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Silicon–silicon interaction in bis(silylene)iron, disilanyliron, and bis(silyl)iron complexes

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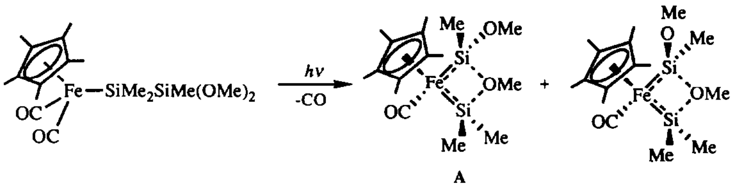
Abstract

^{29}Si NMR coupling constants in a disilanyliron complex $CpFe(CO)_2SiMe_2SiMe(O^tBu)_2$ (**1**: Cp = η^5-C_5H_5), a bis(silylene)iron complex $Cp(OC)Fe\{SiMe_2 \cdots O(^tBu) \cdots SiMeO^tBu\}$ (**2**), and a *cis*-bis(silyl)iron complex $(OC)_4Fe\{SiMe_2CH_2CH_2SiMePh\}$ (**3**) were measured by the INEPT-INADEQUATE technique. The coupling constant for **2** (28.6 Hz) is much smaller than that for **1** (128 Hz) with a direct Si–Si bond, but larger than that for **3** (2.7 Hz) where there is no direct Si–Si bond. Model calculations using the extended Hückel method indicate that there is no direct bond between the two silicon atoms in the bis(silylene)iron complex $Cp(OC)Fe\{SiH_2 \cdots O(H) \cdots SiH_2\}$. This means that the coupling in **2** can be described as the sum of the two *geminal* couplings, ^2J(SiFeSi) and ^2J(SiOSi).

Introduction

The synthesis of silylene complexes is a recent topic in silicon-transition metal chemistry. Several base-stabilized silylene complexes have been isolated and characterized [1–3] and, recently, base-free silylene complexes were reported by Tilley [4] and Jutzi [5].

We previously reported that the irradiation of a C_6D_6 solution of an alkoxy-substituted disilanyliron complex $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_2SiMe(OMe)_2$ resulted in the formation of a mixture of novel bis(silylene)iron complexes with *anti*- and *syn*-configurations (eq. 1) [1].



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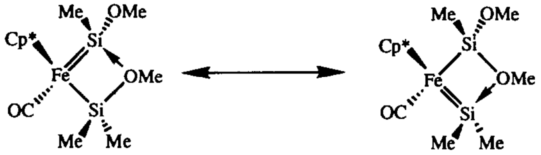
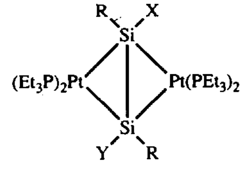


Scheme 1.

The crystal structure analysis of the *anti*-isomer **A** revealed several characteristic features: (i) The Fe–Si bonds (2.222(3) and 2.207(3) Å) are quite short compared to known Fe–Si bonds, (ii) the Si–O(bridge) bonds (1.793(9) and 1.799(8) Å) are significantly longer than the usual Si–O single bonds, and (iii) each silicon atom and the three atoms attached directly to it, apart from the bridging oxygen, have geometry that is almost planar. From these structural features and the fact that the ^{29}Si NMR signals of **A** appear at very low field (δ 121.1 and 101.9 ppm), we proposed a combination of two resonance forms as a bonding model for **A**, using a classical bonding description (Scheme 1, $Cp^* = \eta^5\text{-}C_5Me_5$) [1].

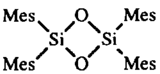
However, an alternative bonding description is possible. As the Si ··· Si interatomic distance in **A** (2.622(4) Å) is greater than the normal Si–Si single bond (2.34 Å), but still lies within the range of known Si–Si single bond lengths (2.32–2.70 Å) [6], a single bond could indeed exist between silicon atoms in **A**.

Recently, Youngs *et al.* reported the preparation and crystal structure of $[(Et_3P)_2Pt(SiRX)(SiRY)Pt(PEt_3)_2]$ (**B**: R = Ph, Cy; X, Y = H, Cl) [7]. The cross-ring silicon–silicon distance (2.55–2.65 Å) in **B** is again longer than the usual Si–Si single bond (2.34 Å) but within the range of known single Si–Si bonds (2.32–2.70 Å) [6]. From the structural evidence as well as the results of MO calculations, they concluded that complex **B** is a disilene complex with a $\mu^2\text{-}\eta^2$-disilene ligand [8].



B: R = Ph, Cy; XY=H_2, HCl, Cl_2

In contrast to the long Si–Si direct bond in the Young's complex **B**, the interatomic separation between silicon atoms in West's 1,3-tetramesitylcyclodisiloxane **C** (2.306 Å) is slightly shorter than the usual Si–Si single bonds (2.34 Å) [9]. Judging from this short distance, a Si–Si single bond may exist in **C**, but many MO calculations on 1,3-cyclodisiloxanes suggest that there is no direct Si–Si bond [10].

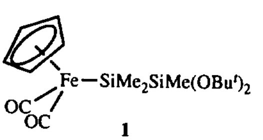


C: Mes = 2,4,6-trimethylphenyl

It is well known that the NMR coupling constant between two nuclei depends on bond parameters and structural factors such as atomic *s* densities, formal hybridization, and the number of bonds separating the two nuclei. It has also been observed that, for a given pair of nuclei X and Y, the coupling constants decrease in the order $^1J(XY) \gg {}^3J(XY) > {}^2J(XY) > {}^4J(XY)$ and that longer-range coupling is two or more orders of magnitude smaller than one-bonded coupling [11]. Because of low natural abundance, negative and relatively small magnetogyric ratio, and long spin-lattice relaxation times, it is more difficult to determine the coupling constant between silicon-29 nuclei than that between carbon-13 nuclei even though ^{29}Si is more abundant than ^{13}C [12]. Recent advances in high-field Fourier Transform NMR instruments and the development of multipulse techniques such as INEPT-INADEQUATE, however, have made the determination of the $^{29}Si-^{29}Si$ coupling constant possible [13].

The INEPT-INADEQUATE technique comprises a sequence of two series of pulses. The INEPT (Insensitive Nuclei Enhancement by Polarization Transfer) pulse enhances the intensities of signals coupled to proton by polarization transfer, and the INADEQUATE (Incredible Natural Abundance Double Quantum Transfer Experiment) pulse sequence enables only the homocoupled signals to be observed. When West *et al.* applied this INEPT-INADEQUATE technique to the 1,3-cyclodisiloxane they observed small ^{29}Si NMR coupling constants (3.8–4.0 Hz) which could be clearly assigned to $^2J(SiOSi)$ [13]. This result supports the absence of direct Si–Si bonds from 1,3-cyclodisiloxanes.

To investigate the nature of bonding in the bis(silylene)iron complexes, we applied the INEPT-INADEQUATE ^{29}Si NMR technique to silicon-transition metal complexes. To measure the coupling constants, we prepared three complexes with non-equivalent silicon nuclei, a disilanyliron complex $CpFe(CO)_2SiMe_2SiMe(O^tBu)_2$ (**1**: $Cp = \eta^5\text{-}C_5H_5$), a bis(silylene)iron complex $Cp(OC)Fe\{SiMe_2 \cdots O(^tBu) \cdots SiMeO^tBu\}$ (**2**) and a *cis*-bis(silyl)iron complex $(OC)_4Fe\{SiMe_2CH_2CH_2SiMePh\}$ (**3**). In this paper, we report the ^{29}Si NMR coupling constants for these three complexes and discuss the nature of bonding in the bis(silylene)iron complex.



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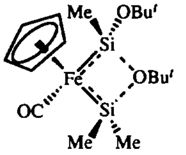

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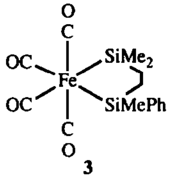

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Experimental

All experiments were performed under a nitrogen atmosphere by standard Schlenk or high-vacuum-line techniques. Benzene-d_6 was dried over a potassium mirror and distilled to the NMR sample tubes under high-vacuum immediately before use. Hydrocarbon solvents, THF, and diethylether were distilled under nitrogen from sodium benzophenone ketyl prior to use. $Cl_2MeSiCH{=}CH_2$, Me_2SiHCl, and $LiAlH_4$ were used as received from commercial sources. H_2PtCl_6 was prepared according to a published procedure [14]. $CpFe(CO)_2SiMe_2SiMe(O^tBu)_2$ (**1**) and $Cp(OC)Fe\{SiMe_2 \cdots O(^tBu) \cdots SiMeO^tBu\}$ (**2**) were prepared by using procedures described previously [1]. The usual NMR measurements were obtained on either a JEOL FX-90Q or a Varian XL-200 spectrometer. Low and high resolution mass spectra were recorded with a JEOL HX-110 spectrometer.

$(OC)_4Fe\{SiMe_2CH_2CH_2SiMePh\}$ (3)

Complex **3** was prepared according to a procedure similar to that reported for the synthesis of $(OC)_4Fe\{SiMe_2CH_2CH_2SiMe_2\}$ [15].

(i) Preparation of $PhMeSi(Cl)CH{=}CH_2$: To a solution of $Cl_2MeSiCH{=}CH_2$ (108 g, 0.77 mol) in Et_2O (300 ml) was added a solution of PhMgCl (1 mol) in THF (230 ml) with vigorous stirring. The reaction mixture was refluxed for 1 h, and then filtered. The filtrate was concentrated and distilled under reduced pressure (bp. 78°C at 7 Torr). $PhMeSi(Cl)CH{=}CH_2$ was obtained as a colorless liquid in 82.5% yield (115.4 g, 0.632 mol). Anal. Found: C, 59.51; H, 5.96. $C_9H_{11}ClSi$ calcd.: C, 59.16; H, 6.07%.

(ii) Preparation of $PhMe(H)SiCH_2CH_2Si(H)Me_2$: Me_2SiHCl (13.2 g, 0.140 mol) was added dropwise to a mixture of $PhMeSi(Cl)CH{=}CH_2$ (18.8 g, 0.102 mol) and 2 drops of an isopropyl alcohol solution of H_2PtCl_6 (*ca.* 10 m*M*) with vigorous stirring for about 1 h. The temperature of the reaction mixture was maintained at 70°C during the addition. After refluxing for 2 h, the reaction mixture was added dropwise to $LiAlH_4$ (10.6 g, 0.28 mol) in Et_2O (130 ml) with vigorous stirring. The suspension was refluxed for 5 h, and then concentrated under reduced pressure. The residue was extracted with 300 ml of hexane. The extract was filtered and concentrated under reduced pressure. Molecular distillation of the residue gave a colorless liquid of $PhMe(H)SiCH_2CH_2Si(H)Me_2$ in 82.6% yield (17.5 g, 0.084 mol). ^1H NMR (C_6D_6) δ 7.5–7.1 (m, 5H, Ph), 4.58 (q, $J = 3.6$ Hz, 1H, Si–H), 4.08 (sep, $J = 3.6$ Hz, 1H, Si–H), 0.8–0.5 (m, 4H, CH_2CH_2), 0.26 (d, $J = 3.6$ Hz, 3H, Si–Me), -0.02 (d, $J = 3.6$ Hz, 6H, Si–Me). Anal. Found: C, 62.32; H, 9.59. $C_{11}H_{20}Si_2$ calcd.: C, 63.38; H, 9.67%.

(iii) Preparation of $(OC)_4Fe\{SiMe_2CH_2CH_2SiMePh\}$ (3). A solution in hexane (200 ml) of $PhMe(H)SiCH_2CH_2Si(H)Me_2$ (2.08 g, 9.81 mmol) and $Fe(CO)_5$ (1.3 ml) was irradiated for 1 h with a 450 W mercury arc lamp. The reaction mixture was concentrated under reduced pressure. Molecular distillation (90°C, 0.001 torr) of the residue afforded the product **3** (1.8 g, 4.8 mmol) as a pale brown air and moisture sensitive oil in 49% yield. When **3** was exposed to air, a green solid was produced. ^1H NMR (C_6D_6) δ 7.5–7.1 (m, 5H, Ph), 1.4–0.9 (m, 4H, CH_2CH_2), 0.69 (s, 3H, Me), 0.50 (s, 3H, Me), 0.46 (s, 3H, Me). ^{13}C NMR (C_6D_6) δ 208.5 (CO), 207.6 (CO), 141.7 (Ph), 133.1 (Ph), 129.2 (Ph), 128.0 (Ph), 17.8 (Me), 15.0 (Me), 4.4 (Me), 3.8 (Me). ^{29}Si NMR (C_6D_6) δ 51.0, 43.4. MS m/z 374 (10.6, M^+), 347 (14.1), 346 (49.3), 318 (23.4), 291 (14.2), 290 (54.5), 264 (10.3), 263 (25.4), 262 (100), 260 (21.0), 234 (21.4). Exact mass. found 374.0080. $C_{15}H_{18}O_4FeSi_2$ calcd.: 374.0093. Anal. Found: C, 47.66; H, 4.79. $C_{15}H_{18}FeSi_2O_4$ calcd.: C, 48.13; H, 4.85%.

INEPT-INADEQUATE ^{29}Si NMR experiment

Measurements of the coupling constants between ^{29}Si atoms were carried out on a JEOL GX-400 or a Bruker AC-300 spectrometer using the INEPT-INADEQUATE pulse sequence [13]. The C_6D_6 solutions of **1** and **3** were prepared as follows. A flame-dried 5-mm NMR tube with a 15/25 ground glass joint was charged with *ca.* 200 mg of a complex and connected to a vacuum line. About 0.5 ml of C_6D_6 was introduced into the sample tube by the trap-to-trap transfer method. Then the sample solution was freeze-pump-thaw degassed and sealed off with a torch. A solution of **2** was prepared by irradiating a C_6D_6 solution of **1** in a sealed tube prepared as above with a 450 W medium pressure Hg lamp [1].

EHMO calculations

All calculations were carried out using the extended Hückel method [16]. All valence-state ionization potentials and atomic parameters were according to Hoffmann [17]. No refinement, such as the SCCC (Self Consistent Charge and Configuration) method, was applied to the calculations. The structural parameters, *i.e.* bond lengths and bond angles, of the complexes were estimated from the reported data [1,18,19]. In the EHMO calculations, $CpFe(CO)_2SiH_2SiH_2(OH)$, $CpFe(CO)\{SiH_2 \cdots O(H) \cdots SiH_2\}$, $(OC)_4Fe(SiH_3)_2$, Si_2H_6, and Si_2H_4 are used as models for **1**, **2**, **3**, disilanes, and disilenes, respectively. For $CpFe(CO)\{SiH_2 \cdots O(H) \cdots SiH_2\}$, the Fe–Si and Si–O(bridge) lengths were set at 2.214 and 1.796 Å, respectively. The Fe–Si distance in $(OC)_4Fe(SiH_3)_2$ was set at 2.456 Å. For $CpFe(CO)_2SiH_2SiH_2(OH)$, the Fe–Si, Si–Si, and Si–O bond lengths were set at 2.346, 2.373 and 1.632 Å, respectively. Conformation and structural parameters for $H_2Si{=}SiH_2$ were determined according to the conclusion of the literature [20], *i.e.*, the conformation of $H_2Si{=}SiH_2$ is a *trans*-bent form. In the calculations, 2.236 and 1.480 Å were used for the Si–Si and Si–H bond distances in $H_2Si{=}SiH_2$, respectively. In the calculation for the disilane, 2.331 and 1.491 Å were used for the Si–Si and Si–H bond distances, respectively. The atomic coordinates of the calculated models are available from the authors.

Results and discussion

An INEPT-INADEQUATE ^{29}Si NMR spectrum for the bis(silylene)iron complex **2** is given in Fig. 1. This spectrum exhibits two doublet resonances at δ 121.6 and 89.6 ppm with the coupling constant $J(SiSi) = 28.6$ Hz. The 180° phase inversion of the doublet is a characteristic feature of the INEPT spectrum [12]. Observed coupling constants for **1**, **2**, and **3** are summarized in Table 1 along with a range of typical values for disilanes [13,21,22], disilenes [13], and 1,3-cyclodisiloxanes [13].

The typical $^{29}Si-^{29}Si$ coupling constant in disilanes (80–90 Hz) is much larger than that in 1,3-cyclodisiloxanes (3.8–4.8 Hz), but almost half of that in disilenes (155–158 Hz). It has been established that the carbon–carbon coupling constant is related qualitatively to the percentage of *s* character of the carbon orbitals involved in C–C bonding [11,13,23]. Recent *ab initio* calculations indicated that the Si–Si coupling constant, $^1J(SiSi)$, is also controlled mainly by the Fermi contact term, *i.e.*, percentage of *s* orbital character of the Si–Si bond [24]. Thus the difference of the coupling constants in disilanes and disilenes is attributable to the difference in formal hybridization of the silicon atoms, *i.e.*, sp^3 for disilanes and sp^2 for disilenes. The quite small value for 1,3-cyclodisiloxanes is assigned to the coupling separated by two Si–O bonds, $^2J(SiOSi)$ [13]. This is consistent with the general observation that longer-range couplings are two or more orders of magnitude smaller than one-bonded couplings [11].

The coupling constant value of 128 Hz for the disilanyliron complex **1** is slightly larger compared to typical values for organodisilanes. It is well known that the

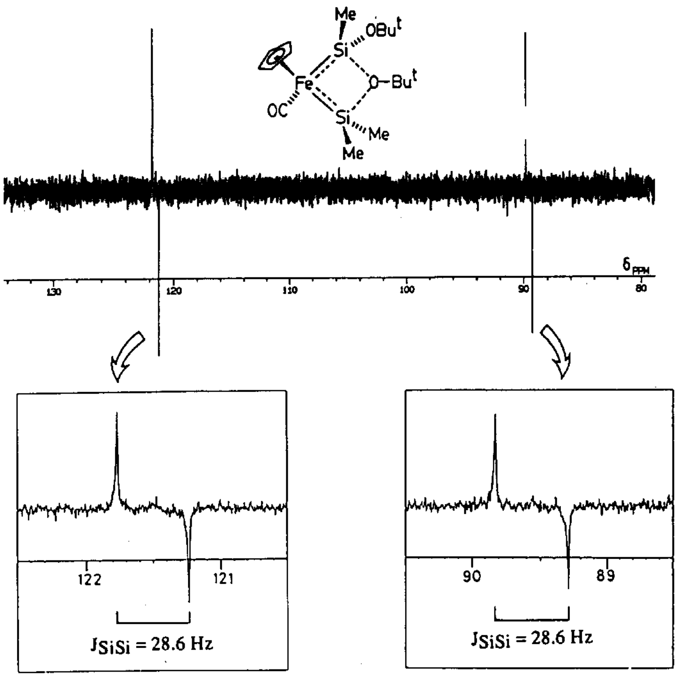


Fig. 1. INEPT-INADEQUATE ^{29}Si NMR spectrum for the bis(silylene)iron complex **2**. Two doublet signals are evident at 121.6 and 89.6 ppm with coupling constant $J(SiSi) = 28.6$ Hz.

magnitude of one-bond coupling increases with increasing electronegativity of substituents on a pair of coupled nuclei [11]. For example, the $^1J(SiSi)$ values for $Me_3SiSiMe_2Ph$, $Me_3SiSiMe_2Cl$, and $Me_3SiSiMe_2F$ are 86.1, 94.0 and 98.7 Hz, respectively, and those for $(Me_3Si)_2SiMe_2$ and $(Cl_3Si)_2SiCl_2$ are 73.2 and 186 Hz, respectively [21,25]. Thus the larger coupling constant for **1** compared to those for typical disilanes is attributable to the electron-attracting effect of the iron fragment and the tert-butoxy group.

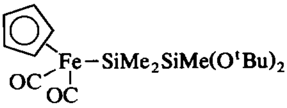
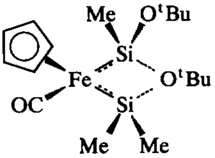
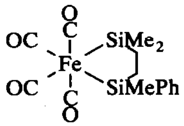
The observed coupling constant in the *cis*-bis(silyl)iron complex **3** (2.7 Hz) is much smaller than that of **1** and even smaller than that of 1,3-cyclodisiloxanes. Complex **3** contains a 5-membered chelate ring which consists of an iron atom and a bidentate ligand, $SiMe_2CH_2CH_2SiMePh$, so that the coupling in complex **3** corresponds to a combination of $^2J(SiFeSi) + {}^3J(SiCCSi)$. Unusually small coupling constants are often observed in systems where the couplings are described as a combination of ^2J and ^3J, because ^2J and ^3J are commonly opposite in sign and the absolute difference between them is not large [11].

The coupling constant of 28.6 Hz for the bis(silylene)iron complex **2** is much smaller than that for the disilanyliron complex **1** with a direct Si–Si single bond, but larger than that for the *cis*-bis(silyl)iron complex **3** with no direct Si–Si bond. This observation suggests that the silicon atoms in **2** interact weakly.

One possible interpretation for the coupling constant in **2** is that a direct but weak interaction exists between the two silicon atoms. By this model, the long Si–Si bond in **2** causes a smaller overlap of the two silicon orbitals than those in the usual disilanes or disilanyliron complex **1**. In addition, coupling through a

Table 1

Silicon-29 NMR coupling constants for disilanyliron complex **1**, bis(silylene)iron complex **2**, and *cis*-bis(silyl)iron complex **3** with typical values for disilanes, disilenes, and 1,3-cyclodisiloxanes

Compound	J(Si–Si) (Hz)	Ref.
 (1)	128	This work
 (2)	28.6	This work
 (3)	2.7	This work
Disilanes	80–90	refs. 13, 20, 21
Disilenes	155–158	ref. 13
1,3-Cyclodisiloxanes	3.8–4.0	ref. 13

SiFeSi or SiOSi bond further decreases the coupling constant slightly since ^2J and ^1J are opposite in sign [11].

One can also rationalize a coupling interaction without a Si–Si direct bond. On this model, the silicon-silicon coupling constant in **2** can be viewed as the sum of two geminal couplings, ^2J(SiFeSi) and ^2J(SiOSi). If the bonding for **2** is assumed to be that shown in Scheme 1, the Fe–Si bond is formally depicted as a resonance mixture of a single bond and a double bond. Thus, a large *s* orbital contribution is expected in the bonding between the iron and silicon atoms. Clark and Schrock [26] reported the coupling constants of ^2J(CWP) and ^1J(CW) in an alkyl(alkylidene)(alkylidyne)tungsten complex W(CCMe$_3$)(CHCMe$_3$)(CH$_2$CMe$_3$)(PMe$_3$)$_2$. The coupling constants ^2J(CWP) for the neopentyl, neopentylidene, and neopentylidyne ligands are 7, 14, and 14 Hz, respectively, and ^1J(CW) are 80, 120, and 210 Hz, respectively. These data show that the coupling constant through unsaturated bonds is larger than that through single bonds, even in the case of transition metal complexes. Thus the magnitude of the coupling constant through the Si–Fe–Si path in **2** is expected to be larger than that of ^2J(SiFeSi) in the bis(silyl)iron complex **3**. ^2J(SiFeSi) for **3** is not actually known but may be larger than the experimentally observed value, 2.7 Hz, which is a combination of ^2J(SiFeSi) and ^3J(SiCCSi) (see above). In contrast to the Fe–Si bond, the silicon atom *p*-orbitals are likely to be the major contributions to the Si–O(bridge)

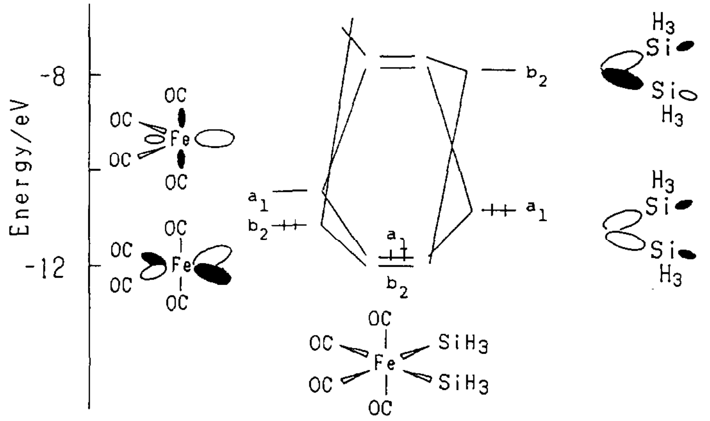


Fig. 2. Orbital interaction diagram between a $(OC)_4Fe$ fragment and a bis(silyl) fragment to yield $(OC)_4Fe(SiH_3)_2$.

bonds, since the geometry of each silicon atom and three atoms bonded to the silicon except the bridging oxygen is almost planar. The bridging oxygen coordinates to this pseudoplane almost perpendicularly [1]. Thus the coupling through the Si–O–Si path is expected to be small compared to that through the iron atom.

To elucidate the interaction mechanism, model calculations using the extended Hückel method [16] were carried out. The interaction between a $(OC)_4Fe$ fragment and a bis(silyl) fragment, obtained from the EHMO calculation for $(OC)_4Fe(SiH_3)_2$, is shown (Fig. 2). The frontier orbitals of the bis(silyl) fragment are the in-phase (HOMO) and the out-of-phase (LUMO) combinations of the two silicon orbitals. These orbitals interact with the LUMO and HOMO of the $Fe(CO)_4$ fragment, respectively, giving two bonding orbitals.

An interaction diagram between the orbitals of a CpFe(CO) fragment and those of a bis(silylene) fragment $\{SiH_2 \cdots O(H) \cdots SiH_2\}$ to yield the bis(silylene)iron complex $CpFe(CO)\{SiH_2 \cdots O(H) \cdots SiH_2\}$ is presented in Fig. 3. The *1a'* and *2a'* orbitals of the bis(silylene)iron complex arise from the in-phase combination of iron 1*a'* and 2*a'* orbitals and a bis(silylene) a_1 orbital. In addition to these interactions, the b_2 orbital of the bis(silylene) fragment interacts with the a'' orbital of the iron fragment to give the a'' bonding orbital of the bis(silylene)iron complex. Thus there are three bonding MOs in terms of inter-fragment interaction. These findings suggest that the interaction between the two fragments is stronger than that in bis(silyl)iron complex and are consistent with the fact that the Fe–Si distances in the bis(silylene)iron complex A are shorter than those of known Fe–Si single bonds.

The a'' orbital (HOMO) of the bis(silylene)iron complex is made up of the a'' orbital of the CpFe(CO) fragment and the b_2 orbital of the $(SiH_2)_2OH$ fragment. Since the b_2 orbital of the $(SiH_2)_2OH$ fragment arises from the out-of-phase interaction between two silicon orbitals and an oxygen orbital, the a'' orbital of the bis(silylene)iron complex also has antibonding character on the Si–O–Si frame. Thus the Si–O bonds are expected to be weak compared to the normal Si–O single bond. In fact, the atomic bond population [27], which is the measure of the

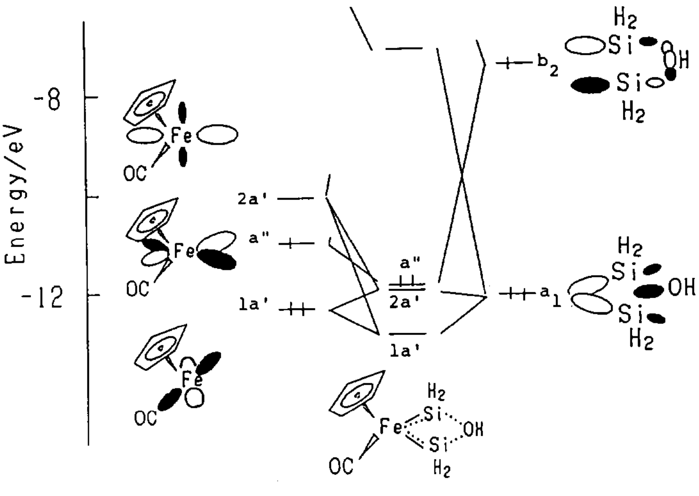


Fig. 3. Orbital interaction diagram of important orbitals between a CpFe(CO) fragment and a bis(silylene) fragment to yield $CpFe(CO)\{SiH_2\cdots O(H)\cdots SiH_2\}$.

bond strength, on the Si–O bond of the bis(silylene)iron complex (0.147) is much smaller than that of $CpFe(CO)_2SiH_2SiH_2(OH)$ (0.184) which has a normal Si–O single bond. This is also consistent with the fact that the Si–O(bridge) bonds in the bis(silylene)iron complex **A** are unusually long (1.793(9) and 1.799(8) Å) compared to the Si–O(terminal) bond (1.632(9) Å) [1].

In the EHMO calculation, the magnitude of overlap between two atomic orbitals is given as an atomic orbital bond population (AOBP) [27]. The atomic orbital bond population between two silicon 3*s* orbitals (3*s*(Si)–3*s*(Si) AOBP) is 0.020 for the bis(silylene)iron complex, whereas it is 0.002 for the bis(silyl)iron complex and 0.067 for the disilanyliron complex. Figure 4 shows a plot of the observed and reported ^{29}Si NMR coupling constants against the AOBP between

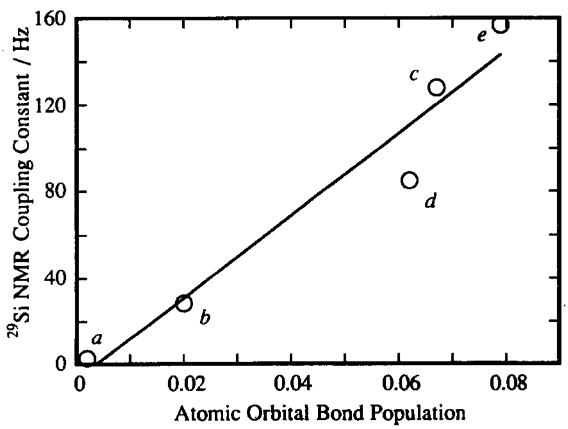


Fig. 4. Plot of ^{29}Si NMR coupling constants against 3*s*(Si)–3*s*(Si) atomic orbital bond populations (AOBP) obtained from extended Hückel MO calculations. (a) bis(silyl)iron complex **3**; (b) bis(silylene)iron complex **2**; (c) disilanyliron complex **1**; (d) disilanes [13,20,21]; and (e) disilenes [13].

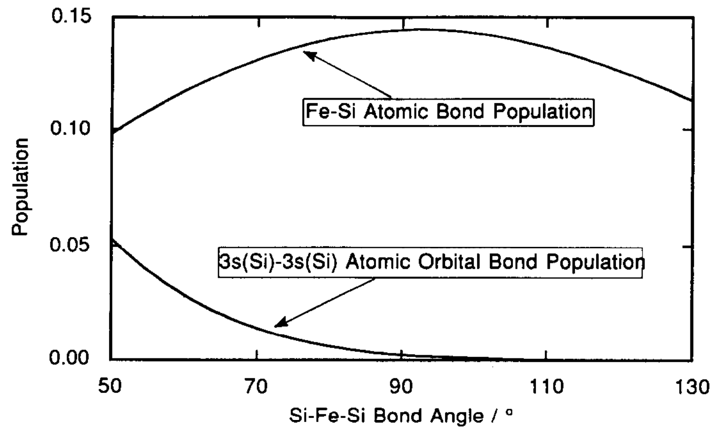


Fig. 5. Angular dependence of the Fe–Si atomic bond population and 3*s*(Si)–3*s*(Si) atomic orbital bond population for $(OC)_4Fe(SiH_3)_2$.

two silicon 3*s* orbitals derived from extended Hückel MO calculations. A nearly linear relationship is found between the 3*s*(Si)–3*s*(Si) AOBP and ^{29}Si NMR coupling constant. This means that the magnitude of ^{29}Si NMR coupling might be estimated from the 3*s*(Si)–3*s*(Si) atomic orbital bond population derived from an EHMO calculation.

The EHMO calculation for the bis(silylene)iron complex indicates that there is no direct silicon–silicon bond along the silicon–silicon axis. This means that the ^{29}Si NMR coupling constant for the bis(silylene)iron complex **2** should be assigned to the sum of two geminal couplings, ^2J(SiFeSi) and ^2J(SiOSi). Why, then, is the coupling in the bis(silylene)iron complex **2** larger than that in the bis(silyl)iron complex **3**? The following three factors appear to be operative in this system. Firstly, the coupling in **2** is described as the combination of two ^2J couplings, while that in **3** is described as the combination of ^2J and ^3J which are generally opposite in sign [11].

Secondly, the bis(silylene) fragment interacts with the iron fragment through three bonding orbitals. Two of these are composed of the bis(silylene) a_1 orbital which contains an in-phase combination of two silicon 3*s* orbitals. In the bis(silyl)iron complex, one of two interfragment bonding orbitals only is suitable for in-phase overlap with the two silicon 3*s* orbitals. Thus a stronger interaction between the two silicon 3*s* orbitals is expected in the bis(silylene)iron complex than in the bis(silyl)iron complex.

Thirdly, the magnitude of the 3*s*(Si)–3*s*(Si) AOBP varies dramatically with change in the Si–Fe–Si bond angle. Figure 5 displays the variation in the calculated 3*s*(Si)–3*s*(Si) AOBP and Fe–Si atomic bond population of the bis(silyl)iron complex $(OC)_4Fe(SiH_3)_2$ as a function of the Si–Fe–Si bond angle. The Fe–Si atomic bond population which corresponds to the electron density in each Fe–Si bond reaches a maximum around 90°. The 3*s*(Si)–3*s*(Si) AOBP, however, increases with a decrease in the Si–Fe–Si bond angle. In the EHMO calculation of the bis(silylene)iron complex, the Si–Fe–Si bond angle of the model was set at 72.6° in accordance with the result of the X-ray crystal structure analysis [1]. The Si–Fe–Si bond angle in the bis(silyl)iron complex **3** is unknown, but

Graham *et al.* reported that the bond angle in *cis*-$(OC)_4Fe(SiMe_3)_2$ is 111.8° [18]. Therefore, considering the Si–Fe–Si bond angle, larger 3*s*(Si)–3*s*(Si) AOBP, *i.e.*, ^{29}Si–^{29}Si coupling, is also expected for the bis(silylene)iron complex **2** than for the bis(silyl)iron complex **3**.

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