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Structural Studies of Organonitrogen Compounds of the Transition Elements. II. The Crystal and Molecular Structure of Di-μ_3-methylimido-tris(tricarbonyliron), $(CH_3N)_2Fe_3(CO)_9$[1,2]

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A single-crystal X-ray structural analysis has confirmed the proposed structure of $(CH_3N)_2Fe_3(CO)_9$, one of several products of the reaction of methyl azide or nitromethane with $Fe_2(CO)_9$. This material crystallizes in space group C_i^1-P$\bar{1}$ of the triclinic system, with reduced cell constants $a = 8.31$ (2) Å, $b = 8.90$ (2) Å, $c = 12.79$ (3) Å, $\alpha = 80°\ 29'$ (10′), $\beta = 108°\ 27'$ (10′), and $\gamma = 111°\ 29'$ (10′). Observed and calculated densities for two molecules per unit cell are 1.89 (2) and 1.90 g/cm^3, respectively. The structural determination was based upon 773 independent film data; full-matrix least-squares refinement resulted in a conventional R factor of 6.5%. The crystal structure is made up of discrete $(CH_3N)_2Fe_3(CO)_9$ molecules, in which the iron atoms of three $Fe(CO)_3$ groups are triangularly situated and triply bridged on opposite sides of the Fe–Fe–Fe plane by the two N–CH_3 groups. Two of the iron–iron distances (mean 2.462 (7) Å) are of a magnitude indicative of iron–iron bonds, and the third is a nonbonded contact of 3.044 (8) Å. The six iron–nitrogen bond distances are equal within experimental error and have an average value of 1.928 (11) Å.

Introduction

A variety of organonitrogen–iron carbonyl derivatives have recently been prepared by the reactions of organic azo, azido, nitro, and isocyanato compounds with the iron carbonyls.[3-7] Several of these reactions have been interpreted as proceeding through nitrene intermediates,[7] and a number of the products may be regarded as containing nitrenes as ligands. The structures of these compounds are of interest because of their possible relevance to the proposed reaction mechanisms, because of the presence of several new types of ligand systems in the proposed structures, and because of the close analogy of some of the proposed structures to the known structures of other compounds, particularly to sulfur-containing iron carbonyl derivatives. Compounds containing one, two, and three iron atoms are known, and a number of these compounds are the subjects of structural investigations in this laboratory. This paper reports the results of a crystallographic analysis of $(CH_3N)_2Fe_3(CO)_9$, for which the proposed structure[7] analogous to that of $S_2Fe_3(CO)_9$[8] has now been confirmed.

Experimental Section

Preliminary precession and Weissenberg photographs of the deep purple crystals of $(CH_3N)_2Fe_3(CO)_9$ suggested that this compound crystallizes in the triclinic crystal system. These photographs were indexed on the basis of a face-centered triclinic unit cell, chosen because of its near-orthogonality. Lattice constants of this cell at 22°, determined from NaCl-calibrated (a(NaCl) = 5.640 Å, λ(Mo Kα) 0.7107 Å) $h0l$ and $hk0$ precession photographs, are: $a = 8.31$ (2) Å, $b = 16.66$ (4) Å, $c = 24.26$ (6) Å, $\alpha = 86°\ 47'$ (10′), $\beta = 90°\ 11'$ (10′), and $\gamma = 96°\ 10'$ (10′). The standard deviations in parentheses are estimates based on the reproducibility of the measurements and on previous experience with this technique. No evidence of higher symmetry resulted from a Delaunay reduction of this cell. The three shortest noncoplanar lattice translations define a reduced cell with $a' = 8.31$ (2) Å, $b' = 8.90$ (2) Å, $c' = 12.79$ (3) Å, $\alpha' = 80°\ 29'$ (10′), $\beta' = 108°\ 27'$ (10′), and $\gamma' = 111°\ 29'$ (10′). All results are reported in terms of the face-centered cell, from which the reduced cell may be derived by the transformations: $a' = -a$, $b' = {}^1/_2(a + b)$, $c' = {}^1/_2(a - c)$. The observed density of 1.89 (2) g/cm^3, determined by flotation in aqueous zinc bromide solution, agrees well with the value of 1.90 g/cm^3 calculated on the basis of eight formula units per face-centered cell. The centrosymmetric space group C_i^1-F$\bar{1}$ $\{$equivalent general positions: $[(0, 0, 0), ({}^1/_2, {}^1/_2, 0), ({}^1/_2, 0, {}^1/_2), (0, {}^1/_2, {}^1/_2)] \pm (x, y, z)\}$ was assumed; no evidence arose in the course of the structural analysis to contradict this assumption. In the centrosymmetric space group with $Z = 8$, all atoms may occupy general positions, and thus no crystallographic molecular symmetry is imposed.

Intensity data for reciprocal lattice levels $0kl$–$7kl$ were collected by the multiple-film equiinclination Weissenberg technique from a fragment of a tabular crystal of dimensions 0.23 × 0.22 × 0.10 mm mounted parallel to its longest dimension in a sealed thin-walled glass capillary. Zirconium-filtered Mo Kα radiation and a Supper nonintegrating Weissenberg camera were employed in the data collection. A full 360° of data was collected for each nonzero reciprocal lattice level, and the intensities of only the reflections recorded on the top halves of the films were measured. Intensities were estimated visually by comparison with a calibrated strip, and the usual Lorentz–polarization and spot-shape corrections were applied. With $\mu = 25.3$ cm^{-1}, the maximum variation due to absorption of the intensities observed on a given layer was estimated to be of the same order of magnitude as the uncertainty in judgment of the data, and hence no absorption correction was attempted. The total number of independent data measured above background was 773, which represents 51% of the experimentally accessible data with $\theta \leq 20°$. Beyond this value of the Bragg angle, very few reflections were above background. No attempt to place the data on a common scale was made prior to the preliminary least-squares refinement; for the calculation of the Patterson map, it was assumed that all data were on a common scale by virtue of the identical exposure times for all levels. In the final refinement, the observed structure factors were assigned standard deviations as follows:

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[1] Part I: R. J. Doedens, *Inorg. Chem.*, **7**, 2323 (1968).

[2] Presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.

[3] T. A. Manuel, *Inorg. Chem.*, **3**, 1703 (1964).

[4] M. M. Bagga, P. L. Pauson, F. J. Preston, and R. I. Reed, *Chem. Commun.*, 543 (1965).

[5] W. T. Flannigan, G. R. Knox, and P. L. Pauson, *Chem. Ind.* (London), 1094 (1967).

[6] M. M. Bagga, P. E. Baikie, O. S. Mills, and P. L. Pauson, *Chem. Commun.*, 1106 (1967).

[7] M. Dekker and G. R. Knox, *ibid.*, 1243 (1967).

[8] C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 493 (1965).

if $F \leq 4F_{\min}$, $\sigma(F) = 1.0$; if $F > 4F_{\min}$, $\sigma(F) = F/4F_{\min}$. $F_{\min}$ is the minimum observed F for the entire data set.

Solution and Refinement of the Structure

Trial coordinates of the three iron atoms were determined from a three-dimensional Patterson function and refined by full-matrix least-squares methods to discrepancy factors $R_1 = 100\Sigma||F_o| - |F_c||/\Sigma|F_o| = 27.6\%$ and $R_2 = 100[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 36.0\%$. A difference Fourier map clearly revealed the locations of the remaining nonhydrogen atoms. Refinement of all atomic positional parameters, isotropic atomic temperature factors, and individual scale factors for each reciprocal lattice level yielded discrepancy factors $R_1 = 8.2\%$ and $R_2 = 9.8\%$. A difference Fourier map revealed positive peaks of up to 1.1 e/Å^3 in the immediate vicinity of the iron atoms and no other peaks greater than 0.6 e/Å^3. For comparison, peaks due to light atoms on the previous difference map ranged in height from 2.0 to 4.1 e/Å^3. Further refinement with anisotropic temperature factors for the iron atoms resulted in a reduction of R_1 and R_2 to their final values of 6.5 and 7.9%, respectively. In the final least-squares cycle, no parameter shifted by more than 10% of its standard deviation. Unit weights were used during the early stages of refinement; commencing with the final cycles of isotropic refinement, weights were taken as $1/\sigma^2(F_o)$ for each reflection. The appropriateness of the weighting scheme was tested by calculation of average values of $\Delta F/\sigma$ for various subsets of the intensity data; it was found that this average was essentially independent of the range of the magnitude of F_o, the uncorrected intensity, or the Bragg angle included in a subset. The final standard deviation of an observation of unit weight was 0.85.

Final observed and calculated structure factors (in electrons) are tabulated in Table I. Unobserved data were not included in the refinement and are not listed. Only six experimentally accessible unobserved data with $\theta \leq 20°$ had calculated structure factors greater than twice the minimum observed value for their reciprocal lattice level. Final positional and thermal parameters are listed in Table II, and intramolecular distances and angles are given in Tables III and IV, respectively. Standard deviations include correlation effects, and in the case of bond lengths and angles the effects of cell constant errors are also included.

The scattering factors tabulated by Ibers[9] were used in all structure factor calculations, and the $\Delta f'$ and $\Delta f''$ values of Cromer[10] were employed in the correction of the calculated structure factors for the anomalous scattering of the iron atoms. Programs for the IBM 360/50 computer used in this structural determination included modified versions of Zalkin's FORDAP Fourier summation program, the Busing–Martin–Levy ORFLS and ORFFE least-squares and error analysis programs, the Brookhaven–Northwestern data reduction programs, and various locally written programs.

Description and Discussion of the Structure

The crystal structure of $(CH_3N)_2Fe_3(CO)_9$ is made up of monomeric molecular units, in which the three iron atoms are triangularly situated. Two of the iron–iron distances (2.436 (7) and 2.488 (7) Å) are of a magnitude generally associated with iron–iron bonding, while the third (3.044 (8) Å) is in the range of nonbonded iron–iron distances. Each iron atom is bonded to three terminal carbonyl groups, and the two methylimido groups triply bridge the iron atoms on opposite sides of the Fe–Fe–Fe plane. The bridging groups are symmetrically situated, as shown by the fact that none of the six Fe–N bond distances deviates significantly from their mean of 1.928 (11) Å and by the small range of 121.9 (14)–128.3 (13)° for the Fe–N–C (methyl) angles. Though no crystallographic symmetry is imposed on the molecule, the plane of the iron atoms is an approximate mirror plane. The molecular structure is shown in Figure 1, and in Figure 2 the central portion of the molecule is viewed from another perspective.

The molecular structure of $(CH_3N)_2Fe_3(CO)_9$ is closely related to that of $[(C_6H_5)_2CNN]_2Fe_3(CO)_9$, the only other compound for which a structure containing three iron atoms bridged by an N–R group has been reported.[11] These two compounds, in turn, are directly related to a variety of binuclear N-bridged iron carbonyls whose structures are known. For example, the structure of the μ_3-methylimido complex may be formally derived from that of the dimethylureylene-bridged compound, $[(CH_3N)_2CO]Fe_2(CO)_6$,[1] by replacement of the carbonyl group of the bridging ligand by a third $Fe(CO)_3$ moiety and formation of a metal–metal bond to the new iron atom from one of the two original iron atoms. The central portion of the resulting configuration may be envisioned as consisting of two Fe_2N_2 tetrahedra which share a N–Fe–N triangular face. The mean iron–nitrogen distance of 1.928 (11) Å is at the low end of the range of 1.94–2.00 Å for mean Fe–N distances in a variety of closely related binuclear and trinuclear species. All of these bonds may be regarded as single bonds, and the variations within this range are reasonable ones. The shorter distances occur for tetrahedral triply bridging nitrogen atoms [1.928 (11) Å in $(CH_3N)_2Fe_3(CO)_9$ and 1.95 Å in $[(C_6H_5)_2CNN]_2Fe_3(CO)_9$] and for trigonal doubly bridging nitrogen atoms [1.94 (1) Å in $[(p\text{-}CH_3C_6H_4)_2CNFe(CO)_3]_2$].[12] Bonds from iron atoms to tetrahedral doubly bridging nitrogen atoms are in general longer than these values [*e.g.*, 1.98 (1) Å in $[H_2NFe(CO)_3]_2$,[13] 1.996 (6) Å in $[(C_6H_5N)_2CO]Fe_2(CO)_6$,[14,15]

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[11] P. E. Baikie and O. S. Mills, *Chem. Commun.*, 1228 (1967).

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[14] J. A. J. Jarvis, B. E. Job, B. T. Kilbourn, R. H. B. Mais, P. G. Owston, and P. F. Todd, *Chem. Commun.*, 1149 (1967).

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TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS) FOR $(CH_3N)_2Fe_3(CO)_9$

K	L	FO	FC
***** H= 0 *****			
0	4	157	155
0	8	51	42
0	10	377	377
0	12	164	158
0	14	213	225
0	16	126	126
0	18	91	90
2	6	107	106
2	10	211	201
2	12	153	149
2	14	177	149
2	16	193	210
2	18	102	100
2	-8	170	153
2	-10	125	117
2	-12	225	217
2	-16	113	112
4	0	168	166
4	2	46	41
4	4	84	81
4	6	61	90
4	8	222	213
4	12	150	160
4	14	74	75
4	16	109	119
4	18	94	98
4	-2	175	168
4	-4	129	129
4	-6	164	162
4	-8	239	234
4	-16	172	183
4	-20	125	124
4	-22	97	92
6	0	78	72
6	2	236	234
6	4	257	253
6	8	215	226
6	12	116	117
6	-2	417	414
6	-4	169	159
6	-6	347	347
6	-8	194	194
6	-10	92	79
6	-14	235	231
6	-16	77	70
6	-18	220	234
8	0	351	365
8	2	126	134
8	4	63	69
8	6	255	277
8	10	241	258
8	14	151	143
8	20	109	112
8	-2	157	152
8	-4	300	314
8	-6	107	110
8	-8	197	203
8	-10	126	113
8	-14	55	77
8	-16	203	196
10	0	121	119
10	2	156	161
10	4	214	209
10	8	224	217
10	12	194	194
10	-2	214	206
10	-6	139	131
10	-14	91	85
12	2	115	97
12	4	82	65
12	-2	78	65
12	-6	116	110
12	-8	96	84
12	-10	127	129
14	0	94	80
14	4	123	134
14	-4	87	78
14	-6	93	94
14	-8	124	139
***** H= 1 *****			
1	5	116	116
1	7	105	87
1	9	105	98
1	13	233	261
1	17	185	172
1	-5	146	118
1	-7	640	761
1	-9	119	98
1	-11	315	363
1	-13	272	308
1	-15	194	191
1	-17	191	189
3	1	354	400
3	3	69	75
3	5	118	103
3	9	81	84
3	11	167	163
3	15	231	241
3	19	140	147
3	-1	168	204
3	-3	179	171
3	-7	96	88
3	-9	238	216
3	-11	213	205
3	-13	220	207
3	-15	177	130
5	1	297	292
5	3	321	304
5	11	66	69
5	13	105	84
5	15	118	114
5	17	142	135
5	-1	352	373
5	-3	230	239
5	-5	102	92
5	-9	176	161
5	-11	104	79
5	-17	119	105
7	7	158	157
7	9	140	123
7	11	106	103
7	13	197	185
7	-1	206	213
7	-3	127	109
7	-5	291	307
7	-7	217	225
7	-9	194	190
7	-15	224	238
7	-19	134	143
9	1	186	183
9	3	199	213
9	5	72	71
9	7	111	98
9	9	210	215
9	11	139	134
9	13	155	154
9	15	87	79
9	-1	118	132
9	-3	256	283
9	-5	254	262
9	-7	231	219
9	-9	79	64
9	-13	186	194
9	-17	199	214
11	1	193	180
11	3	87	79
11	5	92	91
11	7	151	143
11	11	132	123
11	-1	228	209
11	-3	269	286
11	-5	119	119
11	-7	91	84
11	-15	143	153
13	1	91	84
13	7	97	87
13	-1	63	77
13	-7	87	83
15	7	96	47
-1	7	117	99
-1	9	140	116
-1	11	201	192
-1	13	136	134
-1	15	111	112
-1	17	91	82
-1	-9	181	193
-1	-11	213	197
-1	-13	148	144
-1	-15	155	158
-3	3	208	224
-3	5	184	180
-3	7	236	231
-3	11	220	224
-3	17	138	155
-3	19	109	91
-3	21	114	121
-3	-3	136	131
-3	-5	144	124
-3	-7	224	213
-3	-11	80	70
-3	-13	139	130
-3	-15	138	157
-5	1	343	350
-5	3	191	193
-5	7	164	145
-5	9	267	242
-5	15	109	76
-5	17	120	121
-5	19	200	220
-5	-1	222	227
-5	-3	160	155
-5	-5	362	376
-5	-7	92	87
-5	-9	384	404
-5	-11	88	95
-5	-13	108	104
-5	-17	117	112
-7	3	304	311
-7	7	258	259
-7	11	89	78
-7	17	131	128
-7	-3	237	247
-7	-5	161	160
-7	-7	289	318
-7	-9	150	160
-7	-11	209	213
-7	-13	104	105
-7	-17	97	89
-7	-19	122	140
-9	1	177	187
-9	5	112	117
-9	7	92	89
-9	13	100	96
-9	17	110	105
-9	-1	89	93
-9	-3	160	160
-9	-5	80	63
-9	-7	108	96
-9	-9	194	199
-9	-11	122	111
-9	-13	133	142
-11	1	147	148
-11	9	137	135
-11	11	145	145
-11	15	112	111
-11	-3	215	219
-11	-7	108	91
-13	9	198	204
-13	-1	205	223
-13	-5	146	149
-15	-3	137	140
***** H= 2 *****			
0	4	130	129
0	6	385	428
0	8	119	125
0	10	132	117
0	12	69	58
0	14	144	144
0	16	139	120
0	18	77	69
0	-4	54	40
0	-6	119	119
0	-8	162	148
0	-12	220	219
0	-16	129	104
2	0	160	166
2	2	170	161
2	4	323	378
2	6	109	95
2	8	101	89
2	12	127	128
2	16	169	163
2	-4	95	44
2	-6	276	260
2	-8	76	79
2	-10	352	340
2	-12	113	129
2	-14	381	396
4	0	70	97
4	2	401	419
4	4	273	282
4	6	219	236
4	8	79	77
4	12	111	111
4	14	141	136
4	16	93	81
4	18	145	157
4	-2	89	81
4	-8	325	317
4	-10	100	92
4	-12	224	220
4	-16	73	62
6	2	78	68
6	4	152	172
6	6	75	89
6	16	149	149
6	18	82	83
6	20	126	121
6	-2	120	125
6	-6	243	239
6	-8	132	127
6	-10	100	104
6	-12	132	106
6	-18	92	79
8	0	61	54
8	2	61	45
8	4	75	65
8	10	76	73
8	-2	176	187
8	-6	164	137
8	-8	80	73
8	-10	70	53
8	-12	107	100
8	-14	76	63
8	-16	147	159
10	0	237	240
10	4	120	125
10	6	100	93
10	10	154	145
10	12	83	74
10	14	108	106
10	-4	263	277
10	-10	122	112
10	-14	189	186
12	2	157	162
12	10	113	103
12	12	81	84
12	-2	159	172
12	-6	139	146
12	-12	100	123
-2	2	109	95
-2	4	137	108
-2	6	424	407
-2	8	312	291
-2	10	366	376
-2	12	182	182
-2	14	96	89
-2	20	166	189
-2	-2	342	347
-2	-4	153	151
-2	-6	171	164
-2	-8	206	195
-2	-16	107	98
-4	2	119	129
-4	4	270	280
-4	6	81	86
-4	8	203	204
-4	10	199	192
-4	12	245	249
-4	18	178	183
-4	-2	383	388
-4	-4	313	348
-4	-6	213	209
-4	-8	295	295
-4	-10	118	134
-4	-12	127	124
-4	-16	167	168
-6	0	107	100
-6	2	125	125
-6	4	121	89
-6	6	175	170
-6	8	164	150
-6	10	106	102
-6	-2	195	180
-6	-6	240	251
-6	-8	88	90
-6	-10	242	255
-6	-12	87	69
-6	-14	92	66
-6	-16	122	121
-6	-20	136	151
-8	0	74	61
-8	2	90	75
-8	4	106	106
-8	12	136	130
-8	16	121	110
-8	-2	113	115
-8	-4	121	119
-8	-8	106	84
-10	0	136	159
-10	10	204	196
-10	14	203	211
-10	-2	123	136
-10	-4	128	129
-10	-10	95	70
-10	-12	101	76
-10	-16	108	103
-12	0	147	141
-12	2	161	163
-12	8	118	118
-12	12	180	189
-12	-2	192	201
-12	-4	111	101
-12	-14	110	106
-14	-2	105	110
***** H= 3 *****			
1	3	97	91
1	7	150	147
1	11	194	193
1	13	186	192
1	21	99	87
1	-3	159	139
1	-5	173	150
1	-7	149	137
1	-9	163	155
1	-11	85	73
1	-13	101	91
3	1	68	90
3	3	224	228
3	5	81	65
3	7	66	93
3	9	68	66
3	11	125	117
3	17	85	86
3	-1	102	88
3	-5	128	123
3	-7	170	162
3	-9	199	203
3	-11	202	184
3	-13	156	149
5	1	155	175
5	5	347	395
5	9	122	112
5	15	164	159
5	19	127	137
5	-1	76	65
5	-5	205	207
5	-7	186	189
5	-9	225	248
5	-11	118	122
5	-13	125	113
7	3	196	221
7	7	197	194
7	11	90	77
7	13	82	87
7	17	142	148
7	-1	71	64
7	-5	178	193
7	-7	218	224
7	-11	161	154
9	1	76	73
9	5	176	162
9	9	85	79
9	-1	107	97
9	-3	146	157
9	-5	75	67
9	-11	99	119
11	1	83	80
11	3	134	176
11	13	117	109
11	-1	166	151
11	-3	86	79
11	-5	118	126
11	-7	76	58
11	-9	78	65
11	-11	114	117
-1	3	358	365
-1	5	120	99
-1	7	208	206
-1	9	199	209
-1	11	288	293
-1	13	128	116
-1	19	125	100
-1	-3	324	336
-1	-5	79	77
-1	-7	266	269
-1	-9	69	55
-1	-13	107	101
-1	-15	96	92
-1	-17	106	114
-3	5	336	332
-3	7	164	151
-3	9	305	312
-3	11	121	114
-3	13	207	200
-3	-1	252	265
-3	-3	117	98
-3	-5	276	291
-3	-11	128	132
-3	-15	177	168
-3	-17	123	111
-3	-19	150	127
-5	5	132	104
-5	7	189	192
-5	11	82	85
-5	-1	95	107
-5	-3	177	158
-5	-5	75	82
-5	-7	236	260
-5	-15	108	112
-5	-17	148	155
-5	-21	106	94
-7	1	159	159
-7	3	179	187
-7	5	103	100
-7	11	99	109
-7	15	138	134
-7	-1	169	155
-7	-3	119	123
-7	-9	88	76
-7	-11	96	86
-7	-17	108	97
-9	1	269	304
-9	3	230	237
-9	5	140	129
-9	7	94	86
-9	11	141	135
-9	13	188	189
-9	15	158	152
-9	17	106	101
-9	-1	87	67
-9	-3	137	129
-9	-5	77	53
-9	-9	149	149
-9	-13	146	146
-11	1	110	100
-11	3	172	166
-11	9	120	122
-11	11	125	107
-11	13	142	151
-11	-1	265	277
-11	-3	88	69
-11	-5	89	93
-11	-11	194	146
-11	-15	124	139
-13	1	97	84
***** H= 4 *****			
0	4	174	186
0	8	202	211
0	10	261	256
0	14	220	232
0	-4	442	416
0	-6	163	152
0	-8	161	177
0	-10	98	96
0	-12	118	109
0	-14	124	134
0	-16	173	175
0	-18	95	89
2	0	77	83
2	2	109	107
2	8	190	183
2	10	74	73
2	12	217	223
2	16	112	108
2	-2	127	134
2	-4	89	83
2	-8	142	139
2	-10	113	121
2	-14	89	89
4	0	66	47
4	2	79	83
4	8	151	155
4	-2	89	81
4	-6	134	132
4	-8	78	70
4	-10	162	149
6	2	76	65
6	4	188	184
6	6	129	119
6	8	191	194
6	10	110	97
6	12	87	77
6	18	92	85
6	-2	70	76
6	-4	123	117
6	-6	108	103
6	-8	221	227
6	-10	137	132
6	-12	111	95
8	2	115	106
8	4	120	114
8	6	244	253
8	8	114	107
8	10	167	162
8	14	84	73
8	16	91	78
8	-2	97	94
8	-4	121	107
8	-6	153	149
8	-8	116	91
8	-10	100	87
10	4	89	83
10	8	123	121
10	-4	74	74
12	0	97	99
-2	2	193	216
-2	4	67	55
-2	6	104	99
-2	8	261	269
-2	10	79	67
-2	12	277	276
-2	14	100	96
-2	16	222	224
-2	-2	270	282
-2	-4	159	152
-2	-6	238	244
-2	-8	90	93
-2	-10	217	225
-2	-14	129	161
-4	2	93	89
-4	4	191	177
-4	6	81	71
-4	10	116	103
-4	12	121	96
-4	14	102	99
-4	-2	138	141
-4	-4	105	101
-4	-6	120	111
-4	-12	99	90
-4	-16	165	138
-6	2	249	264
-6	12	127	112
-6	16	145	151
-6	-2	140	150
-6	-4	97	91
-6	-8	135	136
-6	-12	138	139
-8	0	285	266
-8	4	285	275
-8	6	78	71
-8	8	107	95
-8	10	98	77
-8	14	165	178
-8	-4	173	183
-8	-6	80	67
-8	-8	91	76
-8	-10	172	169
-8	-14	104	103
-10	2	246	267
-10	6	129	124
-10	12	109	104
-10	-2	154	163
-10	-8	136	125
-10	-12	116	115
-10	-14	110	98
-14	2	97	81
***** H= 5 *****			
1	1	208	244
1	3	133	135
1	7	156	153
1	9	170	157
1	11	130	120
1	13	116	111
1	-1	146	172
1	-3	196	205
1	-5	88	67
1	-7	143	136
1	-13	204	196
1	-17	122	126
3	1	113	107
3	3	149	137
3	5	150	190
3	9	66	88
3	11	156	159
3	15	104	101
3	-1	137	142
3	-3	147	140
3	-5	71	67
3	-7	60	53
3	-11	122	115
3	-15	94	72
5	3	79	70
5	5	110	91
5	7	71	60
5	9	77	71
5	-1	102	98
5	-5	97	82
5	-7	125	112
7	1	64	55
7	3	73	56
7	5	153	146
7	7	148	169
7	9	158	160
7	-1	111	102
7	-5	168	133
7	-9	180	236
9	1	76	63
9	3	114	102
9	5	93	98
9	7	155	174
9	9	107	102
9	11	110	116
9	-1	92	82
9	-3	161	167
9	-7	147	157
-1	3	111	102
-1	5	167	146
-1	9	164	166
-1	11	137	129
-1	13	76	78
-1	-3	108	102
-1	-5	204	215
-1	-7	65	59
-1	-9	72	64
-1	-11	112	116
-1	-15	153	153
-3	3	112	102
-3	7	180	172
-3	9	70	66
-3	-3	58	35
-3	-11	90	84
-3	-13	88	76
-5	1	89	95
-5	3	112	133
-5	5	235	249
-5	9	84	83
-5	15	133	152
-5	-1	59	62
-5	-7	125	130
-5	-9	130	131
-7	1	160	165
-7	3	210	208
-7	5	139	132
-7	7	139	129
-7	13	105	109
-7	-1	127	128
-7	-3	82	76
-7	-5	71	58
-7	-7	133	120
-7	-9	148	141
-7	-11	149	171
-7	-13	112	109
-9	1	134	146
-9	3	223	217
-9	5	80	63
-9	7	66	69
-9	-1	63	49
-9	-5	85	87
-9	-7	88	71
-9	-9	83	62
-9	-11	127	141
-11	7	89	77
-13	-1	91	80
-13	-5	106	105
***** H= 6 *****			
0	2	117	117
0	-2	182	206
0	-4	143	119
0	-12	127	120
2	0	195	211
2	4	135	137
2	-4	167	166
2	-6	69	55
2	-10	137	120
2	-12	114	103
2	-14	148	153
4	2	156	164
4	4	93	76
4	-2	163	176
4	-6	69	54
4	-8	87	78
4	-12	125	117
6	4	86	75
6	-2	103	98
6	-4	124	121
-2	4	122	108
-2	6	123	110
-2	8	85	84
-2	-6	120	116
-2	-10	76	84
-4	2	137	143
-4	4	113	110
-4	6	193	184
-4	8	89	95
-4	-2	54	49
-4	-4	120	119
-4	-8	146	142
-4	-12	83	87
-6	0	81	74
-6	2	76	82
-6	4	148	159
-6	8	79	87
-6	-6	152	150
-6	-10	162	166
-6	-14	63	79
-8	-4	95	97
-8	-12	109	120
-10	6	85	87
***** H= 7 *****			
1	3	67	65
1	-3	81	82
3	1	76	75
3	5	71	69
3	-1	67	67
5	1	100	104
5	3	80	75
5	5	78	82
-1	7	112	118
-1	-3	79	76
-1	-7	122	117
-3	5	131	133
-3	9	116	109
-3	-5	142	151
-3	-9	111	113
-5	7	78	58
-5	-7	84	90
-5	-9	86	72
-7	-3	70	63

TABLE II

Atomic Positional and Thermal Parameters for $(CH_3N)_2Fe_3(CO)_9$

	x	y	z	B, Å²
Fe_1	0.2601 (4)[a]	0.4455 (2)	0.3942 (1)	. . .
Fe_2	0.4516 (4)	0.4027 (2)	0.3249 (1)	. . .
Fe_3	0.4851 (4)	0.3140 (2)	0.4022 (1)	. . .
C_{1-1}	0.2926 (32)	0.5479 (18)	0.4033 (11)	5.4 (7)
O_{1-1}	0.3096 (24)	0.6195 (13)	0.4087 (8)	7.0 (5)
C_{1-2}	0.0844 (32)	0.4514 (15)	0.3576 (10)	4.1 (6)
O_{1-2}	−0.0353 (23)	0.4576 (10)	0.3317 (7)	5.2 (4)
C_{1-3}	0.1616 (29)	0.4266 (14)	0.4572 (11)	4.0 (6)
O_{1-3}	0.0961 (22)	0.4106 (11)	0.4996 (8)	6.0 (5)
C_{2-1}	0.5586 (31)	0.4915 (16)	0.3066 (11)	4.6 (6)
O_{2-1}	0.6346 (23)	0.5553 (12)	0.2963 (8)	6.4 (5)
C_{2-2}	0.3319 (32)	0.3953 (15)	0.2671 (11)	4.5 (6)
O_{2-2}	0.2447 (23)	0.3912 (12)	0.2277 (8)	6.2 (5)
C_{2-3}	0.5884 (32)	0.3386 (15)	0.2971 (11)	4.3 (6)
O_{2-3}	0.6867 (23)	0.3027 (11)	0.2788 (8)	6.0 (5)
C_{3-1}	0.6934 (34)	0.3136 (15)	0.4145 (10)	4.0 (6)
O_{3-1}	0.8286 (25)	0.3110 (11)	0.4276 (8)	6.0 (5)
C_{3-2}	0.4646 (30)	0.2113 (16)	0.3820 (10)	4.3 (6)
O_{3-2}	0.4510 (23)	0.1416 (12)	0.3676 (8)	6.2 (5)
C_{3-3}	0.4271 (29)	0.3002 (15)	0.4719 (11)	3.9 (6)
O_{3-3}	0.4002 (23)	0.3001 (11)	0.5181 (9)	6.5 (5)
N_1	0.2873 (20)	0.3391 (10)	0.3672 (7)	2.9 (4)
N_2	0.4860 (21)	0.4282 (10)	0.4025 (7)	2.4 (4)
C_4	0.1614 (27)	0.2746 (13)	0.3465 (9)	3.3 (5)
C_5	0.6124 (25)	0.4866 (13)	0.4288(9)	2.9 (5)

Anisotropic Thermal Parameters $(\times 10^5)$[b]

	β_{11}	β_{22}	β_{33}	β_{13}	β_{13}	β_{23}
Fe_1	1046 (162)	204 (16)	109 (8)	82 (28)	−28 (17)	5 (8)
Fe_2	1273 (160)	216 (17)	85 (8)	0 (30)	42 (17)	46 (8)
Fe_3	1019 (161)	198 (16)	111 (8)	31 (29)	22 (17)	33 (8)

[a] Numbers in parentheses in tables and in the text are standard deviations in the least significant figures. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

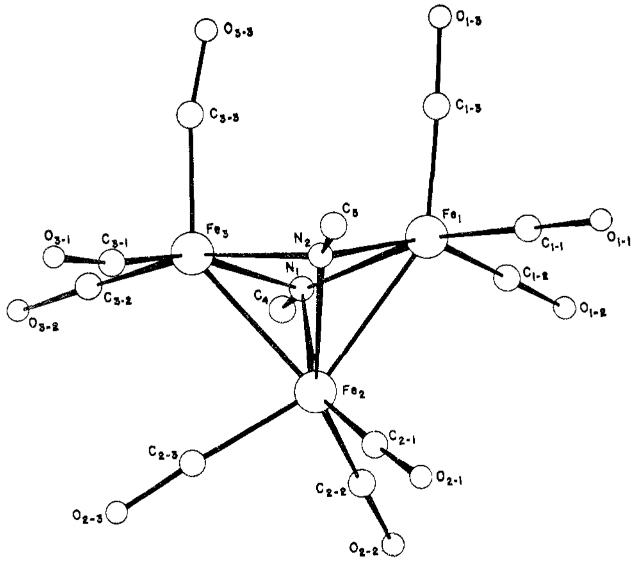

Figure 1.—The molecular configuration of $(CH_3N)_2Fe_3(CO)_9$.

1.965 (10) Å in $[(CH_3N)_2CO]Fe_2(CO)_6$,[1] and *ca.* 2.00 Å in $[(p\text{-}CH_3C_6H_4)_2CNHNFe(CO)_3]_2$.[6] Dihedral angles of 96.9 (9) and 98.4 (10)° are observed between the pairs of planes (Fe_1–Fe_2–N_1, Fe_1–Fe_2–N_2) and (Fe_3–Fe_2–N_1, Fe_3–Fe_2–N_2), respectively. These values are intermediate between the observed dihedral angles of 104.0 (10)° in $[H_2NFe(CO)_3]_2$, in which the amido groups are unconstrained by any bond or bridging group between them, and 84.9 (10)° in $[(CH_3N)_2CO]Fe_2(CO)_6$, in which the bridging nitrogen atoms are bridged in turn by a CO group. The nonbonded N · · · N distance of 2.24 (2) Å between the two triply bridging nitrogen atoms is likewise intermediate between the values of 2.10 (2) and 2.50 (3) Å reported for the corresponding distance in the $(CH_3N)_2CO$-bridged complex and NH_2-bridged dimer, respectively.

The confirmation of the proposed structure of $(CH_3N)_2Fe_3(CO)_9$ extends the analogy between nitrogen- and sulfur-bridged iron carbonyls and permits further comparisons of the geometries of these two types of

TABLE III

BOND LENGTHS AND SELECTED INTRAMOLECULAR NONBONDED CONTACTS (Å)

Fe_1–Fe_2	2.436 (7)	Fe_2–Fe_3	2.488 (7)	$Fe_1 \cdots Fe_3$	3.044 (8)
Mean Fe–Fe	2.462 (7)				
Fe_1–N_1	1.89 (2)	Fe_2–N_1	1.96 (2)	Fe_3–N_1	1.95 (2)
Fe_1–N_2	1.94 (2)	Fe_2–N_2	1.92 (2)	Fe_3–N_2	1.90 (2)
Mean Fe–N	1.928 (11)				
Fe_1–C_{1-1}	1.70 (3)	Fe_2–C_{2-1}	1.72 (3)	Fe_3–C_{3-1}	1.76 (3)
Fe_1–C_{1-2}	1.73 (3)	Fe_2–C_{2-2}	1.72 (3)	Fe_3–C_{3-2}	1.74 (3)
Fe_1–C_{1-3}	1.76 (3)	Fe_2–C_{2-3}	1.75 (3)	Fe_3–C_{3-3}	1.77 (3)
Mean Fe–C	1.739 (9)				
N_1–C_4	1.49 (3)	N_2–C_5	1.48 (2)		
Mean N–C	1.482 (18)				
C_{1-1}–O_{1-1}	1.19 (3)	C_{2-1}–O_{2-1}	1.21 (3)	C_{3-1}–O_{3-1}	1.18 (3)
C_{1-2}–O_{1-2}	1.20 (3)	C_{2-2}–O_{2-2}	1.20 (3)	C_{3-2}–O_{3-2}	1.19 (3)
C_{1-3}–O_{1-3}	1.19 (3)	C_{2-3}–O_{2-3}	1.14 (3)	C_{3-3}–O_{3-3}	1.14 (3)
Mean C–O	1.181 (9)				
$C_{1-1} \cdots C_{1-2}$	2.46 (4)	$C_{2-1} \cdots C_{2-2}$	2.50 (4)	$C_{3-1} \cdots C_{3-2}$	2.51 (4)
$C_{1-1} \cdots C_{1-3}$	2.60 (4)	$C_{2-1} \cdots C_{2-3}$	2.58 (4)	$C_{3-1} \cdots C_{3-3}$	2.60 (4)
$C_{1-2} \cdots C_{1-3}$	2.57 (4)	$C_{2-2} \cdots C_{2-3}$	2.55 (4)	$C_{3-2} \cdots C_{3-3}$	2.60 (4)
$N_1 \cdots C_{1-2}$	2.67 (3)	$N_2 \cdots C_{1-1}$	2.69 (4)		
$N_1 \cdots C_{2-2}$	2.66 (3)	$N_2 \cdots C_{2-1}$	2.65 (3)		
$N_1 \cdots C_{3-2}$	2.76 (3)	$N_2 \cdots C_{3-1}$	2.74 (3)		
$N_1 \cdots C_{1-3}$	2.81 (3)	$N_2 \cdots C_{3-3}$	2.79 (3)		
$N_1 \cdots C_{3-3}$	2.94 (3)	$N_2 \cdots C_{1-3}$	2.99 (3)		
$N_1 \cdots C_{2-3}$	3.01 (3)	$N_2 \cdots C_{2-3}$	3.05 (3)		
$N_1 \cdots N_2$	2.24 (2)				

TABLE IV

INTRAMOLECULAR ANGLES (DEG)

Fe_2–Fe_1–Fe_3	52.6 (2)	Fe_2–Fe_3–Fe_1	51.0 (2)
Fe_2–Fe_1–N_1	51.9 (5)	Fe_2–Fe_3–N_1	50.5 (5)
Fe_2–Fe_1–N_2	50.6 (5)	Fe_2–Fe_3–N_2	49.8 (5)
Fe_2–Fe_1–C_{1-1}	107.7 (9)	Fe_2–Fe_3–C_{3-1}	108.4 (8)
Fe_2–Fe_1–C_{1-2}	104.4 (8)	Fe_2–Fe_3–C_{3-2}	113.3 (9)
Fe_2–Fe_1–C_{1-3}	147.1 (9)	Fe_2–Fe_3–C_{3-3}	141.8 (9)
N_1–Fe_1–N_2	71.5 (7)	N_1–Fe_3–N_2	71.1 (7)
N_1–Fe_1–C_{1-1}	159.6 (10)	N_1–Fe_3–C_{3-1}	158.9 (10)
N_1–Fe_1–C_{1-2}	94.9 (10)	N_1–Fe_3–C_{3-2}	96.3 (10)
N_1–Fe_1–C_{1-3}	100.9 (10)	N_1–Fe_3–C_{3-3}	103.9 (10)
N_2–Fe_1–C_{1-1}	95.0 (11)	N_2–Fe_3–C_{3-1}	96.6 (10)
N_2–Fe_1–C_{1-2}	154.9 (10)	N_2–Fe_3–C_{3-2}	162.9 (10)
N_2–Fe_1–C_{1-3}	107.9 (10)	N_2–Fe_3–C_{3-3}	98.7 (10)
C_{1-1}–Fe_1–C_{1-2}	91.6 (12)	C_{3-1}–Fe_3–C_{3-2}	91.7 (12)
C_{1-1}–Fe_1–C_{1-3}	97.8 (12)	C_{3-1}–Fe_3–C_{3-3}	94.7 (12)
C_{1-2}–Fe_1–C_{1-3}	95.1 (12)	C_{3-2}–Fe_3–C_{3-3}	95.4 (12)
Fe_1–Fe_2–Fe_3	76.4 (2)		
Fe_1–Fe_2–N_1	49.5 (5)	Fe_3–Fe_2–N_1	50.4 (6)
Fe_1–Fe_2–N_2	51.3 (6)	Fe_3–Fe_2–N_2	49.0 (6)
Fe_1–Fe_2–C_{2-1}	104.1 (9)	Fe_3–Fe_2–C_{2-1}	131.8 (9)
Fe_1–Fe_2–C_{2-2}	100.1 (9)	Fe_3–Fe_2–C_{2-2}	134.7 (9)
Fe_1–Fe_2–C_{2-3}	153.9 (9)	Fe_3–Fe_2–C_{2-3}	77.9 (9)
N_1–Fe_2–C_{2-1}	153.7 (10)	N_2–Fe_2–C_{2-1}	93.0 (10)
N_1–Fe_2–C_{2-2}	92.6 (10)	N_2–Fe_2–C_{2-2}	151.4 (10)
N_1–Fe_2–C_{2-3}	108.8 (10)	N_2–Fe_2–C_{2-3}	112.2 (11)
C_{2-1}–Fe_2–C_{2-2}	93.3 (13)		
C_{2-1}–Fe_2–C_{2-3}	96.2 (12)		
C_{2-2}–Fe_2–C_{2-3}	94.8 (13)		
Fe_1–N_1–C_4	128.2 (14)	Fe_1–N_2–C_5	125.5 (14)
Fe_2–N_1–C_4	128.3 (13)	Fe_2–N_2–C_5	127.8 (13)
Fe_3–N_1–C_4	121.9 (14)	Fe_3–N_2–C_5	124.2 (14)
Fe_1–N_1–Fe_2	78.6 (7)	Fe_1–N_2–Fe_2	78.0 (7)
Fe_1–N_1–Fe_3	104.7 (8)	Fe_1–N_2–Fe_3	104.7 (8)
Fe_2–N_1–Fe_3	79.1 (7)	Fe_2–N_2–Fe_3	81.2 (7)
Fe_1–C_{1-1}–O_{1-1}	177.4 (26)	Fe_3–C_{3-1}–O_{3-1}	173.8 (23)
Fe_1–C_{1-2}–O_{1-2}	178.0 (24)	Fe_3–C_{3-2}–O_{3-2}	179.3 (33)
Fe_1–C_{1-3}–O_{1-3}	177.4 (24)	Fe_3–C_{3-3}–O_{3-3}	171.8 (22)
Fe_2–C_{2-1}–O_{2-1}	176.9 (24)		
Fe_2–C_{2-2}–O_{2-2}	178.0 (26)		
Fe_2–C_{2-3}–O_{2-3}	174.1 (23)		

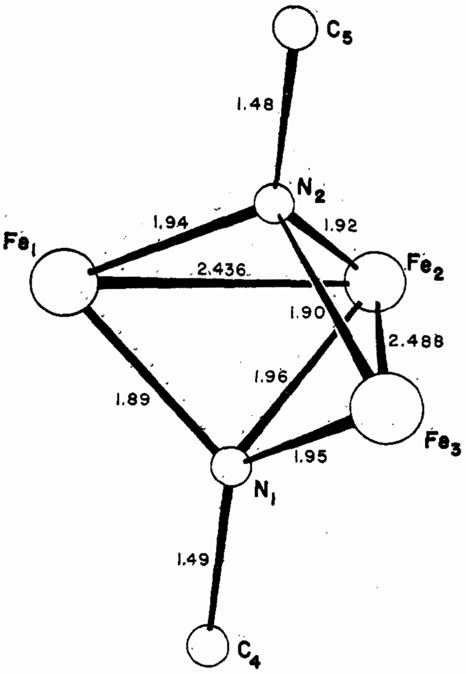

Figure 2.—The central portion of the $(CH_3N)_2Fe_3(CO)_9$ molecule, with bond lengths (in Å).

bridging systems. The methylimido groups in the present compound are analogous to the triply bridging chalcogen atoms in $Se_2Fe_3(CO)_9$[16] and $S_2Fe_3(CO)_9$;[8] the doubly bridging C_2H_5S groups in $[C_2H_5SFe(CO)_3]_2$[17] have found parallels in the nitrogen-bridged compounds $[H_2NFe(CO)_3]_2$ and $[(RN)_2CO]Fe_2(CO)_6$ (R = CH_3, C_6H_5). In these compounds, the SR and NR_2 groups are formal three-electron donors, and the NR group and the S atom function as four-electron donors. The shortening of the mean Fe–N distance from 1.965 (10) Å in $[(CH_3N)_2CO]Fe_2(CO)_6$ to 1.928 (11) Å in $(CH_3N)_2Fe_3(CO)_9$ is closely similar to the contraction in the mean Fe–S distance from 2.259 (6) Å in $[C_2H_5SFe(CO)_3]_2$ to 2.229 (5) Å in $S_2Fe_3(CO)_9$. The mean

[16] L. F. Dahl and P. W. Sutton, *Inorg. Chem.* **2**, 1067 (1963).
[17] L. F. Dahl and C. H. Wei, *ibid.*, **2**, 328 (1963).

values of 79.2 (4) and 104.7 (6)° for the two independent Fe–N–Fe angles are greater than the values of 71.2 (2) and 98.4 (4)° observed for the corresponding Fe–S–Fe angles in $S_2Fe_3(CO)_9$; the difference is of a comparable magnitude to that observed in the corresponding binuclear compounds [*e.g.*, 75.0° in $[(CH_3N)_2CO]Fe_2(CO)_6$ *vs.* 68.4° in $[C_2H_5SFe(CO)_3]_2$].

The two outer iron atoms, Fe_1 and Fe_3, are each coordinated to three terminal carbonyl groups, the two bridging nitrogen atoms, and Fe_2 in a distorted octahedral configuration similar to that found in a variety of related compounds. The central iron atom, Fe_2, has a seven-coordinate geometry of the type observed in the isostructural sulfur complex $S_2Fe_3(CO)_9$[8] and closely related to that of the selenium analog $Se_2Fe_3(CO)_9$.[16] A view of this coordination, projected onto a plane perpendicular to the vector defined by Fe_2 and the point midway between Fe_1 and Fe_2, is shown in Figure 3.

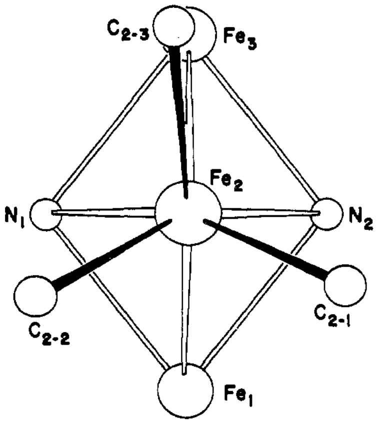

Figure 3.—The coordination of Fe_2, as projected onto the plane perpendicular to the line defined by Fe_2 and the Fe_1–Fe_3 midpoint.

The two iron–iron bond distances of 2.436 (7) and 2.488 (7) Å differ significantly on the basis of their estimated standard deviations. As can clearly be seen in Figure 3, the seven-coordinate configuration about Fe_2 is one which leaves the outer iron atoms Fe_1 and Fe_3 nonequivalent. The steric and electronic factors which might lead to a difference in iron–iron bond lengths cannot be sorted out with any confidence; it is, however, worth noting that the $Fe_3 \cdots C_{2-3}$ contact is a rather short one of 2.72 (3) Å while the $Fe_1 \cdots C_{2-1}$ and $Fe_1 \cdots C_{2-2}$ nonbonded distances are 3.31 (3) and 3.22 (3) Å, respectively. The Fe–Fe bond lengths in $[C_6H_5CNN]_2Fe_3(CO)_9$ are reported to differ by 0.03 Å,[11] but it cannot be determined from the preliminary published results whether this difference is significant or whether it is consistent with that observed in the present case. The mean iron–iron bond distance of 2.462 (5) Å in this compound and that of 2.445 Å in $[C_6H_5CNN]_2Fe_3(CO)_9$ are significantly longer than the range of 2.37–2.40 Å observed for iron–iron bond distances in compounds containing two Fe–N–Fe bridges.[18] This effect is also observed in the analogous doubly and triply bridged sulfur compounds. The nonbonded Fe_1–Fe_3 distance of 3.044 (8) Å is again close to the value of 3.06 Å found for the corresponding distance in $[C_6H_5CNN]_2Fe_3(CO)_9$; it is longer than any reported iron–iron bond, and simple electron-counting considerations suggest that no bond should be required.

The only other compound in which a crystal structure analysis has confirmed the presence of a triangle of metal atoms triply bridged by an N–R group is the paramagnetic nickel complex t-$C_4H_9N(NiC_5H_5)_3$.[19] Though final comment on this structure must be reserved until full structural results are published, the preliminary bond lengths quoted do not appear to fall into the pattern established by the iron compounds.

Normal values are observed for the mean Fe–C, C–O, and N–C bond lengths, with none of the individual bonds of these types showing significant variations from the averages. The Fe–C–O angles range from 171.8 (22) to 179.3 (33)°. Intermolecular contacts are of normal lengths for molecular crystals, with the shortest (not considering the methyl hydrogen atoms) being a distance of 3.11 (3) Å between two carbonyl oxygen atoms. The trends in the isotropic temperature factors of the light atoms are in accord with qualitative expectations, and the anisotropic thermal parameters for the three iron atoms give rise to reasonable principal rms amplitudes of motion—0.165 (8), 0.176 (7), and 0.195 (11) Å for Fe_1; 0.134 (8), 0.188 (6), and 0.214 (13) Å for Fe_2; and 0.155 (7), 0.186 (9), and 0.192 (9) Å for Fe_3.

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(18) See ref 13 for a summary of these bond lengths.

(19) S. Otsuka, A. Nakamura, and T. Yoshida, *Inorg. Chem.*, **7**, 261 (1968).