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CARBONYLIRON COMPLEXES WITH AN AZOMETHYLENE MOIETY

V *. PREPARATION OF $Fe_3(PhCH_2N)(CO)_{10}$ AND $HFe_3(PhCH{=}N)(CO)_9$ FROM BENZALAZINE AND $Fe_3(CO)_{12}$. X-RAY CRYSTAL STRUCTURE OF μ-(o-$C_6H_4CH_2NN{=}CHPh)Fe_2(CO)_6$

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Summary

The precipitate formed by the reaction of benzalazine with $Fe_3(CO)_{12}$ yields the triangular clusters $Fe_3(PhCH_2N)(CO)_{10}$ and $HFe_3(PhCH{=}N)(CO)_9$ when decomposed by concentrated hydrochloric and phosphorous acids, respectively. The structure of μ-(o-$C_6H_4CH_2NN{=}CHPh)Fe_2(CO)_6$, a product obtained from the benzalazine and $Fe_3(CO)_{12}$ reaction, is discussed.

Introduction

In the presence of a hydrogen source nitriles are known to react with $[HFe_3(CO)_{11}]^-$ or $[Fe_2(CO)_8]^{2-}$ anions to form complexes I and II (Scheme 1). The protonation of I and II (reversible in basic medium) yields complexes III and IV [2]. Treatment of III with CO in hexane under mild conditions gives complexes V [3], the structures of which were established by an X-ray diffraction study of Vd [4], and on the basis of analogy between the IR spectra of Va–Vc and Vd [5].

In the present paper we report a novel method of preparing Vc and IIIc (from benzalazine, PhCH=NN=CHPh) and their properties, not described in ref. 3.

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* For part IV see ref. 1.
** Deceased November 1984.
*** Deceased June 1983.

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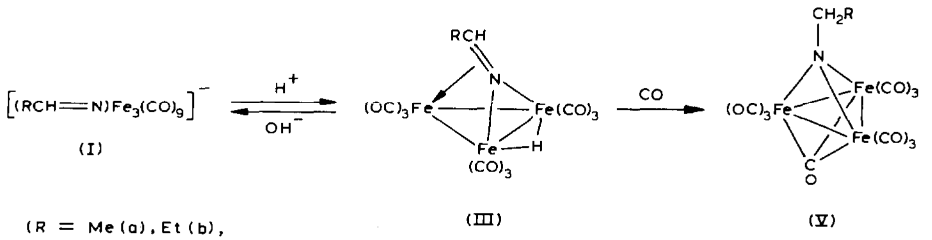


(R = Me (a), Et (b),
Ph (c), SiMe$_3$ (d))

$$\underset{(II)}{[(RC{=}NH)Fe_3(CO)_9]^-} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \underset{(IV)}{(RC{=}NH)Fe_3(CO)_9H}$$

Earlier we published a short communication [6] on the synthesis and preliminary X-ray structure characterization of μ-(o-$C_6H_4CH_2NN{=}CHPh)Fe_2(CO)_6$ (VI), prepared from benzalazine and $Fe_3(CO)_{12}$ in the presence of $M(CO)_6$ (M = Cr, Mo, W). In the present paper the structure of VI is described in detail.

Results and discussion

We prepared Vc by treating a precipitate formed by the interaction of benzalazine and $Fe_3(CO)_{12}$ with concentrated HCl (in hexane). Using H_3PO_4 instead of HCl, we obtained complex IIIc.

The IR spectrum of Vc is essentially the same as the spectra of the other complexes V. It shows six bands of the CO groups, among them one band characteristic of the μ_3-carbonyl group (1736 cm^{-1}). The ^1H NMR spectra of Va and Vc display somewhat different chemical shifts of the methylene group protons, probably because of the different R substituents. The mass spectra of both Va and Vc show weak peaks of molecular ions and demonstrate similar fragmentation modes.

IIIc is isostructural with IIIa, as indicated by the similarity of their IR, ^1H NMR and mass spectra. The IR spectra of IIIa and IIIc exhibit no band of a bridging CO group, and the ^1H NMR spectra show the signals of hydride and imine (–CH=) protons.

Heating Vc in hexane under an inert atmosphere yields IIIc, i.e. Vc (like Va [3]) undergoes elimination of the bridging CO group and isomerization (migration of a hydrogen atom).

It is worth noting that the above-mentioned reaction between benzalazine and $Fe_3(CO)_{12}$, unlike the reaction between nitriles and iron-carbonyl anions, does not yield complexes of type IV.

The molecular structure of VI is shown in Fig. 1; bond distances and angles are listed in Table 1. The two iron atoms, each bearing three linear, terminal carbonyl ligands, are linked by a metal–metal bond bridged by the organic ligand formed from benzalazine via *ortho*-metallation of benzene ring A and hydrogen atom migration from C(9) to C(7). Thus complex VI is an analogue of μ-(o-

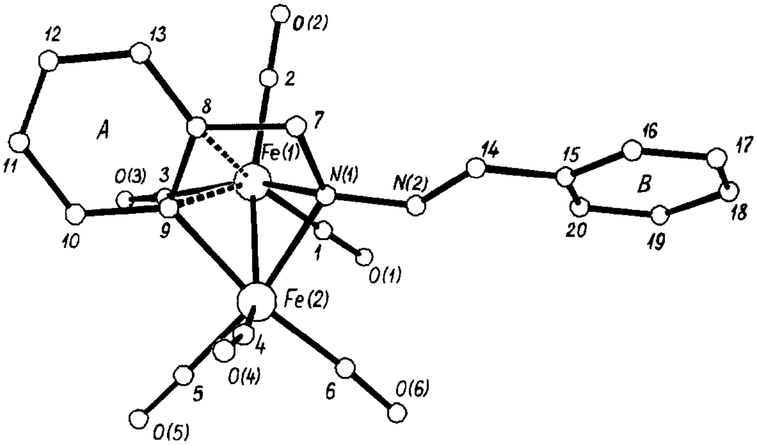


Fig. 1. Molecular structure of VI (the hydrogen atoms have been omitted).

$C_6H_4CH_2NC_6H_4Me)Fe_2(CO)_6$ (VII) [7] and μ-(*o*-$C_6H_4CH_2NPh)Fe_2(CO)_6$ (VIII) [1], differing from the latter only by the non-coordinated substituent at the bridging nitrogen atom.

The Fe(1)–Fe(2) bond distance of 2.417(3) Å in VI is close to the values in VII (2.43 Å) and VIII (2.459(1) Å) and indicates rather strong metal–metal bonding.

The *ortho*-metallated benzene ring A is planar. Its C(9) atom forms a normal length σ-bond (1.99(2) Å) with Fe(2), vs. 2.06 Å in VII, 2.001 Å in VIII and the standard Fe–C(sp^2) bond distance of 1.98 Å [8]. The interaction of ring A with Fe(1) can be considered as a π-olefinic coordination of the C(8)–C(9) bond (Scheme 2). The plane defined by the Fe(1), C(8) and C(9) atoms forms a dihedral angle of 59° with the benzene ring, vs. 90°, the ideal value for such coordination. The Fe(2)–C(9) and C(7)–C(8) bonds are bent out of the ring A plane by 7 and 6° away from Fe(1), indicating partial $sp^2 \rightarrow sp^3$ rehybridization of C(8) and C(9) consistent with π-coordination of the C(8)–C(9) bond. The Fe(1)–C(8) and Fe(1)–C(9) distances are distinctly non-equivalent, viz. 2.47(2) and 2.14(2) Å. The rather large former value is not uncommon, in comparison with 2.401 and 2.404 Å in complex IX with symmetrical η^2-coordination of the phenyl ring (Scheme 2). The non-equivalence of the Fe(1)–C distances is probably caused by steric factors, being smaller in VIII (Fe(1)–C(8) 2.305(8) vs. Fe(1)–C(9) 2.185(8) Å) and absent in VII (both distances of 2.30 Å).

N(1) bridges the iron atoms at equal distances (1.95 Å), although according to Scheme 2 and the EAN rule, the Fe(1)–N(1) bond is covalent and the Fe(2)–N(1) bond is a donor–acceptor one. In VII and VIII the former bond is slightly shorter than the latter, viz. 1.95 vs. 1.96 Å in VII, 1.967(6) vs. 1.982(7) Å in VIII. N(1) has a distorted tetrahedral environment. The N(1)–N(2) and N(1)–C(7) distances (1.45(2) and 1.47(2) Å) correspond to essentially single bonds [10]. The C(7)N(1)N(2)C(14) torsion angle in VI is 11(2) vs. 180° in the molecule of benzalazine, which has a crystallographic inversion centre in the midpoint of the N–N bond [11].

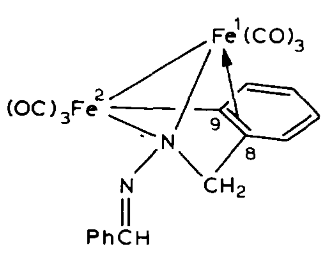
The N(2)=C(14)–Ph moiety does not participate in the coordination with the iron atoms and has essentially the same geometry as in benzalazine. The essentially double bond [10] N(2)=C(14) (1.27(2) Å) has a *trans*-configuration of the sub-

TABLE 1

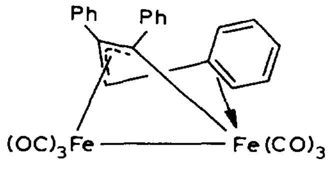
BOND DISTANCES (Å) AND ANGLES (°) IN THE STRUCTURE OF VI

Bond		Bond		Bond	
Fe(1)-Fe(2)	2.417(3)	C(1)-O(1)	1.13(2)	C(11)-C(12)	1.38(2)
Fe(1)-N(1)	1.95(1)	C(2)-O(2)	1.13(2)	C(12)-C(13)	1.39(2)
Fe(1)-C(1)	1.81(2)	C(3)-O(3)	1.14(2)	C(13)-C(8)	1.40(3)
Fe(1)-C(2)	1.77(2)	C(4)-O(4)	1.17(2)	N(2)-C(14)	1.27(2)
Fe(1)-C(3)	1.81(2)	C(5)-O(5)	1.13(2)	C(14)-C(15)	1.47(2)
Fe(1)-C(8)	2.47(2)	C(6)-O(6)	1.13(2)	C(15)-C(16)	1.40(3)
Fe(1)-C(9)	2.14(2)	N(1)-N(2)	1.45(2)	C(16)-C(17)	1.36(3)
Fe(2)-N(1)	1.95(1)	N(1)-C(7)	1.47(2)	C(17)-C(18)	1.35(3)
Fe(2)-C(4)	1.72(2)	C(7)-C(8)	1.53(2)	C(18)-C(19)	1.40(3)
Fe(2)-C(5)	1.78(2)	C(8)-C(9)	1.38(2)	C(19)-C(20)	1.36(3)
Fe(2)-C(6)	1.80(2)	C(9)-C(10)	1.46(2)	C(20)-C(15)	1.35(3)
Fe(2)-C(9)	1.99(2)	C(10)-C(11)	1.40(2)		
Angle		Angle		Angle	
Fe(2)Fe(1)N(1)	51.6(3)	C(4)Fe(2)C(6)	100.1(8)	C(9)C(8)C(13)	125(1)
Fe(2)Fe(1)C(1)	91.7(5)	C(4)Fe(2)C(9)	91.6(7)	C(8)C(9)C(10)	115(1)
Fe(2)Fe(1)C(2)	151.6(5)	C(5)Fe(2)C(6)	91.7(8)	Fe(2)C(9)C(8)	116(1)
Fe(2)Fe(1)C(3)	107.6(5)	C(5)Fe(2)C(9)	93.4(7)	Fe(2)C(9)C(10)	128(1)
N(1)Fe(1)C(1)	92.6(6)	C(6)Fe(2)C(9)	166.5(7)	C(9)C(10)C(11)	120(1)
N(1)Fe(1)C(2)	101.9(6)	Fe(1)C(1)O(1)	178(1)	C(10)C(11)C(12)	122(2)
N(1)Fe(1)C(3)	159.0(6)	Fe(1)C(2)O(2)	179(1)	C(11)C(12)C(13)	118(2)
C(1)Fe(1)C(2)	100.8(7)	Fe(1)C(3)O(3)	179(1)	C(12)C(13)C(8)	120(2)
C(1)Fe(1)C(3)	91.4(7)	Fe(2)C(4)O(4)	172(1)	N(1)N(2)C(14)	122(1)
C(2)Fe(1)C(3)	154.5(6)	Fe(2)C(5)O(5)	178(2)	N(2)C(14)C(15)	121(1)
Fe(1)Fe(2)N(1)	51.7(3)	Fe(2)C(6)O(6)	176(2)	C(14)C(15)C(16)	115(1)
Fe(1)Fe(2)C(4)	141.9(5)	Fe(1)N(1)Fe(2)	76.7(4)	C(14)C(15)C(20)	121(2)
Fe(1)Fe(2)C(5)	104.4(6)	Fe(1)N(1)N(2)	118.9(8)	C(16)C(15)C(20)	124(2)
Fe(1)Fe(2)C(6)	109.4(6)	Fe(1)N(1)C(7)	103.8(8)	C(15)C(16)C(17)	118(2)
Fe(1)Fe(2)C(9)	57.2(4)	Fe(2)N(1)N(2)	116.8(8)	C(16)C(17)C(18)	120(2)
N(1)Fe(2)C(4)	103.8(6)	Fe(2)N(1)C(7)	113.9(8)	C(17)C(18)C(19)	120(2)
N(1)Fe(2)C(5)	155.9(7)	N(2)N(1)C(7)	119(1)	C(18)C(19)C(20)	121(2)
N(1)Fe(2)C(6)	94.0(7)	N(1)C(7)C(8)	101(1)	C(19)C(20)C(15)	117(2)
N(1)Fe(2)C(9)	76.4(5)	C(7)C(8)C(9)	113(1)		
C(4)Fe(2)C(5)	98.2(8)	C(7)C(8)C(13)	122(1)		

stituents and is inclined to phenyl ring B by 15(2)°. An interesting feature of both VI and VII is the short non-bonding distance between Fe(1) and the methylene C(7) atom, viz. 2.70 Å in VI and 2.6 Å in VII.



(VI)



(IX)

Experimental

^{1}H NMR spectra were recorded with Varian T-60 (60 MHz) and Tesla-80 (100 MHz) spectrometers; IR spectra, with a UR-20 spectrometer. Electron-ionization mass spectra were measured with an LKB-2091 instrument (direct injection system, evaporation temperature 50–70°C, ionizing electron energy 70 eV).

An X-ray diffraction experiment was carried out with a Hilger & Watts four-circle autodiffractometer (graphite monochromated Cu-K_α radiation) at room temperature. Calculations were performed with an Eclipse S/200 computer using INEXTL programs [12].

Crystal data: monoclinic, space group $P2_1/n$, a 11.581(1), b 21.472(2), c 8.2956(6) Å, β 96.53(1)°, V 2049.4(6) Å^3, $Z = 4$ $C_{20}H_{12}Fe_2N_2O_6$, d_{calcd} 1.58 g cm^{-3}, μ(Cu-K_α) 119.4 cm^{-1}.

The intensities of 1898 independent reflections were measured by $\theta/2\theta$ scan technique ($\theta \leqslant 57°$). 1661 reflections with $|F| \geqslant 6\sigma$ were used in the calculations, with an analytical absorption correction [13] taking into account the real shape of the crystal (plate with dimensions 0.55 × 0.24 × 0.05 mm). However, after this

TABLE 2

ATOMIC COORDINATES ($\times 10^4$) AND THERMAL FACTORS B_{eq} (Å^2)

Atom	x	y	z	B_{eq}
Fe(1)	835(2)	1834(1)	1431(3)	4.5(1)
Fe(2)	1956(2)	1279(1)	3610(3)	4.8(1)
O(1)	−400(9)	699(6)	224(19)	9.7(5)
O(2)	674(9)	2555(6)	−1543(14)	7.4(4)
O(3)	−1289(9)	2310(6)	2666(14)	9.0(5)
O(4)	4140(9)	1384(6)	5628(15)	8.0(4)
O(5)	425(11)	1240(6)	6156(14)	9.6(5)
O(6)	1727(11)	−70(6)	3141(15)	8.5(5)
N(1)	2362(9)	1452(5)	1441(13)	4.2(3)
N(2)	2490(10)	921(5)	404(14)	5.2(4)
C(1)	92(13)	1128(7)	709(22)	6.0(6)
C(2)	729(13)	2280(8)	−378(20)	5.6(5)
C(3)	−462(14)	2126(8)	2203(18)	6.0(5)
C(4)	3268(14)	1294(8)	4804(17)	5.2(5)
C(5)	1032(15)	1252(9)	5191(21)	7.7(6)
C(6)	1803(17)	453(8)	3263(23)	7.5(7)
C(7)	3149(11)	1986(7)	1363(18)	4.9(5)
C(8)	2562(12)	2470(8)	2359(19)	5.5(5)
C(9)	1915(12)	2203(7)	3478(20)	5.1(5)
C(10)	1455(12)	2645(8)	4584(19)	5.8(5)
C(11)	1644(14)	3282(7)	4424(23)	6.6(6)
C(12)	2294(14)	3522(7)	3270(22)	6.1(6)
C(13)	2754(13)	3109(8)	2216(22)	6.2(6)
C(14)	3356(13)	856(9)	−395(20)	6.7(6)
C(15)	3422(16)	324(7)	−1489(16)	5.4(5)
C(16)	4518(14)	219(9)	−1979(20)	6.9(6)
C(17)	4635(17)	−271(10)	−2984(23)	8.1(8)
C(18)	3716(21)	−644(8)	−3458(22)	7.9(7)
C(19)	2631(16)	−520(10)	−2932(23)	8.8(8)
C(20)	2477(15)	−25(8)	−1952(21)	6.5(6)

correction, the absorption profiles (ψ-scan) of the reference reflections remained far from flattened, although the maximum to minimum intensity ratio was reduced from 6.3 to 1.8. Therefore, after a model of the structure had been found by the direct method (using the MULTAN program) and refined to $R = 0.13$, a further empirical absorption correction (the DIFABS procedure) [14] was applied. Full matrix anisotropic least-squares refinement (including hydrogen atoms as fixed contributions in calculated positions) converged to $R = 0.077$, $R_w = 0.076$, the weighting scheme $W^{-1} = \sigma_F^2 + (0.005\ F_0)^2$ being used. The coordinates and equivalent isotropic thermal factors $B_{eq} = 1/3\ \Sigma B_{ij} a_i^* a_j^* (a_i a_j)$ of the non-hydrogen atoms are listed in Table 2.

Preparation of Vc. The reaction of benzalazine with $Fe_3(CO)_{12}$ was carried out as described in [1]. The black precipitate obtained (13.0 g), insoluble in benzene, was placed under a layer of hexane. Concentrated hydrochloric acid was added until gas bubbles no longer evolved. The hexane extract was washed with water, dried with anhydrous $MgSO_4$, and filtered. The solvent was removed with a rotary evaporator, yielding 0.4 g of VIc, m.p. 94–95°C (hexane). ^1H NMR spectrum (δ, ppm, CCl_4): 7.37t (C_6H_5); 5.4s (CH_2). IR spectrum (CCl_4): $\nu(C \equiv O)$, 2095, 2055, 2025, 2020, 2003, 1736 cm^{-1}. Mass spectrum, m/z: 553 (M), 525, 497, 469, 441, 413, 385, 357, 329, 301, 273, 271, 215, 112, 103, 56.

Preparation of IIIc. 40.9 g of the precipitate from the reaction of benzalazine with $Fe_3(CO)_{12}$ (see above), 200 ml of hexane and 100 ml of concentrated H_3PO_4 were stirred until gas bubbles no longer evolved. Then the coloured hexane solution was washed with water to a neutral reaction, dried with anhydrous $MgSO_4$, and filtered. The solvent was removed with a rotary evaporator, yielding 1.1 g of IIIc. ^1H NMR spectrum (δ, ppm, CCl_4): 7.57d (CH); 7.38t (C_6H_5); 21.2d (hydride). IR spectrum (CCl_4): $\nu(C \equiv O)$ 2092, 2056, 2032, 2018, 2010, 2004, 1979 cm^{-1}. Mass spectrum, m/z: 525 (M), 497, 469, 441, 413, 385, 357, 329, 301, 273, 271, 215, 112, 103, 56.

Conversion of Vc into IIIc. 0.3 g (0.542 mmol) of Vc was warmed at 60°C in hexane for 10 h under argon atmosphere. 0.27 g (95%) of IIIc was isolated.

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