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Photoinduced Direct Synthesis of Silylene-Bridged Dinuclear Iron Complexes $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SiHR)]$ from $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_3]$ and $RSiH_3$ ($R = t\text{-}Bu$, $(CMe_2)_2H$)

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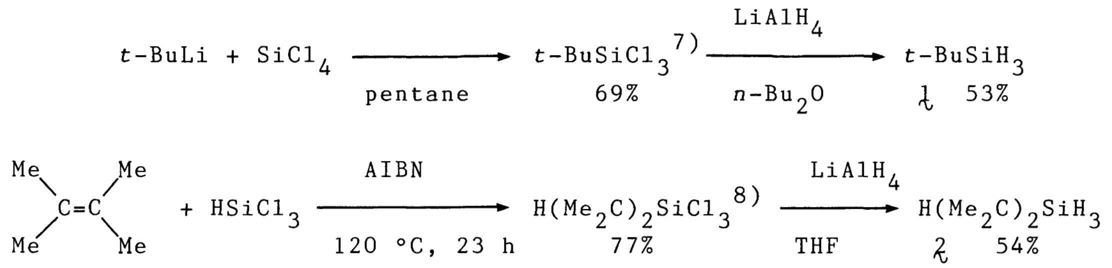
Photolysis of $[CpFe(CO)_2SiMe_3]$ ($Cp = \eta^5\text{-}C_5H_5$) in the presence of $RSiH_3$ ($R = t\text{-}Bu$, $(CMe_2)_2H$) afforded silylene-bridged dinuclear complexes $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SiHR)]$. The structure of the complex $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SiHBu^t)]$ was determined by X-ray crystallography.

Hydrosilanes are well known to react with various transition metal complexes with its Si-H bond and form the complexes containing metal-silicon bonds.[1)] Particularly, polyhydrosilanes (H_nSiR_{4-n}, $n = 2 - 4$) can be potential precursors of bridging ligands because of their plural Si-H bonds. Although there are a number of reports on the reactions of organodihydrosilanes with transition metal complexes,[1,2)] few reactions of that type are known on organotrihydrosilanes.[3)] We now report a new type of photoreaction between alkyltrihydrosilanes and $[CpFe(CO)_2SiMe_3]$ which leads to silylene-bridged dinuclear complexes, and the X-ray crystal structure of one of those dinuclear species.

Two *tert*-alkylsilanes, $t\text{-}BuSiH_3$ (**1**)[4,5)] and $H(Me_2C)_2SiH_3$ (**2**),[6)] which we used for this work, were prepared according to the reactions shown in Scheme 1. Both **1** and **2** are non-pyrophoric, colorless liquid at room temperature (**1**: bp 34 °C; **2**: bp 72 - 73 °C).



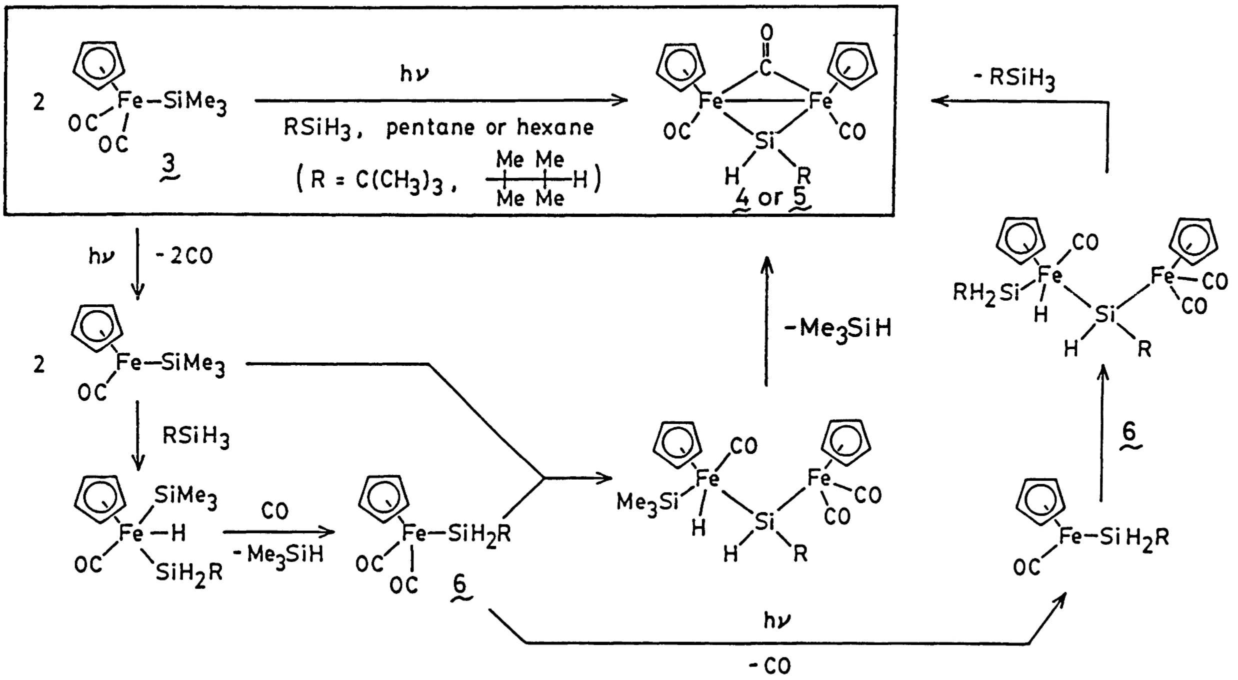
$$AIBN = (NC)(H_3C)_2C\text{-}N{=}N\text{-}C(CH_3)_2(CN)$$

Scheme 1.

A mixture of **1** (0.070 g, 0.79 mmol) and $[CpFe(CO)_2SiMe_3]$ (**3**) (0.32 g, 1.28

mmol) dissolved in deoxygenated pentane (30 ml) was irradiated in a Pyrex tube with a 450 W medium pressure Hg lamp at 0 °C for 4 h. The color of the solution changed from pale yellow to red during the photolysis with evolution of gas. Standing the resultant mixture at -30 °C gave ruby-red needles of [Cp$_2$Fe$_2$(CO)$_3$SiHBu^t] (4),9) which were collected by filtration under a nitrogen atmosphere. Yield: 0.16 g (61%). In a similar procedure, photolysis of a mixture of 2 and 3 provided [Cp$_2$Fe$_2$(CO)$_3$SiH{(CMe$_2$)$_2$H}] (5)10) in 65% yield.

Previously we described the photoinduced silyl exchange reaction of 3 in the presence of Et$_2$MeSiH to give [CpFe(CO)$_2$SiMeEt$_2$].11) For this reaction, we proposed a possible mechanism including oxidative addition and subsequent reductive elimination of hydrosilane on a decarbonylated 16-electron transition metal intermediate based on the studies of Wrighton et al.12) The formation of 4 and 5 can be explained by the same mechanism which is, this time, repeated twice (Scheme 2). Interestingly, a fair amount of 5 was formed even when a mixture of 3 and 2 mol equiv. of 2 was photolyzed. We have not succeeded in the isolation of mononuclear intermediate [CpFe(CO)$_2$SiH$_2$R] (6).



Scheme 2.

The NMR data of a solution of 4 9) or 5 10) at ambient temperature are consistent with the existence of an only isomer with *cis* geometry. This result forms sharp contrast to the fact that the related complex [Cp$_2$Fe$_2$(CO)$_2$(μ-CO)L] (L = μ-SiHMe)13) as well as its carbon (L = μ-CHMe)14) and germanium (L = μ-GeMe$_2$)15,16) analogues exists as a mixture of *cis* and *trans* isomers in solution. The bulkiness of a tertiary alkyl group on a silicon atom of 4 or 5 is undoubtedly responsible for the preferential formation of the *cis* isomer. This is further confirmed by a single-crystal X-ray study of 4.17)

The molecular structure of 4 is shown in Fig. 1. This is the first example

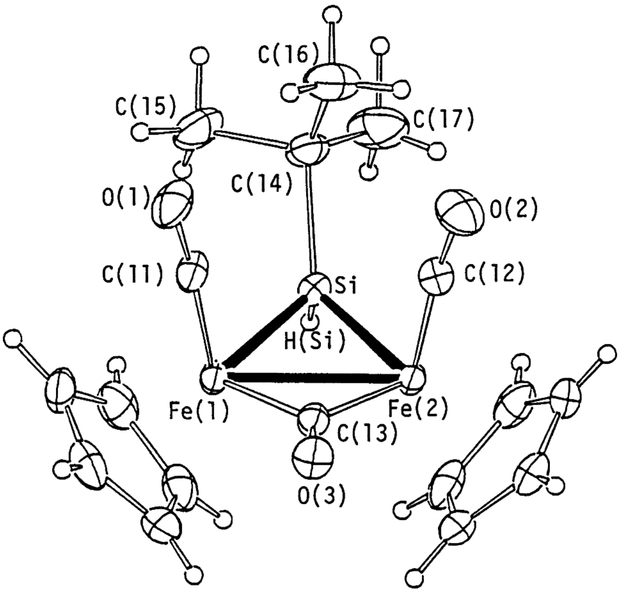


Fig. 1. perspective drawing of **4**. Thermal ellipsoids represent 30% probability surfaces except those of the hydrogen atoms.

of the silylene-bridged dinuclear iron complex on which an X-ray crystallographic determination was carried out. Two cyclopentadienyl groups are mutually *cis* and the dihedral angle between these rings is 91.3(2)° which is close to the value of *cis*-$Cp_2Fe_2(CO)_4$ (92.8°).$^{18)}$ The Fe(1)-Fe(2) distance is 2.614(1) Å which is significantly longer than those of *cis*-$Cp_2Fe_2(CO)_4$ (2.531(2) Å)$^{18)}$ or $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)]$ (2.520(2) Å),$^{19)}$ but slightly shorter than that of $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}GeMe_2)]$ (2.628(1) Å).$^{16)}$ This is attributable to the size of bridging atoms. The Fe-Si bond lengths (2.270(1) and 2.272(1) Å) and the Si-H bond length (1.39(4) Å) are normal. The dihedral angle between the Fe_2Si plane and the $Fe_2C(13)$ plane is 164.0(1)°. The angle between C(14)-Si bond and the Fe_2Si plane is markedly enlarged to 140.4(1)° from the calculated value for ideal tetrahedron (125.3°). This distortion is apparently due to the steric repulsion between the *t*-butyl group and two terminal carbonyl ligands. In fact, the distances of C(16)•••O(1) and C(16)•••O(2) are 3.443(5) and 3.358(4) Å, respectively, which are almost equal to the sum of the van der Waals radii of methyl group and oxygen atom (3.4 Å). Obviously, it looks impossible to place bulky Cp group(s) and a *t*-butyl group on the same side of the Fe_2Si plane. In other words, the cis isomer shown in Fig. 1 is considered to be an only isomer which can exist under normal conditions.

The complexes described here would appear to be precursors for (mixed metal) clusters, since they still have Si-H bonds reactive to transition metal complexes. This aspect is currently under investigation.

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5) ^{1}H NMR ($CDCl_3$) δ 1.05(s, 9H, *t*-Bu), 3.46(s, 3H, Si-H); ^{13}C NMR ($CDCl_3$) δ 15.0 (s, quarternary carbon of *t*-Bu), 28.5(q, J_{CH} = 128.0 Hz, Me); IR ($CHCl_3$ soln.) ν(SiH) 2150 cm^{-1}.

6) ^{1}H NMR ($CDCl_3$) δ 0.91(d, 6H, J = 6.6 Hz, β-Me), 1.00(s, 6H, α-Me), 1.54 (septet, 1H, J = 6.6 Hz, methyne), 3.42(s, 3H, Si-H); IR ($CHCl_3$ soln.) ν(SiH) 2150 cm^{-1}; MS m/e 116(3, M^+), 85(100, $H(Me_2C)_2{}^+$); Anal. Found: C, 61.72; H, 13.63%. Calcd for $C_6H_{16}Si$: C, 61.98; H, 13.87%.

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9) ^{1}H NMR (C_6D_6) δ 1.52(s, 9H, *t*-Bu), 4.13(s, 10H, Cp), 4.23(s, 1H, Si-H); IR (KBr disk) ν(SiH) 2074 cm^{-1}; ν($CO_{term.}$) 1950, 1922 cm^{-1}; ν($CO_{brid.}$) 1720 cm^{-1}; MS m/e 412(29, M^+), 384(51, M^+-CO), 356(100, M^+-2CO), 328(32, M^+-3CO), 270(55); Anal. Found: C, 49.62; H, 5.01%. Calcd for $C_{17}H_{20}Fe_2O_3Si$: C, 49.55; H, 4.89%.

10) ^{1}H NMR (C_6D_6) δ 1.22(d, 6H, J = 6.6 Hz, β-Me), 1.37(s, 6H, α-Me), 2.25(septet, 1H, J = 6.6 Hz, methyne), 4.13(s, 10H, Cp), 4.24(s, 1H, Si-H); IR (KBr disk) ν(SiH) 2074 cm^{-1}; ν($CO_{term.}$) 1948, 1926 cm^{-1}; ν($CO_{brid.}$) 1724 cm^{-1}; MS m/e 440(69, M^+), 412(54, M^+-CO), 384(100, M^+-2CO); Anal. Found: C, 51.77; H, 5.63%. Calcd for $C_{19}H_{24}Fe_2O_3Si$: C, 51.84; H, 5.50%.

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17) Crystal data: Triclinic, space group $P\bar{1}$, a = 9.056(2), b = 15.311(3), c = 6.769(2) Å, α = 101.84(2), β = 104.85(2), γ = 85.36(2)°, V = 887.5(3) $Å^3$, Z = 2; d_x = 1.54 g cm^{-3}, μ(MoKα) = 17.5 cm^{-1}. Intensity of 6483 reflections were measured at 23 °C (3° < 2θ < 65°) on a Rigaku AFC-6A diffractometer using graphite monochromated MoKα (0.71073 Å) radiation. The structure was solved by heavy-atom methods and refined by block-diagonal least-squares calculations using individual anisotropic thermal parameters for the non-hydrogen atoms. The positions of all hydrogen atoms were derived by difference-Fourier synthesis and refined applying isotropic thermal parameters. For 4690 unique reflections ($|Fo| > 3\sigma(Fo)$) R = 0.035 (Rw = 0.036) was obtained.

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