hz, *C*O$_2$CH$_3$], 165.7 [d, $^2J$(C,P) = 6 Hz, *C*O$_2$CH$_3$], 169.9 [d, $^1J$(C,P) = 20.5 Hz, C4]; $^{31}$P NMR ($C_6D_6$): $\delta = -63.5$ (s); IR (film): $\tilde{\nu} = 2950$ (vs), 2900 (q), 1720 (vs), 1600 (w), 1530 (m), 1430 (s), 1360 (w), 1230 (vs), 1070 (m), 1020 (w), 850 (vs), 770 (s), 710 (s), 630 (m) cm$^{-1}$; $C_{27}H_{47}O_4PSi_4$ (578.0): calcd C 56.0, H 8.1; found C 55.9, H 8.1.

**Di-*tert*-butyl [4-*tert*-butyl-3-phenyl-2,2-bis(trimethylsilyl)-1,2-dihydro-1,2-phosphasilet-1-yl)-trimethylsilylmaleate (9b)**: From **8b** (52 mg, 0.23 mmol) and **4a** (100 mg, 0.23 mmol). Crystallization from *n*-pentane at 0 °C yielded **9b** (130 mg, 86 %) as colorless crystals. M.p. 153.5 °C; b.p. 250 °C ($10^{-3}$ mbar); $^1$H NMR ($C_6D_6$): $\delta = 0.4$, 0.5 [each s, 9H, Si(CH$_3$)$_3$], 0.55 [d, $J$(H,P) = 2 Hz, 9H, Si(CH$_3$)$_3$], 1.3, 1.5, 1.7 (each s, 9H, *t*Bu), 7.0–7.3 (m, 5H, phenyl-H); $^{13}$C NMR ($C_6D_6$): $\delta = 0.3$ [s, Si(CH$_3$)$_3$], 1.4 [d, $J$(C,P) = 12 Hz, Si(CH$_3$)$_3$], 1.7 [s, Si(CH$_3$)$_3$], 28.6 [s, C(*C*H$_3$)$_3$], 31.2 [d, $^3J$(C,P) = 3.2 Hz, C(*C*H$_3$)$_3$], 41.3 [d, $^2J$(C,P) = 13.8 Hz, *C*(CH$_3$)$_3$], 80.8, 82.1 [each s, $CO_2C(CH_3)_3$], 125.8, 126.4, 127.7 (each s, phenyl-C), 145.5 [d, $^3J$(C,P) = 5 Hz, *ipso*-C], 149.2 [d, $^2J$(C,P) = 45.6 Hz, C2′], 153.8 [d, $^1J$(C,P) = 58.4 Hz, C1′], 157.8 [d, $^2J$(C,P) = 18.7 Hz, C3], 164.3 [d, $^3J$(C,P) = 16.7 Hz, *C*O$_2$*t*Bu], 166.0 [d, $^2J$(C,P) = 5.5 Hz, *C*O$_2$*t*Bu], 168.9 [d, $^1J$(C,P) = 23.2 Hz, C4]; $^{31}$P NMR ($C_6D_6$): $\delta = -60.2$ (s); IR (KBr): $\tilde{\nu} = 2900$ (vs), 1710 (vs), 1600 (w), 1540 (w), 1425 (w), 1350 (w), 1240 (s), 1050 (m), 840 (s), 770 (m), 710 (m), 630 (w) cm$^{-1}$; $C_{33}H_{59}O_4PSi_4$ (663.1): calcd C 59.77, H 9.0; found C 57.8, H 8.7.

**Methyl (*Z*)-3-[4-*tert*-butyl-3-phenyl-2,2-bis(trimethylsilyl)-1,2-dihydro-1,2-phosphasilet-1-yl)-2-trimethylsilylprop-2-enoate (9c)**: From **8c** (40 mg, 0.48 mmol) and **4a** (200 mg, 0.46 mmol), to afford **9c** (220 mg, 90 %) as



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colorless crystals. M.p. 95 °C; b.p. 200 °C ($10^{-3}$ mbar); $^1$H NMR ($C_6D_6$): $\delta =$ 0.4, 0.5, 0.6 [each s, 9H, $Si(CH_3)_3$], 1.2 (s, 9H, *t*Bu), 3.6 (s, 3H, $CO_2Me$), 7.0–7.3 (m, 5H, phenyl-H), 8.7 [d, $^2J$(H,P) = 5 Hz, 1H, C=CH]; $^{13}$C NMR ($C_6D_6$): $\delta = -0.2$ [s, $Si(CH_3)_3$], 0.5 [s, $Si(CH_3)_3$], 1.0 [d, $J$(C,P) = 8.8 Hz, $Si(CH_3)_3$], 31.3 [d, $^3J$(C,P) = 4.8 Hz, $C(CH_3)_3$], 41.4 [d, $^2J$(C,P) = 12.7 Hz, $C(CH_3)_3$], 51.1 (s, $CO_2CH_3$), 125.8, 126.5, 128.4 (each s, phenyl-C), 142.9 [d, $^2J$(C,P) = 28.5 Hz, C2′], 144.9 [d, $^3J$(C,P) = 5.5 Hz, *ipso*-C], 151.3 [d, $^2J$(C,P) = 20.1 Hz, C3], 164.6 [d, $^1J$(C,P) = 46.3 Hz, $^1J$(C,H) = 154.0 Hz, C=CH], 169.2 [d, $^3J$(C,P) = 14.6 Hz, $CO_2$Me], 169.7 [d, $^1J$(C,P) = 17.0 Hz, C4]; $^{31}$P NMR ($C_6D_6$): $\delta = -82$ (s); IR (film): $\tilde{\nu} =$ 3050 (w), 2950 (s), 2900 (m), 1700 (s), 1590 (w), 1510 (w), 1430 (w), 1350 (w), 1250 (s), 1200 (s), 830 (vs), 760 (w), 700 (m) $cm^{-1}$; $C_{25}H_{45}O_2PSi_4$ (521.0): calcd C 57.6, H 8.7; found C 57.1, H 8.8.

**(*Z*)-3-[4-*tert*-Butyl-3-phenyl-2,2-bis(trimethylsilyl)-1,2-dihydro-1,2-phosphasilet-1-yl)-2-trimethylsilyl-1-phenylpropen-1-one (9d)**: From **8d** (45 mg, 0.35 mmol) and **4a** (150 mg, 0.35 mmol), to furnish **9d** (180 mg, 90 %) as a yellow oil. B.p. 200 °C ($10^{-3}$ mbar); $^1$H NMR ($C_6D_6$): $\delta =$ 0.35, 0.4 [each s, 9H, $Si(CH_3)_3$], 0.6 [s, 9H, $Si(CH_3)_3$], 1.2 (s, 9H, *t*Bu), 7.1–7.4 (m, 8H, phenyl-H), 7.7 [d, $^2J$(H,P) = 4 Hz, 1H, C=CH], 8.0–8.2 (m, 2H, phenyl-H); $^{13}$C NMR ($C_6D_6$): $\delta =$ 0.4 [d, $J$(C,P) = 8.1 Hz, $Si(CH_3)_3$], 0.8, 1.4 [each s, $Si(CH_3)_3$], 31.4 [d, $^3J$(C,P) = 4.6 Hz, $C(CH_3)_3$], 41.4 [d, $^2J$(C,P) = 13 Hz, $C(CH_3)_3$], 125.8, 126.4, 128.3, 128.5, 130.1, 132.6 (each s, phenyl-C), 138.0 (s, *ipso*-C), 144.8 [d, $^3J$(C,P) = 6 Hz, *ipso*-C], 151.8 [d, $^2J$(C,P) = 19 Hz, C3], 155.3 [d, $^1J$(C,P) = 45.8 Hz, $^1J$(C,H) = 152.7 Hz, C=CH], 155.8 [d, $^2J$(C,P) = 27.7 Hz, C2′], 168.9 [d, $^1J$(C,P) = 14.7 Hz, C4], 199.1 [d, $^3J$(C,P) = 16.2 Hz, COPh]; $^{31}$P NMR ($C_6D_6$): $\delta = -82.3$ (s); IR (film): $\tilde{\nu} =$ 3080 (w), 2950 (s), 2900 (w), 1650 (m), 1600 (w), 1260 (s), 1250 (s), 1170 (m), 1050 (m), 830 (s), 770 (w), 700 (m) $cm^{-1}$.

**4-*tert*-Butyl-1-(2′,2′-diphenyl-1′-trimethylsiloxyethenyl)-3-phenyl-2,2-bis(trimethylsilyl)-1,2-dihydro-1,2-phosphasilete (11)**: A solution of diphenylketene (**10**) (70 mg, 0.36 mmol) in diethyl ether (2 mL) was added to a solution of **4a** (150 mg, 0.35 mmol) in diethyl ether (5 mL) at −78 °C. The mixture was allowed to warm to room temperature and was stirred for 12 h. The solvent was removed at 20 °C ($10^{-2}$ mbar) and the residue then purified by bulb-to-bulb distillation to afford **11** (130 mg, 60 %) as a yellow oil. B.p. 250 °C ($10^{-3}$ mbar); $^1$H NMR ($CD_2Cl_2$): $\delta =$ 0.0, 0.1, 0.35 [each s, 9H, $Si(CH_3)_3$], 1.0 (s, 9H, *t*Bu), 7.0–7.3 (m, 15H, phenyl-H); $^{13}$C NMR ($CD_2Cl_2$): $\delta =$ 0.2 [d, $J$(C,P) = 3 Hz, $Si(CH_3)_3$], 1.5, 2.5 [each s, $Si(CH_3)_3$], 31.4 [d, $^3J$(P,C) = 4.6 Hz, $C(CH_3)_3$], 41.5 [d, $^2J$(C,P) = 15 Hz, $C(CH_3)_3$], 125.4–131.0 (phenyl-C), 134.1 [d, $^2J$(C,P) = 38.1 Hz, C=CPh$_2$], 124.6 [d, $^3J$(C,P) = 6.8 Hz, *ipso*-C], 144.1 [d, $^3J$(C,P) = 9.9 Hz, *ipso*-C], 145.6 [d, $^3J$(C,P) = 4.8 Hz, *ipso*-C], 153.3 [d, $^1J$(C,P) = 62.0 Hz, C=COTms], 153.4 [d, $^2J$(C,P) = 20.4 Hz, C3], 166.5 [d, $^1J$(C,P) = 19.6 Hz, C4]; $^{31}$P NMR ($CD_2Cl_2$): $\delta = -58$ (s); IR (film): $\tilde{\nu} =$ 3050 (w), 2950 (s), 2900 (m), 1600 (m), 1550 (w), 1440 (w), 1250 (s), 1200 (b), 960 (m), 800 (s), 700 (s) $cm^{-1}$.

**4-*tert*-Butyl-3,7-diphenyl-2,2,6-tris(trimethylsilyl)-2,8a-dihydrofuro[2,3-*b*]-[1,4,7]oxaphosphasilaepine (14)**: A solution of dibenzoylacetylene (**12**) (170 mg, 0.73 mmol) in dichloromethane (3 mL) was added to a solution of **4a** (300 mg, 0.69 mmol) in dichloromethane (3 mL) at −78 °C. The red reaction mixture was allowed to warm to room temperature. The solvent was removed at 20 °C ($10^{-2}$ mbar) and the residue was dissolved in *n*-pentane (20 mL). Filtration through Celite and recrystallization from *n*-pentane afforded **14** (280 mg, 60 %) as colorless crystals. M.p. 157.2 °C; $^1$H NMR ($C_6D_6$): $\delta =$ 0.2, 0.55, 0.65 [each s, 9H, $Si(CH_3)_3$], 1.1 (s, 9H, *t*Bu), 6.8–8.2 (m, 15H, phenyl-H); $^{13}$C NMR ($C_6D_6$): $\delta = -0.5$ [s, $Si(CH_3)_3$], 1.3 [d, $J$(C,P) = 8.2 Hz, $Si(CH_3)_3$], 1.9 [d, $J$(C,P) = 4 Hz, $Si(CH_3)_3$], 32.6 [d, $^3J$(C,P) = 9.6 Hz, $C(CH_3)_3$], 42.4 [d, $^2J$(C,P) = 22.1 Hz, $C(CH_3)_3$], 111.6 [d, $^2J$(C,P) = 13.2 Hz, C8a], 115.6 [d, $^2J$(C,P) = 31.7 Hz, C6], 125.8, 126.8, 126.9, 127.9, 128.6, 129.6, 130.0, 133.0, 146.3 (each s, phenyl-C), 142.9 [d, $J$(C,P) = 6.1 Hz, *ipso*-phenyl-C], 153.3 (s, C3), 165.8 [d, $^1J$(C,P) = 53.9 Hz, C4], 168.6 [d, $^3J$(C,P) = 31.9 Hz, C7], 193.5 [d, $^1J$(C,P) = 51.3 Hz, C5a]; $^{31}$P NMR ($C_6D_6$): $\delta = +214$ (s); IR (KBr): $\tilde{\nu} =$ 3050 (w), 2950 (s), 1600 (w), 1580 (w), 1450 (m), 1370 (w), 1250 (s), 1050 (s), 950 (w), 830 (s), 760 (m), 690 (m) $cm^{-1}$; $C_{37}H_{51}O_2PSi_4$ (671.1): calcd C 66.2, H 7.6; found C 65.3, H 7.5.

**General procedure for the reaction of 4a with chloromethylenephosphanes 15**: To a solution of **4a** (200 mg, 0.46 mmol) in diethyl ether (3 mL) was added an equimolar amount of chloromethylenephosphane **15**. After stirring for 12 h at room temperature the solvent was removed at 20 °C ($10^{-2}$ mbar).

**4-*tert*-Butyl-3-phenyl-2,2-bis(trimethylsilyl)-1-[bis(trimethylsilyl)methylenephosphanyl]-1,2-dihydro-1,2-phosphasilete (16a)**: Yield: 240 mg, 93 % of **16a** as a nondistillable red oil. $^1$H NMR ($C_6D_6$): $\delta =$ 0.35 [s, 18H, $Si(CH_3)_3$], 0.4 [d, $J$(H,P) = 2 Hz, 9H, $Si(CH_3)_3$], 0.55 [s, 9H, $Si(CH_3)_3$], 1.2 (s, 9H, *t*Bu), 7.0–7.3 (m, 5H, phenyl-H); $^{13}$C NMR: $\delta =$ 0.35, 1.4 [each s, $Si(CH_3)_3$], 1.9 [d, $^3J$(C,P) = 12.4 Hz, $Si(CH_3)_3$], 3.0 [d, $^3J$(C,P) = 8.9 Hz, $Si(CH_3)_3$], 31.6 [d, $^3J$(C,P) = 4.7 Hz, $C(CH_3)_3$], 41.5 [d, $^2J$(C,P) = 11.8 Hz, $C(CH_3)_3$], 125.8, 126.9, 128.2 (each s, phenyl-C), 145.2 [d, $^3J$(C,P) = 3.3 Hz, *ipso*-C], 152.4 [dd, $^2J$(C,P) = 14.6 Hz, $^3J$(C,P) = 5.8 Hz, C3], 168.9 [dd, $^1J$(C,P) = 23.7 Hz, $^2J$(C,P) = 6.8 Hz, C4], 211.2 [d, $^1J$(C,P) = 96.4 Hz, P=C]; $^{31}$P NMR ($C_6D_6$): $\delta = +459.0, -33.0$ [each d, $^1J$(P,P) = 270.5 Hz].

**4-*tert*-Butyl-3-phenyl-2,2-bis(trimethylsilyl)-1-(trimethylsilylbenzylidenephosphanyl)-1,2-dihydro-1,2-phosphasilete (16b)**: Yield: 250 mg, 95 % of **16b** as a nondistillable red oil. $^1$H NMR ($C_6D_6$): $\delta =$ 0.3 [s, 9H, $Si(CH_3)_3$], 0.4 [d, $J$(H,P) = 2 Hz, 9H, $Si(CH_3)_3$], 0.5 (s, 9H, $Si(CH_3)_3$], 1.25 (s, 9H, *t*Bu), 7.0–7.4 (m, 10H, phenyl-H); $^{13}$C NMR ($C_6D_6$): $\delta = -0.2, -0.1$ [each s, $Si(CH_3)_3$], 1.8 [d, $J$(C,P) = 2.8 Hz, $Si(CH_3)_3$], 31.6 [s, $C(CH_3)_3$], 41.5 [d, $^2J$(C,P) = 12 Hz, $C(CH_3)_3$], 125.2–129.1 (phenyl-C), 145.2 [d, $^2J$(C,P) = 3 Hz, *ipso*-C], 147.6 [dd, $J$(C,P) = 11.6 Hz, $J$(C,P) = 12.6 Hz, *ipso*-C], 151.2 [d, $^2J$(C,P) = 12 Hz, C3], 167.5 [dd, $^1J$(C,P) = 21.6 Hz, $^2J$(C,P) = 6.6 Hz, C4], 207.6 [d, $^1J$(C,P) = 81.3 Hz, P=C]; $^{31}$P NMR ($C_6D_6$): $\delta = +352.9, -66.2$ [each d, $^1J$(P,P) = 271.6 Hz].

**General procedure for the isomerization of 16 to 17**: 1,2-Dihydro-1,2-phosphasilete **16** was heated for 2 h at 175–190 °C in a bulb-to-bulb distillation apparatus. Distillation at 200 °C ($10^{-3}$ mbar) gave **17** as a colorless oil. Product **17b** was crystallized from *n*-pentane at −20 °C.

**4-*tert*-Butyl-3-phenyl-2,2,6,6-tetrakis(trimethylsilyl)-1,5,2-diphosphasilabicyclo[3.1.0]-hex-3-ene (17a)**: From **16a** (240 mg, 0.43 mmol), to afford **17a** (190 mg, 80 %). B.p. 180 °C ($10^{-3}$ mbar); $^1$H NMR ($C_6D_6$): $\delta =$ 0.20 [s, 9H, $Si(CH_3)_3$], 0.35 [t, $^4J$(H,P) = 1.8 Hz, 9H, $Si(CH_3)_3$], 0.45 [s, 9H, $Si(CH_3)_3$], 0.50 [s, 9H, $Si(CH_3)_3$], 1.35 (s, 9H, *t*Bu), 7.0–7.3 (m, 5H, phenyl-H); $^{13}$C NMR ($C_6D_6$): $\delta =$ 1.7 [d, $^3J$(C,P) = 4.2 Hz, $Si(CH_3)_3$], 2.5 [dd, $^3J$(C,P) = 8.1 Hz, $^3J$(C,P) = 8.5 Hz, $Si(CH_3)_3$], 2.8 [s, $Si(CH_3)_3$], 6.8 [s, $Si(CH_3)_3$], 16.4 (pseudo-t, $^1J$(C,P) = 88 Hz, C6], 34.2 [d, $^3J$(C,P) = 10.1 Hz, $C(CH_3)_3$], 43.9 [d, $^2J$(C,P) = 27.2 Hz, $C(CH_3)_3$], 127.2 (s, *para*-phenyl-C), 129.7 (s, *meta*-phenyl-C), 126.3, 129.7 (each br, *ortho*,*ortho′*-phenyl-C), 146.1 (s, *ipso*-C), 151.4 (s, C3), 165.5 [d, $^1J$(P,C) = 71.7 Hz, C4]; $^{31}$P NMR ($C_6D_6$): $\delta = -59.8, -261.5$ [each d, $^1J$(P,P) = 195.3 Hz]; IR (film): $\tilde{\nu} =$ 3050 (w), 2950 (vs), 2900 (m), 1590 (m), 1470 (w), 1440 (w), 1400 (w), 1350 (w), 1250 (vs), 1070 (m), 1030 (m), 920 (s), 840 (vs), 760 (m), 700 (m), 690 (m) $cm^{-1}$.

**4-*tert*-Butyl-3,6(*β*)-diphenyl-2,2,6(*β*)-tris(trimethylsilyl)-1,5,2-diphosphasilabicyclo-[3.1.0]hex-3-ene (17b)**: From **16b** (200 mg, 0.36 mmol), to afford **17b** (190 mg, 95 %) as colorless crystals. M.p. 78 °C; b.p. 200 °C ($10^{-3}$ mbar); $^1$H NMR ($C_6D_6$): $\delta =$ 0.10 [s, 9H, $Si(CH_3)_3$], 0.30 [t, $^4J$(H,P) = 1.2 Hz, 9H, $Si(CH_3)_3$], 0.50 [s, 9H, $Si(CH_3)_3$], 1.5 [d, $^4J$(H,P) = 2 Hz, 9H, *t*Bu], 7.0–7.6 (m, 10H, phenyl-H); $^{13}$C NMR ($C_6D_6$): $\delta = -1.3$ [t, $^3J$(C,P) = 4.8 Hz, $Si(CH_3)_3$], 0.7 [d, $^3J$(C,P) = 3.6 Hz, $Si(CH_3)_3$], 30.6 [pseudo-t, $^1J$(C,P) = 67.7 Hz, C6], 33.6 [d, $^3J$(C,P) = 12.2 Hz, $C(CH_3)_3$], 42.4 [d, $^2J$(C,P) = 25.8 Hz, $C(CH_3)_3$], 125.3–134.6 (phenyl-C), 134.6, 140.9 (each s, *ipso*-C), 148.4 (s, C3), 160.4 [d, $^1J$(C,P) = 69.3 Hz, C4]; $^{31}$P NMR ($C_6D_6$): $\delta = -87.9, -283.5$ [each d, $^1J$(P,P) = 177 Hz]; IR (film): $\tilde{\nu} =$ 3050 (m), 2950 (s), 2900 (s), 1590 (s), 1470 (w), 1430 (w), 1390 (m), 1350 (m), 1240 (s), 1070 (w), 1030 (w), 910 (w), 900 (w), 820 (s), 760 (m), 700 (s), 620 (w) $cm^{-1}$; MS (70 eV, EI): *m/z* (%) = 556 (25) [$M^+$], 483 (15) [$M^+$ − Tms], 396 (12) [$M^+$ − Tms − PhC], 73 (100) [$Tms^+$].

**2,4-Di-*tert*-butyl-5-phenyl-6,6-bis(trimethylsilyl)-6*H*-1,3,6-oxaphosphasiline (20a)**: A solution of **18a** (42 mg, 0.35 mmol) in tetrahydrofuran (1 mL) was added slowly to a solution of **4a** (150 mg, 0.35 mmol) in tetrahydrofuran (1 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and was then stirred for 12 h at 20 °C. The solvent was removed at 20 °C ($10^{-2}$ mbar) and the residue was purified by bulb-to-bulb distillation to afford **20a** (80 mg, 51 %) as a yellow oil. B.p. 200 °C ($10^{-3}$ mbar); $^1$H NMR ($CD_2Cl_2$): $\delta =$ 0.15 [s, 18H, $Si(CH_3)_3$], 1.15 (s, 9H, *t*Bu), 1.3 [d, $^4J$(H,P) = 2.0 Hz, 9H, *t*Bu], 7.0–7.4 (m, 5H, phenyl-H); $^{13}$C NMR ($CD_2Cl_2$): $\delta = -0.62$ [s, $Si(CH_3)_3$], 29.1 [d, $^3J$(C,P) = 13.7 Hz, $C(CH_3)_3$], 32.8 [d, $^3J$(C,P) = 14 Hz, $C(CH_3)_3$], 42.8 [d, $^2J$(C,P) = 27.3 Hz, $C(CH_3)_3$], 43.1 [d, $^2J$(C,P) = 24.1 Hz, $C(CH_3)_3$], 125.6, 127.9, 128.2, 145.1 (each s, phenyl-C), 134.6 [d, $^2J$(C,P) = 7.3 Hz, C5], 161.5 [d, $^1J$(C,P) = 58.2 Hz, C4], 217.6 [d, $^1J$(C,P) = 79.3 Hz, C2]; $^{31}$P NMR ($CD_2Cl_2$): $\delta = +91.0$ (s); IR (film): $\tilde{\nu} =$ 2950 (s), 2900 (w), 1700 (m), 1470 (w), 1400 (w), 1360 (w), 1250 (s), 1070 (s), 840 (s), 700 (m) $cm^{-1}$.

**1-(4-*tert*-Butyl-5-phenyl-6,6-bis(trimethylsilyl)-6*H*-1,3,6-oxaphosphasilin-2-yl)ferrocene (20b)**: A solution of **18b** (87 mg, 0.36 mmol) in tetrahydrofuran (1 mL) was added slowly to a solution of **4a** (150 mg, 0.35 mmol) in tetrahydrofuran (1 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and was then stirred for 24 h at 20 °C. The solvent was removed at 20 °C ($10^{-2}$ mbar) and the residue was purified by chromatography (silica gel (12 g), *n*-pentane/diethyl ether 5:1) followed by recrystallization from *n*-pentane at −78 °C to afford **20b** (140 mg, 70 %) as red crystals. M.p. 135 °C; $^1$H NMR ($C_6D_6$): $\delta = 0.4$ [s, 18 H, $Si(CH_3)_3$], 1.5 (s, 9 H, *t*Bu), 4.2–4.5 (m, 7 H, cyclopentadienyl-H), 5.1 (m, 2 H, cyclopentadienyl-H), 7.1–7.4 (m, 5 H, phenyl-H); $^{13}$C NMR ($C_6D_6$): $\delta = -0.3$ [s, $Si(CH_3)_3$], 33.4 [d, $^3J$(C,P) = 14.1 Hz, $C(CH_3)_3$], 42.8 [d, $^2J$(C,P) = 25.8 Hz, $C(CH_3)_3$], 67.7 [d, $^3J$(C,P) = 13.7 Hz, C2′], 70.5 (s, C4′), 70.6 (s, C3′), 86.7 [d, $^2J$(C,P) = 38.0 Hz, C1′], 125.8, 127.6, 128.5 (each s, phenyl-C), 136.0 [d, $^2J$(C,P) = 7.8 Hz, C5], 145.8 (s, *ipso*-C), 163.4 [d, $^1J$(C,P) = 57.3 Hz, C4], 204.3 [d, $^1J$(C,P) = 66.4 Hz, C2]; $^{31}$P NMR ($C_6D_6$): $\delta = +92.0$ (s); IR (film): $\tilde{\nu} = 3080$ (w), 3060 (w), 3040 (w), 2950 (vs), 2895 (s), 1700 (w), 1650 (m), 1590 (m), 1476 (s), 1390 (m), 1360 (m), 1240 (vs), 1190 (m), 1160 (m), 1100 (s), 1060 (s), 1025 (s), 1000 (w), 980 (w), 910 (w), 885 (s), 840 (vs), 770 (s), 750 (s), 700 (s) cm$^{-1}$; $C_{29}H_{41}FeOPSi_3$ (576.7): calcd C 60.4, H 7.2; found C 60.4, H 7.3.

**Methyl 4-*tert*-butyl-5-phenyl-6,6-bis(trimethylsilyl)-6*H*-1,3,6-oxaphosphasiline-2-carboxylate (20c)**: A solution of **18c** (30 mg, 0.25 mmol) in diethyl ether (2 mL) was added dropwise to a solution of **4a** (110 mg, 0.25 mmol) in diethyl ether (3 mL) at −78 °C. The color of the reaction mixture changed to yellow. The solution was allowed to warm to room temperature, the solvent was removed at 20 °C ($10^{-2}$ mbar), and the residue was dissolved in *n*-pentane (10 mL). Filtration through Celite and recrystallization from *n*-pentane gave **20c** (80 mg, 72 %) as yellow crystals. M.p. 83 °C; $^1$H NMR ($C_6D_6$): $\delta = 0.3$ [s, 18 H, $Si(CH_3)_3$], 1.3 (s, 9 H, *t*Bu), 3.55 (s, 3 H, $CO_2Me$), 7.0–7.3 (m, 5 H, phenyl-H); $^{13}$C NMR ($C_6D_6$): $\delta = -0.36$ [s, $Si(CH_3)_3$], 33.1 [d, $^3J$(C,P) = 13.5 Hz, $C(CH_3)_3$], 42.7 [d, $^2J$(C,P) = 27.1 Hz, $C(CH_3)_3$], 51.7 (s, $CO_2CH_3$), 126.3, 127.1, 128.6 (each s, phenyl-C), 142.6 [d, $^2J$(C,P) = 6.2 Hz, C5], 144.3 (s, *ipso*-C), 161.5 [d, $^1J$(C,P) = 54.8 Hz, C4], 165.3 [d, $^2J$(C,P) = 33.4 Hz, $CO_2$Me], 187.1 [d, $^1J$(C,P) = 64.7 Hz, C2]; $^{31}$P NMR ($C_6D_6$): $\delta = +172.0$ (s); IR (film): $\tilde{\nu} = 2950$ (s), 2900 (m), 1750 (s), 1720 (s), 1470 (w), 1430 (w), 1390 (w), 1360 (w), 1250 (s), 1070 (s), 1020 (s), 830 (vs), 700 (m), 620 (w) cm$^{-1}$.

**4-*tert*-Butyl-1-diphenylphosphano-3-phenyl-2,2-bis(trimethylsilyl)-1,2-dihydro-1,2-phosphasilete (22)**: Compound **21** (75 mg, 0.34 mmol) was added to a solution of **4a** (150 mg, 0.35 mmol) in diethyl ether (3 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and was then stirred for 12 h at 20 °C. The solvent was removed at 20 °C ($10^{-2}$ mbar) and the residue was purified by bulb-to-bulb distillation to furnish **22** (150 mg, 80 %) as a yellow oil. B.p. 175 °C ($10^{-3}$ mbar); $^1$H NMR ($C_6D_6$): $\delta = 0.20$, 0.50 [each s, 9 H, $Si(CH_3)_3$], 1.1 (s, 9 H, *t*Bu), 7.0–8.3 (m, 15 H, phenyl-H); $^{13}$C NMR ($C_6D_6$): $\delta = 0.06$ [s, $Si(CH_3)_3$], 1.1 [d, $^3J$(C,P) = 4.9 Hz, $Si(CH_3)_3$], 31.6 [d, $^3J$(C,P) = 4.5 Hz, $C(CH_3)_3$], 41.1 [d, $^2J$(C,P) = 13.3 Hz, $C(CH_3)_3$], 125.6–136.6 (phenyl-C), 141.4 [dd, $^1J$(C,P) = 22.6 Hz, $^2J$(C,P) = 5.8 Hz, *ipso*-C], 142.2 [dd, $^1J$(C,P) = 28.8 Hz, $^2J$(C,P) = 9.8 Hz, *ipso*-C], 145.3 [d, $^3J$(C,P) = 4.4 Hz, *ipso*-C], 151.6 [dd, $^2J$(C,P) = 19.0 Hz, $^3J$(C,P) = 8.6 Hz, C3], 167.9 [dd, $^1J$(C,P) = 27.1 Hz, $^2J$(C;P) = 8.6 Hz, C4]; $^{31}$P NMR ($C_6D_6$): $\delta = -10.8, -79.6$ [each d, $^1J$(P,P) = 186.2 Hz]; IR (film): $\tilde{\nu} = 3050$ (m), 2950 (vs), 2900 (s), 1600 (m), 1580 (w), 1570 (w), 1480 (s), 1430 (s), 1360 (w), 1250 (s), 1070 (w), 1030 (w), 840 (vs), 770 (m), 740 (s), 700 (s) cm$^{-1}$.

**4-*tert*-Butyl-3-phenyl-2,2-bis(trimethylsilyl)-1,2-dihydro-1,2-phosphasilete (23)**: A solution of **4a** (100 mg, 0.23 mmol) in tetrahydrofuran (1 mL) was stirred for 12 h at 70 °C. After removal of the solvent at 20 °C ($10^{-2}$ mbar), the remaining oil was purified by bulb-to-bulb distillation to furnish **23** (70 mg, 80 %) as a colorless oil. Compound **23** is extremely sensitive to moisture. B.p. 130 °C ($10^{-3}$ mbar); $^1$H NMR ($C_6D_6$): $\delta = 0.20$, 0.35 [each s, 9 H, $Si(CH_3)_3$], 1.20 (s, 9 H, *t*Bu), 3.40 [d, $^1J$(H,P) = 160 Hz, 1 H, PH], 7.0–7.3 (m, 5 H, phenyl-H); $^{13}$C NMR ($C_6D_6$): $\delta = -0.6, -0.5$ [each s, $Si(CH_3)_3$], 30.4 [d, $^3J$(C,P) = 4 Hz, $C(CH_3)_3$], 40.4 [d, $^2J$(C,P) = 13.3 Hz, $C(CH_3)_3$], 125.3, 126.4, 127.8 (each s, phenyl-C), 145.0 [d, $^3J$(C,P) = 5 Hz, *ipso*-C], 148.9 [d, $^2J$(C,P) = 18.9 Hz, C3], 164.8 [d, $^1J$(C,P) = 17 Hz, C4]; $^{31}$P NMR ($C_6D_6$): $\delta = -173.2$ [$^1J$(P,H) = 160 Hz].

**Crystallographic data**: Data collection was performed on a four-circle diffractometer (Enraf–Nonius CAD4) with $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å) at room temperature. The structures were solved by direct methods and refined by the full-matrix least-squares method on *F* with SHELXTL (Vers. 4.2); molecule plots were obtained with the program XP from SHELXTL.[41]

**Data for 14**: $C_{37}H_{51}O_2PSi_4$ ($M_r$ = 671.1), colorless prisms; $a$ = 12.247(4), $b$ = 15.282(5), $c$ = 21.096(6) Å, $\beta$ = 96.20(2)°, $V$ = 3925(2) Å$^3$, $\rho_{calcd}$ = 1.136 g cm$^{-3}$, monoclinic, $P2_1/n$ (No. 14), $Z$ = 4, $F_{(000)}$ = 1440, $\omega$-scan, $\mu$ = 0.22 mm$^{-1}$, no absorption correction. In the range $4° \le 2\theta \le 48°$ 4525 reflections were measured, of which 4386 ($R_{int}$ = 0.0212) were independent and 3835 [with $I > 1.5\sigma(I)$] were used for the refinement; 397 parameters, $R$ = 0.0626, $R_w$ = 0.1031, residual density: 0.36 and −0.32 e Å$^{-3}$.

**Data for 20b**: $C_{29}H_{41}FeOPSi_3$ ($M_r$ = 576.7), red prisms; $a$ = 11.561(3), $b$ = 15.343(5), $c$ = 10.504(3) Å, $\alpha$ = 99.25(2), $\beta$ = 111.87(2), $\gamma$ = 106.55(2), $V$ = 1581.1(8) Å$^3$, $\rho_{calcd}$ = 1.211 g cm$^{-3}$, triclinic, $P\bar{1}$ (No. 2), $Z$ = 2, $F_{(000)}$ = 614, $\omega$-scan, $\mu$ = 0.66 mm$^{-1}$, no absorption correction. In the range $4° \le 2\theta \le 48°$ 4887 reflections were measured, of which 4601 ($R_{int}$ = 0.0266) were independent and 4295 [with $I > 1.5\sigma(I)$] were used for the refinement; 316 parameters, $R$ = 0.0430, $R_w$ = 0.0595, residual density: 0.41 and −0.41 e Å$^{-3}$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-103016 (**14**) and CCDC-103015 (**20b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

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