ArP=C=Si(Ph)Tip: The First Allenic Compound with Doubly Bonded Phosphorus and Silicon

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Abstract: The first allenic compound with doubly bonded silicon and phosphorus, the 3-phospha-1-silaallene **1**, has been obtained by dechlorination of the corresponding (chlorosilyl)chlorophosphaalkene **10** with *tert*-butyllithium at low temperature. Compound **1** was characterized by ^{13}C NMR ($\delta = 269.1$ for the allenic carbon), ^{29}Si NMR ($\delta = 75.7$), and ^{31}P NMR spectroscopy ($\delta = 288.7$), and by addition of methanol to the Si=C double bond. In the absence of a trapping agent, **1** dimerizes above $-30\,^{\circ}$C to afford two types of dimers: **14**, formed over one Si=C and one P=C double bond, and **15**, formed over two Si=C double bonds, probably according to a concerted pathway. A thermodynamic equilibrium has been observed between the two stereoisomers **15** and **16** involving an isomerization around the P=C double bond. Compound **16** has been structurally characterized, displaying a nearly planar 1,3-disilacyclobutane ring with the two phenyl (Ph) and the two 2,4,6-tri-*tert*-butylphenyl (Ar) groups on the same side of this ring and the two 2,4,6-triisopropylphenyl (Tip) groups on the other side.

Keywords: disilacyclobutane · phosphaalkenes · phosphasilaallene · phosphorus · silicon

Introduction

Many silenes >Si=C<,[1] heavy homologs of alkenes, and phosphaalkenes −P=C<,[2] heavy homologs of imines, have been synthesized in the last two decades and isolated as monomers owing to a large steric hindrance that is the main stabilizing factor. The preparation of heavy homologs of other important organic functions such as alkynes, dienes, heterocumulenes, and so on is now a fast-growing area and constitutes a great challenge. Among such derivatives, compounds with cumulative double bonds are of particular interest, due to their unique geometric and electronic structure. Phosphaallenes −P=C=X (X: C,[3a–i] Ge,[3j] N,[3k–n] P,[3a,b,d,o,r] As,[3s] O,[3t] S[3u]) have begun to be well-known, since some of them have been prepared recently; however this is not the case for allenic compounds of silicon, germanium, and tin, which are still very rare. Some 1-silaallenes >Si=C=C<[4] have been postulated as intermediates in pyrolysis or photolysis reactions, but only very few of them have been stabilized so far by a large steric hindrance, by West et al.,[5] or by complexation with a complex of ruthenium.[6] A 3-sila-1-azaallene >Si=C=N− has also been postulated by Weidenbruch as intermediate[7a] and a formal 3-stanna-1-azallene has been isolated by Grützmacher.[7b] Recently stable germaallenes >Ge=C=C< have been reported by West[8] and Okazaki.[28]

We describe in this paper the synthesis, the physicochemical data, and the preliminary aspects of the reactivity of the first allenic compound with both doubly bonded silicon and phosphorus, the 3-phospha-1-silaallene ArP=C=Si(Ph)Tip **1** (Ar: 2,4,6-tri-*tert*-butylphenyl, Tip: 2,4,6-triisopropylphenyl).

Results and Discussion

In order to have a phosphasilaallene stable enough to allow its characterization by physicochemical methods, we have used the extremely bulky 2,4,6-tri-*tert*-butylphenyl group (Ar) on phosphorus; this is widely used in P$^{\mathrm{II}}$ chemistry.[2] To afford a further insight into the nature of the dimerization of the Si=C double bond (concerted or multistep diradicalar mechanism that is now controversial), we have attached two different groups: a phenyl and the bulky 2,4,6-triisopropylphenyl group (Tip) to the silicon atom.

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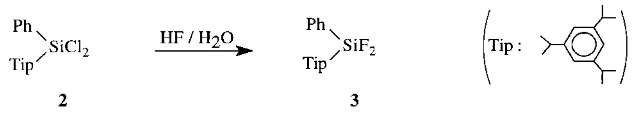
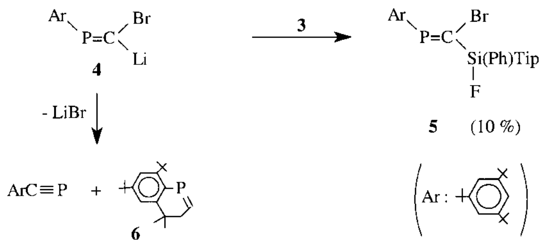
Synthesis and characterization of 1: As the P=C double bond is much less reactive than the Si=C double bond, we first formed the P=C unsaturation, which should be inert during the rest of the process. Thus the synthesis of **1** involved the preliminary preparation of the (halogenosilyl)halogenophosphaalkenes ArP=C(X)Si(Y)(Ph)(Tip) (X = Br, Y = F: **5**; X = Cl, Y = F: **9**,Y = Cl: **10**) followed by a dehalogenation.

Starting compounds for the synthesis of these derivatives are the dichlorosilane **2**[9] and the difluorosilane **3** (Scheme 1). Compound **2** was obtained by a similar procedure to that already described,[9] but with THF instead of hexane as solvent for the preparation of TipLi. Treatment of **2** with aqueous hydrofluoric acid gave its difluoro homolog **3**.

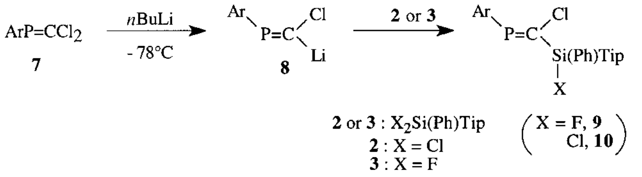


Scheme 1. Synthesis of difluorosilane **3**.

Treatment of **3** with the carbenoid ArP=C(Br)Li **4**, obtained according to the procedure of Bickelhaupt[10] from ArP=CBr$_2$, afforded the silylphosphaalkene **5** [^{31}P NMR: δ = 340.7 (d, ^3J(P,F) = 18.8 Hz)] only in a very poor yield (10 %). The two main products were the phosphaalkene **6**[11] and the phosphaalkyne ArC≡P, arising from the decomposition of ArP=C(Br)Li around $-80\,^\circ$C before its reaction with the difluorosilane **3,** which is very slow at this temperature because of the steric hindrance (Scheme 2); a similar formation of ArC≡P was reported by Bickelhaupt in the decomposition of ArP=C(Li)I.[10a]



Scheme 2. Preparation of **5**.



Scheme 3. Synthesis of **9** and **10**.

By contrast, reaction of **2** or **3** with the chlorocarbenoid **8**,[12] which is much more stable as it can be handled to room temperature without decomposition, afforded **9** and **10** in excellent yields (Scheme 3). Only one isomer was obtained for **9** and **10**, probably the *Z* isomer. The formation of this isomer can be reasonably explained by the preferential substitution of chlorine at the less-hindered side of the P=C double bond to form the *Z* carbenoid.[10] Further reaction with the silanes **2** and **3** afforded **9** and **10** with the silicon group in a *trans* position to the huge Ar group.

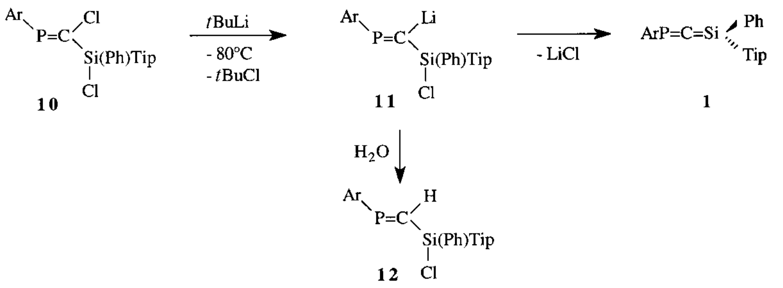
Abstract in French: *Le premier composé allénique comportant à la fois un atome de silicium et un atome de phosphore doublement liés, le 3-phospha-1-silaallène **1**, a été obtenu par déchloration du (chlorosilyl)chlorophosphaalcène **10** correspondant par le tert-butyllithium à basse température. **1** a été caractérisé à la fois par RMN ^{13}C (δ = 269.1 pour le carbone allénique), ^{29}Si (δ = 75.7), ^{31}P (δ = 288.7) et par addition de méthanol sur la double liaison Si=C. En l'absence de réactif de piégeage, **1** se dimérise au-dessus de $-30\,^\circ$C pour conduire à deux types de dimères: **14**, impliquant une double liaison Si=C et une double liaison P=C, et **15**, via deux doubles liaisons Si=C selon probablement un mécanisme radicalaire. Un équilibre thermodynamique a été observé entre les deux stéréoisomères **15** et **16**, dû à une isomérisation Z/E de la double liaison P=C.*

***16** a été caractérisé par une étude cristallographique par rayons X qui montre un cycle 1,3-disilacyclobutane pratiquement plan avec les groupes phényles et Ar du même côté de ce cycle et les groupes Tip de l'autre côté.*

Compounds **9** and **10** were clearly identified by multinuclear NMR spectroscopy and by mass spectroscopy. In the ^{1}H NMR spectrum, the main feature is the presence of two doublets (coupling with phosphorus) for the ortho *tert*-butyl groups; this is due to a hindered rotation of the Ar group. Such a result proves the high steric hindrance occurring in these derivatives. The two diastereotopic methyls of *o-i*Pr resonate as expected as two doublets, while the methyls of *p-i*Pr are isochronous. In the ^{29}Si NMR spectrum, a rather large ^2J coupling constant is observed between silicon and phosphorus (**9**: 54.3 Hz, **10**: 54.7 Hz).

The reaction of **10** with *t*Buli was monitored by variable temperature ^{31}P NMR spectroscopy between $-90\,^\circ$C and 20 °C. Addition of one equivalent of *tert*-butyllithium to **10** in a mixture toluene/Et$_2$O (90:10) immediately afforded the lithio compound **11,** which was evidenced by a low field signal in ^{31}P NMR (δ = 417.6) and by hydrolysis leading to **12** [^{31}P NMR: δ = 347.5 (^2J(P,H) = 24 Hz)]. Gradually warming **11** to $-60\,^\circ$C showed the elimination of LiCl and the formation of the expected phosphasilaallene **1**. The complete decomposition of **11** was observed around $-60\,^\circ$C to afford **1** in about 60 % yield (Scheme 4).

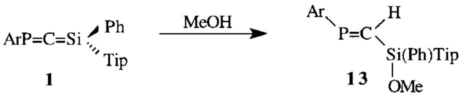
The structure of **1** was proved by characteristic low-field chemical shifts in ^{13}C, ^{29}Si, and ^{31}P NMR spectra, comparable with those reported in sila- or phosphaallenes: ^{31}P NMR: δ = 288.7 (δ = 240.0 in ArP=C=GeMes$_2$[3j]); ^{13}C NMR: δ of the allenic carbon = 269.1 (^1J(C,P) = 45.8 Hz) (δ = 280.9 in ArP=C=GeMes$_2$,[3j] δ = 276.2 in ArP=C=PAr,[3a,o,p] and δ = 299.5 in ArP=C=AsAr[3s]); ^{29}Si NMR: δ = 75.7 (^2J(Si,P) = 18.3 Hz). The allenic carbon and silicon in **1** are slightly deshielded, in comparison with those of West's stable silaallenes, δ = 225.7 and 48.4 in Ar(Ad)Si=C=CR$_2$ (CR$_2$: substituted fluorenyl, Ad: adamantyl[5a]), δ = 227.9 and 55.1 in Ar(*t*Bu)Si=C=CPh$_2$),[5b] δ = 216.3 and 55.1 in Ar(*t*Bu)-Si=C=C(Ph)*t*Bu, respectively.[5b] A much stronger shielding



Scheme 4. Synthesis of the 3-phospha-1-silaallene **1**.

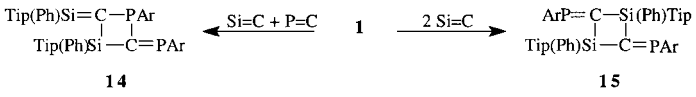
(+13.1 ppm[5b]) was observed in ^{29}Si NMR for the silaallene Tip$_2$Si=C=C(Ph)tBu bearing two aromatic groups on silicon.

Addition of methanol to a solution of **1** at −60 °C results in the formation of adduct **13**; a chemo- and regiospecific reaction was observed with exclusive addition to the Si=C double bond according to the expected Si$^{\delta+}$=C$^{\delta-}$ polarity. The sole *E* isomer was obtained, as proved by the value of the ^{2}J(P,H) coupling constant (23.5 Hz) (Scheme 5). A similar coupling constant was obtained in **12** (23.5 Hz). In a *Z* isomer, this constant should be smaller (the ^{2}J(P,H) in the *E* and *Z* isomers of ArP=C(H)SiMe$_3$ are 24.7 and 18.0 Hz[10], respectively). The magnitude of these ^{2}J(P,H) coupling constants in *Z* and *E* isomers has been discussed by Bickelhaupt,[10a] who postulated that the electronegativity of the substituents on carbon plays a great role (in our case low electronegativity of silicon) to explain this change in the *cis* rule.



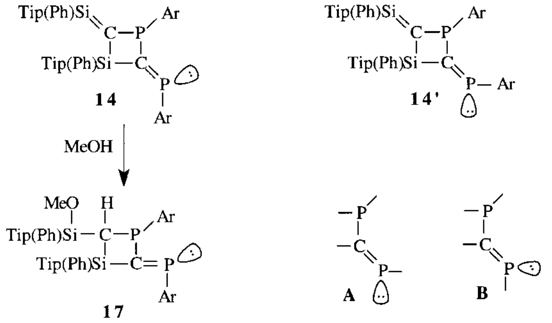
Scheme 5. Reactivity of the phosphasilaallene with MeOH.

Dimerization of 1: Above −20 °C and in the absence of trapping reagent, the phosphasilaallene **1** gives two types of dimer: the unsymmetrical dimer **14** due to the dimerization between one P=C and one Si=C double bond, and the expected head-to-tail dimer **15** resulting from the dimerization over two Si=C double bonds. The ratio between **14** and **15** is about 60:40 (Scheme 6). Compound **15** is not formed through intermolecular elimination of LiCl, since it appears when the signal of **1** decreases, by which time **11** has already completely decomposed. A similar dimerization was reported for the germaphosphaallene Mes$_2$Ge=C=PAr.[3j]



Scheme 6. Dimerization of **1**.

*Unsymmetrical dimer **14***: Attempts to obtain pure **14** by fractional crystallization failed. Its structure was established in ^{31}P NMR spectroscopy and has an AX spectrum with the expected low-field shift for the dicoordinate phosphorus atom ($\delta = +294.9$) and a signal at higher field ($\delta = +66.8$) for the tricoordinate phosphorus atom. From the large ^{2}J(P,P) coupling constant (224 Hz), it seems that the structure of **14** involves the two Ar groups in a *trans* position, which allows a relief of the steric hindrance: the literature data show that the ^{2}J(P,P) coupling constant is generally around 15–30 Hz in *cis* structures **A** (such as **14′**), whereas it is much larger (100 Hz and even more) in *trans* structures **B** (like **14**)[3f, 13, 14] (Scheme 7).



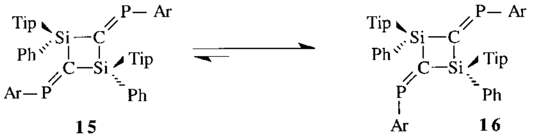
Scheme 7. Unsymmetrical dimer.

Addition of methanol occurred only at the very reactive Si=C double bond of **14**; even with an excess of methanol the P=C double bond was inert. An AX spectrum similar to that of **14** was observed for **17**, with a large ^{2}J(P,P) coupling constant: δ (P=C) = 305, δ (P$^{\mathrm{III}}$) = 40.5 [^{2}J(P,P) = 254 Hz, ^{2}J(P,H) = 17.4 Hz] (according to Albrand et al.[15] who calculated the dihedral dependance of ^{2}J(P,H) spin coupling in phosphorus, the H and the phosphorus lone pair are in a *cis* position; thus, the Ar and Tip(Ph)(OMe)Si groups are also *cis*).

It has been impossible to determine the spatial arrangement around the Si=C double bond and on the tetracoordinate silicon for **14** (Tip in *cis* or in *trans* in relation to the Ar on the tricoordinate phosphorus).

*Dimers formed over the two Si=C bonds, **15** and **16***: Immediately after dimerization, the only dimer formed over the two Si=C bonds was **15**, but when Et$_2$O solutions containing the dimer **15** were kept at room temperature for some days and monitored by ^{31}P NMR, we observed that the signal of **15** at $\delta = 431.9$ decreased and that a new signal at $\delta = 425.4$ attributed to **16** appeared. After 5 days, the ratio **15/16** was about 10:90. This ratio was obtained much faster (2 h) by photolysis in a rayonet ($\lambda = 360$ nm). Isomer **16** was obtained in pure form by crystallization from MeOH/pentane 50:50. When **16** was put again in solution in pentane, the ratio **15/16** rapidly reached (10:90) proving the thermodynamic equilibrium between these two dimers. Interestingly, the color of **16** (red) can be accounted for if some conjugation is made possible through the correct dπ orbital on the ring silicon.

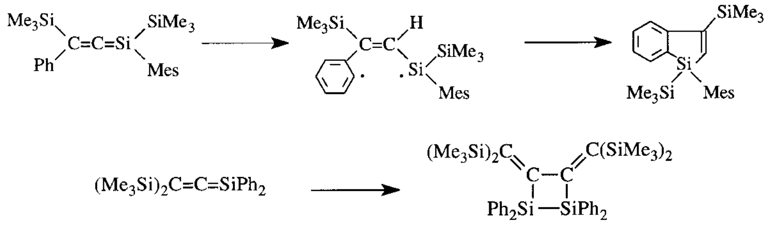
The most characteristic feature in the ^{31}P NMR spectra of **15** and **16** is the very low-field chemical shift, in agreement with a phosphaalkene structure, in which the carbon is bonded to two silicon groups[2a] (for example $\delta = 393$ in $ArP{=}C(SiMe_3)_2$[16l]). The structure of **16** was established by an X-ray structure determination; this shows that the two Tip groups are in a *cis* position and that the two Ar groups are also in a *cis* position relative to the $P{=}C \cdot\cdot C{=}P$ axis. We can deduce from this that **15** has the two Ar groups in a *trans* position, which is the only other possibility of isomerization since silicon is configurationally stable (Scheme 8).



Scheme 8. Isomerization of **15**.

The driving force for this surprising isomerization was the decreasing of the steric hindrance when the two Ar groups are located on the same side as the two phenyl groups in relation to the disilacyclobutane ring instead of being on the same side as the Tip groups.

Dimerization in other main-group allenic derivatives: The formation of the two dimers **14** and **15** does not correspond to the previously reported dimerization of transient silallenes $>Si{=}C{=}C<$; for example, Ishikawa observed a rearrangement leading to a bicyclic compound[4c,d] or a head-to-head dimerization depending on the groups on silicon and carbon (Scheme 9). Various types of dimerization occur from phospha-heterocumulenes $-P{=}C{=}X$: a head-to-tail dimerization between two P=C bonds was reported for tBuP=C=O,[3t] a dimerization involving one P=C and one C=S bonds in ArP=C=S,[3u] two types of dimerization on ArP=C=N–[3n] depending on the experimental conditions (Scheme 10), and a head-to-tail dimerization between two C=Si for $PhN{=}C{=}Si\mathit{t}Bu_2$[7a] (Scheme 11).

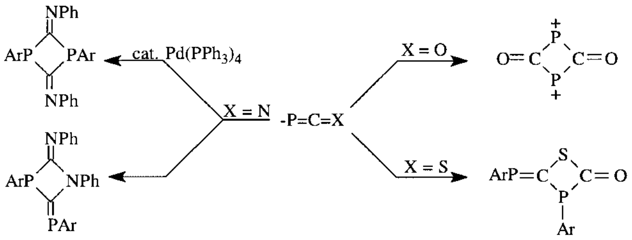


Scheme 9. Dimerization of transient silaallenes.

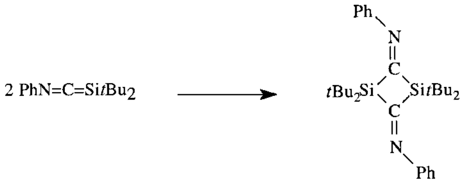
Note that the dimerization of ketenes occurs according to a similar fashion as **1**, since the formation of both symmetrical and unsymmetrical dimers are observed leading to a dione (two C=C bonds involved) and a lactone (one C=C and one C=O bond); with alkyl or aryl groups on carbon, the dione product is generally the major one.

X-ray structure determination of 16 (see Tables 1 and 2, and Figure 1): The four-membered disilacyclobutane ring is nearly planar: the folding is 4.7(8)° along the C1 ··· C2 axis and 5(1)° along the Si1 ··· Si2 axis (distances to the Si1-C1-Si2-C2 mean plane: Si1 0.029(5), C1 −0.029(5), Si2 0.028(5), C2 −0.029(5) Å). The intracyclic Si–C bond lengths (1.897(7) to 1.958(8) Å) lie in the normal range as do the P=C double bonds (1.650(7) and 1.656(9) Å).

The sum of the angles on C1 and C2 are close to 360° (357.2 and 357.9°, respectively), displaying a nearly planar arrangement. As shown in Figure 1, the main features in **16** are that the two Ph and the two Ar groups are on the same side in relation to the disilacyclobutane ring and that the two Tip groups are both on the other side of the ring; the distances of the ipso carbons to the Si1-C1-Si2-C2



Scheme 10. Dimerization of phosphacumulenes.



Scheme 11. Dimerization of a silaazaallene.

Table 1. Selected bond lengths [Å] and angles [°] for **16**.

Si1–C1	1.897(7)	C1-Si1-C2	89.3(4)	C2-Si2-C39	107.8(3)
Si1–C2	1.907(9)	C1-Si2-C2	86.3(3)	C24-Si2-C39	106.3(4)
Si2–C1	1.952(9)	Si1-C1-Si2	92.3(3)	Si1-C1-P1	144.9(5)
Si2–C2	1.958(8)	Si1-C2-Si2	91.9(4)	Si2-C1-P1	120.0(4)
C1–P1	1.650(7)	C1-Si1-C3	115.6(3)	Si1-C2-P2	144.8(5)
C2–P2	1.656(9)	C1-Si1-C18	107.0(3)	Si2-C2-P2	121.2(5)
P1–C45	1.878(8)	C3-Si1-C18	115.1(3)	C1-P1-C45	115.5(4)
P2–C63	1.846(8)	C2-Si1-C3	115.5(3)	C2-P2-C63	112.4(4)
Si1–C3	1.918(7)	C2-Si1-C18	111.4(4)		
Si1–C18	1.888(7)	C1-Si2-C24	121.4(4)		
Si2–C24	1.928(9)	C1-Si2-C39	109.3(4)		
Si2–C39	1.885(9)	C2-Si2-C24	124.1(4)		

Table 2. Selected torsion angles [°] for **16**.

Si1–C1-P1-C45	−6.8(9)
Si2-C1-P1-C45	−161.3(4)
Si1-C2-P2-C63	+8.6(9)
Si2-C2-P2-C63	+165.9(4)
C2-Si1-C1-P1	+154.5(8)
C2-Si2-C1-P1	−162.2(5)
C1-Si1-C2-P2	−157.2(8)
C1-Si2-C2-P2	+163.7(5)

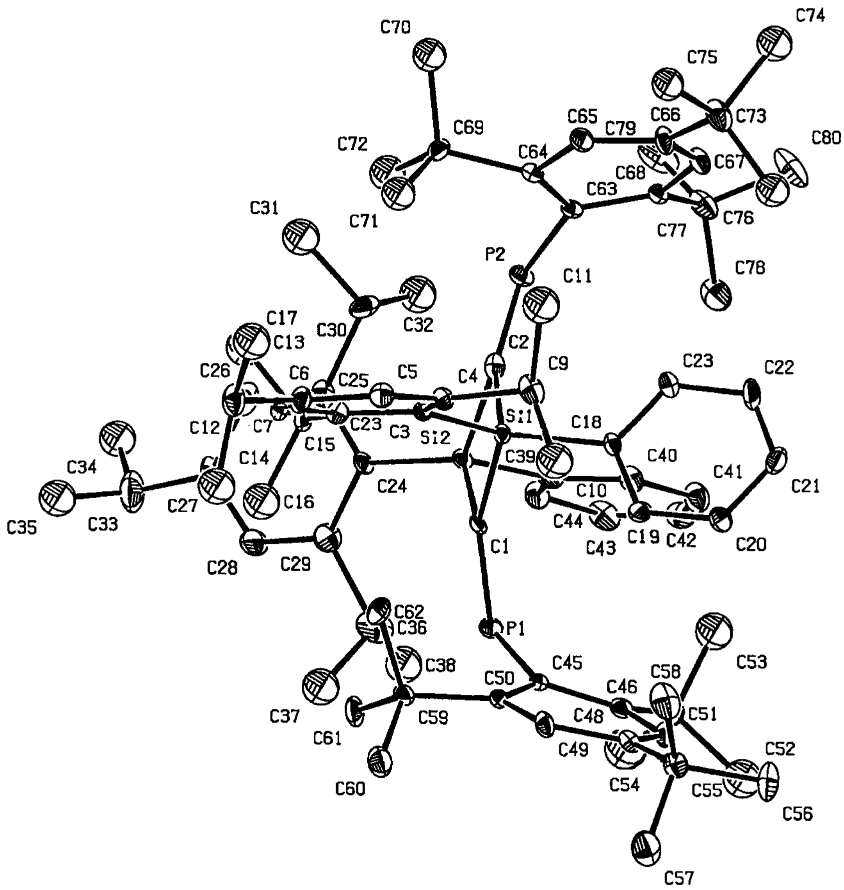


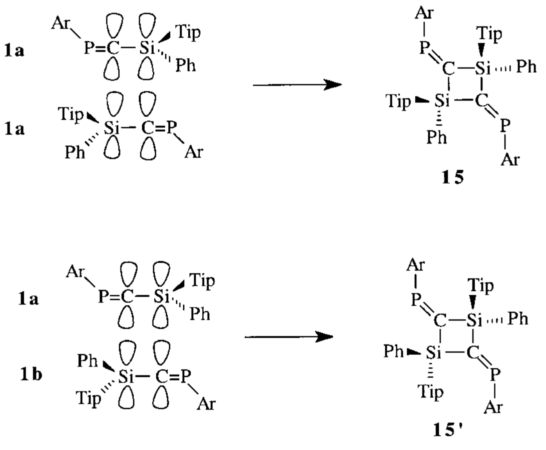
Figure 1. PLATON[26] view of **16**, ellipsoids are drawn at 10 % probability level.

plane are: C18 (Ph): – 1.606(14), C39 (Ph) – 1.645(17) Å; C45 (Ar) – 1.032(29), C63 (Ar) – 0.782(30) Å; C3 (Tip) + 1.611(14), C24 (Tip) + 1.370(16) Å. Owing to the poor refinement of the structure, rather important errors are observed on these distances. However, these values, even if they are only indicative, prove the geometry of **16**.

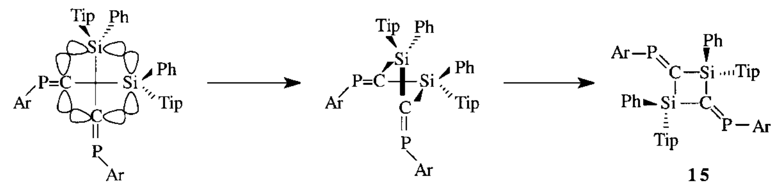
Mechanism of the head-to-tail dimerization to 15: Many theoretical[17, 18] and experimental[19, 20] studies have been devoted to the mechanistic aspects of the dimerization of silenes (to form 1,3-disilacyclobutanes), which remain controversial: Schaefer[17] postulates a concerted $[2\pi_s+2\pi_s]$ mechanism, whereas Bernardi[18] thinks that such a $[2\pi_s+2\pi_s]$ cycloaddition proceeds by a stepwise mechanism involving the formation of a short-lived biradical intermediate. The stereospecificity of the dimerization (only the most crowded isomer with the two bulkier groups (Tip) *cis* in the 1,3-disilacyclobutane ring was obtained) and the lack of dependence on solvent polarity (ether, toluene and so on) suggest a concerted mechanism.

According to the Woodward-Hoffmann rules,[21] a concerted supra–supra process ($[2\pi_s+2\pi_s]$) is forbidden. However, the polarization of the double bond in the reactant (which is the case in **1**) is often supposed to lead to a relaxation of these rules.[22] Due to the large difference of steric hindrance between every group on silicon (Tip and Ph) and on phosphorus (Ar and lone pair), the approach of the two molecules of **1** probably occurs according to Scheme 12. From the two of the same enantiomers, **1a** or **1b**, the dimer **15** is formed, whereas dimer **15′** with the Tip groups *trans* should be obtained by a dimerization between **1a** and **1b**. As only **15** is formed, specific effects due to the nature of the frontier orbitals could favor such a coupling between two same enantiomers in the concerted mechanism.

A concerted supra–antara process ($[2\pi_s+2\pi_a]$) is allowed, but is expected to have higher activation energy because of large steric effects. Thus, such a mechanism is supposed not to occur with silenes, but is considered as the most probable in [2+2] cycloadditions involving ketenes[23] or allenes. In our case, the approach which seems sterically most favorable is displayed on Scheme 13. This would give the dimer **15**.



Scheme 12. Concerted process $[2\pi_s+2\pi_s]$.



Scheme 13. Concerted process $[2\pi_s+2\pi_a]$.

Of course, the observed stereospecificity does not settle the matter of whether the mechanism is concerted or stepwise. The latter two-stage mechanism cannot be totally excluded since, as a result of the large steric hindrance caused by Ar and Tip groups, one type of approach to form the first Si–C bond and then to close into the four-membered ring should be largely favored, thus leading also to stereospecificity.

Experimental Section

All experiments were carried out in flame-dried glassware under N_2 atmosphere with high-vacuum line techniques. Solvents were dried and freshly distilled from sodium benzophenone ketyl and carefully deoxygenated over the vacuum-line by several freeze-pump-thaw cycles. NMR spectra were recorded in $CDCl_3$ on the following spectrometers: ^{1}H, Bruker AC80 (80.13 MHz) and AC200 (200.13 MHz); ^{13}C {^{1}H}, Bruker AC200 (50.32 MHz; reference TMS); ^{29}Si, Bruker AC200 (59.628 MHz; reference TMS); ^{31}P, Bruker AC200 (81.015 MHz; reference H_3PO_4 85 %). Mass spectra were obtained on a Hewlett–Packard 5989 A spectrometer by EI at 70 eV. Melting points were determined on a Wild Leitz-Biomed apparatus. Elemental analyses were performed by the Service de Microanalyse de l'Ecole de Chimie de Toulouse.

Dichloro(phenyl)(2,4,6-triisopropylphenyl)silane (**2**): The procedure was slightly different from the procedure described by Bickelhaupt.[9] A solution of *n*-butyllithium in hexane (1.6 M, 24 mL, 38.40 mmol) was slowly added to TipBr (10.00 g, 35.34 mmol) in THF (50 mL) cooled at −50 °C. After 3 h stirring at −50 °C, trichlorophenylsilane (7.40 g, 35.34 mmol) was added to the solution of TipLi through syringe. The reaction mixture was allowed to warm to room temperature and was refluxed for 1.5 h. After removal of LiCl by filtration, the small amount of TipH, formed by hydrolysis of TipLi, and of the starting TipBr were removed under vacuum. Compound **2** was isolated as a waxy solid and identified by comparison with its literature data[9] (12.02 g, 90 %).

Difluoro(phenyl)(2,4,6-triisopropylphenyl)silane (**3**): A large excess of a solution at 40 % of hydrofluoric acid in water (8.75 g, 158 mmol) was added to **2** (12 g, 31.6 mmol) in benzene. After 2 h stirring at room temperature, the volatile materials were removed under vacuum, and Et_2O and water were added to the residue. The two layers were separated, and the organic layer was dried over Na_2SO_4. After one night, Et_2O was removed under vacuum, and the small amount of TipH formed was removed by distillation. Compound **3** was isolated in the distillation flask as a waxy solid (9.09 g, 83 %, m.p. 56 °C). ^{1}H NMR: $\delta = 1.20$ (d, ^{3}J(H,H) = 6.6 Hz, 12 H; *o*-CH*Me*$_2$), 1.31 (d, ^{3}J(H,H) = 6.6 Hz, 6 H; *p*-CH*Me*$_2$), 2.93 (sept, ^{3}J(H,H) = 6.6 Hz, 1 H; *p*-C*H*Me$_2$), 3.25 (sept, t, ^{3}J(H,H) = 6.6 Hz, ^{5}J(H,F) = 1.6 Hz, 2 H; *o*-C*H*Me$_2$), 7.13 (s, 2 H; arom H of Tip), 7.29–7.72 (m, 5 H; arom H of Ph); ^{13}C NMR: $\delta = 23.86$ (*p*-CH*Me*$_2$), 24.99 (*o*-CH*Me*$_2$), 34.42 (*o*-CHMe$_2$), 34.63 (*p*-CHMe$_2$), 121.79 (*m*-CH of Tip), 128.35 (*m*-CH of Ph), 131.77 (*p*-CH of Ph), 134.22 (*o*-CH of Ph), 153.10 (*p*-C of Tip), 157.36 (*o*-C of Tip); ^{19}F NMR: $\delta = -55.7$ (^{1}J(F,Si) = 291 Hz); ^{29}Si NMR: $\delta = -23.8$ (t, ^{1}J(Si,F) = 291 Hz); EI-MS: *m*/*z* (%) = 346 (31) [M^+], 304 (6) [$M^+ - i$Pr+1], 268 (28) [$TipSiF_2^+ - 1$], 253 (52) [$TipSiF_2^+ - Me - 1$], 143 (27) [$PhSiF_2^+$], 43 (100) [*i*Pr$^+$].

Synthesis of 9: The procedure was the same as for **10** (see below), starting from **7** (3.11 g, 8.67 mmol), *n*BuLi in hexane (1.6 M 5.4 mL, 8.70 mmol), **3** (3.00 g, 8.67 mmol), and THF (50 mL). Pure **9** was obtained after crystallization from pentane (4.85 g, 86 %, m.p. 160 °C). ^{1}H NMR: $\delta = 0.86$ (d, ^{3}J(H,H) = 6.4 Hz, 6 H; *o*-CH*Me*Me′), 1.26 (d, ^{3}J(H,H) = 6.8 Hz, 12 H; *o*-CHMe*Me′* and *p*-CH*Me*$_2$), 1.75 (s, 9 H; *p*-*t*Bu), 1.48 (d, ^{5}J(HP) = 0.6 Hz, 9 H; *o*-*t*Bu), 1.54 (d, ^{5}J(HP) = 0.6 Hz, 9 H; *o*-*t*Bu), 2.93 (sept, ^{3}J(H,H) = 6.8 Hz, 1 H; *p*-CHMe$_2$), 3.32 (sept, t, ^{3}J(H,H) = 6.6 Hz, ^{5}J(H,F) = 1.3 Hz; *o*-C*H*MeMe′), 7.08 (s, 2 H; arom H of Tip), 7.50 (d, ^{4}J(HP) = 1.5 Hz; arom H of Ar), 7.30–7.92 (m; arom H of Ph); ^{13}C NMR: $\delta = 23.89$, 24.31 and 24.99 (Me of *i*Pr), 31.48 (*p*-C*Me*$_3$), 34.32 (*p*-CHMe$_2$), 34.73 (d, ^{4}J(C,F) = 4.3 Hz; *o*-CHMeMe′), 35.19 (*p*-CMe$_3$), 37.84 (d, ^{3}J(C,P) = 6.2 Hz; *o*-CMe$_3$), 121.84 (*m*-CH of Tip), 122.03 and 122.30 (*m*-CH of Ar), 124.80 (dd, ^{2}J(C,F) = 12.7 Hz, ^{3}J(C,P) = 2.6 Hz; ipso-C of Tip), 127.81 (*m*-CH of Ph), 130.16 (*p*-CH of Ph), 133.92 (*o*-CH of Ph), 135.90 (dd, ^{2}J(C,F) = 20.8 Hz, ^{3}J(C,P) = 6.3 Hz; ipso-C of Ph), 150.91 (*p*-C of Ar), 151.91 (*o*-C of Ar), 153.01 (d, ^{2}J(C,P) = 1.4 Hz; *o*-C of Ar), 153.63 (*p*-C of Tip), 157.22 (*o*-C of Tip), 167.90 (dd, ^{1}J(C,P) = 79.3 Hz, ^{2}J(C,F) = 12.3 Hz; C=P); ^{19}F NMR: $\delta = -76.6$ (d, ^{3}J(F,P) = 21.5 Hz, ^{1}J(F,Si) = 288 Hz); ^{29}Si NMR: $\delta = -10.0$ (dd, ^{1}J(Si,F) = 288 Hz, ^{2}J(Si,P) = 54.3 Hz); ^{31}P NMR: $\delta = 322.3$ (d, ^{3}J(F,P) = 21.5 Hz); EI-MS: *m*/*z* (%) = 650 (6) [M^+], 635 (20) [$M^+ - Me$], 607 (48) [$M^+ - i$Pr], 593 (58) [$M^+ - t$Bu], 531 (10) [$M^+ - Ph - i$Pr+1], 405 (16) [$M^+ - Ar$], 277 (20) [ArPH$^+$], 203 (5) [Tip$^+$], 57 (100) [*t*Bu$^+$].

Synthesis of 10: The 1-chloro-2-phosphaethenyllithium ArP=C(Cl)Li was obtained by use of the procedure by Yoshifuji[12] from **7**[10] (5.54 g, 15.40 mmole), *n*-butyllithium in hexane (1.6 M, 10.0 mL, 16 mmol) and THF (50 mL) at −78 °C. After half an hour of stirring at this temperature, a solution of **2** (5.85 g, 15.40 mmol) in THF (20 mL) was added. The reaction mixture was stirred for 2 h at −20 °C then warmed to room temperature giving a brown reaction mixture. THF was removed under vacuum then pentane (100 mL) was added, and the lithium salts were filtered off. Crystallization from pentane afforded **10** as a white powder (m.p. 137 °C, 8.52 g, 83 %). ^{1}H NMR: $\delta = 0.97$ (d, ^{3}J(H,H) = 6.6 Hz, 6 H; *o*-CH*Me*Me′), 1.10 (d, ^{3}J(H,H) = 6.6 Hz, 6 H; *o*-CHMe*Me′*), 1.26 (d, ^{3}J(H,H) = 6.9 Hz, 6 H; *p*-CH*Me*$_2$), 1.34 (s, 9 H; *p*-*t*Bu), 1.40 (d, ^{5}J(HP) = 0.5 Hz, 9 H; *o*-*t*Bu), 1.53 (d, ^{5}J(HP) = 0.6 Hz, 9 H; *o*-*t*Bu), 2.90 (sept, ^{3}J(H,H) = 6.9 Hz, 1 H; *p*-C*H*Me$_2$), 3.34 (sept, ^{3}J(H,H) = 6.6 Hz, 2 H; *o*-C*H*MeMe′), 7.03 (s, 2 H; arom H of Tip), 7.35 (d, ^{4}J(HP) = 2.4 Hz, 2 H; arom H of Ar), 7.24 – 7.70 (m, 5 H; arom H of Ph); ^{13}C NMR: $\delta = 23.75$, 24.79, 25.32 (3s, Me of *i*Pr), 31.38 (*p*-C*Me*$_3$), 32.95 (d, ^{4}J(C,P) = 4.6 Hz; *o*-C*Me*$_3$), 33.08 (d, ^{4}J(C,P) = 6.2 Hz; *o*-C*Me*$_3$), 34.32 (*p*-CHMe$_2$), 34.51 (*o*-CHMeMe′), 35.07 (*p*-CMe$_3$), 37.84 (*o*-CMe$_3$), 122.06, 122.13, 122.21, 122.28 (*m*-CH of Ar and Tip), 124.73 (d, ^{3}J(C,P) = 4.3 Hz; ipso-C of Tip), 127.71 (*m*-CH of Ph), 129.83 (*p*-CH of Ph), 134.55 (*o*-CH of Ph), 137.89 (d, ^{3}J(C,P) = 6.6 Hz; ipso-C of Ph), 150.75, 151.92 (2s, *p*-C of Tip and Ar), 153.29 (d, ^{2}J(C,P) = 2.4 Hz; *o*-C of Ar), 153.70 (*o*-C of Ar), 157.34 (*o*-C of Tip), 168.68 (d, ^{1}J(C,P) = 85.6 Hz; C=P); ^{31}P NMR: $\delta = 319.7$; ^{29}Si NMR: $\delta = -6.8$ (d, ^{2}J(Si,P) = 54.7 Hz); EI-MS: *m*/*z* (%) = 666 (7) [M^+], 631 (49) [$M^+ - Cl$], 623 (65) [$M^+ - i$Pr], 609 (51) [$M^+ - t$Bu], 589 (23) [$M^+ - Ph$], 547 (11) [$M^+ - Ph - i$Pr+1], 533 (5) [$M^+ - Ph - t$Bu+1], 421 (39) [$M^+ - Ar$], 277 (10) [ArPH$^+$], 57 (100) [*t*Bu$^+$]; $C_{40}H_{57}Cl_2PSi$ (667.86): calcd C 71.94, H 8.60; found: C 71.99, H 8.78.

Synthesis of 1: Compound **10** (200 mg, 0.3 mmol), [D$_8$]toluene (3 mL) and Et_2O (0.09 mL, 3 equivalents) were placed in a 10 mm diameter NMR tube. After cooling at −80 °C, one equivalent of *tert*-butyllithium in pentane (1.6 M, 0.185 mL, 10 % of excess) was slowly added. The lithio compound **11** was evidenced by a new signal at $\delta = 417.6$. Phosphasilaallene **1** began to be formed immediately from **11** between −60 °C and −70 °C. Compound **1** was characterized at −60 °C by ^{31}P NMR (C_7D_8): $\delta = 288.7$; ^{13}C NMR: $\delta = 269.1$ (d, ^{1}J(C,P) = 45.8 Hz; the allenic carbon); ^{29}Si NMR: $\delta = 75.7$ (d, ^{2}J(Si,P) = 18.3 Hz). Above −30 °C the signal of **1** decreased and those of the dimers began to be observed. When the temperature was raised from −80 °C to 0 °C over 1 h, **1** could be observed even at 0 °C for a short period.

Synthesis of 13: A solution of *t*BuLi in pentane (1.6 M, 0.98 mL, 1.58 mmol) was added to **10** (1.00 g, 1.50 mmol) dissolved in a mixture toluene (10 mL) and Et_2O (1 mL) cooled at −80 °C. The solution immediately became orange then red. After 20 min stirring at −60 °C, a two-fold excess of methanol was added leading to a yellow reaction mixture. The solvents were removed under vacuum, pentane (50 mL) was added, and the lithium salts filtered off. Crystallization from MeOH/pentane (50:50) afforded 0.47 g of white crystals (m.p. 162 °C, 50 %) of **13**. ^{1}H NMR: $\delta = 0.89$ (d, ^{3}J(H,H) = 6.7 Hz, 6 H; *o*-CH*Me*Me′), 1.09 (d, ^{3}J(H,H) = 6.7 Hz, 6 H; *o*-CHMe*Me′*), 1.24 (d, ^{3}J(H,H) = 6.8 Hz, 6 H; *p*-CH*Me*$_2$), 1.34 (s, 9 H; *p*-*t*Bu), 1.50 (s, 18 H; *o*-*t*Bu), 2.95 (sept, ^{3}J(H,H) = 6.8 Hz, 1 H; *p*-C*H*Me$_2$), 3.41 (s, 3 H; OMe), 3.43 (sept, ^{3}J(H,H) = 6.7 Hz, 2 H; *o*-C*H*MeMe′), 6.97 (s, 2 H; arom. H of Tip), 7.24 - 7.55 (m, 5 H; arom. H of Ph), 7.38 (d, ^{4}J(HP) = 1.0 Hz, 2 H; arom H of Ar), 8.16 (d, ^{2}J(HP) = 23.5 Hz, 1 H; P=CH); ^{13}C NMR: $\delta = 23.85$, 24.61, 25.37 (3s, Me of *i*Pr), 31.43 (*p*-C*Me*$_3$), 33.26, 33.85, 34.00, 34.15 (*o*-C*Me*$_3$, *o*-CHMeMe′, *p*-CHMe$_2$), 34.99 (*p*-CMe$_3$), 38.14 (*o*-CMe$_3$), 51.09 (OMe), 121.36 and 121.81 (*m*-CH of Tip and Ar), 126.96 (ipso-C of Tip), 127.61 (*m*-CH of Ph), 129.09 (*p*-CH of Ph), 134.44 (*o*-CH of Ph), 138.70 (d, ^{3}J(C,P) = 5.6 Hz; ipso-C of Ph), 145.00 (d, ^{1}J(C,P) = 71.6 Hz; ipso-C of Ar), 149.44 and 150.38 (*p*-C of Tip and Ar), 152.48 (*o*-C of Ar), 156.91 (*o*-C of Tip), 171.30 (d, ^{1}J(C,P) = 69.3 Hz; P=C); ^{31}P NMR: $\delta = 347.3$; EI-MS: *m*/*z* (%) = 627 (3) [$M^+ - 1$], 585 (3) [$M^+ - i$Pr], 571 (13) [$M^+ - t$Bu], 384 (13)

[M^+ – Ar+1], 352 (15) [M^+ – ArP], 231 (28) [$\mathrm{TipSi^+}$], 43 (100) [$i\mathrm{Pr^+}$]; $\mathrm{C_{41}H_{61}OPSi}$ (628.99): calcd C 78.29, H 9.78; found: C 78.25, H 10.01.

Dimerization of 1: In the absence of trapping reagent, **1** prepared as previously described from **10** (2.00 g, 3.00 mmol) dimerizes above $-20\,°\mathrm{C}$ to afford **14** and **15** in the ratio 60:40. Attempts to separate these two dimers by fractional crystallization from pentane, $\mathrm{Et_2O}$, THF, toluene failed, but **14** and **15** were characterized by their physicochemical data. An excess of methanol was added to this reaction mixture. The ^{31}P NMR study showed that **15** did not react, whereas **14** was transformed into **17**, which could not be obtained in pure form by crystallization and was identified by ^{31}P NMR spectroscopy. After about 10 days in a mixture MeOH/pentane 50/50, red crystals of **16** (formed from **15**) appeared from the solution and were removed by filtration (0.54 g, 30 %, m.p. 90 °C).

*Dimer **14***: ^{31}P NMR: $\delta = 294.9$ (P=C), 66.8 (dd, $^2J(\mathrm{P,P}) = 224$ Hz; $\mathrm{P^{III}}$); ^{29}Si NMR: $\delta = 86.9$ (dd, $^2J(\mathrm{Si,P}) = 70.1$ Hz, $^4J(\mathrm{Si,P}) = 4.3$ Hz).

*Dimer **15***: ^{31}P NMR: $\delta = 431.9$.

*Dimer **16***: ^{1}H NMR: $\delta = 0.80 - 1.32$ (m, 36H; *o*-CH*MeMe′* and *p*-CH*MeMe′*), 1.14 and 1.15 (2s, 2 × 18H; *o*-*t*Bu), 1.30 (s, 18H; *p*-*t*Bu), 2.98 (sept, $^3J(\mathrm{H,H}) = 6.8$ Hz, 2H; *o*-C*H*MeMe′), 3.42 (sept, $^3J(\mathrm{H,H}) = 6.8$ Hz, 1H; *p*-C*H*MeMe′), 3.73 (sept, $^3J(\mathrm{H,H}) = 6.8$ Hz, 1H; *p*-C*H*MeMe′), 4.70 (sept, $^3J(\mathrm{H,H}) = 6.8$ Hz, 2H; *o*-C*H*MeMe′), 6.10 – 7.63 (m, arom H of Ar, Ph and Tip); ^{13}C NMR: $\delta = 23.79$, 24.07 and 24.19 (Me of *i*Pr), 33.65, 33.85, 33.98, 34.09 and 34.27 (Me of *t*Bu, *o*-*C*HMeMe′, and *p*-*C*HMeMe′), 34.88 (*p*-*C*Me$_3$), 38.37 (d, $^3J(\mathrm{PC}) = 5.5$ Hz, *o*-*C*Me$_3$), 121.65, 121.81 and 122.81 (*m*-CH of Tip and *m*-CH of Ar), 126.26, 126.68, 126.91 and 128.21 (*m*-CH of Ph and *p*-CH of Ph), 135.93 and 137.18 (*o*-CH of Ph), 139.52 (d, $^1J(\mathrm{C,P}) = 79.3$ Hz; ipso C of Ar), 149.30, 149.75, 149.83, 153.17 and 156.89 (*o*-C and *p*-C of Tip and Ar); ^{31}P NMR: $\delta = 425.4$; EI-MS: *m*/*z* (%) = 948 (16) [M^+ – Ar+1], 892 (4) [M^+ – Ar+2 – *t*Bu], 687 (17) [M^+ – 2 Ar – Me], 597 (12) [$M/2^+$+1], 539 (13) [$M/2^+$ – *i*Pr – Me+1], 351 (15) [$M/2^+$ – Ar], 275 (22) [$\mathrm{ArP^+}$ – 1], 231 (100) [$\mathrm{TipSi^+}$], 203 (12) [$\mathrm{Tip^+}$], 57 (80) [$t\mathrm{Bu^+}$].

*Compound **17***: ^{31}P NMR: $\delta = 305.0$ (P=C), 40.5 ($^2J(\mathrm{P,P}) = 254$ Hz, $^2J(\mathrm{P,H}) = 17.4$ Hz; $\mathrm{P^{III}}$).

Crystal structure determination for 16: Diffraction data were collected on a Huber diffractometer ($\mathrm{Mo_{K\alpha}}$ radiation graphite monochromator) at room temperature. Lattice parameters were obtained from the centering of 21 reflections ($6 < 2\theta < 30°$). A standard reflection (3, 3, 0) checked every 50 reflections showed no significant deviation. Data: $\mathrm{C_{80}H_{114}P_2Si_2}$; red; $0.28 \times 0.30 \times 0.35\ \mathrm{mm^3}$; $M_r = 1193.83$, triclinic; space group 0 $P\bar{1}$; $a = 13.335$ (2), $b = 14.665$ (3), $c = 21.710$ (6) Å; $\alpha = 83.29$ (2), $\beta = 81.50$ (2), $\gamma = 74.71$ (2)°; $V = 4037$ (2) Å^3; $\rho_{\mathrm{calcd}} = 0.98\ \mathrm{g\,cm^{-3}}$; $Z = 2$, $F(000) = 1304$; μ for $\mathrm{MoK_\alpha}$ radiation = 0.12 mm^{-1}; 2θ range = $4 < 2\theta < 52°$; index ranges: $0 < h < 16$, $-17 < k < 18$, $-26 < l < 26$; $T = 293$ K; 15859 reflections were measured of which 5352 were considered observed with $I > 3\sigma(I)$; number of parameters = 642; residual electron density = 0.95 e Å^{-3}; $R = 0.151$; S (goodness of fit) = 0.91. The structure was solved by Patterson method and subsequent Fourier syntheses with SHELXS-86[24] program. The least-squares refinement was performed by using SHELXL-93[25] program against F^2. In spite of many attempts we have not been successful in the preparation of a good quality crystal. Moreover a very great thermal agitation was observed for some carbons of *i*Pr and *t*Bu groups; thus, we have been obliged to fix the position of these groups in order to refine the structure. In order to decrease the number of parameters to refine (only 5352 observed reflections on 15859 measured reflections) we have used for these atoms global thermal isotropic agitation parameters. All the hydrogen atoms were placed in calculated positions also with global thermal agitation parameters. For these reasons, the refinement is relatively poor.

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[27] 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-102119. 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).

[28] Note added in proof: a second germaallene has been reported recently by N. Tokitoh, K. Ishikawa, R. Okazaki, *Chem. Lett.* **1998**, 811.

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