CHEMISTRY LETTERS, pp. 293-296, 1989.

Stepwise Reactions of Dimethylsilyl Acetylenes with Octacarbonyldicobalt

Sonae KOTANI, Toshihiro MATSUMOTO, Hidemasa YAMAGUCHI,
Kyo SHIINA, and Kenkichi SONOGASHIRA*
Research Institute for Atomic Energy, Osaka City University,
Sugimoto, Sumiyoshi-ku, Osaka 558

Treatment of bis(dimethylsilyl)acetylene 1 with more than two molar amount of octacarbonyldicobalt in cyclohexane gave the complex $[(CO)_4CoSiMe_2C{\equiv}C\text{-}SiMe_2Co(CO)_4]Co_2(CO)_6$, while treatment of 1 with one or 1.5 molar amount of octacarbonyldicobalt produced the complexes $[HSiMe_2C{\equiv}CSiMe_2H]Co_2(CO)_6$ and $[HSiMe_2C{\equiv}CSiMe_2Co(CO)_4]Co_2(CO)_6$, respectively. The reactions of dimethyl(phenylethynyl)silane and its homologs with $Co_2(CO)_8$ were also investigated.

Recently, there is considerable interest in hydrocarbon-bridged dinuclear organometallic complexes,1) partly since such compounds can act as a model for metal cluster and metal surface. In order to obtain information about the possibility of alkynylsilanes as a valuable precursor for metal clusters, we have investigated the reaction of bis(dimethylsilyl)acetylene2) 1 and its homologs with octacarbonyldicobalt and organotransition-metal complexes. A feature of 1 is that it has three reactive centers to transition metal complexes : the acetylene and two Si-H groups. Eaborn et al.3) reported the preparation of the complex cis-$[PtH(SiMe_2C{\equiv}CSiMe_2H)(PPh_3)_2]$ by oxidative addition of 1 to Pt^0 complex with a Si-H group in preference to π-coordination of the acetylene group.

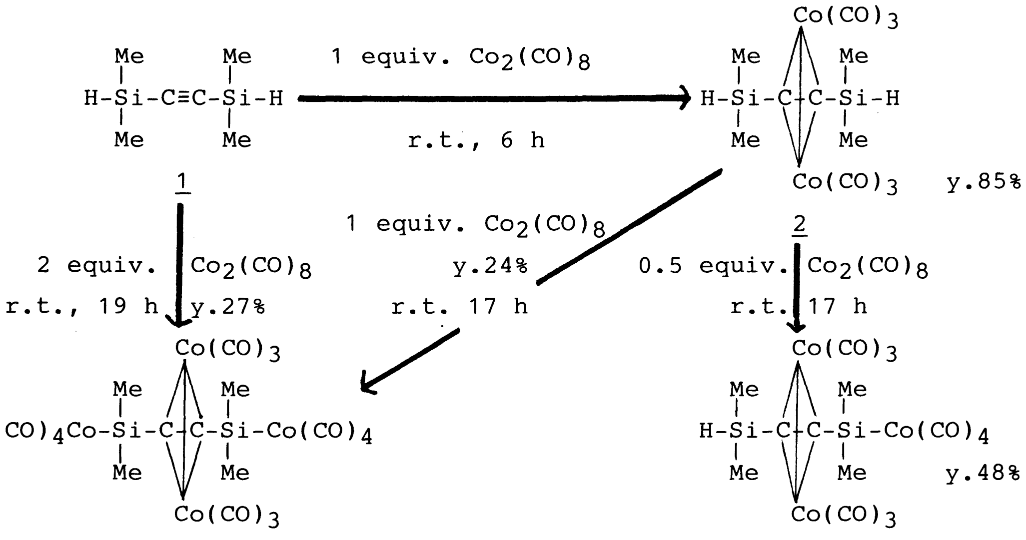
On the other hand, it is well known that $Co_2(CO)_8$ reacts easily with a large variety of alkynes or hydroorganosilanes to produce the μ-alkyne complexes $Co_2(CO)_6(RC_2R')$2,4) or the complexes containing a Si-Co bond,5) respectively. The reaction of 1 with octacarbonyldicobalt is of special interest since such reaction should allow the formation of a new metal cluster system.

In this communication, we would like to report our new finding that silylacetylene 1 reacts with $Co_2(CO)_8$ to afford at first the μ-alkyne complex followed by stepwise formation of two Si-Co bonds.

First, we investigated the reaction of 1 with equimolar $Co_2(CO)_8$ to compare the reactivity of the acetylene group and the Si-H groups.

A solution of 1 (860 mg, 6.14 mmol) and octacarbonyldicobalt (1.71 g, 5 mmol) in cyclohexane (10 ml) was stirred for 6 h at room temperature under an atmosphere of argon. After purification by silica-gel column chromatography (30 mm x 50 mm, hexane) and sublimation (0.1 mmHg, 25 °C), dark red crystals of μ-alkyne complex (2)$^{6)}$ were obtained in 85% yield (Scheme 1). The infrared spectral pattern of 2 in the CO stretching region is very similar to alkyne complexes and the $\nu_{C\equiv C}$ band shifts to 1540 cm^{-1} by coordination for the $Co_2(CO)_6$ group.$^{7)}$ The ^{1}H-and ^{13}C{^{1}H}-NMR and mass spectra are also consistent with the formulation of the μ-complex.

Tricobalt and tetracobalt derivatives of 1, 3,$^{8)}$ and 4,$^{9)}$ were also prepared by the reaction of 2 with half- or equi-molar amount of octacarbonyldicobalt, respectively, under similar conditions at a longer reaction time (17 h) as shown in Scheme 1.



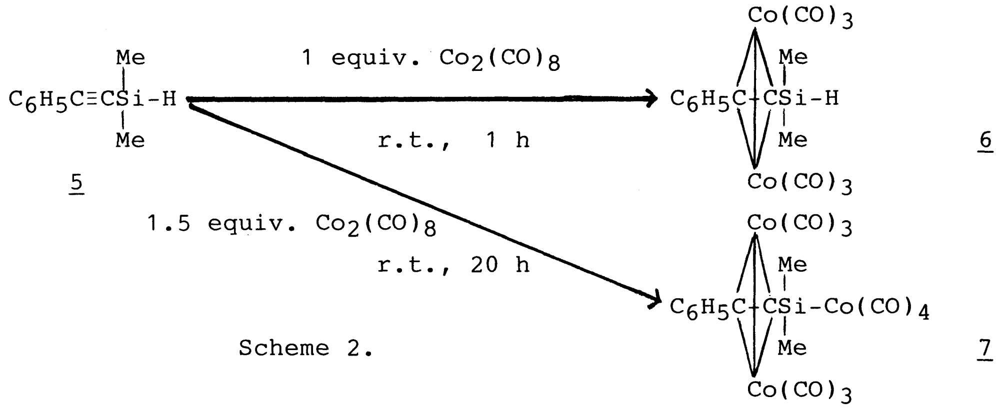
Scheme 1.

Complexes 3 and 4 were also obtained directly from 1. The composition of these complexes which are dark red crystals (stable in air for a few days and under argon in refrigerator for a few weeks) has been confirmed by elemental analysis and mass spectra. ^{1}H-NMR spectra show the formation of Si-Co bond by the chemical shift of Si-Me and disappearance of Si-H resonance peak. As the number of cobalt atoms increases, the positions of the ^{1}H-NMR signal of Si-Me and $\nu_{C\equiv C}$ band of IR shift successively as follows: δ(Si-Me, ppm, in C_6D_6); 0.22 for 2, 0.31 and 0.77 for 3, 0.88 for 4. $\nu_{C\equiv C}$ (cm^{-1}); 1550 for 2, 1540 for 3, 1520 for 4. Thus it has been proved that the Si-H groups of 1 react much more slowly than the C≡C group and 1 → 4 proceeds in three steps via the isolable intermediates 2 and 3.

We have also been successful in preparing stepwise stable dicobalt$^{10)}$ and tricobalt$^{11)}$-complexes of dimethyl(phenylethynyl)silane in good yield as shown in Scheme 2.

The reaction of dimethysilylacetylens $HC\equiv CSiMe_2H$ (8),$^{12)}$ $HSiMe_2C\equiv CC\equiv CSiMe_2H$

(9),[13)] and p-$C_6H_4(C{\equiv}CSiMe_2H)_2$(10)[14)] with $Co_2(CO)_8$ was also investigated. μ-Alkyne complexes of the above acetylenes were isolated and characterized.[15)] However, none of σ-bonded Si-Co complexes was isolated because of their instability ascribed to Si-Co bond.



Scheme 2.

Electronic spectra of the complexes described above provide information about the interaction between cobalt atoms in the complexes. Based on comparison of λ_{max} of LMCT bands for 3 and 4 with those for 2, we conclude that the interaction between cobalt atoms μ-coordinated to the acetylene group with cobalt atom σ-bonded to silicon atom is weak.

Attempts to obtain stable σ-bonded silicon derivatives of other transition metals by the reaction of the silylacetylenes with low valent metal complexes such as dodecacarbonyltriruthenium and platinum(0) complexes were unsuccessful because of high reaction temperature used.

Further works are in progress. The present work is supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (Grant-in-Aid for Special Project Research, No. 61225023).

References

1) C. P. Casey and J. D. Audet, Chem. Rev., 86, 339 (1986); W. Beck, M. J. Scweiger, and G. Muller, Chem. Ber., 120, 889 (1987).

2) D. Seyferth and D. L. White, J. Organomet. Chem., 32, 317 (1971).

3) C. Eaborn, P. N. Kapoor, D. J. Tune, C. L. Turpin, and D. R. M. Walton, J. Organomet. Chem., 63, 107 (1973).

4) H. Greenfield, H. W. Sternberg, R. A. Friedel, J. H. Wotiq, R. Markby, and I. Wender, J. Am. Chem. Soc., 78, 120 (1956); R. S. Dickson and P. J. Fraser, Adv. Organomet. Chem., 12, 323 (1974).

5) A. T. Chalk and J. F. Harrod, J. Am. Chem. Soc., 87, 1133 (1965).

6) Dark red crystals, 85% yield; mp 50-52 °C (dec.) under N_2; Elemental analysis, Found: C, 33.18; H, 3.12%. Calcd for $C_{12}H_{14}Co_2O_6Si_2$: C,33.65; H, 3.29%; UV λ_{max} 208 nm (ε 47000 $dm^3\ mol^{-1}\ cm^{-1}$), 260 (24000), 352 (8000), 424 (830), 529 (360)(c-C_6H_{12}); ^{1}H-NMR (400 MHz, C_6D_6, TMS) δ(ppm) 0.22(12H, d, J = 3.0 Hz,

Si-CH_3), 4.74 (2H, sept, J = 3.0 Hz, Si-H); $^{13}C\{^1H\}$-NMR (100.6 MHz, C_6H_6, TMS) δ(ppm) 1.75 (Si-CH_3), 91.2 (C≡C), 202.6 (br, $Co(CO)_3$); IR (KBr, cm^{-1}) ν_{CO} (2120, 2080, 2050), ν_{Si-H} (2170, 2150), $\nu_{C\equiv C}$ (1550), δ_{Si-Me} (1260); MS m/z 428(M^+).

7) Y. Iwashita, F. Tamura, and A. Nakamura, Inorg. Chem., 8, 1179 (1979); K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd ed, John Wiley & Sons, New York (1978), p. 387.

8) Dark red crystals, 48% yield from 2; mp 45-47 °C (dec.) under N_2; Elemental analysis, Found: C 31.45; H 2.05%. Calcd for $C_{16}H_{13}Co_3O_{10}Si_2$: C, 32.12%; H, 2.19%; UV λ_{max} 206 nm (ε 54000), 263 (26000), 354 (51000), 426 (870), 552 (390) (c-C_6H_{12}); ^1H-NMR (C_6D_6, TMS) δ(ppm) 0.31 (6H, br), 0.77 (6H, br), 4.86 (1H, br); $^{13}C\{^1H\}$-NMR (C_6D_6, TMS) δ(ppm) 0.5, 11.4 (br, Si-CH_3), 91.6, 96.9 (-C≡), 202.3, 200.9 (br, $Co(CO)_3$), 200.9 (br, $Co(CO)_4$); IR (KBr, cm^{-1}) ν_{CO} (2120, 2070, 2030, 2010, 1990), ν_{Si-H} (2150), δ_{Si-Me} (1260), $\nu_{C\equiv C}$ (1540).

9) Dark red crystals, 27% yield from 1; mp 117-119 °C (dec.) under N_2; Elemental analysis, Found: C, 31.30; H 1.52%. Calcd for $C_{20}H_{12}Co_4O_{14}Si_2$: C, 31.30; H, 1.57%; UV λ_{max} 206 nm (ε 87000), 266 (52000), 358 (9500), 424 (800), 532 (470) (c-C_6H_{12}); ^1H-NMR (C_6D_6, TMS) δ(ppm) 0.88 (s, Si-Me); IR (KBr, cm^{-1}) ν_{CO} (2120, 2070, 2050, 2020, 1980), $\nu_{C\equiv C}$ (1520), δ_{Si-Me} (1260); MS m/z 740 (M^+-CO).

10) Dark red crystals, 85% yield, mp 64-65 °C(dec.) under N_2; UV λ_{max} 210 (42000), 260 (21000), 310 (9700), 355 (4800) 427 (1100), 545 (560) (c-C_6H_{12}); ^1H-NMR (C_6D_6, TMS) δ(ppm) 0.30 (6H, d, J = 3.0 Hz, Si-CH_3), 4.91 (1H, sept, J = 3.0 Hz, Si-H), 7.01, 7.60 (5H, phenyl); IR (KBr, cm^{-1}), ν_{CO} (2120, 2080, 2050), $\nu_{C\equiv C}$ (1580).

11) Dark red crystals, 50% yield; mp 91-93 °C(dec.) under N_2; Elemental analysis, Found: C, 38.88%, H, 1.88%. Calcd for $C_{20}H_{11}Co_3O_{10}Si$: C, 38.99; H, 1.80%; UV λ_{max} 208 (56000), 272 (24000), 324 (12000), 369 (3400), 423 (890), 571 (410); ^1H-NMR (C_6D_6, TMS) δ(ppm) 0.88 (6H, s, Si-CH_3), 7.05, 7.54 (5H, phenyl); IR (KBr, cm^{-1}) ν_{CO} (2120, 2080, 2020, 2000), $\nu_{C\equiv C}$ (1580); MS m/z 616(M^+).

12) G. Stehlik and V. Hoffmann, Z. Naturforsch., A, 27, 1764 (1972).

13) G. Chandra, J. Owen, N. C. Lloyd, and B. E. Cooper, U.S.P. 3714118, 30 Jan, 1973; Chem. Abstr., 78, 137285b (1973).

14) Compound 10 was prepared by the reaction of $LiC\equiv CC_6H_4C\equiv CLi$ with $HSiMe_2Cl$. Y. 90%, mp 55-56 °C, white crystals from ethanol.

15) For example $(HMe_2SiC\equiv CH)Co_2(CO)_6$. Dark red oil, 85% yield, Elemental analysis, Found: C,31.89; H, 2.22%. Calcd for $C_{10}H_8Co_2O_6Si$: C, 32.45; H, 2.17%; UV λ_{max} 215 nm(ε 36000), 263 (17000), 313 (8100), 353 (3500), 432 (740), 537 (300)(c-C_6H_{12}); ^1H-NMR (C_6D_6, TMS) δ(ppm) 0.18 (6H, d, J = 2.7 Hz, Si-Me), 4.67 (1H, sept, J = 2.7 Hz, Si-H), 5.76 (1H, s, ≡CH); IR (liq., cm^{-1}) ν_{CO} (2130, 2090, 2050), $\nu_{C\equiv C}$ (1490), δ_{Si-Me}(1260).

(Received November 21, 1988)