

PREPARATION OF 1,3-BIS(η^5 -CYCLOPENTADIENYLDICARBONYLIRON)-1-CYANO-2,4-DIPHENYLCYCLOBUT-2-ENE AND ITS TRANSFORMATION INTO 1,3-BIS(η^5 -CYCLOPENTADIENYLDICARBONYLIRON)-1-CYANO-2,4-DIPHENYLBUTA-1,3-DIENE; FACILE C–C BOND CLEAVAGE IN A CYCLOBUTENE RING *

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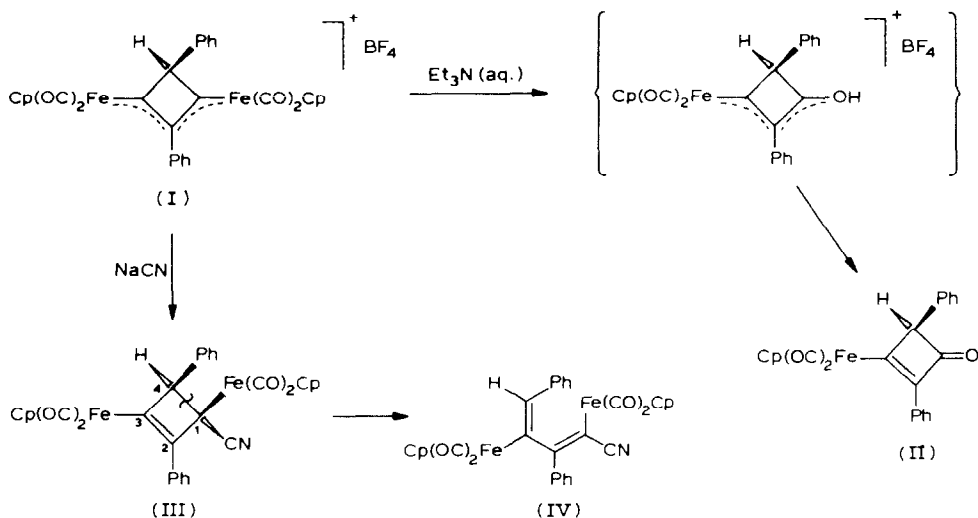
Summary

The reaction between the cationic diiron complex $[\text{Cp}(\text{CO})_2\text{-FeC}\equiv\text{CPh}\equiv\text{C}\{\text{Fe}(\text{CO})_2\text{Cp}\}\text{CHPh}]^+ \text{BF}_4^-$ (I) and sodium cyanide gives the neutral complex $\text{Cp}(\text{OC})_2\text{FeC}(\text{CN})\text{CPh}=\text{C}\{\text{Fe}(\text{CO})_2\text{Cp}\}\text{CHPh}$ (III). By heating in solution III undergoes an opening of its cyclobutene ring via C–C bond cleavage, yielding the butadiene derivative $\text{Cp}(\text{OC})_2\text{FeC}(\text{CN})=\text{CPhC}\{\text{Fe}(\text{CO})_2\text{Cp}\}=\text{CHPh}$ (IV). III and IV are characterized by X-ray diffraction studies, IR and NMR spectroscopy.

Introduction

Cationic vinylideneiron complexes can be prepared by two routes. Protonation of the σ -phenylethynyl complex yielding the unstable intermediate $[\text{Cp}(\text{OC})_2\text{Fe}=\text{C}=\text{CHPh}]^+ \text{BF}_4^-$ [1,2], while the reaction of the σ -acyl complexes $\text{Cp}(\text{OC})\text{LFeCOCHR}_2$ with $(\text{F}_3\text{CSO}_2)_2\text{O}$ in the presence of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ produces the stable compounds $[\text{Cp}(\text{OC})\text{LFe}=\text{C}=\text{CR}_2]^+ \text{BF}_4^-$ ($\text{L} = \text{PPh}_3$, $\text{R} = \text{H, Me}$; $\text{L} = \text{PMe}_2\text{Ph}$, $\text{P}(\text{C}_6\text{H}_{11})_3$, $\text{R} = \text{H}$) [3]. Both types of vinylidene complexes are reactive, adding neutral nucleophiles to the α -carbon atom of the vinylidene ligand. σ -Phenylethynyliron complexes are added to the same (electrophilic) atom yielding cationic diiron complexes with bridging cyclobutenylidene ligands [1–3]. The properties of these interesting complexes were not investigated previously.

* Dedicated to Prof. Oleg A. Reutov on the occasion of his 65th birthday.



SCHEME 1

In the present work we have studied the reactivity to neutral and anionic nucleophiles of one of such complexes, I (Scheme 1), prepared and characterized by some of us earlier [1].

Results and discussion

We have found that I does not react with water and alcohols (MeOH, EtOH) neither at room temperature nor upon heating. However, aqueous Et_3N causes cleavage of one Fe–C bond, yielding η^5 -cyclopentadienyl- η^1 -(2,4-diphenyl-3-oxocyclobut-2-ene-1-yl)iron dicarbonyl (II) [6], probably through the hydroxylation. The ^1H and ^{13}C NMR spectra of II (Table 1) in agreement with its structure established by an X-ray single crystal study [7].

II can also be obtained by the reactions of I with anionic nucleophiles e.g. MeCO_2Na , MeONa , NaF , $\text{PhC}\equiv\text{CNa}$, BuLi and PhSNa . Probably all these nucleophilic reagents only form a basic medium, which promotes the Fe–C(cyclobutenylidene) bond cleavage in I.

With NaCN complex I reacts differently, adding the cyanide anion to the α -carbon atom of the cyclobutenylidene ligand and producing neutral 1,3-bis(η^5 -cyclopentadienyldicarbonyliron)-1-cyano-2,4-diphenylcyclobut-2-ene (III) in a stoichiometric yield [8] (Scheme 1). Complex III is a yellow crystalline substance, poorly soluble in aliphatic hydrocarbons but readily soluble in polar and aromatic solvents. The IR spectrum of III exhibits stretching bands of carbonyl groups at 2030, 2020 and 1975 cm^{-1} , and a weak band at 2180 cm^{-1} , characteristic of the CN group. Both ^1H and ^{13}C NMR spectra of III indicate the unequivalence of the two Cp rings, unlike I, wherein both Cp ligands are equivalent and exhibit one proton singlet at 5.20 ppm and one ^{13}C singlet at 88.27 ppm [5]. NMR spectra of III (Table 1) are consistent with its X-ray structure (see below).

III is stable in the solid state, but in solutions (especially on heating) it undergoes

TABLE 1
CHEMICAL SHIFTS (ppm) IN NMR ^1H AND ^{13}C SPECTRA OF II-IV ^a

Compound	Nucleus	$\delta(\text{Cp})$	$\delta(\text{Ph})$	$\delta(\geq\text{C}-\text{H})$	$\delta(-\text{CH}=\text{C})$	$\delta(\text{C}=\text{O})$
II	^1H	4.78s	7.8–7.3m	4.67s	–	
II	^{13}C	84.78	126.08; 126.51; 126.89; 127.69; 78.37 127.84; 138.29		166.22(Fe–C \leftarrow) 131.9(Ph–C \leftarrow)	213.42; 212.09; 211.80
III	^1H	4.53s; 4.11s	7.5–7.1m	4.13s		
III	^{13}C	86.13 84.82	126.59; 126.83; 127.66; 127.80; 129.35; 130.71; 142.36; 147.64	70.46	166.61(Fe–C \leftarrow) 138.47(Ph–C \leftarrow)	215.18; 214.64 214.35; 213.38
IV	^1H	4.88s; 4.37s	7.4–6.9		6.38s	
IV	^{13}C	86.47 85.25	142.79; 138.52; 129.40; 127.80; 127.36; 126.93; 125.08; 127.51		138.81	216.29; 214.98; 212.12

^a Measured in CDCl_3 medium, but recalculated referring to TMS as standard.

cleavage of the C(1)–C(4) bond in the cyclobutenediyl ligand with isomerization into 1,3-bis(η^5 -cyclopentadienyldicarbonyliron)-1-cyano-2,4-diphenylbuta-1,3-diene (IV). IV is an air-stable orange crystalline substance, which is readily soluble in polar and aromatic solvents. Its IR spectrum exhibits stretching bands of four terminal carbonyl groups at 2040, 2020, 1990 and 1970 cm^{-1} , and an intense characteristic band of the CN group at 2170 cm^{-1} . The latter frequency is situated 10 cm^{-1} lower than in the spectrum of III, indicating a conjugation between the $\text{C}\equiv\text{N}$ and C(1)=C(2) bonds.

When a freshly prepared solution of III was kept for several hours at room temperature, its ^1H and ^{13}C NMR spectra indicated slow transformation of III into IV (viz. the $\geq\text{CH}$ group signals of III vanished and the $-\text{CH}=\text{C}$ group signals of IV appeared) as confirmed by thin-layer chromatography.

The molecular structures of III and IV (Fig. 1 and 2, Table 2) were determined by an X-ray single crystal diffraction study. Complex III was studied in the form of the $\text{III} \cdot \text{C}_6\text{H}_6$ solvate, crystallized from benzene.

Molecules III and IV both consist of two $\text{Cp}(\text{OC})_2\text{Fe}$ moieties (designated A and C), σ -bonded to a bridging $\text{C}_4\text{HPh}_2\text{CN}$ ligand (designated B). In III ligand B is 1-cyano-2,4-diphenylcyclobut-2-ene-1,3-diyl. Its cyclobutene ring is planar with the C(2B)=C(3B) double bond. The $\text{Cp}(\text{OC})_2\text{Fe}$ moiety A and the phenyl substituent E are in a *cis* arrangement to each other, the Fe(A)–C(1B) and C(4B)–C(41B) bonds being inclined by 46.5 and 43° to the plane of the 4-membered ring.

The C(2B) and C(3B) atoms have planar-trigonal geometry. The C(2B)–C(21B) bond is co-planar with the cyclobutene ring, while the Fe(C)–C(3B) bond is 7° bent out of its plane in the same direction as A and E moieties. The phenyl ring D forms a dihedral angle of 54° with the 4-membered ring, i.e. D does not conjugate with the C(2B)=C(3B) bond.

The Fe(A)–C(1B) bond distance (2.08(3) Å) is not uncommon for Fe–C(sp^3)

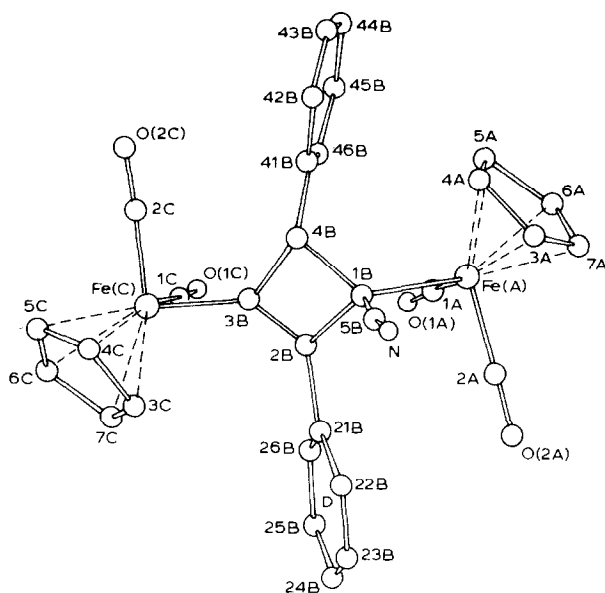


Fig. 1. Molecular structure of III (hydrogen atoms omitted for clarity).

σ -bonds (2.08–2.16, average 2.11 Å [9]). The Fe(C)–C(3B) bond (1.89(3) Å) is somewhat shorter than the standard Fe–C(sp^2) bond (1.98 Å [9]). Though this shortening (ca. 3σ) is at the limit of statistical significance, it is comparable with the shortening of the Fe–C(sp^2) σ -bond (up to 1.935(6) Å) in the more accurately determined structure of II [7].

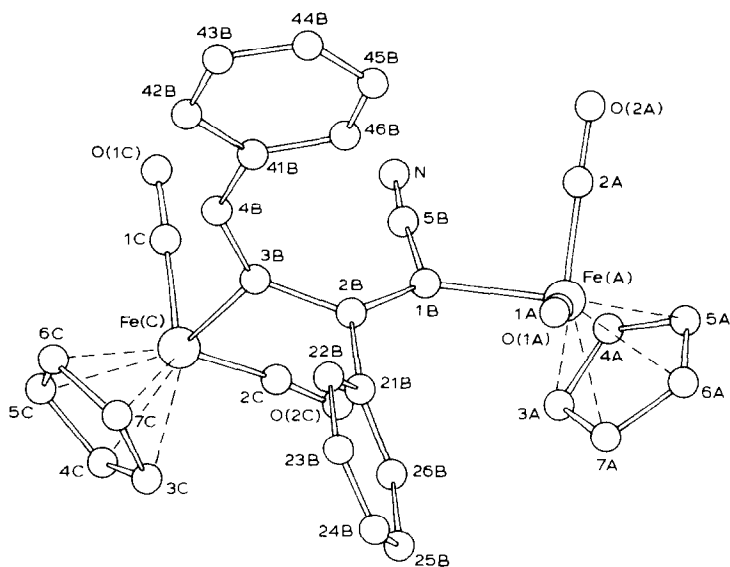


Fig. 2. Molecular structure of IV (hydrogen atoms omitted for clarity).

TABLE 2a

BOND DISTANCES (Å) AND ANGLES (°) IN Cp(OC)₂Fe, MOIETIES A AND C

	Structure III		Structure IV	
	A	C	A	C
<i>Bonds</i>				
Fe–C(1)	1.72(3)	1.69(3)	1.766(3)	1.762(3)
Fe–C(2)	1.81(4)	1.73(4)	1.768(4)	1.756(3)
Fe–C(3)	2.05(3)	2.13(4)	2.094(3)	2.098(3)
Fe–C(4)	2.13(3)	2.07(4)	2.088(3)	2.105(4)
Fe–C(5)	2.12(3)	2.06(4)	2.101(4)	2.102(3)
Fe–C(6)	2.05(4)	2.15(4)	2.092(4)	2.077(4)
Fe–C(7)	2.07(4)	2.09(4)	2.082(4)	2.093(4)
C(1)–O(1)	1.19(4)	1.19(4)	1.139(4)	1.137(4)
C(2)–O(2)	1.12(4)	1.16(4)	1.135(4)	1.142(4)
C(3)–C(4)	1.45(5)	1.37(5)	1.392(5)	1.400(5)
C(4)–C(5)	1.42(4)	1.39(5)	1.396(5)	1.383(5)
C(5)–C(6)	1.51(5)	1.36(5)	1.389(6)	1.409(6)
C(6)–C(7)	1.28(5)	1.44(5)	1.392(6)	1.384(5)
C(7)–C(3)	1.38(5)	1.41(4)	1.382(5)	1.382(5)
<i>Angles</i>				
C(1)FeC(2)	97(2)	98(2)	94.1(2)	95.4(1)
C(1)FeX ^a	90(1)	85(1)	91.4(1)	83.9(1)
C(2)FeX ^a	92(1)	91(1)	89.7(1)	94.2(1)
FeC(1)O(1)	175(3)	175(3)	176.8(3)	177.3(3)
FeC(2)O(2)	173(3)	178(3)	177.2(3)	176.9(3)
C(7)C(3)C(4)	108(3)	105(3)	108.0(3)	108.5(3)
C(3)C(4)C(5)	108(3)	110(3)	107.9(3)	107.8(3)
C(4)C(5)C(6)	101(3)	111(3)	107.9(3)	107.6(3)
C(5)C(6)C(7)	113(3)	105(3)	107.8(4)	108.1(3)
C(6)C(7)C(3)	109(3)	109(3)	108.4(3)	108.0(3)

^a X = C(1B) for Fe(A) and C(3B) for Fe(C).

TABLE 2b

BOND DISTANCES (Å) AND ANGLES (°) IN BRIDGING C₄HPh₂CN LIGAND (B)

	B			B	
	III	IV		III	IV
<i>Bonds</i>					
Fe(A)–C(1B)	2.08(3)	2.024(3)	C(1B)–C(5B)	1.44(4)	1.454(4)
Fe(C)–C(3B)	1.89(3)	2.035(3)	C(5B)–N	1.16(4)	1.144(4)
C(1B)–C(2B)	1.47(4)	1.344(4)	C(2B)–C(21B)	1.59(5)	1.497(4)
C(2B)–C(3B)	1.32(5)	1.483(4)	C(4B)–C(41B)	1.48(4)	1.473(4)
C(3B)–C(4B)	1.57(4)	1.345(4)	C–C(Ph)	1.33(5)–1.43(4)	
C(4B)–C(1B)	1.58(4)	–	average	1.40(3)	
<i>Angles</i>					
Fe(A)C(1B)C(2B)	121(2)	133.7(2)	C(2B)C(3B)C(4B)	86(2)	124.5(3)
Fe(A)C(1B)C(4B)	123(2)	–	C(3B)C(4B)C(1B)	88(2)	–
Fe(A)C(1B)C(5B)	106(2)	110.2(2)	C(3B)C(4B)C(41B)	122(2)	131.3(3)
C(2B)C(1B)C(4B)	81(2)	–	C(1B)C(4B)C(41B)	121(2)	–
C(2B)C(1B)C(5B)	112(3)	116.0(2)	C(1B)C(5B)N	174(3)	174.6(3)
C(4B)C(1B)C(5B)	113(3)	–	C(2B)C(21B)C(22B)	121(3)	121.7(3)
C(1B)C(2B)C(3B)	104(3)	122.7(2)	C(2B)C(21B)C(26B)	117(3)	119.9(3)
C(1B)C(2B)C(21B)	126(3)	122.6(2)	C(22B)C(21B)C(26B)	122(3)	118.4(3)
C(3B)C(2B)C(21B)	130(3)	114.6(2)	C(4B)C(41B)C(42B)	124(3)	118.2(3)
Fe(C)C(3B)C(2B)	141(3)	115.8(2)	C(4B)C(41B)C(46B)	120(2)	125.1(3)
Fe(C)C(3B)C(4B)	132(2)	119.5(2)	C(42B)C(41B)C(46B)	116(3)	116.7(3)

In IV the bridging C_4HPh_2CN ligand (B) is 1-cyano-2,4-diphenylbuta-1,3-diene-1,3-diyl. All four carbon atoms of the acyclic butadiene moiety have planar-trigonal geometry, but the repulsion between bulky $Cp(OC)_2Fe$ and Ph substituents causes torsion around the $C(1B)=C(2B)$ and $C(3B)=C(4B)$ double bonds (9.7 and 3.2°) and rotation (88.4°) around the $C(2B)-C(3B)$ single bond, preventing any π -conjugation between the double bonds. The D and E phenyl planes are inclined (59.0 and 24.3°) to the coordination planes of the $C(2B)$ and $C(4B)$ atoms, respectively. The $Fe(A)-C(1B)$ and $Fe(C)-C(3B)$ σ -bonds are somewhat longer ($2.024(3)$ and $2.035(3)$ Å) than the standard $Fe-C(sp^2)$ bond (1.98 Å) and $Fe-C$ (vinyl) bonds in $Cp(OC)_2Fe(\sigma$ -vinyl) complexes ($1.987-1.996$ Å) [10-12].

In molecule IV the $Cp(OC)_2Fe$ moiety A and the phenyl group D are mutually *cis*, while moiety C and the phenyl group E are mutually *trans*. In III the mentioned pairs of substituents are compelled to adopt *gauche* arrangement.

Comparison of the geometry of molecules I, III and IV provides some fruitful conclusions on the stereochemistry of the above-mentioned reactions.

In cation I both iron atoms are bent out of the 4-membered ring plane (0.15 and 0.27 Å) in the same direction as the phenyl substituent at the sp^3 -hybridized carbon atom of the ring (corresponding to the phenyl group E and the $C(4B)$ atom in III). This bending is the same in both crystallographically independent cations I, hence it represents intramolecular rather than intermolecular features and is probably retained in solution. By widening the corresponding coordination site of the metallated $C(1B)$ atom such a distortion favours the cyanide anion addition to this atom in the *trans*-position to the phenyl group E. The opposite coordination site is narrowed and screened by one carbonyl ligand at $Fe(A)$, directed perpendicularly to the 4-membered ring plane, which hinders *cis*-addition of CN^- . Therefore in molecule III formed the bulky A and E substituents adopt an overcrowded *cis*-arrangement, giving rise to straining of the $C(1B)-C(4B)$ bond (note that the $Fe(C)$ atom remains bent out of the 4-membered ring plane by 0.23 Å in the same direction as in I). The cyano group increases steric overcrowding and weakens adjacent C-C bonds ($50-63$ kJ/mol) [13]. Combination of these two (steric and energetic) effects leads to easy cleavage of the $C(1B)-C(4B)$ bond, i.e. to the transformation of III into IV. In the latter complex the steric strain is relieved due to twisting of the butadiene moiety.

Experimental

Absolute solvents and L100/160 μ silica gel were used. IR spectra were recorded with a UR-20 Zeiss spectrophotometer (in KBr pellets) and 1H and ^{13}C NMR spectra with a Bruker WP 200 SY spectrometer (200.13 and 50.35 MHz, resolution of 2000 Hz (1H) or 20000 Hz (^{13}C) per 16 channels). The signal assignment in ^{13}C NMR spectra was based on the known chemical shifts of the related compounds [14] and the increment scheme for monosubstituted benzenes [15] as well as on experiments without 1H frequency suppression.

X-ray diffraction experiments were carried out with 4-circle autodiffractometers. Calculations were performed with an Eclipse S/200 computer using INEXTL programs [16]. Crystal data and experimental details are listed in Table 3. Structure III was solved by Patterson and Fourier methods and refined by full matrix least squares in isotropic (anisotropic for Fe atoms) approximation. No attempt was made to locate hydrogen atoms. Structure IV was solved by a direct method and refined

TABLE 3
CRYSTAL DATA AND X-RAY EXPERIMENTAL DETAILS

Compound	III	IV
Formula	$C_{31}H_{21}Fe_2NO_4 \cdot C_6H_6$	$C_{31}H_{21}Fe_2NO_4$
a , Å	10.60(3)	12.0201(5)
b , Å	12.40(3)	12.2660(8)
c , Å	12.31(4)	18.585(1)
α , °	107.8(3)	90
β , °	91.91(3)	104.623(4)
γ , °	100.8(2)	90
V , Å ³	1506(12)	2651.4(3)
Space group	$P\bar{1}$	$P2_1/c$
Z	2	4
d_{calcd} , g cm ⁻³	1.46	1.49
Diffractionmeter	Syntex P2 ₁	Hilger & Watts
Radiation	graphite-monochromated Mo- K_α	graphite-monochromated Mo- K_α
Temperature, °C	-120	20
Scan mode	$\theta/2\theta$	$\theta/2\theta$
θ_{max} , °	25	30
No. of reflections with $I \geq 2\sigma(I)$	1133	3278 ^a
Weighting scheme	$W=1$	$W^{-1} = \sigma^2 F + (0.011 F_o)^2$
R	0.097	0.036
R _w	0.110	0.034

^a Except 4 rejected low-angle reflections, affected by extinction

by block diagonal anisotropic least squares for non-hydrogen atoms. All H atoms, located in the difference Fourier map, were refined in isotropic approximation. Final positional and thermal atomic parameters are listed in Tables 4 and 5.

Preparation of II. Aqueous Et₃N (0.6 g, 6 mmol) in THF (5 ml) was added to a solution of I (0.2 g, 0.31 mmol) in THF (50 ml). The mixture was stirred for 5 h at 20°C, the solvent was removed in vacuo and the residue was chromatographed on silica gel using benzene as the eluent, 0.12 g (ca. 100%) of yellow crystalline II was isolated, m.p. 147–148°C (from petroleum ether/CH₂Cl₂ (2/1)). Found: C, 69.08; H, 4.40; Fe, 14.23. C₂₃H₁₆O₃Fe calcd.: C, 69.18; H, 4.04; Fe, 14.76%. IR spectrum: $\nu(\text{C}\equiv\text{O})$ 2025, 1980, $\nu(\text{C}=\text{O})$ 1705 cm⁻¹.

Preparation of III. NaCN (0.1 g, 2.04 mmol) in absolute ethanol (25 ml) was added to a solution of I (0.75 g, 1.15 mmol) in THF (200 ml) and cooled to -30°C. The mixture was left to warm up to 20°C. The solvent was removed in vacuo and the residue was extracted with benzene/heptane (1/1). 0.66 g (ca. 99%) of yellow crystalline III was isolated, m.p. 115–116°C (from benzene/heptane (3/2)). Found: C, 63.96; H, 3.56; N, 2.50; Fe, 19.39. C₃₁H₂₁NO₄Fe₂ calcd.: C, 63.84; H, 3.60; N, 2.40; Fe, 19.17%. Mass spectrum: 527 ($M^+ - 2\text{CO}$), 471 ($M^+ - 4\text{CO}$). IR spectrum: $\nu(\text{C}\equiv\text{O})$ 2030, 2020, 1975; $\nu(\text{C}\equiv\text{N})$ 2180 cm⁻¹.

Preparation of IV. A benzene solution of III was refluxed for ca. 1 h (monitored by thin layer chromatography) and then filtered. The solvent was removed in vacuo and the residue recrystallized from benzene/heptane. Orange crystalline IV was isolated in ca. 100% yield, m.p. 180–180.5°C (dec.). Found: C, 63.84; H, 3.72; N,

(Continued on p. 256)

TABLE 4
 ATOMIC COORDINATES ($\times 10^3$, for Fe $\times 10^4$) AND THERMAL FACTORS B_{iso} (for Fe $B_{\text{iso}}^{\text{Fe}} = \frac{1}{3} \sum_{i,j} B_{ij} a_i^* a_j^* (\mathbf{a}_i, \mathbf{a}_j)$) IN THE STRUCTURE III

Atom	x	y	z	B (\AA^2)	Atom	x	y	z	B (\AA^2)
Fe(A)	4897(5)	2571(4)	3099(4)	1.6(2)	C(24B)	665(3)	525(3)	1(3)	2.4(7)
Fe(C)	9629(4)	2037(4)	1005(4)	1.4(2)	C(25B)	654(3)	408(3)	-52(3)	1.8(7)
O(1A)	473(2)	128(2)	67(2)	2.1(4)	C(26B)	677(3)	343(3)	22(3)	1.5(6)
O(2A)	441(2)	466(2)	267(2)	2.7(5)	C(41B)	733(3)	99(2)	304(2)	0.5(5)
O(1C)	770(2)	42(2)	-73(2)	2.3(5)	C(42B)	753(3)	63(3)	399(3)	2.1(7)
O(2C)	1012(2)	47(2)	222(2)	2.4(5)	C(43B)	701(3)	-47(3)	393(3)	2.5(7)
N	752(2)	489(2)	490(2)	1.9(5)	C(44B)	636(3)	-134(3)	298(3)	2.1(7)
C(1A)	479(3)	177(3)	168(3)	1.9(7)	C(45B)	620(3)	-107(3)	194(3)	1.5(6)
C(2A)	464(3)	390(3)	289(3)	2.4(7)	C(46B)	671(3)	11(3)	202(3)	1.7(6)
C(3A)	449(3)	306(3)	478(3)	2.9(8)	C(1C)	845(3)	111(3)	2(3)	2.4(7)
C(4A)	522(3)	216(2)	464(2)	1.2(6)	C(2C)	990(3)	109(3)	173(3)	2.6(7)
C(5A)	454(3)	116(3)	376(3)	1.9(7)	C(3C)	1035(3)	383(3)	125(3)	2.3(7)
C(6A)	333(3)	156(3)	349(3)	3.2(8)	C(4C)	1121(4)	336(3)	171(3)	3.5(8)
C(7A)	334(3)	261(3)	408(3)	1.9(7)	C(5C)	1157(3)	248(3)	86(3)	1.0(6)
C(1B)	688(3)	306(3)	311(3)	1.3(6)	C(6C)	1098(3)	237(3)	-18(3)	3.3(8)
C(2B)	747(3)	316(3)	207(3)	2.4(7)	C(7C)	1014(3)	318(3)	7(3)	1.4(6)
C(3B)	827(3)	244(2)	190(2)	0.9(6)	C(15) ^a	156(4)	669(3)	334(3)	3.4(8)
C(4B)	782(3)	219(2)	302(2)	0.8(6)	C(25) ^a	45(4)	650(3)	381(3)	3.6(8)
C(5B)	727(3)	411(3)	407(3)	1.6(6)	C(35) ^a	-33(4)	734(3)	394(3)	3.9(9)
C(21B)	716(3)	396(2)	135(2)	1.2(6)	C(45) ^a	2(4)	825(3)	346(3)	3.4(8)
C(22B)	726(3)	518(3)	188(2)	1.4(6)	C(55) ^a	111(3)	832(3)	297(3)	3.1(8)
C(23B)	697(3)	577(3)	112(3)	2.5(7)	C(65) ^a	194(4)	762(3)	285(3)	3.6(8)

^a Atoms of the solvate benzene molecule.

TABLE 5
 ATOMIC COORDINATES ($\times 10^4$, for $\times 10^5$, for $\text{H} \times 10^{-3}$) AND THERMAL FACTORS $B_{\text{iso}}^{\text{eq}} = \frac{1}{3} \sum_{i,j} B_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$ (FOR HYDROGEN ATOMS B_{iso}) IN THE STRUCTURE IV

Atom	x	y	z	B (\AA^2)	Atom	x	y	z	B (\AA^2)
Fe(A)	67434(3)	4049(4)	67184(2)	3.57(1)	C(6C)	7953(3)	6233(3)	6138(2)	6.2(1)
Fe(C)	68625(3)	48925(3)	59701(2)	3.37(1)	C(7C)	8049(3)	5717(3)	6813(2)	5.7(1)
O(1A)	9015(2)	275(2)	7731(2)	7.3(1)	C(1B)	7091(2)	1852(2)	6300(1)	3.0(1)
O(2A)	7384(3)	-734(2)	5514(2)	8.1(1)	C(2B)	7742(2)	2714(2)	6590(1)	2.9(1)
O(1C)	6695(2)	4460(2)	4413(1)	6.0(1)	C(3B)	7989(2)	3624(2)	6127(1)	3.0(1)
O(2C)	4904(2)	3590(2)	6084(1)	5.4(1)	C(4B)	8922(2)	3683(2)	5855(2)	3.6(1)
N	6034(2)	1910(2)	4897(1)	5.2(1)	C(5B)	6540(2)	1909(2)	5508(2)	3.6(1)
C(1A)	8131(3)	356(3)	7329(2)	4.8(1)	C(21B)	8209(2)	2868(2)	7410(1)	3.4(1)
C(2A)	7159(3)	-277(3)	5990(2)	5.1(1)	C(22B)	9372(3)	3004(3)	7725(2)	4.5(1)
C(3A)	5226(3)	1058(3)	6898(2)	5.1(1)	C(23B)	9787(3)	3139(3)	8479(2)	6.1(1)
C(4A)	4959(3)	259(3)	6349(2)	5.4(1)	C(24B)	9031(4)	3144(3)	8926(2)	7.5(2)
C(5A)	5414(3)	-728(3)	6667(2)	5.9(1)	C(25B)	7888(4)	3054(4)	8631(2)	7.3(2)
C(6A)	5979(3)	-529(3)	7404(2)	6.4(1)	C(26B)	7465(3)	2920(3)	7869(2)	5.1(1)
C(7A)	5861(3)	574(3)	7543(2)	5.7(1)	C(41B)	9904(2)	2937(3)	5924(1)	3.7(1)
C(1C)	6734(3)	4634(3)	5020(2)	4.2(1)	C(42B)	10933(3)	3363(3)	5831(2)	5.2(1)
C(2C)	5687(2)	4080(3)	6030(2)	3.9(1)	C(43B)	11883(3)	2712(4)	5881(2)	6.7(1)
C(3C)	6983(3)	5742(3)	6967(2)	5.3(1)	C(44B)	11839(3)	1635(4)	6019(2)	6.5(1)
C(4C)	6213(3)	6286(3)	6386(2)	5.4(1)	C(45B)	10847(3)	1202(3)	6106(2)	6.0(1)
C(5C)	6812(3)	6600(3)	5875(2)	6.0(1)	C(46B)	9882(3)	1830(3)	6060(2)	4.8(1)
H(3A)	507(2)	175(2)	684(2)	5.4(7)	H(22B)	990(2)	299(2)	742(1)	3.9(6)
H(4A)	460(3)	38(3)	590(2)	6.1(8)	H(23B)	1063(3)	322(3)	866(2)	6.5(8)
H(5A)	534(3)	-144(3)	642(2)	8.4(9)	H(24B)	930(3)	324(3)	943(2)	9(1)
H(6A)	642(3)	-100(3)	773(2)	7.8(9)	H(25B)	736(3)	307(3)	891(2)	7.9(9)
H(7A)	614(3)	95(3)	795(2)	6.3(8)	H(26B)	668(2)	285(2)	767(1)	4.4(6)
H(3C)	678(2)	542(2)	736(1)	4.3(6)	H(42B)	1095(2)	411(2)	576(2)	5.1(7)
H(4C)	544(3)	638(3)	634(2)	6.5(8)	H(43B)	1256(3)	310(3)	585(2)	7.4(9)
H(5C)	654(3)	696(3)	545(2)	8.3(9)	H(44B)	1247(3)	120(3)	605(2)	6.9(8)
H(6C)	852(3)	631(3)	592(2)	6.4(8)	H(45B)	1079(3)	51(3)	619(2)	6.1(8)
H(7C)	869(3)	540(2)	713(2)	5.2(7)	H(46B)	923(2)	155(2)	610(2)	4.9(7)
H(4B)	901(2)	432(2)	560(1)	3.6(6)					

2.63; Fe, 19.18. $C_{31}H_{21}NO_4Fe_2$ calcd.: C, 63.84; H, 3.60; N, 2.40; Fe, 19.17%. IR spectrum: $\nu(C\equiv O)$ 2040, 2020, 1990, 1970; $\nu(C\equiv N)$ 2170 cm^{-1} .

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References

- 1 G.G. Aleksandrov, V.V. Skripkin, N.E. Kolobova and Yu.T. Struchkov, *Koord. Khimiya*, 5 (1979) 453.
- 2 A. Devison and J.P. Solar, *J. Organomet. Chem.*, 155 (1978) C8.
- 3 B.E. Boland-Lussier, M.R. Churchill, R.P. Hughes and A.L. Rheingold, *Organometallics*, 1 (1982) 628.
- 4 B.E. Boland-Lussier and R.P. Hughes, *Organometallics*, 1 (1982) 635.
- 5 N.Ye. Kolobova, V.V. Skripkin, G.G. Alexandrov and Yu.T. Struchkov, *J. Organomet. Chem.*, 169 (1979) 293.
- 6 N.E. Kolobova, V.V. Skripkin and T.V. Rosantseva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1979) 1665.
- 7 Yu.L. Slovokhotov, A.I. Yanovskiy, V.G. Andrianov and Yu.T. Struchkov, *J. Organomet. Chem.*, 184 (1980) C57.
- 8 N.E. Kolobova and T.V. Rosantseva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1984) 2150.
- 9 C. Krüger, D.L. Barnett and D. Brauer, *The organic chemistry of iron*, Academic Press, New York, 1978, p. 1.
- 10 M.R. Churchill and J. Wormald, *Inorg. Chem.*, 8 (1969) 1936.
- 11 M.R. Churchill and J. Wormald, *J. Am. Chem. Soc.*, 93 (1971) 354.
- 12 L.F. Dahl, R.J. Doedens, W. Hübel and J. Nielsen, *J. Am. Chem. Soc.*, 88 (1966) 446.
- 13 E.N. Zil'berman. *Reaktsii nitrilov*, "Khimiya", Moscow, 1972, p. 408 (in Russian).
- 14 G.C. Levy and G.L. Nelson. *Carbon-13 nuclear magnetic resonance for organic chemists*. Wiley, New York, 1972.
- 15 D.F. Ewig, *Org. Magn. Res.*, 12 (1979) 499.
- 16 R.G. Gerr, A.I. Yanovskii and Yu.T. Struchkov, *Kristallogr.*, 28 (1983) 1029.