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# Structural Studies of Incipient Pentacoordination of Silicon in Hydrido Transition-Metal Silyl Compounds.

# II. The Crystal Structure of *trans*-Hydridobis(difluoromethylsilyl)-($\eta$-cyclopentadienyl)monocarbonyliron, $(\eta^5\text{-}C_5H_5)Fe(CO)H(SiF_2CH_3)_2$

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$(\eta^5\text{-}C_5H_5)Fe(CO)H(SiF_2CH_3)_2$ is orthorhombic, *Pnma*, $a = 11{\cdot}821$ (2), $b = 14{\cdot}640$ (2), $c = 7{\cdot}157$ (2) Å, $Z = 4$, $\rho_c = 1{\cdot}64$ g cm$^{-3}$. The hydride was located by direct observation at the point where minimization of intramolecular non-bonded contacts would place it, the latter calculations being simplified by the mirror plane of symmetry present in the molecule. The Fe–Si length of 2·249 (1) Å is compared to that found in compounds with different substituents on the Si. These substituents show an almost constant orientation which suggests a similar position for the H atom in those compounds in which it was not observed. The final *R*, for 981 counter reflexions, was 2·8%.

## Introduction

The comparative study of $(\eta^5\text{-}C_5H_5)M(CO)_2$-$HSi(C_6H_5)_3$ ($M$ = Re, Mn) (Smith & Bennett, 1977; Hutcheon, 1971) clearly demonstrates the difficulties associated with X-ray diffraction studies when relatively precise information concerning H atom locations is required. While this type of problem is more properly tackled by neutron diffraction, X-ray diffraction can yield useful results if the study molecule is carefully chosen. The previous paper indicates two complementary approaches to the location of the H ligand: (1) by direct observation and (2) by inference, from arguments based on non-bonded contacts. Arguments based on non-bonded contacts are optimized by increasing the symmetry of the H ligand environment and assuming a single-well potential. Direct observation should be optimized by choosing a metal in the first transition series. Close Si···H contacts are promoted by high coordination of the metal and highly electronegative substituents on the Si atom. Consideration of all of these factors suggests that molecules containing the structural fragment $(\eta^5\text{-}C_5H_5)Fe(CO)H$-$(SiXX'X'')_2$ (where $X$, $X'$ and $X''$ are various substituents) should be particularly suitable. Data on two molecules [$XX'X''$ = $Cl_3$, Manojlović-Muir, Muir & Ibers (1970); $XX'X''$ = $(CH_3)_2C_6H_5$, Simpson (1973)] are available for comparison. In neither of these was the H atom located directly. The structure determination of the bis(difluoromethylsilyl) derivative was undertaken in an attempt to gain further information on this particular series of hydrido metal silyl compounds.

## Experimental

The pale-yellow prismatic crystals of $(\eta^5\text{-}C_5H_5)Fe$-$(CO)H(SiF_2CH_3)_2$ as supplied by Dr W. A. G. Graham and E. Wood were suitable for an X-ray diffraction study. Since the compound is extremely air-sensitive, crystals were sealed in Lindemann glass capillaries. Preliminary photographs showed the systematic absences $0kl$ for $k + l = 2n + 1$, $h0l$ for $h = 2n + 1$, consistent with *Pnam* (non-standard setting of *Pnma*) and $Pna2_1$. Twelve intense non-axial reflexions were carefully centred in $2\theta$ (no monochromator, Cu $K\alpha_1$ radiation, $\lambda = 1{\cdot}54051$ Å) and used to refine the cell parameters (see abstract). Precise experimental measurement of the density was not possible, but when a few crystals were introduced into a mixture of organic liquids within 1% of the calculated density they showed no marked tendency to rise or fall during the minute or so in which no overt change in their appearance occurred.

A fresh crystal 0·1 × 0·1 × 0·1 mm was mounted on a Picker FACS 1 diffractometer in an arbitrary orientation and the intensities of 1309 reflexions were measured in the coupled $\omega/2\theta$ scanning mode. A scan width of 3° in $2\theta$ was chosen and a scanning rate of 1° min$^{-1}$ employed. Background was measured for 40 s on either side of the peak with the detector stationary. Data (limited by $0 < 2\theta < 50°$) were collected with Mo $K\alpha$ radiation monochromated by an oriented graphite crystal (reflecting plane 002). Of the measured intensities, 981 were judged to be significant ($I/\sigma I > 3{\cdot}0$) and were used in the subsequent calculations. The significant data were reduced to structure amplitudes (Doedens & Ibers, 1967). Absorption effects ($\mu$ = 15 cm$^{-1}$, transmission factors range from 0·90 to 0·95)

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were applied (Coppens, Leiserowitz & Rabinovich, 1965).

### Structure solution and refinement

The structure was solved by the heavy-atom method. The scattering factors were from Cromer & Mann (1968) for all atoms except H, for which the values of Mason & Robertson (1966) were used. The real and imaginary terms for anomalous scattering were included for Fe and Si (Ibers & Hamilton, 1964). The structure refined smoothly in space group *Pnma* and the molecule therefore contains a mirror plane. The positions of the H atoms of the cyclopentadienyl ring were calculated with the following assumptions: (1) H atoms are coplanar with the $C_5$ ring, (2) C—H = 1·0 Å, (3) the C—H vector bisects the appropriate external C—C—C angle. The H atoms of the methyl group were located in a difference map in which a peak consistent with the H ligand was also apparent, but was not accepted at this stage since the data appeared to suffer from extinction (maximum correction of the order of 20% of $F_c$). An extinction correction (Zachariasen, 1963) reduced $R$ to 3·1% and the refined value of $g$ was $1{\cdot}4 \times 10^{-7}$.

At this stage the positive identification of the H ligand was attempted. The general procedure was that of La Placa & Ibers (1965), *i.e.* use of a series of difference maps with varying maximum limits of $\sin\theta/\lambda$ for the contributing data. While the details of this treatment have been criticized by Huber-Buser (1971), the technique does ensure that any observed peak receives appropriate contributions to its electron density from the various shells of the data set. The results of this study are collected in Table 1.

For all maps with a $\sin\theta/\lambda$ limit > 0·25 the largest peak corresponded to an Fe—H distance of 1·44 Å. The $x$, $z$ and isotropic temperature factors of this H atom were refined in two final cycles of least squares. The parameters refined sensibly and $R$ was reduced to 2·8%. The refined coordinates correspond to Fe—H = 1·39 (6) Å. The true distance is probably between 0·05 and 0·15 Å longer because bonding effects (Stewart, Davidson & Simpson, 1965) produce a pronounced deviation from a spherical electron-density distribution for H atoms.

Two caveats are appropriate when discussing the validity of the H location. The unit cell is rather small and thus the number of independent terms in the electron density calculations are small and errors in a few observations can produce substantial effects. The data set also suffers from extinction. However, the peak assigned to the H ligand is located in the same place regardless of the application of the extinction correction and it seems that the known errors in the data are not contributing significantly to this peak.

### Results

The atomic coordinates, thermal parameters and rotor-model parameters are collected in Table 2. Symmetry restrictions prevent some parameters from being refined and these are marked with an asterisk and no standard deviations are reported for them. Intramolecular distances and angles are reported in Tables 3 and 4 respectively.*

### Discussion of the structure

A view of the molecule projected onto the plane of the $C_5$ ring is shown in Fig. 1. The molecular symmetry is as required by the site symmetry. Equivalent views of $(\eta^5\text{-}C_5H_5)Fe(CO)H(SiCl_3)_2$ and $(\eta^5\text{-}C_5H_5)Fe(CO)H[Si(CH_3)_2C_6H_5]_2$ are shown in Figs. 2 and 3 respectively. All three structures show the same gross orientation of the ligands, although minor angular differences occur. To a good approximation the carbonyl group bisects a C—C bond of the cyclopentadienyl ring in all three structures. The largest deviation from this arrangement is shown by the bis(trichlorosilyl) derivative.

Structural data on the $(\eta^5\text{-}C_5H_5)Fe(CO)Si_2$ fragments of the study molecule and of those discussed above are compared in Table 5. The Fe—C(cyclopentadienyl) distances exhibit remarkable consistency

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32187 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Results from a series of difference maps for* $(\eta^5\text{-}C_5H_5)Fe(CO)H(SiF_2CH_3)_2$

| Cut-off limit in $\sin\theta/\lambda$ | Number of terms in calculations | Observed electron density $\rho^E$ | Error in $\rho^E$, $\sigma(\rho)$ (at $y = 0{\cdot}25$) | Ratio $\rho^E/\sigma(\rho)$ | Calculated electron density ($B = 3{\cdot}0$ Å$^2$) | Fe—H distance (Å) |
|---|---|---|---|---|---|---|
| 0·20 | 51 | 0·20 | 0·027 | 7·4 | 0·16 | 1·52 |
| 0·25 | 95 | 0·31 | 0·036 | 8·6 | 0·25 | 1·44 |
| 0·30 | 156 | 0·44 | 0·042 | 10·5 | 0·34 | 1·44 |
| 0·35 | 241 | 0·50 | 0·045 | 11·1 | 0·42 | 1·44 |
| All data | 979 | 0·64 | 0·053 | 12·1 | Not calculated | 1·44 |

Table 2. *Independent atom and group parameters for* $(\eta^5\text{-}C_5H_5)Fe(CO)H(SiF_2CH_3)_2$

Positional parameters

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| Fe | 0·3856 (1) | 0·2500* | 0·1266 (1) |
| C(1) | 0·2997 (3) | 0·2500* | 0·3228 (5) |
| O(1) | 0·2406 (3) | 0·2500* | 0·4513 (4) |
| Si | 0·4529 (1) | 0·3787 (1) | 0·2570 (1) |
| F(1) | 0·4979 (2) | 0·3627 (1) | 0·4654 (2) |
| F(2) | 0·5625 (2) | 0·4190 (1) | 0·1577 (3) |
| C(2) | 0·3547 (3) | 0·4756 (2) | 0·2725 (5) |
| C(3) | 0·4472 (4) | 0·2500* | −0·1475 (5) |
| C(4) | 0·3788 (3) | 0·3281 (2) | −0·1175 (4) |
| C(5) | 0·2701 (3) | 0·2982 (2) | −0·0704 (4) |
| H(1) | 0·497 (3) | 0·2500* | 0·191 (5) |

Thermal parameters (×10$^4$)

| | $U_{11}$ or $U$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Fe | 323 | 329 | 318 | 0 | −8 | 0 |
| C(1) | 386 | 419 | 469 | 0 | −46 | 0 |
| O(1) | 553 | 849 | 511 | 0 | 184 | 0 |
| Si | 409 | 397 | 497 | −68 | −31 | −56 |
| F(1) | 936 | 743 | 589 | −143 | −289 | −93 |
| F(2) | 486 | 604 | 1087 | −192 | 136 | −33 |
| C(2) | 627 | 446 | 953 | 11 | 10 | −203 |
| C(3) | 688 | 877 | 329 | 0 | 107 | 0 |
| C(4) | 888 | 515 | 371 | −45 | −63 | 121 |
| C(5) | 625 | 651 | 455 | 117 | −185 | 49 |
| H(1) | 439 | | | | | |

Group parameters for methyl H atoms

| $x$ | $y$ | $z$ | $B$ | $B_d$ | Radius |
|---|---|---|---|---|---|
| 0·338 (2) | 0·494 (2) | 0·274 (4) | 5·6† | 0·8 (2) | 0·91 (2) Å |

| $D$ | $E$ | $F$ |
|---|---|---|
| 0·82 (3) | 1·72 (6) | 2·25 (7) |

* Constrained by symmetry.
† Not varied.

Table 3. *Intramolecular distances in* $(\eta^5\text{-}C_5H_5)Fe(CO)H(SiF_2CH_3)_2$

(*a*) Bond lengths between heavy atoms, standard deviations in parentheses

| | | | |
|---|---|---|---|
| Fe–Si | 2·249 (1) Å | Si–F(1) | 1·591 (2) Å |
| Fe–C(1) | 1·733 (4) | Si–F(2) | 1·601 (2) |
| Fe–C(3) | 2·092 (4) | Si–C(2) | 1·836 (3) |
| Fe–C(4) | 2·089 (3) | C(3)–C(4) | 1·416 (4) |
| Fe–C(5) | 2·086 (3) | C(4)–C(5) | 1·398 (5) |
| C(1)–O(1) | 1·156 (4) | C(5)–C(5′) | 1·411 (6) |

(*b*) From a heavy atom to the hydrogen

| | | | |
|---|---|---|---|
| Fe–H(1) | 1·49 (6) Å (bonding) | F(2)–H(1) | 2·56 (7) Å |
| F(1)–H(1) | 2·57 (7) | Si–H(1) | 2·06 (7) |

(*c*) Important non-bonding intramolecular distances between heavy atoms

| | | | |
|---|---|---|---|
| Si···Si′ | 3·667 (2) Å | C(5)···C(2) | 3·380 (3) Å |
| Si···C(1) | 2·654 (3) | F(1)···F(1′) | 3·300 (3) |
| F(1)···C(1) | 3·042 (3) | | |

Table 4. *Significant angles* (°) *between bonds*

Standard deviations are in parentheses.

| | | | |
|---|---|---|---|
| Si–Fe–Si′ | 113·9 (1) | Fe–C(1)–O(1) | 178·6 (3) |
| Si–Fe–C(1) | 82·6 (1) | C(4)–C(3)–C(4′) | 107·6 (4) |
| Si–Fe–H(1) | 63 | C(3)–C(4)–C(5) | 108·0 (3) |
| C(1)–Fe–H(1) | 109 | C(4)–C(5)–C(5′) | 108·2 (2) |
| F(1)–Si–F(2) | 105·5 (1) | Fe–Si–F(1) | 112·4 (1) |
| F(1)–Si–C(2) | 105·5 (1) | Fe–Si–F(2) | 114·4 (1) |
| F(2)–Si–C(2) | 104·8 (1) | Fe–Si–C(2) | 116·6 (1) |

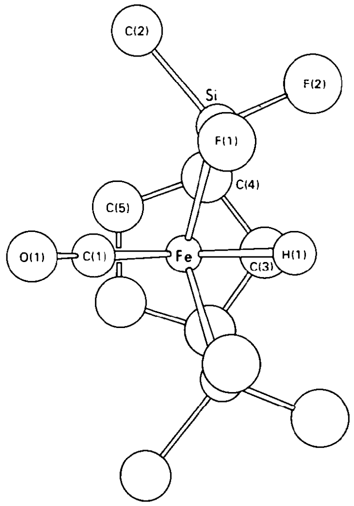

Fig. 1. A skeletal view of *trans*-hydridobis(difluoromethylsilyl)-(cyclopentadienyl)monocarbonyliron viewed down the vector joining the Fe atom to the centre of the cyclopentadienyl group.

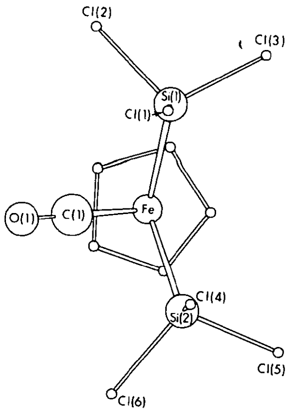

Fig. 2. A view (similar to that in Fig. 1) of the trichlorosilyl analogue.

within each molecule and are independent of the silyl substituents. This provides further evidence that highly electronegative substituents on Si do not cause a contraction of the metal *d* orbitals in carbonyl derivatives. The equality of the Fe—Si bonds in the difluoromethylsilyl and trichlorosilyl derivatives at 2·25 Å would suggest an equality in the electron-withdrawing ability of these groups. Table 6 contains values for the sums of the electronegativities of the Si substituents (excluding the metal) for $SiF_2CH_3$, $SiCl_3$ and $SiF_3$ for three different scales of electronegativity.

The Si—C [1·836 (3) Å] and Si—F [1·591 (2), 1·601 (2) Å] distances of the difluoromethylsilyl substituents are essentially identical with those observed in difluoromethylsilane (Sivalen & Stoichoff, 1958) [Si—C 1·833 (2), Si—F 1·583 (2) Å]. The H ligand is 2·1 Å from each of the two Si atoms.

Any discussion of geometric parameters associated with H atoms bound directly to transition metals must be considered somewhat speculative whenever the experimental method is X-ray diffraction. A perfect X-ray diffraction study would, as discussed earlier, give metal—hydrogen distances that would be systematically short because of the perturbation of electron density by bond formation. If the magnitude of this shortening is estimated to be 0·1 Å, the Fe—H distance can be corrected to 1·5 Å which is reasonable when compared with the value of 1·60 Å observed for a Mn—H length in the neutron diffraction study of $Mn(CO)_5H$ (La Placa, Hamilton & Ibers, 1961), and considering the normal trend in covalent radii.

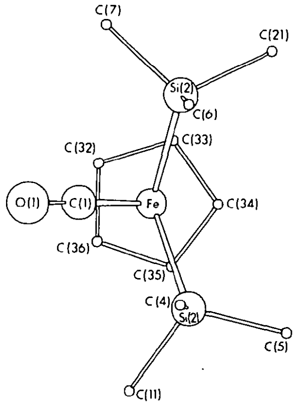

Fig. 3. A view (similar to that in Fig. 1) of the dimethylphenylsilyl analogue.

An error in the Fe—H length makes remarkably little difference to the Si···H contact, provided the angular parameters are constant. In $(\eta^5\text{-}C_5H_5)Fe(CO)H(SiF_2CH_3)_2$, changing the Fe—H distance from 1·4 to 1·6 Å while maintaining Si—Fe—H at 63° produces a change in the Si···H contact from 2·04 to 2·09 Å. Provided that the H atom occupies a single minimum-potential well the molecular mirror plane places a constraint on the direction of the Fe—H vector, and only one variable angular parameter is required to define the vector orientation. The convenient angular parameter is that formed between the Fe-to-centroid (of the cyclopentadienyl ring) vector and the Fe—H vector corresponding to the angle $\theta$ in the equivalent treatment of

Table 6. *Electronegativity sums for silicon substituents (excluding the metal)*

For all three scales the ligand ordering would be $SiF_3 > SiF_2CH_3 > SiCl_3$.

| $SiF_2CH_3$ | $SiCl_3$ | $SiF_3$ | Reference |
|---|---|---|---|
| 10·70 | 8·49 | 12·30 | Allred & Rochow (1958) |
| 10·51 | 9·48 | 11·94 | Allred (1961) |
| 10·45 | 9·00 | 11·73 | Pritchard & Skinner (1955) |

Table 5. *A comparison of the reported structures of the form* $(\eta^5\text{-}C_5H_5)HFeCO(SiR_3)_2$

| | Individual Fe—C distances | Fe—cp* | Fe—C† | Fe—Si |
|---|---|---|---|---|
| ($\eta$-Cpd)HFeCO($SiF_2Me)_2$ | 2·086 (3) Å<br>2·089 (3)<br>2·089 (3)<br>2·092 (4)<br>2·092 (4) | 1·72 (1) Å | 1·73 (1) Å | 2·249 (1) Å |
| ($\eta$-Cpd)HFeCO($SiCl_3)_2$ | 2·10 (1)<br>2·10 (1)<br>2·09 (1)<br>2·09 (1)<br>2·08 (1) | 1·72 (1) | 1·76 (1) | 2·252 (3) |
| ($\eta$-Cpd)HFeCO$[Si(CH_3)_2C_6H_5]_2$ | All 2·10 (1) | 1·72 (2) | 1·71 (1) | 2·336 (3) |

* Centre of cyclopentadiene ring.
† Carbonyl.

$(\eta^5\text{-}C_5H_5)Re(CO)_2HSi(C_6H_5)_3$ in the previous paper. The consequences of allowing this angle to vary by ±5° from the observed $\theta$ value of 122·5° are shown below (Fe–H = 1·5 Å assumed):

| $\theta$ | Si···H | F(1)···H | F(2)···H |
|---|---|---|---|
| 117·5° | 2·11 Å | 2·65 Å | 2·57 Å |
| 122·5 | 2·06 | 2·56 | 2·59 |
| 127·5 | 2·02 | 2·46 | 2·62. |

These results show that the Si···H distance is relatively insensitive to changes in $\theta$, but the F···H contacts become markedly different. The F···H contacts are relatively close to van der Waals contacts and in any non-bonded repulsion calculation with spherical potentials they would constitute little to the overall energy of the system. However, in any sophisticated treatment, that attempted a correction for the perturbation of the spherical electron density as a result of bonding effects, an equality of the H···F contacts would assume greater significance since it would correspond to moving the H atom from a position near an electron-deficient antibonding region of a Si atom towards an electron-rich bonding region where repulsion would be expected to be greater for a given internuclear separation.

$(\eta^5\text{-}C_5H_5)Fe(CO)H(SiCl_3)_2$ and $(\eta^5\text{-}C_5H_5)Fe(CO)H[Si(CH_3)_2C_6H_5]_2$ do not have mirror symmetry in the crystalline state and a comparison of Figs. 1, 2 and 3 shows that some variation in the orientation of the silyl groups is possible because of minor perturbations, such as intermolecular forces. Nevertheless the differences in rotations about the Fe–Si bonds are small and it seems reasonable to conclude that in all three molecules the H atom will be approximately equidistant from two of the substituents on each silyl ligand. This conformational feature is consistently observed in all transition-metal complexes where a H forms a close contact with a *cis* silyl ligand. Only in $Fe(CO)_4HSi(C_6H_5)_3$, where H–Si = 2·7 Å, does the silyl group fail to adopt a special orientation with respect to the H ligand (Simpson, 1973).

In the series of Fe derivatives containing the $(\eta^5\text{-}C_5H_5)Fe(CO)HSi_2$ fragment, the Si···H contacts are estimated to be ≥ 2·1 Å and have been treated as repulsive in nature. For $(\eta^5\text{-}C_5H_5)Mn(CO)_2HSi(C_6H_5)_3$ and $(\eta^5\text{-}C_5H_5)Mn(CO)_2HSiCl_2C_6H_5$, containing the $C_5H_5Mn(CO)_2HSi$ fragments, the Si···H *cis* contacts are both estimated to be about 1·8 Å. The H atom apparently prefers to be closer to the Si atom than to the C atom, which is totally unexpected in view of the relative atom sizes. The original deduction that this indicated a bonding interaction between Si and H atoms (*i.e.* the onset of the pentacoordination) should be reconsidered.

A terminal carbonyl group with its cylindrical electron density would be expected to be uniformly 'hard' with respect to non-bonded contacts with *cis* ligands. A Si atom in an $sp^3$-hybridized state and with an appropriate orientation appears to be capable of contacts which are of the same magnitude as contacts with C atoms of carbonyl groups. The near equality of Si···C and C···C contacts (2·55 and 2·51 Å respectively) in $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$ (Bennett & Simpson, 1971) provides good evidence for this. Thus, the relative ordering of Si···H and C···H contacts in the Mn compounds may not be significant.

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