

## An Unexpected Product of the Reactions of Fluorenylchlorosilanes with Phosphorus Ylides

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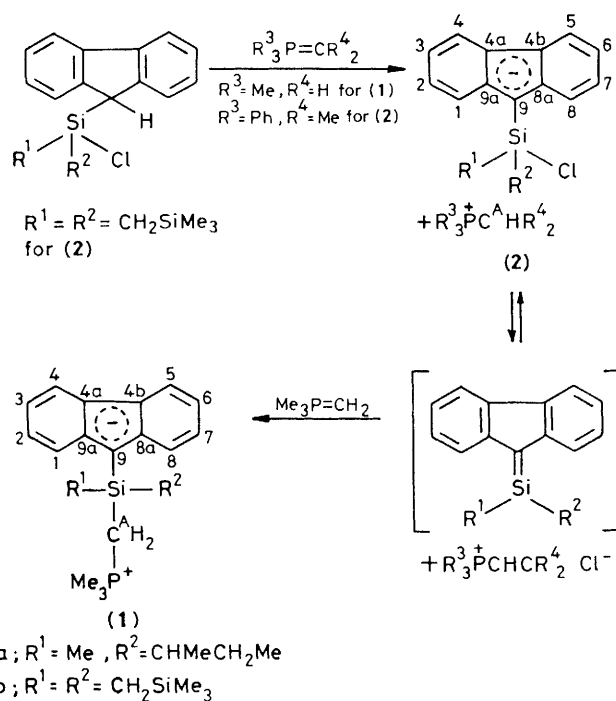
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The reaction of  $\text{Me}_3\text{P}=\text{CH}_2$  with  $\text{R}^1\text{R}^2\text{Si}(\text{C}_{13}\text{H}_9)\text{Cl}$  ( $\text{C}_{13}\text{H}_9$  = fluoren-9-yl), irrespective of the molar ratio of reagents, yields betaines of the  $\text{Me}_3\text{P}^+\text{CH}_2\text{SiR}^2\text{R}^2(\text{C}_{13}\text{H}_8^-)$  type, whereas under similar conditions the reaction of bis(trimethylsilylmethyl)fluoren-9-ylchlorosilane with  $\text{Ph}_3\text{P}=\text{CMe}_2$  gives a stable organosilicon carbanion (*X*-ray analysis); the compounds were characterized by  $^{13}\text{C}$ ,  $^{29}\text{Si}$ , and  $^{31}\text{P}$  n.m.r., and u.v. spectroscopy.

We have recently shown that the reaction of dialkylcyclopentadienylchloro-silane,<sup>1</sup> -germane,<sup>2</sup> or -stannane<sup>3</sup> with  $\text{Ph}_3\text{P}=\text{CH}_2$  yields 6,6-dialkyl-6-sila(or germa)fulvene dimers or the 6,6-dialkyl-6-stannafulvene trimer, probably *via* intermediates with a  $\text{p}_\pi\text{-p}_\pi$  double bond,  $\text{C}=\text{E}$  ( $\text{E} = \text{Si}, \text{Ge}, \text{or Sn}$ ). The 6,6-dimethyl-6-silafulvene dimer has also been obtained independently by other authors<sup>4,5</sup> using flow pyrolysis techniques.

We tried to stabilize the presumed metalla-fulvene intermediates sterically and electronically by using fluorenylchlorosilanes with bulky substituents at the silicon atom. The reaction of compounds  $\text{R}^1\text{R}^2\text{Si}(\text{C}_{13}\text{H}_9)\text{Cl}$  with  $\text{Me}_3\text{P}=\text{CH}_2$  in tetrahydrofuran (thf) *in vacuo* ( $2 \times 10^{-4}$  mmHg), irrespective of the molar ratio of the reagents, gave the organosilicon-phosphorus betaines (**1a**, **b**) as yellow crystalline products in 80–85% yield (Scheme 1). The structures were established from their  $^{13}\text{C}$  and  $^{29}\text{Si}$  n.m.r. spectra, following literature assignments<sup>6,7</sup> for the  $^{13}\text{C}$  resonances. The  $^{13}\text{C}$ - $\{^1\text{H}\}$  off-resonance spectra indicated the absence of a proton at C-9 of the fluorenyl ring. Also important for the structural assignments was the presence of  $^{31}\text{P}$ - $^{29}\text{Si}$  couplings and  $^{31}\text{P}$ - $^{13}\text{C}$  couplings in the substituent  $\text{R}^2$  shown in the  $^{13}\text{C}$  and  $^{29}\text{Si}$  n.m.r. spectra. The u.v. spectrum of (**1b**) showed an absorption maximum at 351 nm.

Under similar conditions, with the more sterically hindered triphenylisopropylidene phosphorane, the phosphonium salt (**2**) was produced in 81% yield (Scheme 1), the structure of which was determined by *X*-ray crystallography.



Scheme 1

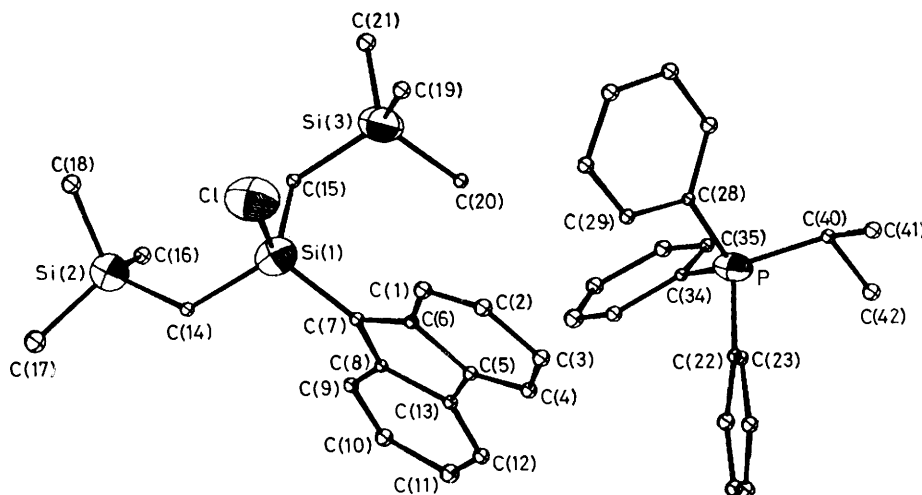


Figure 1. ORTEP view of the crystal structure of (2) showing the crystallographic numbering scheme.

*Crystal data:*  $[\text{C}_{21}\text{H}_{30}\text{ClSi}_3]^- [\text{C}_{21}\text{H}_{22}\text{P}]^+$  (2), monoclinic, space group  $P2_1$ ,  $a = 10.878(3)$ ,  $b = 10.498(3)$ ,  $c = 10.140(5)$  Å,  $\gamma = 118.24(2)^\circ$ ,  $U = 2026$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.16$  g cm<sup>-3</sup>. The intensities of 886 independent reflections with  $I \geq 3\sigma(I)$  were measured on a Syntex  $P\bar{1}$  automatic diffractometer, using Mo- $K_\alpha$  radiation and a graphite monochromator. The structure was solved by direct methods using the SHELXTL (G. M. Sheldrick) program. Refinement with anisotropic thermal parameters for Cl, P, and Si and isotropic thermal parameters for C proceeded to an  $R$ -value of 0.056.† Further refinement was hindered by defects on the crystal surface arising from the sensitivity of compound (2) to oxygen and traces of moisture in the air, and the consequent need to mount the crystal in a capillary. However, the structure determination clearly confirms the conclusion that compound (2) is ionic.

The structure is shown in Figure 1. The Si(1)–C(7) (crystallographic numbering) bond length (1.83 Å) is significantly shorter than the Si(1)–C(14) and Si(1)–C(15) bond lengths (1.88 and 1.89 Å). Together with this shortening of the Si–C (fluorenyl) bond, the Si–Cl distance (2.107 Å) is longer than normal (2.01 Å). The C(7) atom has a trigonal planar coordination, corresponding to  $sp^2$ -hybridization [sum of valence angles  $359(1)^\circ$ ]. In the fluorenyl residue the five-membered ring is planar to within 0.02 Å (the bond lengths are roughly equal, in the range 1.41–1.47 Å); the fact that Si(1) lies outside this plane (by 0.23 Å) may be explained by steric hindrance due to the presence of the bulky trimethylsilylmethyl substituents. The structure found thus differs substantially from structures of other fluorenylsilanes studied by  $X$ -ray crystallography. The phosphonium cation has the usual tetrahedral configuration, and intermolecular contacts correspond to the usual van der Waals interactions.

The <sup>13</sup>C n.m.r. spectrum of the phosphonium salt (2) may be assigned on the basis of previous work.<sup>6,9</sup> The assignment

Table 1. <sup>13</sup>C, <sup>29</sup>Si, and <sup>31</sup>P N.m.r. data for the betaines (1a,b) and the phosphonium salt (2).<sup>a</sup>

Atoms	(1a) <sup>b</sup>	(1b) <sup>c</sup>	(2) <sup>d</sup>
C-1,8	117.83	117.85	119.17
C-2,7	121.46	121.26	120.95
C-3,6	111.81	111.73	111.52
C-4,5	119.60	119.65	119.21
C-9	76.01	79.42	84.88
C-8a,9a	144.80	144.34	144.56
C-4a,4b	128.04	127.99	127.72
C <sup>A</sup>	9.68 (46.4)	13.35 (45.1)	20.07 (45.8)
Si-fluorenyl	-10.6 (5.3)	-13.11 (5.0)	+13.61 [ <sup>2</sup> $J(\text{Si}-\text{CH}_2)$ 9.9]
Si (side chain)	—	0.03 (1.1)	-1.27 [ <sup>2</sup> $J(\text{Si}-\text{CH}_2)$ 6.6, <sup>2</sup> $J(\text{Si}-\text{CH}_3)$ 8.6]
P <sup>+</sup>	21.8	22.1	31.0

<sup>a</sup> The spectra were measured on Jeol FX-100 (48 k memory) and Varian FT-80A (16 k memory) instruments for degassed solutions of the samples in  $\text{C}_5\text{D}_5\text{N}$ . <sup>13</sup>C Chemical shifts are given in p.p.m. relative to  $\text{SiMe}_4$ , and are accurate to  $\pm 0.05$  p.p.m.;  $J(\text{C}-\text{P})$  values, in Hz, are in parentheses, and are accurate to  $\pm 0.1$  Hz. <sup>29</sup>Si Shifts are given in p.p.m. relative to  $\text{SiMe}_4$ , and are accurate to  $\pm 0.05$  p.p.m.;  $J(\text{Si}-\text{P})$  values, in Hz, are shown in parentheses, and  $J(\text{Si}-\text{H})$  values in square brackets. <sup>31</sup>P Shifts are given relative to external 85%  $\text{H}_3\text{PO}_4$  and are accurate to  $\pm 0.5$  p.p.m. Positive values indicate deshielding. <sup>b</sup> Additional <sup>13</sup>C resonances, with  $J(\text{C}-\text{P})$  values in Hz, at 24.73 ( $J$  1.2,  $-\text{CHMeCH}_2\text{Me}$ ), 23.14 ( $J$  6.0,  $-\text{CHMeCH}_2\text{Me}$ ), 13.86 ( $-\text{CHMeCH}_2\text{Me}$ ), 13.65 ( $-\text{CHMeCH}_2\text{Me}$ ), 10.72 ( $J$  55.0,  $\text{PMe}_3$ ), and -2.67 ( $\text{SiMe}$ ). <sup>c</sup> Additional <sup>13</sup>C resonances, with  $J(\text{C}-\text{P})$  values in Hz, at 10.59 ( $J$  54.4,  $\text{PMe}_3$ ), 6.06 ( $J$  3.1,  $\text{SiCH}_2\text{Si}$ ), and 1.98 ( $\text{SiMe}$ ). <sup>d</sup> Additional <sup>13</sup>C resonances, with  $J(\text{C}-\text{P})$  values in Hz, at 16.04 ( $J$  2.4,  $\text{Ph}_3\text{P}^+\text{CHMe}_2$ ), 11.07 ( $\text{SiCH}_2\text{Si}$ ), and 1.72 ( $\text{SiMe}_3$ ); phenyl resonances: 118.51 ( $J$  83.0, C-1'), 134.45 ( $J$  9.2, C-2'), 130.86 ( $J$  12.2, C-3'), and 134.92 ( $J$  2.4, C-4').

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as supplementary publication No. SUP 23413 (7 pp.) from the British Library, Lending Division. For details of how to obtain this material, see Notice to Authors No. 7, *J. Chem. Soc., Dalton or Perkin Trans.*, Index issues.

of an ionic structure for (2) was supported by the following. (a) C-9 and C-3,6 (numbering as in Scheme 1) show downfield (39.2 p.p.m.) and upfield (5.4 p.p.m.) shifts, respectively, in comparison with the corresponding resonances of the initial fluorenylsilane, which are in line with the data obtained for the fluorene–fluorenyl anion pair.<sup>10</sup> (b) <sup>31</sup>P–<sup>13</sup>C-16 and <sup>31</sup>P–<sup>29</sup>Si spin couplings were not observed, which confirms the absence of the covalent bonding which is present in the betaines (1a, b). (c) The Si-1 <sup>29</sup>Si resonance is shifted upfield by only 15.1 p.p.m. compared with the initial silane, showing that the

covalent Si-Cl bond is preserved since, for the corresponding betaine (**1b**), this shift difference increased to 41.6 p.p.m.

The phosphonium salt (**2**) showed a u.v. absorption maximum at 349 nm (Hitachi-124) in tetrahydrofuran (25 °C). The difference in absorption of the free fluorenyl anion<sup>11</sup> and its 9-substituted anions<sup>12</sup> seems to be associated with the nature of the silicon-containing substituent.

In our opinion, compounds (**1**) and (**2**) are formed *via* an intermediate with an Si=C double bond.

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