Synthesis of a Donor-Stabilized Silyl(silylene)iron Complex. Direct Observation of 1,3-Methyl Migration from Silyl to Silylene Ligands

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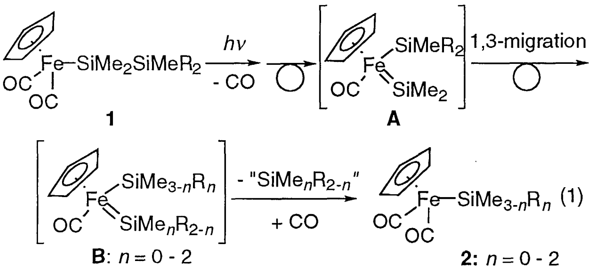
Photolysis of $Cp^*Fe(CO)_2SiMe_2SiMe_3$ ($Cp^* = \eta$-C_5Me_5) in the presence of HMPA (HMPA = $(Me_2N)_3PO$) afforded a donor-stabilized silyl(silylene)iron complex, $Cp^*(OC)Fe(=SiMe_2{\bullet}HMPA)SiMe_3$, almost quantitatively. Variable temperature ^{1}H NMR investigation for solutions of the trimethylsilyl(dimethylsilylene)iron complex allowed the direct observation of 1,3-methyl migration from the silyl ligand to the silylene ligand. It is proposed that 1,3-migration may be a general phenomenon which prevails among compounds with R_nE–M=$E'R_m$ arrangement.

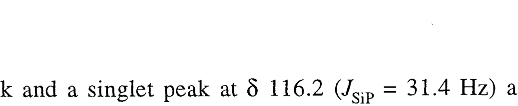
It has been known for many years that transition metal complexes can catalyze the redistribution of substituents on silicon atoms in organosilicon compounds.[1,2] Although the redistribution is considered to be induced by the coordination of the organosilicon compounds to the metal complexes, mechanistic details of the redistribution processes had been long unknown. 1,3-Substituent migration was proposed by Pannell's group[3] and us[4] to occur from silyl to silylene ligands: Photolysis of a disilanyliron complex, $CpFe(CO)_2SiMe_2SiMeR_2$ (**1**: Cp = η-C_5H_5; R = Me, Et, Ph), afforded a mixture of monosilyliron complexes, $CpFe(CO)_2SiMe_{3-n}R_n$ (**2**: $n = 0 - 2$), with scrambling of alkyl and aryl groups on the silicon atoms (eq 1). The reaction was proposed to proceed via the formation of a silyl(silylene)iron intermediate **A** and subsequent rapid intramolecular 1,3-substituent migration from the silyl group to the silylene ligand to form the intermediate **B**. Quite recently, it was supported by several experimental observations[5] that the mechanism is operative in the transition metal catalyzed redistribution reactions of organosilicon compounds. However, no direct observation of the 1,3-migration has been made.



(1)

Here we report the synthesis of the first isolable external base-stabilized silyl(silylene)iron complex $Cp^*(OC)Fe(=SiMe_2{\cdot}HMPA)SiMe_3$ (**3**: $Cp^* = \eta$-C_5Me_5) and direct observation of 1,3-methyl migration from the silyl group to the silylene ligand in complex **3**.[6]

Irradiation of a toluene-d_8 solution containing a disilanyliron complex $Cp^*Fe(CO)_2SiMe_2SiMe_3$ (**4**) and 3.5 eq of HMPA in a Pyrex NMR sample tube with a 450 W medium pressure mercury arc lamp afforded complex **3** almost quantitatively. The ^{29}Si NMR spectrum of the reaction mixture at 230 K showed a doublet peak and a singlet peak at δ 116.2 (J_{SiP} = 31.4 Hz) and 34.7 ppm, respectively. The remarkable downfield shift of the former signal compared to those for the precursor complex **4** (δ 14.6 and -12.2 ppm) and its doublet pattern clearly indicate the formation of a silylene ligand coordinated by a HMPA molecule, while the chemical shift of the latter signal of **3** is comparable with those for (alkylsilyl)iron complexes $CpFe(CO)_2SiR_3$ (R = alkyl).[7] The ^{1}H NMR spectrum of the reaction mixture at 250 K (Figure 1, bottom) shows two doublet peaks for the free and the coordinated HMPA at δ 2.40 and 2.24 ppm, respectively, a singlet peak for Cp* ligand at δ 1.97 ppm, and three peaks for SiMe groups at δ 0.71, 0.69, and 0.68 ppm with the relative intensity ratio of 1:3:1. The SiMe signal at δ 0.69 ppm is assignable to the $SiMe_3$ ligand while the others are to the diastereotopic methyl groups of the HMPA-coordinated $SiMe_2$ ligand. These NMR data strongly support the formulation of the compound $Cp^*(OC)Fe(=SiMe_2{\cdot}HMPA)SiMe_3$ (eq 2).[8] Although complex **3** was isolated as yellow crystals, we could not obtain satisfactory results of elemental analysis for complex **3** due to the extreme sensitivity toward air and moisture.

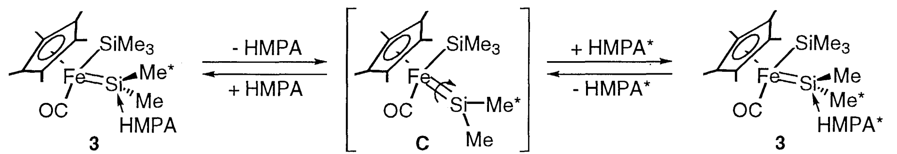


4 **3** (2)

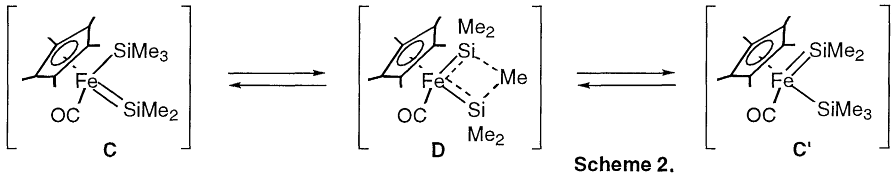
The silyl(silylene)iron complex **3** exhibits dynamic processes (Figure 1). As the temperature is raised from 250 K, two singlet peaks for the diastereotopic methyl groups in the $SiMe_2$ ligand broaden, coalesce, and become a singlet peak at 280 K. Two doublet signals for the free and the coordinated HMPA also broaden, coalesce, and finally become a sharp doublet peak above 280 K. These spectral changes suggest that the exchange between the diastereotopic methyl groups in the $SiMe_2$ ligand occurs concurrently with exchange of the coordinated HMPA molecule with the free HMPA molecule in solution.

Another spectral change is observed above 280 K: The two singlet signals for the $SiMe_2$ and $SiMe_3$ ligands gradually broaden, then coalesce at 318 K, and become a sharp singlet peak with 15 H intensity at 360 K. This spectral change clearly demonstrates that the 1,3-methyl migration from $SiMe_3$ to $SiMe_2$ ligands takes place in the NMR time scale.

A proposed mechanism is given in Scheme 1 for the concurrent occurrence of the exchange between the diastereotopic methyl groups in the $SiMe_2$ ligand and that between the coordinated and free HMPA molecules: The dissociation of the coordinated HMPA molecule from **3** gives a base-free silyl(silylene)iron intermediate **C**. Rotation of the silylene ligand and re-coordination of a free HMPA molecule result in the methyl group exchange in the $SiMe_2$ ligand accompanied by the inversion of the silicon center, and the exchange between the coordinated and free HMPA



Scheme 1.



Scheme 2.

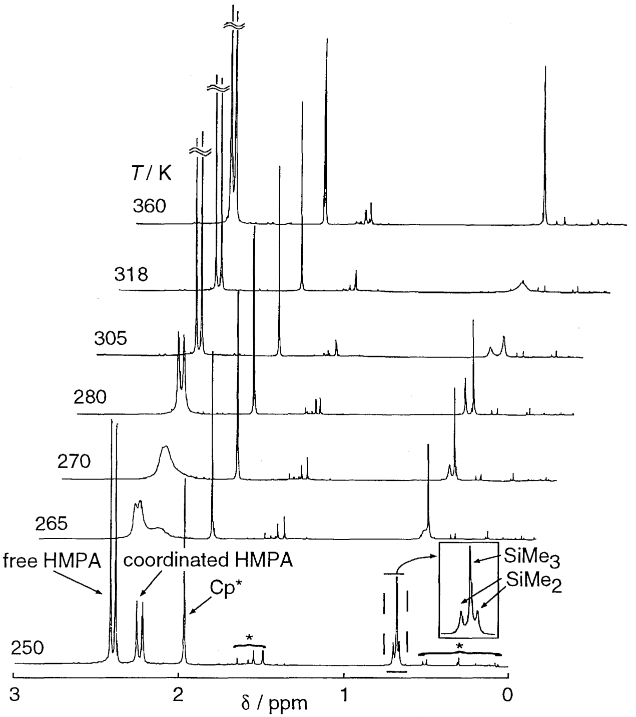


Figure 1. Variable temperature 300 MHz ^{1}H NMR spectra of **3** measured in toluene-d_8. *; Impurity.

·molecules.[9]

Another fluxional behavior observed at higher temperature range (280 - 360 K) may be explained by the mechanism shown in Scheme 2: 1,3-Methyl migration from the $SiMe_3$ group to the electron-deficient silylene ligand in the intermediate **C** takes place to give intermediate **C'** which proceeds most likely via a symmetric transition state (or intermediate) **D**. Recombination of an HMPA molecule to the silylene ligand in **C'** completes the process.

1,3-Migration occurs not only in silyl(silylene) transition metal complexes with the $R_3Si\text{–}M\text{=}SiR_2$ arrangement but also in organosilicon compounds containing an electron-deficient silicon atom such as silenes, $(R_3Si)_2C\text{=}SiR_2$,[10] and cationic silyl compounds.[11] It has also been proposed that facile 1,3-migration occurs in compounds with the $R_nE\text{–}M\text{=}E'R_m$ arrangement, where the combination of elements E and E' (or E' and E) are Si and Si,[3-5] Ge and Ge,[12, 13] Si and Ge,[12, 14] Ge and Sn,[15] and Sn and P,[16] respectively.[17] Photolysis of $Fe(CO)_4\{P(OEt)_3\}$ in the presence of $HSi(NMe_2)_3$ was reported to give $\{P(OEt)(NMe_2)_2\}(CO)_2Fe\text{=}Si(OEt)_2\cdot NHMe_2$.[18] 1,3-Substituent migration between the silicon and phosphorous atoms might be responsible for the formation of the product.

With respect to facile 1,3-migration, it should be noted that the sp^2 E' atom in the compounds must be electron deficient. 1,3-Migration in the compounds with the $R_nE\text{–}M\text{=}E'R_m$ arrangement may be general and prevailing phenomena observed in a variety of organo- and inorganometallic compounds containing group 14, 15, and probably 13 elements as E (and E'). M means not only metal in complexes but also carbon or possibly other main group elements.

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