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SYNTHESIS AND STRUCTURE OF AN *ortho*-METALLATED DIIRON HEXACARBONYL COMPLEX FROM BENZALAZINE AND $Fe_3(CO)_{12}$

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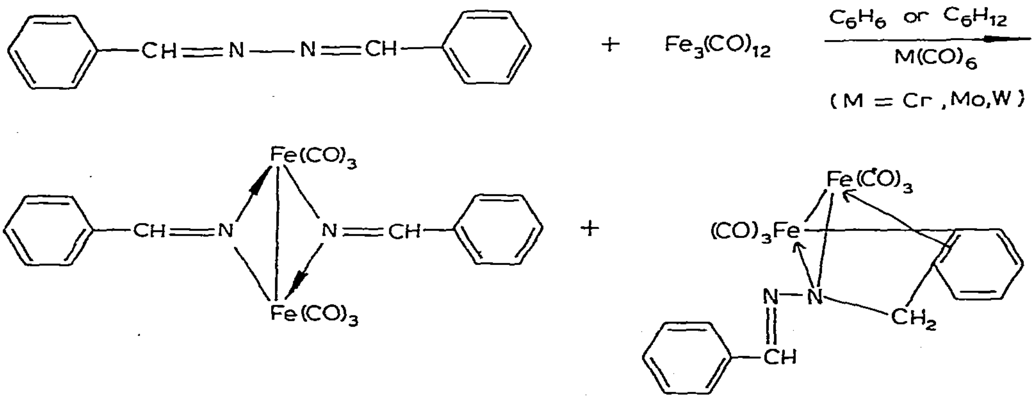
Summary

The synthesis of two diiron hexacarbonyl complexes from benzalazine and $Fe_3(CO)_{12}$ is described. This reaction is catalyzed by Group VIB metal carbonyls. An X-ray study was performed for the *ortho*-metallated complex $o\text{-}C_6H_4CH_2N{-}N{=}CHC_6H_5 \cdot Fe_2(CO)_6$.

All binuclear diiron hexacarbonyl complexes described until now in which two iron atoms are combined via a metal—metal bond and two three-electron or one six-electron heteroatomic bridges occur the two nitrogen atoms always take part in the coordination [1].



(I) (II)

We now show that treatment of benzalazine with $Fe_3(CO)_{12}$ gives a number of complexes (five) with iron carbonyl groups. Two of them (I and II) are characterized spectroscopically.

Compound I is an orange crystalline substance which can be characterized as a binuclear diiron hexacarbonyl compound of the type $N_2Fe_2(CO)_6$ without a direct bond between the nitrogen atoms [2]. Compound II is the main reaction product and forms dark-red crystals whose spectral data correspond to those of complex III, which was prepared from benzalazine and $Fe_2(CO)_9$ [3], but it has a different melting point (III, m.p. 83.5—84.5°C [3]). Experiments with $Fe_2(CO)_9$ under conditions of ref. 3 also lead to complex II (m.p. 115°C (decomp.)). On the basis of spectral data the authors of ref. 3 proposed a structure for complex III retaining the N—N bond and with two nitrogen atoms participating in the coordination with the iron atoms.

With this in mind we performed an X-ray analysis for compound II. Crystal data: monoclinic crystals, a 11.581(1), b 21.472(2), c 8.2956(6) Å, β 96.53(1)°, V 2049.4(6) Å^3, $Z = 4$, space group $P2_1/n$. The structure of II (Fig. 1) is similar to that of the compound prepared from $Fe_2(CO)_9$ and a Schiff base synthesized from p-toluidine and benzaldehyde, $(OC)_3Fe(H_3CC_6H_4CH_2NCH_2C_6H_4)$-$Fe(CO)_3$ (IV) [4]. The Fe(1)—Fe(2) bond (2.42(1) Å) in II is rather short, as it is in IV (2.43 Å). The bridging N(1) atom is almost equidistant from both Fe atoms (mean Fe—N distance 1.94(2) Å), the bridging benzene ring coordinates the Fe(1) atom by η^2 type (Fe(1)—C(3) 2.09(3) Å, Fe(1)—C(2) 2.45(2) Å) and Fe(2) form a σ-bond (Fe(2)—C(2) (1.96(3) Å). The double N(2)=C(4) bond and another benzene ring do not participate in the coordination with the metal. The effective atomic number rule holds for Fe(1) and Fe(2) if the N(1) atom is assumed to be a one-electron donor for Fe(1) and a two-electron donor for Fe(2).

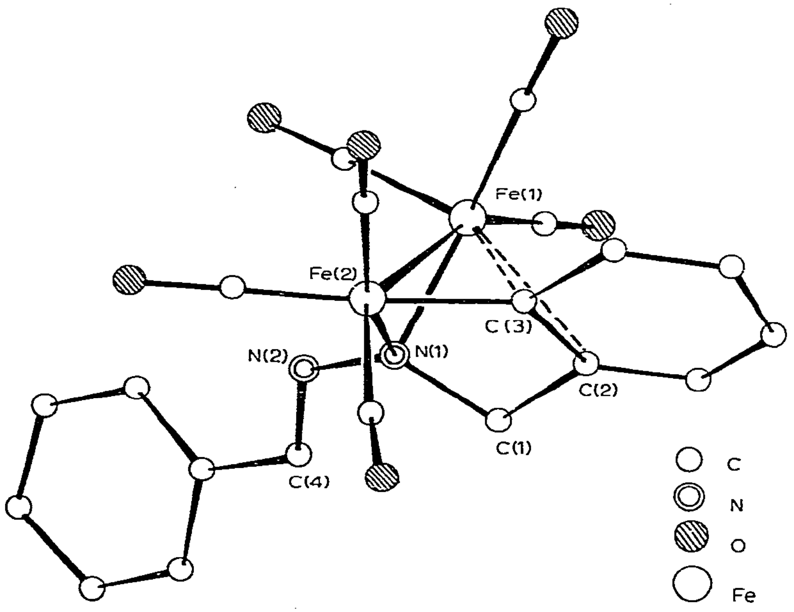


Fig. 1. Structure of complex II.

Compound II is the first example of an *ortho*-metallated binuclear diiron hexacarbonyl complex in which the metal is coordinated via one nitrogen atom only. This fact is important as it may provide different reactions at the double C=N bond and affords new and hardly available complexes including carbonyl clusters.

Significantly higher yields of the complexes are observed in cyclohexane as solvent and in the presence of Group VIB metal carbonyls. The nature of the metal influences the yield of complexes I and II. Group VIB metal carbonyls catalyze this reaction since they can interact with one or two nitrogen atoms via the lone pair electrons [1]. We have found an almost quantitative recovery of $M(CO)_6$ in this reaction.

Experimental

The PMR spectra were recorded on a Perkin—Elmer R-12 spectrometer (60 MHz) in CCl_4 with TMS as internal standard, the IR spectra on a UR-20 spectrophotometer as KBr pellets and in hexane. The mass-spectra were obtained with an LKB 2091 instrument with direct injection of the ion source at 40°C and an ionization energy of 70 eV. The melting points of the complexes were measured on a "Paulik-Paulik-Erdey" derivatograph (Hungary) under argon. A 100 mg sample was used for recording the derivatogram at a heating rate of 3°C/min. Calcined alumina (Al_2O_3) was used as standard.

The structure of complex II was solved by direct method and refined to $R = 0.13$ using 1748 reflections with $I \geqslant 2\sigma(I)$, measured on a "Syntex $P2_1$" diffractometer with Cu-K_α source at 20°C (with correction for absorption).

Reaction of benzalazine with $Fe_3(CO)_{12}$. A mixture of benzalazine, $Fe_3(CO)_1$ and $M(CO)_6$ (1/3/1 mol) in benzene or C_6H_{12} was refluxed with stirring under argon for 14—18 h. After removal of the solvent the residue was chromatographed on a SiO_2 column with hexane as eluent. Complexes I and II were crystallized from hexane. When C_6H_6 was used as solvent the Group VIB metal carbonyls did not take part in the reaction.

Analytical data for I: yield (%): 0.5 (C_6H_6), 3.0 (C_6H_{12}). M.p. 105°C. PMR spectrum (δ, ppm): 7.35—8.00w ($2C_6H_5$), 8.87s (CH), 8.98s (CH). IR spectrum (ν, cm^{-1}, C_6H_{14}): 1955, 1980, 1992, 2004, 2038, 2073 ($C{\equiv}O$). Mass spectrum (m/e): 488 (M^+), 320 ($M^+ - 6CO$). Found: C, 49.35; H, 2.47; Fe, 22.80; N, 5.71. $C_{20}H_{12}Fe_2N_2O_6$ calcd.: C, 49.22; H, 2.48; Fe, 22.88; N, 5.74%. For II: yield (%): 5.0 (C_6H_6), 18.0 (C_6H_{12}), 41.0 (C_6H_{12} + $Cr(CO)_6$). M.p. 115°C (decomp.). PMR spectrum (δ, ppm): 4.37s (CH_2), 7.0—8.3w (C_6H_4, C_6H_5), 8.39s (CH). IR spectrum (ν, cm^{-1}, KBr): 1969, 1988, 2032, 2070 ($C{\equiv}O$). Mass spectrum (m/e): 488 (M^+), 320 ($M^+ - 6CO$). Found: C, 49.10; H, 2.54; Fe, 23.11; N, 6.00. $C_{20}H_{12}Fe_2N_2O_6$ calcd.: C, 49.22; H, 2.48; Fe, 22.88; N, 5.74%.

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