more intense the satellite.[5] However, the satellite of $H[LnPc_2]$ is much more intense than that of $ThPc_2$, though the latter complex must have more covalent character in M–L bonding than the former. Magnetism of the compounds which relates to multiple splitting of core levels also cannot interpret this puzzling question.

Let us now point out that adiabatic relaxation upon the core-hole creation is a crucial factor governing the satellite intensity observed.[20,21] Recent MS Xα calculations of LaF_3 and CeF_3 found a large influx of electrons from the ligands to the 4f shell during core ionization.[22] In the ground state of the lanthanide complexes $H[LnPc_2]$, an occupied molecular orbital (ϕ_L), which is localized on the ligands, is expected to have only small amount of metal 4f admixture. The antibonding counterpart (ϕ_M^*) of the occupied orbital is then essentially 4f orbital. Owing to the electron flow upon core ionization, the antibonding counterpart ($\phi_M^*(i)$) should gain ligand character in core-ionized state. The strong satellite of the La complex can be explained by the large overlap between these MO's, $\langle \phi_L | \phi_M^*(i) \rangle$ under the sudden approximation. The presence of half-occupied 4f orbital(s) appears to cause a decrease in shake-up intensity of $H[CePc_2]$ and a vanishing of the shake-up of $H[PrPc_2]$ and $H[NdPc_2]$. This is likely because the half-occupied 4f orbital(s) can receive electrons, instead of vacant 4f orbitals, from ligand orbitals upon core ionization. The possible electron flow to the half-filled 4f level results in considerable diminution of ligand character in ϕ_M^* orbital and consequently a much smaller overlap $\langle \phi_L | \phi_M^*(i) \rangle$. In the actinide complexes $[AnPc_2]$, the ϕ_L orbital must have some 5f admixture even in their ground states. Thus, the electron flow from ligands to 5f levels is not so significant as it is in the lanthanide case. In such a situation, we cannot anticipate either the large overlap $\langle \phi_L | \phi_M^*(i) \rangle$, i.e., strong satellite, or the significant role of half-occupied 5f orbital(s) to reduce shake-up intensity.

Acknowledgment. This work was supported by the Robert A. Welch Foundation (Grant No. A420) and the Office of Naval Research. We thank Dr. M. B. Hall for stimulating and informative discussions and Dr. F. Lux for having carefully made the $AnPc_2$ complexes.

References and Notes

(1) C. K. Jørgensen, *Struct. Bonding (Berlin)*, **13**, 199 (1973).
(2) J. J. Pireaux, N. Mårtensson, R. Didriksson, K. Siegbahn, J. Riga, and J. Verbist, *Chem. Phys. Lett.*, **46**, 215 (1977), and references therein.
(3) G. K. Wertheim, R. L. Cohen, A. Rosencwaig, and H. J. Guggenheim, in "Electron Spectroscopy", by D. A. Shirley, Ed., North-Holland, Amsterdam, 1972.
(4) C. K. Jørgensen and H. Berthou, *Chem. Phys. Lett.*, **13**, 186 (1972).
(5) H. Berthou, C. K. Jørgensen, and C. Bonnelle, *Chem. Phys. Lett.*, **38**, 199 (1976).
(6) A. J. Signorelli and R. G. Hayes, *Phys. Rev. B*, **8**, 81 (1973).
(7) D. Chadwick, *Chem. Phys. Lett.*, **21**, 291 (1973).
(8) C. Miyake, H. Sakurai, and S. Imoto, *Chem. Phys. Lett.*, **36**, 158 (1975).
(9) R. Dubois, J. C. Carver, and M. Tsutsui, *J. Coord. Chem.*, **6**, 123 (1976).
(10) J. J. Pireaux, J. Riga, E. Thibaut, C. Tenret-Noel, R. Caudano, and J. J. Verbist, *Chem. Phys.*, in press.
(11) (a) I. S. Kirin, P. N. Moskalev, and Yu. A. Makashev, *Russ. J. Inorg. Chem.*, **12**, 369 (1969); (b) S. Misumi and K. Kasuga, *Nippon Kagaku Zasshi*, **92**, 335 (1971).
(12) The peak has been assigned to the carbon atoms of having aromatic hydrocarbon character in the phthalocyanine ring.
(13) The satellite of U $4d_{5/2}$ is so broad that for the moment accurate analysis of ΔE and R values cannot be given. The satellite may involve several shake-up transitions.
(14) G. C. Allen and P. M. Tucker, *Chem. Phys. Lett.*, **43**, 254 (1976). Recently, Bancroft et al.[15a] also found that Th $4d_{5/2}$ peak of $Th(AcAc)_4$ gives narrow satellite of variable intensity ($R = 0.62$) of ~8 eV from the main line. Since the interaction integral (δ value) is small for the interaction configurations $4d^9 4f^{14} \leftrightarrow 4d^{10} 4f^{12} 6d$, the relatively strong satellite is not expected from the CI mechanism[15b] (Coster–Kronig transition) which seems important to interpret 4f, 5s, 5p and 5d satellites of actinides. Compared with the $4d_{5/2}$ satellite of $Th(AcAc)_4$, that of $ThPc_2$ is broad and locates at 4.6 eV from main peak, which is similar to L $\rightarrow$ 5f shake-up satellite of U 4f spectra.
(15) (a) G. M. Bancroft, T. K. Sham, and S. Larsson, *Chem. Phys. Lett.*, **46**, 551 (1977); (b) C. K. Jørgensen, *Struct. Bonding (Berlin)*, **30**, 141 (1976).
(16) K. Tatsumi, M. Tsutsui, G. W. Beall, D. F. Mullica, W. O. Milligan, *J. Electron Spectrosc.*, in press.
(17) W. A. Coghlan and R. E. Clausing, *At. Data*, **5**, 317 (1973).
(18) M. O. Krause, private communication. When the molecular rearrangement can occur during core ionization, there is a possibility of an energy gain by the interatomic shake-up transition. This process may be considered "shake-down".
(19) R. Dubois, J. C. Carver, and M. Tsutsui, *J. Coord. Chem.*, **7**, 31 (1977).
(20) T. Robert and G. Offergeld, *Chem. Phys. Lett.*, **29**, 606 (1974).
(21) S. Larsson, *Chem. Phys. Lett.*, **32**, 401 (1975).
(22) J. Weber, H. Berthou, and C. K. Jørgensen, *Chem. Phys. Lett.*, **45**, 1 (1977).
(23) Robert A. Welch Postdoctoral Fellow, Texas A&M University, 1977–

K. Tatsumi,[23] K. Kasuga, M. Tsutsui*
Department of Chemistry, Texas A&M University
College Station, Texas 77843

Received March 3, 1978

Efficient Trapping of Silylenes through Disilene Intermediates[1]

Sir:

During the course of the study on disilenes, we have found that variously substituted silylenes (**1**) can dimerize efficiently to disilenes (**2**) which are trapped with anthracene. Previously, Margrave and Perry[2] have rationalized results of the reaction of difluorosilylene with acetylene at low temperature in the condensed phase by postulating the existence of tetrafluorodisilene (or diradical), and Conlin and Gaspar[3] have shown recently that dimethylsilylene dimerizes in the gas phase at 600–700 °C to give tetramethyldisilene as an intermediate. Existence of the latter has been evidenced from the reaction product identical with the known rearrangement product found previously in the reaction of disilene.[4]

Cothermolysis of 2,3-benzo-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorbornadiene (**3a**)[5] and anthracene in a sealed tube at 350 °C gave 2,3,5,6-dibenzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**6a**)[4] in 36% yield along with 1,2,3,4-tetraphenylnaphthalene. The formation of **6a** is rationalized most reasonably in terms of the Diels–Alder-type reaction of highly reactive tetramethyldisilene with anthracene, an efficient enephile, as depicted in Scheme I. The phenylmethylsilylene and the diphenylsilylene were also generated similarly from **3b** and **3c** (350 °C, 1 h) and gave **6b** (40% yield) and **6c**[6] (46% yield), respectively, by the reaction with anthracene.

7-Silanorbornadiene is a well-known thermochemical silylene generator[5] and, in fact, on thermolysis of **3a** in the presence of both 2,3-dimethylbutadiene and anthracene, the dimethylsilylene was trapped with the diene affording 1,1,3,4-tetramethyl-1-sila-3-cyclopentene (**7a**)[7] in 36% yield. However, under these conditions, **6a** was not detected in the thermolysate. This fact can be explained well by postulating that the butadiene traps the dimethylsilylene so efficiently that the concentration of the silylene would be too low to undergo dimerization.

Another possible route to **6a** without involving intermediate disilene is a stepwise insertion of the dimethylsilylene into anthracene. Such a route has to involve 2,3,5,6-dibenzo-7,7-dimethyl-7-silabicyclo[2.2.1]hepta-2,5-diene as a direct precursor to **6a**. At this moment, this possibility cannot be excluded completely. However, in carbene chemistry, it is known that only the 1,2 adduct was obtained from the thermal reaction of $:CHCO_2R$ with anthracene.[8a,b] Although in some cases, a hypothetical 9,9a adduct of $:CH_2$ and anthracene, that subsequently isomerized to dibenzonorbornadiene, was obtained as a minor product;[8c] in the case of thermally generated silylenes, such adducts of cyclic dienes gave ring-expanded products predominantly rather than rearranged products.[8d,e] The 7-silanorbornadiene system, such as the precursor itself,

0002-7863/79/1501-0486$01.00/0

Table I. Some Physical Properties of New Compounds

3b: mp 239–241 °C; mass spectrum (rel intensity) M^+ 552 (100); NMR δ (CCl_4) 0.20 (3 H, s, CH_3), 6.4–7.7 (29 H, m, Ph)

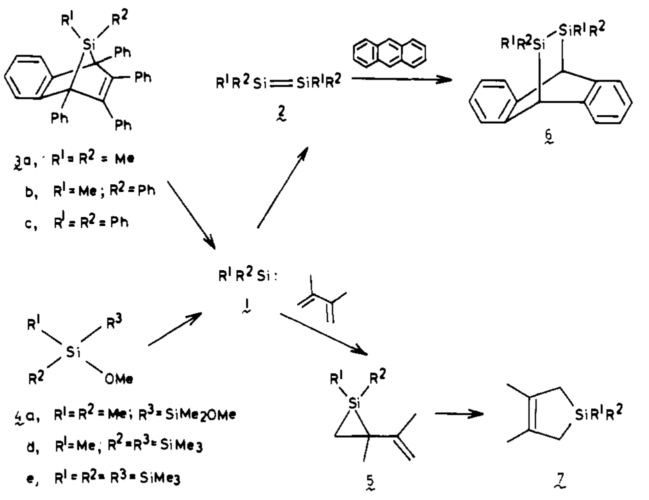
4d: bp 77 °C (20 mmHg); mass spectrum (rel intensity) M^+ 220 (4.9), *m/e* 73 (100); NMR δ (CCl_4) 0.12 (18 H, s), 0.34 (3 H, s), 3.34 (3 H, s)

4e: bp 63 °C (0.5 mmHg); mass spectrum (rel intensity) M^+ 278 (1.5), *m/e* 73 (100); NMR δ (CCl_4) 0.14 (27 H, s), 3.35 (3 H, s)

6d: bp 160–180 °C (0.2 mmHg); mass spectrum (rel intensity) M^+ 410 (24.9), *m/e* 232 (100); NMR δ (CCl_4), trans, −0.07 (6 H, s), −0.12 (18 H, s), 4.08 (2 H, s), 7.0–7.2 (8 H, m, arom), and cis, −0.26 (6 H, s), 0.00 (18 H, s), 4.10 (2 H, s), 7.0–7.2 (8 H, m, arom)

6e: mp 275 °C; mass spectrum (rel intensity) M^+ 526 (4.3), *m/e* 348 (100); NMR δ (CCl_4) 0.06 (36 H, s) 4.27 (2 H, s), 6.8–7.2 (8 H, m, arom)

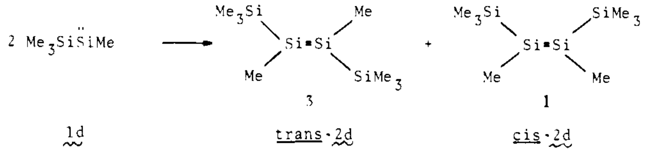
Scheme I



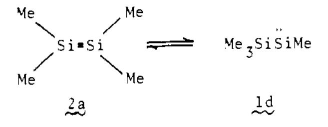
is also not reactive enough to be susceptible to silylene insertion. Therefore, we favor the mechanism shown in Scheme I.

Methoxypolysilanes are also well-defined silylene generators[9] and, indeed, the dimethylsilylene generated from **4a** afforded **6a** by reaction with anthracene. The yield of **6a** from **4a** was highly temperature dependent. Thus, at 300 °C, no adduct was found in the thermolyzed mixture of **4a** and anthracene, but **6a** was obtained as a trace at 350 °C and in 6.2% yield at 390 °C. Methyl(trimethylsilyl)silylene (**2d**) and the bis(trimethylsilyl)silylene (**2e**), more bulky silylenes, generated from **4d** and **4e**, gave the corresponding adducts **6d** (72% yield, 350 °C, 4 h) and **6e** (48% yield, 250 °C, 3 h), respectively, in higher yields. These results indicate that dimerization of silylenes competes with insertion into the Si-OMe bond of the precursor.[10] Some physical properties of new compounds are summarized in Table I.[11]

Interestingly, an ~1:1 mixture of trans and cis isomers of **6b** was obtained from **4b** (350 °C). Since *cis*- and *trans*-1,2-diphenyl-1,2-dimethyldisilene are configurationally stable under these conditions,[12] the result implies no stereochemical preference in the dimerization of the phenylmethylsilylene. However, **4d** gave two isomers of **6d** in the ratio 3:1 at 250 °C. Therefore, the methyl(trimethylsilyl)silylene dimerized stereoselectively to the disilenes in favor of one isomer which was tentatively assigned to be trans.



Very recently, Wulff, Goure, and Barton[13] reported that tetramethyldisilene (**2a**) isomerizes to **1d** and that **1d** also isomerizes to **2a** to some extent in vapor phase.



However, in our experimental conditions, there is no indication of such a rearrangement. In fact, we generated **1d** in the hope of obtaining **2a** which has been known to be trapped by anthracene,[4] but no **6a** was detected. The discrepancy between these experiments may arise from the different experimental conditions, but we reserve the explanation until new experimental results are available.

Acknowledgment. We thank Toshiba Silicone Co., Ltd., for gifts of chlorosilanes.

References and Notes

(1) Chemistry of Organosilicon Compounds. 108.
(2) J. L. Margrave and K. L. Perry, *Inorg. Chem.*, **16**, 1820 (1977).
(3) R. T. Conlin and P. P. Gaspar, *J. Am. Chem. Soc.*, **98**, 868 (1976).
(4) D. N. Roark and G. J. D. Peddle, *J. Am. Chem. Soc.*, **94**, 5837 (1972).
(5) H. Gilman, S. G. Cottis, and W. H. Atwell, *J. Am. Chem. Soc.*, **86**, 1596 (1964).
(6) C. L. Smith and J. Pounds, *J. Chem. Soc., Chem. Commun.*, 910 (1975).
(7) W. H. Atwell and D. R. Weyenberg, *J. Am. Chem. Soc.*, **90**, 3438 (1968).
(8) (a) G. M. Badger, J. W. Cook, and A. R. M. Gibb, *J. Chem. Soc.*, 3456 (1951); (b) S H. Graham, D. M. Pugh, and A. J. S. Williams, *J. Chem. Soc. C*, 68 (1969); (c) E. Müller and H. Kessler, *Justus Liebigs Ann. Chem.*, **692**, 58 (1966); (d) E. A. Chernyshev, N. G. Komalenkova and S. A. Bashkirova, *Dokl. Akad. Nauk SSSR*, **205**, 868 (1972); (e) M. E. Childs and W. P. Weber, *Tetrahedron Lett.*, 4033 (1974).
(9) W. H. Atwell and J. G. Uhlmann, *J. Organomet. Chem.*, **52**, C21 (1973).
(10) D. R. Weyenberg and W. H. Atwell, *Pure Appl. Chem.*, **19**, 343 (1969).
(11) All new compounds gave satisfactory elemental analyses and spectral data.
(12) H. Sakurai, Y. Nakadaira, and T. Kobayashi, *J. Am. Chem. Soc.*, following paper in this issue.
(13) W. D. Wulff, W. F. Goure, and T. J. Barton, *J. Am. Chem. Soc.*, **100**, 6236 (1978).

Yasuhiro Nakadaira, Toshiaki Kobayashi
Tatsuo Otsuka, Hideki Sakurai*
Department of Chemistry, Faculty of Science
Tohoku University, Sendai 980, Japan

Received June 19, 1978

trans- and *cis*-1,2-Dimethyl-1,2-diphenyldisilene. Is Si═Si a True Double Bond?[1]

Sir:

Although disilenes, the silicon–silicon double-bonded species, have been recognized as intermediates in certain reactions,[2] no experimental knowledge has been obtained on the double-bond properties such as geometrical isomerism of the Si═Si bond.[3] We report in this communication the first evidence of the geometrical isomerism of the silicon–silicon double bond.

The reaction of 1,4-dilithio-1,4-diphenylbutadiene[4] with 1,2-difluoro-1,2-dimethyl-1,2-diphenyldisilane in THF gave a mixture of *trans*- and *cis*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexadiene which was separated into each isomer by silica gel chromatography.[5]

The stereochemical assignment of trans (**1a**) and cis isomers (**1b**) is not easy from the NMR results only, but can be accomplished unequivocally by examination of the NMR signals due to Si-Me groups of products of the next step (**2a** and **2b**).

0002-7863/79/1501-0487$01.00/0