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The Crystal and Molecular Structure of Phenyltrimethylenemethaneiron Tricarbonyl

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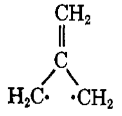
Phenyltrimethylenemethaneiron tricarbonyl, $[(CH_2)_2C(CHC_6H_5)]Fe(CO)_3$, crystallizes in the centrosymmetric monoclinic space group $P2_1/a$ (C_{2h}^5; no. 14) with $a = 16.322 \pm 0.012$ Å, $b = 6.632 \pm 0.005$ Å, $c = 12.542 \pm 0.008$ Å, $\beta = 117.18 \pm 0.05°$, and $Z = 4$. Observed and calculated densities are 1.33 ± 0.05 and 1.289 g cm^{-3}, respectively. A single-crystal X-ray diffraction study has been carried out. Data complete to $\sin\theta = 0.42$ (Mo Kα radiation) were collected with a 0.01°-incrementing Buerger automated diffractometer, and the structure was solved by a combination of Patterson, Fourier, and least-squares refinement procedures. All atoms (including hydrogens) have been located, the final discrepancy index being $R_F = 7.85\%$ for the 1459 independent, nonzero reflections. The crystal is composed of molecular units of $[(CH_2)_2C(CHC_6H_5)]Fe(CO)_3$, separated by normal van der Waals distances. The iron atom is located directly beneath the central atom of the trimethylenemethane residue and is π bonded to the four carbon atoms of this system. The carbon atom skeleton of the trimethylenemethane moiety is significantly nonplanar, the central atom being displaced (away from the iron) by 0.315 Å relative to the plane defined by the three terminal carbon atoms. The trimethylenemethane ligand and the $Fe(CO)_3$ group adopt a mutually staggered conformation.

Introduction

Trimethylenemethane (I) has been the subject of much theoretical discussion, since its central carbon atom attains the maximum total bond order (and mobile bond order) possible for an sp^2-hybridized carbon atom.[1,2] This species has been detected as a stable intermediate in the low-temperature photochemical decomposition of 4-methylene-Δ^1-pyrazoline[3] and 3-methylenecyclobutanone;[4] it has also been postulated as an intermediate in the thermal decomposition of 4-methylene-Δ^1-pyrazoline[5] and esters of 2-methylenepropane-1,3-diol[6] and in the alkali metal dehalogenation of 2-iodomethyl-3-iodopropene.[7,8] Recent electron spin resonance studies on orientated trimethylenemethane [trapped in an irradiated (uv) single-crystal of 3-methylenecyclobutanone] confirm that it has a triplet ground state (*i.e.*, that it is a diradical) and show that its six hydrogen atoms are equivalent—*i.e.*, that the diradical possesses D_3 (or higher) molecular symmetry.[9]



I

As with a number of other highly reactive or intrinsically unstable organic species (such as cyclobutadiene,[10] cyclopentadienone,[11] and azepine[12]), trimethylenemethane has been stabilized as an iron tricarbonyl adduct.[13] Since trimethylenemethane represents a novel type of organic ligand, we decided to investigate the structure of a trimethylenemethaneiron tricarbonyl species. The parent compound, $[(CH_2)_3C]Fe(CO)_3$, has a rather low melting point (28.4–29.6°),[13] but *phenyl*trimethylenemethaneiron tricarbonyl melts

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[1] J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, Inc., New York, N. Y., 1961, p 56.

[2] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, pp 43, 57.

[3] P. Dowd, *J. Am. Chem. Soc.*, **88**, 2587 (1966).

[4] P. Dowd and K. Sachdev, *ibid.*, **89**, 715 (1967).

[5] R. J. Crawford and D. M. Cameron, *ibid.*, **88**, 2589 (1966).

[6] J.-P. Schirmann and F. Weiss, *Tetrahedron Letters*, 5163 (1967).

[7] R. G. Doerr and P. S. Skell, *J. Am. Chem. Soc.*, **89**, 3062 (1967).

[8] P. S. Skell and R. G. Doerr, *ibid.*, **89**, 4688 (1967).

[9] P. Dowd, A. Gold, and K. Sachdev, *ibid.*, **90**, 2715 (1968).

[10] G. F. Emerson, L. Watts, and R. Pettit, *ibid.*, **87**, 131 (1965).

[11] M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 989 (1960).

[12] E. O. Fischer and H. Rühle, *Z. Anorg. Allgem. Chem.*, **341**, 137 (1965).

[13] G. F. Emerson, K. Ehrlich, W. P. Giering, and P. C. Lauterbur, *J. Am. Chem. Soc.*, **88**, 3172 (1966).

at a somewhat higher temperature (62–64°).[14] We have therefore carried out a single-crystal X-ray diffraction study on this latter complex. A preliminary communication concerning this work has appeared previously.[15]

Unit Cell and Space Group

Optical examination and the observed reciprocal-lattice symmetry of C_{2h} indicated that the crystals belong to the monoclinic system. A survey of $h0l$ and $h1l$ Weissenberg photographs and $hk0$ and $0kl$ precession photographs revealed the systematic absences $h0l$ for $h = 2n + 1$ and $0k0$ for $k = 2n + 1$, consistent with space group $P2_1/a$ (C_{2h}^5; no. 14).

Unit cell parameters, obtained from calibrated ($a_{NaCl} = 5.640$ Å) precession pictures taken with Mo Kα radiation ($\bar{\lambda}$ 0.7107 Å) at 23 ± 2° are $a = 16.322 \pm 0.012$ Å, $b = 6.632 \pm 0.005$ Å, $c = 12.542 \pm 0.008$ Å, and $\beta = 117.18 \pm 0.05°$. [Errors given are the "maximum possible errors" based on the sum of the inaccuracies involved in measuring (on precession photographs) the positions of diffraction rows from the crystal under investigation and from our standard (sodium chloride) crystal.] The unit cell volume is 1391 Å^3. The observed density ($\rho_{obsd} = 1.33 \pm 0.05$ g cm^{-3}, by flotation in aqueous zinc iodide solution) is in satisfactory agreement with the value calculated for $M = 270$ and $Z = 4$ ($\rho_{calcd} = 1.289$ g cm^{-3}).

Collection and Reduction of X-Ray Diffraction Data

Pale yellow platelets of phenyltrimethylenemethane-iron tricarbonyl were supplied by the late Professor G. F. Emerson. The crystals have well-developed (100) faces and are extended along the b direction. Two crystals were used during the analysis—crystal I (0.10 × 0.58 × 0.36 mm) was mounted along its b axis and crystal II (0.11 × 0.44 × 0.31 mm) was mounted along its c axis. [Dimensions refer sequentially to a, b, c directions in the crystals.] The compound is rather volatile, so each crystal was enclosed in a thin-walled lithium borate capillary tube.

Intensity data (Mo Kα, $\bar{\lambda}$ 0.7107 Å) were collected with a 0.01°-incrementing Buerger automated diffractometer, using the "stationary-background, ω-scan, stationary-background" counting sequence. The angle scanned (ω) was chosen as $\omega = [2.0 + (0.8/L)]°$ where $1/L$ is the Lorentz factor; initial and final backgrounds (B_1 and B_2) were each counted for one-fourth the time taken for the appropriate ω scan, and $I(hkl)$ (the intensity of the reflection hkl) was calculated as $I(hkl) = C(hkl) - 2[B_1(hkl) + B_2(hkl)]$, where $C(hkl)$ is the count associated with the ω scan. Standard deviations assigned to reflections were: $I(hkl) > 1225$, $\sigma(hkl) = 0.1[I(hkl)]$; $I(hkl) \leqslant 1225$, $\sigma(hkl) = 3.5[I(hkl)]^{1/2}$. Reflections were included in the analysis if (1) $0.333 \leqslant B_1/B_2 \leqslant 3.0$ and (2) $I(hkl) \geqslant 3[C(hkl) + B_1(hkl) + B_2(hkl)]^{1/2}$. Condition 1 removes reflections with a large asymmetry in background count—which is usually symptomatic of overlap of adjacent reflections; condition 2 removes reflections which are not significantly different from zero at the 3σ level. All other experimental details (and concomitant precautions) are identical with those described in a previous publication.[16]

A total of 1575 reflections in the zones $h0l$ through $h7l$ were collected from crystal I. [This represents data complete to $\sin\theta = 0.42$ and includes all reflections photographically visible, save for the few at $\theta \leqslant 4°$ which are shielded from the counter by a lead backstop.] A total of 929 reflections from the zones $hk0$ through $hk8$ was collected from crystal II. All data were corrected for Lorentz and polarization effects, and absorption corrections were applied.[17] [With $\mu = 11.16$ cm^{-1} transmission factors ranged from 0.725 to 0.884 for crystal I (volume 0.021 mm^3) and from 0.674 to 0.935 for crystal II (volume 0.0094 mm^3).] The 17 zones of data were merged to a common scale using a least-squares procedure which minimizes a sum of residuals linear in the logarithms of the individual scale factors.[18] The resulting 1475 independent nonzero reflections were used to calculate a Wilson plot,[19] which yielded an approximate absolute scale factor and an over-all isotropic thermal parameter $\bar{B} = 2.43$ Å^2).

Solution and Refinement of the Structure

A three-dimensional Patterson synthesis,[20] which had been sharpened so that the average intensity was independent of $\sin\theta$ and which had the origin peak removed, indicated an iron position at $x = 0.546$, $y = 0.296$, $z = 0.340$. A three-dimensional difference-Fourier synthesis, phased by the iron atom ($R_F = 0.40$),[21] yielded the positions of the three carbonyl groups. A second difference-Fourier synthesis, phased now by seven atoms ($R_F = 0.35$), showed the positions of all of the remaining nonhydrogen atoms. Seven cycles of full-matrix least-squares refinement of positional and isotropic thermal parameters led to convergence at $R_F = 0.116$ and $R_{wF^2} = 0.053$.[21] A three-dimensional difference-Fourier synthesis at this stage showed evidence of anisotropic motion for many atoms and led to the location of all ten hydrogen atoms. [Peak heights (in e$^-$ Å^{-3}) were: $H(21)$ 0.59, $H(22)$ 0.53, $H(31)$ 0.52, $H(32)$ 0.45, $H(4)$ 0.55, $H(6)$ 0.55, $H(7)$ 0.63, $H(8)$ 0.68, $H(9)$ 0.41, $H(10)$ 0.63. This may be compared with carbon atom peaks heights (on an "observed" Fourier synthesis) of ~5 e$^-$ Å^{-3}.] A structure factor calculation, phased now by all 27 atoms, had discrepancy indices $R_F = 0.113$ and $R_{wF^2} = 0.056$.

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(14) G. F. Emerson and K. Ehrlich, unpublished work.

(15) M. R. Churchill and K. Gold, *Chem. Commun.*, 693 (1968).

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

(17) Using a locally modified version of GNABS—a general absorption correction program by C. W. Burnham.

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

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

(20) All crystallographic computations were performed using CRYRM—an integrated sequence of crystallographic routines for the IBM 7094 computer written by Professor R. E. Marsh and coworkers at the California Institute of Technology.

(21) $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_{wF^2} = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $[(CH_2)_2C(CHC_6H_5)]Fe(CO)_3$ (IN ELECTRONS × 10.00)[a]

K	L	FO	FC
H = -19			
1	7	84	79
H = -18			
0	1	125	127
0	4	147	159
0	7	205	230
0	8	78	31
0	9	144	146
0	10	81	73
0	11	66	51
1	2	117	107
1	5	185	186
1	6	91	71
1	8	182	188
1	9	91	51
2	1	87	88
2	6	106	91
2	7	115	96
H = -17			
1	2	76	50
2	2	118	103
2	3	79	77
2	4	70	59
2	9	67	29
2	10	77	25
3	7	83	99
H = -16			
0	0	117	120
0	1	101	187
0	2	73	86
0	4	158	155
0	5	149	149
0	7	174	183
0	8	134	106
0	10	115	157
0	12	82	88
1	0	110	87
1	2	123	135
1	3	133	139
1	6	191	205
1	7	97	85
1	8	129	121
1	9	137	120
1	12	88	91
2	1	116	77
2	2	95	96
2	4	204	188
2	6	80	65
2	7	176	175
2	8	121	114
2	10	84	87
2	11	94	107
3	2	90	95
3	4	104	114
3	5	72	88
3	6	116	100
3	9	102	100
3	10	79	69
H = -15			
1	2	109	117
1	3	92	65
2	0	88	80
2	3	195	203
2	4	90	93
2	6	94	79
3	0	72	33
3	2	142	135
3	4	157	147
3	5	85	48
3	7	97	108
3	8	123	125
3	10	78	65
4	1	110	115
4	3	116	106
4	4	81	73
4	6	106	122
4	7	139	95
4	8	89	48
4	9	105	101
H = -14			
0	0	92	41
0	1	109	113
0	3	107	79
0	5	90	109
0	6	289	311
0	7	98	86
0	8	164	177
0	11	129	125
0	12	163	157
1	0	133	132
1	1	93	76
1	3	229	224
1	5	151	165
1	6	165	159
1	7	194	199
1	8	91	41
1	9	116	140
1	10	126	126
1	11	125	102
1	13	180	159
2	1	192	185
2	2	126	123
2	3	73	83
2	4	139	157
2	5	211	215
2	6	88	64
2	7	69	71
2	8	141	137
2	9	119	137
2	10	88	84
2	11	111	91
2	12	95	94
3	0	69	70
3	1	175	175
3	3	147	137
3	4	144	125
3	6	146	134
3	7	128	107
3	9	136	129
3	11	103	96
3	12	151	155
4	0	100	75
4	1	108	96
4	3	113	95
4	5	133	113
4	11	99	74
5	8	92	21
H = -13			
1	0	111	106
1	1	96	79
1	2	110	102
1	3	125	147
1	6	117	109
1	7	113	80
1	8	104	98
1	12	95	71
2	1	217	219
2	2	153	129
2	3	94	80
2	4	105	101
2	5	73	89
2	6	107	97
2	7	155	153
2	8	153	135
2	10	133	133
2	11	83	86
2	13	118	115
3	0	69	77
3	2	211	215
3	5	203	202
3	6	172	162
3	8	117	117
3	9	161	166
3	12	86	102
4	0	84	84
4	1	176	171
4	3	134	126
4	4	150	146
4	6	73	69
4	7	205	195
4	9	94	85
5	0	98	82
5	2	161	160
5	5	138	136
5	6	92	76
5	8	108	101
5	9	91	90
H = -12			
0	0	270	259
0	1	93	46
0	2	334	335
0	3	294	307
0	4	179	202
0	5	225	240
0	6	303	324
0	7	163	100
0	8	356	392
0	9	183	171
0	12	183	178
0	13	135	145
0	14	89	87
1	0	150	144
1	1	251	272
1	2	132	112
1	3	176	180
1	4	267	267
1	5	258	284
1	6	136	118
1	7	270	272
1	8	253	275
1	9	186	185
1	10	127	121
1	11	209	195
1	13	163	148
1	14	99	77
2	0	144	141
2	2	356	358
2	5	158	159
2	6	257	252
2	8	130	132
2	9	119	129
2	10	147	153
2	11	83	96
2	12	136	123
3	0	249	230
3	2	139	139
3	3	123	131
3	4	145	138
3	6	76	53
3	7	107	86
3	10	155	146
3	13	204	98
4	0	120	68
4	3	117	99
4	4	84	43
4	8	91	53
4	10	84	55
4	11	106	104
5	3	75	26
5	4	113	72
H = -11			
1	0	211	200
1	1	190	142
1	2	138	116
1	3	80	49
1	5	174	180
1	6	96	85
1	9	207	179
1	12	127	109
2	0	158	171
2	1	278	302
2	2	185	191
2	4	235	237
2	5	204	214
2	7	91	108
2	8	297	298
2	11	187	185
2	13	136	117
2	14	68	49
3	0	153	138
3	1	213	211
3	2	166	174
3	3	274	253
3	4	159	157
3	5	114	108
3	6	283	278
3	7	211	209
3	8	106	92
3	9	143	138
3	10	102	101
3	12	203	197
4	1	86	88
4	2	167	149
4	4	191	183
4	5	186	175
4	7	196	194
4	8	167	170
4	9	76	93
4	10	129	142
4	11	85	96
5	0	167	155
5	2	105	80
5	3	173	183
5	6	185	170
5	9	121	107
5	10	83	93
6	0	90	77
6	1	139	134
6	4	147	137
6	5	83	70
H = -10			
0	0	327	353
0	1	295	335
0	2	570	597
0	3	374	389
0	4	319	382
0	5	173	151
0	6	422	478
0	7	198	208
0	8	257	282
0	9	323	302
0	10	95	83
0	12	217	238
0	14	68	41
1	1	529	543
1	2	301	321
1	4	313	339
1	5	412	440
1	6	73	70
1	7	338	346
1	8	327	333
1	10	183	171
1	11	185	175
1	12	147	137
1	13	82	67
1	14	121	115
2	0	338	342
2	1	238	236
2	2	176	177
2	3	395	407
2	4	240	243
2	5	93	85
2	6	142	150
2	7	412	418
2	8	182	184
2	9	215	201
2	10	189	190
2	12	118	126
2	13	87	101
3	1	146	133
3	2	208	179
3	4	112	109
3	5	278	249
3	6	122	92
3	7	165	149
3	8	80	71
3	9	205	211
3	10	146	159
3	11	77	88
3	13	80	48
4	3	129	51
4	5	85	84
4	6	94	74
4	10	116	109
5	0	72	46
5	3	86	66
5	4	114	42
6	0	87	76
6	3	77	32
H = -9			
1	0	128	80
1	1	221	186
1	4	176	163
1	6	93	37
1	7	125	71
1	8	66	13
1	9	99	73
1	10	107	82
1	11	119	110
1	12	139	130
2	1	130	143
2	2	100	110
2	4	307	294
2	5	164	185
2	6	185	192
2	8	102	113
2	9	139	145
2	11	124	123
2	14	104	82
3	0	347	337
3	1	257	257
3	2	93	94
3	3	316	307
3	4	260	249
3	5	71	62
3	6	182	181
3	7	248	251
3	10	119	134
3	12	132	97
3	13	143	138
4	0	156	149
4	1	159	126
4	2	319	307
4	3	73	58
4	4	134	124
4	5	351	324
4	6	152	136
4	7	100	99
4	8	204	200
4	9	75	77
4	11	192	186
4	12	114	111
5	0	156	169
5	1	144	139
5	3	183	178
5	4	146	131
5	6	171	160
5	7	185	193
5	9	117	113
5	10	147	140
6	1	118	119
6	2	151	158
6	5	159	141
6	6	101	94
6	8	91	101
H = -8			
0	0	361	369
0	1	461	471
0	2	234	223
0	3	315	323
0	4	446	490
0	5	79	80
0	6	365	398
0	7	686	759
0	8	93	98
0	9	343	315
0	10	255	280
0	13	166	168
0	14	85	85
1	0	283	294
1	1	491	493
1	2	667	674
1	3	522	519
1	4	128	129
1	5	211	212
1	6	736	742
1	7	291	282
1	8	318	303
1	9	244	256
1	11	216	221
1	12	147	154
1	14	128	123
2	0	567	568
2	1	473	490
2	3	243	232
2	4	422	436
2	5	179	173
2	6	226	225
2	7	228	224
2	8	154	164
2	9	237	224
2	10	211	205
2	11	63	46
2	12	67	54
2	13	134	119
2	14	76	72
3	0	220	225
3	1	64	73
3	2	325	310
3	3	84	75
3	4	100	104
3	5	274	253
3	6	147	141
3	8	259	247
3	9	119	141
3	11	84	87
3	12	124	118
4	0	91	54
4	1	111	94
4	3	76	80
4	4	270	223
4	6	166	138
4	8	166	162
4	12	75	35
5	1	108	92
5	3	86	82
5	8	89	106
7	3	98	56
7	5	97	75
H = -7			
1	0	264	192
1	2	96	85
1	3	209	196
1	4	420	393
1	5	114	89
1	6	147	150
1	7	372	374
1	8	96	49
1	9	102	36
1	10	108	112
2	0	284	275
2	2	309	296
2	3	267	264
2	4	152	142
2	5	66	47
2	6	388	386
2	7	129	116
2	9	78	65
2	10	98	92
2	11	133	140
2	12	115	122
3	0	120	127
3	1	314	305
3	2	160	149
3	3	248	235
3	4	273	271
3	5	115	108
3	6	188	175
3	7	241	210
3	9	116	101
3	10	127	134
3	11	110	115
3	13	98	115
4	0	176	159
4	2	409	375
4	3	293	281
4	4	67	43
4	5	318	297
4	6	217	199
4	7	126	118
4	8	110	116
4	9	94	87
4	10	72	87
4	12	148	160
5	0	108	99
5	1	254	257
5	3	139	122
5	4	225	220
5	5	152	158
5	6	140	133
5	7	177	170
5	8	194	199
5	10	137	144
5	11	125	119
6	0	145	145
6	2	200	194
6	3	124	107
6	4	89	67
6	5	121	112
6	6	165	154
6	7	68	55
6	8	96	112
6	9	147	156
7	0	92	77
7	1	119	131
7	4	167	153
7	5	83	71
H = -6			
0	0	388	395
0	1	828	872
0	2	528	545
0	4	507	550
0	5	568	576
0	6	219	212
0	7	609	675
0	8	264	296
0	9	135	119
0	10	295	318
0	11	222	243
0	12	66	67
0	14	187	188
1	0	645	665
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2	9	86	70
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2	13	79	77
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3	1	184	186
3	2	418	410
3	3	129	137
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3	5	375	383
3	7	141	128
3	8	118	111
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4	3	477	444
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1	6	262	259
1	7	446	405
1	8	101	95
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1	10	310	307
1	11	102	143
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1	13	204	183
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2	1	144	148
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2	7	195	193
2	8	248	234
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2	11	160	155
2	13	89	94
3	0	435	396
3	1	148	141
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3	3	412	384
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3	5	525	499
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3	12	193	182
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6	1	112	98
6	2	70	39
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6	4	206	195
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7	3	61	50
7	5	78	68
H = -2			
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0	7	376	413
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0	10	171	126
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1	0	291	401
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1	5	563	564
1	6	284	288
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1	8	333	334
1	10	268	270
1	11	222	197
1	12	81	60
1	13	139	112
2	0	458	447
2	1	494	424
2	2	388	337
2	3	632	599
2	5	186	199
2	6	440	418
2	7	163	165
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2	9	254	248
2	11	82	91
2	12	170	167
2	13	72	77
3	0	90	98
3	1	517	458
3	2	82	83
3	3	170	172
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3	7	267	257
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6	2	123	128
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7	3	64	64
H = -1			
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1	4	980	949
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1	6	229	229
1	7	195	206
1	8	85	82
1	11	106	97
2	0	501	478
2	2	464	415
2	4	486	483
2	5	523	510
2	7	450	455
2	8	123	123
2	9	79	60
2	10	140	143
2	11	241	231
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3	0	552	530
3	1	143	140
3	2	409	364
3	3	492	468
3	4	317	304
3	5	189	178
3	6	309	298
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3	9	226	216
3	10	183	202
3	12	178	174
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4	2	115	109
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4	7	154	116
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6	2	202	207
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6	4	110	118
6	5	179	181
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7	3	107	109
7	5	86	92
7	6	62	90
H = 0			
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H = 1			
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H = 2			
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7	5	70	53
H = 3			
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7	4	75	93
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2	3	151	159
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2	5	241	241
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2	7	268	278
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2	9	86	95
2	11	133	120
3	0	466	452
3	2	148	171
3	4	260	271
3	5	290	299
3	6	121	131
3	7	114	95
3	9	120	113
4	0	146	82
4	1	260	268
4	2	155	158
4	3	100	115
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H = 5			
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2	4	193	196
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4	3	206	193
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4	6	150	138
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4	9	107	97
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5	2	207	224
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5	4	189	195
5	5	148	137
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6	0	220	232
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6	2	105	112
6	3	219	237
6	4	83	89
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7	1	119	108
7	2	106	114
H = 6			
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0	3	233	256
0	4	190	203
0	5	369	390
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0	7	81	51
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1	3	325	341
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1	5	71	70
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1	7	229	222
1	8	96	108
1	9	110	115
1	10	150	124
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2	4	191	209
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4	7	90	93
4	8	87	97
5	0	145	37
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6	1	72	47
7	0	77	73
H = 7			
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1	3	138	116
1	4	96	107
1	5	93	76
1	8	71	43
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2	1	297	301
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2	3	71	45
2	4	334	347
2	7	94	107
3	0	125	127
3	1	204	208
3	2	244	249
3	3	424	467
3	4	133	122
3	5	246	269
3	6	122	113
3	8	100	84
4	0	171	159
4	1	203	216
4	2	166	156
4	3	147	135
4	4	184	196
4	6	174	169
4	7	196	173
5	0	98	99
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5	2	232	249
5	3	112	113
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6	0	129	145
6	1	203	207
6	3	127	124
6	4	115	94
7	0	81	77
H = 8			
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0	5	241	265
0	6	198	207
0	7	129	121
0	8	144	134
0	9	95	107
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1	2	103	109
1	3	133	136
1	4	369	387
1	5	97	77
1	7	173	218
1	8	130	124
2	0	572	568
2	2	353	382
2	3	210	213
2	4	102	108
2	5	219	227
2	6	121	104
3	0	204	225
3	1	171	179
3	2	233	259
3	3	256	269
3	4	94	90
3	5	124	103
3	7	107	103
3	8	99	49
4	0	111	54
4	2	149	132
4	4	84	30
4	5	107	106
4	6	113	82
5	2	91	79
5	3	80	52
H = 9			
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1	3	121	120
2	1	157	151
2	2	113	103
2	3	112	114
2	4	221	231
2	5	139	126
2	7	99	95
2	8	82	69
3	0	328	337
3	3	259	259
3	4	181	178
3	6	135	119
4	0	166	149
4	1	124	108
4	2	177	161
4	4	190	170
4	5	137	129
5	0	164	169
5	2	133	125
5	3	140	138
6	1	160	143
6	2	94	80
H = 10			
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0	1	280	299
0	2	177	183
0	3	317	350
0	4	219	201
0	5	162	150
0	6	236	219
0	7	108	105
1	1	341	353
1	2	268	274
1	3	89	52
1	4	284	300
1	5	208	196
1	6	97	79
1	7	110	86
2	0	347	342
2	1	249	233
2	2	136	133
2	3	227	204
2	6	103	95
3	0	70	44
3	1	178	175
3	3	94	72
3	4	128	126
3	5	96	81
3	6	70	23
4	1	84	66
4	3	70	41
4	4	107	78
H = 11			
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1	1	85	21
1	2	103	51
1	4	76	50
1	6	72	76
2	0	179	171
2	2	176	176
2	5	119	82
3	0	145	138
3	1	74	84
3	2	110	123
3	3	111	92
4	1	145	148
4	2	75	87
4	3	97	108
4	4	92	39
5	0	163	155
5	1	114	100
6	0	107	77
H = 12			
0	0	275	259
0	1	189	194
0	2	80	98
0	3	244	275
0	4	158	134
0	6	112	98
1	0	162	144
1	1	106	101
1	2	250	245
1	3	134	140
1	5	145	128
2	0	157	141
2	1	120	116
2	2	105	92
2	3	120	105
2	4	129	109
3	0	244	230
3	1	103	108
3	2	85	55
3	3	105	93
4	0	96	68
4	1	96	74
H = 13			
1	0	121	106
1	5	83	24
2	4	66	31
3	0	100	77
3	1	72	65
4	2	130	110
5	0	115	82
H = 14			
0	0	93	41
0	1	108	102
0	2	160	163
0	4	140	128
1	0	141	132
1	1	109	96
1	2	100	99
1	3	118	111
1	4	205	75
2	1	132	106
2	2	78	62
3	0	93	70
3	2	76	80
H = 15			
2	0	93	80
2	1	86	54
3	1	100	78
H = 16			
0	0	129	120
0	1	136	116
1	0	110	87
1	1	109	111
H = 17			
1	0	83	43

[a] The table shows k, l, $10|F_o|$, $10|F_c|$ in blocks of constant h.

Refinement was continued using anisotropic thermal parameters (T) in the form: $T = \exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl)$. Hydrogen atoms were included in calculated positions,[22] each hydrogen atom being assigned an isotropic thermal parameter equal to that of the carbon atom to which it was attached [see Table II]. Neither the positions nor the thermal parameters of the hydrogen atoms were allowed to refine. Positions were, however, redefined with respect to the new carbon positions after each cycle of refinement. Three cycles of refinement of positional and anisotropic thermal parameters led to convergence at $R_F = 0.0819$ and $R_{wF^2} = 0.0264$. Finally the list of observed and calculated structure factors was examined and 16 reflections were removed from the refinement since they were all low-angle reflections having $F_o \ll F_c$ (probably due to the diffracted beam being partially shielded from the counter by the lead backstop—the effect is far too great to be due simply to extinction). Three further cycles of refinement led to convergence (shift/$\sigma < 0.05$ for each parameter) at $R_F = 0.0785$ and $R_{wF^2} = 0.0253$. [The average error in an observation of unit weight is 1.99,

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[22] With d(C–H) = 1.080 Å and the appropriate sp^2 geometry. All calculated positions are close to the center of the peaks observed on the 11.3% difference Fourier.

Table II

Final Atomic Coordinates[a] for $[(CH_2)_2C(CHC_6H_5)]Fe(CO)_3$, Including Isotropic Thermal Parameters Associated[b] with Hydrogen Atoms

Atom	x	y	z	B, Å^2
Fe	0.55054 (8)	0.29552 (18)	0.34137 (10)	...
O(1)	0.3704 (6)	0.4250 (13)	0.3082 (7)	...
O(2)	0.6580 (6)	0.6590 (10)	0.4344 (8)	...
O(3)	0.6104 (7)	0.0807 (14)	0.5684 (7)	...
C(1)	0.5609 (6)	0.1534 (12)	0.2136 (8)	...
C(2)	0.6517 (6)	0.1596 (13)	0.3061 (10)	...
C(3)	0.4988 (7)	0.0333 (12)	0.2347 (8)	...
C(4)	0.5255 (5)	0.3453 (12)	0.1586 (7)	...
C(5)	0.4319 (5)	0.3772 (10)	0.0613 (7)	...
C(6)	0.3870 (6)	0.5620 (12)	0.0473 (7)	...
C(7)	0.3019 (6)	0.5941 (15)	−0.0515 (8)	...
C(8)	0.2638 (6)	0.4523 (17)	−0.1350 (8)	...
C(9)	0.3087 (6)	0.2715 (14)	−0.1242 (8)	...
C(10)	0.3910 (5)	0.2376 (12)	−0.0283 (8)	...
C(11)	0.4416 (7)	0.3777 (14)	0.3219 (9)	...
C(12)	0.6145 (7)	0.5214 (15)	0.3975 (8)	...
C(13)	0.5878 (7)	0.1630 (15)	0.4813 (9)	...
H(21)	0.6963	0.2464	0.2914	5.55
H(22)	0.6766	0.0253	0.3451	5.55
H(31)	0.5238	−0.1013	0.2734	5.06
H(32)	0.4337	0.0289	0.1683	5.06
H(4)	0.5715	0.4714	0.1922	4.61
H(6)	0.4182	0.6797	0.1131	4.30
H(7)	0.2653	0.7337	−0.0626	4.83
H(8)	0.1981	0.4826	−0.2094	5.01
H(9)	0.2793	0.1554	−0.1919	5.05
H(10)	0.4252	0.0953	−0.0222	4.43

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit of the preceding number. [b] Isotropic thermal parameters for hydrogen atoms are equal to the final isotropic parameter of the carbon atoms to which they are bonded (see text).

indicating a slight underestimation in the standard deviations assigned (*vide supra*) to the intensity data.] A final difference-Fourier synthesis showed no significant features, thus confirming the correctness of the structural analysis.

Throughout the analysis, scattering factors for neutral oxygen, carbon, and hydrogen were used.[23a] The values for neutral iron[23b] were corrected to allow specifically both for the real ($\Delta f' = 0.4$ e$^-$) and for the imaginary ($\Delta f'' = 1.0$ e$^-$) components of dispersion.[23c] Observed and calculated structure factors (in electrons × 10.00) are shown in Table I. Final atomic positions are given in Table II. Thermal parameters are collected in Table III, and their associated atomic vibration ellipsoids are defined in Table IV.

The Molecular Structure

Intramolecular distances and their estimated standard deviations (esd's) are shown in Table V; interatomic angles (with esd's) are given in Table VI. The scheme used for numbering atoms is shown in Figure 1.

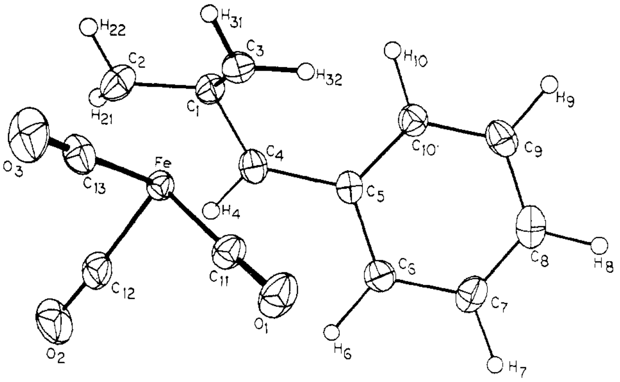

Figure 1.—Numbering of atoms within the $[(CH_2)_2C(CHC_6H_5)]$-$Fe(CO)_3$ molecule. The molecule is shown projected onto the least-squares plane of the phenyl ring. This diagram also shows the 68% probability contours of the atomic vibration ellipsoids. [Constructed using otlips, an IBM 1620 program by P. H. Bird.]

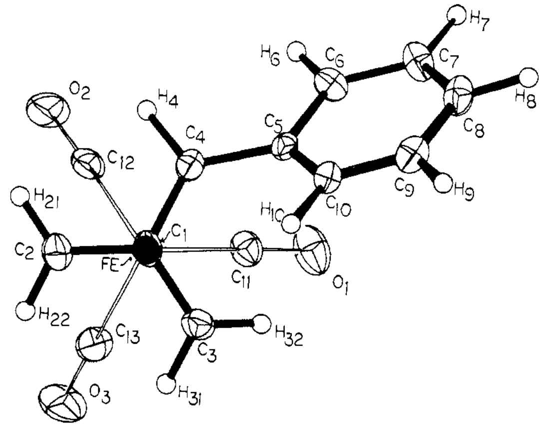

Figure 2.—The molecule projected onto the plane defined by C(2), C(3), and C(4).

The diamagnetic compound may be considered as an Fe(0) derivative in which the d^8 iron atom reaches the anticipated rare gas (Kr) configuration by the donation of two electrons from each of the three carbonyl ligands and four electrons from the trimethylenemethane residue. The iron atom is located directly beneath the central carbon atom of the trimethylenemethane system and is π bonded to all four carbon atoms of this ligand, individual distances being Fe–C(1) = 1.932 ± 0.010 Å, Fe–C(2) = 2.098 ± 0.011 Å, Fe–C(3) = 2.118 ± 0.010 Å, and Fe–C(4) = 2.161 ± 0.009 Å. As may be seen in Figure 2, the phenyltrimethylenemethane ligand and the $Fe(CO)_3$ moiety adopt a mutually staggered conformation.

The Phenyltrimethylenemethane Ligand

The carbon atom skeleton of the trimethylenemethane residue is significantly nonplanar, the central atom [C(1)] being displaced 0.315 Å (*away* from the iron atom) relative to the plane $-0.4763X + 0.4984Y$

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[23] "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962: (a) pp 202, 203; (b) p 210; (c) p 215.

TABLE III

ANISOTROPIC THERMAL PARAMETERS (WITH ESD'S) FOR $[(CH_2)_2C(CHC_6H_5)]Fe(CO)_3$

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	44.8 (0.6)	211.3 (2.7)	66.3 (1.1)	0.1 (2.5)	42.8 (1.2)	17.5 (3.3)
O(1)	73 (5)	618 (27)	130 (8)	157 (20)	101 (10)	50 (26)
O(2)	111 (6)	256 (17)	167 (10)	−148 (18)	−25 (12)	40 (22)
O(3)	130 (7)	592 (29)	96 (8)	−18 (24)	66 (12)	226 (26)
C(1)	44 (4)	278 (22)	82 (8)	43 (17)	43 (10)	−43 (22)
C(2)	48 (5)	332 (25)	138 (12)	66 (19)	76 (12)	64 (29)
C(3)	62 (5)	207 (18)	98 (9)	10 (18)	53 (11)	24 (23)
C(4)	44 (4)	279 (21)	65 (7)	−26 (16)	49 (9)	−43 (20)
C(5)	37 (4)	233 (18)	60 (6)	−28 (15)	45 (8)	15 (19)
C(6)	65 (5)	263 (21)	59 (7)	32 (18)	63 (10)	4 (21)
C(7)	53 (5)	393 (26)	73 (8)	94 (20)	67 (11)	38 (27)
C(8)	44 (5)	486 (33)	73 (8)	−11 (22)	57 (10)	8 (30)
C(9)	58 (5)	342 (27)	78 (8)	−49 (20)	70 (11)	−67 (25)
C(10)	41 (4)	249 (21)	85 (8)	−9 (15)	55 (10)	−16 (21)
C(11)	55 (5)	327 (25)	99 (9)	51 (21)	75 (12)	25 (26)
C(12)	66 (6)	269 (24)	79 (8)	4 (21)	19 (11)	87 (24)
C(13)	74 (6)	339 (28)	84 (9)	−69 (23)	56 (12)	−15 (28)

TABLE IV

DIRECTION COSINES FOR THE ATOMIC VIBRATION ELLIPSOIDS IN $[(CH_2)_2C(CHC_6H_5)]Fe(CO)_3$[a-c]

Atom	B_{max} (dc's major axis)	B_{med} (dc's, median axis)	B_{min} (dc's, minor axis)
Fe	4.15 (−875, 408, 632)	3.74 (478, 812, 80)	3.17 (75, −418, 771)
O(1)	12.36 (−417, −899, 69)	6.34 (−51, −127, 905)	4.32 (−908, 420, 421)
O(2)	18.61 (−863, 233, 793)	6.03 (326, −419, 604)	3.14 (385, 877, 78)
O(3)	14.28 (−770, 600, 544)	10.36 (631, 668, 62)	3.15 (−92, −440, 837)
C(1)	6.12 (−554, −746, 581)	3.76 (167, 334, 749)	3.19 (−815, 576, 319)
C(2)	7.42 (−63, 477, 809)	5.98 (−518, −766, 574)	3.32 (−853, 431, 127)
C(3)	6.13 (−908, 44, 786)	4.73 (412, 291, 580)	3.52 (83, −956, 213)
C(4)	5.10 (−362, 930, 112)	3.57 (−882, −362, 134)	3.17 (−303, −56, 985)
C(5)	4.47 (−438, 893, 291)	3.07 (410, 97, 619)	2.57 (−800, −439, 729)
C(6)	5.93 (−864, −445, 184)	4.29 (−407, 893, 14)	2.71 (−297, 71, 983)
C(7)	7.86 (−434, −884, 43)	3.68 (411, −367, 555)	3.09 (−802, 290, 831)
C(8)	8.55 (−58, 998, 45)	3.81 (608, 19, 429)	3.34 (−792, −59, 902)
C(9)	6.65 (330, −866, 184)	4.40 (−895, −414, 259)	3.39 (−302, 281, 948)
C(10)	4.53 (−26, −809, 534)	4.09 (−253, 573, 809)	3.38 (−967, −128, 246)
C(11)	6.30 (423, 859, 63)	4.79 (−120, −262, 907)	3.90 (−898, 440, 417)
C(12)	8.13 (−886, 284, 731)	5.08 (429, 803, 172)	2.86 (177, −524, 660)
C(13)	7.91 (−817, 577, 368)	5.05 (−553, −780, 512)	4.12 (164, 241, 776)

[a] Direction cosines (dc's) are referred to the monoclinic axes. They have been multiplied by 1000. [b] The atomic vibration ellipsoids are presented in terms of the isotropic thermal parameter B (Å^2). The transformation to root-mean-square displacement is: $(\overline{u^2})^{1/2} = [B/8\pi^2]^{1/2}$. [c] The 68% probability contours of the vibration ellipsoids are illustrated in Figure 1.

TABLE V

INTRAMOLECULAR DISTANCES FOR $[(CH_2)_2C(CHC_6H_5)]Fe(CO)_3$[a]

Atoms	Dist, Å	Atoms	Dist, Å	Atoms	Dist., Å	Atoms	Dist., Å
(a) Bond Distances				(b) Intramolecular Contacts (⩽3.5 Å)			
C(1)–C(2)	1.405 (13)	Fe–C(1)	1.932 (10)	Fe···C(5)	3.189 (9)	C(12)···C(4)	2.910 (12)
C(1)–C(3)	1.406 (13)	Fe–C(2)	2.098 (11)	Fe···H(4)	2.36	C(12)···C(2)	2.839 (13)
C(1)–C(4)	1.436 (12)	Fe–C(3)	2.118 (10)	Fe···H(21)	2.74	C(13)···C(2)	2.831 (13)
C(4)–C(5)	1.472 (11)	Fe–C(4)	2.162 (09)	Fe···H(22)	2.71	C(13)···C(3)	2.884 (13)
C(5)–C(6)	1.396 (12)	Fe–C(11)	1.768 (11)	Fe···H(31)	2.74	O(1)···H(6)	3.35
C(5)–C(10)	1.370 (11)	Fe–C(12)	1.776 (11)	Fe···H(32)	2.77	O(2)···H(4)	2.97
C(6)–C(7)	1.392 (13)	Fe–C(13)	1.802 (12)	C(11)···C(3)	2.865 (12)	O(2)···H(21)	3.48
C(7)–C(8)	1.331 (14)	O(1)–C(11)	1.139 (13)	C(11)···C(4)	2.946 (12)	O(3)···H(22)	3.45
C(8)–C(9)	1.379 (14)	O(2)–C(12)	1.118 (13)				
C(9)–C(10)	1.351 (13)	O(3)–C(13)	1.121 (14)				

[a] Esd's, shown in parentheses, are right-adjusted to the last digit of the preceding number.

TABLE VI

BOND ANGLES WITHIN THE $[(CH_2)_2C(CHC_6H_5)]Fe(CO)_3$ MOLECULE[a]

Fe-C(11)-O(1)	178.0 (1.0)	C(5)-C(6)-C(7)	120.0 (0.8)
Fe-C(12)-O(2)	177.1 (1.0)	C(6)-C(7)-C(8)	120.7 (0.9)
Fe-C(13)-O(3)	179.5 (1.0)	C(7)-C(8)-C(9)	119.9 (1.0)
C(11)-Fe-C(12)	99.7 (0.5)	C(8)-C(9)-C(10)	120.0 (0.9)
C(11)-Fe-C(13)	99.0 (0.6)	C(9)-C(10)-C(5)	122.1 (0.8)
C(12)-Fe-C(13)	98.5 (0.5)	C(1)-C(4)-C(5)	124.3 (0.8)
C(2)-C(1)-C(3)	116.2 (0.9)	C(10)-C(5)-C(6)	117.2 (0.8)
C(2)-C(1)-C(4)	114.4 (0.8)	Fe-C(1)-C(2)	76.1 (0.6)
C(3)-C(1)-C(4)	115.0 (0.8)	Fe-C(1)-C(3)	77.0 (0.6)
C(4)-C(5)-C(6)	121.2 (0.7)	Fe-C(1)-C(4)	78.3 (0.5)
C(4)-C(5)-C(10)	117.2 (0.8)		

[a] See footnote *a*, Table V.

TABLE VII

IMPORTANT PLANES WITHIN THE $[(CH_2)_2C(CHC_6H_5)]Fe(CO)_3$ MOLECULE[a-c]

Atoms	Dev, Å	Atoms	Dev, Å
I: $-0.7810X - 0.3786Y + 0.4964Z = -5.8591$			
C(5)*	+0.017 (8)	C(8)*	+0.008 (10)
C(6)*	−0.014 (9)	C(9)*	−0.004 (10)
C(7)*	+0.002 (10)	C(10)*	−0.008 (9)
II: $-0.4763X + 0.4984Y + 0.7243Z = -1.2340$			
C(2)*	0.000	Fe	+1.616 (5)
C(3)*	0.000	C(1)	−0.315 (9)
C(4)*	0.000		
III: $-0.7163X + 0.1763Y + 0.6751Z = -3.8988$			
C(4)*	0.000	C(7)	+0.46 (1)
H(4)*	0.000	C(8)	−0.23 (1)
C(5)*	0.000	C(9)	−0.84 (1)
C(6)	+0.58 (1)	C(10)	−0.73 (1)

Dihedral Angles: I-II, 57° 8′; I-III, 34° 7′; II-III, 23° 21′

[a] Planes are defined as $c_1X + c_2Y + c_3Z = d$, where X, Y, Z are Cartesian coordinates which are related to the monoclinic cell coordinates (x, y, z) by the transformations: $X = xa + zc \cos \beta$, $Y = yb$, $Z = zc \sin \beta$. [b] Least-squares planes are calculated using unit weights for all atoms marked with an asterisk. [c] Esd's are shown in parentheses.

$+ 0.7243Z = -1.2340$,[24] which passes through the terminal carbon atoms C(2), C(3), and C(4) [see Table VII]. The trigonal-pyramidal conformation of the trimethylenemethane residue is emphasized by the angles Fe-C(1)-C(2), Fe-C(1)-C(3), and Fe-C(1)-C(4), which are 76.1 ± 0.6, 77.0 ± 0.6, and 78.3 ± 0.5°, respectively.

Carbon-carbon distances within the trimethylenemethane moiety are: C(1)-C(2) = 1.405 ± 0.013 Å, C(1)-C(3) = 1.406 ± 0.013 Å, and C(1)-C(4) = 1.436 ± 0.012 Å (average 1.416 Å). Interatomic angles are: C(2)-C(1)-C(3) = 116.2 ± 0.9, C(2)-C(1)-C(4) = 114.4 ± 0.8, and C(3)-C(1)-C(4) = 115.0 ± 0.8° (average 115.2°).

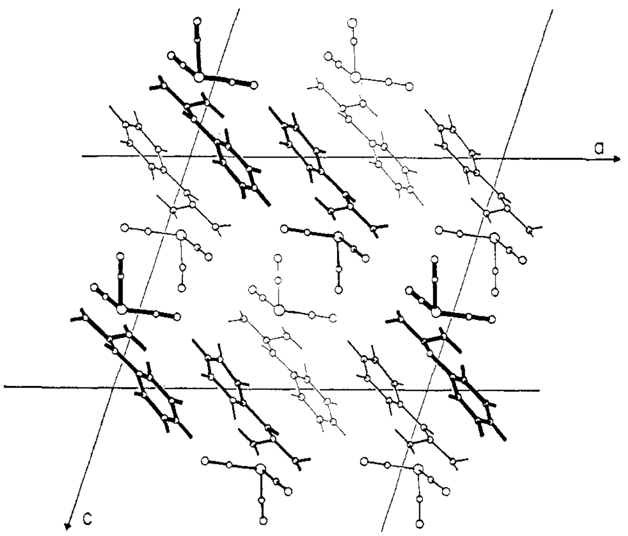
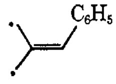


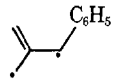
Figure 3.—Packing diagram for $[(CH_2)_2C(CHC_6H_5)]Fe(CO)_3$. The crystal is viewed down *b*.

As may be seen in Figure 1, the phenyl substituent has the expected D_{6h} symmetry within the limits of experimental error. Individual carbon-carbon distances vary from 1.331 ± 0.014 to 1.396 ± 0.012 Å (average 1.363 Å), bond angles range from 117.2 ± 0.8 to 122.1 ± 0.8° (average 120.0°), and the six carbon atoms have a root-mean-square deviation of only 0.010 Å from the least-squares plane:[24] $-0.7810X - 0.3787Y + 0.4964Z = -5.8591$. The phenyl group is not fully conjugated with the trimethylenemethane ligand as can be seen from two measurements. (i) The plane of the carbon atom adjacent to the phenyl ring [*i.e.*, C(4), H(4), C(5)] makes an angle of 34° 7′ with the phenyl group, indicating that the pπ–pπ overlap integral for the C(4)–C(5) bond is reduced to approximately 83% of the value it would take if C(4), H(4), and C(5) were coplanar with the phenyl group. (ii) The C(4)–C(5) bond distance of 1.472 ± 0.011 Å is not distinguishable from the C(sp^2)–C(sp^2) *single* bond distance of 1.465 ± 0.005 Å.[25]

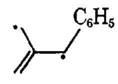
A final rather interesting geometric feature of the phenyltrimethylenemethane ligand concerns the fact that the Fe–C(4) bond distance of 2.162 ± 0.009 Å is significantly longer than the average (2.108 ± 0.008 Å) of the Fe–C(2) and Fe–C(3) distances; similarly the C(1)–C(4) bond is longer (although by only ~2σ) than the C(1)–C(2) and C(1)–C(3) bonds. A possible explanation for this involves a consideration of the resonance forms of the phenyltrimethylenemethane ligand



II



III



IV

Canonical structures III and IV are energetically more favorable than structure II, since they involve an unpaired electron adjacent to the electron-withdrawing phenyl group. Carried forward to the metal complex this leads to the prediction that (*as observed*)

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(24) Cartesian coordinates—see Table VII, footnote *a*.

(25) "Tables of Interatomic Distances and Configuration in Molecules and Ions," Supplement 1956–1959, Special Publication No. 18, The Chemical Society, London, 1965, p S15s.

TABLE VIII

INTERMOLECULAR CONTACTS (TO 3.4 Å) WITHIN THE $[(CH_2)_2C(CHC_6H_5)]Fe(CO)_3$ CRYSTAL

Atoms	Transformation	Dist, Å
O(1)···H(9)	$-x + 1/2, y + 1/2, -z$	2.68
H(21)	$x - 1/2, -y + 1/2, z$	2.98
H(7)	$-x + 1/2, y - 1/2, -z$	3.13
H(8)	$-x + 1/2, y - 1/2, -z$	3.18
O(2)···H(31)	$x, y + 1, z$	2.71
H(22)	$x, y + 1, z$	2.75
O(3)···C(3)	$-x + 1, -y, -z + 1$	3.38
H(8)	$x + 1/2, -y + 1/2, z + 1$	2.52
C(1)···H(10)	$-x + 1, -y, -z$	3.00
C(2)···H(9)	$-x + 1, -y, -z$	3.02
C(3)···H(6)	$x, y - 1, z$	2.78
H(8)	$-x + 1/2, y - 1/2, -z$	3.10
C(5)···H(4)	$-x + 1, -y + 1, -z$	3.31
H(7)	$-x + 1/2, y - 1/2, -z$	3.36
C(6)···H(4)	$-x + 1, -y + 1, -z$	3.37
H(7)	$-x + 1/2, y - 1/2, -z$	3.37
H(32)	$x, y + 1, z$	3.37
C(7)···H(21)	$-x + 1, -y + 1, -z$	3.20
H(7)	$-x + 1/2, y - 1/2, -z$	3.22
H(4)	$-x + 1, -y + 1, -z$	3.30
C(8)···H(21)	$-x + 1, -y + 1, -z$	3.07
H(7)	$-x + 1/2, y - 1/2, -z$	3.09
C(8)···H(32)	$-x + 1/2, y + 1/2, -z$	3.10
H(4)	$-x + 1, -y + 1, -z$	3.13
C(9)···H(4)	$-x + 1, -y + 1, -z$	3.00
H(7)	$-x + 1/2, y - 1/2, -z$	3.10
C(10)···H(4)	$-x + 1, -y + 1, -z$	3.08
H(7)	$-x + 1/2, y - 1/2, -z$	3.24
C(11)···H(8)	$-x + 1/2, y - 1/2, -z$	3.33
C(12)···H(31)	$x, y + 1, z$	2.96
H(21)···H(8)	$-x + 1, -y + 1, -z$	2.98
H(9)	$-x + 1, -y, -z$	3.04
H(7)	$-x + 1, -y + 1, -z$	3.21
H(31)···H(6)	$x, y - 1, z$	2.44
H(4)	$x, y - 1, z$	3.22
H(8)	$-x + 1/2, y - 1/2, -z$	3.38
H(32)···H(6)	$x, y - 1, z$	2.39
H(8)	$-x + 1/2, y - 1/2, -z$	2.45
H(7)	$-x + 1/2, y - 1/2, -z$	3.20
H(6)···H(10)	$x, y + 1, z$	3.26
H(8)	$-x + 1/2, y + 1/2, -z$	3.34
H(7)···H(9)	$x, y + 1, z$	3.29
H(10)···H(10)	$-x + 1, -y, -z$	2.58

the Fe–C(4) and C(1)–C(4) distances should be greater than the other iron–carbon and carbon–carbon bond lengths of the system. This will, however, operate as only a minor perturbation on the bonding scheme outlined below.

Trimethylenemethane–Iron Bonding

A qualitative picture of trimethylenemethane-to-metal bonding may be obtained from simple Hückel molecular orbital theory. Using point group D_3 (which is the lowest possible for unperturbed trimethylenemethane, *vide supra*) the four $p\pi$ orbitals can be shown to form the basis for molecular orbitals of symmetry A_2 (twice) and E. If the individual atomic $p\pi$ orbitals are labeled ϕ_1 through ϕ_4 (with ϕ_1 being associated with the *central* carbon atom) then, neglecting overlap, the appropriate orthonormalized molecular orbitals (with their energies) are

$$A_2(1) = \frac{1}{\sqrt{6}}(\sqrt{3}\phi_1 + \phi_2 + \phi_3 + \phi_4),\ E = \alpha + \sqrt{3}\beta$$

$$\left.\begin{aligned} E(a) &= \frac{1}{\sqrt{2}}(\phi_2 - \phi_4) \\ E(b) &= \frac{1}{\sqrt{6}}(\phi_2 - 2\phi_3 + \phi_4) \end{aligned}\right\} E = \alpha$$

$$A_2(2) = \frac{1}{\sqrt{6}}(-\sqrt{3}\phi_1 + \phi_2 + \phi_3 + \phi_4),\ E = \alpha - \sqrt{3}\beta$$

The lowest lying ligand orbital, $A_2(1)$, has symmetry appropriate for overlap with any combination of metal s, p_z and d_{z^2} orbitals; energetically (by comparison with ferrocene[26]) it is probable that a $d_{z^2}s$ hybrid will be used. The next lowest trimethylenemethane energy level is doubly degenerate (*i.e.*, has E symmetry) and may overlap with the d_{xy} and d_{yz} orbitals of the iron atom. The highest molecular orbital, $A_2(2)$, is antibonding and will not be utilized to any appreciable extent.

The $Fe(CO)_3$ Group

Within experimental error, the $Fe(CO)_3$ group has exact C_{3v} symmetry. Individual OC–Fe–CO angles vary from 98.5 ± 0.5 to 99.7 ± 0.5° and average 99.1°. Average Fe–CO and C–O bond lengths are 1.782 and 1.126 Å, in good agreement with values observed in such other $Fe(CO)_3$-containing species as $C_6F_8Fe(CO)_3$[27] [1.802 and 1.126 Å] and $C_{10}H_8Fe_2(CO)_5$[28] [1.780 and 1.128 Å].

Intermolecular Contacts

The molecular packing within the crystal lattice (viewed down *b*) is shown in Figure 3. Quantitative data on intermolecular contacts are collected in Table VIII. The individual molecules of $[(CH_2)_2C(CHC_6H_5)]Fe(CO)_3$ are separated by normal van der Waals distances, closest approaches (of each type) being: oxygen···carbon, 3.38 Å; oxygen···hydrogen, 2.52 Å; carbon···hydrogen, 2.78 Å; and hydrogen···hydrogen, 2.39 Å.[29]

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(28) M. R. Churchill, *Inorg. Chem.*, **6**, 190 (1967).

(29) NOTE ADDED IN PROOF.—An electron diffraction study of unsubstituted trimethylenemethaneiron tricarbonyl [A. Almenningen, H. Haaland, and K. Wahl, *Chem. Commun.*, 1027 (1968)] shows the molecular geometry of this species to be substantially the same as the present phenyl-substituted complex.