the shortest yet reported for a metal–silicon bond.[29] In the ruthenium complexes the two Ru–P bonds involving phosphorus atoms which are mutually *trans* to one another are normal, the mean values being 2.393 (6) Å (X = Cl) and 2.345 (4) Å (X = H), whereas the third Ru–P distance, involving the phosphorus atom which is *cis* to the other two, is in each case much shorter, being 2.230 (8) Å (X = Cl) and 2.206 (4) Å (X = H).[8,9] These results may be rationalized if one assumes that transition metal–phosphine and –silyl bonds involve some back-donation from the metal; short metal–phosphorus and metal–silicon distances occur when there is no competing π-bonding ligand in the *trans* position. Since the covalent radius of phosphorus is some 0.07 Å shorter than the covalent radius of silicon, while the covalent radii of Ru and Rh differ by about 0.01 Å,[30] it would then appear, from the near equality of the short Ru–P distance in $RuHCl(P(C_6H_5)_3)_2$ with the Rh–Si distance found here, that back-bonding occurs more readily with $SiCl_3$ than with $P(C_6H_5)_3$. Such an explanation is consistent with the relative stabilities of these complexes formed with different substituted silanes.[12]

Acknowledgment.—We are grateful to the National Science Foundation for its support of this study.

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[29] Further discussion of metal–silicon bond lengths appears in the following paper: Lj. Manojlović-Muir, K. W. Muir, and J. A. Ibers, *ibid.*, **9**, 447 (1970).

[30] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS 60201

The Crystal and Molecular Structure of Hydridobis(trichlorosilyl)carbonyl-π-cyclopentadienyliron, $(\pi\text{-}C_5H_5)FeH(SiCl_3)_2(CO)$

BY LJUBICA MANOJLOVIĆ-MUIR, KENNETH W. MUIR, AND JAMES A. IBERS

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The crystal structure of hydridobis(trichlorosilyl)carbonyl-π-cyclopentadienyliron, $(\pi\text{-}C_5H_5)FeH(SiCl_3)_2(CO)$, has been determined by X-ray diffraction methods. A monoclinic unit cell of dimensions a = 7.493 (5) Å, b = 11.867 (9) Å, c = 8.651 (5) Å, and β = 99.73 (2)° contains two monomeric molecules; the observed and calculated densities are, respectively, 1.88 (2) and 1.835 g cm^{-3}, and the space group is $C_2^2\text{-}P2_1$. The structure has been refined by least-squares methods to a conventional R factor of 0.041 over 1245 counter-diffractometric data. The absolute configuration of the molecules in the crystal used in the analysis has been determined by least-squares methods and Bijvoet ratio tests. The coordination polyhedron around the Fe atom can be regarded as a distorted tetragonal pyramid, with the centroid of the cyclopentadienyl ring at the apex and the remaining ligands in the basal plane. The Fe atom is displaced from the basal plane toward the ring. The two Fe–Si distances are equal at 2.252 (3) Å. This is the first determination of the length of such a bond. Structural data on transition metal-silicon bonds are summarized and arguments are presented in favor of some $d_\pi\text{-}d_\pi$ back-bonding being involved in these bonds.

Introduction

Although complexes containing metal–silicon bonds are known for a wide variety of transition metals, there is still very little structural information on such compounds. The recent work on silylcobalt complexes of the type $Co(SiX_3)(CO)_4$[1-3] (where X = Cl, F, and H) tends to confirm the suggestion of Hagen and McDiarmid[4] that the empty silicon d orbitals may be involved in the Co–Si bonding. We have pointed out in the previous paper that the Rh–Si distance in $RhHCl(SiCl_3)(P(C_6H_5)_3)_2$ provides evidence that the silicon d orbitals are used in the Rh–Si bonding.[5] In order to obtain further insight into the behavior of substituted silyl groups as ligands in transition metal complexes, we have determined the structure of $\pi\text{-}CpFeH(SiCl_3)_2(CO)$ (Cp = cyclopentadienyl = $C_5H_5^-$). This is the first reported structure of a compound which contains an Fe–Si bond. The work also reflects our interest in the geometries of five-coordinated[6] transition metal complexes and, in particular, those containing a hydridic hydrogen bonded to the transition metal.

Collection and Reduction of Intensity Data

A sample of $\pi\text{-}CpFeH(SiCl_3)_2(CO)$ was kindly supplied by Graham.[7] The crystals are pale yellow needles, moderately stable in air. A preliminary X-ray photographic examination showed that they possess monoclinic symmetry. According to the photographs of the $0kl$, $hk0$, $h0l$, and $h1l$ reciprocal lattice nets, taken with Mo Kα radiation, systematic absences occur only

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[1] W. T. Robinson and J. A. Ibers, *Inorg. Chem.*, **6**, 1208 (1967).

[2] K. Emerson, P. R. Ireland, and W. T. Robinson, *ibid.*, **9**, 436 (1970).

[3] A. G. Robiette, G. M. Sheldrick, R. N. F. Simpson, B. J. Aylett, and J. A. Campbell, *J. Organometal. Chem.* (Amsterdam), **14**, 279 (1968).

[4] A. P. Hagen and A. G. McDiarmid, *Inorg. Chem.*, **6**, 686 (1967).

[5] K. W. Muir and J. A. Ibers, *ibid.*, **9**, 440 (1970).

[6] In this paper the cyclopentadienyl ring is regarded as occupying one vertex of the iron coordination polyhedron. Some authors assume that a cyclopentadienyl ring occupies three vertices of the coordination polyhedron and would therefore describe the iron as heptacoordinate in the present case.

[7] W. A. G. Graham and W. Jetz, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., March–April 1968, No. M 082.

for the 0*k*0 reflections when *k* is odd. Such absences are compatible with the space groups C_{2h}^1-$P2_1/m$ and C_2^2-$P2_1$. The distribution of peaks in the three-dimensional Patterson function indicated that the true space group is C_2^2-$P2_1$; this assignment has been confirmed by a successful structure analysis. The unit cell dimensions, at 22°, are $a = 7.493$ (5) Å, $b = 11.867$ (9) Å, $c = 8.651$ (5) Å, and $\beta = 99.73$ (2)°. These values were obtained by a least-squares procedure outlined below, and they are based on a value of 0.70930 Å for the wavelength of Mo Kα_1 radiation. The density of the crystals, measured by flotation in a mixture of carbon tetrachloride and dibromomethane, is 1.88 (2) g cm^{-3}; it is in tolerable agreement with the value of 1.835 g cm^{-3} calculated for two molecules in the unit cell.

For the intensity measurements a large needle-shaped crystal was cut so that its final dimensions were 0.30 mm × 0.54 mm × 0.08 mm parallel to *a*, *b*, and *c*, respectively. It was then sealed in a glass capillary and mounted on a Picker four-circle diffractometer, in such a way that the *b* axis of the crystal made an angle of approximately 5° with the axis of the φ circle. The half-widths of a number of narrow source–open counter ω scans[8] ranged from 0.08 to 0.21°, thus indicating that the crystal mosaicity was small, albeit somewhat anisotropic. Twelve reflections were accurately centered through a narrow vertical slit at a takeoff angle of roughly 0.5°. These observations were used to determine the crystal orientation and the dimensions of the unit cell by the method of least squares.[9] The intensity measurements were made with the θ–2θ scan technique, using procedures already described.[10] Each reflection was scanned through a 2θ range of -0.7 to $+0.7°$ from the center of the Mo Kα_1 peak; the takeoff angle was 2°, and the scan rate was 1°/min. The background was counted for 10 sec at each end of the scan range. Molybdenum radiation was used in conjunction with a 3-mil niobium β filter and a pulse height analyzer set to accept roughly a 90% window centered on the Mo Kα_1 peak. Coincidence losses were minimized by inserting copper foil attenuators into the diffracted beam until the maximum counting rate was less than 7000 counts/sec. The crystal–source and crystal–counter distances were 21 and 34 cm, respectively. The dimensions of the counter aperture were 5 mm × 5 mm.

The intensities of four strong independent reflections were measured periodically in order to monitor crystal and electronic stability. Although the crystal darkened during the experiment, no significant trend was apparent in the intensities of these standards. The greatest random fluctuation observed in the intensity of a standard was less than 3% of its mean value. The intensities were corrected for background, and their standard deviations were estimated in the way described earlier; a value for *p* of 0.04 was used.[10] The data were then corrected for Lorentz and polarization effects. In order to correct for absorption, the six faces of the crystal were indexed on the X-ray diffractometer. All members of the forms $\{100\}$, $\{010\}$, and $\{001\}$ were exhibited. The dimensions of the crystal were measured with a micrometer eyepiece. The calculated transmission coefficients, based on a linear absorption coefficient of 21.9 cm^{-1} for Mo Kα radiation, ranged from 0.53 to 0.83.

The intensities of 1924 independent reflections within the sphere $2\theta(\text{Mo K}\alpha_1) \leq 56°$ were measured. Of these, 1251 were found to be greater than three times their estimated standard deviations. Only these reflections were used in subsequent Fourier and least-squares calculations. Continuation past $2\theta = 56°$ did not seem worthwhile, since in the shell with $2\theta >$ 52° there were only a few reflections with intensities significantly above background. For 1872 reflections only the *hkl* intensities were measured; for the remainder, which were all strong low-angle reflections, the intensities of hkl, $\bar{h}k\bar{l}$, $h\bar{k}l$, and $\bar{h}\bar{k}\bar{l}$ were measured. After absorption corrections had been applied, the intensities of the hkl and $\bar{h}k\bar{l}$ spectra were averaged, and so also were those of the $h\bar{k}l$ and $\bar{h}\bar{k}\bar{l}$ spectra, yielding the intensities of 52 Friedel pairs. These were later used to check the absolute configuration of the molecules in the crystal employed in the analysis. Reflections with negative *k* indices were not included in any of the least-squares calculations.

Structure Determination and Refinement

A three-dimensional Patterson synthesis revealed the positions of the iron, chlorine, and silicon atoms. The sites of the oxygen and carbon atoms were obtained from subsequent electron density syntheses. The model so derived was refined by the method of full-matrix least squares. The function minimized was $\Sigma w\Delta^2$, where $w = 1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$ and where $\Delta = |F_o| - |F_c|$, $|F_o|$ and $|F_c|$ being the observed and calculated structure amplitudes, respectively. The atomic scattering factors were taken from ref 11, with the exception of those for the Fe[12] and H[13] atoms. Throughout the refinement the anomalous scattering of the Fe, Cl, and Si atoms was taken into account in the calculation of structure factors.[14] Cromer's values for $\Delta f'$ and $\Delta f''$ were used.[15]

A refinement in which the scale factor and the positional and isotropic temperature factors of all the nonhydrogen atoms were adjusted converged with $R =$ 0.127 and $R_w = 0.146$, where $R = \Sigma|\Delta|/\Sigma|F_o|$ and $R_w =$

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(8) T. C. Furnas, "The Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

(9) Using the program PICK for the CDC 6400 computer. In addition to the various local programs, local versions of Hamilton's GONO absorption correction program, Busing and Levy's ORFFE function and error program, Johnson's ORTEP thermal ellipsoid plotting program, and Zalkin's FORDAP Fourier program were employed in this work. The local least-squares program NUCLS used in this work in its nongroup form closely resembles the Busing–Levy ORFLS program.

(10) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(11) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962.

(12) D. T. Cromer and J. A. Waber, *Acta Cryst.*, **18**, 104 (1965).

(13) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(14) J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).

(15) D. T. Cromer, *ibid.*, **18**, 17 (1965).

TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS × 10) FOR π-CpFeH$(SiCl_3)_2$(CO)

K	L	FO	FC
*****	H =	0	*****
0	0		4129
0	4	342	333
0	5	92	88
0	6	163	164
0	7	102	103
0	8	328	328
0	9	161	167
0	10	99	117
1	2	675	613
1	3	1013	944
1	4	169	161
1	5	123	117
1	6	205	199
1	7	169	175
1	8	123	126
1	9	123	124
1	10	131	132
1	11	87	89
2	-1	437	372
2	2	369	336
2	3	410	398
2	4	339	328
2	5	113	109
2	6	109	92
2	7	217	217
2	8	184	190
2	9	72	38
2	10	86	73
2	11	90	76
3	1	835	757
3	2	430	406
3	3	281	261
3	4	307	291
3	5	492	467
3	6	355	348
3	7	254	251
3	8	100	96
3	9	124	123
4	-4	885	863
4	0	312	282
4	1	239	221
4	2	644	617
4	3	217	200
4	5	216	217
4	6	74	78
4	7	104	109
4	8	89	88
4	10	61	17
5	1	639	605
5	2	235	216
5	3	276	270
5	4	166	162
5	5	258	245
5	6	156	145
5	7	176	171
5	9	133	139
6	0	67	66
6	1	302	284
6	2	383	372
6	3	430	387
6	4	192	202
6	6	74	65
6	7	76	73
6	8	213	219
7	1	233	225
7	2	430	401
7	3	67	63
7	5	264	267
7	9	87	106
8	0	558	519
8	1	90	88
8	2	146	138
8	3	107	103
8	5	92	103
8	6	108	107
8	7	87	98
8	8	242	242
9	1	190	193
9	3	291	285
9	5	193	188
9	6	81	80
9	7	125	126
10	0	170	164
10	1	91	94
10	2	130	130
10	3	118	112
10	4	211	203
10	5	92	93
10	6	120	102
11	1	126	125
11	6	102	137
12	0	118	109
12	2	87	103
12	4	153	166
13	1	112	116
14	0	114	107
*****	H =	1	*****
0	-11	79	81
0	-10	133	150
0	-9	130	144
0	-8	124	126
0	-7	278	284
0	-6	100	87
0	-5	369	365
0	-3	262	273
0	-2	454	455
0	2	855	856
0	3	496	487
0	4	166	157
0	5	824	812
0	6	72	70
0	7	98	95
0	8	175	175
0	9	82	104
0	10	179	185
0	11	104	102
1	-11	101	99
1	-8	346	351
1	-7	141	132
1	-6	312	297
1	-5	349	335
1	-4	245	234
1	-3	471	465
1	-2	148	146
1	-1	67	67
1	1	528	536
1	2	1004	998
1	3	302	283
1	4	174	170
1	5	241	240
1	6	290	281
1	7	169	170
1	8	315	313
1	9	72	61
2	-11	79	63
2	-9	123	127
2	-8	230	228
2	-7	239	237
2	-6	286	282
2	-5	490	465
2	-4	548	540
2	-3	225	227
2	-2	61	61
2	-1	695	697
2	0	817	821
2	1	434	443
2	2	350	348
2	3	582	571
2	4	202	203
2	5	152	144
2	6	114	116
2	7	176	173
2	8	122	115
2	9	90	89
2	10	105	100
3	-9	141	148
3	-8	254	252
3	-7	254	246
3	-6	201	198
3	-5	134	137
3	-4	678	669
3	-3	175	175
3	-2	654	650
3	-1	496	502
3	0	416	427
3	1	645	640
3	2	318	322
3	3	124	122
3	4	838	824
3	5	129	125
3	6	163	159
3	7	85	90
3	8	95	94
3	9	65	63
3	10	115	109
4	-9	124	121
4	-8	94	83
4	-7	168	166
4	-6	225	212
4	-5	441	417
4	-4	79	74
4	-3	201	202
4	-2	562	555
4	-1	433	451
4	0	357	360
4	1	766	792
4	2	165	168
4	3	445	438
4	4	212	212
4	5	154	147
4	6	381	386
4	7	272	268
4	8	73	80
4	9	132	135
5	-9	117	126
5	-6	126	117
5	-5	172	160
5	-4	374	371
5	-3	222	227
5	-2	479	480
5	-1	115	116
5	0	223	231
5	1	255	261
5	2	174	183
5	3	307	301
5	4	599	577
5	5	144	130
5	6	146	139
5	7	131	138
5	8	107	118
5	10	78	72
6	-9	167	165
6	-8	159	156
6	-7	128	114
6	-5	77	59
6	-4	213	198
6	-3	455	445
6	-2	302	305
6	-1	242	259
6	0	431	438
6	1	307	306
6	2	84	87
6	3	302	311
6	4	215	210
6	5	70	56
6	6	95	109
6	7	289	288
7	-8	122	123
7	-7	81	64
7	-6	228	233
7	-5	198	198
7	-4	130	137
7	-3	335	329
7	-2	99	99
7	-1	104	100
7	0	681	701
7	1	116	113
7	2	63	68
7	3	199	193
7	4	153	157
7	5	146	136
7	6	136	127
7	8	134	139
8	-9	142	148
8	-5	175	179
8	-4	104	109
8	-3	296	290
8	-2	224	230
8	-1	217	216
8	0	223	220
8	1	71	83
8	2	203	207
8	3	202	214
8	4	257	258
8	5	241	234
8	7	176	171
8	8	98	90
9	-8	136	146
9	-7	92	84
9	-6	108	118
9	-5	83	92
9	-4	67	44
9	-2	104	107
9	-1	78	94
9	0	254	252
9	1	137	154
9	2	288	303
9	4	147	144
9	6	97	112
9	7	82	90
9	8	102	98
10	-8	74	65
10	-6	93	92
10	-5	222	216
10	-4	134	133
10	-1	101	88
10	0	99	92
10	1	100	91
10	2	127	117
10	3	203	219
10	4	73	74
10	5	145	143
10	7	102	104
11	-7	81	88
11	-6	191	189
11	-1	198	214
11	0	77	87
11	1	115	120
11	2	80	90
11	4	142	142
12	-5	112	102
12	-4	103	103
12	-1	105	111
12	0	63	84
12	1	132	141
12	3	102	129
13	-3	90	81
13	-2	98	106
13	2	90	119
14	-3	75	42
14	-1	105	106
*****	H =	2	*****
0	-10	67	69
0	-9	82	75
0	-7	87	85
0	-6	182	188
0	-5	709	724
0	-4	65	74
0	-3	373	387
0	-1	117	103
0	0	112	112
0	1	60	68
0	2	215	213
0	3	369	379
0	4	277	288
0	5	116	121
0	6	150	152
0	8	145	148
0	9	83	80
0	10	113	114
1	-9	148	164
1	-8	206	204
1	-7	262	270
1	-6	150	163
1	-5	303	299
1	-4	358	356
1	-3	453	458
1	-2	491	497
1	-1	327	331
1	0	541	540
1	1	156	150
1	2	463	471
1	3	266	260
1	4	564	557
1	5	291	288
1	6	94	84
1	7	349	346
1	8	135	142
2	-9	150	143
2	-8	123	125
2	-7	118	126
2	-6	264	264
2	-5	309	308
2	-4	425	432
2	-3	107	115
2	-2	1059	1062
2	-1	592	605
2	0	287	292
2	1	723	718
2	2	636	651
2	3	97	106
2	4	338	341
2	5	133	142
2	6	268	270
2	7	177	182
2	8	172	173
2	10	104	112
3	-9	73	69
3	-8	211	205
3	-7	144	144
3	-6	221	219
3	-5	442	443
3	-4	271	264
3	-3	462	450
3	-2	160	157
3	-1	284	303
3	0	263	277
3	1	545	560
3	2	66	90
3	3	605	602
3	4	416	412
3	5	71	63
3	6	110	102
3	7	203	200
3	8	139	131
3	9	144	147
4	-9	240	241
4	-8	78	73
4	-7	237	239
4	-6	146	155
4	-5	205	201
4	-4	341	343
4	-3	130	121
4	-2	208	205
4	-1	663	699
4	0	297	290
4	1	235	232
4	2	182	193
4	3	125	133
4	4	262	257
4	5	104	101
4	6	261	253
4	7	134	133
4	9	74	67
4	10	105	128
5	-9	121	114
5	-8	235	241
5	-7	194	199
5	-6	154	159
5	-5	121	116
5	-4	543	543
5	-3	306	300
5	-2	123	118
5	-1	395	401
5	0	465	480
5	1	120	119
5	2	317	330
5	3	458	454
5	4	85	80
5	5	99	106
5	6	256	248
5	7	147	152
5	8	69	95
5	9	87	96
6	-9	99	117
6	-7	105	96
6	-6	137	123
6	-5	116	126
6	-4	272	274
6	-3	275	277
6	-2	342	347
6	-1	248	252
6	0	345	351
6	1	72	83
6	2	481	491
6	3	323	314
6	5	190	193
6	6	298	296
6	8	133	127
6	9	68	71
7	-8	108	103
7	-6	99	101
7	-5	124	124
7	-4	166	163
7	-3	179	175
7	-2	169	163
7	-1	588	611
7	0	260	259
7	1	98	95
7	2	101	108
7	3	157	161
7	4	155	165
7	5	334	328
7	6	74	81
7	7	175	178
8	-9	77	78
8	-8	89	68
8	-5	265	255
8	-4	206	202
8	-3	160	151
8	-1	132	131
8	0	191	192
8	1	251	252
8	2	185	187
8	3	253	263
8	4	80	77
8	5	76	76
8	6	192	186
9	-8	126	129
9	-7	102	96
9	-5	109	109
9	-4	221	224
9	-3	149	150
9	-2	94	86
9	-1	119	112
9	0	210	206
9	1	189	194
9	2	133	131
9	3	119	132
9	4	81	90
9	7	77	78
10	-7	108	108
10	-6	125	125
10	-3	64	46
10	-2	139	139
10	-1	106	104
10	0	82	98
10	1	180	192
10	2	102	105
10	4	146	144
11	-6	89	77
11	-5	157	168
11	-4	64	59
11	-3	70	76
11	-2	87	91
11	0	118	121
11	1	201	202
11	3	116	134
11	4	112	121
11	6	62	28
12	-4	72	61
12	-2	90	98
12	-1	110	98
12	1	103	97
12	2	80	82
12	4	91	96
13	-4	91	82
13	1	65	51
*****	H =	3	*****
0	-11	73	83
0	-10	65	76
0	-6	250	266
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0	1	62	57
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1	-9	155	161
1	-8	66	59
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1	-1	414	420
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2	3	466	477
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2	7	167	178
2	8	98	103
2	9	107	116
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4	-7	92	93
4	-6	194	206
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4	1	356	361
4	2	172	187
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4	4	228	236
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4	6	124	124
4	8	174	175
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5	2	404	399
5	3	144	152
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7	3	183	180
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7	5	141	161
7	6	144	145
8	-7	139	145
8	-6	154	158
8	-5	87	91
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8	0	173	169
8	1	76	78
8	2	152	165
8	3	99	101
8	4	182	187
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8	7	77	64
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9	-3	188	185
9	-2	223	218
9	-1	143	145
9	0	101	97
9	1	186	189
9	2	148	149
9	3	154	143
9	5	80	74
9	6	80	70
9	7	95	92
10	-8	80	77
10	-6	78	76
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10	-4	92	90
10	-3	145	142
10	-2	153	158
10	-1	116	107
10	0	131	140
10	1	142	142
10	3	146	154
10	6	68	92
11	-4	104	106
11	-3	68	65
11	-1	161	148
11	0	154	159
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11	3	91	97
11	4	54	27
12	-6	64	32
12	-4	93	91
12	-3	63	80
12	-2	63	47
12	-1	56	35
12	0	99	97
13	-3	86	93
13	-1	91	81
14	2	71	66
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1	-9	101	98
1	-8	146	145
1	-7	166	171
1	-6	209	204
1	-5	155	148
1	-4	313	315
1	-3	162	185
1	-2	468	468
1	-1	162	165
1	0	133	128
1	1	190	184
1	2	596	606
1	3	101	96
1	4	80	86
1	5	303	309
1	6	148	146
1	8	112	101
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2	-7	148	157
2	-6	94	96
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2	-4	237	242
2	-3	416	429
2	-2	164	166
2	-1	468	476
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2	4	101	103
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2	6	73	63
2	7	182	166
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3	-7	122	110
3	-6	230	235
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3	-3	108	110
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3	2	335	336
3	3	120	102
3	4	220	223
3	5	80	76
3	6	184	184
3	7	62	49
3	8	94	87
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4	-5	91	98
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4	-2	66	67
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4	2	152	150
4	3	259	269
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4	5	137	140
4	7	224	221
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5	-8	125	126
5	-7	115	108
5	-6	87	104
5	-5	164	173
5	-4	96	103
5	-3	141	138
5	-2	133	143
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5	1	331	330
5	2	143	147
5	3	115	108
5	4	83	78
5	5	61	51
5	6	178	173
5	7	94	99
6	-9	124	128
6	-8	92	83
6	-7	166	169
6	-6	120	112
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6	-4	62	68
6	-3	273	275
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6	1	166	171
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6	4	72	64
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6	6	106	102
6	7	176	184
7	-6	236	248
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7	-4	83	96
7	-2	184	184
7	-1	109	101
7	0	249	236
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8	-5	171	168
8	-4	61	61
8	-3	84	74
8	-2	83	82
8	-1	163	196
8	0	63	67
8	1	162	187
8	2	88	81
8	3	289	289
8	5	84	78
8	6	71	76
8	7	91	102
9	-6	92	90
9	-4	104	115
9	-3	159	164
9	-2	142	145
9	0	160	157
9	1	96	99
9	2	111	116
9	3	114	135
9	5	107	101
9	6	148	149
10	-5	86	82
10	-4	95	93
10	-3	114	100
10	-1	168	165
10	0	69	68
10	2	152	146
10	3	114	117
10	5	78	80
11	-6	83	74
11	-2	175	170
11	0	68	60
11	2	78	75
12	-5	90	79
12	-1	117	124
12	1	85	83
13	2	102	108
14	-2	66	46
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0	-4	74	72
0	-3	57	46
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0	6	69	57
0	7	150	145
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1	-7	236	232
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1	0	94	89
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1	4	62	81
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2	-8	85	78
2	-7	71	91
2	-6	208	205
2	-5	72	74
2	-4	252	256
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2	2	297	293
2	3	58	65
2	4	162	164
2	5	98	99
2	6	215	217
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3	-5	80	83
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3	-2	83	82
3	-1	368	370
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3	3	197	188
3	5	222	219
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4	-6	206	209
4	-5	198	202
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4	1	120	124
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4	3	162	164
4	4	145	143
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4	6	150	148
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5	-7	110	106
5	-6	160	153
5	-5	83	96
5	-3	174	180
5	-1	232	241
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5	2	125	121
5	3	116	122
5	4	66	57
5	5	177	178
5	7	78	76
6	-9	82	63
6	-8	148	148
6	-6	131	131
6	-5	147	153
6	-4	140	129
6	-3	82	72
6	-2	177	176
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6	2	410	424
6	6	166	166
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7	-5	127	116
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7	-1	220	224
7	0	71	65
7	1	197	192
7	3	178	172
7	5	116	124
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8	-7	70	56
8	-6	88	101
8	-4	65	63
8	-2	130	126
8	-1	110	129
8	0	74	70
8	2	201	210
8	5	108	101
8	6	98	104
9	-7	89	95
9	-5	89	87
9	-4	113	124
9	-3	116	109
9	-2	110	105
9	-1	58	45
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9	5	83	70
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10	-5	91	80
10	-4	103	98
10	-2	142	145
10	-1	78	78
10	0	74	81
10	2	94	80
10	4	120	134
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11	-1	87	84
12	-2	95	78
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0	2	168	168
0	3	221	211
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0	6	167	177
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1	-8	89	88
1	-7	92	97
1	-4	127	124
1	-3	102	99
1	-2	170	173
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2	-7	125	131
2	-6	156	157
2	-4	75	77
2	-3	175	182
2	-2	95	102
2	-1	141	141
2	1	154	163
2	2	121	121
2	3	140	148
2	4	90	94
2	5	157	173
2	6	129	120
3	-7	108	104
3	-6	170	170
3	-5	139	134
3	-4	139	145
3	-3	100	103
3	-2	145	155
3	0	62	30
3	1	107	101
3	2	209	209
3	3	148	137
3	4	191	205
3	6	132	136
4	-7	101	117
4	-6	202	207
4	-5	112	119
4	-4	69	55
4	-3	251	260
4	-2	95	103
4	-1	116	123
4	0	81	79
4	1	214	210
4	2	223	230
4	3	67	76
4	5	195	206
5	-6	212	212
5	-5	101	118
5	-4	177	175
5	-3	67	69
5	-2	186	184
5	0	111	107
5	1	81	82
5	2	202	208
5	3	101	104
5	4	182	191
6	-7	85	85
6	-6	70	69
6	-5	72	68
6	-3	192	193
6	-2	111	98
6	1	267	268
6	2	67	73
6	5	133	137
7	-8	69	66
7	-7	97	94
7	-6	94	92
7	-4	61	56
7	-3	71	77
7	-2	142	148
7	-1	65	72
7	0	97	92
7	4	105	94
7	6	67	36
8	-7	80	81
8	-6	68	67
8	-5	136	127
8	-4	102	96
8	-3	76	68
8	-2	213	206
8	1	136	132
8	2	101	99
8	4	71	65
9	-4	126	125
9	-2	102	113
9	-1	84	101
9	0	99	89
9	1	81	74
9	3	62	35
10	-3	107	103
10	-1	86	65
10	1	85	87
10	3	104	96
11	-4	71	60
12	0	71	72
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0	-2	215	211
0	0	167	176
0	1	78	74
0	2	64	53
0	4	101	102
0	5	120	129
1	-6	125	117
1	-4	85	92
1	-3	81	84
1	-2	212	207
1	-1	97	105
1	0	140	129
1	1	211	206
1	2	69	64
1	4	82	75
1	5	152	151
2	-7	107	119
2	-6	63	73
2	-5	132	132
2	-4	115	103
2	-3	143	147
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2	-1	84	73
2	0	83	79
2	1	153	154
2	2	90	80
2	3	85	86
2	4	114	118
2	5	135	134
3	-8	81	75
3	-7	71	76
3	-6	168	165
3	-4	77	86
3	-3	104	101
3	-2	159	156
3	-1	70	66
3	0	100	94
3	1	123	123
3	2	198	190
3	3	163	155
3	5	111	104
4	-7	88	91
4	-6	90	90
4	-4	143	145
4	-3	144	135
4	-1	77	68
4	0	109	120
4	1	150	142
4	2	62	80
4	3	85	95
4	4	174	175
4	6	70	56
5	-6	108	105
5	-4	104	104
5	-3	124	131
5	0	105	104
5	1	75	71
5	2	111	104
5	3	108	96
6	-7	74	77
6	-5	90	95
6	-4	84	75
6	-3	157	171
6	-1	79	71
6	0	139	127
6	1	65	56
6	3	78	64
7	-6	80	62
7	-4	109	110
7	-3	97	106
7	-2	168	166
7	-1	102	104
7	4	64	51
8	-4	66	55
8	-3	107	96
8	-2	102	95
8	-1	71	60
8	0	140	147
8	1	68	57
8	2	62	51
8	3	72	73
9	1	69	69
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0	-2	129	129
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0	4	122	117
1	-7	105	97
1	-5	89	85
1	-3	202	195
1	-1	61	46
1	0	121	122
1	1	98	[illegible]
1	2	95	87
1	3	76	83
1	4	76	89
2	-8	67	55
2	-4	117	113
2	-2	80	92
2	0	136	132
2	1	76	65
2	3	83	73
2	4	100	119
3	-4	66	51
3	-3	104	111
3	-1	107	103
3	1	127	129
3	2	96	81
3	4	84	86
4	-5	73	61
4	-3	72	60
4	-2	107	103
4	0	105	[illegible]
4	2	113	106
4	3	74	67
5	-5	89	76
5	-4	61	60
5	-3	95	88
5	-1	99	96
5	0	63	45
5	1	101	93
6	-4	90	[illegible]
6	-2	108	100
5	-1	72	74
6	0	76	75
6	2	94	89
7	-2	88	[illegible]
7	0	84	75
7	1	67	65
*****	H =	9	*****
0	-5	101	[illegible]
0	-3	83	77
0	-1	114	116
1	-4	123	122
1	0	90	98
1	2	107	102
2	-2	67	40
2	-1	106	96
3	-4	69	56
3	-3	69	59
3	0	111	105
4	-3	89	34
4	-2	59	30
4	-1	60	[illegible]
4	1	90	92
5	-4	61	[illegible]
5	0	111	96
6	-3	76	[illegible]

$(\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$. The poor agreement of this model is due mainly to the anisotropy of the atomic thermal vibrations. Adjustment of anisotropic thermal parameters for all the nonhydrogen atoms brought the agreement indices R and R_w to 0.046 and 0.053, respectively.

At this point the absolute configuration of the molecules in this particular crystal was considered. Let A be the configuration of the molecule assumed hitherto. The signs of the indices of all reflections were now reversed, thus assuming the enantiomorphic model B. Model B was refined in exactly the same way as model A. This refinement converged with $R = 0.048$ and $R_w = 0.055$. Assuming that the data contain only random errors, B is a poorer model than A at the 0.5% significance level.[16] The difference between $|F_o(h)|$ and $|F_o(\bar{h})|$ was greater than 2% of the mean $|F_o|$ for 15 of the 52 reflections for which Friedel pair intensities had been measured. Comparison of the ratio $|F_o(h)|/|F_o(\bar{h})|$ with $|F_c(h)|/F_c(\bar{h})|$[17] again indicated that A was a better model than B; model A correctly predicted these ratios for all of the 15 reflections which showed Bijvoet differences of more than 2%, whereas model B failed to predict any correctly. Furthermore, the agreement between chemically equivalent bond lengths was better for model A than it was for model B; thus the two Fe–Si distances differed by 0.006 Å (at this stage) for model A and by 0.027 Å for model B. These results are conclusive evidence that the correct absolute configuration is given by model A.

A difference map was now calculated, with the data for which $\lambda^{-1}\sin\theta < 0.30$ Å^{-1}, in order to locate the hydrogen atoms. The maximum electron density in this map was 0.32 e$^-$/Å^3, while the estimated standard deviation of the electron density $\sigma(\rho)$[18] was 0.08 e$^-$/Å^3. Only one of the hydrogen atoms of the cyclopentadienyl ring was found to lie on a peak higher than $3\sigma(\rho)$; the remaining four lay in regions higher than $1.5\sigma(\rho)$, and the hydridic hydrogen atom could not be located from the map. Our failure to detect one hydrogen atom and the poor signal to noise ratio for the "peaks" associated with the five we did detect reflect the general experience that for Fourier syntheses in noncentrosymmetric space groups the peaks associated with atoms excluded from the structure factor calculations tend to be low in height. This failure does not seem to be due to a lack of sensitivity of our data to the hydrogen

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(16) W. C. Hamilton, "Statistics in Physical Science," The Ronald Press, New York, N. Y., 1964.

(17) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," The Macmillan Co., New York, N. Y., 1968, p 426.

(18) D. W. J. Cruickshank, *Acta Cryst.*, **7**, 519 (1954).

Table II

Final Fractional Coordinates and Anisotropic Thermal Parameters of Atoms

	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0.1963(1)[b]	1/4[c]	0.2563(1)	1204(17)	627(9)	748(13)	−14(14)	106(12)	−1(13)
Si(1)	0.3726(3)	0.3921(3)	0.3663(3)	1619(46)	850(24)	986(32)	−224(27)	152(31)	−253(25)
Si(2)	0.0903(3)	0.2689(3)	−0.0019(2)	1901(43)	717(24)	734(26)	−65(27)	−21(27)	−37(23)
Cl(1)	0.2454(4)	0.5205(3)	0.4628(3)	3481(73)	926(26)	1716(43)	252(35)	241(44)	−499(28)
Cl(2)	0.5659(3)	0.3380(3)	0.5494(3)	2080(51)	1484(33)	1686(40)	−93(34)	−660(37)	−175(33)
Cl(3)	0.5236(4)	0.4715(3)	0.2232(3)	3565(78)	1621(40)	1629(42)	−1448(47)	806(46)	−343(35)
Cl(4)	−0.1685(3)	0.3298(3)	−0.0570(3)	2299(55)	1258(32)	1787(43)	204(34)	−599(39)	313(32)
Cl(5)	0.2397(4)	0.3702(3)	−0.1231(3)	3731(74)	1241(31)	974(30)	−589(40)	545(38)	142(26)
Cl(6)	0.0808(4)	0.1173(3)	−0.1192(3)	4204(85)	946(29)	1399(40)	−65(38)	224(45)	−532(28)
O	0.5194(9)	0.1647(9)	0.1562(9)	2025(161)	1829(110)	2412(149)	536(109)	632(122)	−459(113)
C	0.3937(11)	0.2008(9)	0.1939(10)	1394(169)	1084(94)	1050(121)	13(101)	−60(117)	15(89)
C(1)	−0.0393(11)	0.1541(9)	0.2554(10)	1584(167)	962(94)	1249(128)	−294(102)	286(115)	107(98)
C(2)	−0.0426(11)	0.2493(11)	0.3495(11)	2014(164)	1103(93)	1729(142)	129(153)	1177(130)	−87(133)
C(3)	0.1062(14)	0.2429(12)	0.4718(10)	3161(240)	1322(120)	874(112)	−675(183)	584(136)	−109(122)
C(4)	0.2028(14)	0.1451(11)	0.4506(12)	2674(240)	1052(113)	1371(162)	−14(134)	23(156)	559(117)
C(5)	0.1099(13)	0.0885(9)	0.3125(12)	2486(224)	850(95)	1601(165)	−80(118)	615(154)	−44(104)

[a] The anisotropic temperature factor used was: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The values of β_{ij} are multiplied by 10^5. [b] Limits of error are standard deviations, given in units of the least significant digit of the quantity to which they refer. [c] This value is arbitrarily chosen to fix the origin.

scattering; when fixed contributions for the scattering of the hydrogen atoms of the cyclopentadienyl ring were added to the structure factors, further refinement resulted in agreement indices $R = 0.043$ and $R_w = 0.048$. The positions of the hydrogen atoms were idealized for these calculations: the C–H distance was taken to be 1.0 Å; each hydrogen atom was assigned an isotropic thermal parameter $B = 5.0$ Å^2.

At this stage the six reflections for which $2\theta < 14°$ were removed from the refinement; for these reflections $|F_o|$ was much greater than $|F_c|$, apparently because of errors in estimating the local background. After further calculations the refinement converged with $R = 0.041$ and $R_w = 0.044$. All parameters shifted by less than their estimated standard deviations in the last cycle of refinement. The standard deviation of an observation of unit weight was 1.26, close to the expected value of unity. The relative correctness of the weighting scheme was satisfactory, on the basis of the variation of the mean $w\Delta^2$ with $|F_o|$ and $\lambda^{-1} \sin \theta$. Extinction corrections did not appear to be necessary. The final difference map showed no important features; the largest function value was 0.47 e$^-$/Å^3, or 9% of the average height of a carbon atom in the final electron density synthesis. For none of the 673 reflections omitted from the refinements for which $F_o^2 < 3\sigma(F_o^2)$ did $|F_o^2 - F_c^2|$ exceed $3\sigma(F_o^2)$.

The final observed and calculated structure amplitudes for those reflections used in the refinements are listed in Table I. The final positional and thermal parameters of the nonhydrogen atoms are presented in Table II, and the calculated positional parameters of the hydrogen atoms are given in Table III.

Description of the Structure

The crystal structure of π-CpFeH(SiCl$_3$)$_2$(CO) is built by packing of discrete monomeric molecules. An inspection of all intermolecular contacts shorter than 3.9 Å reveals none which is appreciably smaller than the sum of the corresponding van der Waals radii. No intermolecular contacts are therefore listed here.

Table III

Calculated Fractional Coordinates of Hydrogen Atoms

	x	y	z
H(1)[a]	−0.1336	0.1364	0.1578
H(2)	−0.1352	0.3136	0.3335
H(3)	0.1431	0.3017	0.5567
H(4)	0.3167	0.1171	0.5189
H(5)	0.1457	0.0150	0.2724

[a] Each hydrogen is marked with the same number as the carbon atom to which it is bonded.

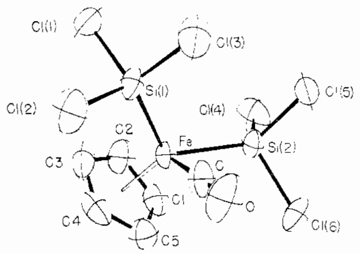

Figure 1.—A perspective view of the π-CpFeH(SiCl$_3$)$_2$(CO) molecule. The 50% probability ellipsoids of thermal motion are shown. Hydrogen atoms have been omitted for the sake of clarity.

A perspective view of the structure is shown in Figure 1 (from which the located hydrogen atoms have been omitted for the sake of clarity). The coordination polyhedron around the iron atom is of an unusual type. Although it may be described with equal validity in other terms, we choose to regard it as a distorted tetragonal pyramid, with the centroid of the cyclopentadienyl ring (CCp) at the apex; the carbonyl and trichlorosilyl ligands then lie in the basal plane, with the trichlorosily ligands *trans* to one another. The iron atom is placed above the basal plane, in the direction toward the cyclopentadienyl ring, so that the CCp–Fe–C angle is 126° (Table IV) and the CCp–Fe–Si angles are, respectively, 118 and 119°; as a result of the Si–Fe–Si angle is 115°. Inspection of molecular models indicates that a hydrogen atom can be accommodated *trans* to the carbonyl in the basal plane and at a reasonable Fe–H distance, without impossibly short non-

TABLE IV

SELECTED INTERMOLECULAR DISTANCES AND ANGLES

Distance	Value, Å	Angle	Value, deg
Fe–Si(1)	2.252 (3)	CCp–Fe–Si(1)	119.4
Fe–Si(2)	2.252 (3)	CCp–Fe–Si(2)	118.1
Fe–C	1.758 (9)	CCp–Fe–C	125.8
Fe–CCp[a]	1.718	Si(1)–Fe–Si(2)	115.3 (1)
Fe–C(1)	2.099 (8)	Si(1)–Fe–C	85.1 (3)
Fe–C(2)	2.084 (7)	Si(2)–Fe–C	84.4 (3)
Fe–C(3)	2.089 (8)	Fe–C–O	177.0 (10)
Fe–C(4)	2.086 (10)	Fe–Si(1)–Cl(1)	116.7 (1)
Fe–C(5)	2.106 (11)	Fe–Si(1)–Cl(2)	112.2 (2)
Fe–C_{ring} (av)[b]	2.093 (4)	Fe–Si(1)–Cl(3)	115.8 (1)
Si(1)–Cl(1)	2.049 (4)	Fe–Si(2)–Cl(4)	115.3 (1)
Si(1)–Cl(2)	2.060 (4)	Fe–Si(2)–Cl(5)	115.8 (1)
Si(1)–Cl(3)	2.043 (4)	Fe–Si(2)–Cl(6)	112.2 (1)
Si(2)–Cl(4)	2.049 (4)	Fe–Si–Cl (av)	114.7 (8)
Si(2)–Cl(5)	2.048 (4)	Cl(1)–Si(1)–Cl(2)	103.5 (2)
Si(2)–Cl(6)	2.061 (4)	Cl(1)–Si(1)–Cl(3)	104.3 (2)
Si–Cl (av)	2.052 (3)	Cl(2)–Si(1)–Cl(3)	102.7 (2)
C–O	1.132 (10)	Cl(4)–Si(2)–Cl(5)	104.6 (2)
C(1)–C(2)	1.395 (14)	Cl(4)–Si(2)–Cl(6)	103.9 (2)
C(2)–C(3)	1.404 (13)	Cl(5)–Si(2)–Cl(6)	103.7 (2)
C(3)–C(4)	1.396 (17)	Cl–Si–Cl (av)	103.8 (3)
C(4)–C(5)	1.443 (15)	C(5)–C(1)–C(2)	109.9 (9)
C(5)–C(1)	1.383 (13)	C(1)–C(2)–C(3)	107.8 (10)
C–C (av)	1.404 (10)	C(2)–C(3)–3(4)	108.0 (10)
		C(3)–C(4)–C(5)	107.9 (9)
		C(4)–C(5)–C(1)	106.3 (10)
		C–C–C (av)	108.0 (6)

[a] CCp is the centroid of the cyclopentadienyl ring. [b] Standard deviations of averaged quantities are estimated from the range of the individual measurements.

bonded intermolecular or intramolecular contacts. Our results, therefore, do not contradict the chemical evidence for the composition of this compound.

The geometry about the metal found here shows a strong resemblance to that found in the complexes π-$CpMoR(CO)_3$ (R = C_2H_5,[19] C_3F_7[20]). In the molybdenum compounds the ring centroid occupies the apex of a tetragonal pyramid, with the alkyl and carbonyl ligands in the basal plane. The metal is again displaced from the basal plane toward the cyclopentadienyl ring so that the CCp–Mo–B angles (B = R, CO) are in the range 110–120°, and the B_1–Mo–B_2 angles (B_1 *trans* to B_2) are smaller than 135°. No other structural studies on mononuclear iron complexes with similar geometries are known to us.

The thermal motions of the atoms (Figure 1 and Table V) show no unexpected features. The trichlorosilyl groups appear to be oscillating about the Fe–Si vectors. The directions of maximum vibration of the ring carbon atoms are all approximately normal to the corresponding ring carbon–CCp vectors and in the plane of the ring. Libration of the ring about the Fe–CCp vector would explain these results. The maximum root-mean-square amplitudes of all the nonhydrogen atoms are, however, quite small, and there is no evidence for disorder of the cyclopentadienyl ring.

Discussion

TABLE V

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å) ALONG PRINCIPAL AXES OF THERMAL ELLIPSOIDS

Atom	Min	Intermed	Max
Fe	0.165 (1)	0.185 (1)	0.212 (2)
Si(1)	0.172 (4)	0.211 (3)	0.261 (4)
Si(2)	0.161 (3)	0.225 (4)	0.239 (3)
Cl(1)	0.194 (4)	0.284 (3)	0.330 (4)
Cl(2)	0.179 (3)	0.310 (3)	0.329 (4)
Cl(3)	0.204 (3)	0.235 (3)	0.416 (4)
Cl(4)	0.185 (3)	0.302 (4)	0.323 (4)
Cl(5)	0.176 (3)	0.267 (3)	0.351 (4)
Cl(6)	0.176 (4)	0.296 (4)	0.345 (4)
O	0.202 (10)	0.291 (9)	0.384 (11)
C	0.177 (12)	0.221 (12)	0.278 (12)
C(1)	0.189 (12)	0.216 (11)	0.275 (13)
C(2)	0.159 (12)	0.283 (12)	0.289 (11)
C(3)	0.170 (12)	0.247 (15)	0.348 (16)
C(4)	0.177 (15)	0.271 (13)	0.313 (15)
C(5)	0.228 (12)	0.244 (14)	0.272 (12)

The cyclopentadienyl ring is planar within experimental error. The equation of the least-squares plane[21] through the ring carbon atoms (based on monoclinic coordinates) is: $4.900X + 5.994Y - 5.758Z = -0.734$. The deviations of the atoms from this plane are (Å): C(1), −0.005 (8); C(2), 0.007 (9); C(3), −0.006 (10); C(4), 0.003 (10); C(5), 0.003 (10). The ring C–C distances range from 1.383 (13) to 1.443 (15) Å, with a mean of 1.404 Å. On the basis of a χ^2 test the deviations of the individual values from the mean are not significant at the 1% probability level. Our results, therefore, do not suggest that localization of the ring electron density had occurred, although such localization has been reported in Cp–metal complexes where the electron density round the metal lacks effective cylindrical symmetry.[22] The mean ring C–C distance is slightly shorter than that found in electron diffraction studies of ferrocene.[23,24] This difference is probably due to our failure to correct the bond distances for librational motion of the ring rather than to electronic factors. The ring carbon–Fe distances range from 2.084 (7) to 2.106 (11) Å and are therefore equal within the experimental errors; their mean value is 2.093 (4) Å, and the Fe–CCp distance is 1.718 Å. The metal–cyclopentadienyl bonding is therefore somewhat weaker than in ferrocene, where values of 2.03 and 2.06 Å were obtained for the Fe–C distance in two separate electron diffraction analyses.[23,24] Such a change is to be expected when one of the two rings of a sandwich molecule is replaced by strongly π-accepting ligands.[25] The geometry of the Fe–C–O group is normal.

The geometries of the two trichlorosilyl ligands are extremely similar. The same distortions from tetrahedral symmetry are found in the coordination about each silicon atom. The mean of the six Si–Cl distances is 2.052 Å, and the individual values all lie within

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[19] M. J. Bennett, Doctoral Dissertation, Sheffield University, 1965.

[20] M. R. Churchill and J. P. Fennessy, *Inorg. Chem.*, **6**, 1213 (1967).

[21] W. C. Hamilton, *Acta Cryst.*, **14**, 185 (1965).

[22] M. J. Bennett, M. R. Churchill, M. Gerloch, and R. Mason, *Nature*, **201**, 1318 (1964).

[23] R. K. Bohn and A. Haaland, *J. Organometal. Chem.* (Amsterdam), **5**, 470 (1966).

[24] A. F. Berndt, Doctoral Dissertation, California Institute of Technology, Pasadena, Calif., 1957.

[25] P. J. Wheatley, *Perspect. Struct. Chem.*, **1**, 1 (1967).

TABLE VI

DISTANCES (Å) AND ANGLES (DEG) IN SILYL–TRANSITION METAL COMPLEXES M–SiX$_3$[a]

Compound	M—Si Obsd	M—Si Calcd[b]	Si–X	∠M–Si–X	∠X–Si–X	Ref
π-CpFeH(SiCl$_3$)$_2$(CO)	2.252 (3)	2.51	2.052 (3)	115	104	c
Co(SiH$_3$)(CO)$_4$	2.381 (7)	2.51				d
Co(SiCl$_4$)(CO)$_4$	2.254 (3)	2.51	2.035	113	105	e
Co(SiF$_3$)(CO)$_4$	2.226 (5)	2.51	1.51	115	104	f
Mn(Si(CH$_3$)$_3$)(CO)$_5$	2.497 (5)	2.63	1.91 (2)			g
RhHCl(SiCl$_3$)(P(C$_6$H$_5$)$_3$)$_2$	2.203 (4)	2.48	2.054 (6)	109–121	103	h
trans-PtCl(SiCH$_3$(C$_6$H$_5$)$_2$)(P(CH$_3$)$_2$C$_6$H$_5$)$_2$	2.29	2.46				i

[a] Averaged values are given whenever possible. [b] See text for covalent radii used. [c] Present work. [d] Reference 3. [e] Reference 1. [f] Reference 2. [g] R. S. Hamilton and E. R. Corey, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, No. INOR 025. [h] Reference 5. [i] P. Kapoor, Doctoral Dissertation, University of Sussex, 1968.

±0.009 Å of this mean. The two Fe–Si distances are equal at 2.252 Å.

The available structural data on transition metal–silyl complexes are summarized in Table VI. Prediction of the length of a metal–silicon single bond from covalent radii is rendered difficult by the sensitivity of bond lengths involving transition metals to electronegativity effects, and to the coordination number and oxidation state of the metal; the special problems posed by Fe[26] and Co[27] in this respect have been recently pointed out. For Fe we propose a covalent radius of 1.34 Å; this value is based on the Fe–C$_{sp^3}$ distances of 2.123 (15) and 2.11 (2) Å found, respectively, in Fe$_2$(C$_2$H$_2$)$_3$(CO)$_6$[28] and π-CpFe(σ-Cp)(CO)$_2$[29] and on the Fe–Fe distance of 2.679 (3) Å found in the former compound, where the metal atoms are not linked by a three-center bond. The upper limit of Fe–Fe distances in a number of iron-cluster compounds[30–32] is around 2.70 Å. The Co–Co distances in [(CH$_3$CN)$_5$Co]$_2^{2+}$[33] and Co$_2$(CO)$_6$(P(C$_4$H$_9$)$_3$)$_2$[34] of 2.74 and 2.62 Å, respectively, lead to a Co radius of 1.34 Å. The Rh–CH$_3$ distance of 2.08 Å in RhI$_2$(CH$_3$)(P(C$_6$H$_5$)$_3$)$_2$[35] gives an Rh radius of 1.31 Å. For Mn a value of 1.46 Å has been proposed from the Mn–Mn distance in Mn$_2$(CO)$_{10}$.[36] The Pauling radius for platinum is 1.29 Å.[37] The metal–silicon single-bond distances predicted from these radii and from the accepted value of 1.17 Å for the covalent radius of silicon[37] are also given in Table VI.

From Table VI it can be seen that the observed metal–silicon distances are all shorter than their predicted values, the differences ranging from 0.13 to 0.28 Å. Errors in the covalent radii used do not seem an adequate explanation for these differences, and we therefore conclude that some electronic effect is involved and that the shortening cannot be explained entirely by σ bonding. The shortening appears to be greatest when the silyl ligand carries electronegative substituents such as Cl and F; however, from the near equivalence of the Co–Si distances in Co(SiF$_3$)(CO)$_4$ and Co(SiCl$_3$)(CO)$_4$ it appears that the shortening is not purely a function of electronegativity. It would therefore seem that some d$_\pi$–d$_\pi$ back-bonding from the metal is involved and that the shortening is not entirely due to contraction of the metal d orbitals by a strongly electron-withdrawing ligand. Owing to a lack of data and to inadequacies in the values for the covalent radii, no firm conclusion is possible regarding trends in metal–silicon bonds as a given transition series is ascended. Yet consistent with the conjectured π-bonding effects, the shortest metal–silicon bond yet found involves the second transition series element rhodium in a structure where there is no π-bonding ligand *trans* to and competing with the silyl group.

From Table VI it can be seen that the mean silicon–halogen distances in the complexes differ little from the values of 2.02 and 1.56 Å found for Si–Cl and Si–F distances in halogenosilanes.[38] The coordination polyhedron about the silicon atom in the metal complexes is a distorted tetrahedron; the metal–Si–X angle (X = Cl, F, etc.) is usually some 5° greater than the tetrahedral angle, whereas the X–Si–X angles are typically about 5° less than 109°. Similar distortions have been repeatedly noticed in the coordination about tin in transition metal–stannyl complexes.[39,40]

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(26) L. F. Dahl, R. J. Doedens, W. Hubel, and J. Nielson, *J. Am. Chem. Soc.*, **88**, 446 (1966).

(27) P. W. Sutton and L. F. Dahl, *ibid.*, **89**, 261 (1967).

(28) J. Meunier-Piret, P. Piret, and M. van Meerssche, *Acta Cryst.*, **19**, 85 (1965).

(29) M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Moorhouse, *J. Am. Chem. Soc.*, **88**, 4371 (1966).

(30) C. H. Wei and L. F. Dahl, *ibid.*, **88**, 1821 (1966).

(31) D. J. Dahm and R. A. Jacobson, *Chem. Commun.*, 496 (1966).

(32) J. F. Blount, L. F. Dahl, C. Hoozgand, and W. Hubel, *J. Am. Chem. Soc.*, **88**, 292 (1966).

(33) F. A. Cotton, T. G. Dunne, B. F. G. Johnson, and J. S. Wood, *Proc. Chem. Soc.*, 175 (1964).

(34) J. A Ibers, *J. Organometal. Chem.* (Amsterdam), **14**, 423 (1968).

(35) P. G. M. Troughton and A. C. Skapski, *Chem. Commun.*, 575 (1968).

(36) R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2576 (1965).

(37) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N. Y., 1960.

(38) L. E. Sutton, Ed., Special Publication No. 18, The Chemical Society, London, 1965.

(39) F. G. A. Stone in "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, Cambridge, England, 1968.

(40) B. J. Aylett, *Advan. Inorg. Chem. Radiochem.*, **11**, 249 (1968).