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Preliminary communication

PENTAMETHYLDISILYLMETHYL AND RELATED COMPLEXES OF IRON INVOLVING SKELETAL REARRANGEMENTS, Fe—C—Si—Si → Fe—Si—C—Si

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Summary

For the new complex $Me_3Si{-}Me_2Si{-}CH_2Fe(CO)_2Cp$ the metal—carbon bond undergoes normal insertion reactions; however, under certain conditions the Si—Si—C—Fe framework rearranges to the silicon—iron bonded system Si—C—Si—Fe.

Initial reports on the synthesis and chemical properties of various monosilylmethyliron complexes, $CpFe(CO)_2CH_2SiMe_2R$ [1,2] were followed by considerable interest in the use of the silylmethyl ligand. In particular, the laboratories of Lappert and of Wilkinson have used this ligand to produce many novel alkylmetal complexes of great kinetic stability unavailable using simple unsubstituted alkyl groups [3,4].

Our continuing interest in this area led us to attempt the synthesis of polysilylmethyl complexes and study their properties. The cyclopentadienyliron dicarbonyl derivatives are readily formed using the standard salt elimination reaction outlined below. Recovered yields range from 45—80%.

$$CpFe(CO)_2^- + Me_3Si{-}Me_2Si{-}CH_2Cl \rightarrow \underset{\text{(I)}}{CpFe(CO)_2{-}CH_2{-}SiMe_2{-}SiMe_3}$$

Complex I reacts with sulphur dioxide and with triphenylphosphine in refluxing THF to produce the insertion type products expected from such reactions, i.e.:

$$CpFe(CO)_2CH_2SiMe_2SiMe_3 + SO_2 \rightarrow \underset{\text{(II)}}{CpFe(CO)_2{-}SO_2{-}CH_2{-}SiMe_2{-}SiMe_3}$$

$$CpFe(CO)_2CH_2SiMe_2SiMe_3 + PPh_3 \rightarrow \underset{\text{(III)}}{CpFe(CO)(PPh_3){-}CO{-}CH_2{-}SiMe_2{-}SiMe_3}$$

Photochemical treatment of the starting disilylmethyl complex (I) leads to a facile rearrangement resulting in the formation of a silicon—iron bonded complex $CpFe(CO)_2SiMe_2—CH_2—SiMe_3$ (IV). If this photochemical reaction is carried out in the presence of phosphine the corresponding rearranged phosphine monocarbonyl complex is obtained, $CpFe(CO)(PPh_3)SiMe_2—CH_2—SiMe_3$ (V). Photochemical treatment of the rearrangement complex IV with phosphine also leads, as would be expected, to complex V.

$$CpFe(CO)_2CH_2SiMe_2SiMe_3 \xrightarrow{h\nu} \underset{\text{(IV)}}{CpFe(CO)_2SiMe_2CH_2SiMe_3}$$

$$CpFe(CO)_2CH_2SiMe_2SiMe_3 \xrightarrow[PPh_3]{h\nu} \underset{\text{(V)}}{CpFe(CO)(PPh_3)—SiMe_2—CH_2—SiMe_3}$$

$$CpFe(CO)_2SiMe_2—CH_2—SiMe_3 \xrightarrow[PPh_3]{h\nu} CpFe(CO)(PPh_3)—SiMe_2—CH_2—SiMe_3$$

The spectral data for the new complexes are recorded in Table 1 and are in accord with the proposed structures. A few points may be pertinent. (a) Complex I exhibits singlets for the cyclopentadienyl, trimethylsilyl, dimethylsilyl and methylene protons in accord with a silylmethyl complex. By way of comparison the data for $CpFe(CO)_2CH_2SiMe_3$ (VI) is included in Table 1. (b) Complex IV, related to I via the new rearrangement, also exhibits singlets for the sets of distinct protons present. The new resonances are shifted relative to those in complex I in the expected fashion due to the formation of a silicon—iron bond at the expense of the carbon—iron bond. A comparison may be drawn with the changes observed between $CpFe(CO)_2CH_2SiMe_3$ (VI) and $CpFe(CO)_2SiMe_3$ (VII). Thus τ(Cp) (ppm) (VI→VII) 5.19→5.36; (I→IV) 5.23→5.32: $\tau(CH_3Si)$ (VI→VII) 9.94→9.61; (I→IV) 9.92, 9.96→9.47, 9.85. The methylene protons change from τ10.21 for complex I where they are bonded directly to the transition metal to τ9.78 in the rearranged silicon—iron bonded complex reflecting an expected loss of electron density. The infrared stretching frequencies for the terminal carbonyl groups for the two complexes also change in the manner to be expected by comparison of the known values for the trimethylsilylmethyliron (VI) and trimethylsilyliron

TABLE 1

INFRARED AND PMR SPECTRAL DATA OBTAINED FOR THE COMPLEXES I—VII

Complex	IR [a] $\nu(C{\equiv}O)$ (cm^{-1})	PMR [b] (τ) (ppm)			
		Cp	Me_3Si	Me_2Si	CH_2
I	1960; 2013	5.23	9.96	9.92	10.21
II	2000; 2021	4.92	9.89	9.83	6.91
III	1921	5.62	9.99	9.99	(7.10, 7.32, 7.94, 8.16) [c]
IV	1947; 2000	5.32	9.85	9.47	9.78
V	1901	5.89 (d, J 0.2 Hz)	9.98	(9.84, 9.97)	10.22 (d, J 4 Hz)
VI	1960; 2008	5.19	9.94		10.32
VII	1940; 1995	5.36	9.61		

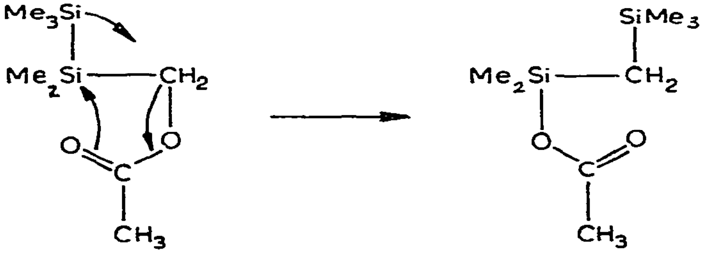
[a] Cyclohexane solution. [b] Carbon disulfide solution. [c] AB quartet centered at 7.63 ppm, J_{AB} 13 Hz, $\Delta\tau$(AB) 0.84.

dicarbonyl complex (VII), i.e., (VI→VII) 1960, 2008→1940, 1995; (I→IV) 1960, 2013→1947, 2000.

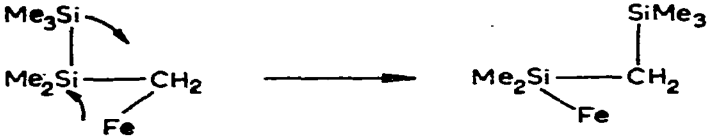
(c) The asymmetric complexes III and VI also exhibit those characteristic features previously observed for such complexes. Thus the methylene protons of III form an AB quartet centered at τ7.63 while the dimethylsilyl methyl groups of complex V, being non-equivalent, appear as two distinct signals at τ9.84 and 9.97. The methylene protons in complex V exhibit a completely different pattern from those of previously reported asymmetric silylmethyl-iron complexes. $\mathrm{CpFe(CO)(PR_3)\text{—}CH_2SiMe_2R'}$. Such protons exhibit a complex ABX pattern, at τ11.2 and 10.2 with J_{AX} and J_{BX} having greatly differing values of 2 and 13 Hz [2]. The methylene protons in complex V appear as an apparent doublet. The splitting is probably due to PH coupling, however, varying temperature and decoupling experiments etc. are underway to determine the exact nature of this aspect of the spectrum.

The rearrangements reported here appear to be related to the thermal rearrangement of pentamethyldisilylmethyl acetate [5]:

cf. (a)



(b)

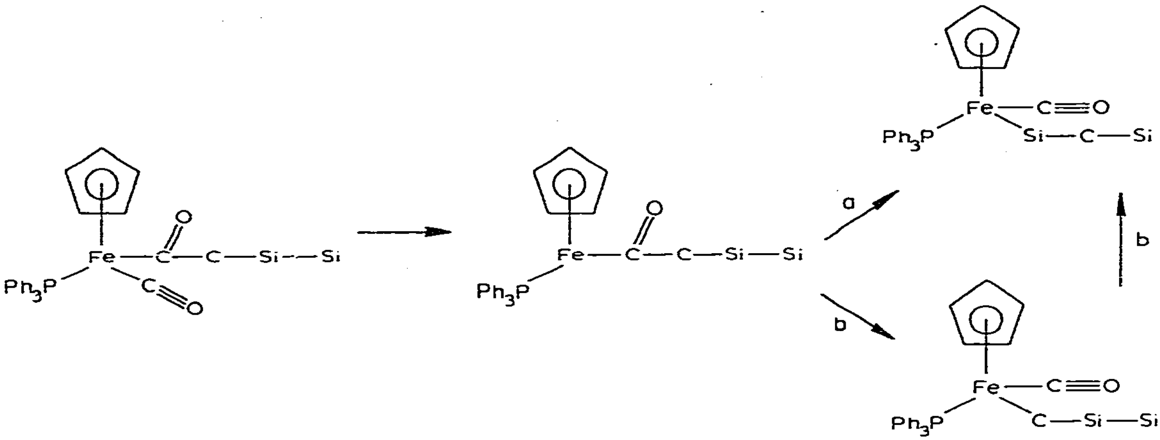


Decarbonylation of the disilylacyl complex (III) affords some insight into the nature of the rearrangement. Photochemical decarbonylation leads to the formation of V exclusively.

The thermal decarbonylation is more complex. We have recently drawn attention to the decarbonylation of the general system $\mathrm{CpFe(CO)(PPh_3)COR}$ and pointed out that two products are formed, a kinetically controlled iron dicarbonyl complex, $\mathrm{CpFe(CO)_2R}$ and the thermodynamically controlled $\mathrm{CpFe(CO)(PPh_3)R}$ [6]. The thermal decarbonylation of III leads to I as the kinetically-controlled product and V as the thermodynamically-controlled product. No rearranged dicarbonyl complex IV and no unrearranged phosphine iron complex $\mathrm{CpFe(CO)(PPh_3)CH_2\text{—}SiMe_2\text{—}SiMe_3}$ were isolated or observed as transient species, i.e.,

$$\begin{array}{l} \mathrm{CpFe(CO)(PPh_3)\text{—}CO\text{—}CH_2\text{—}SiMe_2\text{—}SiMe_3} \rightarrow \mathrm{CpFe(CO)(PPh_3)SiMe_2CH_2SiMe_3} \\ \qquad\qquad\quad \uparrow\downarrow \\ \mathrm{CpFe(CO)_2\text{—}CH_2\text{—}SiMe_2\text{—}SiMe_3} + \mathrm{PPh_3} \end{array}$$

It has previously been established that silyliron dicarbonyl complexes containing a silicon—iron bond will not undergo carbonyl displacement reactions with tertiary phosphine thermally [7]. Thus product V must form via a very unstable transient species $CpFe(CO)(PPh_3)CH_2{-}SiMe_2{-}SiMe_3$ which almost immediately rearranges to V or the rearrangement might occur as the alkyl group migrates from the acyl carbon atom to the iron atom. The two possibilities are outlined; a and b. Whichever pathway operates, it is unambiguous that replacement of a carbonyl group by a triphenylphosphine ligand dramatically increases the tendency of the disilylmethyl group to rearrange to the dimethylsilylmethyltrimethylsilane group.



This enhancement may be understood since replacement of the carbon monoxide by the tertiary phosphine will increase the π electron density of the iron atom. This not only increases the ability of the iron to undertake a nucleophilic attack upon the silicon atom, but also increases the need to delocalize such π density to the attached ligands. A metal—silicon bond may perform this function via a $d_\pi{-}d_\pi$ interaction in contrast to the metal—carbon bond.

These rearrangements are related to the observed photochemical fragmentation of polysilyliron complexes [8]; e.g.:

$$CpFe(CO)_2{-}SiMe_2{-}SiMe_3 \xrightarrow{h\nu} CpFe(CO)_2{-}SiMe_3 + (SiMe_2)_n$$

and further illustrates the ready cleavage of silicon—silicon bonds in a transition metal environment.

It is worth noting that the polysilylmethyl complexes will probably have less potential as homogeneous catalysts, cf., monosilylmethyl complexes [9], being prone to rearrangement involving loss of the crucial metal—carbon linkage. Our studies are continuing with other transition metals.

Acknowledgements

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