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Preliminary Communication

Synthesis of Me_2Si-η^5-$C_5H_4(CO)Fe(CO)_2$-$Fe(CO)$-η^5-$C_5H_4SiMe_2$ and a novel reaction between its Si–Si and Fe–Fe bonds

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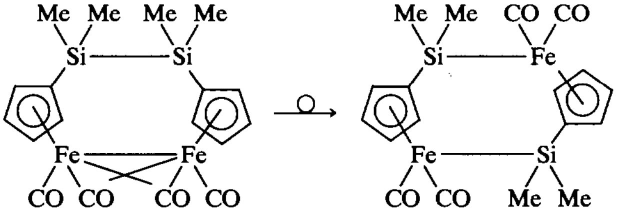
Abstract

Me_2Si-η^5-$C_5H_4(CO)Fe(CO)_2Fe(CO)$-η^5-$C_5H_4SiMe_2$ (**1**) was synthesized by reaction of 1,2-bis(cyclopentadienyl)tetramethyldisilane and pentacarbonyliron. An unexpected product, Me_2Si-η^5-$C_5H_4Fe(CO)_2SiMe_2$-η^5-$C_5H_4Fe(CO)_2$ (**2**), was obtained from the reaction, which was evidently formed *via* a novel metathesis reaction between Si–Si and Fe–Fe bonds in **1**. The molecular structures of **1** and **2** were determined by single-crystal X-ray diffraction studies.

Ring-bridged bis(cyclopentadienyl)tetracarbonyldiiron derivatives in which two cyclopentadienyls are linked together by certain alkyl or silyl groups have been studied extensively over the past years [1]. Polysilanyl bridged derivatives of this kind, however, have never been reported up to now. The introduction of tetramethyldisilanylene as a linking group into this type of compound is of interest to us, as we have long been interested in polysilane chemistry, and here we report on our recent investigation.

1,2-Bis(cyclopentadienyl)tetramethyldisilane [2] was prepared from 1,2-dichlorotetramethyldisilane and cyclopentadienylsodium [3*], and reacted with pentacarbonyliron on refluxing in xylene [4*]. After refluxing for 24 h, only a small amount of **1** was obtained in a yield of about 1% [5*]. An unexpected by-product, which was confirmed to have the novel cyclic structure of **2**, was isolated from the reaction in 35% yield [6*]. When the reaction was repeated and the time of reflux was shortened to 10 h, the yield of **1** increased to 24% and the yield of product **2** became as little as 11%.

$$ClMe_2SiSiMe_2Cl + 2NaC_5H_5 \xrightarrow{THF} C_5H_5Me_2SiSiMe_2C_5H_5 \xrightarrow[xylene]{Fe(CO)_5}$$



(1) (2)

Compound **2**, having Si–Fe bonds, is clearly a rearranged isomer of **1** formed *via* breaking of the Si–Si and Fe–Fe bonds. As the total yield of the two products remained unchanged upon shortening the reaction time while individual yields of **1** and **2** rose and fell, respectively, compound **1** was most likely transformed into **2** upon further reaction. Since the Si–Si bond is well known to be reactive towards halogen–halogen bonds [7], and the Fe–Fe bond, as well as other metal–metal bonds in metal carbonyl dimers, has been shown to have similar properties as halogens [8], it could be possible that the Si–Si bond in compound **1** would react with the Fe–Fe bond, leading to the transformation of **1** into **2** under the above reaction conditions. Thus, product **1** was put back into xylene and subjected to further refluxing. It was noteworthy that compound **1** was converted into **2** almost completely after refluxing for 24 h [9*].

The rearrangement of compound **1** into **2** is a metathesis reaction of Si–Si and Fe–Fe bonds which has not yet been discovered. Although these two bonds had been shown to be non-interactive in intermolecular cases [10], the combination of them in one molecule seems to make their interaction more easy to occur.

In order to find out how the reaction could happen, both structures were determined by single crystal X-ray

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[*] Reference number with asterisk indicates a note in the list of references.

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diffraction studies. Compound **1**, of crystalline state * as illustrated in Fig. 1, has an unsymmetric configuration. Although all of its bond lengths and angles are normal in value, its twisted boat conformation of the six membered ring formed by silicon, iron and the bridgehead cyclopentadienyl carbon atoms must cause a certain degree of molecular strain. However, the configuration of compound **2**, also of crystalline state ** as shown in Fig. 2, has C_i symmetry, and the conformation of the six membered ring takes a strainless chair one. Thus, the rearrangement from **1** into **2** would be favourable, with a reduction in molecular strain.

In addition, the distance of Si–Fe (2.315(2) Å) in compound **2** is much shorter than the average bond length of Si–Si (2.346(4) Å) and Fe–Fe (2.526(2) Å) in compound **1** and is slightly shorter than distances in acyclic molecules of the same kind [11]. Thus the Si–Fe bond has extra stability which greatly promotes the rearrangement of **1** into **2**. The carbonyl bridges at the Fe–Fe bond in crystalline **1**, which have been reported to be broken in solution [12], were not able to hinder the reaction of Fe–Fe and Si–Si bonds.

Compound **1** was found to be stable in solution as well as in the solid state at room temperature. Compound **2** was not only stable in both states, but also no longer sensitive to moisture and air owing to formation of the tremendously stable cyclic structure. Further research on the chemistry of both **1** and **2**, and on details of the metathesis reaction is currently in progress.

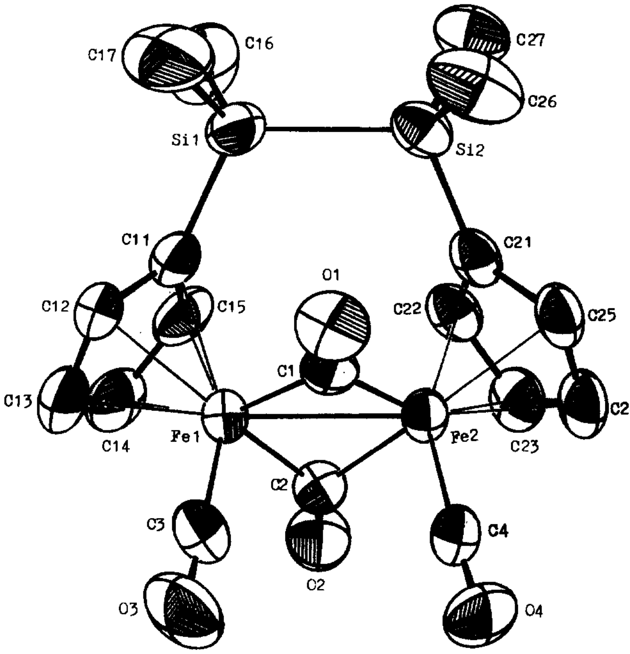

Fig. 1. Structure and atom labelling scheme for non-hydrogen atoms of **1**. Important bond lengths (Å), angles (°) and torsion angles (°): Si1–Si2 2.346(4), Si1–C11 1.85 (2), Si2–C21 1.848(9), Fe1–Fe2 2.526(2), Si2–Si1–C11 114.8(3), Si1–Si2–C21 112.3(4), C11–Si1–Si2–C21 13.32, C11–Fe1–Fe2–C21 1.22(0), Si1–C11–Fe1–Fe1 26.30(0), Fe1–C11–Si1–Si2 20.57(0), Si1–Si2–C21–Fe1 41.74(0), Si2–C21–Fe2–Fe1 21.82(0).

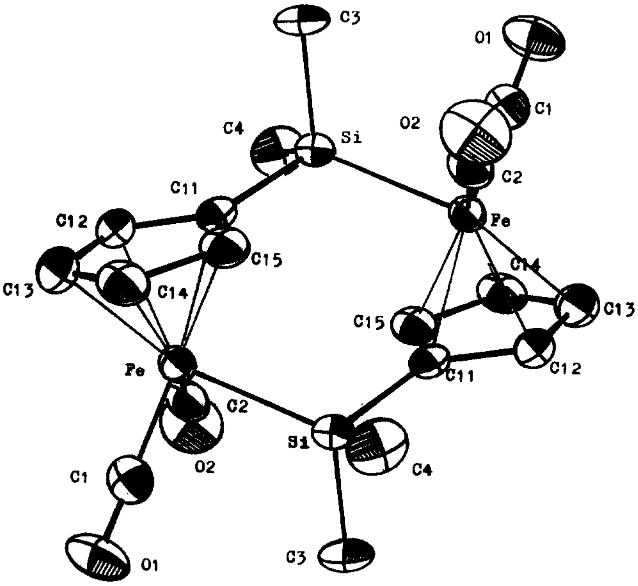

Fig. 2. Structure and atom labelling scheme for non-hydrogen atoms of **2**. Important bond lengths (Å), angles (°) and torsion angles (°): Si–Fe 2.315(2), Si–C11 1.881(5), Si–Fe–C11 99.8(1), Fe–Si–C11 112.0(2), Fe–C11–Si 132.8(3), C11–Si–Fe–C11 35.57(23), Si–C11–Fe–Si 47.28(9), Fe–Si–C11–Fe 51.37(13).

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* Crystal data for **1**: $C_{18}H_{20}O_4Si_2Fe_2$, $M = 468.22$; triclinic, space group $P\bar{1}$; a 6.998(1), b 10.106(2), c 15.475(2) Å; α 75.26(1), β 79.671(1), γ 74.00(1)°; $V = 1010.4$ Å^3, $Z = 2$, $D_x = 1.539$ g cm^{-3}, $\mu = 15.708$ cm^{-1}, $F(000) = 480$. 3704 independent reflections were collected; 2765 reflections have $I > 3\sigma(I)$ (ω–2θ scan, $2 < \theta < 25°$, Mo Kα, λ 0.71073 Å, room temperature, Lp and empirical absorption correction). The structure was solved by direct methods (MULTAN 82). $R = 0.057$, $R_w = 0.080$ (anisotropic, nonhydrogen atoms, final height 0.66 e Å^3). Details of atomic coordinates, thermal parameters, bond parameters and structural factors may be obtained from the authors.

** Crystal data for **2**: $C_{18}H_{20}O_4Si_2Fe_2$, $M = 468.22$; monoclinic, space group $P2_1/n$; a 8.985(1), b 10.526(1), c 10.621(2) Å; β 95.609(9)°; $V = 998.8$ Å^3, $Z = 2$, $D_x = 1.557$ g cm^{-3}, $\mu = 15.89$ cm^{-1}, $F(000) = 480$. 1975 independent reflections were collected; 1369 reflections have $I > 3\sigma(I)$ (ω–2θ scan, $2 < \theta < 25°$, room temperature, Mo Kα, λ 0.71073 Å, Lp and empirical absorption correction). $R = 0.046$; $R_w = 0.067$ (anisotropic, nonhydrogen atoms, final height 0.66 e Å^3). Details as for **1** may also be obtained from the authors.

Acknowledgments

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3 Refer to procedures in ref. 2.

4 Procedures of preparation: 1,2-bis(cyclopentadienyl)tetramethyldisilane (2.46 g, 10 mmol) and pentacarbonyliron (3.92 g, 20 mmol) were refluxed in xylene (50 ml) for 24 h. Cooling and distilling off xylene under reduced pressure (residue of pentacarbonyliron was collected by a cooling well) gives a dark silt of crude product.

5 Compound **1**: Extraction of the crude product with n-hexane (50 ml) and purification through a column (Al_2O_3/n-hexane) gave 0.46 g (1%) of dark-red crystals. M.p. 170–172°C. Anal. Found: C, 46.15; H, 4.35. $C_{18}H_{20}Fe_2O_4Si_2$ calcd.: C, 46.17; H, 4.31%. ^1H NMR ($CDCl_3$): δ 0.29 (s, 2×6H, $SiMe_2$), 4.72 (m, 2×2H, C_5H_4), 5.40 (m, 2×2H, C_5H_4). ^{13}C NMR ($CDCl_3$): δ −3.056 ($SiMe_2$), 96.178, 91.431, 88.15 (C_5H_4), 209.59 (CO). ^{29}Si NMR ($CDCl_3$): δ 25.34 ($SiMe_2$); IR (KBr): ν(CO) 1991.4, 1942.1, 1810.9, 1979.0, 1761.7 cm^{-1}.

6 Compound **2**: The extracted residue was purified through a column (Al_2O_3/n-hexane) to give 1.6 g (35%) of yellow crystals. M.p. 180°C (decomposition). Anal. Found: C, 46.66; H, 4.45. $C_{18}H_{20}Fe_2O_4Si_2$ calcd.: C, 46.17; H, 4.31%. ^1H NMR ($CDCl_3$): δ 0.48 (s, 2×6H, $SiMe_2$), 4.99 (s, 2×4H, C_5H_4). ^{13}C NMR ($CDCl_3$): δ 6.97 ($SiMe_2$), 96.49, 93.16, 83.75 (C_5H4), 215.45 (CO). ^{29}Si NMR ($CDCl_3$): δ 35.46 ($SiMe_2$). IR (KBr): ν(CO) 1975.0, 1925.8 cm^{-1}.

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9 Rearrangement reaction: compound **1** (0.33 g) in xylene (10 ml) was refluxed for 24 h. The product was separated through a column (Al_2O_3/n-hexane), giving 0.2 g (60%) of yellow crystals of **2**. No significant amount of **1** was recovered.

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