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Phosphonium Sila-ylide: Reaction Pathway Different from Ammonium Sila-ylide but Similar to Phosphonium Ylide

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Recently, we reported the novel reaction of an amine-coordinated silylene or an ammonium sila-ylide[1] bearing an 8-(dimethylamino)-1-naphthyl group with diphenylacetylene to afford the cyclized product containing the 1-silaphenalene skeleton.[2] During this cyclization reaction, the acetylene carbons were incorporated between the silicon atom and the naphthyl carbon atom bearing the amino group accompanied by the migration of the amino group to the silicon center. Reported herein is a completely different reaction pathway of a phosphine-coordinated silylene[3] or a phosphonium sila-ylide[1] bearing an 8-phosphino-1-naphthyl group during the reaction with diphenylacetylene. The observed behavior reflects the propensity of phosphorus, the heavier congener of nitrogen, to form a pentavalent phosphonium ylide or phosphorane.

The pentacoordinate fluorodisilanes **1a** and **1b** bearing an 8-diethylphosphino- and 8-diphenylphosphino-1-naphthyl group, respectively, the precursors of the phosphonium sila-ylide **2**, were prepared by the reaction of 8-phosphino-1-naphthyllithium with 1,1-difluoro-1,2-dimethyl-2,2-diphenyldisilane in a way similar to that for the amine-coordinated counterpart **1c**.[2] The coordination of the phosphorus atom to the silicon atom has been shown in the solid state and in solution by the X-ray crystallographic analysis of **1b** (Figure 1)[4−7] and by NMR spectroscopy,[8] respectively.

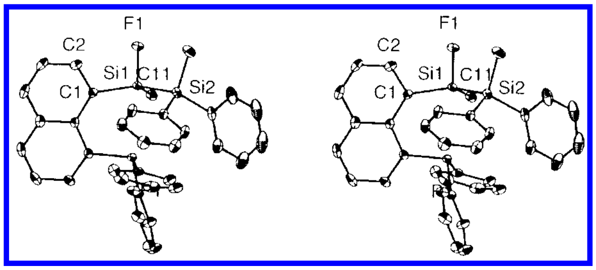
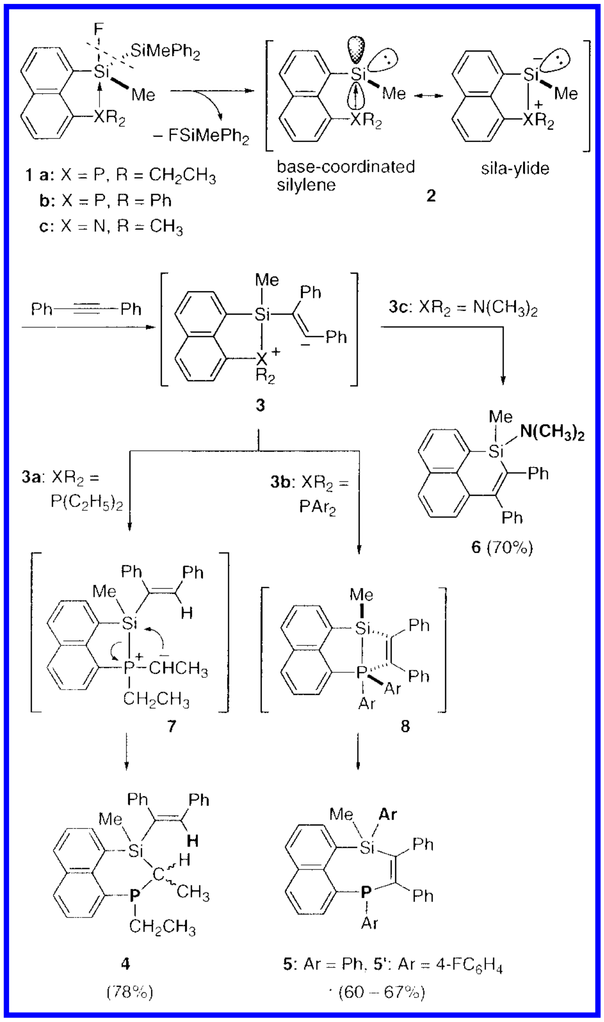


Figure 1. X-ray structure of **1b** in stereoview at 50% probability level. All hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [deg]: Si1−F1 1.651(2), Si1−Si2 2.348(1), Si1⋯P1 2.9866(9), Si1−C1 1.901(3), F1−Si1⋯P1 175.89(8), F1−Si−Si2 98.09(8), Si2−Si1−C1 122.43(9), Si2−Si1−C11 113.9(1), C1−Si1−C11 116.1(1), Si1−C1−C2 113.5(2).

Scheme 1



All of the reaction courses observed during the thermal degradation of **1a** and **1b** are summarized in Scheme 1. When a solution of pentacoordinate fluorodisilane **1a** bearing the di*ethyl*phosphino group in toluene was heated at 110 °C for 12 h under nitrogen, the α-elimination product, fluoromethyldiphenylsilane, was obtained in almost quantitative yield.[9] The thus produced phosphonium sila-ylide **2a** was trapped by diphenylacetylene to afford a six-membered cyclic product **4** as a mixture of stereoisomers (ca. 2:1) in the total yield of 78%, which contains an ethylydene bridge between the silicon atom and the phosphorus atom and a *(Z)*-diphenylethenyl group on the silicon atom, indicative of the hydrogen migration from the methylene in the diethylphosphino group to the alkenyl carbon atom.

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[1] In this paper, we call this species the sila-ylide for simplicity.

[2] (a) Tamao, K.; Asahara, M.; Saeki, T.; Feng, S.-G.; Kawachi, A.; Toshimitsu, A. *Chem. Lett.* **2000**, 660−661. (b) Review: Tamao, K.; Asahara, M.; Saeki, T.; Toshimitsu, A. *J. Organomet. Chem.* **2000**, *600*, 118−123.

[3] Phosphine-coordinated silylenes: (a) Müller, G.; Waldkircher, M.; Pape, A. In *Organosilicon Chemistry III From Molecules to Materials*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, Germany, 1998; pp 452−459 and references therein. (b) Karsch, H. H.; Witt, E. In *Organosilicon Chemistry III From Molecules to Materials*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, Germany, 1998; pp 65−69.

[4] Crystal data for **1b**: orthorhombic, $P2_12_12_1$, colorless, $a = 17.2502(8)$ Å, $b = 17.8934(6)$ Å, $c = 9.8489(2)$ Å, $T = 173$ K, $Z = 4$, $R = 0.036$, $R_w = 0.049$, GOF = 0.94.

[5] The phosphine coordination in the fluorodisilane **1b** has been found to be similar to the amine coordination in analogous **1c**[2] as follows. The geometry of Si1 adopts a pseudotrigonal bipyramid as shown by the %TBPe[6] of 76% with fluorine atom and phosphino group at the two pseudoapical positions, having the P1⋯Si1−F1 angle of 175.89(8)° and P1⋯Si1 distance of 2.9866(9) Å which is ca. 0.9 Å shorter than the sum of the van der Waals radii.[7]

[6] Tamao, K.; Hayashi, T.; Ito, Y.; Shiro, M. *Organometallics* **1992**, *11*, 2099−2114.

[7] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

[8] In ^{13}C NMR of **1a** at room temperature, two kinds of signals are observed for each of the methylene and methyl carbons of the diethylphosphino group. This result indicates that the coordination of phosphorus to silicon is strong enough to prevent the equilibration of the two ethyl groups via the rotation about the phosphino-naphthyl bond. Moreover, spin−spin couplings through the silicon−phosphorus bond are observed in the ^{1}H, ^{13}C, ^{19}F, ^{29}Si, and ^{31}P NMR spectra of **1a** and **1b** as follows. **1a**: ^1J(P,Si) = 15 Hz, ^2J(P,Si) = 51 or 38 Hz [one of which is ^2J(F,Si)], ^2J(P,F) = 108 Hz, ^2J(P,C) = 16 Hz, ^3J(P,C) = 6 Hz, ^3J(P,H) = 12 Hz. **1b**: ^2J(P,Si) = 48 or 32 Hz [one of which is ^2J(F,Si)], ^2J(P,F) = 89 Hz, ^2J(P,C) = 15 Hz, ^3J(P,C) = 7 Hz, ^3J(P,H) = 10 Hz.

[9] It should be noted that this temperature is 30 °C lower than that required for the thermal degradation of the amine-coordinated **1c**.[2]

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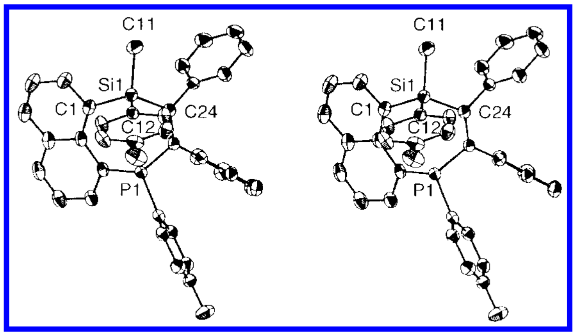

Figure 2. X-ray structure of **5′** in stereoview at 40% probability level. All hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [deg]: Si1−C1 1.888(2), Si1−C11 1.868(2), Si1−C12 1.880(2), Si1−C24 1.888(2), Si1···P1 3.0593(7), C11−Si1···P1 167.87(8), C1−Si1−C12 112.10(8), C1−Si1−C24 107.63(8), C11−Si1−C12 106.43(9), C12−Si1−C24 112.48(8).

Thermal degradation of pentacoordinate fluorodisilane **1b** bearing the di*phenyl*phosphino group was carried out at 140 °C, and the generated phosphonium sila-ylide **2b** was trapped by diphenylacetylene to afford a seven-membered cyclic product **5** in the yield of 67%, in which the diphenylacetylene has been incorporated between the silicon atom and the phosphorus atom, and one phenyl group has migrated from the phosphorus to silicon. The P-to-Si phenyl migration has been confirmed by a similar experiment using the di(4-fluorophenyl)phosphino analogue, in which the 4-fluorophenyl group has migrated to afford **5′**. The structures of these products were confirmed by X-ray crystallographic analyses, the structure of **5′** being shown in Figure 2.[10,11]

The cyclization reactions described above are best understood by the nucleophilic attack of the phosphonium sila-ylide **2** on the diphenylacetylene to form the zwitterionic intermediate **3** bearing alkenyl anion and phosphonium ion moieties as also shown in Scheme 1.[12,13] For the di*ethyl*phosphino derivative **3a** [$XR_2 = P(C_2H_5)_2$], the alkenyl anion abstracts a proton from the methylene of the di*ethyl*phosphino group to form the phosphonium ylide **7**. The formed ylide carbanion nucleophilically attacks the silicon atom causing the silicon-phosphorus bond fission, resulting in the formation of the six-membered cyclic product **4**. The reaction course of **3a** is different from that of the nitrogen analogue **3c**, presumably because the proton abstraction from the dimethylamino group in **3c** is not possible due to the lower ability of nitrogen to stabilize the ylide.

For the di*aryl*phosphino derivative **3b** ($XR_2 = PAr_2$) where the proton abstraction is not possible from the di*aryl*phosphino group, the reaction course is still different from that of **3a** and **3c**. Thus, as shown in Scheme 1, the alkenyl anion **3** nucleophilically attacks the phosphorus atom to form a pentavalent phosphorane intermediate **8** (or a transition structure), which undergoes ligand coupling of the aryl group and the silicon atom on the phosphorus center,[14−16] resulting in the formation of the seven-membered cyclic product **5** and **5′**. This route seems to have emerged due to the intrinsic ability of phosphorus to form pentavalent species.

It is significant to compare the present sila-ylide chemistry with the carbon protocol ylide chemistry. In the carbon chemistry, a similar aryl group migration from phosphorus to carbon has been observed during the reaction of a triarylphosphonium ylide with benzyne.[17] This reaction may also be explained by the ligand coupling in the phosphorane species.

It may be concluded that the reaction pathway of the phosphonium sila-ylide with acetylene is similar to that of the carbon protocol phosphonium ylide and different from that of the ammonium sila-ylide.[18] Thus, the reaction pathways of the sila-ylides with acetylenes clearly reflect the character of the cationic center. Further studies on the reaction pathways of sila-ylides bearing other cationic moieties should contribute to clarifying the character of the element.

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Supporting Information Available: Experimental details and spectroscopic data (PDF) and X-ray crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[10] Crystal data for **5**: monoclinic, $P2_1/c$, colorless, $a = 16.667(1)$ Å, $b = 9.2935(6)$ Å, $c = 17.903(1)$ Å, $\beta = 94.538(3)°$, $T = 173$ K, $Z = 4$, $R = 0.065$, $R_w = 0.085$, GOF = 1.21. Crystal data for **5′**: triclinic, P-1, colorless, $a = 12.4740(7)$ Å, $b = 13.1328(6)$ Å, $c = 11.3443(5)$ Å, $\alpha = 107.217(3)°$, $\beta = 115.824(3)°$, $\gamma = 63.616(2)°$, $T = 173$ K, $Z = 2$, $R = 0.043$, $R_w = 0.065$, GOF = 1.07.

[11] The seven-membered ring in **5** (and **5′**) adopts a puckered structure with the aryl group on the silicon atom and the unshared electron pair of the phosphorus located at the "axial" positions. Judging from this direction, the unshared electron pair of the phosphorus does not seem to coordinate to the silicon center, despite the short P1···Si1 distance [2.9416(9) and 3.0593(7) Å] and the linear P1···Si1−F1 arrangement [168.1(1)° and 167.87(8)°].

[12] Pioneering work of Seyferth et al. has demonstrated the nucleophilic character of the phosphine-coordinated silylene in the reaction with carbonyl compounds; Seyferth, D.; Lim, T. F. O. *J. Am. Chem. Soc.* **1978**, *100*, 7074−7075.

[13] Judging from this reactivity, we feel it better to describe this species as a phosphonium sila-ylide.[1]

[14] (a) Wittig, G.; Maercker, A. *Chem. Ber.* **1964**, *97*, 747−767. (b) Seyferth, D.; Fogel, J.; Heeren, J. K. *J. Am. Chem. Soc.* **1966**, *88*, 2207−2212. (c) Newkome, G. R.; Hager, D. C. *J. Am. Chem. Soc.* **1978**, *100*, 5567−5568. (d) Oae, S.; Uchida, Y. *Acc. Chem. Res.* **1991**, *24*, 202−208.

[15] The ligand coupling reaction has been clarified to occur between two apical groups by careful analyses of the thermolysis of pentaarylantimony compounds.[16] For the phosphorane **8**, if it is involved as an intermediate, the reaction pathway is expected to be the apical-equatorial coupling because three ligands are incorporated in the rigid bicyclic structure.

[16] Akiba, K. *Pure Appl. Chem.* **1996**, *68*, 837−842.

[17] Zbiral, E. *Tetrahedron Lett.* **1964**, 3963−3967; *Monatsh. Chem.* **1964**, *95*, 1759−1780.

[18] To the best of our knowledge, in carbon chemistry, the reaction of an ammonium ylide with acetylenes has not been reported.