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Crystallographic Studies on Sulfur Dioxide Insertion Compounds. III. The Structure of an *S*-Sulfinate Derivative, $[\pi\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2CH_2CH{=}CH(C_6H_5)$[1]

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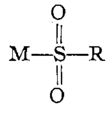
$[\pi\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2CH_2CH{=}CH(C_6H_5)$, prepared by the reaction of $[\pi\text{-}C_5(CH_3)_5]Fe(CO)_2CH_2CH{=}CH(C_6H_5)$ and SO_2, crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ (C_{2h}^5; no. 14) with $a = 16.327\ (14)$ Å, $b = 12.891\ (12)$ Å, $c = 9.785\ (8)$ Å, $\beta = 94.03\ (3)°$, $Z = 4$, $\rho_{obsd} = 1.39 \pm 0.01$ g cm^{-3}, and $\rho_{calcd} = 1.384$ g cm^{-3}. Diffraction data to $\sin\theta = 0.38$ (Mo Kα radiation) were collected on a 0.01°-incrementing Supper-Pace "Buerger Automated Diffractometer." The structure was solved by Patterson, Fourier, and least-squares refinement techniques, the final discrepancy index being $R_F = 6.65\%$ for the 2135 independent nonzero reflections. The crystallographic analysis has confirmed that this molecule is formed by "insertion" of an SO_2 molecule into the iron–(σ-allyl) bond without rearrangement of the allyl fragment.

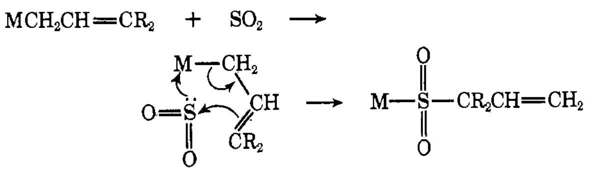
Introduction

A crystallographic study[3] of *cis*-$(CH_3SO_2)Mn(CO)_3$(bipy) (bipy = 2,2′-dipyridyl) confirms the accumulated chemical evidence[4–10] that SO_2 "inserts" into a metal–alkyl or metal–aryl (M–R) bond to form an *S*-sulfinate (I). The reaction of SO_2 with *σ-allyls* is rather more complicated. Following the observation that $(OC)_5MnCH_2CH{=}CH_2$ inserts SO_2 much faster than do the analogous methyl or benzyl derivatives,[5] Wojcicki and coworkers have studied the products of SO_2 insertion into a number of manganese carbonyl complexes containing unsymmetrically substituted allyl groups.[11,12] Thus $(OC)_5MnCH_2CH{=}CH(CH)_3$ and $(OC)_5MnCH_2CH{=}C(CH_3)_2$ each are found to undergo rearrangement upon insertion of SO_2, yielding the products $(OC)_5MnSO_2CH(CH_3)CH{=}CH_2$ and $(OC)_5MnSO_2C(CH_3)_2CH{=}CH_2$, respectively. The suggested mechanism (eq 1) is compatible with the fact that $Mn(CO)_5CH_2CH{=}CHCl$ reacts with SO_2 to form $Mn(CO)_5Cl$ and $C_3H_4(SO_2)_x$.[12] The complex $(OC)_5MnCH_2CH{=}CH(C_6H_5)$, however, reacts with SO_2 to form $(OC)_5MnSO_2CH_2CH{=}CH(C_6H_5)$, with no rearrangement. Presumably the conjugation of the allyl double bond with the phenyl group prevents a mechanism such as (1), and the organic ligand behaves essentially as an alkyl group, with SO_2 insertion occurring by a mechanism such as (2) or (3). With $\pi\text{-}C_5H_5Fe(CO)_2CH_2CH{=}C(CH_3)_2$, insertion of SO_2 leads to both $\pi\text{-}C_5H_5Fe(CO)_2SO_2CH_2CH{=}C(CH_3)_2$ and $\pi\text{-}C_5H_5Fe(CO)_2SO_2C(CH_3)_2CH{=}CH_2$, with low temperatures favoring formation of the latter (rearranged) product.



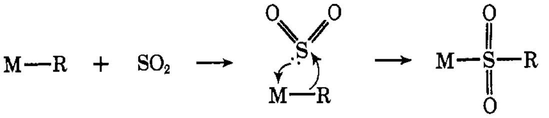
$$\begin{array}{c} \mathrm{O} \\ \| \\ \mathrm{M{-}S{-}R} \\ \| \\ \mathrm{O} \end{array}$$

I



(1)

$$M(CO)R + SO_2 \longrightarrow M(COR)(SO_2) \longrightarrow M(CO)(SO_2R) \quad (2)$$



(3)

We now report the results of an X-ray diffraction study on $[\pi\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2CH_2CH{=}CH(C_6H_5)$ prepared from $[\pi\text{-}C_5(CH_3)_5]Fe(CO)_2CH_2CH{=}CH(C_6H_5)$ and SO_2.[13]

Unit Cell and Space Group

A sample of the complex $[\pi\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2CH_2CH{=}CH(C_6H_5)$ was kindly supplied by Professor A. Wojcicki of The Ohio State University. Crystals suitable for an X-ray diffraction study were grown by slow evaporation of a *sym*-dichloroethane–methylcyclohexane solution; they are air and X-ray stable. Optical examination and a reciprocal lattice symmetry of $2/m$ (C_{2h}) indicate that the crystals belong to the monoclinic system. Unit cell dimensions measured from high-angle reflections on precession photographs (Mo Kα radiation, calibration with $Pb(NO_3)_2$) taken at 24 ± 2° are $a = 16.327\ (14)$ Å, $b = 12.891\ (12)$ Å, $c = 9.875\ (8)$ Å, and $\beta = 94.03\ (3)°$. The unit cell volume is 2054 Å^3.

A survey of *hk*0–*hk*1 Weissenberg photographs and *h*0*l*–*h*1*l*, 0*kl*–1*kl* precession photographs in conjunction with *c*-axis rotation and *a*- and *b*-axis cone-axis photographs revealed the systematic absences *h*0*l* for $h + l = 2n + 1$ and 0*k*0 for $k = 2n + 1$, compatible only

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(1) Part II: M. R. Churchill and J. Wormald, *J. Amer. Chem. Soc.*, **93**, 354 (1971).

(2) Fellow of the Alfred P. Sloan Foundation, 1968–1970.

(3) D. R. Swift and K. Knox, personal communication.

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(5) F. A. Hartman and A. Wojcicki, *ibid.*, **88**, 844 (1966).

(6) J. P. Bibler and A. Wojcicki, *ibid.*, **88**, 4862 (1966).

(7) F. A. Hartman and A. Wojcicki, *Inorg. Chem.*, **7**, 1504 (1968).

(8) F. A. Hartman and A. Wojcicki, *Inorg. Chim. Acta*, **2**, 351 (1968).

(9) P. J. Pollick, J. P. Bibler, and A. Wojcicki, *J. Organometal. Chem.*, **16**, 201 (1969).

(10) M. Graziani, J. P. Bibler, R. M. Montesano, and A. Wojcicki, *ibid.*, **16**, 507 (1969).

(11) F. A. Hartman, P. J. Pollick, R. L. Downs, and A. Wojcicki, *J. Amer. Chem. Soc.*, **89**, 2493 (1967).

(12) F. A. Hartman and A. Wojcicki, *Inorg. Chim. Acta*, **2**, 289 (1968).

(13) A. Wojcicki, private communication.

with space group $P2_1/n$ [a nonstandard setting of C_{2h}^5; no. 14[14] with equipoints $\pm(x, y, z)$, $\pm(^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$]. The observed density ($\rho_{\text{obsd}} = 1.39 \pm 0.01$ g cm^{-3} by flotation in aqueous zinc iodide solution) is consistent with $\rho_{\text{calcd}} = 1.384$ g cm^{-3} for $M = 428.33$ and $Z = 4$. No crystallographic symmetry is imposed upon the molecule.

Collection and Reduction of the X-Ray Diffraction Data

Two crystals were used in the course of data collection. Crystal I approximated to a regular parallelepiped of dimensions 0.70 × 0.41 × 0.23 mm (referred to $11\bar{1}$, $\bar{1}11$, 101) and was mounted on its *b* axis; crystal II (0.51 × 0.41 × 0.19 mm, referred to $1\bar{1}1$, 110, $\bar{1}11$) was mounted on its *c* axis.

Intensity data were collected with Mo Kα radiation (molybdenum X-radiation filtered through a 3.0-mil zirconium foil at the source) on a 0.01°-incrementing Supper-Pace "Buerger Automated Diffractometer." Details of the "stationary-background, ω-scan, stationary-background" counting sequence have appeared previously.[15] Experimental details specific to the present investigation include the following. (i) Generator power was 49 kV/19 mA. (ii) Angle scanned was $\omega = [1.4 + 0.7/L]°$.[16] (iii) $d\omega/dt = 2.0°$/min. (iv) Initial and final background counts (B_1, B_2) were each measured for one-fourth the time for the ω scan, the count associated with the ω scan being C. (v) Within each zone, a carefully preselected check reflection was remeasured after every 20 reflections. (There were no deviations $\geqslant 2\%$ from the mean.)

Equiinclination Weissenberg geometry was used to collect data for quadrants *hkl* and $\bar{h}kl$ of the zones *h*0*l*–*h*13*l* from crystal I; this set of data is complete to $\sin\theta = 0.38$ except for the few reflections in the range $0 < \theta \leqslant 4°$ which lie behind the backstop. Data for quadrants *hkl* and $\bar{h}kl$ of zones *hk*0–*hk*2 were collected from crystal II for the purpose of correlation.

The integrated intensity of a reflection, $I(hkl)$, is calculated by $I(hkl) = C(hkl) - 2.0[B_1(hkl) + B_2\cdot(hkl)]$. The 3σ (maximum probable) error in $I(hkl)$ *based solely on counting statistics* is given by $\delta(hkl) = 3.0[C(hkl) + 4\{B_1(hkl) + B_2(hkl)\}]^{1/2}$. Based on previous experience with the ω-scan technique, the following weighting scheme was used for the data: if $I(hkl) \geqslant 4900$, $\sigma(I) = 0.1(I)$; if $4900 > I(hkl) \geqslant \delta(hkl)$ $\sigma(I) = 7.0(I)^{1/2}$; if $\delta(hkl) > I(hkl)$, the reflection was rejected as not significantly above background.

Of 2757 reflections collected from crystal I, 467 were rejected; of 1088 reflections from crystal II, 233 were rejected. Intensities were corrected for Lorentz, polarization, and absorption effects;[17] with $\mu = 8.57$ cm^{-1}, transmission coefficients ranged from 0.759 to 0.856 for crystal I (volume 29.7×10^{-6} cm^3) and from 0.706 to 0.759 for crystal II (volume 46.9×10^{-6} cm^3). Equivalent reflections (*i.e.*, *hk*0, $\bar{h}k0$) within a zone were averaged and the 17 zones were merged to a common scale by a least-squares analysis of common reflections.[18] The resulting 2135 independent, nonzero reflections were used in a Wilson plot[19] which yielded the approximate absolute scale and an overall isotropic thermal parameter.

Elucidation and Refinement of the Structure

Unless otherwise stated all crystallographic routines were performed under the CRYRM system[20] using the Harvard University IBM 7094 computer.

Discrepancy indices referred to below are

$$R_F = \sum||F_o| - |F_c||/\sum|F_o|$$

$$R_{wF^2} = \sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^4$$

The positions of iron and sulfur atoms were obtained from a three-dimensional Patterson map. All carbon and oxygen atoms were located *via* a difference Fourier synthesis phased by the two "heavy" atoms ($R_F = 39.0\%$). Three cycles of full-matrix least-squares refinement[21] of the scale factor along with positional and isotropic thermal parameters for all nonhydrogen atoms led to convergence at $R_F = 11.13\%$, $R_{wF^2} = 8.05\%$. A difference Fourier map now showed evidence of anisotropic motion of many atoms; no hydrogen atoms could be located from this map. Hydrogen atoms (excluding those of the methyl groups, whose positions are indeterminate) were now included in calculated positions[22] with $B = 4.0$ Å^2. Keeping these parameters constant, three cycles of refinement of positional and anisotropic thermal parameters of nonhydrogen atoms led to convergence at $R_F = 7.24\%$, $R_{wF^2} = 4.33\%$. Hydrogen atom positions were now recalculated (using the up-dated carbon positions). No hydrogen atom had to be relocated by more than 0.05 Å. Because of the good quality of the crystals, three more cycles of refinement were performed, now including a secondary extinction factor (based on the model of Zachariasen[23]). This resulted in convergence with $R_F = 6.65\%$, $R_{wF^2} = 3.36\%$, $(\Delta/\sigma)_{\max} = 0.15$. The final value for the extinction coefficient (χ) was 4.91×10^{-6} where $F_{\text{calcd}}^2(\text{cor}) = F_{\text{calcd}}^2/(1 + \chi\beta F_{\text{calcd}}^2)$ and $\beta = (1 + \cos^4 2\theta)/[\sin 2\theta(1 + \cos^2 2\theta)]$.

A final difference Fourier synthesis showed no features higher than 0.4 e$^-$ Å^{-3}, and the structure was judged to be correct and complete. The standard deviation in an observation of unit weight was 1.68. A final structure factor calculation *omitting* hydrogens gave $R_F = 7.12\%$, $R_{wF^2} = 4.00\%$.

Hamilton *R* factor ratio tests[24] confirm that (i)

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(14) "International Tables for X-Ray Crystallography," Vol. 1, Kynoch Press, Birmingham, England, 1965, p 99.

(15) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 1123 (1968).

(16) $1/L$ is the Lorentz factor.

(17) Using the IBM 360 Fortran IV program IMBIBE (by J. Wormald).

(18) A. D. Rae, *Acta Crystallogr.*, **19**, 683 (1965).

(19) A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942).

(20) CRYRM is an integrated sequence of crystallographic routines for the IBM 7094 computer, compiled under the direction of Professor R. E. Marsh at the California Institute of Technology.

(21) The residual minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w = [\sigma(F^2)]^{-2}$ and $\sigma(F^2)$ is derived from $\sigma(I)$ by adjustment for Lorentz, polarization, absorption, and scale factors.

(22) Using d(C–H) = 1.080 Å and assuming idealized geometry about the appropriate carbon atom.

(23) W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963).

(24) W. C. Hamilton, *ibid.*, **18**, 502 (1965).

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (IN ELECTRONS × 10.00) FOR $[\pi\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2CH_2CH{=}CH(C_6H_5)$

K	L	FO	FC
H = -17			
0	1	246	256
0	3	312	319
1	1	289	297
2	1	215	205
2	2	136	137
3	1	198	185
H = -16			
0	2	318	311
1	1	79	20
1	2	132	125
1	4	239	252
2	1	108	102
2	2	222	234
2	4	113	102
3	1	193	186
3	2	84	96
3	3	339	318
4	1	76	24
5	1	283	283
5	2	198	205
H = -15			
0	1	253	254
0	3	203	190
0	5	296	283
1	1	267	267
1	3	93	92
2	1	157	154
2	2	195	205
2	4	177	159
2	5	87	76
3	1	251	262
3	2	193	180
3	4	72	67
4	1	169	193
4	2	312	312
4	3	174	176
4	4	299	274
4	5	159	154
5	1	204	198
5	2	182	167
5	3	188	191
5	4	75	52
6	1	242	261
6	2	247	238
6	3	235	236
7	1	204	184
H = -14			
0	2	110	104
0	5	71	72
1	2	61	36
1	3	67	84
1	4	165	175
1	5	137	146
1	6	211	224
2	1	143	123
2	2	150	126
2	4	101	84
2	5	89	105
2	6	86	72
3	1	180	181
3	3	179	164
3	5	156	130
4	1	412	399
4	2	313	304
4	3	247	222
4	4	105	125
4	5	123	94
4	6	132	111
5	2	155	168
5	3	116	117
5	5	113	128
6	1	348	351
6	2	419	412
6	3	231	220
6	4	255	246
7	1	78	23
7	2	95	95
7	3	79	61
8	1	170	172
8	2	258	252
H = -13			
0	1	96	97
0	3	278	294
0	5	190	203
0	7	360	356
1	1	117	136
1	2	122	125
1	3	175	175
1	4	88	97
1	5	128	124
2	1	126	121
2	2	122	118
2	3	168	173
2	4	134	123
2	5	200	[illegible]
2	6	177	164
2	7	[illegible]	193
3	1	154	153
3	2	236	221
3	4	191	161
3	6	79	67
4	1	76	59
4	2	172	163
4	3	192	180
4	4	103	85
5	1	92	63
5	2	202	169
5	3	215	215
5	4	195	159
5	5	277	263
5	6	178	165
6	1	186	183
6	2	183	184
6	3	70	76
6	4	74	67
6	5	94	73
7	1	291	286
7	2	140	115
7	3	399	392
7	4	115	118
7	5	169	151
8	1	96	94
8	2	132	130
9	1	212	192
H = -12			
0	2	379	367
0	4	517	491
0	5	313	295
0	8	284	287
1	1	160	113
1	4	145	145
1	5	358	391
1	7	87	74
1	8	223	234
2	2	246	263
2	3	195	212
2	4	243	243
2	5	131	115
2	6	134	131
3	1	363	383
3	2	110	113
3	3	132	129
3	4	162	150
3	5	137	136
3	6	271	255
3	7	128	117
4	1	152	132
4	2	143	149
4	3	165	164
4	4	137	115
4	5	302	282
5	1	224	187
5	2	171	165
5	3	168	176
5	4	138	133
5	6	105	84
5	7	114	116
6	2	80	72
6	4	166	165
6	5	125	118
7	1	276	277
7	2	267	251
7	3	171	162
7	4	116	114
7	5	105	105
8	2	280	265
8	3	84	86
8	4	317	299
9	1	144	108
9	2	206	199
H = -11			
0	1	260	245
0	3	214	232
0	5	156	145
0	7	199	205
1	1	400	437
1	2	246	50
1	3	377	403
1	4	257	256
1	5	536	559
1	6	134	137
1	7	273	289
1	8	63	52
2	1	368	380
2	2	379	387
2	3	330	328
2	4	215	212
2	6	141	149
2	7	192	193
2	8	181	172
3	1	489	484
3	2	123	163
3	3	235	245
3	4	220	202
3	5	182	175
3	6	268	257
3	7	262	260
4	1	269	259
4	2	258	231
4	4	129	115
4	6	160	130
5	1	123	146
5	2	139	130
5	3	173	163
5	4	264	247
5	6	243	226
5	7	155	143
6	1	69	46
6	2	220	220
6	3	106	89
6	4	171	173
6	5	111	98
6	6	109	89
6	7	81	82
7	1	70	74
7	2	75	73
7	3	190	189
7	5	300	286
7	6	81	96
8	1	269	265
8	2	72	78
8	3	289	281
9	2	184	186
9	3	282	269
9	4	154	142
10	1	249	239
10	2	129	140
10	3	141	142
H = -10			
0	2	259	253
0	4	320	321
0	6	383	379
0	8	188	173
1	1	138	61
1	2	795	825
1	3	279	311
1	4	381	410
1	5	211	227
1	6	126	125
1	8	147	144
2	1	370	224
2	4	210	224
2	5	232	222
2	6	264	253
2	7	141	153
2	8	202	203
3	1	227	203
3	2	564	590
3	3	417	429
3	4	243	231
3	5	232	226
3	6	214	[illegible]
3	7	255	237
4	1	545	527
4	2	77	74
4	4	71	72
4	5	262	247
4	6	119	108
4	7	356	331
4	8	146	126
5	1	273	280
5	2	147	142
5	3	211	227
5	5	107	77
5	6	111	109
5	7	156	151
5	8	139	135
6	2	79	70
6	3	165	162
6	4	78	67
6	5	184	156
6	6	258	255
7	1	98	100
7	2	163	167
7	3	84	105
7	4	113	110
7	5	76	84
8	1	72	17
8	2	65	80
8	3	78	60
8	4	217	219
8	6	308	304
9	1	262	271
9	2	263	266
9	3	195	193
9	4	149	196
9	5	195	190
10	1	114	115
10	3	81	64
10	4	147	153
11	1	374	386
11	2	169	157
H = -9			
0	1	769	776
0	3	741	768
0	5	663	667
0	7	201	186
0	9	134	120
1	1	295	281
1	2	97	90
1	3	109	108
1	5	91	70
1	6	87	86
1	9	132	116
2	1	992	990
2	2	377	406
2	3	385	389
2	4	237	246
2	5	177	182
2	6	164	175
2	7	94	86
3	1	609	594
3	2	668	648
3	3	367	351
3	5	101	79
3	6	222	218
3	7	126	113
3	8	199	176
4	1	292	300
4	2	573	546
4	3	104	95
4	4	327	321
4	5	198	202
4	8	92	78
5	2	68	69
5	3	200	195
5	4	104	121
5	5	241	215
5	6	225	201
5	7	76	86
5	8	292	273
6	2	207	208
6	3	345	330
6	4	329	330
6	6	89	85
6	7	74	55
7	1	227	209
7	2	196	196
7	3	90	92
7	4	204	199
7	5	234	223
7	6	299	289
8	1	184	168
8	3	172	169
8	4	66	69
8	5	214	214
8	6	139	144
9	1	169	163
9	2	198	202
9	3	155	144
9	4	89	70
9	5	209	201
10	1	151	164
10	2	298	301
10	3	118	112
10	4	260	261
10	5	126	113
11	1	185	178
11	2	71	45
H = -8			
0	2	867	874
0	4	292	302
0	8	99	98
1	1	360	395
1	2	261	286
1	3	332	368
1	4	326	361
1	6	145	144
1	7	88	82
1	8	85	[illegible]
2	1	624	616
2	2	666	664
2	3	191	162
2	4	277	277
2	5	135	145
2	6	137	148
2	7	119	100
3	1	185	168
3	2	93	87
3	3	549	558
3	5	181	177
3	6	89	87
3	9	161	141
4	1	262	247
4	2	89	73
4	3	320	304
4	4	268	266
4	6	355	343
4	7	150	156
4	8	123	122
4	9	204	160
5	1	239	246
5	2	154	161
5	3	525	545
5	4	257	226
5	5	413	405
5	6	64	80
5	7	86	56
5	8	132	123
6	1	301	302
6	2	81	76
6	3	151	168
6	4	221	213
6	5	369	356
6	6	256	250
6	7	351	328
7	1	312	310
7	2	248	225
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1	9	86	108
2	0	45	86
2	1	528	539
2	2	136	112
2	3	110	129
2	4	159	159
2	5	112	56
2	6	178	168
2	7	631	639
2	8	158	198
2	9	285	269
2	10	131	98
3	0	572	522
3	2	903	805
3	3	286	243
3	4	860	807
3	5	63	54
3	6	573	544
4	0	1096	946
4	2	215	190
4	3	671	628
4	4	155	145
4	5	122	104
4	6	368	345
4	7	233	226
4	8	253	243
4	9	139	99
5	0	403	381
5	1	258	275
5	2	161	183
5	3	243	229
5	4	521	504
5	5	452	451
5	6	514	508
5	7	406	404
5	9	108	104
6	0	450	464
6	1	106	91
6	2	565	564
6	4	139	139
6	5	119	119
6	6	169	158
6	7	155	151
7	0	448	447
7	1	781	769
7	2	302	287
7	3	597	574
7	4	321	324
7	5	683	624
8	0	93	60
8	1	218	189
8	2	390	389
8	3	189	190
8	4	73	72
8	5	128	140
8	6	122	113
8	7	96	82
9	0	174	156
9	1	414	420
9	2	96	82
9	3	389	359
9	5	366	347
9	6	112	113
9	7	89	65
10	0	210	[illegible]
10	1	223	219
10	4	88	[illegible]
10	6	163	178
11	0	171	165
11	1	79	24
11	2	186	192
11	3	145	134
11	4	87	79
11	5	115	124
12	0	161	150
12	1	79	64
12	2	59	43
12	3	52	28
13	0	57	23
13	1	196	186
13	2	121	125
H = 4			
0	0	834	890
0	2	529	493
0	4	349	361
0	6	634	647
0	8	486	504
1	0	150	52
1	1	211	168
1	2	176	[illegible]
1	3	140	103
1	4	[illegible]	[illegible]
1	6	150	151
1	7	191	188
1	8	431	447
2	0	699	576
2	1	231	232
2	2	672	627
2	3	335	314
2	4	504	494
2	5	657	623
2	6	373	391
2	7	358	338
2	8	274	298
3	0	290	268
3	1	1376	1326
3	2	159	142
3	3	341	321
3	5	133	155
3	6	492	467
3	7	288	290
3	8	398	373
3	9	206	208
4	1	429	358
4	2	186	170
4	3	355	364
4	4	130	102
4	7	444	412
4	8	176	168
5	0	580	549
5	1	954	915
5	2	197	209
5	3	432	424
5	4	173	136
5	5	159	163
5	6	323	342
5	8	104	110
5	9	126	117
6	0	216	212
6	2	374	351
6	3	309	305
6	4	347	356
6	5	354	331
6	6	460	447
6	7	70	50
6	8	145	148
7	0	654	637
7	1	155	162
7	2	391	362
7	3	391	372
7	4	412	387
7	5	299	290
7	6	163	183
8	0	99	62
8	1	287	280
8	2	231	232
8	4	345	333
8	5	74	65
8	6	428	417
8	7	111	121
9	0	622	627
9	1	267	272
9	2	366	364
9	3	131	115
9	4	300	297
9	6	104	95
9	7	105	123
10	0	106	47
10	1	94	95
10	2	202	175
10	4	160	142
10	5	253	257
10	6	203	202
11	0	91	75
11	1	72	48
11	2	239	239
11	3	95	85
11	4	133	117
11	5	139	133
12	2	96	70
12	3	165	168
12	4	73	51
13	0	175	186
13	1	127	122
H = 5			
0	1	923	826
0	3	88	104
0	5	282	276
0	9	155	138
1	0	1409	1593
1	1	599	608
1	2	91	68
1	3	332	354
1	4	229	251
1	5	516	550
1	6	266	284
1	7	798	870
1	9	246	272
2	0	999	913
2	1	837	784
2	2	404	400
2	3	504	450
2	4	358	356
2	5	200	184
2	6	117	108
2	8	261	257
2	9	96	81
3	0	1140	1057
3	1	507	458
3	2	133	123
3	3	414	407
3	5	490	484
3	6	208	211
3	7	331	335
3	8	187	169
3	9	203	196
4	0	824	748
4	1	147	171
4	2	848	799
4	3	255	218
4	4	748	678
4	5	84	73
4	6	227	209
4	7	90	91
4	8	166	151
5	0	682	623
5	1	91	87
5	2	104	79
5	3	133	133
5	4	417	407
5	6	137	126
5	7	87	97
5	8	219	[illegible]
6	[illegible]	402	425
6	1	315	267
6	2	373	340
6	3	279	261
6	4	303	289
6	5	122	135
6	6	141	136
6	7	114	137
7	0	257	246
7	1	311	304
7	2	326	340
7	3	89	63
7	4	57	42
7	5	269	256
7	7	255	260
8	0	149	175
8	1	778	764
8	2	163	141
8	3	602	626
8	5	228	232
8	7	74	76
9	0	187	143
9	1	360	341
9	2	87	69
9	3	145	143
9	3	145	143
9	4	142	135
9	5	215	183
9	6	320	375
9	7	211	190
10	1	122	114
10	3	270	265
10	5	232	224
11	2	132	138
11	4	269	260
11	5	144	135
12	0	184	189
12	1	67	57
12	2	367	395
12	3	101	109
13	0	63	45
H = 6			
0	0	470	412
0	4	633	597
0	6	454	442
0	8	333	345
1	0	654	145
1	1	272	310
1	2	893	903
1	3	287	266
1	4	629	649
1	6	359	377
1	7	106	103
2	0	206	133
2	1	699	678
2	2	217	186
2	3	272	243
2	4	278	264
2	5	101	101
2	6	392	391
2	7	197	188
2	8	321	324
2	9	73	72
3	0	409	431
3	1	686	637
3	2	470	431
3	3	674	625
3	4	561	561
3	5	397	378
3	6	384	383
3	8	241	251
3	9	109	81
4	0	724	638
4	1	736	635
4	2	58	61
4	3	239	233
4	4	247	246
4	5	149	126
4	6	122	114
4	7	179	178
4	9	169	175
5	0	370	310
5	1	220	213
5	2	172	134
5	3	520	480
5	4	121	108
5	5	231	173
5	6	133	105
5	7	73	53
5	8	133	133
6	0	747	719
6	1	572	543
6	2	57	41
6	3	63	48
6	4	179	164
6	5	99	66
6	6	235	251
6	7	125	121
6	8	123	120
7	0	195	98
7	1	81	23
7	2	365	339
7	3	179	174
7	4	235	225
7	5	171	157
7	6	84	87
7	7	130	137
8	0	582	586
8	2	310	308
8	3	134	126
8	5	195	197
8	6	172	143
8	7	83	66
9	0	79	55
9	1	220	220
9	2	338	347
9	3	80	76
9	4	297	295
9	6	192	177
10	0	238	241
10	1	257	279
10	2	346	342
10	3	108	109
10	5	209	204
11	0	101	89
11	1	222	215
11	3	383	381
11	4	168	133
12	1	104	106
12	3	95	86
H = 7			
0	1	502	500
0	3	708	709
0	5	716	728
0	7	294	248
1	0	255	227
1	1	965	987
1	3	242	259
1	4	121	108
1	5	128	187
1	6	177	175
1	7	144	134
1	8	228	238
1	9	65	44
2	0	728	677
2	1	823	799
2	2	361	308
2	3	591	587
2	4	300	292
2	5	656	666
2	6	77	39
2	7	143	140
2	8	72	79
3	0	828	773
3	1	224	204
3	2	266	237
3	3	126	[illegible]
3	4	105	143
3	5	153	162
3	6	190	172
3	8	237	236
4	0	166	76
4	1	91	91
4	2	544	512
4	3	294	259
4	4	460	445
4	5	412	387
4	6	99	85
4	7	174	169
5	0	527	522
5	1	172	162
5	2	214	198
5	3	64	62
5	4	68	71
5	5	261	273
5	6	131	124
5	7	261	254
5	8	190	198
6	0	188	180
6	1	66	44
6	2	417	391
6	3	129	120
6	5	113	124
7	0	255	119
7	1	463	437
7	2	214	191
7	3	90	103
7	4	171	164
7	5	199	199
7	6	122	107
7	7	331	328
8	0	113	102
8	1	205	184
8	3	126	133
8	4	149	126
8	5	149	191
8	7	150	139
9	0	341	336
9	1	257	237
9	2	298	327
9	5	247	237
10	0	69	13
10	1	78	76
10	2	248	240
10	3	274	273
10	4	229	224
10	5	149	164
11	0	351	349
11	1	94	104
11	2	260	251
11	3	95	100
12	0	238	249
12	2	393	408
H = 8			
0	0	1113	1098
0	2	736	777
0	4	454	466
0	6	221	209
1	0	129	108
1	1	378	351
1	2	404	412
1	4	634	659
1	5	136	138
1	6	247	251
1	7	75	34
1	8	67	28
2	0	629	591
2	1	370	390
2	2	627	583
2	3	356	355
2	4	333	320
2	5	189	179
2	6	240	219
2	7	159	149
3	0	451	394
3	1	316	287
3	2	187	128
3	3	56	45
3	4	387	389
3	5	153	156
3	6	176	163
3	7	299	285
4	0	187	168
4	1	499	486
4	2	175	164
4	3	171	180
4	4	159	130
4	6	270	268
4	7	118	120
4	8	128	121
5	0	302	307
5	1	380	372
5	2	312	312
5	3	484	469
5	4	174	154
5	5	304	286
5	6	231	251
5	7	296	279
5	8	114	114
6	0	141	125
6	1	300	314
6	2	65	64
6	5	69	72
6	6	158	158
6	7	300	281
7	0	211	189
7	1	134	161
7	2	241	223
7	3	167	137
7	4	223	213
7	5	92	69
7	6	319	316
7	7	101	90
8	0	468	444
8	1	272	290
8	2	327	333
8	3	168	162
8	5	169	153
8	6	317	306
9	0	64	7
9	2	73	70
9	4	257	252
10	0	127	111
10	1	451	462
10	3	211	207
10	5	148	124
11	0	65	15
11	2	82	67
11	3	236	243
12	0	82	70
12	1	475	472
H = 9			
0	1	195	186
0	3	184	187
0	5	168	148
0	7	132	102
1	0	356	348
1	1	797	838
1	2	120	134
1	3	427	446
1	5	396	425
1	6	100	118
1	7	69	12
2	1	696	693
2	2	288	316
2	3	75	84
2	4	111	120
2	5	130	120
2	6	68	86
2	8	225	207
3	0	674	626
3	1	328	294
3	2	651	659
3	3	174	180
3	4	294	284
3	5	153	135
3	6	179	147
3	7	109	75
4	0	212	146
4	2	256	259
4	3	89	91
4	4	274	290
4	5	137	135
4	6	319	307
4	7	283	282
4	8	387	367
5	0	429	401
5	1	374	352
5	2	530	533
5	4	218	216
5	5	76	55
5	6	175	176
6	1	87	92
6	2	160	154
6	3	274	276
6	4	136	155
6	5	283	283
6	6	406	396
6	7	373	374
7	0	73	71
7	1	528	517
7	2	81	90
7	3	219	220
7	5	90	71
8	0	260	186
8	1	197	215
8	2	156	143
8	3	257	261
8	4	173	174
8	5	240	226
8	6	254	265
9	0	307	292
9	1	259	261
9	2	156	151
9	3	241	241
9	4	129	122
9	5	132	119
10	0	374	390
10	3	181	178
11	0	346	342
11	1	110	47
11	2	348	343
H = 10			
0	0	752	712
0	2	670	649
0	4	322	337
0	6	195	184
0	8	137	108
1	0	1094	1024
1	1	309	312
1	2	185	189
1	3	115	123
1	4	107	116
1	5	61	77
1	7	187	197
1	8	134	[illegible]
2	0	75	69
2	1	109	216
2	3	240	238
2	5	202	209
2	7	312	323
3	0	287	257
3	1	448	443
3	2	180	206
3	3	152	157
3	4	72	[illegible]
3	5	162	146
3	7	203	179
4	0	132	131
4	1	718	711
4	2	204	217
4	3	571	560
4	5	436	417
4	[illegible]	137	133
4	7	362	353
5	0	84	103
5	1	134	136
5	2	61	11
5	3	62	66
5	5	153	153
5	6	89	100
5	7	170	163
6	0	281	280
6	1	316	297
6	2	493	488
6	3	222	219
6	4	345	349
6	5	331	330
6	6	185	190
7	0	252	231
7	4	91	99
7	5	206	211
7	6	145	134
8	0	231	235
8	1	81	91
8	2	306	305
8	3	95	91
8	4	324	307
[illegible]	[illegible]	137	124
[illegible]	[illegible]	147	144
9	1	381	396
9	3	91	110
9	4	175	169
10	0	291	269
10	1	149	125
10	2	271	264
10	3	84	47
11	0	153	107
11	1	238	234
H = 11			
0	1	413	411
1	0	401	116
1	1	84	63
1	2	327	321
1	3	70	64
1	4	196	204
1	5	75	87
1	6	137	120
2	0	211	226
2	1	175	175
2	2	303	306
2	3	193	182
2	5	87	79
2	7	185	175
3	0	84	12
3	1	229	238
3	2	399	395
3	4	360	342
3	5	79	69
3	6	492	393
3	7	85	87
4	0	478	411
4	1	170	177
4	2	605	376
4	4	189	183
4	5	190	167
4	7	98	77
5	0	294	271
5	1	244	248
5	2	279	277
5	3	163	170
5	4	442	452
5	5	275	275
5	6	377	393
6	0	232	240
6	1	387	362
6	2	213	215
6	3	211	193
6	4	96	91
6	5	126	113
7	0	118	100
7	1	174	170
[illegible]	[illegible]	330	299
7	4	191	171
7	5	240	230
[illegible]	[illegible]	308	411
[illegible]	3	129	121
[illegible]	[illegible]	172	165
9	1	126	119
9	2	130	133
9	3	363	339
10	0	107	86
10	1	190	[illegible]
[illegible]	2	135	[illegible]
H = 12			
0	2	139	119
0	4	127	130
[illegible]	6	357	347
1	0	334	324
1	1	93	101
1	2	90	71
1	3	[illegible]	73
1	[illegible]	210	223
2	[illegible]	[illegible]	339
2	1	141	151
2	3	86	79
[illegible]	[illegible]	212	221
[illegible]	4	77	[illegible]
[illegible]	5	391	374
[illegible]	[illegible]	205	202
[illegible]	[illegible]	195	165
[illegible]	[illegible]	541	573
[illegible]	[illegible]	74	113
[illegible]	[illegible]	[illegible]	319
[illegible]	4	151	181
[illegible]	[illegible]	223	216
[illegible]	[illegible]	136	127
4	[illegible]	121	96
4	3	224	225
4	4	70	83
4	5	189	171
[illegible]	[illegible]	273	263
5	1	368	367
5	2	176	174
5	[illegible]	188	173
5	4	322	326
[illegible]	[illegible]	293	276
5	6	114	84
6	1	166	163
6	2	117	117
6	3	91	73
6	5	251	225
7	0	254	231
7	2	376	363
7	3	113	117
7	4	252	230
8	0	91	72
8	4	217	198
9	0	211	222
9	1	147	157
9	2	325	324
H = 13			
0	1	120	100
0	3	134	135
1	0	212	156
1	1	99	59
1	3	101	120
1	4	71	68
1	5	429	478
1	6	174	200
2	0	235	219
2	1	182	187
2	2	249	253
2	4	284	262
3	0	204	175
3	1	134	77
3	3	159	157
3	4	179	175
3	5	135	157
3	6	292	269
4	0	91	62
4	2	493	482
4	4	454	433
5	0	297	292
5	1	112	136
5	3	98	88
5	4	141	128
5	5	70	97
6	0	256	216
6	1	262	244
6	2	210	214
6	3	225	220
6	4	205	202
7	0	293	295
7	1	275	232
7	2	252	272
8	0	157	165
8	1	261	270
9	0	76	36
H = 14			
0	0	247	242
0	4	246	259
1	0	367	342
1	1	159	158
1	2	413	449
1	3	68	79
1	4	256	275
1	5	66	68
2	0	110	98
2	1	292	294
2	2	103	98
2	4	126	123
2	5	87	93
3	0	112	109
3	1	76	37
3	2	191	181
3	3	350	351
3	4	142	151
3	5	260	250
4	1	440	432
5	0	114	123
5	1	164	174
5	2	102	98
5	3	330	346
6	0	302	285
6	1	244	259
6	2	299	294
6	3	141	147
7	0	80	35
7	1	120	138
7	2	161	152
8	0	316	322
H = 15			
0	1	129	133
0	3	428	421
1	0	118	34
1	1	465	490
1	2	200	203
1	3	168	168
2	0	337	356
2	1	145	112
2	2	176	177
2	3	318	323
2	4	91	85
3	0	283	289
3	1	219	221
3	2	307	315
3	3	136	194
4	0	157	157
4	1	194	213
4	2	178	177
5	0	249	285
5	1	148	147
5	2	266	269
6	0	147	131
6	1	100	124
6	2	92	107
7	0	172	152
H = 16			
0	0	323	309
0	2	692	619
1	0	141	132
1	1	173	107
1	3	98	116
2	0	377	377
2	1	219	221
2	2	319	320
3	0	75	15
3	1	113	108
3	2	44	[illegible]
4	0	265	255
4	1	195	184
5	0	208	212
H = 17			
0	1	251	251
1	0	113	107
1	1	239	244
2	0	107	56
2	1	273	268

anisotropic thermal parameter refinement and (ii) inclusion of nonmethyl hydrogen atoms each result in an improvement significant at (or beyond) the 95% confidence level. As complete omission of hydrogen atoms raises R_F to only 7.12% and their positions were in fact so slightly adjusted, the refinement of a secondary extinction factor[25] can also be accepted at the 95% confidence level. The marked improvement in R_{wF^2} that results speaks for the reduction in discrepancies for intense, low-angle reflections.

Scattering factors for *neutral* iron, sulfur, oxygen, carbon, and hydrogen were used throughout the analyses.[26] The real part of the anomalous dispersion correction was applied by adding $\Delta f'$ to f for iron ($\Delta f' = +0.4\ e^-$) and sulfur ($\Delta f' = +0.1\ e^-$).

Observed and calculated structure factor amplitudes are collected in Table I. Final atomic coordinates are shown in Table II. Thermal parameters are given

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(25) It should be remembered that the Zachariasen treatment of secondary extinction assumes that extinction effects within the crystal are isotropic. While this is probably not the case for crystals of low symmetry (such as the present, monoclinic, case), the approximation is certainly better than neglecting secondary extinction.

(26) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 202–207, 216.

TABLE II

FINAL ATOMIC COORDINATES FOR $[\pi\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2CH_2CH{=}CH(C_6H_5)$, WITH ESD'S[a,b]

Atom	x	y	z
Fe	0.56659 (6)	0.31170 (7)	0.69999 (11)
S	0.68380 (11)	0.23108 (14)	0.75903 (21)
O(1)	0.6945 (3)	0.2148 (4)	0.9074 (6)
O(2)	0.6935 (4)	0.1373 (4)	0.6744 (7)
O(3)	0.6219 (5)	0.5088 (5)	0.8172 (8)
O(4)	0.5967 (4)	0.3439 (5)	0.4135 (7)
C(1)	0.7727 (5)	0.3124 (6)	0.7244 (9)
C(2)	0.7807 (5)	0.3316 (6)	0.5779 (9)
C(3)	0.7839 (5)	0.4238 (6)	0.5214 (9)
C(4)	0.7893 (5)	0.4465 (6)	0.3766 (9)
C(5)	0.7742 (5)	0.3725 (6)	0.2718 (9)
C(6)	0.7772 (6)	0.3971 (7)	0.1390 (10)
C(7)	0.7958 (6)	0.4993 (8)	0.0971 (10)
C(8)	0.8122 (6)	0.5708 (6)	0.1979 (11)
C(9)	0.8080 (5)	0.5473 (6)	0.3350 (10)
C(10)	0.5025 (4)	0.1766 (5)	0.7605 (9)
C(11)	0.4743 (4)	0.2072 (5)	0.6254 (9)
C(12)	0.4415 (4)	0.3111 (5)	0.6376 (9)
C(13)	0.4503 (4)	0.3435 (6)	0.7725 (8)
C(14)	0.4905 (4)	0.2606 (6)	0.8540 (9)
C(15)	0.5317 (5)	0.0692 (5)	0.8023 (11)
C(16)	0.4746 (5)	0.1426 (6)	0.4988 (10)
C(17)	0.3962 (5)	0.3679 (6)	0.5176 (10)
C(18)	0.4174 (5)	0.4434 (7)	0.8303 (11)
C(19)	0.5072(6)	0.2594 (8)	1.0060 (10)
C(20)	0.6020 (5)	0.4319 (6)	0.7692 (9)
C(21)	0.5905 (5)	0.3331 (5)	0.5295 (10)
H(1)	0.7701	0.3861	0.7750
H(2)	0.8302	0.2741	0.7660
H(3)	0.7841	0.2649	0.5117
H(4)	0.7824	0.4896	0.5895
H(5)	0.7592	0.2944	0.3010
H(6)	0.7650	0.3380	0.0619
H(7)	0.7983	0.5194	−0.0097
H(8)	0.8271	0.6490	0.1688
H(9)	0.8202	0.6064	0.4121

[a] Esd's (estimated standard deviations), shown in parentheses, are right-adjusted to the last digit of the preceding number. [b] Hydrogen atoms are in calculated positions.

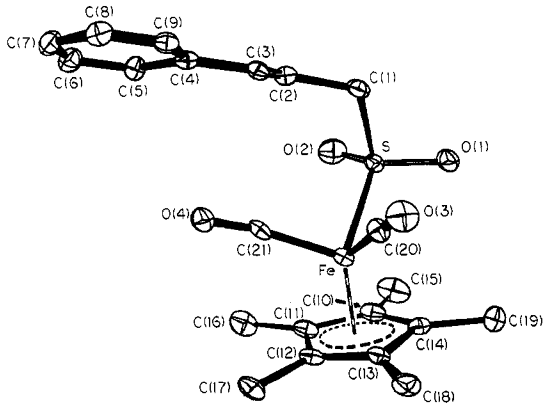

Figure 1.—Molecular geometry and atomic vibration ellipsoids[27] for $[\pi\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2CH_2CH{=}CH(C_6H_5)$.

in Table III; the associated atomic vibration ellipsoids are listed in Table IV and displayed pictorially[27] in Figure 1.

The Molecular Structure

Interatomic distances with estimated standard deviations (esd's) are collected in Table V; bond angles (with esd's) are shown in Table VI. The labeling of atoms and the molecular stereochemistry are shown in Figures 1 and 2. The molecular structure corresponds to the case of SO_2 insertion *without* allylic rearrangement.

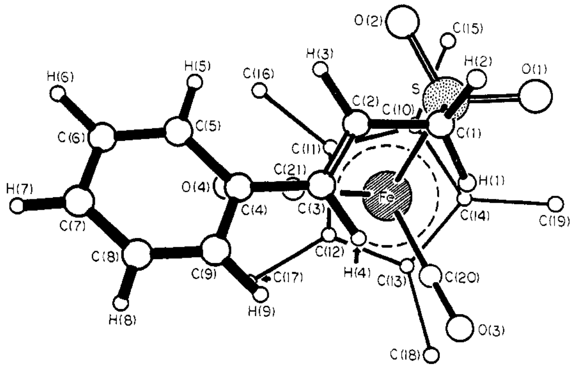

Figure 2.—The $[\pi\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2CH_2CH{=}CH(C_6H_5)$ molecule, projected onto the plane of its cyclopentadienyl ring.

The formally d^6 Fe(II) ion achieves the expected noble gas configuration by the donation of six electrons from the π-pentamethylcyclopentadienyl ion, two electrons from each of the carbonyl ligands, and two electrons from the S-bonded sulfinate moiety. The iron atom may be regarded as pseudo-octahedrally coordinated since it is linked to three monodentate ligands and to a formally tridentate $\pi\text{-}C_5(CH_3)_5$ ligand. The monodentate ligands are disposed about the iron atom with a very regular geometry, the appropriate angles being S–Fe–C(20) = 93.3 (3)°, S–Fe–C(21) = 94.3 (3)°, and C(20)–Fe–C(21) = 97.9 (4)°. They also have pseudo-threefold symmetry relative to the π-pentamethylcyclopentadienyl ligand where the angles are Cp–Fe–S = 122.7 (3)°, Cp–Fe–C(20) = 123.0 (4)°, and Cp–Fe–C(21) = 118.8 (4)° (Cp being the centroid of the five membered ring).

The ring carbon atoms of the π-pentamethylcyclopentadienyl system, *i.e.*, C(10)–C(11)–C(12)–C(13)–C(14), have a root-mean-square deviation of only 0.010 Å from their least-squares plane (see Table VII). The iron atom lies 1.730 Å to one side of this plane; the carbon atoms of the methyl substituents each lie to the opposite side of the ring carbon atoms; *i.e.*, they are bent *away from* the iron atom by the following amounts: C(15), 0.191 Å; C(16), 0.025 Å; C(17), 0.140 Å; C(18), 0.136 Å; C(19), 0.075 Å. The different distortions presumably reflect steric interaction between adjacent methyl groups. Bond lengths within the cyclopentadienyl ring range from 1.382 (10) to 1.460 (10) Å, averaging 1.431 ± 0.030 Å. This agrees precisely with the C–C(π-cyclopentadienyl) bond length of 1.431 ± 0.005 Å determined from an electron diffraction study on ferrocene,[28] is close to our average value

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(27) Atomic vibration ellipsoids were drawn using OTLIPS, an IBM 1620/CALCOMP program by Dr. P. H. Bird.

(28) R. K. Bohn and A. Haaland, *J. Organometal. Chem.*, **5**, 470 (1966).

TABLE III

ANISOTROPIC THERMAL PARAMETERS FOR $[\pi\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2CH_2CH{=}CH(C_6H_5)$[a]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Fe	21.5 (0.5)	33.2 (0.7)	87.8 (1.6)	1.1 (0.8)	−12.2 (1.2)	−3.7 (1.5)
S	22.1 (0.8)	51.1 (1.2)	81.9 (2.6)	8.9 (1.5)	−8.3 (2.1)	13.5 (2.9)
O(1)	33 (2)	82 (4)	100 (8)	2 (5)	−10 (7)	68 (9)
O(2)	43 (3)	58 (4)	162 (10)	33 (5)	24 (8)	−19 (10)
O(3)	70 (4)	54 (4)	219 (12)	−34 (7)	7 (11)	−82 (12)
O(4)	42 (3)	89 (5)	109 (9)	6 (6)	−9 (8)	48 (11)
C(1)	22 (3)	80 (6)	106 (12)	−15 (7)	−15 (9)	47 (14)
C(2)	25 (3)	73 (3)	106 (12)	2 (7)	14 (10)	−4 (14)
C(3)	23 (3)	64 (5)	99 (12)	−19 (7)	−5 (9)	−17 (13)
C(4)	23 (3)	55 (5)	115 (13)	−4 (6)	13 (10)	7 (13)
C(5)	40 (4)	58 (5)	90 (12)	0 (8)	17 (10)	9 (13)
C(6)	43 (4)	89 (7)	115 (14)	−3 (9)	36 (12)	−45 (17)
C(7)	45 (4)	92 (7)	106 (13)	29 (9)	41 (12)	30 (17)
C(8)	43 (4)	47 (5)	158 (16)	14 (8)	27 (13)	50 (15)
C(9)	31 (3)	49 (5)	134 (14)	−6 (7)	6 (11)	−6 (13)
C(10)	23 (3)	47 (5)	135 (13)	−10 (6)	1 (10)	15 (13)
C(11)	22 (3)	39 (4)	125 (12)	−5 (6)	−9 (10)	−12 (12)
C(12)	17 (3)	41 (4)	129 (12)	5 (6)	−7 (9)	0 (12)
C(13)	21 (3)	53 (5)	110 (11)	7 (6)	−7 (9)	−22 (12)
C(14)	22 (3)	73 (6)	108 (12)	−8 (7)	20 (9)	12 (14)
C(15)	42 (4)	37 (5)	217 (17)	0 (7)	−19 (13)	88 (14)
C(16)	46 (4)	48 (5)	150 (13)	−11 (7)	−19 (12)	−67 (13)
C(17)	42 (4)	52 (5)	150 (13)	21 (8)	−56 (12)	−15 (14)
C(18)	40 (4)	84 (6)	167 (15)	46 (8)	−1 (12)	−78 (16)
C(19)	47 (4)	119 (8)	94 (12)	−11 (10)	18 (11)	40 (17)
C(20)	40 (4)	50 (5)	111 (12)	−18 (7)	−7 (11)	−15 (13)
C(21)	25 (3)	43 (5)	102 (12)	0 (6)	−41 (10)	13 (13)

[a] The anisotropic thermal parameter (T) is defined as $T = \exp[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl]$.

TABLE IV

THERMAL VIBRATION ELLIPSOIDS FOR ATOMS IN $[\pi\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2CH_2CH{=}CH(C_6H_5)$[a,b]

Atom	$B_{\max}$, Å^2	B_{med}, Å^2	$B_{\min}$, Å^2
Fe	3.66	2.20	2.06
S	3.62	3.30	2.01
O(1)	6.58	3.81	2.52
O(2)	6.26	5.65	2.64
O(3)	9.13	7.82	2.50
O(4)	6.56	4.81	3.30
C(1)	6.28	3.39	2.14
C(2)	4.89	4.04	2.58
C(3)	4.63	3.88	2.02
C(4)	4.45	3.64	2.38
C(5)	4.33	3.95	3.24
C(6)	6.60	4.79	3.31
C(7)	7.19	4.36	3.30
C(8)	6.66	4.44	2.61
C(9)	5.12	3.50	3.03
C(10)	5.27	3.26	2.25
C(11)	4.93	2.73	2.13
C(12)	5.02	2.81	1.76
C(13)	4.67	3.23	2.09
C(14)	4.95	4.13	2.11
C(15)	9.33	4.34	1.68
C(16)	6.87	4.89	2.12
C(17)	7.66	3.60	2.66
C(18)	8.69	4.97	2.56
C(19)	8.19	4.96	3.25
C(20)	4.85	4.30	2.70
C(21)	5.08	2.85	1.68

[a] The magnitudes of the major, median, and minor axes of the atomic vibration ellipsoids defined in terms of the isotropic thermal parameter, B. This is related to the rms displacement by $(\bar{U}^2)^{1/2} = [B/8\pi^2]^{1/2}$. [b] The 68% probability envelopes are depicted in Figure 1.

of 1.436 Å for the C–C distance in bis(fulvalene)diiron,[29] and is rather longer than the mean X-ray value of 1.419 Å from studies on unsubstituted π-cyclopentadienyl derivatives.[30] Thus, the central C_5 ring of the π-pentamethylcyclopentadienyl system is probably more rigidly held than the corresponding ring in a π-C_5H_5 system, since no significant librational contraction of the C–C bond is observed. Iron–carbon distances range from 2.090 (9) to 2.137 (8) Å averaging 2.115 ± 0.016 Å. This mean value appears to be rather greater than that observed in nonmethylated π-cyclopentadienyliron–carbonyl species, *viz.*, 2.089 Å in $[\pi\text{-}C_5H_5Fe(CO)_2]_2C_4H_4$,[31] 2.093 Å in (azulene)$Fe_2(CO)_5$,[32] and 2.094 Å in π-$C_5H_5Fe(CO)_2C_4H_5$-SO_2.[1] However, since the present complex is the first $[\pi\text{-}C_5(CH_3)_5]$ complex of iron to be examined crystallographically, we feel that further results are necessary before any firm conclusions on this point can be reached.

Bond distances from the ring carbons to the methyl carbons range from 1.492 (12) to 1.530 (11) Å, averaging 1.509 ± 0.015 Å. This value is in excellent agreement with the recognized C(sp^2)–C(sp^3) single-bond distance of 1.510 ± 0.005 Å.[33]

The terminal carbonyl groups are quite normal with a mean iron–carbon distance of 1.766 ± 0.007 Å and a mean carbon–oxygen distance of 1.145 ± 0.014 Å.

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(29) M. R. Churchill and J. Wormald, *Inorg. Chem.*, **8**, 1970 (1969).

(30) P. J. Wheatley in "Perspectives in Structural Chemistry," Vol. 1, J. D. Dunitz and J. A. Ibers, Ed., Wiley, New York, N. Y., 1967, p 9.

(31) M. R. Churchill and J. Wormald, *Inorg. Chem.*, **8**, 1936 (1969).

(32) M. R. Churchill, *ibid.*, **6**, 190 (1967).

(33) *Chem. Soc., Spec. Publ.*, **No. 18**, S10s–22s (1965).

TABLE V

INTERATOMIC DISTANCES (WITH ESTIMATED STANDARD DEVIATIONS[a]) FOR THE $[\pi\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2CH_2CH{=}CH(C_6H_5)$ MOLECULE

Atoms	Dist, Å	Atoms	Dist, Å
(a) Distances Involving the Sulfur Atom			
Fe–S	2.218 (2)	S–O(1)	1.465 (5)
S–C(1)	1.840 (8)	S–O(2)	1.480 (6)
		Av	1.473 (10)
(b) Iron–$[\pi\text{-}C_5(CH_3)_5]$ Distances			
Fe–C(10)	2.137 (8)	Fe···C(15)	3.344 (9)
Fe–C(11)	2.112 (8)	Fe···C(16)	3.236 (9)
Fe–C(12)	2.090 (8)	Fe···C(17)	3.279 (9)
Fe–C(13)	2.113 (7)	Fe···C(18)	3.297 (9)
Fe–C(14)	2.124 (8)	Fe···C(19)	3.281 (9)
Av	2.115 (16)	Av	3.287 (–)[b]
(c) Distances Involving Carbonyl Ligands			
Fe–C(20)	1.771 (8)	C(20)–O(3)	1.135 (10)
Fe–C(21)	1.761 (8)	C(21)–O(4)	1.154 (10)
Av	1.766 (7)	Av	1.145 (14)
(d) Distances within Phenylallyl Moiety			
C(1)–C(2)	1.469 (11)	C(4)–C(5)	1.409 (11)
C(2)–C(3)	1.312 (11)	C(5)–C(6)	1.341 (12)
C(3)–C(4)	1.456 (11)	C(6)–C(7)	1.418 (13)
		C(7)–C(8)	1.363 (13)
		C(8)–C(9)	1.381 (12)
		C(9)–C(4)	1.401 (11)
		Av	1.386 (29)
(e) Distances within $[\pi\text{-}C_5(CH_3)_5]$ Ligand			
C(10)–C(11)	1.424 (10)	C(10)–C(15)	1.510 (11)
C(11)–C(12)	1.449 (10)	C(11)–C(16)	1.493 (11)
C(12)–C(13)	1.382 (10)	C(12)–C(17)	1.530 (11)
C(13)–C(14)	1.460 (10)	C(13)–C(18)	1.519 (12)
C(14)–C(10)	1.439 (10)	C(14)–C(19)	1.492 (12)
Av	1.431 (30)	Av	1.509 (16)

[a] Esd's for individual distances are obtained from the least-squares refinement process *via* the matrix inverse to the normal equation matrix. Esd's for average bond lengths were calculated from the equation

$$\sigma^2 = \left\{\left[\sum_{i=1}^{i=N}(\chi_i - \bar{\chi})^2\right]\Big/(N-1)\right\}$$

where χ_i is the ith bond length, and $\bar{\chi}$ is the mean of the N equivalent bond lengths. [b] The above distances are not expected to be equivalent, since there appears to be steric repulsion between adjacent methyl groups.

TABLE VI

ANGLES WITHIN THE $[\pi\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2CH_2CH{=}CH(C_6H_5)$ MOLECULE

Atoms	Angle, deg	Atoms	Angle, deg
(a) Angles around Iron Atom[a]			
S–Fe–C(20)	93.3 (3)	Cp–Fe–S	122.7 (3)
S–Fe–C(21)	94.3 (3)	Cp–Fe–C(20)	123.0 (4)
C(20)–Fe–C(21)	97.9 (4)	Cp–Fe–C(21)	118.8 (4)
(b) Angles around Sulfur Atom			
Fe–S–O(1)	111.4(2)	C(1)–S–O(1)	102.9 (3)
Fe–S–O(2)	111.1 (2)	C(1)–S–O(2)	104.2 (4)
Fe–S–C(1)	111.2 (3)	O(1)–S-O(2)	115.3 (3)
(c) Angles within Phenylallyl Moiety			
S-C(1)-C(2)	113.6(6)	C(4)-C(5)-C(6)	121.9 (8)
C(1)–C(2)–C(3)	124.9 (8)	C(5)–C(6)–C(7)	121.5 (9)
C(2)–C(3)–C(4)	126.8 (8)	C(6)–C(7)–C(8)	117.0 (9)
C(3)–C(4)–C(5)	123.5 (7)	C(7)–C(8)–C(9)	122.3 (9)
C(3)–C(4)–C(9)	119.9 (7)	C(8)–C(9)–C(4)	120.8 (8)
		C(9)–C(4)–C(5)	119.9 (9)
(d) Angles Subtended at Fe by the Five-Membered Ring			
C(10)–Fe–C(11)	39.2 (3)	C(13)–Fe–C(14)	40.3 (3)
C(11)–Fe–C(12)	40.4 (3)	C(14)–Fe–C(10)	39.5 (3)
C(12)–Fe-C(13)	38.4 (3)		
(e) Internal Angles of the $[\pi\text{-}C_5(CH_3)_5]$ Ligand			
C(14)–C(10)–C(11)	109.4 (7)	C(12)–C(13)–C(14)	108.2 (7)
C(10)–C(11)–C(12)	106.1 (6)	C(13)–C(14)–C(10)	106.2 (7)
C(11)–C(12)–C(13)	110.1 (6)		
(f) External angles of the $[\pi\text{-}C_5(CH_3)_5]$ Ligand			
C(11)–C(10)–C(15)	125.5 (7)	C(13)–C(12)–C(17)	126.9 (7)
C(14)-C(10)-C(15)	124.9 (7)	C(12)–C(13)–C(18)	126.6 (7)
C(10)–C(11)–C(16)	126.6 (7)	C(14)–C(13)–C(18)	125.0 (7)
C(12)–C(11)–C(16)	127.3 (7)	C(13)–C(14)–C(19)	126.5 (7)
C(11)–C(12)–C(17)	122.7 (7)	C(10)–C(14)–C(19)	127.0 (7)

[a] "Cp" represents the centroid of the cyclopentadienyl ring.

TABLE VII

IMPORTANT LEAST-SQUARES PLANES WITHIN THE $[\pi\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2CH_2CH{=}CH(C_6H_5)$ MOLECULE[a,b]

Atom	Dev, Å	Atom	Dev, Å
(a) $\pi\text{-}C_5(CH_3)_5$ Group			
$-0.9126X - 0.3767Y + 0.1584Z + 6.7051 = 0$			
C(10)*	0.014	C(15)	0.191
C(11)*	−0.010	C(16)	0.025
C(12)*	0.002	C(17)	0.140
C(13)*	0.007	C(18)	0.136
C(14)*	−0.012	C(19)	0.075
Fe	−1.730		
(b) The Phenyl Ring			
$0.9700X - 0.2376Y + 0.0495Z - 11.0666 = 0$			
C(4)*	−0.002	C(3)	−0.044
C(5)*	0.004	C(2)	0.176
C(6)*	0.001	C(1)	0.082
C(7)*	−0.009		
C(8)*	0.012		
C(9)*	−0.007		

[a] Planes are defined in Cartesian coordinates (X, Y, Z) which are related to the monoclinic fractional cell coordinates (x, y, z) by the transformations $X = xa + zc \cos\beta$, $Y = yb$, and $Z = zc \sin\beta$. [b] Planes are calculated using unit weights for all atoms marked with an asterisk.

The iron–sulfur distance of 2.218 (2) Å is significantly shorter than the sum of the appropriate covalent radii (r(Fe) = 1.34 Å[34] and r(S) = 1.04 Å[35]), suggesting some double-bond character is this linkage. The sulfur atom is tetrahedrally coordinated, angles from the iron atom being very similar [Fe–S–O(1) = 111.4 (2)°, Fe–S–O(2) = 111.1 (3)°, Fe–S–C(1) = 111.2 (3)°] whereas the remaining angles are C(1)–S–O(1) = 102.9 (3)°, C(1)–S–O(2) = 104.2 (4)°, and O(1)–S–O(2) = 115.3 (3)°. This last value is seen to be consistent with the Gillespie–Nyholm rules[36] concerning bond angles, since it separates two sulfur–oxygen double bonds, S—O(1) = 1.465 (5) Å and S—O(2) = 1.480

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[34] This is taken specifically from studies on $\pi\text{-}C_5H_5Fe(CO)_2R$ molecules: see M. R. Churchill, *Perspect. Struct. Chem.*, **3**, 157 (1970).

[35] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 224.

[36] R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, 339 (1957), especially pp 371–372.

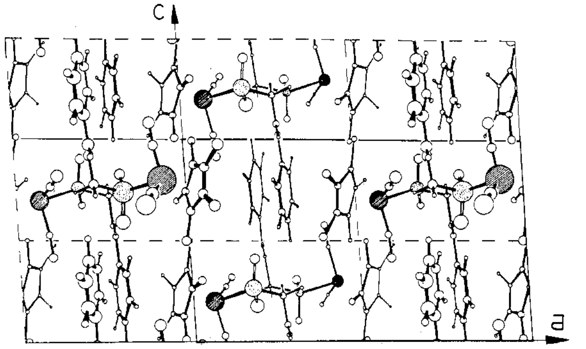

Figure 3.—Packing of $[\pi\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2CH_2CH{=}CH(C_6H_5)$ molecules within the unit cell, viewed down *b*. The dashed lines represent the half-periods in the unit cell.

(6) Å. These distances are closely similar to the S═O bond length of 1.480 (8) Å in π-$C_5H_5Fe(CO)_2C_4H_5SO_2$.[1,37] The present sulfur–sp^3 carbon bond, S–C(1), is 1.840 (8) Å long; this is consistent with the sulfur–sp^2 carbon distance of 1.781 (9) Å found in π-$C_5H_5Fe(CO)_2C_4H_5SO_2$,[1,37] since there is a difference of 0.03–0.04 Å in the covalent radii of sp^2- and sp^3-hybridized carbon atoms.

As may be seen from Tables V–VII, distances within the phenylallyl moiety are in keeping with the structure as illustrated in Figures 1 and 2.

TABLE VIII

INTERMOLECULAR CONTACTS TO 3.5 Å[a]

Atoms	Dist, Å	Trans[b]	Atoms	Dist, Å	Trans[b]
O(1)···H(6)	2.42	I	C(16)···H(2)	3.34	II
H(1)···H(7)	2.72	I	S···H(6)	3.43	I
H(1)···H(6)	2.87	I	C(17)···H(6)	3.46	III
C(17)···H(2)	3.20	II	O(1)···C(6)	3.47	II
O(3)···H(7)	3.23	I	H(1)···C(7)	3.48	I
H(2)···H(6)	3.25	I	C(11)···H(6)	3.49	III
C(1)···H(6)	3.31	I	C(11)···C(6)	3.50	III

[a] Note that hydrogen atoms belonging to methyl groups of the π-$C_5(CH_3)_5$ ligand have not been located and are not included in these calculations. [b] The translations are as follows: (I) $x, y, 1 + z$; (II) $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (III) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

Crystal Packing

The packing of molecules in the crystal is shown in Figure 3; intermolecular contacts are collected in Table VIII. The shortest contact is O(1)···H(6) $[x, y, 1 + z]$ = 2.42 Å. This and all other contacts are greater than the sum of the appropriate van der Waals radii.

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The Bonding of Molecular Nitrogen. III. The Crystal and Molecular Structure of Chlorodinitrogentetrakis(dimethylphenylphosphine)rhenium(I)

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The crystal and molecular structure of the molecular nitrogen complex chlorodinitrogentetrakis(dimethylphenylphosphine)rhenium(I), $ReCl(N_2)(P(CH_3)_2C_6H_5)_4$, has been determined from three-dimensional X-ray data collected by counter techniques. The central rhenium atom is octahedrally coordinated to four phosphorus atoms, to the chlorine atom, and to a nitrogen atom of the molecular nitrogen group. The chlorine and nitrogen atoms are *trans*. The Re–Cl bond distance is 2.521 (4) Å, the Re–N bond distance is 1.97 (2) Å, and the four Re–P bond distances have a mean value of 2.422 (10) Å. The molecular nitrogen group is linear with an Re–N–N bond angle of 177 (1)° and a Cl–Re–N bond angle of 175.6 (4)°. Owing to partial disorder between the chlorine atom and the molecular nitrogen entity, a precise determination of the N–N distance has not been possible. Crystal data are as follows: triclinic, space group C_i^1-$P\bar{1}$; $a = 12.730$ (6) Å, $b = 12.771$ (6) Å, $c = 11.523$ (6) Å, $\alpha = 103.25$ (3)°, $\beta = 103.96$ (2)°, $\gamma = 95.37$ (2)° (temperature 22°), $Z = 2$; $d_{obsd} = 1.57$ (3) g/cm^3, $d_{calcd} = 1.53$ g/cm^3. The structure was refined using 1968 independent reflections for which $F^2 > 3\sigma(F^2)$ and the refinement converged to a conventional R factor (on F) of 3.7%.

Introduction

In the previously reported structures of transition metal complexes which contain molecular nitrogen as a coordinating ligand, $CoH(N_2)(P(C_6H_5)_3)_3$, $Ru(N_2)(NH_3)_5^{2+}$, and $[Ru(N_3)(N_2)(NH_2CH_2CH_2NH_2)_2][PF_6]$, it has been shown that molecular nitrogen bonds in a manner similar to the isoelectronic species carbon monoxide.[1-3] In continuing our studies and collaboration with the Unit of Nitrogen Fixation at the University of Sussex, Brighton, England, to determine factors con-

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