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Studies of some Carbon Compounds of the Transition Metals. IV. The Structure of Butadiene Irontricarbonyl

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The structure of the complex $C_4H_6Fe(CO)_3$, prepared from butadiene and iron pentacarbonyl, has been determined, at -40 °C, by three-dimensional Fourier methods and refined by least-squares techniques. The compound crystallizes in the orthorhombic system, space group *Pnma*, with four molecules in a unit cell of dimensions $a = 11.6$, $b = 11.1$, $c = 6.2$ Å. The molecule contains the butadiene group in the cisoid form π-bonded to the iron atom to which are also bonded the carbonyl groups in roughly trigonal arrangement. The Fe–C(butadiene) distances are 2.06 and 2.14 Å, whilst the average Fe–C(carbonyl) distance is 1.76 Å. The C–C distances are 1.46 and 1.45 Å and are in agreement with delocalization of the π-electrons.

Introduction

Although Rheilen, Gruhl, Hessling & Pfrengle (1930) first reported the preparation of butadiene irontricarbonyl, it has only recently been reinvestigated (Hallam & Pauson, 1958) and reformulated as a π-complex (II). The earlier structural proposal of Rheilen *et al.* (I) would yield a 34-electron configuration in conflict with the observed diamagnetism and remarkable chemical stability. More recently, Green, Pratt & Wilkinson (1959), mainly on the basis of nuclear magnetic resonance measurements, have considered in addition the structure (III). To determine the exact structural geometry in the hope of being able to infer the type of bonding possible within the molecule, a three-dimensional X-ray analysis was undertaken. A preliminary report of the structure has been published (Mills & Robinson, 1960).

Experimental

A sample of butadiene irontricarbonyl was kindly supplied by Prof. Pauson and approximately 1 cm
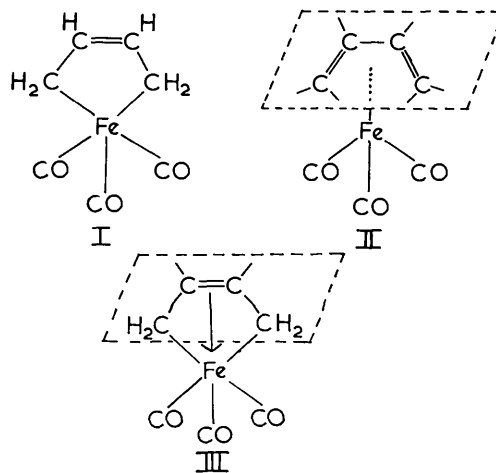
of the liquid was placed in a Lindemann glass tube (0.2 mm diameter). The sample was cooled by a stream of cold nitrogen whilst mounted inside the low-temperature equipment supplied with the Nonius

Table 1. *Final positional parameters and estimated standard deviations*

	x/a	y/b	z/c	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Fe	0·0788	$\frac{1}{4}$	0·1000	0·002 Å	0 Å	0·002 Å
C(1)	−0·0434	$\frac{1}{4}$	−0·0634	0·013	0	0·013
O(1)	−0·1271	$\frac{1}{4}$	−0·1717	0·010	0	0·010
C(2)	0·1630	0·1345	−0·0194	0·008	0·015	0·008
O(2)	0·2144	0·0585	−0·0928	0·007	0·011	0·007
C(4)	0·0012	0·1226	0·3154	0·011	0·016	0·009
C(5)	0·0997	0·1848	0·4082	0·010	0·011	0·008

Weissenberg goniometer. A single crystal was eventually grown in the tip and subsequently maintained at −40 °C throughout the analysis. Oscillation and Weissenberg photographs, taken with Co $K\alpha$ radiation, yielded the following data.

Butadiene irontricarbonyl $C_4H_6Fe(CO)_3$, m.p. 19 °C.
Formula weight 193·97.
Orthorhombic

$a = 11·6$, $b = 11·1$, $c = 6·2$ Å, all $\pm 0·1$ Å.

D_m (in aq. zinc chloride at 0 °C) *ca.* 1·5 g.cm^{-3}.
D_c (at −40 °C) 1·61 g.cm^{-3}.
Number of molecules per unit cell, $Z = 4$.
Systematic absences:

$hk0$ absent when $h = 2n + 1$ and
$0kl$ absent when $k + l = 2n + 1$.

Possible space groups $Pnma$ and $Pn2_1a$.
Linear absorption coefficient: $\mu = 40$ cm^{-1}.

Three-dimensional intensity data were collected by the equi-inclination technique. Because of the difficulty of growing crystals in other orientations, only those levels perpendicular to the b axis were collected ($h0l$ to $h5l$) and these were estimated visually by the multiple-film method. In this way 390 reflexions were included of which 21 were too weak to be measured. The data were processed and put on an approximately absolute scale with the programme written for the Mercury computer by Dr J. Bland (Mills & Rollett, 1961).

Solution of the structure

A two-dimensional Patterson synthesis projected down the b axis gave the (x, z) iron positions and an electron-density projection was calculated with phases based on this atom alone. The molecule was not recognized in this projection, because of the considerable overlap which occurs near the origin, and so we turned directly to the three-dimensional data.

The space group $Pnma$ requires the molecule to have mirror symmetry, and so the Fe atoms must lie in the planes $y = \frac{1}{4}, \frac{3}{4}$; if the space group is $Pn2_1a$, the y coordinate of one atom is arbitrary and we can set that of the Fe atom to $\frac{1}{4}, \frac{3}{4}$. The coordinates of the iron atom are thus completely determined by the (010) projection.

The first three-dimensional electron-density synthesis was based on phases from the iron atoms alone.

This synthesis thus contained mirror planes at $y = \frac{1}{4}, \frac{3}{4}$ irrespective of the true space group. The trigonal arrangement of CO groups was clearly recognizable with one CO group in the mirror plane. There was no evidence of two 'half sets' of tricarbonyl groups and we conclude that the true space group is $Pnma$ and subsequent calculations were based upon this symmetry. A second synthesis, with phases based upon the Fe(CO)$_3$ group, was calculated from those reflexions for which $|F_c| > \frac{1}{8}$th of the maximum iron contribution for the reflexion. The whole molecule was revealed at this stage and the agreement index $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ for non-zero intensities was 29%. The successive levels were scaled onto the trial structure and after two difference syntheses R was 21·9%.

The refinement was completed by least-squares methods. The scattering factors used were those of Berghuis *et al.* (1955) for carbon and oxygen and that of Freeman & Wood (1959) for iron. An allowance was made for the anomalous scattering by iron, due to the proximity of the absorption edge to the wavelength used, by subtracting 3·8 electrons over the whole range before application of the temperature factor. The refinement was carried out on the Mercury computer with the SFLS programme written by Dr J. S. Rollett (Mills & Rollett, 1961). When the shifts were negligibly small, the R factor for all non-zero reflexions was 7·7%. Estimated standard deviations of the positional parameters were obtained from the diagonal elements of the inverted 3×3 matrices used to obtain the final (negligible) shifts. From these the average standard deviations were found to be 0·002 Å for Fe, 0·009 Å for oxygen and 0·011 Å for carbon. The final positional parameters, together with standard deviations, are given in Table 1 and thermal

Table 2. *Thermal exponent coefficients*

Allowance was made for anisotropic thermal motion by the expression

$$2^{-10-4}(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$$

for the thermal exponent

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Fe	48	77	152	−1	0	0
C(1)	74	234	220	−7	0	0
O(1)	96	391	379	−216	0	0
C(2)	93	52	276	−32	96	−128
O(2)	157	73	501	14	111	−98
C(4)	184	129	217	−4	−173	122
C(5)	146	138	160	58	0	87

parameters in Table 2. The calculated reflexion 011 was always greater than that observed, and was omitted from the least-squares refinement on the

Table 3. Interatomic distances and angles

The bond-length errors listed are three standard deviations (excluding errors in the unit-cell parameters)

Fe–C(4), Fe–C(7)	2.14 ± 0.04 Å	Fe–C(1)–O(1)	179°
Fe–C(5), Fe–C(6)	2.06 ± 0.03	Fe–C(2)–O(2)	178
Fe–C(2), Fe–C(3)	1.77 ± 0.03	Fe–C(4)–C(5)	67
Fe–C(1)	1.74 ± 0.04	Fe–C(5)–O(4)	73
C(4)–C(5), C(6)–C(7)	1.46 ± 0.05	C(4)–C(5)–C(7)	118
C(5)–C(6)	1.45 ± 0.06	C(1)–Fe–C(2)	102
C(1)–O(1)	1.18 ± 0.05	C(2)–Fe–C(3)	93
C(2)–O(2), C(3)–O(3)	1.13 ± 0.04	C(2)–Fe–C(4)	91
C(2)–C(3)	2.56 ± 0.05	C(4)–Fe–C(7)	83
C(3)–C(7)	2.80 ± 0.05		
C(4)–C(7)	2.83 ± 0.05		

The standard deviation of the difference between Fe–C(4) and Fe–C(5) is 0.016 Å.

supposition that this was due to extinction. The 'unobserved' reflexions were also omitted.

Bond lengths and angles were calculated with the programme written by Dr R. A. Sparks and are shown in Table 3.

Discussion of the structure

The structure (Fig. 1) is essentially that suggested by Hallam & Pauson with the butadiene residue in a cisoid arrangement. The space group implies that the molecule has m-symmetry: the mirror plane passes through the atoms O(1), C(1) and Fe, and bisects the C(5)–C(6) bond, which requires the atoms C(4), C(5), C(6) and C(7) of the butadiene residue to be strictly coplanar. The trigonal axis of the carbonyl groups makes an angle of 61° with this plane. The iron–carbon distances (2.14 and 2.06 Å; Fe–C(4)–C(5) 67° and Fe–C(5)–C(4) 73°) seem to exclude the possibility of

Table 4. Observed and calculated structure factors

These are arranged in the order k, h, l, $10|F_o|$, $10|F_c|$

l	10|Fo|	10Fc
*k 0 h 0		
*0 0		
2	560	586
4	498	-495
6	218	-202
*0 1		
1	567	722
2	167	143
3	132	99
4	197	171
5	231	-247
6	56	59
*0 2		
0	497	452
1	622	-678
2	305	-234
3	488	-469
4	189	-168
5	46	49
6	82	-68
*0 3		
1	531	-530
2	773	-773
3	168	132
4	204	-205
5	192	-191
6	93	82
*0 4		
0	286	-284
1	645	-666
2	228	-189
3	694	-741
4	83	86
5	105	-110
6	60	75
*0 5		
1	29	21
2	205	-198
3	303	285
4	232	-235
5	27	-17
6	14	-4
*0 6		
0	380	-362
1	226	203
2	145	-127
3	70	66
4	348	355
5	45	-40
6	233	270
*0 7		
1	389	-388
2	74	53
3	192	170
4	64	-59
5	220	222
*0 8		
0	181	-170
1	132	121
2	225	-209
3	164	160
4	95	95
5	43	22
*0 9		
1	171	-174
2	141	130
3	59	-51
4	80	86
*0 10		
0	113	104
1	119	118
2	65	-55
3	226	206
4	87	-90
*0 11		
1	0	17
2	163	165
3	39	26
*0 12		

l	10|Fo|	10Fc
0	171	160
1	0	14
2	77	70
*1 0		
1	575	-460
3	445	-428
5	60	59
*1 1		
1	404	-392
2	156	80
3	147	-128
4	216	-189
5	101	91
6	173	176
*1 2		
0	983	-972
1	626	-577
2	556	-520
3	349	-329
4	272	261
5	56	52
6	201	210
*1 3		
1	119	-68
2	179	-158
3	56	43
4	124	-102
5	179	184
6	19	31
*1 4		
0	336	-344
1	35	-16
2	18	8
3	415	389
4	326	364
5	91	94
6	200	174
*1 5		
1	175	-152
2	331	344
3	272	267
4	122	117
5	169	174
6	59	-44
*1 6		
0	146	-118
1	275	202
2	130	107
3	442	481
4	76	66
5	46	45
6	40	-45
*1 7		
1	0	-6
2	332	377
3	0	-12
4	44	43
5	94	-85
*1 8		
0	391	389
1	158	143
2	96	90
3	158	131
4	251	-254
5	35	-51
*1 9		
1	255	269
2	147	146
3	123	-104
4	34	-34
*1 10		
0	325	358
1	116	-103
2	90	83
3	133	-129
4	99	-120
*1 11		
1	204	196

l	10|Fo|	10Fc
2	135	-147
3	20	-21
*1 12		
0	0	44
1	162	-162
2	0	7
*2 0		
2	209	-188
4	366	344
6	189	188
*2 1		
1	492	-532
2	557	573
3	180	170
4	126	99
5	191	173
6	73	-62
*2 2		
0	818	-929
1	682	759
2	325	-285
3	593	617
4	305	264
5	0	5
6	179	166
*2 3		
1	271	241
2	403	401
3	56	-58
4	82	78
5	115	110
6	78	-66
*2 4		
0	650	683
1	282	283
2	63	49
3	397	387
4	214	-199
5	63	55
6	87	-83
*2 5		
1	399	397
2	344	330
3	198	-175
4	224	229
5	161	-158
6	45	-26
2 6		
0	504	513
1	24	16
2	133	119
3	208	176
4	240	-238
5	66	61
6	117	-167
*2 7		
1	150	170
2	51	-38
3	36	-16
4	54	45
5	155	-155
*2 8		
0	185	170
1	255	-244
2	128	118
3	250	-242
4	89	-86
5	0	-10
*2 9		
1	185	178
2	189	-188
3	0	21
4	108	-117
*2 10		
0	0	-15
1	90	-85
2	0	10
3	156	-147

l	10|Fo|	10Fc
4	24	19
*2 11		
1	67	-74
2	100	-101
3	0	-9
*2 12		
0	146	-152
1	45	-38
2	59	-63
*3 0		
1	262	265
3	690	749
5	74	74
*3 1		
1	407	-372
2	514	467
3	55	-44
4	112	90
5	95	-91
6	95	-87
*3 2		
0	56	41
1	240	-203
2	82	69
3	77	63
4	262	-260
5	39	-32
6	185	-194
*3 3		
1	502	505
2	40	30
3	105	-149
4	211	-198
5	287	-301
6	0	4
*3 4		
0	741	789
1	110	-83
2	295	260
3	124	-101
4	258	-279
5	50	-43
6	129	-135
*3 5		
1	216	235
2	34	-32
3	108	-85
4	162	-161
5	50	-43
6	88	105
*3 6		
0	121	-101
1	364	-376
2	121	-100
3	341	-345
4	43	19
5	33	32
*3 7		
1	136	-133
2	408	-400
3	91	-66
4	157	-164
5	60	61
*3 8		
0	298	-294
1	240	-232
2	188	-124
3	142	-129
4	100	83
5	41	48
*3 9		
1	248	-256
2	20	3
3	69	55
4	18	-5
*3 10		
0	302	-330
1	62	45

l	10|Fo|	10Fc
2	40	-43
3	120	117
4	168	169
*3 11		
1	121	-121
2	140	142
3	75	77
*3 12		
0	0	-12
1	106	102
*4 0		
2	135	127
4	379	-382
6	247	-263
*4 1		
1	527	557
2	350	-354
3	370	-377
4	108	-96
5	218	-191
6	0	25
*4 2		
0	269	266
1	410	-414
2	324	322
3	367	-374
4	109	-89
5	37	-34
6	121	-127
*4 3		
1	269	299
2	516	-565
3	72	65
4	210	-195
5	97	103
6	97	88
*4 4		
0	322	-332
1	327	-287
2	222	205
3	348	-347
4	183	171
5	27	-18
6	0	7
*4 5		
1	274	-275
2	230	-221
3	30	9
4	130	-130
5	177	179
*4 6		
0	589	-622
1	32	14
2	196	-152
3	81	-78
4	118	104
5	45	-34
*4 7		
1	320	-318
2	93	98
3	83	-79
4	43	-27
5	162	185
*4 8		
0	248	-258
1	117	102
2	58	-46
3	105	98
4	140	128
*4 9		
1	38	28
2	152	157
3	0	13
4	87	83
*4 10		
0	50	49
1	113	96
2	78	69

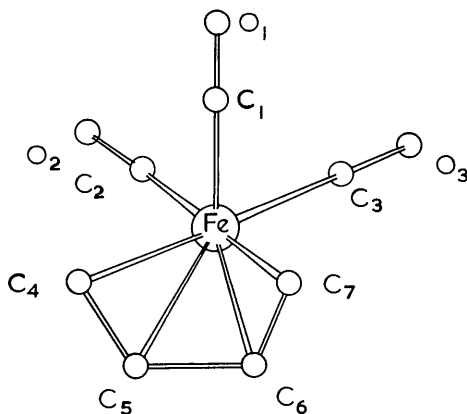| l	10|Fo|	10Fc
3	170	170
*4 11		
1	60	71
2	128	129
*4 12		
0	20	30
1	53	42
*5 0		
1	180	126
3	140	-156
5	53	-57
*5 1		
1	295	-281
2	409	-406
3	152	152
4	129	-110
5	246	262
6	62	86
*5 2		
0	205	-207
1	102	-149
2	13	-20
3	282	-285
4	256	253
5	0	-1
6	129	142
*5 3		
1	178	-184
2	200	-189
3	97	79
4	124	102
5	208	221
6	47	50
*5 4		
0	321	-282
1	187	184
2	130	-105
3	213	206
4	82	75
5	33	34
*5 5		
1	354	-344
2	358	362
3	53	21
4	242	244
5	99	92
*5 6		
0	279	-289
1	222	203
2	17	-10
3	193	178
4	104	96
5	67	-69
*5 7		
1	220	218
2	170	143
3	66	47
4	80	64
5	51	-48
*5 8		
0	372	372
1	179	194
2	186	184
3	126	-118
4	102	-87
*5 9		
1	281	268
2	90	77
3	90	-90
4	49	56
*5 10		
0	145	128
1	17	21
2	0	-2
3	36	-16
*5 11		
1	39	30
2	171	-179

Fig. 1. Schematic representation of molecular geometry.

a simple σ-bond between the iron atom and any of the carbons, and the bonding is essentially that of a π-complex. The Fe atom is closer to the centres of the butadiene bonds than to the carbons themselves: Fe–(C4–C5) 1·97 Å and Fe–(C5–C6) 1·92 Å. The C–C bond lengths, 1·45 and 1·46 Å, are identical within the rather large experimental error, and we cannot be certain from these results that they are significantly shorter than a C–C single bond formed between two sp^2 hybridized atoms as in butadiene itself, where a value of $1·48 \pm 0·01$ Å has been determined (Almenningen, Bastiansen & Traetteberg, 1958). The lengths of those bonds, originally double in butadiene itself, have undoubtedly increased, and the values reported are consistent with complete delocalization of the π-electrons.

The coordination of the Fe atom can be described as square pyramidal, the base of the pyramid being formed by two of the carbons of the linear carbonyls and the terminal carbon atoms of the butadiene. The Fe atom is displaced 0·18 Å out of the basal plane in the direction of the third carbonyl group. This feature is similar to those found in $Fe_2(COH)_2(CO)_6MeCCMe$ (Hock & Mills, 1961), and $Co_2(CO)_9HCCH$ (Mills & Robinson, 1959). The mean Fe–C (carbonyl) distance of 1·76 Å is in good agreement with those found in related compounds, e.g. $Fe_2(COH)_2(CO)_6MeCCMe$, $Fe_2(CO)_4(C_5H_5)_2$ (Mills, 1958) and $C_8H_8Fe_2(CO)_6$ (Dickens & Lipscomb, 1961a).

The two Fe–C distances, 2·14 and 2·06 Å, are, on the basis of probability estimations (Cruickshank & Robertson, 1953), significantly different, and this same feature has since been observed in two cyclo-octatetraene derivatives (Dickens & Lipscomb, 1961a,

1961b) and in two tropolone derivatives (Dodge & Schomaker, 1961; Dahl, 1961), where the same geometry of a four-carbon-atom conjugated double-bond system prevails although in these cases the terminal carbon atoms are now members of cyclic systems.

If the hydrogen atoms attached to the terminal carbons in the butadiene residue are not coplanar with the carbon atoms, but instead are arranged so that one is directed towards the adjacent carbon position in one of these cyclic systems, then the proton resonances reported by Green et al. are explained.

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