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Crystal and Molecular Structure of a Bis(tricarbonyliron) Complex Containing Bridging Isopropylidenamido and 2-Propanoximato(*O*,*N*) Ligands

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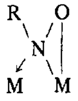
The structure of μ-isopropylidenamido-μ-2-propanoximato(*O*,*N*)-bis(tricarbonyliron) has been determined by a crystallographic study. Crystals of this complex are triclinic, space group $P\bar{1}$, with reduced cell parameters a = 12.061 (10) Å, b = 9.119 (7) Å, c = 8.599 (7) Å, α = 66.81 (2)°, β = 99.94 (3)°, γ = 107.08 (2)°. Observed and calculated (Z = 2) densities are 1.60 (4) and 1.63 g/cm^3, respectively. Least-squares refinement, based upon 1363 independent nonzero counter data, converged to a conventional discrepancy factor of 0.036. The binuclear structure contains two tricarbonyliron groups linked by bridging $N{=}C(CH_3)_2$ and $ON{=}C(CH_3)_2$ ligands and by an iron–iron bond of length 2.484 (2) Å. The 2-propanoximato ligand bridges diatomically, forming a novel Fe–N–O–Fe linkage. Relatively little perturbation of the orientations of the $Fe(CO)_3$ groups or of the iron coordination spheres is observed, despite the presence of both monatomic and diatomic bridging ligands. Distances and angles within the $ON{=}C(CH_3)_2$ group are consistent with the presence of a C═N double bond (1.291 (7) Å) and a N–O single bond (1.351 (6) Å). The Fe–N distances range in length from 1.902 (4) to 1.982 (5) Å, with the shorter distances involving the monatomically bridging isopropylidenamido ligand. The Fe–O bond length is 1.952 (4) Å.

Introduction

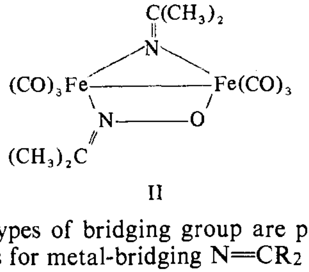
Although only a relatively small number of investigations of reactions of transition metal systems with simple organic C-nitroso compounds have been reported, a variety of types of products have been obtained from such reactions. Two modes of binding to transition metal atoms have been fully characterized for nitrosobenzene and its ring-substituted derivatives. Monodentate N binding has been demonstrated in $(C_6H_5NO)_2PdCl_2$[1] and a bridging configuration which may be represented as I has been found in an iron carbonyl dimer[2]



I

and in a palladium tri-*tert*-butylphosphine trimer.[3] Oxygen binding of *p*-nitroso-*N*,*N*-dimethylaniline in certain of its metal complexes has been suggested,[4] though this has not to date been confirmed.

Recently, King and Douglas reported the results of their investigations of the reactions of several metal carbonylate anions with 2-bromo-2-nitrosopropane.[5] Several types of products were formed including complexes containing the dimethylketimine and isopropylidenamido ligands as well as two compounds in which the CNO grouping was preserved. One of the latter two complexes was a binuclear hexacarbonyldiiron species of stoichiometry $[(CH_3)_2C{=}N]_2O\text{-}Fe_2(CO)_6$. On the basis of its infrared and proton NMR spectra, the material was assigned the structure II, in which



II

two different types of bridging group are present. Ample precedent exists for metal-bridging $N{=}CR_2$ ligands,[6-10] but no previous examples of the proposed diatomic bridging $R_2C{=}NO$ group were known. Because of the novelty of the proposed structure and because of our continuing interest in metal complexes derived from C-nitroso compounds[1] and in nitrogen-bridged metal complexes,[11-15] we have now completed a crystal structure analysis of II.

Table I. Crystal Data and Experimental Parameters

	A. Crystal Data		
Formula	$Fe_2C_{12}H_{12}N_2O_7$	V, A^3	826.5
Formula wt	407.93	Z	2
a, A	12.061 (10)	Density (obsd), g/cm^3	1.60 (4)
b, A	9.119 (7)		
c, A	8.599 (7)	Density (calcd), g/cm^3	1.63
α, deg	66.81 (2)		
β, deg	99.94 (3)	Space group	$P\bar{1}$
γ, deg	107.08 (2)	μ(Mo Kα), cm^{-1}	18.23
	B. Experimental Parameters		
Radiation	Mo Kα λ(Kα$_1$) = 0.70930 A 3.0-mil Nb filter	Scan range	−0.50° to +0.55° in 2θ from Kα$_1$ peak
Temp	22°C	Background counting	20 sec fixed counts at each end of scan
Receiving aperture	5 mm square, 30 cm from crystal	2θ(max), deg	40
		Data collected	1550
Takeoff angle	1.5°	Data with $F_0^2 > 3\sigma(F_0^2)$	1363
Scan rate	1.0°/min in 2θ		

Experimental Section

Collection and Reduction of the Intensity Data. A sample of $[(CH_3)_2CN]_2OFe_2(CO)_6$ was provided by Professor R. B. King. Suitable single crystals could be obtained by recrystallization from a CH_2Cl_2–C_6H_{14} mixture. Preliminary precession photography showed no evidence of monoclinic or higher symmetry; the centrosymmetric space group $P\bar{1}$ was assumed initially and confirmed by the successful solution and refinement of the structure. Cell parameters were determined from least-squares refinement of the setting angles of 16 reflections which had been accurately centered on a Picker four-circle diffractometer.[16] All results are reported in terms of the reduced unit cell defined by the three shortest noncoplanar lattice translations. Crystal data are tabulated in Table IA.

The crystal used for data collection was an irregularly shaped orange plate-like fragment of dimensions 0.46 × 0.35 × 0.09 mm mounted on a glass fiber approximately along a^*. The c^* axis was parallel to the 0.09 mm dimension; other bounding planes belonged to the {100}, {010}, {110}, and {1$\bar{1}$0} forms. The general procedures used in data collection by the θ–2θ scan technique on a Picker diffractometer have previously been described.[17] Experimental parameters specific to the present study are listed in Table IB. Four standard reflections were measured at intervals of 100 reflections throughout data collection. These reflections declined in intensity by a total of 19% during data collection; this effect was isotropic and was a simple function of the time of exposure of the crystal to the x-ray beam. Because of this crystal deterioration, data collection was terminated at 2θ = 40°.

The data were processed according to previously described methods.[17] The intensities were scaled upward to compensate for the

Table II. Atomic Positional and Thermal Parameters for $[(CH_3)_2CN][(CH_3)_2CNO]Fe_2(CO)_6$

Atom	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	−0.17133 (6)[a]	0.05691 (9)	0.10878 (9)	59.1 (.9)	122.5 (1.7)	112.7 (1.8)	27.9 (0.8)	5.6 (0.9)	−46.1 (1.3)
Fe(2)	−0.23948 (6)	0.26543 (9)	0.15964 (10)	64.4 (.9)	115.9 (1.7)	129.5 (1.9)	22.8 (0.8)	9.6 (0.9)	−53.1 (1.3)
N(1)	−0.3009 (3)	0.1530 (5)	0.0063 (5)	48 (4)	122 (8)	115 (9)	18 (4)	−7 (5)	−56 (7)
N(2)	−0.2593 (4)	−0.0527 (5)	0.3164 (5)	67 (4)	109 (8)	110 (9)	23 (5)	1 (5)	−35 (7)
O(1)	0.0473 (4)	0.0505 (6)	0.3207 (6)	79 (4)	253 (10)	183 (9)	37 (5)	−13 (5)	−39 (8)
O(2)	−0.0438 (4)	0.2784 (6)	−0.1892 (6)	123 (5)	224 (9)	167 (9)	36 (5)	58 (6)	−24 (8)
O(3)	−0.2129 (4)	−0.2314 (5)	0.0123 (6)	156 (6)	177 (8)	236 (11)	60 (5)	2 (6)	−112 (8)
O(4)	−0.0684 (5)	0.3334 (6)	0.4267 (6)	145 (6)	310 (12)	191 (10)	24 (6)	−47 (7)	−121 (9)
O(5)	−0.1204 (4)	0.5550 (5)	−0.1075 (5)	112 (5)	148 (8)	188 (9)	26 (5)	38 (5)	−31 (8)
O(6)	−0.4115 (4)	0.4207 (6)	0.1932 (8)	128 (5)	266 (11)	445 (16)	83 (6)	68 (7)	−152 (11)
O(7)	−0.3105 (3)	0.0550 (4)	0.3299 (5)	76 (4)	132 (7)	153 (8)	24 (4)	38 (4)	−45 (6)
C(1)	−0.0376 (6)	0.0512 (7)	0.2399 (8)	3.85 (12)[c]					
C(2)	−0.0934 (5)	0.1928 (7)	−0.0730 (8)	3.67 (12)					
C(3)	−0.1966 (5)	−0.1202 (7)	0.0514 (7)	3.67 (12)					
C(4)	−0.1334 (6)	0.3086 (7)	0.3222 (9)	4.41 (13)					
C(5)	−0.1672 (5)	0.4424 (8)	−0.0011 (8)	3.54 (11)					
C(6)	−0.3474 (5)	0.3600 (8)	0.1778 (8)	4.26 (13)					
C(7)	−0.3751 (5)	0.1582 (7)	−0.1165 (8)	3.61 (12)					
C(8)	−0.3908 (6)	0.0558 (8)	−0.2240 (9)	5.39 (15)					
C(9)	−0.4583 (6)	0.2696 (8)	−0.1713 (9)	5.09 (14)					
C(10)	−0.2753 (5)	−0.1942 (7)	0.4389 (8)	3.73 (12)					
C(11)	−0.2225 (6)	−0.3255 (8)	0.4439 (8)	5.02 (14)					
C(12)	−0.3459 (6)	−0.2312 (8)	0.5825 (9)	5.12 (14)					

[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: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Tabulated β values are $\times 10^4$. [c] For atoms refined isotropically, the isotropic thermal parameter (in Å) is tabulated under β_{11}.

Table III. Atomic Parameters of Hydrogen Atoms[a]

Atom	x	y	z
H(1)[b]	−0.350	−0.025	−0.175
H(2)	−0.354	0.120	−0.314
H(3)	−0.480	0.005	−0.248
H(4)	−0.467	0.308	−0.102
H(5)	−0.400	0.305	−0.275
H(6)	−0.510	0.290	−0.290
H(7)	−0.277	−0.386	0.407
H(8)	−0.150	−0.275	0.375
H(9)	−0.154	−0.336	0.525
H(10)	−0.400	−0.325	0.600
H(11)	−0.320	−0.140	0.600
H(12)	−0.300	−0.275	0.700

[a] Hydrogen atoms were assigned thermal parameters one unit greater than those of the corresponding carbon atoms. [b] Hydrogen atoms numbered 1-3 are bound to C(8), those numbered 4-6 are bound to C(9), etc.

Table IV. Intramolecular Distances, Å

Fe(1)-Fe(2)	2.484 (2)	N(2)-O(7)	1.351 (6)
Fe(1)-N(1)	1.921 (4)	N(2)-C(10)	1.291 (7)
Fe(1)-N(2)	1.982 (5)	C(1)-O(1)	1.131 (6)
Fe(1)-C(1)	1.799 (7)	C(2)-O(2)	1.132 (7)
Fe(1)-C(2)	1.776 (7)	C(3)-O(3)	1.144 (7)
Fe(1)-C(3)	1.798 (6)	C(4)-O(4)	1.132 (7)
Fe(2)-N(1)	1.902 (4)	C(5)-O(5)	1.143 (7)
Fe(2)-O(7)	1.952 (4)	C(6)-O(6)	1.123 (7)
Fe(2)-C(4)	1.805 (7)	C(7)-C(8)	1.510 (9)
Fe(2)-C(5)	1.762 (7)	C(7)-C(9)	1.520 (9)
Fe(2)-C(6)	1.812 (7)	C(10)-C(11)	1.494 (9)
N(1)-C(7)	1.254 (7)	C(10)-C(12)	1.492 (9)

Table V. Bond Angles (deg)

Fe(2)-Fe(1)-N(1)	49.2 (1)	Fe(1)-Fe(2)-N(1)	49.8 (1)
Fe(2)-Fe(1)-N(2)	71.1 (1)	Fe(1)-Fe(2)-O(7)	75.0 (1)
Fe(2)-Fe(1)-C(1)	102.4 (2)	Fe(1)-Fe(2)-C(4)	101.8 (2)
Fe(2)-Fe(1)-C(2)	97.4 (2)	Fe(1)-Fe(2)-C(5)	98.4 (2)
Fe(2)-Fe(1)-C(3)	152.2 (2)	Fe(1)-Fe(2)-C(6)	155.2 (2)
N(1)-Fe(1)-N(2)	85.6 (2)	N(1)-Fe(2)-O(7)	83.9 (2)
N(1)-Fe(1)-C(1)	151.1 (2)	N(1)-Fe(2)-C(4)	151.6 (2)
N(1)-Fe(1)-C(2)	88.6 (2)	N(1)-Fe(2)-C(5)	92.0 (2)
N(1)-Fe(1)-C(3)	106.1 (2)	N(1)-Fe(2)-C(6)	109.0 (2)
N(2)-Fe(1)-C(1)	89.2 (2)	O(7)-Fe(2)-C(4)	88.8 (2)
N(2)-Fe(1)-C(2)	168.3 (2)	O(7)-Fe(2)-C(5)	173.3 (2)
N(2)-Fe(1)-C(3)	97.7 (2)	O(7)-Fe(2)-C(6)	91.7 (2)
C(1)-Fe(1)-C(2)	91.0 (3)	C(4)-Fe(2)-C(5)	92.3 (3)
C(1)-Fe(1)-C(3)	102.7 (3)	C(4)-Fe(2)-C(6)	98.6 (3)
C(2)-Fe(1)-C(3)	93.7 (3)	C(5)-Fe(2)-C(6)	94.6 (3)
Fe(1)-N(1)-Fe(2)	81.1 (2)	Fe(2)-O(7)-N(2)	104.0 (3)
Fe(1)-N(1)-C(7)	138.8 (4)	Fe(1)-N(2)-O(7)	108.7 (3)
Fe(2)-N(1)-C(7)	139.3 (4)	Fe(1)-N(2)-C(10)	136.2 (4)
N(1)-C(7)-C(8)	123.8 (5)	O(7)-N(2)-C(10)	115.1 (5)
N(1)-C(7)-C(9)	122.8 (5)	N(2)-C(10)-C(11)	121.6 (6)
C(8)-C(7)-C(9)	113.5 (5)	N(2)-C(10)-C(12)	120.8 (5)
		C(11)-C(10)-C(12)	117.7 (5)
Fe(1)-C(1)-O(1)	178.8 (5)	Fe(2)-C(4)-O(4)	178.5 (6)
Fe(1)-C(2)-O(2)	179.5 (5)	Fe(2)-C(5)-O(5)	178.4 (5)
Fe(1)-C(3)-O(3)	178.9 (5)	Fe(2)-C(6)-O(6)	177.4 (6)

loss in intensity of the standard reflections. The p factor in the expression for the standard deviations of the observed intensities was assigned a value of 0.05. Only the 1363 data with $F_o^2 > 3\sigma(F_o^2)$ were employed in subsequent calculations. Absorption corrections were applied; the range in transmission factors was from 0.47 to 0.87.

Solution and Refinement of the Structure. The structure was solved by Patterson and difference Fourier methods. Isotropic full-matrix least-squares refinement of all nonhydrogen atoms converged to discrepancy factors $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o| = 0.086$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.113$. Further refinement with anisotropic thermal parameters assigned to the Fe, O, and N atoms yielded $R_1 = 0.058$ and $R_2 = 0.080$. All refinements up to this stage had been based upon the data uncorrected for absorption effects. Application of the absorption correction and an additional least-squares cycle gave $R_1 = 0.045$ and $R_2 = 0.068$. A difference Fourier map at this point clearly showed the methyl hydrogen atoms among its most prominent features. The heights of peaks attributable to these atoms ranged from 0.56 to 0.26 e/Å^3; the largest peak not assignable as a hydrogen atom was 0.40 e/Å^3 in height. The hydrogen atoms were included in the final refinement as fixed atoms at the positions observed on this difference map. This final refinement, still employing the anisotropic/isotropic thermal model, converged to $R_1 = 0.036$ and $R_2 = 0.052$. In the final cycle the largest parameter shift was 0.35 of its estimated standard deviation.

In all structure factor calculations, the atomic scattering factors tabulated in ref 18 were used for C, N, and O, those of Cromer and Waber[19] were used for Fe, and those of Stewart et al.[20] were employed for H. The $\Delta f'$ and $\Delta f''$ values of Cromer[21] were used in correcting for anomalous scattering by the Fe atoms. In all least-squares refinements, the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized and weights of the observed structure amplitudes were taken as $w = 4F_o^2/\sigma^2(F_o^2)$. The final standard deviation of an observation of unit weight was 1.76 e. Calculation of structure factors for the 187 data with $F_o^2 < 3\sigma(F_o^2)$ showed 13 reflections with $F_c^2 > 3\sigma(F_o^2)$; of these, only three had $F_c^2 > 5\sigma(F_o^2)$.

Table VI. Principal Root-Mean-Square Amplitudes of Thermal Motion (Å)

Atom	Maximum	Intermediate	Minimum
Fe(1)	0.207 (1)	0.192 (1)	0.182 (1)
Fe(2)	0.209 (1)	0.203 (1)	0.183 (1)
N(1)	0.321 (6)	0.252 (6)	0.211 (7)
N(2)	0.312 (6)	0.285 (6)	0.197 (8)
O(1)	0.324 (6)	0.277 (6)	0.202 (7)
O(2)	0.363 (6)	0.313 (6)	0.202 (7)
O(3)	0.286 (6)	0.252 (6)	0.212 (7)
O(4)	0.385 (7)	0.317 (6)	0.191 (8)
O(5)	0.251 (5)	0.210 (6)	0.180 (6)
O(6)	0.205 (6)	0.195 (7)	0.166 (8)
O(7)	0.212 (7)	0.196 (7)	0.183 (8)

Table VII. Molecular Planes[a]

1. $0.5743X + 0.5407Y - 0.6147Z = -1.617$

N(1)	0.000	C(8)	0.000
C(7)	0.000	C(9)	0.000

2. $-0.6516X - 0.5709Y - 0.4995Z = 0.698$

O(7)	−0.005	C(11)	−0.006
N(2)	0.004	C(12)	0.000
C(10)	0.007		

3. $0.5001X + 0.5103Y - 0.6997Z = -1.363$

Plane defined by Fe(1), Fe(2), and N(1)

4. $-0.6810X - 0.4215Y - 0.5988Z = 0.710$

Fe(1)	0.042[b]	O(7)	0.076
Fe(2)	−0.041	N(2)	−0.077

Angles between perpendiculars to these planes

Planes	Angle, deg	Planes	Angle, deg
1-2	112.1	2-4	10.4
1-3	6.7	3-4	97.8

[a] Atoms listed for each plane were all given unit weights in the calculation of the plane. The equations of the planes are expressed with respect to coordinates (X, Y, Z,) referred to an orthogonal system (A, B, C) oriented with respect to the crystallographic axes such that A is parallel to a, B is parallel to $c^* \times a$, and C is parallel to $A \times B$. [b] These atoms are not strictly coplanar; the plane is included for purposes of comparison of dihedral angles with those in related structures.

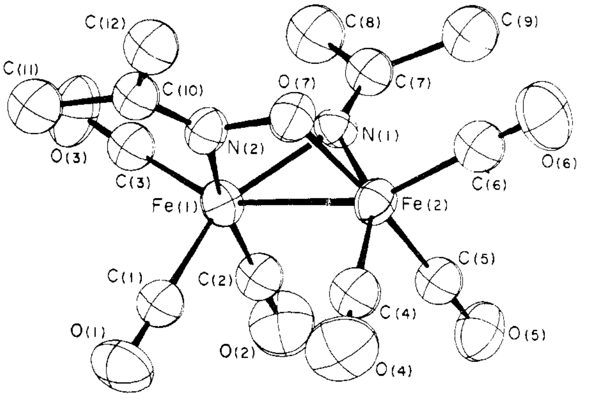


Figure 1. A view of the molecular structure of $[(CH_3)_2CNO][(CH_3)_2CN]Fe_2(CO)_6$. Thermal ellipsoids are drawn at the 50% probability level. Methyl hydrogen atoms are not shown.

Final positional and thermal parameters for the nonhydrogen atoms are listed in Table II and hydrogen atom positional parameters are tabulated in Table III. Bond distances and angles are given in Tables IV and V, respectively. Table VI contains information on principal amplitudes of thermal motion and selected data on molecular planes are shown in Table VII. A listing of observed and calculated structure factors is available.[22]

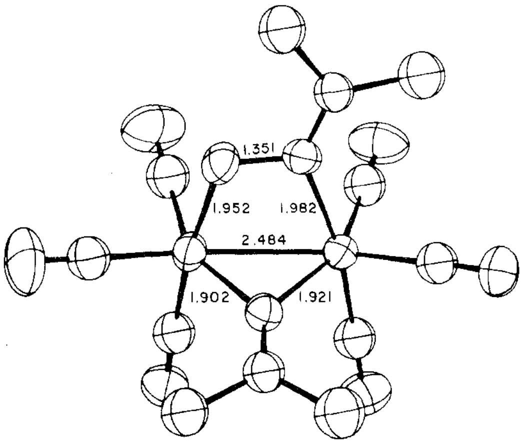


Figure 2. An alternative view of the molecular structure, with selected bond lengths. Atom numbering may be determined by reference to Figure 1.

Table VIII. Comparison of Configurations of Bridging $(CH_3)_2CNO$ and C_6H_5CO Ligands in Bis(tricarbonyliron) Compounds

	$(CH_3)_2CNO$ (X = N)	C_6H_5CO (X = C)
Fe-Fe, Å	2.484 (2)	2.568 (2)
Fe-X, Å	1.982 (5)	1.945 (6)
Fe-O, Å	1.952 (4)	1.967 (5)
X-O, Å	1.351 (6)	1.262 (8)
X-C, Å	1.291 (7)	1.490 (8)
Fe-X-O, deg	108.7 (3)	114.6 (5)
Fe-O-X, deg	104.0 (3)	104.5 (5)
Fe-X-C, deg	136.2 (4)	131.1 (4)
O-X-C, deg	115.1 (5)	114.3 (6)

Description of the Structure and Discussion

Two views of the molecular structure of μ-isopropylidenamido-μ-2-propanoximato(*O,N*)-bis(tricarbonyliron)(*Fe-Fe*) are shown in Figures 1 and 2. The molecule is of the familiar doubly bridged binuclear structure, with two $Fe(CO)_3$ groups linked by bridging $N{=}C(CH_3)_2$ and $ON{=}C(CH_3)_2$ ligands and by an iron–iron bond. These results confirm the structure proposed by King and Douglas[5] and document the presence of a new type of bridging ligand. The possibility of an Fe–N–O–Fe bridge of the sort found here was previously considered[23-25] for the tricarbonyliron dimers $[LFe(CO)_3]_2$ (L = nitrosobenzene or substituted nitrosobenzene), but was ruled out on the basis of Mössbauer data.[25,26] This conclusion was subsequently confirmed by a crystallographic study[2] of the 3-chloro-2-methylnitrosobenzene complex, which showed that the two aryl nitroso ligands adopted the unsymmetrical bridging configuration I. The Mössbauer results suggest a similar bridged structure for bis(tricarbonyliron) complexes derived from other substituted nitrosobenzenes. This type of bridging ligand has also been found in trimeric $[Pd(C_6H_5NO)PR_3]_3$ (R = *tert*-butyl). The only other metal complex of a C-nitroso ligand for which structural data are available is $PdCl_2(C_6H_5NO)_2$, in which the two nitrosobenzenes are monodentate and N bonded.[1]

Distances and angles within the bridging $(CH_3)_2CNO$ ligand are consistent with bonding representation II. The N–C distance of 1.291 (7) Å and the N–O distance of 1.351 (6) Å are within the ranges expected for a double and a single bond, respectively. As is evident from the data in Table VII, the nonhydrogen atoms of this ligand are closely coplanar while the Fe(1)–Fe(2)–O(7)–N(2) ring is slightly puckered. The closest analogues of the bridging RNO ligand found here are the bridging RCO groups found in a bis(tricarbonyliron) dimer[25,27] and in a bridged heterodinuclear Ir–Mn species.[28,29] Both of these molecules contain diatomic M–C–O–M bridges, though only the former also has a metal–metal bond. Details of the configuration of the bridges in the iron dimer are compared with those observed in the present case in Table VIII. Despite a difference of 0.089 Å between the lengths of the C=O and N—O bonds, the overall bridging geometry is similar in both compounds. In each case, a short Fe–Fe bond is maintained in part by acceptance by the C (or N) and O atoms of relatively acute bridging angles. The angles at the oxygen atoms are virtually identical in the two compounds while the angle at the carbon atom is greater by 5.9° than that at the N atom. All of these bridging angles are significantly smaller than their ideal trigonal or tetrahedral values. The Fe–N(2) distance of 1.982 (5) Å is within the range previously observed for Fe–N single bond distances in nitrogen-bridged bis(tricarbonyliron) species.[30] The Fe–O distance of 1.952 (4) Å is likewise a reasonable single bond value; it is marginally shorter than the distance of 1.967 (5) Å observed in the C_6H_5CO-bridged complex.

The bridging configuration of the $N{=}C(CH_3)_2$ ligand is of the type previously found in substituted methylenamido-bridged iron[6] and manganese[9] carbonyl dimers. The two Fe–N(1) distances of 1.921 (4) and 1.902 (4) Å differ by a marginally significant amount and are shorter than the Fe(1)–N(2) distance. However, these distances are still within the range which has been observed for Fe–N single bond lengths.[30] In contrast, substantial metal–nitrogen multiple bonding has been invoked to account for a short Mo–N bond to the terminal di(*tert*-butyl)methylenamino ligand in (η-C_5H_5)$Mo(CO)_2N{=}C(t\text{-}C_4H_9)_2$.[31] This is consistent with the view that both terminal and bridging $N{=}CR_2$ ligands function as three-electron donors. The two Fe–N(1) distances and the bridging Fe(1)–N(1)–Fe(2) angle of 81.1 (2)° are nearer to the values typically found in Fe_2N_2 bridging units which contain a N–N bond than to those in molecules in which the nitrogen atoms are not directly linked.[13] This apparently is related to the longer Fe–Fe bond which is spanned in the present case (vide infra). The N(1)=C(7) distance of 1.254 (7) Å is a normal double bond value and falls within the range of 1.24–1.29 Å observed in other $N{=}CR_2$ ligands.[6,9,31] In particular, it may be noted that our N=C distance is identical within experimental error to the values of 1.258 (9) and 1.259 (9) Å observed for the two independent C=N bonds in $Mn_2[(CF_3)_2C{=}N]_2(CO)_7$[9] and to the value of 1.26 (1) Å found in a terminal $N{=}C(t\text{-}C_4H_9)$ ligand.[31]

The Fe–Fe distance of 2.484 (2) Å is toward the long end of the range previously observed for nitrogen-bridged iron–iron bonds.[30] Characteristic values for such distances in doubly bridged Fe_2N_2 systems have been ~2.40 Å in compounds not containing a N–N bond and ~2.50 Å where such a bond is present. Since the constraints induced by the presence of a bond between the two bridging nitrogen atoms are absent in the present case, it is likely that the diatomic bridging group is responsible for an elongation of ~0.08 Å in the Fe–Fe distance from the value expected if the only bridging ligands were methylenamido groups. Aside from this modest increase in the iron–iron distance, the relative orientation of the two tricarbonyliron moieties is closely similar to that observed in dimers containing only monatomic nitrogen bridges. This is qualitatively evident in Figure 2, where only a slight bending of the two axial carbonyl groups away from the diatomic bridge is evident. The effect of the diatomic bridging group on the distorted octahedral iron coordination polyhedra can best be seen by comparing the angles N(1)–Fe(1)–C(1) = 152.2 (2)° and N(1)–Fe(2)–C(4) = 151.6 (2)° with N(2)–Fe(1)–C(2) = 168.3 (2)° and O(7)–Fe(2)–C(5) = 173.3 (2)°. These rather large angular differences have remarkably little effect on any other parameters of the iron coordination sphere.

In addition to documenting the existence of a new type of bridging ligand, this structure analysis has confirmed a new route for preparation of transition metal complexes of methylenamido-type ligands, $R_2C{=}N$. Such complexes have previously been obtained by a variety of other methods of which the most widely used has been the reaction of metal carbonyl halides with substituted methylenamine, RR′C=NH, or its derivaties RR′C=NM, (M = Li, $Si(CH_3)_3$, $Sn(CH_3)_3$, or $Sn(C_2H_5)_3$).[7-10,32-34] Both terminal and bridging groups have been obtained by this route. The first reported compound containing substituted methylenamido groups bridging two transition metal atoms was a product of the reaction of 4,4′-dimethylbenzophenoneazine with iron pentacarbonyl.[6] Finally, a series of rhenium complexes containing an unsubstituted methylenamido ligand has been prepared by deprotonation of coordinated methylnitrene by bases such as pyridine.[35] Structures of the type found here could be of pertinence to the understanding of reactions of metal-coordinated nitrosyl and nitroso groups. Nucleophilic attack on coordinated NO is well-documented.[36-39] Under appropriate conditions, one could envision interaction of the oxygen atom of a N-bonded RNO ligand with a second metal atom, yielding ultimately a binuclear structure with bridging groups either of the sort found in the present study or of the type depicted in I. Furthermore, coordinated nitrosobenzene has been shown to undergo NO bond cleavage followed by additional chemical reactions.[40] In view of these results, further studies of the chemical and structural properties of metal–nitroso complexes seem warranted.

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Registry No. $[(CH_3)_2CN]_2OFe_2(CO)_6$, 50986-64-6.

Supplementary Material Available: A listing of structure factor amplitudes, ten pages. Ordering information is given on any current masthead page.

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Preparation and Fluxional Behavior of μ-Acetylene-hexakis(trifluorophosphine)dirhodium Complexes

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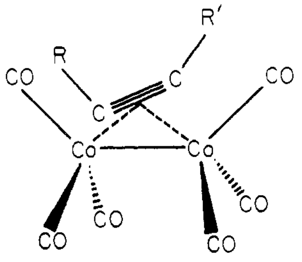
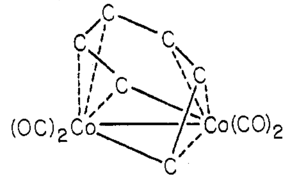
Acetylenes react with octakis(trifluorophosphine)dirhodium, $Rh_2(PF_3)_8$, to give a series of binuclear complexes $Rh_2(PF_3)_6(RC_2R')$ which have been characterized by elemental analysis, ^1H and ^{19}F NMR spectroscopy, and mass spectrometry. Like the well-known $Co_2(CO)_6(RC_2R')$ complexes, the rhodium compounds contain a bridging acetylene ligand lying over and perpendicular to a metal–metal bond. The phenylacetylene derivative ($R = C_6H_5$, $R' = H$) catalyzes the linear polymerization of phenylacetylene, unlike the corresponding cobalt carbonyl complex, which catalyzes cyclotrimerization. Variable-temperature ^{19}F NMR studies show that the PF_3 groups of $Rh_2(PF_3)_6(RC_2R')$ undergo intramolecular exchange leading to NMR equivalence at room temperature. At low temperatures the ^{19}F resonances appear in a 2:1 ratio when $R = R'$ and a 1:1:1 ratio when $R \neq R'$. ^{31}P noise decoupling has been used to simplify the spectra, and the apparatus for removing the large ^{31}P–^{19}F coupling ($\sim$1400 Hz) is described. The free energy of activation ($\Delta G^{\ddagger}$) is of the order 6–10 kcal/mol, being higher for electron-withdrawing and for sterically hindered acetylenes. Possible mechanisms for the exchange process are discussed.

Introduction

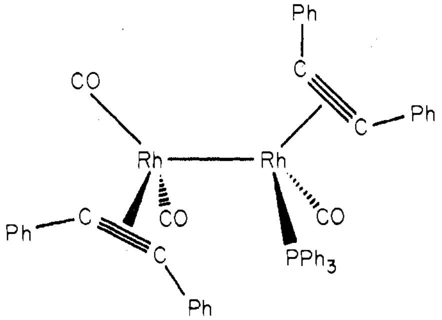
The reaction of dicobalt octacarbonyl, $Co_2(CO)_8$, with a range of mono- and disubstituted acetylenes (ac) gives two types of complexes of general formulas $Co_2(CO)_6(ac)$ and $Co_2(CO)_4(ac)_3$, the first type being formed at room temperature using stoichiometric quantities of reagents, the second being formed at higher temperatures with excess acetylene.[1-5] Single-crystal X-ray studies of members of the first series, e.g., $Co_2(CO)_6(C_6H_5C_2C_6H_5)$[6] and $Co_2(CO)_6(C_6F_6)$[7] (C_6F_6 = hexafluoro-1,3-cyclohexenyne) and related molecules,[8-11] have shown that the common structural feature is an acetylene moiety bridging two metal atoms and lying above and at right angles to the metal–metal bond axis (I). X-Ray studies of two members of the second series[12,13] have shown that the three acetylene units are joined to form a six-carbon "fly-over" bridge between two dicarbonylcobalt units (II). Thermal decomposition of $Co_2(CO)_4(ac)_3$ gives the 1,2,4-trisubstituted benzene,[2] and complexes of this type may be involved in the cobalt carbonyl catalyzed cyclotrimerization of acetylenes to benzenes.[3,14] Less extensive series of complexes analogous to I are formed by other transition metals, e.g., $Ni_2(C_5H_5)_2(ac)$,[15] $Mo_2(C_5H_5)_2(CO)_2(ac)$,[16] and $Rh_2(C_5H_5)_2(CO)_2(ac)$,[17] but the rhodium analogues of $Co_2(CO)_6(ac)$ are unknown, probably because the precursor, $Rh_2(CO)_8$, is stable only under high pressures of CO.[18] A rhodium(0) complex $Rh_2(CO)_3[P(C_6H_5)_3](C_6H_5C_2C_2H_5)_2$, which has been isolated from the reaction of $Rh_4(CO)_{12}$, diphenylacetylene, and triphenylphosphine, is thought to contain one diphenylacetylene attached to each rhodium atom (III).[19] In view of the well-established similarity of CO and PF_3 as ligands[20,21] and in particular the marked similarities of $Co_2(CO)_8$ and $Rh_2(PF_3)_8$ in their reactions with hydrogen and with group 4 hydrides,[22] it seemed worthwhile to investigate the reactions of $Rh_2(PF_3)_8$ with acetylenes. It was also hoped that ^{19}F NMR studies would reveal intramolecular and intermolecular ligand-exchange processes in the resulting complexes similar to those which have been studied by ^{13}C NMR in analogous carbonyl complexes.[23] Our results, which have appeared in a preliminary report,[24] are described in this series of papers.



I



II
(substituents on carbon chain omitted for clarity)



III

Experimental Section

Starting Materials. Reactions were carried out either under dry nitrogen or by using standard vacuum-line techniques. Solvents were dried and degassed before use; those which were gaseous at room temperature were condensed into NMR tubes directly from cylinders. The complex $Rh_2(PF_3)_8$ was prepared as described previously[22] but in variable and often poor yields (5–20% based on $[RhCl(PF_3)_2]_2$).