

A Surprisingly Stable 1-(Chlorosilyl)-2-phosphaethenyllithium Compound, $\text{RCl}_2\text{SiC}(\text{Li})=\text{PMes}^*$

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$\text{RCl}_2\text{Si}-\text{C}(\text{Li})=\text{PMes}^*$ (**1**) (R = 9-methylfluoren-9-yl, Mes^* = 2,4,6-tri-*tert*-butylphenyl), considered as a key intermediate in the synthesis of the heteroallene $\text{RClSi}=\text{C}=\text{PMes}^*$, was obtained from $\text{RCl}_2\text{Si}-\text{C}(\text{Cl})=\text{PMes}^*$ by lithium/chlorine exchange with *n*BuLi and evidence for its identity was obtained by hydrolysis. Remarkably, however, it failed to undergo a lithium salt elimination to form the corresponding chlorophosphasilallene, $\text{RClSi}=\text{C}=\text{PMes}^*$, even under prolonged heating in toluene. As shown by theoretical studies (RHF/3-21G* and RHF/6-31G**//RHF/3-21G* level), interactions

between the lithium ion and the π -systems of the substituents at the phosphorus and silicon atoms could partly account for this stability. The lithium compound **1** reacts with methanol or chlorotrimethylsilane leading to new silylphosphaalkenes. The reaction of the lithium derivative **1** with benzaldehyde gave a four-membered heterocycle with an exocyclic $\text{P}=\text{C}$ bond which virtually corresponds to the product of a [2+2] cycloaddition between the $\text{Si}=\text{C}$ and $\text{C}=\text{O}$ double bonds. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2005)

Introduction

Silenes, the silicon counterparts of olefins, have challenged chemists for many years. Although the initial claim for producing an $\text{Si}=\text{C}$ linkage dates back to 1912,^[1] isolation of a stable silene was first achieved in 1981.^[2] This major breakthrough, combined with the syntheses of the stable disilene $\text{Mes}_2\text{Si}=\text{SiMes}_2$ (Mes = 2,4,6-trimethylphenyl)^[3] and diphosphene $\text{Mes}^*\text{P}=\text{PMes}^*$ (Mes^* = 2,4,6-tri-*tert*-butylphenyl)^[4] paved the way for the remarkable and thriving chemistry of heavier multiple-bonded main group elements from which other bonding patterns such as heterocumulative double-bond systems have emerged.^[5] A stable 1-silaallene $>\text{Si}=\text{C}=\text{C}<$, in which the carbon atom involved in the double bond to the silicon atom adopts sp -hybridisation, was reported a decade later.^[6] We have been interested in 1,3-phosphasilallenes, i.e. compounds with phosphorus and silicon atoms (thus, two heavier group 14 and 15 elements) at the terminal positions of the heteroallene skeleton and reported the hitherto unique $>\text{Si}=\text{C}=\text{P}-$ derivative some years ago.^[7] The latter readily undergoes dimerisation above -30°C . Clearly, the

steric shielding of the bulky groups in $\text{PhTipSi}=\text{C}=\text{PMes}^*$ (Tip = 2,4,6-triisopropylphenyl) is not sufficient to prevent the target molecule from coupling with itself and, consequently, the study of its chemical behaviour was limited. Due to the presence of three reaction sites (the $\text{Si}=\text{C}$ and $\text{P}=\text{C}$ double bonds as well as the phosphorus lone pair), such compounds should be extremely interesting from a synthetic point of view. Various cycloadducts could be obtained with unsaturated species, making these allenic derivatives powerful building blocks in heterocyclic and organometallic chemistry. In order to increase the synthetic utility of such compounds, we have tried to attach a chlorine atom to the silicon atom which could allow functionalisation of SiCP systems. Thus, it seemed interesting to prepare a phosphasilallene, the main objective being to obtain a stable derivative to facilitate the study of its reactivity.

Herein we describe the synthesis of the stable chloro-lithio compound $\text{RCl}_2\text{Si}-\text{C}(\text{Li})=\text{PMes}^*$ (R = 9-methylfluoren-9-yl) **1** from dichlorophosphasilapropene **2**, along with its characterisation showing that it exhibits a chemical behaviour which could be theoretically expected from the target phosphasilallene $\text{RClSi}=\text{C}=\text{PMes}^*$ **3**.

Results and Discussion

Vicinal dihalophosphametallapropenes $>\text{M}(\text{X})-\text{C}(\text{Cl})=\text{P}-$ (X = F, Cl; M = Si,^[7] Ge^[8]) are suitable precursors to the corresponding heteroallenes. Lithiation of the central carbon atom occurs smoothly at low temperature through a lithium/halogen exchange and the subsequent

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lithium salt elimination gives rise to a metal–carbon double bond adjacent to the existing P=C bond which remains intact throughout the whole procedure. The final step in the synthesis of stable 1-silaallenes also involves lithium salt elimination from the closely related 3-fluoro-2-lithio-3-silapropenes $>\text{Si}(\text{F})\text{--C}(\text{Li})\text{=C}<$.^[5e,6,9]

The above-described synthetic approach was applied for the target chlorophosphasilallene. Substitution with the 9-methylfluorenyl group at the silicon atom was intended to provide extra steric protection for the desired double bond. The coupling of the carbenoid $\text{Cl}(\text{Li})\text{C=PMes}^*$ ^[10] with trichloro(9-methylfluoren-9-yl)silane^[11] afforded the anticipated trichlorophosphasilapropene **2** in good yield. A ³¹P NMR analysis of the reaction mixture suggested that only one isomer of compound **2** was formed ($\delta_{\text{P}} = 328.1$ ppm). Because of the severe steric hindrance of the Mes* group, the more accessible *trans*-chlorine atom in $\text{Cl}_2\text{C=PMes}^*$ can be expected to undergo an easier lithium/halogen exchange with *n*BuLi. This favours the formation of the (*E*)-carbenoid $\text{Cl}(\text{Li})\text{C=PMes}^*$ which hence led to the (*Z*)-phosphasilapropene **2** when mixed with the starting trichlorosilane. The (*Z*) configuration of derivative **2** was confirmed by an X-ray diffraction study (Figure 1). The P=C distance [1.669(3) Å] matches the average value reported for such bonds (1.67 Å).^[5c]

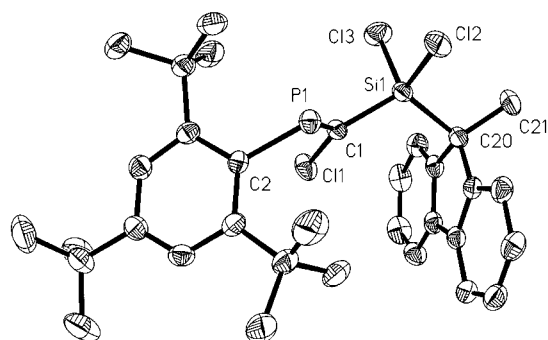
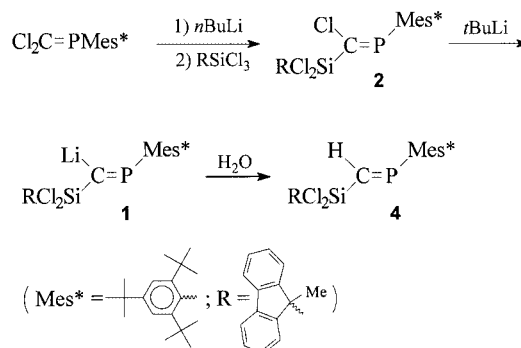


Figure 1. Molecular structure of **2** (thermal ellipsoids at the 50% probability level; H atoms are omitted for clarity); selected bond lengths [Å] and angles [°]: C(1)–P(1) 1.669(3), C(1)–Cl(1) 1.747(2), C(1)–Si(1) 1.850(3), P(1)–C(2) 1.833(3), Si(1)–C(20) 1.883(3), Si(1)–Cl(2) 2.040(9), Si(1)–Cl(3) 2.0524(10); P(1)–C(1)–Cl(1) 125.92(15), P(1)–C(1)–Si(1) 119.65(14), C(1)–P(1)–C(2) 104.42(11), C(1)–Si(1)–C(20) 115.89(11), C(20)–Si(1)–Cl(2) 109.47(8), C(20)–Si(1)–Cl(3) 109.97(8).

Treatment of **2** with *tert*-butyllithium resulted in the expected metallation and caused the ³¹P NMR signal to shift downfield ($\delta_{\text{P}} = 441.4$ ppm). Further evidence for the ensuing lithium derivative $\text{RCl}_2\text{SiC}(\text{Li})\text{=PMes}^*$ **1** was obtained by formation of its hydrolysis product (Scheme 1).

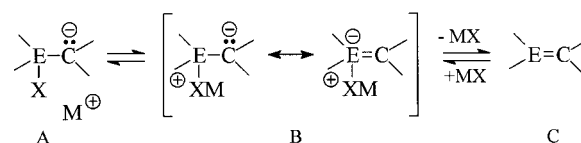
Compound **1** is stable under a rigorously maintained inert gas at room temperature and fails to eliminate lithium chloride to give **3** even under prolonged heating at reflux in toluene. However, attempts to isolate the highly air- and moisture-sensitive **1** by crystallisation at -30 °C led to the hydrolysis product **4** due to adventitious water. The (*E*) isomer was exclusively obtained, as expected from the configuration of starting **1** and was proved by the $^1J_{\text{P=C}}$ coupling



Scheme 1.

constant (67.9 Hz). A similar value (66.4 Hz) was reported by Bickelhaupt et al. for the (*E*) isomer of $\text{Mes}^*\text{P}=\text{C}(\text{H})\text{SiMe}_3$ ^[10a] whereas the coupling constant for the (*Z*) isomer is smaller (54.4 Hz).

According to Wiberg, the 1,2-elimination of LiX to form an Si=C double bond involves dipolar intermediates B (Scheme 2).^[12]



Scheme 2.

In our case, the non-elimination of LiCl means that the position of the equilibrium is shifted to form A, probably because of the presence of two chlorine atoms on the silicon atom. The natural charges on the carbon atom in the model carbanions $[\text{Cl}_{3-x}\text{H}_x\text{Si-C=PH}]^-$ at the RHF/6-31+G** level (Table 1) show that by increasing the number of chlorine atoms on the silicon atom, the negative charge on the carbon atom increases. This in turn favours the A form in Scheme 2.

Table 1. Natural charges on the carbon atom in the $[\text{Cl}_{3-x}\text{H}_x\text{Si-C=PH}]^-$ anions

Model	Natural charge on the carbon atom
$[\text{H}_3\text{Si-C=PH}]^-$	−1.224
$[\text{ClH}_2\text{Si-C=PH}]^-$	−1.315
$[\text{Cl}_2\text{HSi-C=PH}]^-$	−1.362
$[\text{Cl}_3\text{Si-C=PH}]^-$	−1.393

In order to obtain a deeper understanding of the observed reluctance of **1** to lose LiCl, molecular orbital calculations on various conformers of the model $\text{Cp}'\text{Cl}_2\text{SiC}(\text{Li})\text{=PMes}^*$ system ($\text{Cp}' = 1\text{-methylcyclopentadienyl}$) were carried out at the RHF/3-21G* level of theory, with full optimisation of the geometry. Note that this model retains the main steric and electronic features of **1** (through the Mes* group on P and the Cp' group on Si). The influence of the solvent on the relative stability of these conformers has been inferred from single point calculations with the PCM solvation model of Tomasi by using two sol-

Table 2. Relative energies [kJ mol⁻¹] and natural charges on Li in **1a** and **1b**

Conformer	Gas phase		DMSO		Toluene	
	Relative energy	Natural charge	Relative energy	Natural charge	Relative energy	Natural charge
1a	30.00	0.897	47.00	0.900	40.42	0.898
1b	0.0	0.885	0.0	0.887	0.0	0.886

vents (DMSO and toluene). The two lowest energy conformers (**1a** and **1b**) are shown in Figure 2. Table 2 includes the relative energies of these conformers calculated in the gas phase and in the two solvents as well as the natural charges on Li.

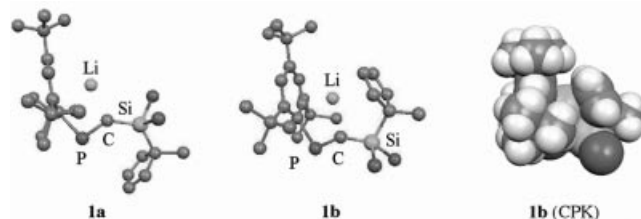


Figure 2. Lowest energy conformers of Cp'Cl₂SiC(Li)=PMes* (hydrogen atoms omitted); note the special position of Li in **1b** allowing for strong cation-π interactions

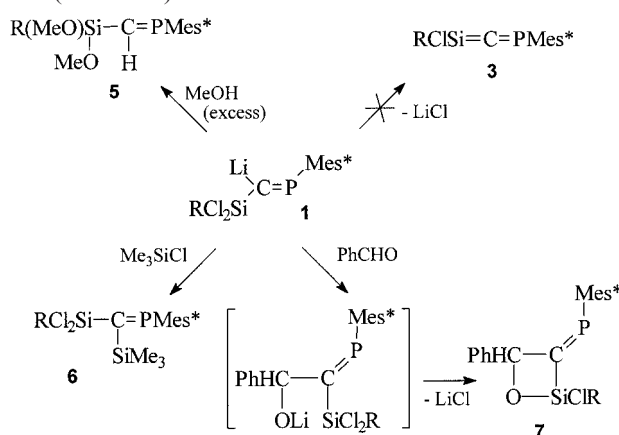
The lowest energy conformer **1b** exhibits strong electrostatic interactions between Li and both π systems (Mes* and Cp') as shown by the following distances: Li-ipso-C(Mes*) 2.357 Å, Li-centroid(Mes*) 2.380 Å, Li-ipso-C(Cp') 2.325 Å, Li-centroid(Cp') 2.247 Å. These distances are in good agreement with those determined from X-ray analyses of similar interactions.^[13]

The chlorine atoms in **1b** are located in unfavourable positions for intramolecular elimination of LiCl. Intermolecular condensation is also quite improbable due to the very efficient steric protection of the Li cation (see the CPK representation of **1b** in Figure 2). Note also that because of these cation-π interactions, the natural charge on Li does not change on going from gas phase to DMSO or toluene solution. Conformer **1a** is higher in energy both in the gas phase and in solution and, presumably, this arrangement is more difficult to achieve in the real system **1**. This order is also maintained at the RHF/6-31G**//RHF/3-21G* level where **1a** is still higher by 15.22 kJ mol⁻¹. Thus, cation-π interactions between Li and the Mes* and fluorenyl groups in **1** could account for its failure to eliminate lithium chloride. Such interactions have been recently highlighted by an X-ray diffraction analysis of a lithium (difluorosilyl)phosphide -Si(F₂)-P(Li)- which failed to undergo lithium fluoride elimination up to 100 °C.^[14]

Lithium-π interactions in the case of RCl₂SiC(Li)=PMes* **1** also favour a shift in the position of the equilibrium to form **A** in accordance with the calculations and this could also explain the lack of elimination of LiCl. A similar reluctance to form an Si=C double bond by salt elimination has been previously reported.^[15]

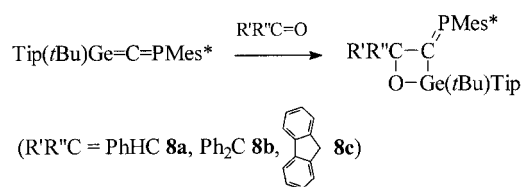
The lithio compound **1** reacts with excess methanol or chlorotrimethylsilane to give the silylphosphaalkenes **5** and **6**, respectively. The same derivatives should also be obtain-

able from the chlorophosphasilaallene **3** with these reactants (Scheme 3).



Scheme 3.

Interestingly, compound **1** readily reacts with benzaldehyde to afford oxasiletane **7** with an exocyclic P=C double bond in the form of one isomer as shown by ³¹P NMR spectroscopy (δ_P = 339.4 ppm) (Scheme 3). From the ²J_{P,CO} coupling constant (10.2 Hz) it seems that **7** exists as the (*E*) isomer (Mes* and Si *trans* to each other). This stereochemistry is in agreement with the postulated configuration of **1** and the mechanism of the reaction. Similar values were obtained by Appel and Bickelhaupt^[16] for ²J_{P,C} in Mes*P=C-C systems [(*E*) isomer 10–15 Hz, (*Z*) isomer 20–60 Hz]. In the closely related germanium compound **8c**, the structure of which was established by an X-ray determination, a ²J_{P,CO} coupling constant of 38.7 Hz was observed for the (*Z*) isomer (Scheme 4). In the absence of an X-ray structural study, the stereochemistry of the four-membered ring (Ph and Cl in *cis* or *trans* positions) could not be determined.



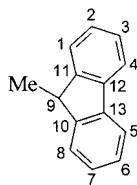
Scheme 4.

Though the latter reaction likely proceeds through an addition/elimination pathway, the four-membered ring **7** virtually conforms to the cycloaddition product of the Si=C double bond of the corresponding chlorophosphasilaallene with the starting aldehyde without participation of the contiguous P=C double bond as was found earlier for the Ge congener *t*BuTipGe=C=PMes*.^[8]

Similarly, a silenoid, $>\text{Si}(\text{Cl})\text{--C}(\text{Li})<$, has already been observed to behave as a synthetic equivalent of the corresponding silene in its reaction with carbonyl compounds.^[15c] The study of the chemical behaviour of **1** towards various unsaturated species is now under investigation.

Experimental Section

General Remarks: All manipulations were carried out under N_2 or Ar using standard Schlenk techniques with solvents freshly distilled from sodium/benzophenone. ^1H , ^{13}C and ^{31}P NMR spectra were recorded in CDCl_3 with a Bruker AC 200 instrument at 200.1, 50.1 and 81.01 MHz, respectively, except for compound **1** which was measured in $[\text{D}_8]\text{toluene}$ with a Bruker AC 400 spectrometer at 100.6 MHz. Mass spectra were recorded with a Hewlett–Packard 5989 A spectrometer by EI at 70 eV. Melting points were determined using a Leitz microscope heating stage 250. Elemental analyses were performed by the “Service de Microanalyse de l’Ecole de Chimie de Toulouse”. The carbon atoms of the fluorenyl group are numbered as shown in Scheme 5.



Scheme 5.

Synthesis of $\text{RCl}_2\text{Si--C}(\text{Cl})=\text{PMes}^*$ (2**):** A sample of $\text{Cl}_2\text{C}=\text{PMes}^*$ (1.14 g, 3.18 mmol) was dissolved in THF (15 mL) and cooled to -80°C . Under nitrogen, $t\text{BuLi}$ (2 mL of a 1.7 M hexane solution, 1 equiv.) was added to form $\text{ClLiC}=\text{PMes}^*$. This solution was slowly added to a solution of trichloro(9-methylfluoren-9-yl)silane (1.00 g, 3.18 mmol) in THF (10 mL) at -80°C . The mixture was slowly warmed to room temperature with magnetic stirring over 2 h. After filtration, the solution was concentrated in vacuo and pentane (10 mL) was added. Cooling to -20°C led to **2** as a crystalline product. Yield 1.49 g (78%). M.p. 131°C . ^1H NMR (CDCl_3): δ = 1.12 (s, 18 H, *o*- CMe_3), 1.23 (s, 9 H, *p*- CMe_3), 1.88 (s, 3 H, Me), 7.28–7.85 (m, 10 H, arom. H of R and *m*-CH of Mes^*) ppm. ^{13}C NMR (CDCl_3): δ = 21.4 (br., Me), 30.3 (br., CMe_3), 35.0 (*p*- CMe_3), 37.8 (*o*- CMe_3), 46.2 (C-9), 120.3 and 122.0 (C-4, -5 and *m*-CH of Mes^*), 125.2 and 127.2 (C-1–3, C-6–8), 134.0 (d, J_{PC} = 63.0 Hz, *i*-C of Mes^*), 141.1 and 146.1 (C-10–13), 151.0 and 153.1 (*o*- and *p*-C of Mes^*), 155.7 (d, J_{PC} = 83.5 Hz, $\text{P}=\text{CCl}$) ppm. ^{31}P NMR (CDCl_3): δ = 328.1 ppm. MS (EI): m/z (%) = 602 (5) $[\text{M}]^+$, 587 (10) $[\text{M} - \text{Me}]^+$, 565 (5) $[\text{M} - \text{Cl}]^+$, 423 (30) $[\text{M} - \text{R}]^+$, 179 (95) $[\text{R}]^+$, 57 (100) $[t\text{Bu}]^+$. $\text{C}_{33}\text{H}_{40}\text{Cl}_3\text{PSi}$ (602.09): calcd. C 65.83, H 6.70; found C 66.10, H 6.91.

Synthesis of $\text{RCl}_2\text{Si--C}(\text{Li})=\text{PMes}^*$ (1**):** A solution of $\text{RCl}_2\text{Si--C}(\text{Cl})=\text{PMes}^*$ (1.30 g, 2.16 mmol) in diethyl ether (20 mL) was cooled to -80°C under nitrogen. To the stirred solution was slowly added $t\text{BuLi}$ (1.27 mL of a 1.7 M hexane solution, 1 equiv.) and the solution was then warmed to room temperature with magnetic stirring over 2 h. ^{13}C and ^{31}P NMR spectroscopic analyses of the brown solution showed nearly quantitative formation of **1**. ^{13}C NMR (400 MHz, $[\text{D}_8]\text{toluene}$): δ = 18.6 (Me), 31.2 and 33.9 (CMe_3), 33.3 (CMe_3), 38.4 (C-9), 120.0 (C-4, -5), 124.7, 126.7 and 127.1 (C-1–3, C-6–8), 141.0 and 145.7 (C-10–13), 144.4 (d, J_{PC} =

74.6 Hz, $\text{P}=\text{C}$ or *i*-C of Mes^*), 149.1 and 151.6 (*o*- and *p*-C of Mes^*) ppm. ^{31}P NMR (Et_2O , $[\text{D}_8]\text{toluene}$): δ = 441.4 ppm.

Formation of $\text{RCl}_2\text{Si--C}(\text{H})=\text{PMes}^*$ (4**):** A white waxy solid of **4** (95% purity) was obtained due to hydrolysis when a solution of the lithium compound **1** in Et_2O , prepared as described previously from **2** (1.00 g, 1.66 mmol), was kept at -30°C for a week. Yield 0.85 g (90%). ^1H NMR (CDCl_3): δ = 1.25 (s, 18 H, *o*- CMe_3), 1.32 (s, 9 H, *p*- CMe_3), 1.85 (s, 3 H, Me), 6.75 (d, $^2J_{\text{PH}}$ = 22.5 Hz, 1 H, CH), 7.28–7.91 (m, 10 H, arom. H of R and *m*-CH of Mes^*) ppm. ^{13}C NMR (CDCl_3): δ = 19.1 (br. s, Me), 31.6 and 34.3 (br., CMe_3), 35.0 and 35.2 (*o*- and *p*- CMe_3), 38.1 (C-9), 120.2 and 122.0 (C-4, -5 and *m*-CH of Mes^*), 124.9 and 127.2 (C-1–3, C-6–8), 141.0, 146.0, 150.2 and 152.6 (*o*- and *p*-C of Mes^* , C-10–13), 156.6 (d, $^1J_{\text{PC}}$ = 67.9 Hz, $\text{P}=\text{C}$) ppm. ^{31}P NMR (CDCl_3): δ = 375.3 ($^2J_{\text{PH}}$ = 22.5 Hz) ppm.

Synthesis of $\text{R}(\text{OMe})_2\text{Si--C}(\text{H})=\text{PMes}^*$ (5**):** $\text{RCl}_2\text{Si--C}(\text{Li})=\text{PMes}^*$ (1.66 mmol) prepared as previously described was treated with excess methanol (1 mL). The reaction mixture was filtered and the solution concentrated in vacuo followed by addition of pentane. Cooling to -20°C gave **5** as a white solid (90% purity). Yield 0.87 g (88%). ^1H NMR (CDCl_3): δ = 1.28 (s, 18 H, *o*- CMe_3), 1.34 (s, 9 H, *p*- CMe_3), 1.66 (s, 3 H, Me), 3.27 (s, 6 H, OMe), 6.98 (d, $^2J_{\text{PH}}$ = 22.0 Hz, 1 H, CH), 7.20–7.80 (m, 10 H, arom. H of R and *m*-CH of Mes^*) ppm. ^{13}C NMR (CDCl_3): δ = 19.1 (Me), 31.5 and 33.8 (br., CMe_3), 35.1, 38.1 and 38.9 (*o*- and *p*- CMe_3 , C-9), 45.5 (br., OMe), 119.9 (br., C-4, -5 and *m*-CH of Mes^*), 124.8 and 126.5 (C-1–3, C-6–8), 140.4, 145.8, 152.2 and 153.1 (*o*- and *p*-C of Mes^* , C-10–13) ppm. ^{31}P NMR (CDCl_3): δ = 362.2 (d, $^2J_{\text{PH}}$ = 22.0 Hz) ppm. MS (EI): m/z (%) = 558 (5) $[\text{M}]^+$, 527 (1) $[\text{M} - \text{OMe}]^+$, 379 (40) $[\text{M} - \text{R}]^+$, 323 (33) $[\text{M} - \text{R} - t\text{Bu} + 1]^+$, 179 (100) $[\text{R}]^+$.

Synthesis of $\text{RCl}_2\text{Si--C}(\text{SiMe}_3)=\text{PMes}^*$ (6**):** $\text{RCl}_2\text{Si--C}(\text{Li})=\text{PMes}^*$ (1.66 mmol) in Et_2O (10 mL) was treated with excess chlorotrimethylsilane (0.5 mL) at room temperature. The lithium salt was removed by filtration and the solution concentrated in vacuo followed by addition of pentane. Cooling to -20°C afforded **6** as a white solid. Yield 0.90 g (85%). M.p. 116°C . ^1H NMR (CDCl_3): δ = -0.33 (s, 9 H, SiMe_3), 1.12 (s, 18 H, *o*- CMe_3), 1.28 (s, 9 H, *p*- CMe_3), 1.92 (s, 3 H, Me), 7.23–7.91 (m, 10 H, arom. H of R and *m*-CH of Mes^*) ppm. ^{13}C NMR (CDCl_3): δ = 0.4 (SiMe_3), 19.6 (Me), 29.9 and 31.6 (br., CMe_3), 37.1 and 37.6 (*o*- and *p*- CMe_3), 45.3 (C-9), 118.3 and 119.6 (C-4, -5 and *m*-CH of Mes^*), 125.1 and 127.2 (C-1–3, C-6–8), 141.0, 146.0, 150.1 and 153.2 (*o*- and *p*-C of Mes^* , C-10–13), 177.2 (d, $^1J_{\text{PC}}$ = 90.5 Hz, $\text{P}=\text{CSi}$) ppm. ^{31}P NMR (CDCl_3): δ = 433.7 ppm. MS (EI): m/z (%) = 638 (15) $[\text{M}]^+$, 623 (15) $[\text{M} - \text{Me}]^+$, 566 (20) $[\text{M} - \text{SiMe}_3 + 1]^+$, 459 (20) $[\text{M} - \text{R}]^+$, 403 (15) $[\text{M} - \text{R} - t\text{Bu} + 1]^+$, 275 (22) $[\text{ArP} - 1]^+$, 179 (65) $[\text{R}]^+$, 57 (100) $[t\text{Bu}]^+$. $\text{C}_{36}\text{H}_{49}\text{Cl}_2\text{PSi}_2$ (638.83): calcd. C 67.58, H 7.72; found C 67.81, H 7.88.

Synthesis of Oxasiletane **7:** A solution of $\text{RCl}_2\text{Si--C}(\text{Li})=\text{PMes}^*$, prepared from **2** (1.00 g, 1.66 mmol) in diethylether (20 mL), was cooled to -60°C under nitrogen. To the stirred solution was slowly added benzaldehyde (0.19 g, 1.75 mmol). The solution was warmed to room temperature with magnetic stirring over 2 h. The reaction mixture was then filtered to remove LiCl and the solution concentrated in vacuo. Addition of pentane and cooling to -20°C gave a waxy yellow solid which could not be obtained completely pure (90% purity) but was unambiguously identified as **7** by NMR spectroscopy and mass spectrometry. Yield 0.85 g (77%). ^1H NMR (CDCl_3): δ = 1.35 (br., 27 H, CMe_3), 1.80 (s, 3 H, Me), 5.80 (d, $^3J_{\text{PH}}$ = 13.6 Hz, 1 H, OCH), 6.75–8.10 (m, 15 H, Ph, arom. H of R and *m*-CH of Mes^*) ppm. ^{13}C NMR (CDCl_3): δ = 13.8 (Me), 31.4 and 33.6 (br., CMe_3), 37.1 and 38.3 (*o*- and *p*- CMe_3) 47.7 (C-

9), 113.1 (d, $^2J_{\text{PCO}} = 10.2$ Hz, OCH), 120.2–130.0 (C-1–8 and *m*-CH of Mes*), 140.8–154.0 (*o*- and *p*-C Mes*, C-10–13) ppm. ^{31}P NMR (CDCl_3): $\delta = 339.4$ (d, $^3J_{\text{PH}} = 13.6$ Hz) ppm. MS (EI): m/z (%) = 636 (2) $[\text{M}]^+$, 545 (3) $[\text{M} - \text{PhCH} - 1]^+$, 456 (5) $[\text{M} - \text{R} - 1]^+$, 394 (3) $[\text{M} - \text{ClSiR}]^+$, 379 (3) $[\text{ArP}=\text{CCHPh}]^+$, 350 (8) $[\text{ArP}=\text{C}-\text{SiCl} + 1]^+$, 179 (35) $[\text{R}]^+$, 105 (30) $[\text{PhCO}]^+$, 57 (100) $[\text{tBu}]^+$.

Computational Details: A complete search of the conformational space of **1** was carried out using Spartan02^[17] and the conformers thus obtained were further subjected to complete geometry optimisation at the RHF/3-21G* level with the same package. Single point calculations, taking into account the effect of solvents with the PCM model of Tomasi,^[18] were performed using the G98 system Gaussian98, revision A.11.3.^[19] The NBO analysis^[20] was carried out within the NBO module implemented in G98.

Crystal Data for 2: $\text{C}_{33}\text{H}_{40}\text{Cl}_3\text{PSi}$, $M = 602.06$, monoclinic, $C2/c$, $a = 16.661(2)$ Å, $b = 10.730(1)$ Å, $c = 36.380(3)$ Å, $\beta = 90.284(2)^\circ$, $V = 6504.0(11)$ Å³, $Z = 8$, $T = 193(2)$ K. 18162 reflections (6577 independent, $R_{\text{int}} = 0.0340$) were collected at low temperature using an oil-coated shock-cooled crystal with a Bruker-AXS CCD 1000 diffractometer with Mo- K_α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods (SHELXS-97)^[21] and all non-hydrogen atoms were refined anisotropically using the least-squares method on F^2 .^[22] Largest electron density residue: $0.403 \text{ e} \cdot \text{Å}^{-3}$, $R_1/[I > 2\sigma(I)] = 0.0511$ and wR_2 (all data) = 0.1187 with $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$. CCDC-233371 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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