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Structural Studies of Organonitrogen Compounds of the Transition Elements. III. The Crystal and Molecular Structure of μ-Methazo-bis(tricarbonyliron)[1,2]

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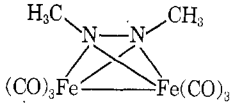
The crystal and molecular structure of μ-methazo-bis(tricarbonyliron), $[CH_3NFe(CO)_3]_2$, has been determined by a single-crystal X-ray analysis. This compound crystallizes in space group C_{2h}^2-$P2_1/m$ of the monoclinic crystal system with two dimeric molecules in a unit cell of dimensions $a = 7.326$ (8) Å, $b = 13.090$ (14) Å, $c = 6.913$ (8) Å, and $\beta = 96°\ 44'$ (1′). Observed and calculated densities are 1.66 (2) and 1.70 g/cm^3, respectively. Full-matrix anisotropic least-squares refinement of 659 independent counter data yielded a final conventional R factor of 2.8%. The dimeric $[CH_3NFe(CO)_3]_2$ molecule contains two $Fe(CO)_3$ groups related by a crystallographic mirror plane and doubly bridged through the nitrogen atoms of the H_3C–N–N–CH_3 ligand. The over-all molecular symmetry is approximately C_{2v}-2mm. The two bridging nitrogen atoms are bonded to each other at a distance of 1.366 (8) Å, resulting in an acute N–Fe–N angle of 42.7 (2)°. Other molecular parameters which differ significantly from those of related nitrogen-bridged iron carbonyl derivatives include the Fe–Fe and mean Fe–N distances of 2.496 (3) and 1.878 (3) Å, respectively.

Introduction

The reactions of azobenzene[4] and azomethane[5] with diiron enneacarbonyl both yield binuclear complexes of chemical composition $R_2N_2Fe_2(CO)_6$ ($R = C_6H_5$, CH_3). A crystal structure analysis of the product of the azobenzene reaction has shown that in its formation the azo linkage is ruptured and that the complexed ligand is present in a form based upon an *o*-semidine skeleton.[6] On the basis of ir, nmr, and mass spectral data, it has been proposed[5] that in the methyl compound the nitrogen–nitrogen bond is maintained, yielding a structure (I) analogous to that of the sulfur-bridged dimer $[SFe(CO)_3]_2$.[7] A similar structure had previously been proposed[7] for the complex obtained by Hieber and Buetner from the reaction of $Fe(CO)_4{}^{2-}$ with nitrite ion or hydroxylamine and formulated by them as $[HNFe(CO)_3]_2$.[8] Recently, however, it has been shown independently by two groups[9,10] that this compound is in fact $[H_2NFe(CO)_3]_2$ and that it contains two bridging amido ligands with no N–N bond.



I

The proposed structure I for $[CH_3NFe(CO)_3]_2$ is a unique one in that previous structural studies of a variety of products obtained from reactions of iron carbonyls with organonitrogen ligands containing nitrogen–nitrogen bonds[2,6,11–15] have revealed no cases of two nitrogen atoms being directly bonded to each other and both participating in Fe–N bonds. In most instances the nitrogen–nitrogen bond is broken, and in a few cases it is maintained with coordination of only one nitrogen atom to the metal. The structural analysis of $[CH_3NFe(CO)_3]_2$ was carried out in order to determine the mode of coordination of the azo ligand and to provide further detailed stereochemical data on nitrogen-bridged iron carbonyls.

Collection and Reduction of the Intensity Data

Crystals of $[CH_3NFe(CO)_3]_2$, prepared from azomethane and diiron enneacarbonyl, were kindly supplied by Dr. G. R. Knox of the University of Strathclyde. Preliminary X-ray photographic examination of several of the orange prismatic crystals revealed the presence of monoclinic symmetry. Lattice parameters were obtained by the least-squares refinement of the setting angles of 13 reflections which had been accurately centered on a Picker four-circle X-ray diffractometer. A takeoff angle of 0.7° was employed throughout the centering process. The unit cell constants (temperature 23°, λ(Mo Kα_1) 0.70930 Å) obtained in this manner are: $a = 7.326$ (8) Å, $b = 13.090$ (14) Å, $c = 6.913$ (8) Å, and $\beta = 96°\ 44'$ (1′). The standard deviations in parentheses are those from the least-squares refinement of the setting angles. A density of 1.70 g/cm^3 is calculated on the basis of two dimers per unit cell; this is in satisfactory agreement with the experimental density of 1.66 (2) g/cm^3, observed by flotation in aqueous zinc bromide solution. The only systematic absence observed on $hk0$, $hk1$, $h0l$, and $h1l$ precession photographs and a $0kl$ Weissenberg photo-

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[2] Part II: R. J. Doedens, *Inorg. Chem.*, **8**, 570 (1969).

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Table I

Observed and Calculated Structure Amplitudes (×10) in Electrons for $[CH_3NFe(CO)_3]_2$

K	L	FO	FC
***** H = 0 *****			
0	1	424	366
0	2	812	730
0	3	704	706
0	4	71	88
0	5	363	357
0	6	178	178
1	1	1106	977
1	2	179	178
1	3	74	77
1	4	322	328
1	5	105	101
1	6	106	103
2	0	354	352
2	1	110	102
2	2	144	141
2	3	142	146
2	4	86	91
2	6	78	89
3	1	92	84
3	2	296	293
3	4	128	128
4	0	706	684
4	1	138	138
4	2	183	189
4	3	285	298
4	5	271	270
4	6	99	98
5	1	546	569
5	2	227	231
5	3	272	270
5	4	370	371
5	5	67	59
5	6	133	127
6	0	268	279
6	1	198	202
6	2	372	383
6	3	288	288
6	4	94	96
6	5	217	216
7	1	104	111
7	2	266	271
7	3	146	142
7	4	168	168
8	0	279	280
9	1	260	255
9	2	137	137
9	3	62	57
9	4	135	126
10	0	369	371
10	1	134	133
10	2	230	232
10	3	194	190
11	1	225	224
11	2	163	161
11	3	78	79
12	0	72	69
12	2	51	56
***** H = 1 *****			
0	0	112	100
0	1	1052	935
0	2	585	570
0	3	478	479
0	4	470	488
0	6	205	200
0	-1	1165	1050
0	-2	382	365
0	-3	544	595
0	-4	337	347
0	-5	243	242
0	-6	130	128
1	0	1060	964
1	1	454	411
1	2	299	298
1	3	321	331
1	4	82	85
1	5	235	239
1	6	126	121
1	-1	369	333
1	-2	896	886
1	-3	448	449
1	-5	287	287
1	-6	154	170
2	0	105	108
2	1	259	253
2	2	226	215
2	-1	143	131
2	-2	371	359
2	-3	34	38
2	-4	236	238
2	-5	160	159
2	-6	75	72
3	0	201	195
3	1	129	131
3	2	57	61
3	3	203	202
3	5	97	95
3	6	51	47
3	-1	637	617
3	-2	309	302
3	-3	41	42
3	-4	72	76
3	-5	79	82
4	0	966	954
4	1	180	192
4	2	202	204
4	3	241	239
4	4	231	224
4	5	47	45
4	6	135	138
4	-1	233	241
4	-2	377	383
4	-3	106	106
4	-4	221	226
4	-5	78	83
5	0	633	643
5	1	220	227
5	2	329	337
5	3	356	397
5	4	73	73
5	5	256	286
5	-1	462	464
5	-2	394	397
5	-3	310	310
5	-4	63	55
5	-5	207	207
5	-6	74	77
6	0	109	114
6	1	523	544
6	2	284	279
6	3	187	190
6	4	304	303
6	-1	405	409
6	-2	311	313
6	-3	109	116
6	-4	366	305
7	0	183	189
7	1	86	86
7	2	263	261
7	3	131	131
7	5	117	118
7	-1	130	134
7	-3	213	219
7	-5	84	96
8	0	95	98
8	-5	79	85
9	0	291	289
9	1	52	56
9	2	117	115
9	3	89	90
9	-1	108	110
9	-2	177	182
9	-3	174	171
10	0	78	72
10	1	333	328
10	2	157	160
10	3	92	93
10	-1	311	305
10	-2	153	152
10	-3	109	111
10	-4	181	180
11	0	229	223
11	2	185	183
11	-2	107	103
11	-3	168	162
12	1	102	100
12	-1	76	82
***** H = 2 *****			
0	0	395	358
0	1	671	667
0	2	472	472
0	3	373	362
0	5	335	332
0	6	60	53
0	-1	31	20
0	-2	434	429
0	-3	447	460
0	-4	121	121
0	-5	291	293
0	-6	90	101
1	0	179	183
1	1	919	923
1	2	304	312
1	3	312	312
1	4	275	273
1	6	138	136
1	-1	133	139
1	-2	537	538
1	-3	196	188
1	-4	419	425
1	-5	144	147
1	-6	140	135
2	0	213	217
2	2	361	362
2	4	108	108
2	-1	364	362
2	-2	159	154
2	-3	150	155
2	-4	65	83
2	-5	176	174
2	-6	66	69
3	0	222	237
3	1	345	355
3	3	98	97
3	4	147	148
3	-2	443	451
3	-4	124	129
3	-6	62	64
4	0	422	426
4	1	56	57
4	2	254	248
4	3	153	155
4	4	90	84
4	5	221	215
4	-1	375	378
4	-2	210	207
4	-3	525	533
4	-4	74	77
4	-5	79	86
4	-6	56	59
5	0	255	264
5	1	491	499
5	2	287	291
5	3	175	180
5	4	327	325
5	-1	349	361
5	-2	538	557
5	-3	112	109
5	-4	346	347
5	-5	126	126
5	-6	63	55
6	0	467	475
6	1	60	55
6	2	278	291
6	3	312	312
6	4	115	113
6	5	200	201
6	-1	366	374
6	-2	223	220
6	-3	347	353
6	-4	73	75
6	-5	121	117
7	0	113	120
7	1	179	176
7	2	80	85
7	3	125	126
7	4	134	129
7	-1	412	421
7	-2	143	144
7	-3	56	53
7	-4	95	96
8	0	60	58
8	1	55	57
8	-3	53	58
9	1	225	228
9	2	126	124
9	3	85	79
9	4	111	103
9	-1	160	155
9	-2	124	129
9	-3	108	109
9	-4	152	149
10	0	220	225
10	1	70	67
10	2	183	173
10	3	161	162
10	-1	84	83
10	-2	155	149
10	-3	141	136
11	1	176	170
11	2	69	69
11	-1	168	166
11	-2	112	107
12	0	116	119
12	-1	67	57
***** H = 3 *****			
0	0	174	177
0	1	501	511
0	2	397	390
0	3	234	238
0	4	270	275
0	5	57	70
0	-1	441	439
0	-2	275	283
0	-3	168	162
0	-4	518	519
0	-5	130	137
0	-6	135	137
1	0	391	408
1	1	45	39
1	2	336	339
1	3	222	221
1	4	236	238
1	5	173	176
1	-1	115	114
1	-2	104	105
1	-3	350	358
1	-4	127	133
1	-5	206	206
2	0	40	45
2	1	231	232
2	2	61	60
2	3	273	275
2	5	83	88
2	-1	223	221
2	-2	161	168
2	-4	171	169
2	-6	72	68
3	0	248	251
3	1	93	94
3	2	39	36
3	3	161	157
3	-1	102	103
3	-2	80	79
3	-3	74	77
4	0	257	258
4	1	608	621
4	2	197	202
4	3	167	169
4	4	227	223
4	5	50	47
4	-1	386	382
4	-2	310	318
4	-3	50	43
4	-4	332	330
4	-5	137	137
5	0	400	408
5	1	116	118
5	2	327	336
5	3	222	223
5	4	98	102
5	5	148	144
5	-1	296	304
5	-2	134	132
5	-3	435	442
5	-4	117	114
5	-5	147	143
6	0	132	136
6	1	376	388
6	2	121	122
6	3	163	163
6	4	173	176
6	-1	269	269
6	-2	359	366
6	-3	121	122
6	-4	210	204
6	-5	84	89
7	0	254	258
7	2	211	212
7	3	112	119
7	-1	168	171
7	-2	185	169
7	-3	151	152
8	1	59	64
8	2	68	65
8	3	59	47
8	-4	85	88
9	0	127	129
9	1	69	70
9	2	171	167
9	3	97	94
9	-1	46	50
9	-2	55	51
9	-3	133	133
10	1	160	156
10	2	78	86
10	-1	99	101
10	-2	145	147
11	0	135	138
11	-1	159	149
***** H = 4 *****			
0	0	139	151
0	1	163	157
0	2	474	478
0	3	162	164
0	4	173	172
0	5	146	140
0	-1	345	345
0	-2	79	85
0	-3	354	342
0	-4	184	189
0	-5	122	116
1	0	204	201
1	1	374	381
1	2	170	170
1	3	315	311
1	4	164	164
1	-1	215	220
1	-2	274	280
1	-4	263	241
1	-5	102	108
2	0	150	165
2	1	73	66
2	2	242	232
2	3	138	143
2	4	116	123
2	-1	74	75
2	-3	201	197
2	-5	79	80
3	1	147	147
3	2	149	154
3	-1	188	191
3	-2	74	80
3	-3	86	88
3	-5	83	85
4	0	272	275
4	2	324	329
4	3	73	68
4	4	71	69
4	-1	237	249
4	-2	210	215
4	-3	170	173
4	-4	164	163
4	-5	69	71
5	0	177	183
5	1	414	423
5	2	44	40
5	3	179	173
5	4	80	75
5	-1	319	323
5	-2	329	333
5	-4	197	190
5	-5	129	133
6	0	368	378
6	2	239	239
6	3	98	91
6	-1	214	221
6	-2	156	156
6	-3	247	249
6	-4	70	76
7	1	126	126
7	-1	110	112
7	-2	104	110
7	-4	51	56
8	2	88	93
9	1	128	123
9	2	57	53
9	-1	65	63
9	-2	51	51
10	0	126	126
10	1	45	47
10	-1	114	107
***** H = 5 *****			
0	0	210	205
0	1	435	430
0	3	116	118
0	4	150	143
0	-1	160	160
0	-2	409	403
0	-4	160	159
0	-5	89	88
1	0	286	284
1	1	106	112
1	2	266	263
1	3	147	137
1	-1	284	278
1	-3	304	294
1	-4	79	76
2	0	106	110
2	1	144	144
2	2	79	80
2	3	68	70
2	4	102	101
2	-1	45	40
2	-2	180	180
2	-4	69	56
3	1	53	55
3	2	62	62
3	-2	49	55
3	-3	47	43
3	-4	56	51
4	0	82	56
4	1	225	226
4	2	59	58
4	3	90	95
4	-1	178	189
4	-2	153	152
4	-4	105	102
5	0	270	266
5	1	119	120
5	2	278	273
5	3	49	41
5	-1	202	200
5	-2	166	171
5	-3	227	221
5	-4	97	92
6	0	121	111
6	1	164	162
6	-1	175	181
6	-2	160	150
6	-4	107	109
7	0	44	39
7	-1	66	56
***** H = 6 *****			
0	0	185	184
0	1	126	126
0	2	144	139
0	-1	294	294
0	-2	93	88
0	-3	260	254
0	-4	104	103
1	0	160	156
1	1	112	112
1	-1	135	141
1	-2	276	269
1	-4	111	105
2	0	69	71
2	2	61	54
2	-1	111	111
2	-2	49	45
2	-3	115	112
3	0	97	90
4	0	116	117
4	1	116	119
4	2	118	122
4	-1	140	139
4	-3	118	110
5	0	155	151
5	1	176	173
5	-1	113	111
5	-2	151	149
6	0	98	111
6	-1	112	109
***** H = 7 *****			
0	0	119	116
1	-1	160	159

graph was that of $0k0$ reflections for k odd. This single absence is consistent with either space group C_2^2-$P2_1$ or C_{2h}^2-$P2_1/m$. The former space group imposes no symmetry on the $[CH_3NFe(CO)_3]_2$ molecule, while the centrosymmetric space group $P2_1/m$ requires the dimer to contain either a mirror plane or a center of symmetry. The proposed configuration was one which could well have one or two mirror planes, but could not, in the absence of disorder, contain a molecular center of symmetry.

The crystal used for the collection of intensity data was a prism of length 0.39 mm and a nearly square cross section measuring 0.20 × 0.19 mm. It was mounted in a thin-walled glass capillary roughly parallel to its longest dimension and mounted on the diffractometer with a^* approximately coinciding with the ϕ axis. Procedures previously described in detail[16] were used for the collection of intensity data on the Picker automatic diffractometer. The diffracted beam was filtered through 3.0-mil Nb foil. The counter aperture, 4 mm high by 6 mm wide, was positioned 29.5 cm from the crystal. Data were collected by the θ–2θ scan technique, with a symmetric scan range of $\pm 0.9°$ in 2θ from the calculated scattering angle employed for all reflections. The takeoff angle was 1.2°. The scan rate was 1.0°/min, and background counts of 10 sec were taken at each end of the scan. Copper foil attenuators were automatically inserted in the path of the diffracted beam whenever the counting rate exceeded ~7000 counts/sec. Attenuation was required only for the eight strongest reflections. Three standard reflections, monitored at regular intervals throughout the period of data collection, showed no variations in intensity beyond those expected from counting statistics. The intensities of a total of 659 independent reflections with $\theta \leqslant 20°$ were measured. Beyond this value of the Bragg angle, the proportion of nonzero intensities became very small.

Processing of the data was carried out by use of previously described methods.[16] In estimation of the standard deviations of the individual intensities, a value of 0.04 was used for the factor p, which determines the minimum value of $\sigma(I)/I$ in the absence of any contribution from counting statistics. Of the 659 data collected, 518 had intensities above background by three or more standard deviations. Correction of the observed intensities for absorption was made; the calculated transmission factors, based on a linear absorption coefficient of 22.2 cm^{-1}, varied from 0.68 to 0.75.

In addition to the independent data, the $h\bar{k}l$ reflections with $\theta \leqslant 20°$ were also collected in order to determine whether any systematic differences in intensity between the hkl and $h\bar{k}l$ data existed as a result of anomalous dispersion by the iron atoms in a noncentrosymmetric crystal structure. No such differences were observed, and hence the centrosymmetric space group $P2_1/m$ was judged to be the most probable one.

Solution and Refinement of the Structure

A three-dimensional Patterson function had as its most prominent feature a vector of length ~2.5 Å parallel to the b axis. This vector, assumed to be an intramolecular iron–iron vector, lent further support to the choice of $P2_1/m$ as the most probable space group and identified the required molecular symmetry element as a mirror plane perpendicular to the iron–iron vector. Least-squares refinement of the trial iron coordinates derived from the Patterson map, together with a scale factor and an isotropic temperature factor, yielded discrepancy factors $R_1 = 100\Sigma||F_o| - |F_c||/\Sigma|F_o| = 33.8\%$ and $R_2 = 100[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 40.7\%$. Coordinates of the ten remaining independent nonhydrogen atoms were obtained from a difference Fourier map, and least-squares refinement of positional and isotropic thermal parameters of these atoms converged to discrepancy factors $R_1 = 7.1\%$ and $R_2 = 9.5\%$. In this and all subsequent refinements, only the 518 independent data with $F_o^2 \geqslant 3\sigma(F_o^2)$ were utilized. Two further least-squares cycles with

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(16) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967); R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

TABLE II

ATOMIC POSITIONAL AND THERMAL PARAMETERS FOR $[CH_3NFe(CO)_3]_2$[a]

Atoms	x	y	z	$10^4\beta_{11}$[b]	$10^4\ \beta_{22}$	$10_4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Fe	0.23097 (9)	0.15464 (5)	−0.19225 (10)	216 (2)	68 (1)	246 (2)	−2 (1)	17 (1)	−6 (1)
C_1	0.3458 (9)	0.0365 (5)	−0.2214 (9)	366 (18)	91 (5)	338 (19)	26 (9)	−95 (14)	−23 (9)
O_1	0.4202 (8)	−0.0393 (4)	−0.2385 (8)	604 (19)	104 (4)	635 (20)	108 (7)	−207 (15)	−87 (7)
C_2	0.1459 (9)	0.1272 (5)	0.0323 (11)	369 (18)	106 (6)	342 (20)	−64 (8)	36 (15)	2 (8)
O_2	0.0932 (8)	0.1107 (5)	0.1775 (8)	705 (21)	213 (7)	377 (16)	−152 (10)	179 (16)	39 (8)
C_3	0.0233 (9)	0.1263 (4)	−0.3390 (9)	227 (14)	81 (5)	342 (17)	7 (7)	43 (13)	−16 (7)
O_3	−0.1119 (6)	0.1089 (4)	−0.4345 (7)	247 (10)	136 (5)	499 (16)	4 (6)	−35 (11)	−68 (7)
N_1	0.3544 (7)	$^1/_4$	−0.3317 (9)	167 (12)	90 (5)	224 (17)	0	49 (12)	0
N_2	0.4225 (7)	$^1/_4$	−0.1391 (8)	170 (14)	83 (5)	215 (16)	0	−5 (12)	0
C_4	0.4724 (11)	$^1/_4$	−0.4912 (12)	244 (20)	161 (11)	279 (24)	0	70 (18)	0
C_5	0.6210 (10)	$^1/_4$	−0.0719 (12)	203 (19)	130 (8)	305 (23)	0	−9 (17)	0
H_1C_4	0.3966	$^1/_4$	−0.6217	c					
H_2C_4	0.5556	0.3124	−0.4842	c					
H_1C_5	0.6428	$^1/_4$	0.0743	c					
H_2C_5	0.6800	0.1876	−0.1219	c					

[a] Numbers in parentheses in all tables and in the text are estimated standard deviations in the least significant figures. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{23} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [c] Hydrogen atoms were assigned isotropic thermal parameters of 7.0 Å^2.

anisotropic thermal parameters assigned to all nonhydrogen atoms further reduced R_1 and R_2 to 3.8 and 5.7%, respectively. At this stage a difference Fourier map was calculated, on which the maximum peak height was 0.6 e$^-$/Å^3. This may be compared with a peak height range 3.8–5.6 e$^-$/Å^3 observed for carbon atoms on the previous difference map. Four of the positive peaks on the final difference Fourier map, ranging in height from 0.27 to 0.41 e$^-$/Å^3, were at plausible locations for methyl hydrogen atoms, as determined by calculation of the hydrogen atom positions for "ideal" methyl groups (C–H = 1.00 Å; ∠H–C–H = 109.5°) centered at C_4 and C_5 as a function of rotation angle about the N–C bond. These methyl hydrogen atoms were included as fixed atoms in the next three cycles of least-squares refinement, during which the R factors were significantly reduced to their final values of R_1 = 2.8% and R_2 = 3.4%. In the final cycle, the largest relative change in a positional parameter was 0.8 standard deviation, and no parameter shifted by more than 1.3 standard deviations.

Final values of the observed and calculated structure factors are listed in Table I. The four strongest reflections ($10\bar{1}$, 011, 110, 101) all have calculated structure factors which are ~10% below the corresponding F_o values. This systematic discrepancy could arise from a variety of causes, including inadequacies in scattering factors, thermal parameters, hydrogen atom parameters, or treatment of background for these reflections. This problem was not pursued further. The nature of these discrepancies suggests that secondary extinction is not a problem in this structural analysis. Data with $F_o^2 \leqslant 3\sigma(F_o^2)$ are not included in Table I; a structure factor calculation for these data was carried out, and, with the exception of one reflection (221) which had been misset, none of them had $F_c^2 > 5\sigma(F_o^2)$. Final atomic positional and thermal parameters are tabulated in Table II, principal root-mean-square amplitudes of thermal motion are given in Table III, and intramolecular distances and angles are presented in Tables IV and V, respectively. In all cases, standard deviations were estimated from the full inverse matrix of the normal equations and hence include interatomic correlation effects.

TABLE III

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

	Max	Intermed	Min
Fe	0.250(1)	0.243(1)	0.234(1)
C_1	0.368(8)	0.272(8)	0.240(8)
O_1	0.514(7)	0.307(6)	0.248(6)
C_2	0.357(8)	0.286(8)	0.253(8)
O_2	0.510(7)	0.370(7)	0.245(7)
C_3	0.291(7)	0.262(8)	0.241(8)
O_3	0.393(6)	0.305(6)	0.247(6)
N_1	0.280(8)	0.237(9)	0.201(8)
N_2	0.268(8)	0.238(8)	0.204(9)
C_4	0.373(13)	0.274(11)	0.234(12)
C_5	0.336(10)	0.280(10)	0.226(12)

TABLE IV

BOND LENGTHS AND SELECTED INTRAMOLECULAR NONBONDED CONTACTS (Å)

Fe–Fe′[a]	2.496(3)	N_1–N_2	1.366(8)
Fe–N_1	1.873(4)	N_1–C_4	1.478(9)
Fe–N_2	1.882(4)	N_2–C_5	1.474(9)
Mean Fe–N	1.878(3)	Mean N–C	1.476(6)
Fe–C_1	1.783(7)	C_1–O_1	1.146(7)
Fe–C_2	1.776(8)	C_2–O_2	1.137(7)
Fe–C_3	1.767(7)	C_3–O_3	1.147(6)
Mean Fe–C	1.775(4)	Mean C–O	1.143(4)
$C_1 \cdots C_2$	2.689(10)	$N_1 \cdots C_1$	2.900(8)
$C_1 \cdots C_3$	2.679(9)	$N_1 \cdots C_3$	2.913(8)
$C_2 \cdots C_3$	2.618(10)	$N_2 \cdots C_1$	2.894(7)
		$N_2 \cdots C_2$	2.943(9)

[a] Primes refer to atoms related to those in the asymmetric unit by the crystallographic mirror plane.

Throughout the refinement, weights of the observed structure amplitudes were taken as $w = 4F_o^2/\sigma^2(F_o^2)$ and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The final value of the standard deviation of an observation of unit weight was 1.35. The scattering factors for Fe, C, N, and O tabulated by Ibers[17] and those for

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(17) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962.

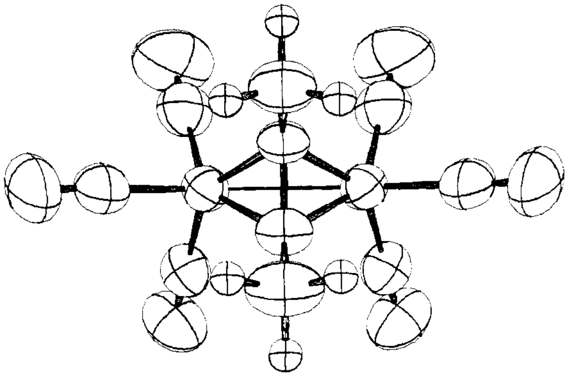


Figure 1.—The molecular structure of $[CH_3NFe(CO)_3]_2$, projected down the direction defined by the N–N and Fe–Fe midpoints. The crystallographic *b* axis is parallel to the Fe–Fe vector. The ellipsoids enclose 50% of the probability distribution, with the exception that the methyl hydrogen atoms have been assigned artificially low thermal parameters for clarity.

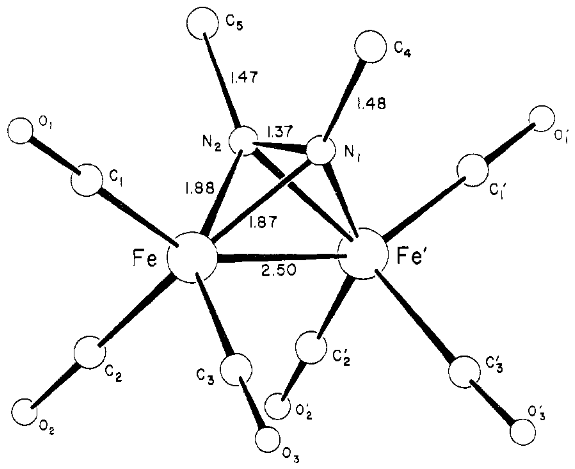


Figure 2.—Another view of the molecular structure of $[CH_3NFe(CO)_3]_2$, with selected bond lengths in ångströms.

Table V

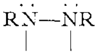
Bond Angles (deg)

Fe′–Fe–N_1	48.2 (1)	Fe–N_1–Fe′	83.6 (2)
Fe′–Fe–N_2	48.4 (1)	Fe–N_1–N_2	69.0 (3)
Fe′–Fe–C_1	150.2 (2)	Fe–N_1–C_4	138.0 (1)
Fe′–Fe–C_2	101.7 (2)	N_2–N_1–C_4	123.2 (5)
Fe′–Fe–C_3	102.1 (2)		
N_1–Fe–N_2	42.7 (2)	Fe–N_2–Fe′	83.1 (2)
N_1–Fe–C_1	104.9 (3)	Fe–N_2–N_1	68.3 (2)
N_1–Fe–C_2	145.6 (3)	Fe–N_2–C_5	138.3 (1)
N_1–Fe–C_3	106.3 (3)	N_1–N_2–C_5	122.8 (5)
N_2–Fe–C_1	104.3 (3)		
N_2–Fe–C_2	107.1 (3)	Fe–C_1–O_1	179.4 (29)
N_2–Fe–C_3	145.5 (2)	Fe–C_2–O_2	178.9 (18)
C_1–Fe–C_2	98.1 (3)	Fe–C_3–O_3	179.3 (35)
C_1–Fe–C_3	98.0 (3)		
C_2–Fe–C_3	95.3 (3)		

H of Stewart, *et al.*,[18] were used in all structure factor calculations. The $\Delta f'$ and $\Delta f''$ values of Cromer[19] were employed in the correction of the calculated structure factors[20] for the anomalous scattering of the iron atoms. Programs utilized in this structural determination included the cell refinement and diffractometer setting program PICK2, the data-processing program PICKOUT, Hamilton's GONO9 absorption correction program, the least-squares programs NUCLS and UCILS2 (both based on the Busing–Martin–Levy program ORFLS), modified versions of Zalkin's FORDAP Fourier summation program and the Busing–Martin–Levy function and error program ORFFE, and Johnson's ORTEP plotting program.

Description of the Structure

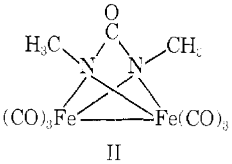
The dimeric $[CH_3NFe(CO)_3]_2$ molecule contains two $Fe(CO)_3$ groups related by a crystallographic mirror plane at $y = {}^1/_4$ and doubly bridged through the nitrogen atoms of the H_3C–N–N–CH_3 ligand. Though only C_s-m molecular symmetry is required, the configuration is very nearly one of C_{2v}-2mm symmetry. This symmetry can clearly be seen in Figure 1, a view down the pseudo-twofold axis defined by the N_1–N_2 and Fe–Fe midpoints. A second view of the molecular structure is shown in Figure 2. The results of this structural analysis agree with the formulation of Dekker and Knox[5,21] for $[RNFe(CO)_3]_2$ (R = C_6H_5, CH_3) and thus provide the first confirmed example of a binuclear transition metal complex bridged by a



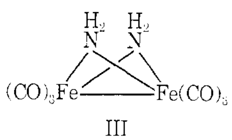
$R\ddot{N}-\ddot{N}R$

group. If the bridging ligand is viewed in this manner as the methyl analog of the hydrazo radical, the compound might be named μ-methazo-bis(tricarbonyliron). The iron–iron distance of 2.496 (3) Å and the configuration of the bridging system are consistent with the presence of an iron–iron bond, as proposed by Dekker and Knox.

In Table VI selected structural features of the Fe_2N_2 tetrahedron in $[CH_3NFe(CO)_3]_2$ are compared with the corresponding parameters of the related molecules $[(CH_3N)_2CO]Fe_2(CO)_6$[14] (II) and $[H_2NFe(CO)_3]_2$[10] (III). In the former compound the two bridging nitrogen atoms are not bonded to each other, but rather are



II



III

linked by a seventh CO group to form a bridging dimethylureylene ligand, while the structure of the latter compound is one in which the bridging nitrogen atoms are not constrained by a direct bond or by a bridging group. The tabulated structural parameters are representative of those of a variety of closely related compounds.[6,11,12,14,22] Obvious structural effects of the N–N bond in $[CH_3NFe(CO)_3]_2$ include the short N_1–N_2 distance of 1.366 (8) Å, the very acute N_1–Fe–N_2

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

[19] D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).

[20] J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

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bond angle of 42.7 (2)°, and the (Fe–N_1–Fe′)–(Fe–N_2–Fe′) dihedral angle of 58.3 (2)°. In addition to these direct effects of the N–N bond in $[CH_3NFe(CO)_3]_2$, the dimensions of the two essentially identical Fe–N–Fe triangles vary considerably from their values in other N-bridged iron carbonyl complexes. The iron–iron distance of 2.496 (3) Å is the longest reported length for an N-bridged Fe–Fe bond, the range of previously reported values being 2.372 (2)[6]–2.488 (7) Å.[2] Iron–iron distances in the compounds most closely related to the present one—those with two Fe–N–Fe bridges—have previously ranged only from 2.372 (2) to 2.416 (3) Å.[22] The long iron–iron distance is reflected in the mean Fe–N–Fe angle of 83.4 (1)°, larger by *ca.* 9° than the typical values of 74–75° which have been found consistently in previous N-bridged iron carbonyl dimers. Finally, the mean Fe–N bond length of 1.878 (3) Å is 0.1 Å shorter than comparable distances in closely related compounds.[23]

TABLE VI

COMPARISON OF STRUCTURAL PARAMETERS OF $[CH_3NFe(CO)_3]_2$, $[(CH_3N)_2CO]Fe_2(CO)_6$, AND $[H_2NFe(CO)_3]_2$

	$[CH_3NFe(CO)_3]_2$	$[(CH_3N)_2CO]$-$Fe_2(CO)_6$	$[H_2NFe(CO)_3]_2$
		Distance, Å	
Fe–Fe	2.496 (3)	2.391 (7)	2.402 (6)
Fe–N	1.878 (3)[a]	1.97 (1)[a]	1.98 (1)[a]
N–N	1.366 (8)	2.10 (2)	2.50 (3)
		Angle, deg	
Fe–N–Fe	83.4 (1)[a]	75.0 (2)[a]	74.4 (5)[a]
N–Fe–N	42.7 (2)	64.8 (5)[a]	77.8 (6)[a]
b	91.1 (2)	92.2 (8)	101.9 (8)
c	58.3 (2)	84.8 (10)	104.0 (10)

[a] Mean value. [b] Dihedral angle between the two Fe–N–N planes. [c] Dihedral angle between the two Fe–Fe–N planes.

The carbonyl groups have their expected configurations, with mean Fe–C and C–O distances of 1.775 (4) and 1.143 (4) Å, respectively. None of the Fe–C–O angles deviates significantly from linearity, and the individual Fe–C and C–O bond lengths are equal within experimental error. Thus, even with the high degree of precision attained in this analysis, no structural differences are observed between the two stereochemically distinct types of carbonyl groups. As expected, the two N–C bond lengths are identical; their mean value of 1.476 (6) Å is typical for an N–C single bond.

No abnormal intra- or intermolecular nonbonded contacts are observed. The shortest intermolecular contacts of various types include: O···H, 2.63 Å; H···H, 2.92 Å; C···H, 3.18 Å; O···O, 3.14 (1) Å. The rms amplitudes of thermal vibration listed in Table III are qualitatively reasonable; their magnitudes are rather high in some cases. No attempt was made to correct the interatomic distances for thermal motion.

Discussion

The central portion of the $[CH_3NFe(CO)_3]_2$ molecule resembles quite closely the M_2C_2 tetrahedra in the diphenylacetylene-bridged dimers $(C_6H_5C_2C_6H_5)[Co(CO)_3]_2$[24] and $(C_6H_5C_2C_6H_5)(NiC_5H_5)_2$.[25] In particular, the C–C distances and C–M–C angles of these two compounds differ by no more than 0.02 Å and 2°, respectively, from the values observed in the present case. Sly[24] has outlined the two simplest models which might be advanced to describe the bonding of the bridging system in the $(C_6H_5C_2C_6H_5)[Co(CO)_3]_2$ molecule. The first involves six-coordinate cobalt atoms σ-bonded to tetrahedrally hybridized carbon atoms, while in the second an acetylenic C–C linkage is π-bonded to five-coordinate cobalt atoms. Though the "best" bonding description for a given compound will in general be between these two extremes, it is nevertheless of interest to inquire which, if either, of these limiting models is in best accord with the observed structural parameters for a particular compound. The π-bonded model was chosen by Brown[26] as the starting point of a molecular orbital calculation for the cobalt dimer; this choice was based primarily on the bridging C–C distance of 1.37 Å which was considered to be inconsistent with the σ-bonded model. For $[CH_3NFe(CO)_3]_2$, on the other hand, the N–N distance of 1.37 Å cannot be used in a similar manner to contradict a bonding description which incorporates six-coordinate iron atoms. A covalent radius of 0.70 Å is in best agreement with the bulk of the data on nitrogen single-bond lengths.[27] Bonds between two tetravalent nitrogen atoms are rather rare; in the $N_2H_6^{2+}$ cation, N–N distances of 1.40–1.42 Å have been reported.[28–30] It hence appears plausible that under appropriate conditions an N–N bond of formal unit order might be as short as 1.37 Å. Also, the $Fe(CO)_3$ group has a configuration which does not differ materially from that found in a variety of other compounds in which six-coordination is unambiguous. We thus conclude that a model with distorted octahedral coordination about the iron atoms is a serviceable first approximation for description of the bonding in $[CH_3NFe(CO)_3]_2$.

These differences in Fe–Fe and Fe–N distances and Fe–N–Fe bridging angles in $[CH_3NFe(CO)_3]_2$ and $[H_2NFe(CO)_3]_2$ may be compared with the corresponding differences between the electronically and structurally analogous pair of compounds $[SFe(CO)_3]_2$[7] and $[C_2H_5SFe(CO)_3]_2$.[31] The values for these parameters in the S-bridged compounds (with the value for $[SFe(CO)_3]_2$ listed first in each case) are: Fe–Fe = 2.552 (2), 2.537 (10) Å; mean Fe–S = 2.228 (2), 2.259 (7) Å; mean ∠Fe–S–Fe = 69.9 (1), 68.3 (3)°. In each case, the differences are in the same direction as for the N-bridged pair, but considerably smaller in magnitude.

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[23] More detailed summaries of structural parameters of related compounds are given in ref 10 and 14.

[24] W. G. Sly, *J. Am. Chem. Soc.*, **81**, 18 (1959), and private communication.

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[28] M. L. Kronberg and D. Harker, *J. Chem. Phys.*, **10**, 309 (1942).

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A correlation exists in the nitrogen- and sulfur-bridged iron carbonyls between the Fe–Fe and mean Fe–X (X = N, S) bond lengths, with a longer Fe–Fe bond associated with a shorter Fe–X bond. This relationship has previously been pointed out[32] for the sulfur-bridged compounds and is more clearly illustrated in the nitrogen-bridged series because of the larger bond length differences involved.

The first question which must be asked in any attempt to understand the basis of the long Fe–Fe and short Fe–N bonds in $[CH_3NFe(CO)_3]_2$ is whether these distances are simply a stereochemical consequence of the presence of the bond linking the two bridging nitrogen atoms or whether they stem from some other property of the bridging group. One possible approach to resolving this question is through structural analyses of other compounds having the same basic bridging configuration but different bridging ligands. Such studies are now in progress, and further discussion of this point will be reserved until their completion.

Acknowledgments.—This work was supported by the National Science Foundation and by the Petroleum Research Fund, administered by the American Chemical Society. Computation was supported in part by a National Science Foundation institutional grant to the University of California, Irvine, Calif.

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The Structure of Chlorodicarbonylbis(triphenylphosphine)iridium(I)–Benzene, $IrCl(CO)_2(P(C_6H_5)_3)_2 \cdot C_6H_6$

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The structure of chlorodicarbonylbis(triphenylphosphine)iridium(I)–benzene, $IrCl(CO)_2(P(C_6H_5)_3)_2 \cdot C_6H_6$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes with four formula units in space group C_{2h}^5-$P2_1/c$ of the monoclinic system in a cell of dimensions a = 18.019 (4) Å, b = 12.240 (4) Å, c = 18.237 (6) Å, and β = 102.51 (1)°. The measured density of 1.51 (1) g/cm³ agrees well with the calculated value of 1.50 g/cm³. The benzene molecule is well separated from the iridium atom. The coordination about iridium is that of a trigonal bipyramid, with *trans* phosphines at the apices. Partial disorder among the chlorine atom and carbonyl groups in the equatorial plane precludes a precise determination of all features of the molecular structure. Nevertheless, the fact that the coordination about iridium in this complex is very different from that in the isoelectronic $IrCl(CO)(NO)(P(C_6H_5)_3)_2^+$ cation has been established. The conventional R factor for the 1657 independent reflections above background is 0.093.

Introduction

We recently reported the preparation[1] and molecular structures[2,3] of the compounds $[IrX(CO)(NO)(P(C_6H_5)_3)_2][BF_4]$, where X = Cl and I. Both compounds were prepared by reaction of $NOBF_4$ with the parent d^8 complexes $IrX(CO)(P(C_6H_5)_3)_2$. In these compounds the coordination about iridium is that of a tetragonal pyramid, with *trans* phosphines, the halogen, and the carbonyl in the basal plane, and the nitrosyl group at the apex. The Ir–N–O linkage is bent, with an Ir–N–O angle of approximately 125°. These structure determinations represented the first well-authenticated cases of such a bent nitrosyl linkage in transition metal compounds.

As CO is isoelectronic with NO^+, we thought it would be of interest to examine the structure of the compound formed by addition of CO to the parent molecule. The results of such an examination are reported here.

Experimental Section

Preparation of the Crystal.—Vaska[4] has reported the preparation and characterization of the complex $IrCl(CO)_2(P(C_6H_5)_3)_2$ and on the basis of infrared evidence (ν_{CO} 1923, 1976 cm^{-1}) deduced a trigonal-bipyramidal structure, with *trans*-triphenylphosphine groups. The observed bands were assigned to the normal modes of vibration expected for a planar $IrCl(CO)_2$ fragment, with C_{2v} symmetry, and equivalent CO ligands.

Crystals suitable for data collection were prepared by an adaptation of Vaska's method. A deoxygenated, saturated solution of chlorocarbonylbis(triphenylphosphine)iridium(I) in benzene was prepared under dry nitrogen gas. Into the refluxing solution a stream of carbon monoxide was passed for 10 min; then the solution was allowed to cool under an atmosphere of carbon monoxide. Pale yellow crystals were formed, a Nujol mull of which showed absorption bands attributable to ν_{CO} at 1925 and 1975 cm^{-1}. Elemental analysis suggested the presence of a benzene molecule of crystallization. *Anal.*[5] Calcd for $IrC_{44}H_{36}O_2P_2Cl$ ($IrCl(CO)_2(P(C_6H_5)_3)_2 \cdot C_6H_6$): C, 59.62; H, 4.09. Found: C, 59.66; H, 3.98.

Collection and Reduction of the X-Ray Intensity Data.—An optical and X-ray analysis of the crystals showed monoclinic symmetry, Laue group 2/m. The systematic absences observed on Weissenberg photographs of the layers *h*0*l* through *h*2*l* and on precession photographs of the layers 0*kl*, 1*kl*, *hk*0, and *hk*1 are *h*0*l* for *l* odd and 0*k*0 for *k* odd. These absences are consistent with space group C_{2h}^5-$P2_1/c$. The unit cell dimensions, as established from a least-squares refinement of the setting angles of 13

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[1] D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Am. Chem. Soc.*, **90**, 4486 (1968).

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[4] L. Vaska, *Science*, **152**, 769 (1966).

[5] Analyses were performed by Miss Hilda Beck of this department.