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IRON CARBONYL COMPLEXES CONTAINING AZOMETHYLENE FRAGMENTS

II *. THE TRINUCLEAR *ortho*-METALLATED $Fe_3[\mu_2\text{-}\eta^6\text{-}o\text{-}C_6H_4CH_2N(N{=}CHC_6H_5)](CO)_8$ FROM BENZALAZINE AND $Fe_3(CO)_{12}$

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Summary

(*o*-Phenylenemethylenebenzylideneiminoamine)triiron octacarbonyl, $Fe_3[\mu_2\text{-}\eta^6\text{-}o\text{-}C_6H_4CH_2N(N{=}CHC_6H_5)](CO)_8$ (II), was isolated from the reaction products of benzalazine and $Fe_3(CO)_{12}$ (I). The structure of II was confirmed from the data of mass, IR, PMR and ^{13}C NMR spectra and elemental analysis. It is shown that compound II is generated by reaction of $Fe_2[\mu_2\text{-}\eta^2\text{-}o\text{-}C_6H_4CH_2N(N{=}CHC_6H_5)](CO)_6$ (III) with I. Thermal decomposition of II in heptane solution gives III.

Results and discussion

Two complexes have been isolated and specified from the reaction of benzalazine and $Fe_3(CO)_{12}$ (I): $(PhCH{=}N)_2Fe_2(CO)_6$ and $Fe_2[\mu_2\text{-}\eta^2\text{-}o\text{-}C_6H_4CH_2N(N{=}CHC_6H_5)](CO)_6$ (III) [1]. This paper is concerned with the isolation and thermal behaviour in the solid state and in solution of $Fe_3[\mu_2\text{-}\eta^6\text{-}o\text{-}C_6H_4CH_2N(N{=}CHC_6H_5)](CO)_8$ (II) and its synthesis from III and I. Complex II was obtained by treating benzalazine with I; the precipitate generated being washed with benzene. The first trinuclear complex, $Fe_3(\mu_2\text{-}\eta^6\text{-}o\text{-}C_6H_4CH_2NC_6H_5)(CO)_8$ (IV), with an unusual σ, π-bridged arene was prepared from *N*-(benzylidene)aniline and I [2].

It was of interest to introduce the *ortho*-metallated complex III into reaction with iron carbonyl. The presence of an uncoordinated C=N double bond and phenyl ring could open a possibility of preparing new clusters. However, the reaction of III with I yields neither an *ortho*-metallated second arenic ring nor a coordinated C=N bond.

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* For part I see ref. 2.

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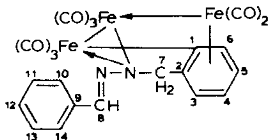
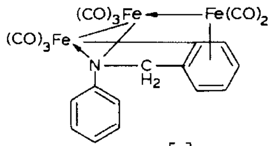
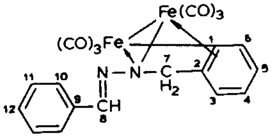
TABLE 1

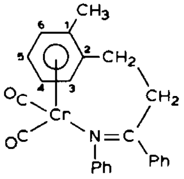
^{1}H NMR AND ^{13}C NMR DATA OF COMPOUNDS I–IV

	 (II)				 (IV) [2]			
	CH	CH_2	C_6H_4	C_6H_5	CH	CH_2	C_6H_4	C_6H_5
^{1}H NMR (δ ppm,$CDCl_3$)	7.6(s)	[AB] H(A)2.65(d) H(B)2.98(d) ^{2}J 13.7 Hz	[KLMN] H(K)4.22(d) H(L)5.01(d) H(M)5.51(t) H(N)6.73(t) ^{3}J 5.9 Hz	7.3–7.6(m)	–	[AB] H(A)2.45(d) H(B)3.88(d) ^{2}J 14.8 Hz	[KLMN] H(K)4.24(d) H(L)4.88(d) H(M)5.53(t) H(N)6.71(t) ^{3}J 5.9 Hz	7.16(s)

	C≡O	C=N	C–N	C_6H_4	C(9)–C(14)	
^{13}C NMR (δ, ppm, $CDCl_3$)	212.9 209.8	147.5	69.2	C(1)116.0 C(2)109.0 C(3) 95.1 C(4) 87.0 C(5) 87.9 C(6) 95.6	133.9; 127.6; 128.8; 130.3;128.9; 127.6	not measured



(III) [1]



(V) [3]

	CH	CH$_2$	C$_6$H$_4$	C$_6$H$_5$	CH	CH$_2$	C$_6$H$_4$
^{1}H NMR (δ, ppm, CDCl$_3$)	8.39(s)	4.37(s)	7.0–8.3(m)	7.0–8.3(m)	– (aceton-d_6)	3.45–2.20(m)	[KLMN] H(K)5.32(d) H(L)4.16(d) H(M)4.75(t) H(N)3.77(t) ^3J 6 Hz

	C≡O	C=N	C–N	C$_6$H$_4$	C(9)–C(14)	C≡O	C=N	C$_6$H$_4$
^{13}C NMR (δ, ppm, CDCl$_3$)	210.4	149.7	71.4	C(1)151.3 C(2)145.1 C(3)128.7 C(4)124.5 C(5)125.8 C(6)130.7	133.3; 127.8; 128.9; 130.4; 128.9; 127.8	242.4 (C$_6$D$_6$)	182.19	C(1)106.3 C(2)103.2 C(3) 98.2 C(4) 80.5 C(5) 88.8 C(6) 87.1

One may suggest that the formation of the trinuclear complex II involves insertion of the $Fe(CO)_2$ group into the Fe–arene π-bond with all six arene π-electrons taking part in coordination to the metal.

$$\mathrm{III} \underset{80^\circ\mathrm{C}}{\overset{\mathrm{Fe_3(CO)_{12}};\ 80^\circ\mathrm{C}}{\rightleftarrows}} \mathrm{II}$$

This case is interesting although there is no definite evidence to the iron carbonyl fragment coordinating the already substituted arene.

Elimination of the $Fe(CO)_2$ group from complex II occurs during its thermal decomposition in heptane solution, giving a high yield of III.

Since we failed to obtain crystals of adequate quality for X-ray analysis, the structure of the trinuclear complex II was analyzed by comparison of the NMR parameters of complexes II-V (cf. Table 1).

Introduction of the $Fe(CO)_2$ group into III causes an almost additive strong field shift of the signals of ^{13}C nuclei C(1)–C(6): C(1) 35.3; C(2) 36.1; C(3) 33.6; C(4) 37.5; C(5) 37.9; C(6) 35.0 ppm, confirming the formation of an η^6-areneiron dicarbonyl complex. The formation of an η^6-type complex with an iron dicarbonyl group is also confirmed by comparison of the PMR spectra of compound IV, for which an X-ray analysis was performed [2] and an arenechromium dicarbonyl complex [3]. As reported [2], here we also observe distinct signals for all four *ortho*-metallated aromatic ring protons forming a [KLMN] spin-system with $^3J \simeq 6$ Hz and $^4J \simeq 0$ Hz. The PMR spectrum of compound II also showed magnetic inequivalence of CH_2-N group protons which could be due to magnetic anisitropy of the $Fe(CO)_2$ group.

Thermal decomposition of II on a derivatograph under argon atmosphere showed that the decomposition starts at 105°C. The first step involves an endothermic elimination of 8 CO groups up to 160°C. The second step (160–500°C) includes the cleavage of an organic ligand of the molecule without any thermal effects; Fe remains in the residue. The experimental results obtained are in good agreement with the calculated data. Compared to the dinuclear complex III [4], compound II is less stable but it is more stable then IV (decomp. pt. 50°C) [2]. The TG curve pattern specifying decomposition is similar for complexes II and III.

Experimental

The PMR spectra were registered on a Bruker WH-90 (90Mz) spectrometer with TMS as standard. The ^{13}C NMR spectra were taken on a Bruker WP-80 (20.115 MHz) spectrometer. The IR spectra were recorded on an UR-20 spectrophotometer. The mass-spectra were obtained on a LKB-2091 instrument with direct inlet into the ion source at 40°C and ionization energy of 12 eV. Thermal decomposition was performed on a Paulik-Paulik-Erday derivatograph (Hungary) in argon; 100 mg of the sample was used for recording a derivatogram at a heating rate 3°C/min. Calcinated Al_2O_3 was employed as standard.

Isolation of II from the reaction of benzalazine with I

The procedure of the reaction of benzalazine with I is described elsewhere [1]. Complex II was isolated by cooling and filtering the reaction mixture and washing the residue with hexane and benzene. The benzene fraction was separated, evaporated on a rotary evaporator and the solid recrystallized from a heptane-benzene mixture; 5.0 g (2.4 mmol) of benzalazine and 36.3 g (7.2 mmol) of I gave 2.4 g of II (16.7%). Complex II is a dark-red solid with limited solubility in hydrocarbon solvents, and good solubility in the polar organic solvents. In solution it decomposes slowly in air giving III. In the solid state in air it generates benzonitrile. IR spectrum (ν, cm^{-1}; KBr): 1952, 1967, 1983, 2005, 2030, 2062 ($C\equiv O$). IR spectrum (ν, cm^{-1}; CCl_4): 1952, 1992, 2005, 2039, 2076, 2100 ($C\equiv O$). Mass spectrum (*m/e*): 600(M^+), 376 ($M^+ - 8CO$). Found: C, 43.82; H, 2.17; Fe, 27.78; N, 4.69. $C_{22}H_{12}Fe_3N_2O_8$ calcd.: C, 44.04; H, 2.02; Fe, 27.93; N, 4.67%. Molecular weight (in benzene) 588 (calculated 600).

Reaction of (III) with (I)

A solution of 6.0 g of III (12.3 mmol) and 18.6 g of I (36.9 mmol) in heptane was stirred in Ar for 10 h (until disappearance of I) at 80°C. The hot solution was filtered and cooled to room temperature. The solid precipitated was dried in vacuum; 5.1 g (69%) of II was obtained.

Thermal decomposition of II

A solution of 3.0 g of II (5 mmol) in heptane was heated at 80°C for 8 h under Ar. The reaction mixture was cooled to room temperature, filtered, and the solvent was evaporated on a rotary evaporator; 1.85 g (76%) of practically pure III was obtained.

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