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CARBONYLIRON COMPLEXES CONTAINING AN AZOMETHYLENE MOIETY

IV *. SYNTHESIS AND X-RAY STRUCTURAL STUDY OF THE COMPLEX $Fe_2[\mu_2\text{-}\eta^2\text{-}o\text{-}C_6H_4CH_2NC_6H_5](CO)_6$

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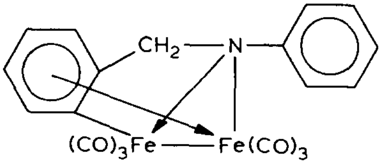
Summary

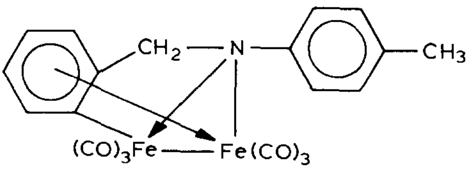
$Fe_2[\mu_2\text{-}\eta^2\text{-}o\text{-}C_6H_4CH_2N\text{-}C_6H_5](CO)_6$ (I) was obtained from the products of the reaction of benzalazine with $Fe_3(CO)_{12}$. The structure of I was confirmed by IR, NMR and mass spectra, and by X-ray structural data.

Results and discussion

In the process of studying the reaction of benzalazine with $Fe_3(CO)_{12}$, besides the previously isolated and described [2,3] polynuclear iron complexes $Fe_2(PhCH{=}N)_2(CO)_6$ (II), $Fe_2[\mu_2\text{-}\eta^2\text{-}o\text{-}C_6H_4CH_2N(N{=}CHPh)](CO)_6$ (III) and $Fe_3[\mu_2\text{-}\eta^6\text{-}o\text{-}C_6H_4CH_2N(N{=}CHPh)](CO)_8$ (IV), a dark-red substance, I, was ob-



(I)



(V)

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* For part III see ref. 1.

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tained in a 1% yield. Its spectral data coincided completely with the data for binuclear complexes of benzaniline and its derivatives with carbonyliron compounds [4,5].

It is known that elimination of the middle part of the molecule can occur either during thermal destruction of benzalazine with the formation of stilbene [6], or on electron impact with HCN removal [1,7]. The reaction of azines with carbonyliron compounds usually leads to only the disruption of the N–N bond (complex II). Cases are also where phenyl breaks off from alkylphenylsulphides under the influence of $Os_3(CO)_{12}$ [8].

The structure of I was solved by an X-ray structural study (Fig. 1). Complex I contains the polydentate $PhCH_2NC_6H_4$ (L) ligand-product of PhCH=NPh regrouping, which is formed during HCN elimination.

The crystals of I are triclinic, *a* 15.866(9), *b* 7.614(4), *c* 8.405(6) Å, α 100.13(4), β 97.42(4), γ 106.55(4)°, *V* 941(1) Å^3, $Z = 2$, space group $P\bar{1}$. The molecule of I

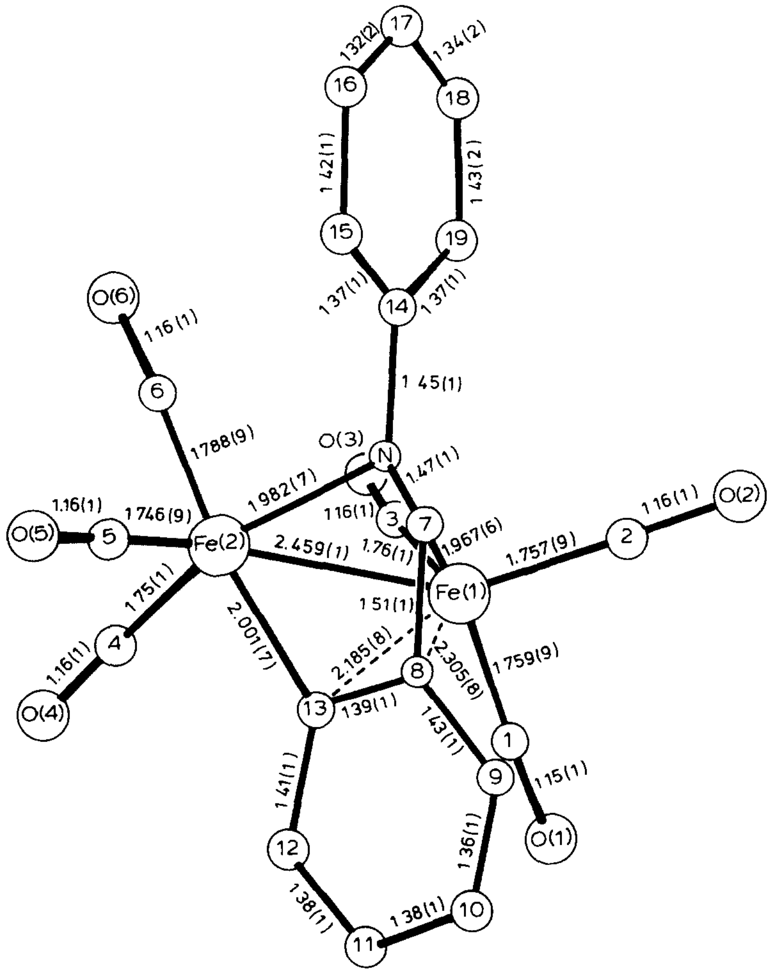

Fig. 1. Structure of the complex $Fe_2[\mu_2\text{-}\eta^2\text{-}o\text{-}C_6H_4CH_2NC_6H_5](CO)_6$ (I).

TABLE 1

ATOMIC COORDINATES ($\times 10^4$; Fe, $\times 10^5$) AND THEIR TEMPERATURE FACTORS B_j (Å^2)

Atom	x	y	z	B_j	Atom	x	y	z	B_j
Fe(1)	22424(8)	49688(14)	36200(12)	[a]	C(6)	2885(6)	6428(12)	7920(10)	4.0(2)
Fe(2)	19705(8)	43452(15)	63120(12)	[a]	C(7)	3194(5)	2913(11)	4655(9)	3.6(2)
O(1)	819(5)	4314(9)	816(8)	5.7(1)	C(8)	2275(5)	1955(10)	3582(8)	2.8(1)
O(2)	3578(5)	6183(10)	1626(9)	6.9(2)	C(9)	2114(6)	527(11)	2115(9)	3.6(2)
O(3)	1910(4)	8398(9)	5129(7)	5.6(1)	C(10)	1254(6)	−456(12)	1371(10)	4.3(2)
O(4)	141(5)	4187(9)	6556(8)	6.5(2)	C(11)	542(6)	−141(12)	2032(10)	4.1(2)
O(5)	2145(5)	1699(10)	8341(9)	7.3(2)	C(12)	687(6)	1226(11)	3444(9)	3.7(2)
O(6)	2610(4)	7763(9)	8977(7)	5.9(2)	C(13)	1565(5)	2324(10)	4246(9)	2.9(1)
N	3091(4)	4715(8)	5423(7)	2.9(1)	C(14)	3911(6)	6096(11)	6396(10)	3.8(2)
C(1)	1364(6)	4564(11)	1957(10)	3.9(2)	C(15)	4145(7)	7913(13)	6203(11)	5.1(2)
C(2)	3039(6)	5677(12)	2397(10)	4.4(2)	C(16)	4900(7)	9282(15)	7266(13)	6.4(2)
C(3)	2048(6)	7008(12)	4630(10)	4.1(2)	C(17)	5393(7)	8782(14)	8389(12)	5.8(2)
C(4)	870(6)	4239(12)	6466(10)	4.3(2)	C(18)	5203(7)	7004(15)	8568(13)	6.5(3)
C(5)	2072(6)	2767(12)	7545(10)	4.6(2)	C(19)	4436(7)	5584(13)	7540(11)	5.5(2)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe(1)	3.35(6)	2.60(5)	2.53(5)	0.44(5)	0.17(4)	0.47(4)
Fe(2)	3.18(6)	3.12(6)	2.49(5)	0.74(5)	0.44(4)	0.34(4)

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[a] Anisotropic temperature factors of Fe atoms in the form $T = \exp[-1/4(B_{11}h^2a^{*2} + \ldots + 2B_{23}kfb^*c^*)]$.

(Tables 1–4, Fig. 1) comprises two $Fe(CO)_3$ groups bonded by an ordinary Fe–Fe bond and a bridge ligand L, whose N atom and one benzene fragment is bonded to both Fe atoms, with the benzene fragment being a σ,π-bridge. As a result of such coordination, L is a donor of six electrons ($3e^-$ from the bridge atom, $3e^-$ from the σ,π-bridge C(8)–C(13), forming a σ-bond, Fe(2)–C(13), and an η^2-bond, Fe(1) with C(8)=C(13), with the benzene fraction double bond) and the Fe atoms, forming another Fe–Fe bond, attain an 18-electron shell, which is in accordance with the diamagnetism of I. On the other hand, the Fe atoms in I are, strictly speaking,

TABLE 2

BOND LENGTHS *d* (Å) OF I

Bond	*d*	Bond	*d*	Bond	*d*
Fe(1)–Fe(2)	2.459(1)	Fe(2)–C(13)	2.001(8)	C(8)–C(13)	1.39(1)
Fe(1)–N	1.967(6)	O(1)–C(1)	1.15(1)	C(9)–C(10)	1.36(1)
Fe(1)–C(1)	1.759(9)	O(2)–C(2)	1.16(1)	C(10)–C(11)	1.38(1)
Fe(1)–C(2)	1.757(7)	O(3)–C(3)	1.16(1)	C(11)–C(12)	1 38(1)
Fe(1)–C(3)	1.762(9)	O(4)–C(4)	1.16(1)	C(12)–C(13)	1.41(1)
Fe(1)–C(8)	2.305(8)	O(5)–C(5)	1.16(1)	C(12)–C(15)	1.37(1)
Fe(1)–C(13)	2.185(8)	O(6)–C(6)	1.16(1)	C(14)–C(19)	1.37(1)
Fe(2)–N	1.982(7)	N–C(7)	1.47(1)	C(15)–C(16)	1.42(1)
Fe(2)–C(4)	1.75(1)	N–C(14)	1.45(1)	C(16)–C(17)	1 32(2)
Fe(2)–C(5)	1.746(9)	C(7)–C(8)	1.51(3)	C(17)–C(18)	1.34(2)
Fe(2)–C(6)	1.788(9)	C(8)–C(9)	1.43(1)	C(18)–C(19)	1.43(2)

TABLE 3

BOND ANGLES ω (°) OF I

Angles	ω	Angles	ω	Angles	
Fe(2)Fe(1)N	51.8(2)	Fe(2)C(6)	95.8(3)	C(7)C(8)C(9)	122.9(7)
Fe(2)Fe(1)C(1)	122.3(3)	Fe(2)C(13)	78.8(3)	C(7)C(8)C(13)	115.4(7)
Fe(2)Fe(1)C(2)	146.9(3)	C(4)Fe(2)C(5)	97.0(4)	C(9)C(8)C(13)	120.9(7)
Fe(2)Fe(1)C(13)	75.9(3)	C(4)Fe(2)C(6)	90.4(4)	C(8)C(9)C(10)	118.8(8)
Fe(2)Fe(1)C(13)	50.6(2)	C(4)Fe(2)C(13)	92.1(4)	C(9)C(10)C(11)	121.2(8)
NFe(1)C(1)	165.1(3)	C(5)Fe(2)C(6)	96.7(4)	C(10)C(11)C(12)	120.7(8)
NFe(1)C(2)	95.7(4)	C(5)Fe(2)C(13)	92.7(4)	C(11)C(12)C(13)	120.6(8)
NFe(1)C(3)	98.5(3)	C(6)Fe(2)C(13)	169.8(4)	Fe(1)C(13)Fe(2)	71.8(2)
NFe(1)C(13)	74.8(3)	Fe(1)NFe(2)	77.0(2)	Fe(1)C(13)C(8)	76 7(5)
C(1)Fe(1)C(2)	90.8(4)	Fe(1)NC(7)	99.3(5)	Fe(1)C(13)C(12)	121.5(6)
C(1)Fe(1)C(3)	92.2(4)	Fe(1)NC(14)	129.2(5)	Fe(2)C(13)C(8)	113.0(5)
C(1)Fe(1)C(13)	91.2(4)	Fe(2)NC(7)	111.8(5)	Fe(2)C(13)C(12)	129.2(6)
C(42)Fe(1)C(3)	107.2(4)	Fe(2)NC(14)	119.0(5)	C(8)C(13)C(12)	117.8(7)
C(2)Fe(1)C(13)	135.5(4)	C(7)NC(14)	114.6(6)	NC(14)C(15)	120.1(8)
C(3)Fe(1)C(13)	117.1(4)	Fe(1)C(1)O(1)	176.6(8)	NC(14)C(19)	119.6(8)
Fe(1)Fe(2)N	51.2(2)	Fe(1)C(2)O(2)	178.2(8)	C(15)C(14)C(19)	120.2(9)
Fe(1)Fe(2)C(4)	109.0(3)	Fe(1)C(3)O(3)	172.6(8)	C(14)C(15)C(16)	119.4(9)
Fe(1)Fe(2)C(5)	140.2(3)	Fe(2)C(4)O(4)	179.1(9)	C(15)C(16)C(17)	120(1)
Fe(1)Fe(2)C(6)	112.3(3)	Fe(2)C(5)O(5)	178.7(9)	C(16)C(17)C(18)	122(1)
Fe(1)Fe(2)C(13)	57.6(2)	Fe(2)C(6)O(6)	176.6(8)	C(17)C(18)C(19)	120(1)
NFe(2)C(4)	160.1(4)	NC(7)C(8)	100.5(6)	C(14)C(19)C(18)	119(1)
NFe(2)C(5)	101.1(4)				

non-equivalent: while Fe(1) is coordinated along the η^2-type with a double C(8)=C(13) bond, Fe(2) is only σ-bonded to the C(13) atom (the remaining ligands of the Fe atoms are identical: three CO groups and an N bridge). It seems that such electron "poverty" of the Fe(2) atom, as compared to the Fe(1) atom, is compensated by the weak interaction of Fe(2) with the carbonyl group of the "alien" Fe(1) atom (Fe(2)... C(3) 2.652(9) Å is comparable to the unsymmetrical carbonyl group bridges found in other Fe structures [9]). Such weak interaction leads to somewhat irregular linearity of the Fe(1)C(3)O(3) moiety (angle Fe(1)C(3)O(3) 172.6(8)°, i.e. somewhat smaller than the other FeCO, which vary in the range of 177–179° (cf. Table 3).

The coordination with the metal atoms is analogous to the structurally studied $Fe_2(CO)_6(PhCH_2NC_6H_4CH_3)$ (V) complex [10], which was obtained by direct reaction of $Fe_2(CO)_9$ with a corresponding Schiff base, and is characterized by comparable geometrical parameters: the Fe–Fe bond lengths are 2.459(1) and 2.43 Å in I and V, respectively. Fe–NFeN 1.982(7), 1.967(6) in II, and 1.95, 1.96 Å in V; Fe–C(13) 2.001(7) in I and 2.06 Å in V; the lengths of Fe(1)–C(8) and Fe(1)–C(13), 2.185(5) and 2.305(5) Å, are comparable to the mean value of 2.30 Å established for V. The length of the π-coordinated double bond C(8)=C(13) equals 1.39(1) Å (1.38 Å in V).

The five-membered Fe(2)C(13)C(8)C(7)N metallocycle has an "easy chair" conformation with the N and C(7) atoms situated on either side of the C(8)C(13)Fe(2) plane at distances of 0.46 and 0.25 Å, respectively. Table 4 contains deviations from the plane through the benzene moiety C(8)–C(13), since the Fe(2) atom is practically coplanar to it. The torsion angles around the Fe(2)–C(13), C(13)–C(8), C(8)–C(7), C(7)–N and N–Fe(2) bonds equal 15.3, 8.8–35.7, 48.3 and −37.7°, respectively. The ligand L has a transoid configuration with the torsion angle of C(8)C(7) C(14) being −172.6°. The dihedral angle between the planes of the benzene rings (cf. Table 4) equals 77.6°. These rings, in turn, form dihedral angles of 8.3 and 81.0° with the metallocycle plane.

Experimental

NMR spectra were obtained with a Varian-T-60 spectrometer (60 MHz; solvent CCl_4; internal standard TMS). IR spectra were taken with a UR-20 spectrophotometer in CCl_4 solution. Mass spectra were obtained with a MAT-311A device using a direct input into the ionic source at 100°C and ionization energies of 12 and 70 eV.

TABLE 4

$Ax + By + Cz = D$ EQUATIONS OF THE PLANES OF SOME OF THE PLANAR MOIETIES AND DEVIATIONS OF THE ATOMS FROM THESE PLANES (Å)

Planes	Atoms									A	B	C	D
1	C(8)	C(9)	C(10)	C(11)	C(12)	C(13)	Fe(2)[a]	N[a]	C(7)[a]	−0.1497	0.8196	−0.5531	−1.4024
	0.00	0.00	0.01	−0.01	0.01	−0.01	−0.02	0.46	−0.25				
2	C(14)	C(15)	C(16)	C(17)	C(18)	C(19)				0.7467	−0.0493	−0.6634	−0.4636
	−0.02	0.02	−0.01	−0.01	0.01	0.01							
3	Fe(2)	C(13)	N	C(7)	C(8)					−0.2712	0.7556	−0.5963	−1.9515
	−0.01	0.17	0.27	−0.42	0.03								

[a] Not included in the equations.

The method of the reaction of benzalazine with $Fe_3(CO)_{12}$ has been described previously [2]. For I: m.p. 80–81°C (hexane) (according to [5] m.p. 82–82.5°C). NMR spectrum (δ, ppm) 7.0–8.3m (C_6H_4, C_6H_5), 4.37s (CH_2). IR spectrum (ν, cm^{-1}) 1955, 1963, 2005, 2037, 2052, 2085 (C≡O). Mass spectrum (m/z): 461 [M^+], 293 [$M^+ - 6CO$], 181 [$M^+ - (2Fe + 6CO)$].

The X-ray structural study of I was carried out on a Syntex-$P\bar{1}$ diffractometer (graphite monochromator, λMo-K_α-irradiation, $\theta/2\theta$-scan $2 \leqslant 2\theta \leqslant 50°$, 1970 reflections with $F^2 \geqslant 2\sigma$). The structure was solved by the Patterson method and refined by the method of least-squares in anisotropic (Fe)-isotropic full-matrix approximation to $R = 0.058$ and $R_W = 0.062$. The atomic coordinates and their temperature factors are given in Table 1; bond lengths and bond angles in Tables 2 and 3, respectively. Table 4 contains the equations of the mean planes and deviations of the atoms (Å) of some of the planar moieties in I.

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