be analogous to complex III, whose formulation is uncertain at the present time. A structural study of III is clearly needed and will be carried out. It is not clear at this stage why the carbonyl ligands which are present in II are not also present in the binuclear compound reported by Connelly and McCleverty,[3] but a possible reason could be in the relative π acidities of the two ligands $S_2C_2(CF_3)_2$ and tdt. The former is a stronger π acid which may be able to withdraw enough electron density from the vicinity of the iridium atom

to make the carbonyl ligand more susceptible to dissociation. With the weaker π-acid ligand tdt, the carbonyl ligands are retained in the binuclear species.

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Structural Studies of Organonitrogen Compounds of the Transition Elements. V. The Structure of μ-2,3-[2,3-Diazabicyclo[2.2.1]heptane]diyl-bis(tricarbonyliron), C5H8N2Fe2(CO)6, an Iron Carbonyl Complex of a Bicyclic Aliphatic Azo Compound

BY R. G. LITTLE AND ROBERT J. DOEDENS*

The crystal and molecular structure of $C_5H_8N_2Fe_2(CO)_6$, an iron carbonyl adduct of 2,3-diazabicyclo[2.2.1]hept-2-ene, has been determined by a single-crystal X-ray analysis. This compound crystallizes in space group $P2_1/c$ of the monoclinic system, with eight molecules in a unit cell of dimensions $a = 9.118$ (4), $b = 22.210$ (2), $c = 13.787$ (7) Å, $\beta = 92.78$ (2)°. Observed and calculated densities are 1.75 (2) and 1.79 g/cm³, respectively. Least-squares refinement, based upon 2513 independent observed counter data, converged to a conventional R factor of 0.056. The two discrete crystallographically independent $C_5H_8N_2Fe_2(CO)_6$ molecules have nearly identical configurations, with two Fe(CO)₃ groups linked by the two ligand nitrogen atoms through Fe–N–Fe bridges and also by an iron–iron bond of length 2.490 (2) Å. A N–N bond is retained in the complex; its length of 1.404 (9) Å is close to that expected for a single bond. Iron–nitrogen distances range from 1.906 (7) to 1.937 (7) Å. Both molecules exhibit small but significant departures from C_s-m symmetry.

Introduction

The coordination chemistry of the azo group has become a matter of considerable interest. Much of this interest stems from the potential intermediacy of metal complexes of diimide, the simplest azo compound, in the biological nitrogen-fixation process. Even apart from this, it is of interest to define the various possible modes of coordination of simple azo compounds (R—N=N–R'), to examine the factors influencing which of these modes will be adopted in a particular instance, and to compare the –N=N– grouping with the closely related >C=N– and >C=C< functions. Excluding cases in which the azo link is completely ruptured, four principal modes of coordination have been demonstrated to result from the reactions of simple azo compounds with transition metal systems: coordination through the lone pair of a single nitrogen atom (I), π coordination (II), and two types of bridging configuration (III and IV). Structures of type I in which coordination of the azo ligand is *solely* through one nitrogen lone pair have been proposed in a number of instances,[1-3] but to date no X-ray studies confirming such structures have been reported. Coordination of a single nitrogen of the azo group is often observed in
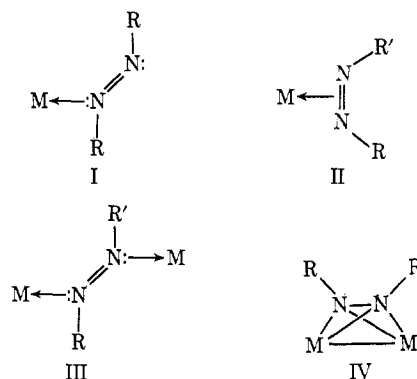
chelate structures containing a metal–carbon,[4-9] metal–oxygen,[10,11] or metal–nitrogen[11] bond to an atom of R or R'. Structurally characterized examples of the other types of coordination include (II) a recently reported nickel(0)–azobenzene adduct,[12] (III) the

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cuprous chloride–azomethane complex,[13] and (IV) iron carbonyl derivatives of azomethane and benzo[c]cinnoline.[14,15] In each of the last two compounds the bonding was considered to conform qualitatively to a valence-bond structure like that shown, with N—N and Fe—N single bonds. One thus could regard structures of type IV as resulting from addition across the N=N bond.

Coordination compounds of the bicyclic aliphatic azo compound 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) have recently been investigated by several workers.

DBH
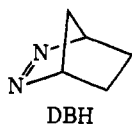
Denning and Thatcher[1] reported several platinum chloride derivatives of DBH including compounds proposed to have structures of types I (with the azo group constrained to a cis configuration) and III. Bennett[16] prepared an iron carbonyl derivative, (DBH)-Fe₂(CO)₆, presumably having a structure of type IV. This compound was also reported by Herberhold and Golla,[3] together with chromium carbonyl and cyclopentadienylmanganese carbonyl complexes of DBH.

We report now the results of an X-ray structural investigation of (DBH)Fe₂(CO)₆, carried out to establish the mode of coordination of this new type of azo ligand and to compare the structure of the complex with the structures of the previously studied azomethane and benzo[c]cinnolineiron carbonyl derivatives.

Collection and Reduction of the Intensity Data

A sample of C₅H₈N₂Fe₂(CO)₆ was generously supplied by Dr. R. P. Bennett. Suitable single crystals could be prepared by recrystallization from acetone. Precession photographs (*hk*0, *hk*1, *h*0*l*, *h*1*l*) displayed monoclinic symmetry with systematic absences (*h*0*l*, *l* = 2*n*; 0*k*0, *k* = 2*n*) consistent with space group C_{2h}^5-$P2_1/c$. Lattice parameters were obtained by least-squares refinement[17] of the setting angles of 14 reflections with $2\theta \geq 18°$ which had been accurately centered on a Picker four-circle X-ray diffractometer. The unit cell constants (23°, λ(Mo Kα₁) 0.70926 Å) obtained in this manner are $a = 9.118$ (4), $b = 22.210$ (12), $c = 13.787$ (7)Å, $\beta = 92.78$ (2)°. The numbers in parentheses are the standard deviations obtained from the least squares refinement of the setting angles. The density of 1.79 g/cm³ calculated on the basis of eight formula units per cell agrees reasonably well with a density of 1.75 (2) g/cm³ obtained by floatation in aqueous zinc bromide solution.

Intensity data were collected from a well-formed, orange, tabular crystal of dimensions 0.20 × 0.33 × 0.60 mm mounted in a thin-walled glass capillary with its longest dimension (the crystallographic [100] direction) parallel to the capillary walls. The 0.20-mm dimension was perpendicular to the well-developed {010} faces; other bounding planes belonged to the {011} and {121̄} forms. The data were collected on a Picker

automatic diffractometer by use of procedures previously described.[18] A takeoff angle of 1.3° was employed. The diffracted beam was filtered through 3.0-mil Nb foil. The counter aperture was 5 × 5 mm and was positioned 28 cm from the crystal. The pulse-height analyzer was set to admit ~95% of the Mo Kα peak. Data were collected by the θ–2θ scan method. A symmetric scan range of ±0.80° in 2θ from the calculated scattering angle was employed for reflections with $2\theta < 35°$; above 35° an additional 0.1° was added to each end of this range. The intensities of all independent reflections with $2\theta \leq 45°$ were measured. The scan rate was 1°/min and stationary background counts of 10 sec were taken at each end of the scan range. Copper foil attenuators were automatically inserted whenever the count rate exceeded ~10,000 counts/ sec; only five reflections required attenuation. Four standard reflections, chosen to lie in widely separated regions of reciprocal space, were monitored regularly throughout the collection of data. During the data collection there was a 6% overall decrease in the intensity of these standards. This decrease was of a comparable magnitude for all four standards and was a roughly linear function of the time of exposure of the crystal to the X-ray beam.

Previously described methods were employed in processing the data.[18] The *p* factor in the expression for the standard deviation of the observed intensities was assigned a value of 0.05. Of the 3529 independent data collected, 2513 were above background by three or more standard deviations. The observed intensities were scaled upward to compensate for the systematic decrease in intensity of the standards. An absorption correction was applied; based on a linear absorption coefficient of 21.2 cm⁻¹ the calculated transmission factors ranged from 0.59 to 0.72.

Solution and Refinement of the Structure

The coordinates of the iron atoms were determined by direct methods. Normalized structure factors (*E*'s) were calculated and 233 reflections with $E \geq 1.80$ were phased by use of Long's program for reiterative application of the Sayre equation.[19] An *E* map based on the solution of greatest internal consistency yielded four peaks with the configuration expected of the iron atoms—two well-separated pairs with a distance of ~2.5 Å between the peaks in each pair. Least-squares refinement of positional and isotropic thermal parameters for the four iron atoms and a scale factor yielded the discrepancy factors $R_1 = \Sigma||F_o| - |F_o||/\Sigma|F_o| = 0.391$ and $R_2 = [\Sigma w(|F_o| - |F_o|)^2/\Sigma w|F_o|^2]^{1/2} = 0.478$. Positional parameters of the 38 carbon, nitrogen, and oxygen atoms were obtained by standard heavy-atom methods. Refinement of positional and isotropic thermal parameters for all nonhydrogen atoms, based upon all data with $F_o^2 \geq 3\sigma(F_o^2)$, converged to $R_1 = 0.069$ and $R_2 = 0.090$. A difference Fourier map at this point showed peaks of about 1.2 e/Å³ very near the iron atoms and no other peaks greater than 0.86 e/Å³. Further refinement employed anisotropic thermal parameters for the iron atoms and isotropic *B*'s for all other atoms. The 16 hydrogen atoms were included as fixed contributions to F_c based upon their "ideal" tetrahedral positions (C–H = 1.08 Å). This final refinement converged to $R_1 = 0.056$ and $R_2 = 0.071$, with the largest parameter shift in the last cycle equal to 0.22σ.

Throughout the least-squares refinement, the 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 standard deviation of an observation of unit weight was 2.0. Calculation of $w(\Delta F)^2$ for subsets of the data as a function of uncorrected intensity, observed *F*, and Bragg angle showed no significant trends, thus confirming that the relative weights were appropriate. Calculations of structure factors for data with $F_o^2 \leq 3\sigma(F_o^2)$ revealed 19 reflections with $||F_o| - |F_o||/\sigma(F_o) \geq 3$; only three of these had $\Delta F/\sigma > 4$. Scattering factors for Fe, C, N, and O were taken from ref 20 and those of Stewart, *et al.*,[21] were employed for H. Structure factor calculations included provisions for the real and imaginary parts of anomalous scattering by the iron atoms.[22]

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(17) This refinement was accomplished by use of J. A. Ibers' diffractometer setting program PICK. Other computer programs employed in this structural analysis included local versions of PICKOUT (R. J. Doedens, J. A. Ibers) for data processing, GONO (W. C. Hamilton) for absorption correction, FAME (R. B. K. Dewar) for scaling and calculation of *E*'s, REL (R. E. Long) for initial phasing, FORDAP (A. Zalkin) for Fourier summation, UCIGLS (derived from Busing, Martin, and Levy's ORFLS) for structure factor calculations and least-squares refinement, ORFFE (Busing, Martin, and Levy) for function and error calculations, PLANET (D. L. Smith) for least-squares plane calculations, DANFIG (R. J. Dellaca, W. T. Robinson) and ORTEP (C. K. Johnson) for preparation of the figures, and RSCAN (R. J. Doedens) for evaluation of the weighting scheme. All computations were carried out on the local PDP-10 computer.

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TABLE I: ATOMIC POSITIONAL AND THERMAL PARAMETERS[a]

Atom	x	y	z	B, Å^2
		Molecule A		
Fe(1)	−0.25482 (13)	0.07569 (5)	0.11416 (9)	...
Fe(2)	−0.30070 (13)	0.11841 (6)	−0.05154 (8)	...
C(1)	−0.2563 (10)	0.0726 (4)	0.2420 (7)	4.1 (2)
O(1)	−0.2477 (8)	0.0678 (3)	0.3260 (5)	5.8 (2)
C(2)	−0.0626 (11)	0.0729 (4)	0.1085 (7)	4.5 (2)
O(2)	0.0648 (9)	0.0716 (3)	0.1046 (5)	6.4 (2)
C(3)	−0.2801 (10)	−0.0019 (4)	0.0962 (6)	3.9 (2)
O(3)	−0.3004 (8)	−0.0528 (3)	0.0866 (5)	6.0 (2)
C(4)	−0.3853 (11)	0.1624 (4)	−0.1443 (7)	4.4 (2)
O(4)	−0.4359 (8)	0.1887 (4)	−0.2106 (6)	6.5 (2)
C(5)	−0.1203 (11)	0.1334 (4)	−0.0836 (7)	4.6 (2)
O(5)	−0.0006 (8)	0.1467 (3)	−0.1013 (5)	6.2 (2)
C(6)	−0.3188 (10)	0.0506 (4)	−0.1141 (7)	3.9 (2)
O(6)	−0.3339 (7)	0.0049 (3)	−0.1568 (5)	5.4 (2)
N(1)	−0.4265 (7)	0.1124 (3)	0.0550 (5)	3.2 (1)
N(2)	−0.3142 (7)	0.1547 (3)	0.0738 (5)	2.9 (1)
C(7)	−0.5639 (10)	0.1406 (4)	0.0923 (7)	4.1 (2)
C(8)	−0.4961 (10)	0.1757 (4)	0.1381 (7)	4.5 (2)
C(9)	−0.3843 (10)	0.2075 (4)	0.1220 (6)	3.9 (2)
C(10)	−0.4801 (11)	0.2377 (5)	0.0461 (7)	5.0 (2)
C(11)	−0.6008 (11)	0.1931 (5)	0.0271 (7)	4.8 (2)
H1C7[b]	−0.6529	0.1101	0.1059	5.3
H2C9	−0.3090	0.2369	0.1619	5.3
H3C8	−0.4470	0.1468	0.2386	5.3
H4C8	−0.5724	0.2060	0.2154	5.3
H5C10	−0.4211	0.2460	−0.0187	5.3
H6C10	−0.5223	0.2797	0.0724	5.3
H7C11	−0.7052	0.2123	0.0442	5.3
H8C11	−0.6051	0.1792	−0.0481	5.3
		Molecule B		
Fe(1)	−0.00958 (14)	0.32864 (6)	0.02231 (9)	...
Fe(2)	0.17724 (13)	0.38145 (6)	0.12896 (8)	...
C(1)	−0.0959 (13)	0.3034 (5)	−0.0857 (9)	6.3 (3)
O(1)	−0.1586 (10)	0.2835 (4)	−0.1557 (7)	8.6 (2)
C(2)	−0.1712 (13)	0.3549 (5)	0.0692 (8)	6.3 (3)
O(2)	−0.2735 (11)	0.3742 (4)	0.1068 (7)	8.8 (2)
C(3)	−0.0049 (11)	0.2584 (5)	0.0817 (7)	4.7 (2)
O(3)	0.0046 (8)	0.2122 (4)	0.1214 (5)	6.2 (2)
C(4)	0.3395 (11)	0.4225 (4)	0.1607 (7)	4.3 (2)
O(4)	0.4457 (8)	0.4475 (3)	0.1873 (5)	6.1 (2)
C(5)	0.0623 (10)	0.4240 (4)	0.2020 (7)	4.2 (2)
O(5)	−0.0128 (8)	0.4539 (3)	0.2470 (5)	5.7 (2)
C(6)	0.2111 (9)	0.3230 (4)	0.2150 (6)	3.7 (2)
O(6)	0.2295 (7)	0.2845 (3)	0.2695 (5)	5.4 (2)
N(1)	0.1913 (7)	0.3475 (3)	0.0003 (5)	3.3 (1)
N(2)	0.1031 (7)	0.3992 (3)	0.0006 (5)	3.5 (1)
C(7)	0.2812 (11)	0.3520 (5)	−0.0851 (7)	5.0 (2)
C(8)	0.1747 (12)	0.3829 (5)	−0.1575 (8)	5.9 (3)
C(9)	0.1420 (12)	0.4338 (5)	−0.0876 (8)	5.5 (2)
C(10)	0.2938 (12)	0.4598 (5)	−0.0650 (8)	5.9 (2)
C(11)	0.3906 (12)	0.4037 (5)	−0.0644 (8)	5.9 (2)
H1C7	0.3280	0.3103	−0.1094	6.6
H2C9	0.0603	0.4657	−0.1142	6.6
H3C8	0.0796	0.3559	−0.1778	6.6
H4C8	0.2255	0.3981	−0.2223	6.6
H5C10	0.2999	0.4820	0.0048	6.6
H6C10	0.3243	0.4912	−0.1203	6.6
H7C11	0.4696	0.4063	−0.1201	6.6
H8C11	0.4478	0.3978	0.0054	6.6

Anisotropic Thermal Parameters (×10^5)[c]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
			Molecule A			
Fe(1)	894 (18)	148 (3)	464 (8)	37 (6)	31 (9)	14 (4)
Fe(2)	918 (18)	165 (3)	426 (8)	12 (6)	56 (9)	9 (4)
			Molecule B			
Fe(1)	945 (19)	184 (3)	525 (9)	−63 (6)	−85 (10)	32 (4)
Fe(2)	874 (18)	159 (3)	364 (8)	−7 (6)	42 (9)	10 (4)

[a] Numbers in parentheses in all tables and in the text are estimated standard deviations in the least significant figures. [b] Coordinates of the hydrogen atoms are calculated values (see text). The designation of a hydrogen atom includes a specification of the carbon atom to which it is bound. Thermal parameters of the hydrogen atoms were set at one unit greater than the average of the temperature factors of the ring carbon atoms in the molecule under consideration. [c] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Final atomic positional and thermal parameters are listed in Table I and intramolecular distances and angles are tabulated in Tables II and III, respectively. A table of observed and calculated structure factors is available.[23]

TABLE II
INTRAMOLECULAR DISTANCES (Å)

	Molecule A	Molecule B
Fe(1)–Fe(2)	2.490 (2)	2.489 (2)
Fe(1)–N(1)	1.913 (7)	1.917 (7)
Fe(1)–N(2)	1.912 (7)	1.906 (7)
Fe(2)–N(1)	1.912 (7)	1.937 (7)
Fe(2)–N(2)	1.916 (7)	1.905 (7)
Mean Fe–N = 1.915 (10)[a]		
Fe(1)–C(1)	1.764 (10)	1.743 (13)
Fe(1)–C(2)	1.759 (10)	1.738 (12)
Fe(1)–C(3)	1.756 (10)	1.762 (11)
Fe(2)–C(4)	1.759 (10)	1.775 (10)
Fe(2)–C(5)	1.756 (10)	1.763 (10)
Fe(2)–C(6)	1.739 (10)	1.775 (9)
Mean Fe–C = 1.757 (12)		
N(1)–N(2)	1.405 (9)	1.402 (9)
N(1)–C(7)	1.512 (11)	1.471 (12)
N(2)–C(9)	1.504 (10)	1.495 (12)
Mean N–C = 1.495 (18)		
C(7)–C(8)	1.576 (13)	1.522 (14)
C(8)–C(9)	1.526 (12)	1.524 (14)
C(9)–C(10)	1.490 (13)	1.519 (14)
C(10)–C(11)	1.494 (13)	1.527 (15)
C(11)–C(7)	1.502 (13)	1.540 (14)
Mean C–C = 1.522 (23)		
C(1)–O(1)	1.162 (10)	1.183 (13)
C(2)–O(2)	1.166 (11)	1.170 (13)
C(3)–O(3)	1.152 (10)	1.164 (11)
C(4)–O(4)	1.161 (10)	1.160 (10)
C(5)–O(5)	1.168 (10)	1.155 (10)
C(6)–O(6)	1.179 (10)	1.146 (10)
Mean C–O = 1.164 (11)		

Estimated Contacts ≤2.6 Å between Ligand
H Atoms and CO Groups

H3C8···C(1)	2.39	2.39
H5C10···C(4)	2.57	2.53
H8C11···C(4)	2.49	2.46

[a] The figure in parentheses following mean values of bond distances in this table is the standard deviation of an *individual* distance as estimated by $S = [\{1/(n-1)\}\Sigma_{i=1}{}^n(\bar{x} - x_i)^2]^{1/2}$, where x_i is an individual distance and $\bar{x}$ is the mean value of the n measurements of presumably equivalent bond distances.

Description of the Structure

The binuclear μ-2,3-[2,3-diazabicyclo[2.2.1]heptane]-diyl-bis(tricarbonyliron) molecule contains two Fe(CO)$_3$ groups linked by two Fe–N–Fe bridges through the nitrogen atoms of the bicyclic ligand and also by an iron–iron bond. This is the structure proposed by Bennett. With the exception of a few angular differences (*vide infra*) the two crystallographically independent molecules are identical within experimental error. An overall view of the molecular structure (of molecule A) is shown in Figure 1. Table IV presents a comparison of the structural parameters of the central portion of the molecule with the corresponding parameters for the closely related compounds μ-methazo-bis(tricarbonyliron)[14] and benzo[c]cinnolinebis(tricarbonyliron).[15] It can be seen that the distances and angles within the Fe$_2$N$_2$ tetrahedron are closely similar for the three compounds. The N–N distance of 1.404 (9) Å[24]

(23) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1392. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(24) Bond distances quoted in the text are averages over the two independent molecules. Numbers in parentheses following average distances are mean standard deviations of an *individual* measurement.

Structure of $C_5H_8N_2Fe_2(CO)_6$ *Inorganic Chemistry, Vol. 11, No 6, 1972* **1395**

TABLE III
BOND ANGLES (DEG)

	Molecule A	Molecule B
Fe(2)–Fe(1)–N(1)	49.4 (2)	50.1 (2)
Fe(2)–Fe(1)–N(2)	49.5 (2)	49.2 (2)
Fe(2)–Fe(1)–C(1)	157.2 (3)	157.5 (4)
Fe(2)–Fe(1)–C(2)	95.5 (3)	101.0 (4)
Fe(2)–Fe(1)–C(3)	103.3 (3)	98.2 (3)
N(1)–Fe(1)–N(2)	43.1 (3)	43.0 (3)
N(1)–Fe(1)–C(1)	113.4 (4)	109.3 (4)
N(1)–Fe(1)–C(2)	142.4 (4)	145.0 (4)
N(1)–Fe(1)–C(3)	105.0 (4)	105.4 (4)
C(1)–Fe(1)–C(2)	95.7 (4)	94.0 (5)
C(1)–Fe(1)–C(3)	95.5 (4)	96.4 (5)
C(2)–Fe(1)–C(3)	94.8 (4)	97.2 (5)
Fe(1)–Fe(2)–N(1)	49.4 (2)	49.4 (2)
Fe(1)–Fe(2)–N(2)	49.3 (2)	49.2 (2)
Fe(1)–Fe(2)–C(4)	158.0 (3)	157.9 (3)
Fe(1)–Fe(2)–C(5)	100.7 (3)	100.5 (3)
Fe(1)–Fe(2)–C(6)	97.6 (3)	98.2 (3)
N(1)–Fe(2)–N(2)	43.1 (3)	42.8 (3)
N(1)–Fe(2)–C(4)	109.8 (4)	109.5 (4)
N(1)–Fe(2)–C(5)	144.2 (4)	143.1 (4)
N(1)–Fe(2)–C(6)	105.9 (4)	108.0 (4)
C(4)–Fe(2)–C(5)	95.4 (4)	95.4 (4)
C(4)–Fe(2)–C(6)	95.3 (4)	95.5 (4)
C(5)–Fe(2)–C(6)	96.1 (4)	95.7 (4)
Fe(1)–N(1)–Fe(2)	81.3 (3)	80.5 (2)
Fe(1)–N(1)–N(2)	68.4 (4)	68.1 (4)
Fe(1)–N(1)–C(7)	134.9 (5)	135.6 (6)
Fe(2)–N(1)–N(2)	68.6 (4)	67.4 (4)
Fe(2)–N(1)–C(7)	140.4 (6)	140.5 (6)
N(2)–N(1)–C(7)	105.6 (6)	106.8 (6)
Fe(1)–N(2)–Fe(2)	81.2 (2)	81.6 (3)
Fe(1)–N(2)–N(1)	68.5 (4)	68.9 (4)
Fe(1)–N(2)–C(9)	135.0 (5)	134.5 (6)
Fe(2)–N(2)–N(1)	68.3 (4)	69.8 (4)
Fe(2)–N(2)–C(9)	140.6 (5)	140.8 (6)
N(1)–N(2)–C(9)	106.3 (6)	105.1 (6)
N(1)–C(7)–C(8)	100.1 (7)	101.1 (8)
N(1)–C(7)–C(11)	106.4 (7)	106.4 (8)
C(8)–C(7)–C(11)	99.1 (8)	99.9 (8)
C(7)–C(8)–C(9)	92.1 (7)	93.4 (8)
N(2)–C(9)–C(8)	101.2 (7)	101.2 (8)
N(2)–C(9)–C(10)	106.7 (7)	106.2 (8)
C(8)–C(9)–C(10)	102.2 (8)	102.0 (9)
C(9)–C(10)–C(11)	103.1 (8)	102.2 (9)
C(10)–C(11)–C(7)	105.5 (8)	103.8 (8)
Fe(1)–C(1)–O(1)	174.6 (8)	175.8 (11)
Fe(1)–C(2)–O(2)	179.4 (9)	174.8 (11)
Fe(1)–C(3)–O(3)	177.6 (9)	177.1 (9)
Fe(2)–C(4)–O(4)	174.8 (9)	175.5 (9)
Fe(2)–C(5)–O(5)	175.6 (9)	177.0 (9)
Fe(2)–C(6)–O(6)	178.7 (8)	178.1 (8)

TABLE IV
COMPARISON OF STRUCTURAL PARAMETERS OF THREE AZO-BRIDGED BINUCLEAR IRON CARBONYLS, LFe₂(CO)₆

	L = (CH₃N)₂[a]	L = C₁₂H₈N₂[b]	L = C₅H₈N₂[c]
N–N–C, deg	123.0 (5)	120.5 (5)	106.0 (6)
N–C, Å	1.476 (6)	1.414 (9)	1.495 (11)
N–N, Å	1.366 (8)	1.399 (8)	1.404 (9)
Fe–Fe, Å	2.496 (3)	2.508 (3)	2.490 (2)
Fe–N, Å	1.878 (4)	1.914 (6)	1.915 (7)
Fe–N–Fe, deg	83.4 (2)	81.9 (2)	81.2 (3)
N–Fe–N, deg	42.7 (2)	42.9 (2)	43.0 (3)
d	91.1 (2)	89.5 (2)	91.4 (2)

[a] Reference 14. [b] Reference 15. [c] This work. [d] Dihedral angle (deg) between the two Fe–N–N planes.

is equal to twice the generally accepted single-bond covalent radius of a tetravalent nitrogen atom.[25] The iron–iron distance of 2.490 (2) Å is longer by *ca.* 0.1 Å

(25) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 221–230; F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 106.
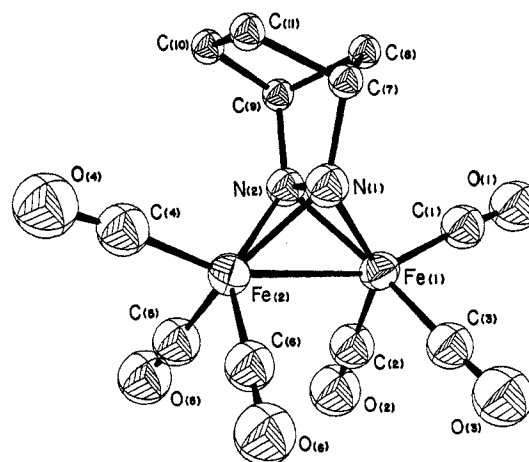

Figure 1.—A perspective view of the C₅H₈N₂Fe₂(CO)₆ molecule. Thermal ellipsoids are those for molecule A and are 50% probability surfaces, with the exception that the thermal parameters of carbon atoms 7–11 have been reduced for clarity.

and the mean iron–nitrogen distance of 1.915 (7) Å is shorter by a comparable amount than the lengths found for these bonds in nitrogen-bridged iron carbonyls not containing an N–N bond.[26]

The molecular configuration of C₅H₈N₂Fe₂(CO)₆ could ideally possess a mirror plane (containing the two iron atoms and the midpoint of the N–N bond); in fact both molecules are found to exhibit small but significant departures from C_s-m symmetry. Figure 2, in
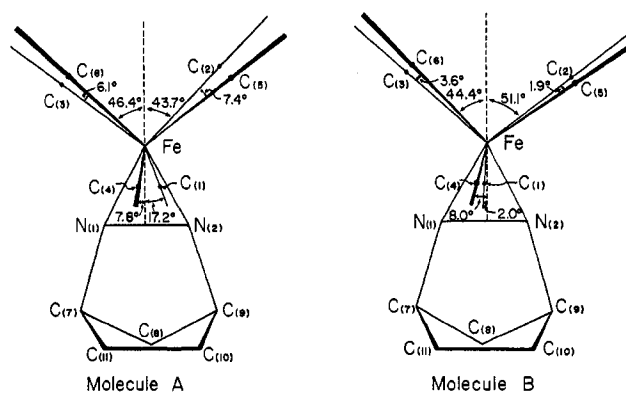

Figure 2.—A schematic view of the structures of the two independent molecules, as projected onto a plane perpendicular to the iron–iron bond. The dotted line represents the projection of the plane defined by the iron atoms and the N(1)–N(2) midpoint.

which both molecules are viewed down their iron–iron bonds, shows the nature of this asymmetry and also displays the major differences between the two independent molecules. If a plane is defined by the two iron atoms and the N(1)–N(2) midpoint, then the departure of the carbonyl groups from their idealized symmetry may be seen by examining the dihedral angles between this plane and the Fe–Fe–C(carbonyl) planes. The pertinent information is tabulated, along with other data on molecular planes and dihedral angles, in Table V.

The carbonyl groups have their expected configurations, with mean Fe–C and C–O distances of 1.757 (12) and 1.164 (11) Å. The Fe–C–O angles are all within 5° of linearity; some deviate from 180° by apparently

(26) This comparison was made in detail in ref 14.

TABLE V

MOLECULAR PLANES AND DIHEDRAL ANGLES[a]

1. Plane Containing Fe(1), Fe(2), and the
Point Midway between N(1) and N(2)

Molecule A: $-0.7208X - 0.6691Y - 0.1811Z = 0.3204$
Molecule B: $-0.5693X + 0.8218Y - 0.0236Z = 6.0491$

	——Distances to plane, Å——	
Atoms	Molecule A	Molecule B
C(1)	−0.202	−0.018
C(2)	−1.210	1.320
C(3)	1.356	−1.303
C(4)	0.088	−0.091
C(5)	−1.344	1.377
C(6)	1.252	−1.238
C(7)	1.111	−1.090
C(8)	−0.040	0.023
C(9)	−1.123	1.126
C(10)	−0.790	0.815
C(11)	0.704	−0.712

	Angles between plane 1 and planes defined here, deg	
Atoms	Molecule A	Molecule B
Fe(1), Fe(2), C(1)	17.2 (8)	2.0 (10)
Fe(1), Fe(2), C(2)	43.7 (4)	51.1 (5)
Fe(1), Fe(2), C(3)	52.5 (4)	48.0 (4)
Fe(1), Fe(2), C(4)	7.8 (9)	8.0 (9)
Fe(1), Fe(2), C(5)	51.1 (4)	53.0 (4)
Fe(1), Fe(2), C(6)	46.4 (4)	44.4 (4)

2. Plane Containing N(1), N(2), C(7), and C(9)

Molecule A: $-0.1569X + 0.4166Y - 0.8955Z = 0.9784$
Molecule B: $-0.6842X - 0.4848Y - 0.5448Z = -4.9417$

	——Distances to plane, Å——	
Atoms	Molecule A	Molecule B
N(1)	−0.0004	0.0042
N(2)	0.0004	−0.0041
C(7)	0.0003	−0.0026
C(9)	−0.0003	0.0026

3. Plane Containing C(7), C(9), C(10), and C(11)

Molecule A: $0.5599X - 0.4171Y - 0.7159Z = -5.1285$
Molecule B: $0.1713X + 0.1052Y - 0.9796Z = 2.423$

	——Distances to plane, Å——	
Atoms	Molecule A	Molecule B
C(7)	0.0031	−0.0040
C(9)	−0.0031	0.0040
C(10)	0.0046	−0.0058
C(11)	−0.0046	0.0058

4. Plane Containing C(7), C(8), and C(9)

Molecule A: $-0.6400X + 0.7467Y - 0.1814Z = 5.430$
Molecule B: $0.7720X + 0.5319Y - 0.3480Z = 6.589$

	——Angles between planes, deg——	
Planes	Molecule A	Molecule B
2–3	112.3	111.4
2–4	125.0	126.6
3–4	122.7	122.0

[a] Unit weights were employed in the calculation of planes 2 and 3. Equations of planes are expressed with respect to coordinates (X, Y, Z) referred to an orthogonal system (A, B, C) oriented with A along a, B along b, and C in the direction of $A \times B$.

TABLE VI

PRINCIPAL ROOT-MEAN-SQUARE THERMAL
DISPLACEMENTS OF THE IRON ATOMS (Å)

	Max	Intermed	Min
	Molecule A		
Fe(1)	0.213 (2)	0.201 (2)	0.183 (2)
Fe(2)	0.208 (2)	0.200 (2)	0.194 (2)
	Molecule B		
Fe(1)	0.244 (2)	0.207 (2)	0.186 (2)
Fe(2)	0.201 (2)	0.192 (2)	0.184 (2)

the same configuration as complexed norbornadiene[27] which, in turn, does not differ greatly from that of the free diene.[28] The ligand has a plane of symmetry within experimental error; its C–C distances average to 1.522 (23) Å. Data on planes and dihedral angles within the ligand are included in Table V.

The principal root-mean-square amplitudes of thermal motion of the iron atoms are tabulated in Table VI. It is evident from these values that the degree of anisotropy is not great. The isotropic thermal parameters of the light atoms show their expected trends. Intermolecular contacts are of normal magnitudes for this type of crystal, with the shortest contacts of various types including H$\cdots$H = 2.43 Å, H$\cdots$O = 2.58 Å, H$\cdots$C = 2.99 Å, and O$\cdots$O = 3.04 Å.

Discussion

As is evident from the information tabulated in Table IV, the nature of the parent azo ligand in the three N-bridged binuclear iron carbonyls of structure type IV studied to date has little effect on the structural parameters of the Fe$_2$N$_2$ tetrahedra in these molecules. The major structural features of DBH which could conceivably cause its binding to metal atoms to differ from that of previously studied azo compounds are its N–N–C angle of 106.0 (6)° (in contrast to values of *ca.* 120° for this angle in benzo[c]cinnoline and azomethane) and its asymmetry. No effect of either of these variations on the Fe–N bonding is evident. This is in contrast to an apparent asymmetry in Fe–N distances observed in the binuclear nitrogen-bridged complex derived from Fe$_2$(CO)$_9$ and 3,5,7-triphenyl-4H-1,2-diazepine.[29] In the present case, only the disposition of the carbonyl groups (*vide supra*) seems to be affected by the ligand symmetry.

In view of the close similarities of the structures of the three compounds represented in Table IV, the comments made previously[14,15] concerning the bonding in the two other examples of this structure type may be applied without modification to (DBH)Fe$_2$(CO)$_6$. In particular, the increase of ∼0.1 Å in the Fe–Fe distance observed in nitrogen-bridged iron carbonyls containing an N–N bond relative to those in which no direct bond links the bridging atoms appears to be a general phenomenon. An explanation based upon strain at the bridging atom has previously been offered for this effect.[15]

(27) Bond distances and angles in metal-coordinated norbornadiene molecules have been tabulated and compared: B. Granoff and R. A. Jacobson, *Inorg. Chem.*, **7**, 2328 (1968).

(28) T. W. Muecke and M. I. Davis, Abstracts, American Crystallographic Association Meeting, Austin, Texas, Feb 1966, No. F1.

(29) A. J. Carty, D. P. Madden, M. Mathew, G. J. Palenik, and T. Birchall, *J. Chem. Soc. D*, 1664 (1970). The diazepine derivative does not possess an N–N bond and so is not strictly analogous to the present complex. Nonetheless it does provide an instance in which asymmetry of the bridging ligand appears to be reflected in a distortion of the normally symmetric Fe$_2$N$_2$ bridging system.

significant amounts. As can be seen from the estimated H$\cdots$C contacts listed in Table II, the carbonyl carbon atoms C(1) and C(4) are relatively close (2.39–2.57 Å) to the calculated positions of certain of the ligand hydrogen atoms. These close contacts could be related to the molecular asymmetry and to the apparent nonlinearity of carbonyl groups 1 and 4.

The structural parameters of the C$_5$H$_8$N$_2$ ligand may be compared with those observed for norbornadiene and its metal complexes. Apart from the expected differences stemming from the saturation and nitrogen substitution of the bicyclic system, the ligand has much

Finally, this study has confirmed one of the three modes of metal coordination proposed for 2,3-diazabicyclo[2.2.1]hept-2-ene. It will be of interest to examine this bicyclic azo compound in other types of metal-coordinated configurations.

The Crystal and Molecular Structure of [Mn(CO)₄(C₂P(C₆H₅)₃)Br]. A Coordination Compound of the Unusual Carbonyl–Ylide Reaction Product (C₆H₅)₃P⁺—C≡C:⁻

BY STEPHEN Z. GOLDBERG,[1a] EILEEN N. DUESLER, AND KENNETH N. RAYMOND*[1b]

The crystal and molecular structure of the unusual compound [Mn(CO)₄(C₂P(C₆H₅)₃)Br] has been determined from single-crystal, three-dimensional X-ray data collected by counter methods. The material crystallizes as yellow-orange needles in the monoclinic space group $P2_1/c$ (C_{2h}^5). The lattice constants are $a = 9.564$ (3), $b = 12.019$ (3), $c = 21.237$ (8) Å, and $\beta = 107.02$ (2)°. The calculated density for four molecules per unit cell is 1.52 g/cm³, as compared with an observed density of 1.47 (2) g/cm³. Full-matrix least-squares refinement on F for 1214 independent reflections with $F^2 > 3\sigma(F^2)$ converged to a weighted R factor of 6.33%. The structure consists of discrete molecular units of octahedrally coordinated manganese with the C₂P(C₆H₅)₃ ligand cis to Br. The C–C distance in the MnC₂ group is 1.216 (14) Å; the Mn–C–C angle is 176.3 (12)° and the P–C–C angle is 164.0 (12)°. These values indicate that the C₂P(C₆H₅)₃ ligand may be best represented as a phosphonium molecule, (C₆H₅)₃P⁺—C≡C:⁻, in which one of the organic groups is the acetylide anion. There is partial disorder between the bromine and one of the carbonyl groups. This disorder is satisfactorily treated in the model refined.
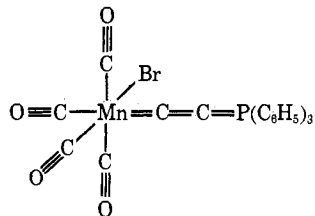
Introduction

In their studies of the reactions of transition metal complexes with ylides, Mitchell, Korte, and Kaska[2] observed that Mn(CO)₅Br reacts readily with the bis ylide hexaphenylcarbodiphosphorane[3,4] according to eq 1. The yellow-orange manganese complex comes

$$Mn(CO)_5Br + (C_6H_5)_3P{=}C{=}P(C_6H_5)_3 \longrightarrow$$
$$[Mn(CO)_4(C_2P(C_6H_5)_3)Br] + (C_6H_5)_3P{=}O \quad (1)$$
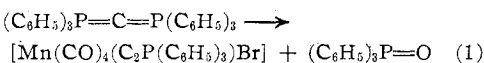
out of benzene solution as an oil which may be separated as crystalline needles from the accompanying triphenylphosphine oxide by repeated crystallization from toluene–pentane or methylene chloride–pentane solutions. Reaction 1 is formally analogous to the Wittig reaction of ylides with carbonyl-containing organic molecules.[5] This, however, appears to be the first instance of the reaction of an ylide with a coordinated carbonyl group in a transition metal complex.

In the original formulation of the manganese complex the cumulene structure

was suggested. Infrared evidence was used to support the formulation of the complex as the cis isomer.[2] The crystal structures of triphenylphosphoranylideneketene, (C₆H₅)₃PC₂O, and its sulfur analog have been reported previously and they have been considered as cumulene molecules.[6,7] As a first step in establishing the structural chemistry of the new class of compounds, of which [Mn(CO)₄(C₂P(C₆H₅)₃)Br] is the first member, we have determined the crystal and molecular structure of this complex by X-ray diffraction methods. A preliminary report of the structure determination has already been published.[8] We now present the complete details and the results of the final refinement of the structure.

Experimental Section

Crystals of [Mn(CO)₄(C₂P(C₆H₅)₃)Br] were provided by Professor W. C. Kaska. The yellow-orange needles darken upon prolonged exposure to air, so crystals for this study were mounted in thin-walled capillaries under an argon atmosphere. Precession photographs showed monoclinic symmetry with systematic absences $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$. The space group was thus uniquely determined as $P2_1/c$ (C_{2h}^5).

The crystal orientation and unit cell constants were determined by a least-squares refinement of 12 carefully centered reflections with 2θ angles in the range 20–30°.[9] Since the Mo Kα₁ and Kα₂ peaks are not well resolved in this range, the reflections were centered on Mo Kᾱ (λ 0.71069 Å). The lattice parameters at 22° are $a = 9.564$ (3), $b = 12.019$ (3), $c = 21.237$ (8) Å, and $\beta = 107.02$ (2)°. The calculated density for four molecules in the unit cell is 1.54 g/cm³. The observed density as determined by flotation in solutions of hexafluorobenzene and pentane is 1.47 (2) g/cm³.

(1) (a) National Institutes of Health Predoctoral Fellow. (b) Fellow of the Alfred P. Sloan Foundation.

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(7) J. J. Daly, *ibid.*, 1913 (1967).

(8) S. Z. Goldberg, E. N. Duesler, and K. N. Raymond, *J. Chem. Soc. D*, 826 (1971).

(9) The programs for refinement of lattice constants and automated operation of the diffractometer are those of Busing and Levy as modified by Picker Corp. for the PDP 8/I.