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Chemistry of organosilicon compounds. 181. Silylene-to-disilene and disilene-to-silylene rearrangements

Hideki Sakurai, Yasuhiro Nakadaira, and Hiroyuki Sakaba

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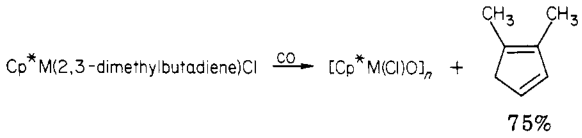
are in fact group 4B metallacyclo-3-pentenes. Additional support for this is found in the IR spectra, where an absorption at 1530–1550 cm^{-1} can be assigned to the double bond of the metallacyclo-3-pentene.[7c]

The chemistry of the compounds Cp*M(1,3-diene)Cl is very interesting. The chlorine atom can be easily substituted by organic groups R by treatment with appropriate Grignard or lithium reagents.[11] The coordinatively strongly unsaturated (14-electron) compounds react readily with donor ligands (e.g., THF or PR_3) to give 16-electron systems Cp*M(1,3-diene)(Cl)(L). Formation of 18-electron complexes Cp*M(1,3-diene)(Cl)$(L)_2$ was not observed.

With CO, adduct formation is the initial step,[12] but the adducts are unstable and react further in what is probably an intramolecular reaction of the carbonyl ligand with the coordinated diene.



M = Zr, Hf

The reaction proceeds under moderate conditions (1 atm of CO, 25 °C) and leads to complete reduction of the carbon monoxide molecule with incorporation of the carbon atom into the 4-position of the product 1,2-dimethyl-1,3-cyclopentadiene, as could be demonstrated by reaction with ^{13}C-enriched CO.[13] The oxygen atom ends up at the transition-metal atom, forming a complex of composition [Cp*M(O)Cl]$_n$,[15] which is most likely oligomeric. To the best of our knowledge this reaction is the first example of carbon monoxide reduction, with complete separation of the carbon–oxygen bond, on a mononuclear transition-metal species under mild conditions. Insertion of CO into several early transition-metal metallacycles has been observed, and normally cyclic ketones are formed directly or isolated after quenching.[16,17]

The closely related compounds Cp_2Zr(cis-diene) react with CO similarly with formation of dimethylcyclopentenone, and cleavage of the C–O bond is not observed.[18] The pentamethylcyclopentadienyl 1,3-diene complexes are unique in showing that the oxophilicity of early transition metals is so great that it can lead to split the CO molecule completely.

Further reactions of these types of complexes and the related compounds Cp*M(1,3-diene)R (R = alkyl, aryl) with CO, and isocyanides are under investigation at the moment.

Acknowledgment. Dr. E. J. Kwak is thanked for his able assistance. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No. 1, 87050-41-7; 2, 87050-42-8; 3, 87050-43-9; 4, 87050-44-0; Cp*$ZrCl_3$, 75181-07-6; Cp*$HfCl_3$, 75181-08-7; Cp*Hf(2,3-dimethylbutadiene)Me, 87050-45-1; Cp*Hf(2,3-dimethylbutadiene)Et, 87050-46-2; Cp*Hf(2,3-dimethylbutadiene)*neo*-pent, 87050-47-3; Cp*Hf(2,3-dimethylbutadiene)Ph, 87050-48-4; Cp*Hf(2,3-dimethylbutadiene)allyl, 87050-49-5; Cp*Hf(2,3-dimethylbutadiene)Cl(CO), 87050-50-8; [Cp*Hf(O)Cl]n, 87050-52-0; [Cp*Zr(O)Cl]n, 87050-54-2; CO, 630-08-0; 1,2-dimethyl-1,3-cyclopentadiene, 4784-86-5.

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[11] For 4 this substitution has been worked out in detail: Cp*Hf(2,3-dimethylbutadiene)R (R = Me, Et, neo-Pent, Ph, allyl) was prepared and characterized (analyses, ^{1}H NMR ^{13}C NMR, IR).

[12] The IR spectrum of a pentane solution of 4 showed, after admission of CO, a strong absorption at 2114 cm^{-1} due to Cp*Hf(2,3-dimethylbutadiene)Cl(CO). The absorption disappears quickly to give new absorptions at 1589 and 1630 cm^{-1} due to C–C stretching frequencies of free 1,2-dimethyl-1,3-cyclopentadiene.

[13] A solution of 2 or 4 (about 1 M) in benzene-d_6 was treated with CO (1 atm, 25 °C). After the uptake of CO had ceased, the reaction mixture was evaporated in vacuo and the volatile components were condensed into a cold trap (−78 °C). 1,2-Dimethyl-1,3-cyclopentadiene was identified (MS, ^{1}H NMR, ^{13}C NMR) by comparison with an authentic sample.[14] ^{13}C NMR (50.3 MHz, benzene-d_6, 34 °C, δ): 136.9 (d, J = 160 Hz, $CH_2CH{=}CH$), 135.6 (s, $C(CH_3)$), 134.7 (s, $C(CH_3)$), 129.4 (d, J = 165 Hz, $CH_2CH{=}CH$), 45.8 (t, J = 124 Hz, $CH_2CH{=}CH$), 13.1 (q, J = 127 Hz, $C(CH_3)$, and 12.6 (q, J = 127 Hz, $C(CH_3)$). With ^{13}C-enriched CO the intensity of the absorption at 129.4 ppm increased strongly, demonstrating the incorporation of ^{13}C at the 4-position of the cyclopentadiene.

[14] Skattebøl, L. S. *Tetrahedron* **1967**, *23*, 1107.

[15] After the solution was washed, the compound [Cp*Hf(O)Cl]$_n$ was isolated, as a white powder. Anal. Calcd: C, 32.89; H, 4.14; Hf, 48.87; Cl, 9.80. Found: C, 33.08; H, 4.19; Hf, 48.31; Cl, 9.71. ^{1}H NMR (60 MHz, $CDCl_3$, 34 °C, δ): 2.15(s).

[16] Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716.

[17] McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529.

[18] Erker, G.; Engel, K.; Krüger, C.; Chiang, A.-P. *Chem. Ber.* **1982**, *115*, 3311.

Silylene to Disilene and Disilene to Silylene Rearrangements[1]

Hideki Sakurai,* Yasuhiro Nakadaira, and Hiroyuki Sakaba

Department of Chemistry, Tohoku University
Sendai 980, Japan

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Summary: The silylene to disilene rearrangement was further confirmed by generating $Me_3SiMe_2SiMeSi$: from 3-methoxyundecamethylpentasilane to afford $Me_2Si{=}SiMe(SiMe_3)$. However, at the same time the reverse rearrangement from the latter disilene to the former disilanylsilylene was also demonstrated by generating $Me_2Si{=}SiMe(SiMe_3)$. Results of photochemically generated disilanylsilylene and silyldisilene were compared with those of thermal reactions.

Recently we have reported the first clear evidence of the silylene to disilene rearrangement by generating $Me_3SiMe_2SiMeSi$: (1) from the newly prepared precursor 2,3-benzo-1,4-diphenyl-7-methyl-7-(pentamethyldisilanyl)-7-silanorbornadiene (2).[2] The silylene 1 rearranges to $Me_2Si{=}SiMe(SiMe_3)$ (3) by the 1,2-trimethylsilyl shift. Although the mechanism of the thermal decomposition of 7-silanorbornadiene derivatives has been well established to give a sound basis for giving the silylene, it is desirable to generate the silylene by an alternative route in order to confirm the previous result. Thus we have synthesized 3-methoxyundecamethylpentasilane (4) and conducted its thermolysis (sealed tube, 300 °C, 7 h) in the hope to generate 1.

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[1] Chemistry of Organosilicon Compounds. 181.

[2] Sakurai, H.; Sakaba, H.; Nakadaira, Y. *J. Am. Chem. Soc.* **1982**, *104*, 6156.

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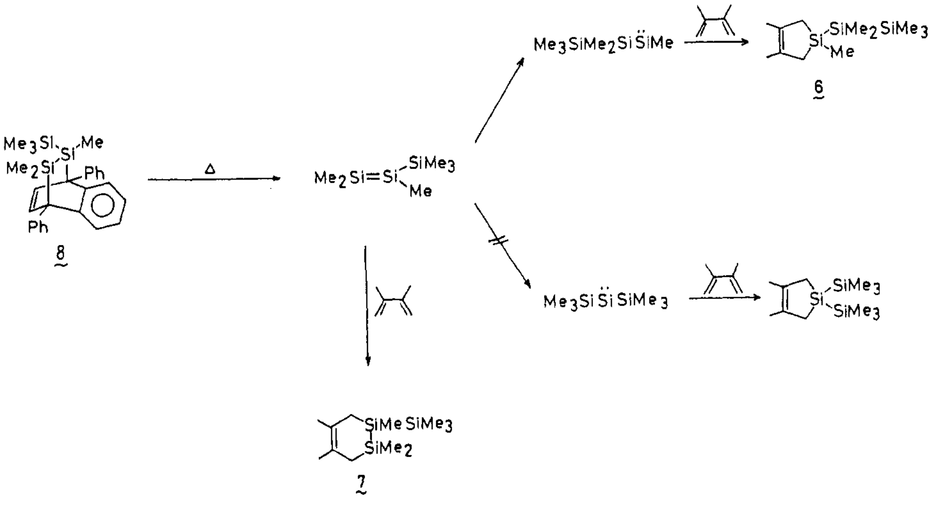
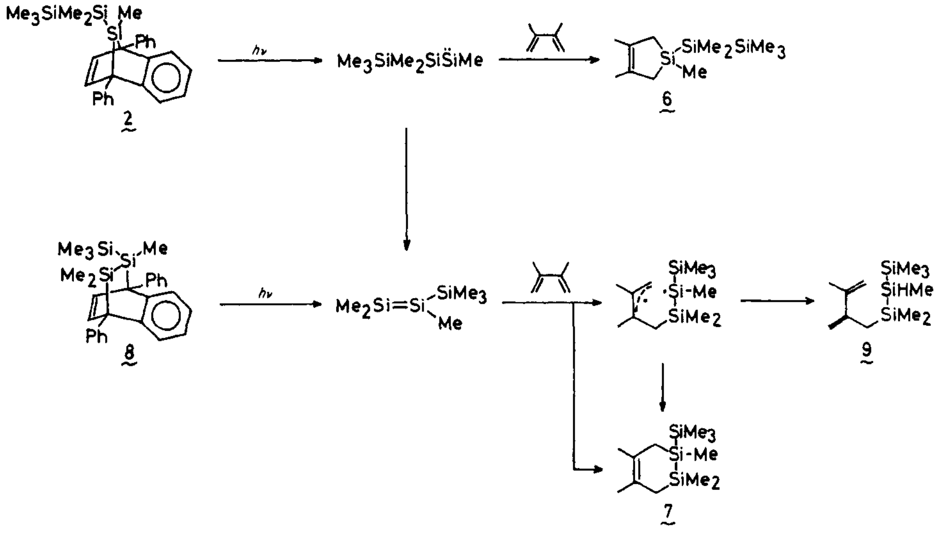
Scheme I



Scheme II



$$\underset{4}{(\mathrm{Me_3SiMe_2Si})_2\mathrm{SiMe(OMe)}} \xrightarrow{\Delta} \underset{1}{\mathrm{Me_3SiMe_2SiMeSi\colon}} + \underset{5}{\mathrm{Me_3SiMe_2Si(OMe)}}$$

Thermolysis of **4** resulted in the formation of many products and turned out to be not a clean reaction for the production of the silylene. However, the fact that **5** was obtained in ca. 15% yield together with 1-methoxyheptamethyltrisilane and methoxytrimethylsilane in thermolysis of **4** in the presence of 2,3-dimethyl-1,3-butadiene at 300 °C supports the formation of **1**. In the product, both 1,2,4-trimethyl-4-pentamethyldisilanyl-4-silacyclopent-1-ene (**6**) and 1,2,4,4,5-pentamethyl-5-(trimethylsilyl)-4,5-disilahex-1-ene (**7**) were detected in a 1:1.4 ratio (29% yield). Since these compounds can reasonably be assigned to the expected products from **1** and **3**, respectively, it can be concluded that the silylene **1** was certainly generated from **4** and underwent the thermal rearrangement to **3**. Moreover, thermolsis of **2** under a similar condition afforded **6** and **7** in a 1:1.1 ratio (46% yield), close to the ratio obtained from **4**. It is then reasonable to conclude that both precursors generate the same silylene **1**, which undergoes the rearrangement in the same fashion.

$$\underset{1}{\mathrm{Me_3SiMe_2SiMeSi\colon}} \rightarrow \underset{3}{\mathrm{Me_2Si{=}SiMe(SiMe_3)}}$$

It is now clear that at least the disilanylsilylene **1** rearranges thermally to the silyldisilene **3**. However, the silylsilylene–disilene rearrangement is a matter of controversy from both experimental[3] and theoretical[4] points of view, and it is also desirable to generate the disilene **3** in order to gain information for the rearrangement. Thus we have prepared a new disilene generator, 2,3-benzo-1,4-diphenyl-7,7,8-trimethyl-8-(trimethylsilyl)-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**8**),[5] and conducted the pyrolysis in the presence of 2,3-dimethyl-1,3-butadiene (sealed tube, 300 °C, 15 h), and actually **6** (9%) was obtained in addition to **7** (34%).

1,2-Dimethyl-4,4-bis(trimethylsilyl)-4-silacyclopent-1-

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[3] Wulff, W. D.; Goure, W. F.; Barton, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 6236.

[4] Köler, H. J.; Lischka, H. *J. Am. Chem. Soc.* **1982**, *104*, 5584 and references cited therein.

[5] **8**: mp 116–117.5 °C; ^{1}H NMR (CCl$_4$) δ 0.11 (3 H, s, SiMe), 0.16 (9 H, s, SiMe$_3$), 0.19 (3 H, s, SiMe), 0.44 (3 H, s, SiMe), 6.18 (2 H, s, vinyl protons), 6.20–6.90 (4 H, m, benzo protons), 7.15–7.55 (10 H, m, phenyl protons); MS, *m/e* (relative intensity) M$^+$ 453 (3), 174 (100); high-resolution MS, found 454.1969, calcd for $C_{28}H_{34}Si_3$ 454.1969. **9**: ^{1}H NMR (CCl$_4$) δ 0.09 (3 H, d, *J* = 5.0 Hz, SiMe), 0.10 (9 H, s, SiMe), 1.85–1.95 (5 H, m, CCH$_2$ and CCH$_3$), 3.03 (1 H, q, *J* = 5.0 Hz, SiH), 4.65–5.05 (4 H, m, vinyl protons); MS, *m/e* (relative intensity) M$^+$ 256 (6), 182 (87), 123 (75), 73 (100); high-resolution MS, found 256.1499, calcd for $C_{12}H_{28}Si_3$ 256.1499.

ene,[6] which should arise from bis(trimethylsilyl)silylene after 1,2-methyl migration of **3**, was not detected. Therefore, the trimethylsilyl group migrates far more readily than the methyl group in both silylsilylene and silyldisilene. A similar facile migration of the trimethylsilyl group from silylsilene ($Me_3SiSiMe{=}CH_2$) to β-silylsilylene ($Me\ddot{S}iCH_2SiMe_3$) has been reported recently.[7]

Benzodisilabicyclo[2.2.2]octadienes of type **8** generate disilenes photochemically,[8] and we have found that benzosilanorbornadienes also generate silylenes photochemically and have compared the above-mentioned results with photochemical ones at room temperature (15 ± 2 °C).

Photolysis of **2** in *n*-hexane in the presence of a large excess of 2,3-dimethyl-1,3-butadiene (23 equiv) with a 450-W high-pressure mercury lamp in a quartz reactor for 6 h resulted in the formation of **6** (31%) and **7** (~3%). In addition, a new product (**9**) was obtained in 34% yield. On the other hand, photolysis of **8** under the identical conditions gave **7** (6%) and **9** (43%). No trace of **6** was detected. Clearly the disilanylsilylene **1** rearranges to the silyldisilene **3** at room temperature, but the reverse rearrangement was not observed at least under this condition.

The formation of **9** may be explained by an ene-type reaction or more adequately by a free radical reaction.

Thermal reaction of the disilene **3** did not give **9** at all. Because of the thermal instability of **9**, we should be silent to the problem of whether **9** was formed actually in thermal reactions. However, predominant formation of **9** over **7** in photochemical reactions raises an interesting question, that disilenes generates by photochemical means or under photolytic conditions should behave like diradicals. This question may be related to the rather small energy difference between singlet and triplet disilenes predicted by theoretical calculations.[4] Very recently free radical hydrogen abstraction by the electronically excited tetramesityldisilene has been reported.[9]

Acknowledgment is made to Toshiba Silicone Co., Ltd., for gifts of chlorosilanes.

Registry No. 1, 87116-34-5; 2, 83363-81-9; 3, 87116-35-6; 4, 87116-36-7; 5, 18107-29-4; 6, 83363-88-6; 7, 51342-18-8; 8, 87116-37-8; 9, 87116-38-9; methoxytrimethylsilane, 1825-61-2; 1-methoxyheptamethyltrisilane, 87116-39-0; 2,3-dimethyl-1,3-butadiene, 513-81-5.

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(6) Nakadaira, Y.; Kobayashi, T.; Otsuka, T.; Sakurai, H. *J. Am. Chem. Soc.* **1979**, *101*, 486.

(7) Barton, T. J.; Burns, S. A.; Burns, G. T. *Organometallics*. **1982**, *1*, 210.

(8) Nakadaira, Y.; Otsuka, T.; Sakurai, H. *Tetrahedron Lett.* **1981**, *22*, 2417.

(9) Fink, M. J.; DeYoung, D. J.; West, R. *J. Am. Chem. Soc.* **1983**, *105*, 1070.

Book Reviews

Metal Interactions with Boron Clusters. Edited by Russell N. Grimes. Plenum Press, New York. 1982. xiv + 327 pages. $42.50.

This volume is the first in a series entitled "Modern Inorganic Chemistry" edited by John P. Fackler, Jr. The stated objective of this book is to further develop the relationship between polyboranes and metal clusters by reviewing and exploring the structure and properties of metal–boron systems. To present information on these compounds, which are logically considered to lie at the interface between metal chemistry and boron chemistry, two criteria were used: "selective and up-to-date coverage" of metal–boron chemistry and topic selection based on subjects "not previously reviewed per se". The major objective is a commendable one, but the criteria chosen to organize the book are seemingly incompatible with this aim. Effective development of the proposed theme is extremely difficult if based on material not previously reviewed. The net result is a useful book consisting of well-written individual chapters, each of which can be profitably read without consulting the other chapters. It is a book that both complements and supplements the volume "Boron Hydride Chemistry" edited by Muetterties in 1975 but does not possess the unity sought which would have placed this volume above the standard multiauthor review.

The first chapter (36 pages) by M. E. O'Neill and K. Wade deals with a phenomenological description of the structure and bonding of metallaboranes and metallacarboranes. These ideas can now be found in several sources (even some text books), but the emphasis on metal–boron systems provides a good introductory chapter. Chapter 2 (71 pages) by N. N. Greenwood and J. D. Kennedy is devoted to transition-metal derivatives of *nido*-boranes. Comparison of the contents with Chapter 12 in the Muetterties volume demonstrates the rapid development of this area in the last 8 years. The chapter is packed with information and will be a useful source for the short term. Chapter 3 (23 pages) by D. F. Gaines and S. J. Hildebrandt discusses interactions of metals with B_3H_x ligands exclusively. Because this chapter is so highly focused, it has considerable depth. This provides good insight into the metal–boron interaction, particularly that taking place via a metal–hydrogen–boron bridge bond. The fourth chapter (24 pages) by L. J. Todd describes metal–boron cage compounds containing main-group metals. Even more than Chapter 2, this contribution is a straightforward review of the defined area. Chapter 5 (59 pages) by S. Bresadola focuses on carborane–metal complexes containing metal carbon σ bonds. The σ bonds discussed are exo to the cluster framework and are one step removed from the metal–boron interface. This chapter contains a large amount of information; however, only about 25% was published after 1975. The sixth chapter (28 pages) by W. E. Geiger, Jr., presents some electrochemistry of metal–boron compounds from the point of view of an electrochemist. Unfortunately, some recent preparative approaches to metalloboranes via electrochemical methods, though referenced, have not been discussed. Despite this, it is a valuable chapter simply because this information has never been treated as a whole previously. Chapter 7 (47 pages) by R. N. Grimes treats boron clusters with transition-metal hydrogen bonds. Given this reviewer's bias, he finds it the most fascinating topic treated in the book. There are a number of similarities between compounds containing metal–hydrogen–boron interactions and transition-metal systems containing hydrides on the one hand and borane cages on the other. Not surprisingly, next to Chapter 1, it is this chapter that comes closest to the stated objectives of the book.

Thomas P. Fehlner, *University of Notre Dame*