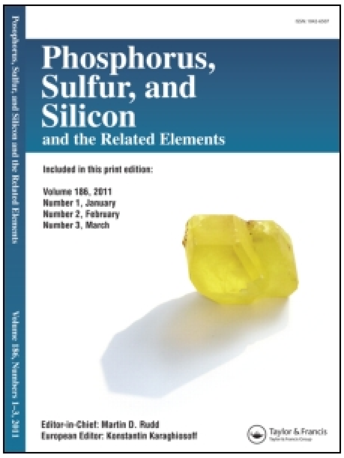

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Intramolecularly Base-Coordinated Silylenes That Behave as Sila-Ylides

Akio Toshimitsu[a]; Tomoyuki Saeki[a]; Kohei Tamao[a]
[a] Institute for Chemical Research, Kyoto University, Kyoto, Japan

To cite this Article Toshimitsu, Akio , Saeki, Tomoyuki and Tamao, Kohei(2002) 'Intramolecularly Base-Coordinated Silylenes That Behave as Sila-Ylides', Phosphorus, Sulfur, and Silicon and the Related Elements, 177: 6, 1409 — 1412
To link to this Article: DOI: 10.1080/10426500212275
URL: http://dx.doi.org/10.1080/10426500212275

Phosphorus, Sulfur and Silicon, 2002, Vol. 177:1409–1412

1042-6507/02 $12.00 + .00
DOI: 10.1080/10426500290092811

INTRAMOLECULARLY BASE-COORDINATED SILYLENES THAT BEHAVE AS SILA-YLIDES

Akio Toshimitsu, Tomoyuki Saeki, and Kohei Tamao
Institute for Chemical Research, Kyoto University, Kyoto, Japan

(Received July 29, 2001; accepted December 25, 2001)

Divalent silicon species bearing an 8-amino- or 8-phosphino-1-naphthyl group have been shown to behave as nucleophilic sila-ylides in the presence of diphenylacetylene to afford zwitterionic intermediates containing alkenyl anion and ammonium or phosphonium cation moieties. The reaction pathways of these zeitterionic intermediates have been clarified to be highly dependent on the character of the cationic center such as N and P.

Keywords: Base-coordinated silylene; ligand coupling; pentacoordinate silicon; phosphonium ylide; sila-ylide; thermolysis

It is well known that the ground state of a divalent silicon species, silylene, is a singlet with an electron pair in σ orbital and a vacant orbital of π symmetry. A priori, silylenes can behave as ambiphiles because both the electron pair and the vacant orbital can take part in the reactions. In the reported examples, however, the first step has been shown to have an electrophilic character; that is, the reaction proceed through the vacant orbital. By the coordination of Lewis base to this vacant orbital, the electrophilic character is expected to be reduced. In the case where the coordination be strong enough as to make a bond, such a silicon center would no longer show the electrophilic character but behave as nucleophile; some examples that strongly suggest the nucleophilic character of base-coordinated silylenes have been reported.[1–6] We report herein that (1) the silylenes bearing an 8-amino- or 8-phosphino-1-naphthyl group behave as nucleophilic sila-ylides during the reaction with diphenylacetylene and (2) the reaction pathways of the intermediates produced by this reaction are highly dependent on the character of the coordinating element, nitrogen or phosphorus.

Address correspondence to Akio Toshimitsu, Institute for Chemical Research, Kyoto University, Uji Kyoto 611-0011, Japan.

RESULTS AND DISCUSSIONS

The pentacoordinate fluorodisilanes **1a–1c** bearing an 8-amino- or 8-phosphino-1-naphthyl group, the precursors of the ammonium or phosphonium sila-ylide, were prepared by the reaction of 8-amino- or 8-phosphino-1-naphthyllithium with 1,1-difluoro-1,2-dimethyl-2,2-diphenyldisilane. The coordination of the nitrogen or phosphorus atom to the silicon atom has been shown in the solid state and in solution by X-ray crystallographic analysis* and by NMR spectroscopy, respectively.

Thermal degradation of **1a–1c** was completed at 110–140°C† to afford the α-elimination product, fluoromethyldiphenylsilane, in almost quantitative yield. The other products, base-coordinated silylenes **2**, were trapped with diphenylacetylene to afford various types of cyclized products **4–6** shown in Figure 1.

In the case of **1a** containing the *dimethylamino* group, the 1-silaphenalene skeleton was formed through the incorporation of diphenylethenyl group between the silicon atom and naphthyl carbon accompanied by the migration of the amino group to the silicon atom to afford **4**.

In the case of **1b** containing the *diethylphosphino* group, the products were the mixture of stereoisomers (ca. 2:1) of the six-membered cyclic compound **5**, which contained an ethylydene bridge between the silicon atom and the phosphorus atom and a (Z)-diphenylethenyl group on the silicon atom, indicative of hydrogen migration from the methylene in the diethylphosphino group to the alkenyl carbon atom.

In the case of **1c** containing the *diphenylphosphino* group, the product was a seven-membered cyclic compound **6**, in which the diphenylethenyl group was incorporated between the silicon atom and the phosphorus atom and one phenyl group migrated from the phosphorus to silicon. The P to Si phenyl migration was confirmed by a similar experiment using the di(4-fluorophenyl)phosphino analogue, in which the 4-fluorophenyl group migrated to afford **6′**.

All of the cyclization reactions just described are best understood by assuming that the silicon center in **2** nucleophilically adds to diphenylacetylene to afford the zwitterionic intermediates **3**, which contain

---

*Coordination of phosphorus to silicon in **1c** has been shown to be similar to that of nitrogen to silicon in **1a′** ($SiPh_3$ instead of $SiMePh_2$ in **1a**) in the following parameters. %TBPe: **1c**, 76%; **1a′**, 80%: X· · ·Si–F angle: **1c** (X = P), 175.89(8)°; **1a′** (X = N), 166.10(9)°: X· · ·Si distance/van der Waals radii: **1c** (X = P), 77%; **1a′** (X = N), 78%.

†Temperatures required for the thermal degradation of **1a** (140°C), **1b** (110°C), and **1c** (140°C) indicate that the formation of phosphine-coordinated silylenes **2b** and **2c** is not less favorable than that of nitrogen-coordinated silylene **2a**.

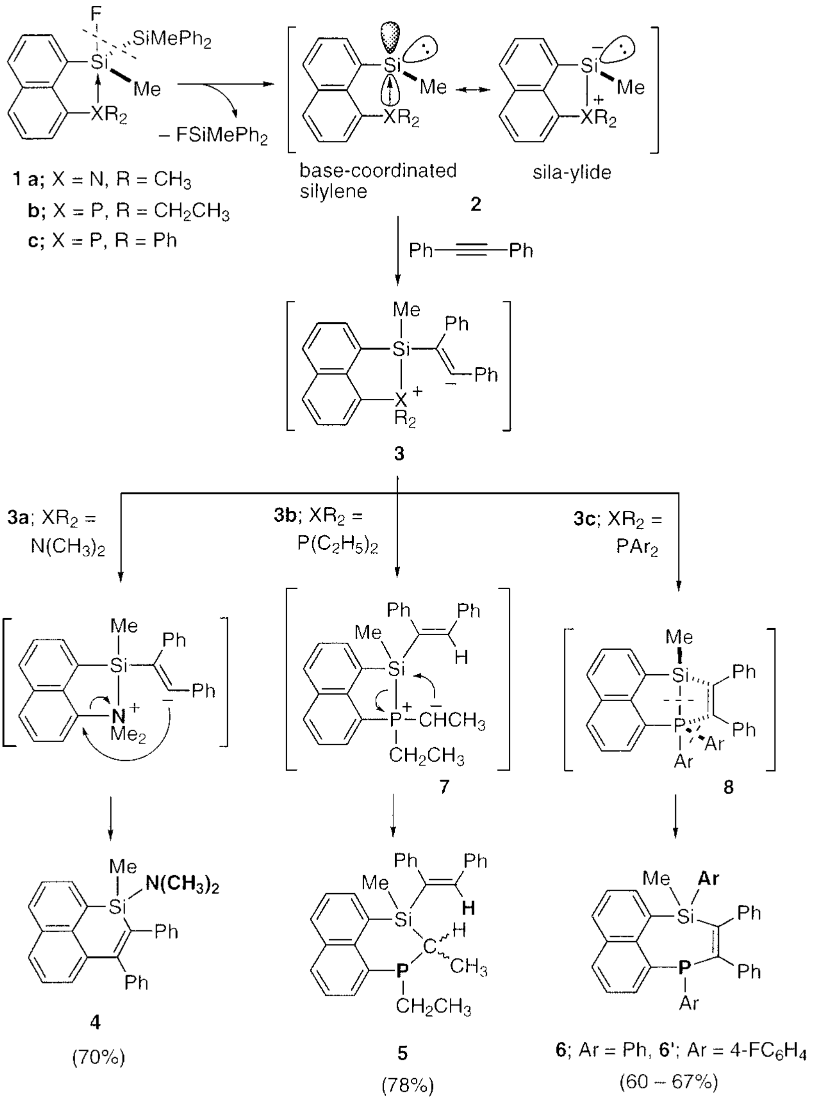

FIGURE 1

alkenyl anion and ammonium or phosphonium cation moeities. For the diethylphosphino derivative **3b**, the alkenyl anion abstracts a proton from the methylene of the diethylphosphino group to form the phosphonium ylide **7**. The formed ylide carbanion nucleophilically attacks the silicon atom, causing silicon—phosphorus bond fission, resulting in the formation of the six-membered cyclic product **5**. The reaction course of the nitrogen analogue **3a** is different from that of **3b**, presumably because the proton abstraction from the dimethylamino group in **3a** is not possible due to the lower ability of nitrogen to stabilize the ylide. Thus, the alkenyl anion nucleophilically attacks the naphthyl carbon, accompanied by carbon—nitrogen bond fission, which is equivalent to the migration of the amino group from carbon to silicon. For the diarylphosphino derivative **3c** where the proton abstraction is also not possible from the diarylphosphino group, the reaction course is still different from that of **3a**. As also shown in Figure 1, the alkenyl anion in **3c** nucleophilically attacks the phosphorus atom to form a pentavalent phosphorane intermediate **8** (or a transition structure), which undergoes ligand coupling[7–10] of the aryl group and the silicon atom on the phosphorus center, resulting in the formation of the seven-membered cyclic product **6** or **6′**. This route seems to have emerged due to the intrinsic ability of phosphorus to form pentavalent species.

The reaction course of the sila-ylide with acetylenes clearly reflect the character of the cationic center. Further studies on the reaction pathways of sila-ylide bearing other cationic moieties should contribute to clarifying the character of the element.

REFERENCES

[1] D. Seyferth and T. F. O. Lim, *J. Am. Chem. Soc.*, **100,** 7074 (1978).

[2] R. J. P. Corriu, G. Lanneau, C. Priou, F. Soulairol, N. Auner, R. Probst, R. Conlin, and C. Tan, *J. Organomet. Chem.*, **466,** 55 (1994).

[3] N. Takeda, H. Suzuki, N. Tokitoh, and R. Okazaki, *J. Am. Chem. Soc.*, **119,** 1456 (1997).

[4] J. Belzner, U. Dehnert, H. Ihmels, M. Hübner, P. Müller, and I. Usón, *Chem. Eur. J.*, **4,** 852 (1998).

[5] J. Belzner, In *Organosilicon Chemistry III. From Molecules to Materials*, eds. N. Auner and J. Weis (VCH, Weinheim, 1998), p. 58.

[6] K. Tamao, M. Asahara, T. Saeki, S.-G. Fen, and A. Toshimitsu, *Chem. Lett.*, 660 (2000).

[7] G. Wittig and A. Maercker, *Chem. Ber.*, **97,** 747 (1964).

[8] D. Seyferth, J. Fogel, and J. K. Heeren, *J. Am. Chem. Soc.*, **88,** 2207 (1966).

[9] G. R. Newkome and D. C. Hager, *J. Am. Chem. Soc.*, **100,** 5567 (1978).

[10] S. Oae and Y. Uchida, *Acc. Chem. Res.*, **24,** 202 (1991).