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The Reaction of Disilylacetylenes with Cyclopentadienyl Manganese. Formation of Vinylidene Complexes by 1,2-Silyl Shift[1]

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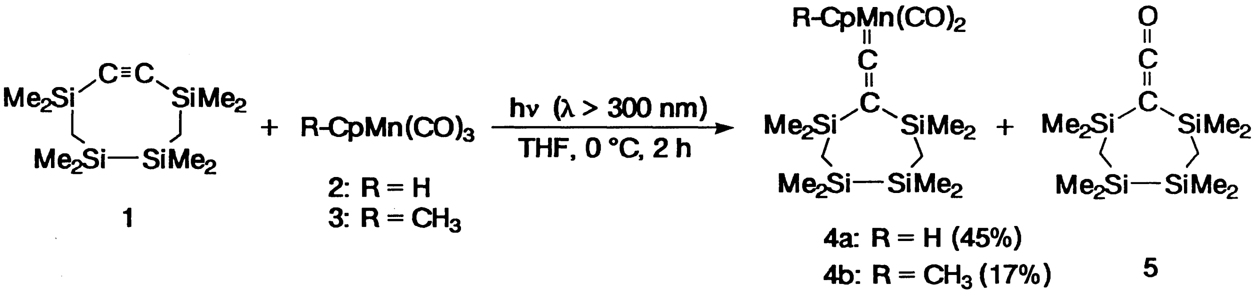
Both cyclic and acyclic acetylenes substituted by two silyl groups on each end undergo facile 1,2-silyl shift in the reaction with cyclopentadienyltricarbonylmanganese under photochemical conditions to give 2,2-disilylvinylidene complexes. Several interesting reactions of the novel complexes are described.

Recently we have reported the formation of novel iron carbonyl complexes of fulvene,[2] methylenecyclopropene,[3] and trimethylenemethane[4] from silicon containing cyclic polyacetylenes. A key step of the reaction is the 1,2-silyl shift in the 1,2-disilyl-substituted acetylenes to give 2,2-disilylvinylidene complexes. The latter undergoes further transformations to give respective products under the conditions.[5] A key intermediate in the cyclotrimerization reactions has been isolated and the structure has been determined by an X-ray crystallography.[3]

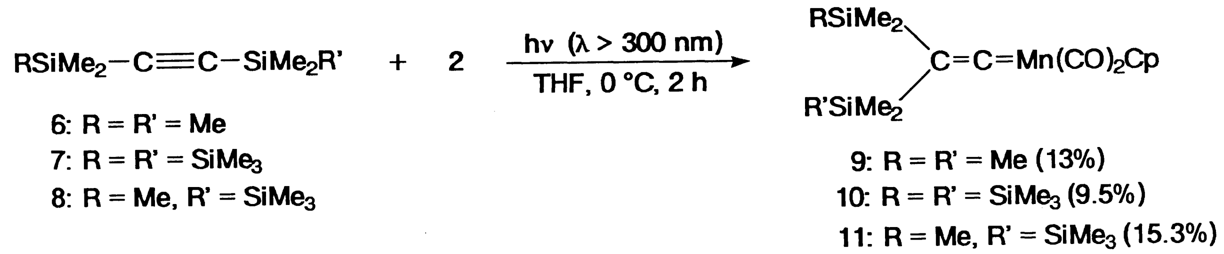
It is extremely interesting to examine whether this sort of 1,2-silyl shift is a general reaction or not because the precedent examples were observed only for cyclic polyacetylenes of rather special structures. We herein report that the reaction is indeed general even for acyclic monoacetylenes. Recently, Schneider and Werner have reported a similar work on the isolation of silylvinylidene rhodium complexes,[6] which prompted us to communicate our own results.

First, we have examined the reaction of cyclic monoacetylene (**1**)[7] with cyclopentadienyltricarbonylmanganese (**2**) and (methylcyclopentadienyl)tricarbonylmanganese (**3**) under photochemical conditions. The expected vinylidene complexes (**4**) were obtained together with a small amount of disilylketenes (**5**).



After the starting materials and **5** were removed from the reaction mixture by column chromatography (silica gel/hexane), the products **4a** and **4b** were obtained as yellow materials.[8] The structure of **4a** was determined by a characteristic low field signal of ^{13}C NMR at 336.5 ppm[9] and a C=C stretching at 1610 cm^{-1} in IR.[2] Both **4a** and **4b** were photochemically unstable and decomposed to **1**.

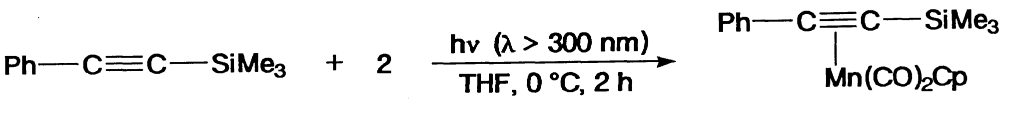
Next, we have examined the reactions of acyclic disilylacetylenes with **2**. Acetylenes **6**, **7**, and **8** gave the corresponding manganese complexes **9**, **10**, and **11** under photochemical conditions.[10)]



6: R = R' = Me
7: R = R' = SiMe$_3$
8: R = Me, R' = SiMe$_3$

9: R = R' = Me (13%)
10: R = R' = SiMe$_3$ (9.5%)
11: R = Me, R' = SiMe$_3$ (15.3%)

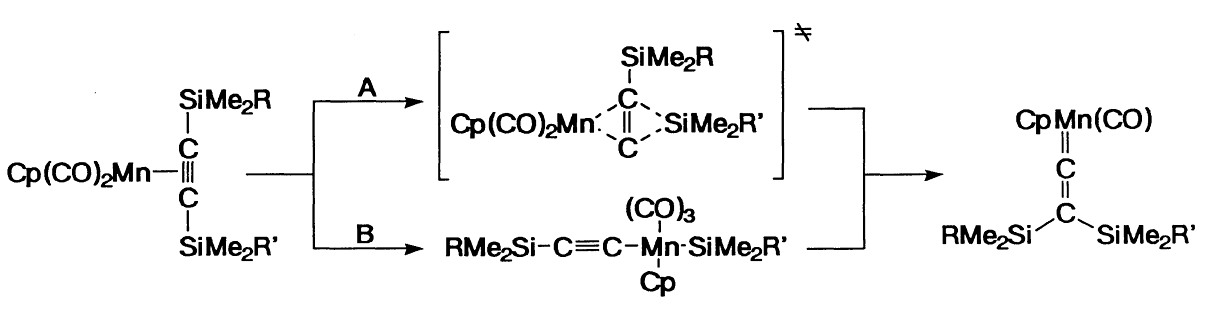
These results indicate that ring strain is not the requisite conditions for the 1,2-silyl shift in the reaction of disilylacetylenes. However, existence of two silyl groups on each terminal of acetylene seemed to be essential for the reaction at least under the conditions because phenyl(trimethylsilyl)acetylene (**12**) did not afford the corresponding vinylidene complexes. Instead, an unstable acetylene complex (**13**) was obtained.[11)] A similar result has been reported for phenyl(triphenylsilyl)acetylene.[12)] In the case of rhodium monosilylacetylene complexes, further heating or irradiation resulted in the formation of the corresponding vinylidene complexes.[6)]



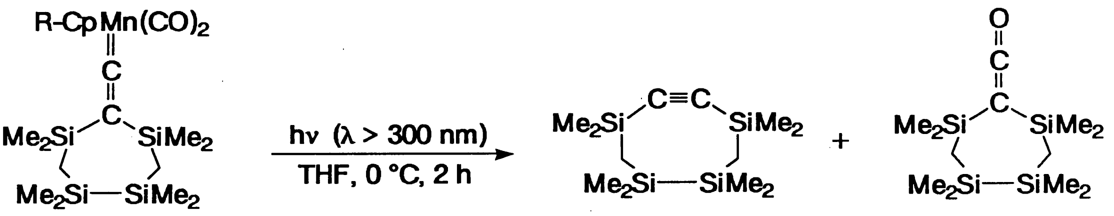
12

13 (24%)

These Mn-complexes are obtained under photochemical conditions. The first step must be dissociation of a carbonyl ligand from **2** or **3** generating a reactive intermediate. The reaction of the latter such as (cyclopentadienyl)(thf)(dicarbonyl)manganese, generated from **2**, with **6** gave **9** in 3.9% yield. Therefore it is concluded that 1,2-silyl shift is a dark reaction.

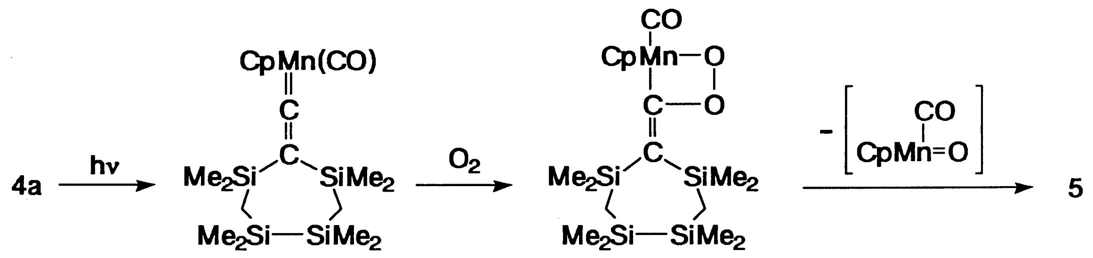


Thermolysis of Mn-vinylidene complexes, **4a** and **9**, in sealed tubes at 200 °C afforded the starting acetylenes, **1** and **6** in 79 and 96% yield, respectively. The manganese complex **2** was also recovered in 62 and 63% yield, respectively. Attempted trapping of the possible intermediate with dimethyl acetylenedicarboxylate, dimethyl maleate, 3,3-dimethyl-2-butene, cyclohexene, and oxygen failed. In every case, acetylenes were regenerated in high yield. These results suggest that 1,2-silyl shift is a reversible process occurring in the coordination sphere of manganese. Between the acetylene complex and the vinylidene complex, two intermediates (or transition states) are possible as shown above. However, judging from the fact that eight-membered ring **1** was regenerated in high yield from **4a**, we propose that the path A may be plausible. Photolysis of **4a** in THF also regenerated the acetylene **1** in 90% yield together with ketene **5**.



4a: R = H 1 (90%) 5 (10%)

Photolysis of **4a** under the same reaction conditions but in the presence of oxygen gave **1** and **5** in 51 and 35% yield, respectively. As described above, no reaction of **4a** with oxygen takes place in the dark. Apparently, **5** is derived by the reaction of a photochemically generated intermediate with oxygen. We suggest the following mechanism for the formation of **5**, which may correspond to the mechanism of ketone formation by the reaction of a carbene complex with oxygen.$^{13)}$



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References

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2) H. Sakurai, Y. Nakadaira, A. Hosomi, Y. Eriyama, K. Hirama, and C. Kabuto, *J. Am. Chem. Soc.*, **106**, 8315 (1984).
3) H. Sakurai, K. Hirama, Y. Nakadaira, and C. Kabuto, *J. Am. Chem. Soc.*, **109**, 6880 (1987).

4) H. Sakurai, K. Hirama, Y. Nakadaira, and C. Kabuto, *Chem. Lett.*, **1988**, 485.

5) H. Sakurai, *Nippon Kagaku Kaishi*, **1990**, 439.

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7) **1**: Colorless crystals; mp 58.5 – 60.5 °C, bp 76 °C/0.9 mmHg; ^{1}H NMR (C_6D_6, δ) –0.02 (s, 4H), 0.19 (s, 12H), 0.31 (s, 12H); $_{13}$C NMR (C_6D_6, δ) 0.1, 0.6, 3.7, 119.5; ^{29}Si NMR (C_6D_6, δ) –17.9, –16.5; IR (NaCl, ν/cm^{-1}) 2954 (m), 1242 (m), 1033 (s), 816 (s), 790 (s); MS m/e (%) 284 (M$^+$, 6.6), 269 (100), 211 (8.5), 113 (8.8), 73 (38.7); High Resolution MS Found: 284.1277, Calcd for $C_{12}H_{28}Si_4$: 284.1268.

8) **4a**: Mp 69 – 70 °C; ^{1}H NMR (C_6D_6, δ) –0.03 (s, 4H), 0.27 (s, 12H), 0.38 (s, 12H), 4.36 (s, 5H); ^{13}C NMR (C_6D_6, δ) –0.6, 3.7, 5.3, 85.6, 112.2, 228.3, 336.5; ^{29}Si NMR (C_6D_6, δ) –19.4, –3.1; IR (CCl_4, ν/cm^{-1}) 2953 (m), 1984 (s), 1922 (s), 1610 (s), 1252 (m); MS m/e (%) 460 (M$^+$, 1.1), 404 (25.0), 284 (100), 269 (81.9); High Resolution MS Found: 460.0936, Calcd for $C_{19}H_{33}O_2Si_4Mn$: 460.0938. **4b**: Yellow oil, ^{1}H NMR (C_6D_6, δ) –0.06 (s, 4H), 0.22 (s, 12H), 0.32 (s, 12H), 1.65 (s, 3H), 4.14–4.18 (m, 2H), 4.22–4.26 (m, 2H); IR (CCl_4, ν/cm^{-1}) 1981 (s), (s), 1608 (m); MS m/e (%) 474 (M$^+$, 6.2), 418 (100), 284 (9.1), 269 (5.4), 79 (10.2); High Resolution MS: 474.1097, Calcd for $C_{20}H_{35}O_2Si_4Mn$: 474.1095.

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10) **9**: Yellow crystals, mp 46 – 51 °C; ^{1}H NMR (C_6D_6, δ) 0.29 (s, 18H), 4.32 (s, 5H); ^{13}C NMR (C_6D_6, δ) 2.0, 85.5, 111.7, 228.8, 336.8; ^{29}Si NMR (C_6D_6, δ) –3.0; IR (CCl_4, ν/cm^{-1}) 2281 (m), 1984 (s), 1923 (s), 1616 (m), 1450 (m), 1331 (m), 858 (m); UV (Hexane) λ_{max} / nm (log ε) 205 (3.38), 242 (3.41), 298 (2.78), 323 (2.76); MS m/e (%) 346 (M$^+$, 16.1), 290 (100), 170 (2.6), 155 (2.5), 84 (6.9), 65 (10.0); High Resolution Mass Found : 346.0613, Calcd for $C_{15}H_{23}O_2Si_2Mn$: 346.0617. **10**: Yellow crystals, ^{1}H NMR (C_6D_6, δ) 0.33 (s, 18H), 0.43 (s, 12H), 4.43 (s, 5H); ^{13}C NMR (C_6D_6, δ) –1.4, –0.1, 85.8, 107.7, 229.3, 333.1; MS m/e (%) 462 (M$^+$, 0.7), 406 (8.8), 286 (22.0), 213 (83.6), 116 (18.9), 73 (19.8), 66 (100), 65 (75.5), 57 (15.3); IR (CCl_4, ν/cm^{-1}) 2953 (w), 2895 (w), 1983 (s), 1923 (s), 1599 (m), 1246 (m). **11**: Yellow oil; ^{1}H NMR (C_6D_6, δ) 0.20 (s, 9H), 0.26 (s, 9H), 0.32 (s, 6H), 4.31 (s, 5H); ^{13}C NMR (C_6D_6, δ) –1.6, –0.4, 2.3, 85.6, 109.5, 229.0, 335.4; IR (CCl_4, ν/cm^{-1}) 1984 (s), 1923 (s), 1606(m), 1248 (m), 849 (m); MS m/e (%) 404 (M$^+$, 0.9), 348 (20.8), 228 (100), 213 (7.6), 140 (5.6), 66 (34.6), 65 (7.7).

11) **13**: Red orange oil; ^{1}H NMR ($(CD_3)_2CO$, δ) 0.41 (s, 9H), 4.79 (s, 5H), 7.1–8.0 (m, 5H); IR (CCl_4, ν/cm^{-1}) 2958 (m), 2008 (m), 1971 (s),1905 (s), 1876 (m), 858 (m); MS m/e (%) 350 (M$^+$, 0.2), 294 (3.6), 204 (7.4), 185 (24.6), 174 (100), 159 (75.4), 148 (8.9), 78 (32.3), 66 (89.1), 65 (15.9); High Resolution Mass Found : 350.0568, Calcd for $C_{19}H_{21}O_2SiMn$: 350.0535.

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