Journal of Organometallic Chemistry, 137 (1977) 207—216

IRON COMPLEXES OF *N*-ALLYLBENZOTRIAZOLES

A.N. NESMEYANOV, G.G. ALEKSANDROV, M.YU, ANTIPIN, YU.T. STRUCHKOV,
YU.A. BELOUSOV *, V.N. BABIN and N.S. KOCHETKOVA

Institute of Organo-Element Compounds of the Academy of Sciences of the U.S.S.R., Moscow (U.S.S.R.)

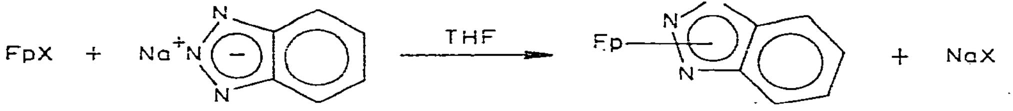
(Received March 24th, 1977)

Summary

Sodium benzotriazolide reacts with π-$C_3H_5Fe(CO)_3I$ to give 1-*N*-allylbenzotriazoletricarbonyliron (I). The same product and the isomeric complex, 2-*N*-allylbenzotriazoletricarbonyliron (II), have been prepared independently, from the corresponding *N*-allylbenzotriazoles and $Fe_2(CO)_9$. The IR, ^1H NMR, and mass spectra of the complexes are reported. The structure of isomer I has been determined by X-ray diffraction. The crystals are monoclinic, $P2_1/c$, $a = 10.65(1)$, $b = 9.95(1)$, $c = 12.90(1)$ Å, $\beta = 113.69(7)°$, $d_{calc} = 1.39$ g cm^{-3}, $Z = 4$.

Introduction

Unlike diazole ligands, triazole anions, even symmetric ones (point group C_{2v}), contain nitrogen atoms of two types. This leads to position isomerism and isomerization rearrangements. We have observed such phenomena in iron cyclopentadienyldicarbonyl complexes with vicinal triazoles [1,2]. Under kinetically controlled conditions, cyclopentadienyldicarbonyliron halides react with sodium benzotriazolide to yield the symmetric 2-isomer, which can rearrange to the asymmetric 1-isomer (the latter is the main reaction product under thermodynamic control):



(1)

$Fp = (\pi-C_5H_5)Fe(CO)_2$, $X = Cl, Br, I$

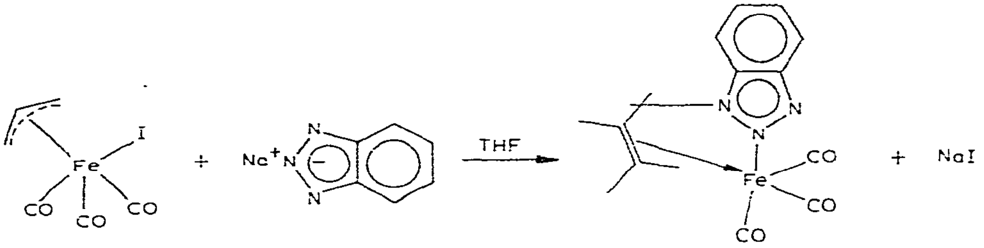
In these transformations the Fp fragment behaves as a whole, remaining intact.

Reaction of π-allyltricarbonyliron iodide with pyrazolyl borates [3], however, proceeds via deep transformations in the iron coordination sphere, deeper than with Fp.

The purpose of this work is to find out if deep transformations in the (π-C_3H_5)-$Fe(CO)_3$ fragment can occur in reactions with metal triazole salts.

Results

The data obtained in this work show that the reaction of π-allyltricarbonyliron iodide with sodium benzotriazolide also proceeds via deep transformations of the (π-C_3H_5)$Fe(CO)_3$ fragment:

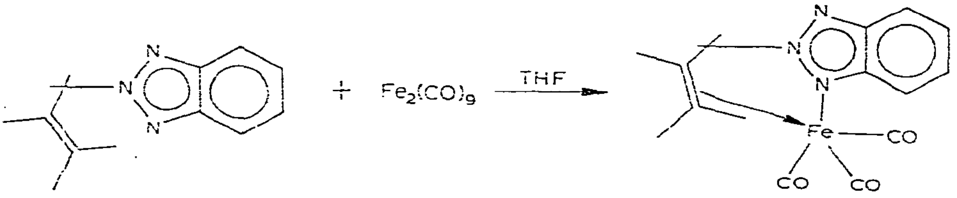


(2)

(I)

Unlike reaction (1), this process however yields no isomer with iron attached at the N(1) nitrogen.

We obtained isomer II from the usual reaction of azoles with iron carbonyls [4,5], by the action of 2-allylbenzotriazole [6] on iron nonacarbonyl (eq. 3):



(3)

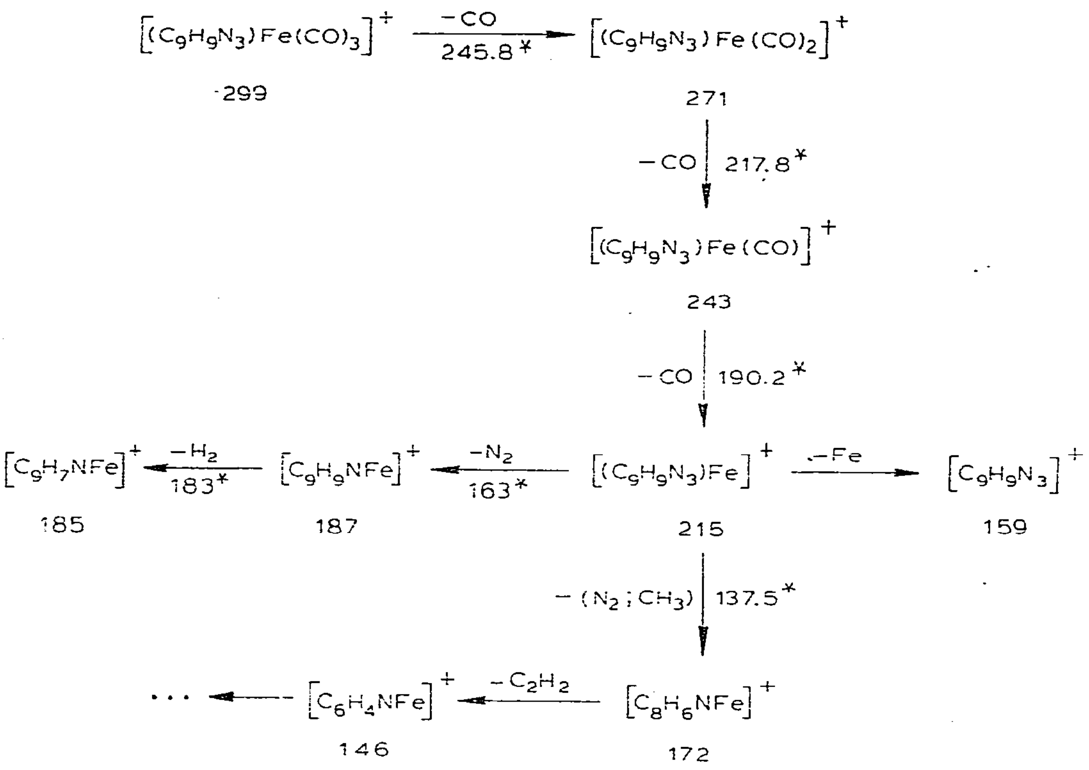
(II)

1-Allylbenzotriazole reacts likewise to give isomer I. Spectral characteristics of the two isomers are closely similar. Their mass spectra contain rather strong peaks of molecular ions, which as usual undergo successive decarbonylation. The fragmentation pathways of both $[LFe]^+$ ions are practically identical (Scheme 1).

The IR spectra of the isomers each contain three bands in the region of 2000 to 1900 cm^{-1} arising from stretching vibrations of coordinated CO molecules (Table 1). The characteristic vibration of the olefinic bond, $\nu(C{=}C)$, shows a low frequency shift from the free ligand, as is usually observed in π-complexes.

The ^1H NMR spectra are listed in Table 2. In both cases, olefinic proton signals undergo considerable upfield shifts on complex formation, which is again a usual effect. Fixation of the olefinic fragment results in magnetic nonequivalence of the methylene protons. The spin-spin coupling constants of these protons with the olefinic methyne proton have different values in both compounds.

SCHEME 1



Apart from that, they markedly increase in absolute value from the free ligand.

The coordination of the heterocyclic nucleus to iron has little effect on the chemical shifts of the ring protons. However, a symmetrical *AA'BB'* pattern of the four-spin system of the free 2-allylbenzotriazole radically changes to an asymmetric *ABCD* one for complex II.

In order to obtain direct structural data, we carried out an X-ray study of single crystals of isomer I. The molecular structure of this compound is shown in Fig. 1. Bond lengths and valence angles are summarized in Table 3. Table 4 lists the atomic coordinates and temperature factors. The compound has a discrete molecular structure. The coordination polyhedra about iron are slightly distorted trigonal bipyramids, two carbonyl ligands and the ethylene fragment forming the equatorial plane. The third carbonyl group and the benzotriazole

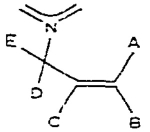
TABLE 1

IR SPECTRA OF THE ISOMERS

Compound (KBr discs)	Wave numbers (cm^{-1})			
	ν_1(C≡O)	ν_2(C≡O)	ν_3(C≡O)	ν(C=C)
1-allylbenzotriazoletricarbonyliron	2038	1973	1948	1451?
2-allylbenzotriazoletricarbonyliron	2037	1970	1959	1450?

TABLE 2

^{1}H NMR SPECTRA [a]

	Chemical shifts of the heterocyclic protons (ppm)		The allyl protons Chemical shifts (ppm)		
			H_A	H_B	H_C
1-Allylbenzotriazole	8.19(m) (1)	7.55(m) (3)	5.10(dd) (1)	5.44(dd) (1)	6.12(m) (1)
1-Allylbenzotriazole-tricarbonyliron	8.19(m) (1)	7.58(m) (3)	1.34(dd) (1)	2.39(dd) (1)	4.47(m) (1)
2-Allylbenzotriazole	7.92(m) (2)	7.28(m) (2)	5.14(dd) (1)	5.31(dd) (1)	6.17(m) (1)
2-Allylbenzotriazole-tricarbonyliron	7.81(m) (2)	7.48(m) (2)	1.33(dd) (1)	2.42(dd) (1)	3.94(m) (1)

[a] Measured in CS_2; the chemical shifts from HMDS are listed; parenthesized are signal multiplicities and relative intensities.

N(2) atom are in axial positions. The deviations from the geometry of a regular bipyramid are not very large, the principal ones being: the distortions of the valence angles in the equatorial plane (C(2)FeC(3) 111.9(4)°, C(2)FeA and C(3)FeA 125.0 and 123.1°, respectively), and the departure of the angle between the two *trans*- bonds from 180° (N(2)FeC(1) 173.2(4)°). Such angular distortions are characteristic of pentacoordinate olefinic π-complexes of iron in the d^8 configuration; cf., for instance, the results of structure determinations of $[C_2H_2(C_6H_5CO)_2]Fe(CO)_4$ [7], (acenaphthylene)$Fe(CO)_4$ [8], $[CH_2{=}CHC(NMe_2)N(Me)C(O)]Fe(CO)_3$ and $\{[CH_2{=}CHC(\text{piperidyl})N(Me)C(OEt)]Fe(CO)_3\}^+(BF_4)^-$ [9].

The coordinated double bond C(4)=C(5) is only insignificantly out of the

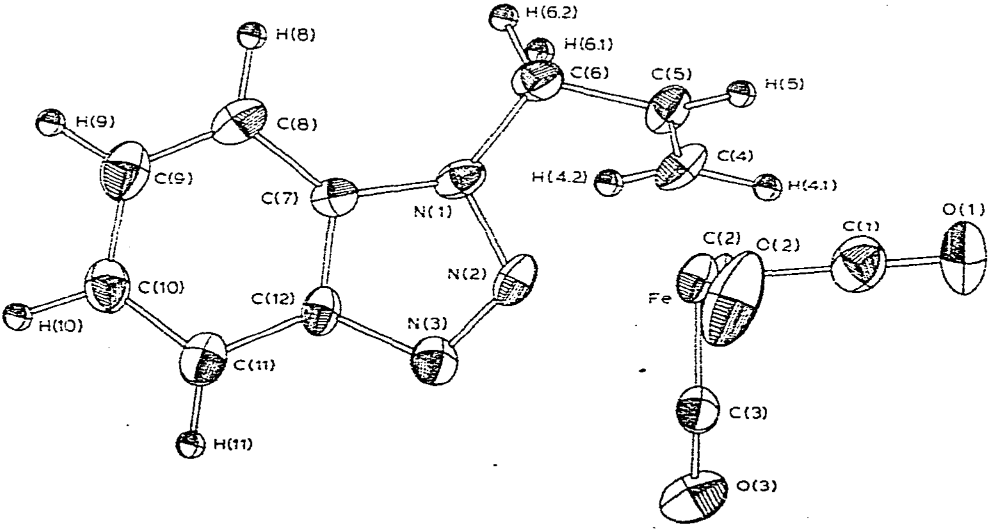


Fig. 1.

		Spin-spin coupling constants (Hz)					
H_D	H_E	J(AC)	J(BC)	J(AB)	J(DC)	J(EC)	J(ED)
5.37(d) (2)		4.5	2.5	1.5	1.0		0
5.47(dd) (1)	5.28(dd) (1)	10.5	9.0	2.9	11.1	6.8	2.1
5.42(s) (2)		3.0	2.5	1.8	0		0
4.77(dd) (1)	5.03(dd) (1)	10.8	8.5	3.0	14.2	13.5	6.4

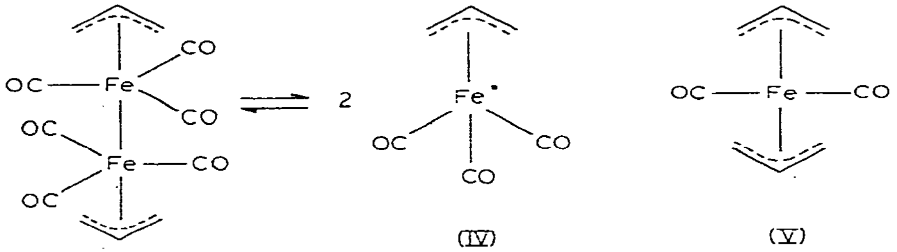
FeC(2)C(3)A plane (the angle between this bond and the plane is 9.9°). The C(4)—C(5) bond length (1.40(1) Å) and the Fe—olefin distance (the Fe—C(4) and Fe—C(5) distances are 2.083(9) and 2.085(8) Å, respectively) have values usual for iron η^2-complexes.

The allyl bridge contracts the FeN(2)N(1) (115.8(5)°) and N(2)N(1)C(6) (118.2(6)°) bond angles, so that they are narrower than the two other angles between similar bonds, FeN(2)N(3) (132.1(6)°) and C(7)N(1)C(6) (134.2(6)°).

The Fe—N bond length (1.978(7) Å) is very near to that reported for an octahedrally coordinated iron in the *v*-triazole complex $[(\pi\text{-}C_5H_5)Fe(CO)_2(N_3C_2H_3)]^+HSO_4^-$ (Fe—N 1.961(4) Å) [10].

The benzotriazole ligand is planar and its geometric parameters have their usual values. The ethylene bond is out of the benzotriazole plane: the torsion angle about the C(5)—C(6) bond amounts to 49.5°.

Complex I is not the only carbonyl-containing product of reaction (2). Other compounds that occur in this reaction are III and IV (which are the usual products from reactions of $(\pi\text{-}C_3H_5)Fe(CO)_3I$ with certain sodium derivatives [11] and complex V.



(III) (IV) (V) (4)

All these compounds were isolated and identified by comparison of their IR and mass spectra with the literature data [11,12]. It also proved possible to obtain

(continued on p. 214)

TABLE 3

BOND DISTANCES d (Å) AND VALENCE ANGLES ω (°)

Bond	d	Bond	d	Angle	ω	Angle	ω	Angle	ω
Fe—N(2)	1.978(7)	C(5)—C(6)	1.52(1)	C(1)FeN(2)	173.2(4)	FeN(2)N(1)	115.8(5)	C(6)N(1)C(7)	134.2(6)
Fe—C(1)	1.76(1)	C(6)—N(1)	1.45(1)	C(1)FeC(2)	90.9(5)	FeN(2)N(3)	132.1(6)	C(7)C(8)C(9)	113.8(8)
Fe—C(2)	1.79(1)	N(1)—N(2)	1.35(1)	C(1)FeC(3)	91.6(4)	N(1)N(2)N(3)	111.9(7)	C(8)C(9)C(10)	123.8(8)
Fe—C(3)	1.77(1)	N(2)—N(3)	1.30(1)	C(1)FeA	89.7	N(2)N(3)C(12)	105.4(7)	C(9)C(10)C(11)	121.4(8)
Fe—C(4)	2.083(9)	N(3)—C(12)	1.39(1)	C(2)FeC(3)	111.9(4)	N(3)C(12)C(7)	109.8(7)	C(10)C(11)C(12)	115.7(8)
Fe—C(5)	2.085(8)	C(12)—C(7)	1.37(1)	C(2)FeN(2)	94.4(4)	C(12)C(7)N(1)	105.3(7)	C(11)C(12)C(7)	121.1(8)
Fe—A[a]	1.962	C(7)—N(1)	1.37(1)	C(2)FeA	125.0	C(7)N(1)N(2)	107.6(7)	C(12)C(7)C(8)	124.0(8)
C(1)—O(1)	1.15(1)	C(7)—C(8)	1.40(1)	C(3)FeN(2)	90.4(4)	C(4)C(5)C(6)	118.3(7)	N(1)C(7)C(8)	130.5(8)
C(2)—O(2)	1.15(1)	C(8)—C(9)	1.37(1)	C(3)FeA	123.1	C(5)C(6)N(1)	109.1(6)	N(3)C(12)C(11)	129.1(8)
C(3)—O(3)	1.17(1)	C(9)—C(10)	1.40(1)	N(2)FeA	83.7	C(6)N(1)N(2)	118.2(6)		
C(4)—C(5)	1.40(1)	C(10)—C(11)	1.38(1)						
		C(11)—C(12)	1.41(1)						

[a] A is the centrum of the C(4)—C(5) bond.

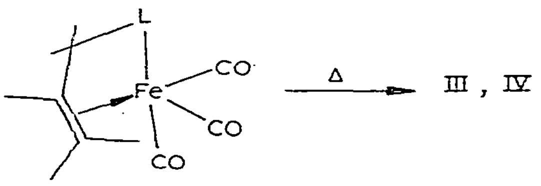
TABLE 4

ATOMIC COORDINATES (X10^4) AND THEIR TEMPERATURE FACTORS $T = \exp[(-10^{-1}/4)(B_{11}a^{*2}h^2 + \ldots + 2\,B_{12}a^*b^*hk + \ldots)]$

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	2896(1)	978(1)	5700(1)	19.5(5)	21.1(5)	28.5(6)	1.3(7)	14.0(5)	−0.5(7)
O(1)	5209(6)	−856(7)	6544(5)	40(4)	69(5)	57(4)	33(4)	17(3)	7(4)
O(2)	4711(6)	3108(6)	5527(6)	45(4)	34(4)	117(6)	−5(3)	58(4)	−2(4)
O(3)	1603(6)	−554(6)	3590(5)	49(4)	37(4)	37(4)	−1(3)	22(3)	−12(3)
N(1)	961(6)	2613(7)	6113(5)	18(3)	24(4)	20(4)	−6(3)	12(3)	−7(3)
N(2)	1239(6)	2115(6)	5255(6)	22(3)	14(3)	34(4)	−2(3)	19(3)	−2(3)
N(3)	281(6)	2412(7)	4270(6)	24(4)	21(4)	28(4)	4(3)	14(3)	8(3)
C(1)	4304(9)	−119(10)	6214(8)	31(5)	43(6)	38(5)	4(4)	20(5)	4(5)
C(2)	3967(9)	2308(9)	5588(8)	29(5)	28(5)	73(7)	13(4)	34(5)	5(5)
C(3)	2144(9)	59(8)	4428(7)	30(4)	30(5)	24(5)	13(4)	19(4)	16(4)
C(4)	2198(8)	6(9)	6792(2)	32(5)	32(5)	34(5)	3(4)	26(4)	−5(4)
C(5)	2954(8)	1204(9)	7292(6)	23(4)	27(5)	30(4)	2(4)	16(4)	−4(4)
C(6)	1974(7)	2420(9)	7263(7)	18(4)	36(5)	21(4)	−5(4)	8(4)	−8(4)
C(7)	−269(7)	3276(8)	5647(7)	14(14)	18(4)	17(4)	−5(3)	7(4)	−2(4)
C(8)	−1033(8)	3926(9)	6162(6)	28(4)	23(4)	30(4)	−6(4)	17(4)	−6(4)
C(9)	−2261(9)	4422(8)	5413(8)	30(5)	26(5)	42(6)	3(4)	21(5)	4(4)
C(10)	−2710(8)	4330(8)	4233(7)	23(4)	27(5)	34(5)	3(4)	15(4)	7(4)
C(11)	−1942(8)	3682(8)	3744(7)	30(4)	24(5)	36(5)	4(4)	20(4)	6(4)
C(12)	−686(8)	3139(8)	4501(7)	21(4)	11(4)	30(5)	4(3)	13(4)	5(4)
H(4.1)[a]	2752	−827	6799						
H(4.2)	1167	−86	6476						
H(5)	3875	1232	7609						
H(6.1)	1516	2288	7807						
H(6.2)	2531	3259	7534						
H(8)	−705	4020	7034						
H(9)	−2881	4901	5717						
H(10)	−3669	4740	3719						
H(11)	−2260	3609	2864						

[a] The numbering of H atoms follows the numbering of adjacent carbon atoms; for all the H atoms, B_{iso} is equal to 3.0 Å.

compounds III and IV by thermal decomposition of complexes I and II.

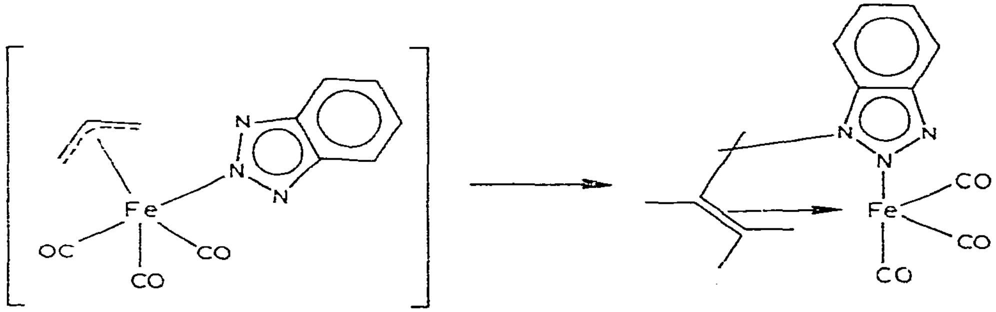


(5)

Discussion

The experimental results show that the coordination sphere of the pseudooctahedral (π-C_3H_5)Fe(CO)$_3$I complex with iron in the formally divalent d^6 state undergoes deep transformations in the formation of isomer I. These transformations include not only the nucleophilic replacement of the halo ligand with the heterocyclic one, but also implanting of the heterocycle at the π-allyl—iron bond via: (*a*) the η^3—η^2 rearrangement of the allyl moiety; and (*b*) the addition of the latter to the unprotected benzotriazole nitrogen atom.

As a result, the Fe—olefin and Fe—heterocyclic nitrogen N(2) bonds are formed.



(6)

(I)

It seems likely that transformation (6) should reduce the difference between the allyl and heterocyclic ligands in terms of the HSAB theory, thus improving the situation from the point of view of the symbiotic principle. Iron changes its pseudooctahedral coordination for a trigonal bipyramidal one. The latter is characteristic for iron in the Fe(0) state with the d^8 electronic configuration. As all the ligands in I are neutral, the net effect of the transformations in the iron coordination sphere may be regarded as reduction. The d^8 configuration thus proves favoured over the d^6 one with the pseudooctahedral coordination. It is reasonable to suggest that both kinetic factors (the presence of lone electron pairs on the heterocyclic imino group that can interact with the allyl electronic system) and thermodynamic ones (entropy gain in the formation of the chelate ligand) contribute to the observed effect.

The formation of isomer I in reaction (2) may be explained by the fact that the first reaction step of the nucleophilic replacement of the halo ligand by the heterocyclic one involving the highest electron density site, that is the N(2) atom, is followed by the intraspherical addition of the allyl ligand to one of the free nitrogen atoms, which leads to the conservation of the first structure formed and prevents metallotropic isomerization.

The trigonal bipyramidal geometry of the complex is in agreement with the stereochemical principles of the HSAB theory. The hardest center in I, the nitrogen atom, is, as usual [5,13], in an axial position, whereas a softer olefinic fragment lies in the equatorial plane. The IR spectra in the region of the C≡O stretching frequencies show that a similar situation occurs in complex II.

Experimental

All preparative work and spectral measurements were carried out under argon.

The ^1H NMR spectra were registered on a R-20 (Perkin Elmer—Hitachi) spectrometer. The IR spectra were recorded on a UR-10 spectrophotometer (DDR), and the mass spectra were obtained using MS-30 (AEI) and CH-8 (Varian) instruments.

Structure of I

The X-ray patterns for I were obtained on a Syntex-$P2_1$ diffractometer, λ Mo, equipped with a graphite monochromator. Measurements were made at —120° C. A total of 1167 reflections with $F^2 \geqslant 1.96\ \sigma$ were registered in the range $2\theta \leqslant 46°$ at the $v/2v$ scan rate. The structure was solved as a heavy atom problem and refined by a full-matrix least squares procedure using anisotropic temperature factors * to R of 0.059 and R_w of 0.040. The atomic coordinates and temperature factors are listed in Table 4. Isomer I crystallyzes in a monoclinic lattice, $P2_1/c$, a = 10.65(1), b = 9.95(1), c = 12.90(1) Å, β = 113.69(7)°; d_{calc} = 1.39 g cm^{-3}, Z = 4.

Reaction of sodium benzotriazolide with π-allyltricarbonyliron iodide

(π-C_3H_5)Fe(CO)$_3$I (3.08 g, 0.01 mol) and $C_6H_4N_3Na$ (1.41 g, 0.01 mol) were stirred in tetrahydrofuran (70 ml) for 2.5 h. The solution was then concentrated and pressure transferred under argon into a column with Al_2O_3 (the 2nd Brockman activity grade). The product mixture gave a rust-coloured layer which was washed out with THF. After the removal of the solvent, the mixture was repeatedly subjected to chromatography on Al_2O_3 (the 2nd activity grade) using hexane. Two fractions were obtained.

The first fraction, after distilling off of the solvent and sublimation of the residue under vacuum, yielded V (0.02 g, 1%). IR spectrum (cyclohexane): ν(C=O) 2012, 1963 cm^{-1} (literature [12]: 2020, 1965 cm^{-1}). The mass spectrum of V gave **: $[(C_3H_5)_2Fe(CO)_2]^+$ 194; $[(C_3H_5)_2Fe(CO)]^+$ 166; $[(C_3H_5)Fe(CO)_2]^+$ 153; $[(C_3H_5)_2Fe]^+$ 138; $[(C_3H_5)Fe(CO)]^+$ 125; $[Fe(CO)_2]^+$ 112; $[(C_3H_5)_2CO]^+$ 110; $[C_3H_4Fe]^+$ 96. Metastable ions:

$$[(C_3H_5)_2Fe(CO)_2]^+ \xrightarrow[-28]{-CO} [(C_3H_5)_2Fe(CO)]^+ \qquad 141.8\ ^*$$

$$[(C_3H_5)_2Fe(CO)]^+ \xrightarrow[-28]{-CO} [(C_3H_5)_2Fe]^+ \qquad 114.6\ ^*$$

---

* All parameters for H atoms were fixed during the refinement.

** Ions with low m/e are omitted.

$[(C_3H_5)_2Fe]^+ \xrightarrow[-42]{-C_3H_6} [C_3H_4Fe]^+$ 66.8 *

The second fraction contained complexes III and IV (0.05 g, yield based on $C_3H_5Fe(CO)_3$ 2.8%). The same compounds were obtained by fractional sublimation of solvent-free product mixture. IR spectra (cyclohexane): 2040, 2011, 1963, 1958 cm^{-1} (literature [11]: 2046, 2015, 1968—1960 cm^{-1}).

Ether extracts one more band containing 1-allylbenzotriazoletricarbonyliron (0.07 g, 2.3%). Recrystallization of the product from hexane gave yellow crystals, decomposing at 137—138° C. Analysis found: C, 48.12; H, 2.91; N, 13.43. $C_{12}H_9N_3O_3Fe$ calcd. C, 48.16; H, 3.01; N, 14.05%.

Synthesis of 1-allylbenzotriazoletricarbonyliron from 1-allylbenzotriazole and iron nonacarbonyl

1-Allylbenzotriazole (3.02 g, 0.019 mol) and $Fe_2(CO)_9$ (6.92 g, 0.019 mol) were stirred in tetrahydrofuran for 3 h at ambient temperature. The solvent was then removed and the residue was extracted with ether and separated on Al_2O_3 (the 2nd Brockman activity grade) using a 1 : 10 ether/hexane mixture to give I in the yield of 3.14 g (55.3%).

Synthesis of 2-allylbenzotriazoletricarbonyliron from 2-allylbenzotriazole and iron nonacarbonyl

The compound was obtained by a similar procedure to that described above from 2-allylbenzotriazole (2.65 g, 0.017 mol) and $Fe_2(CO)_9$ (6.05 g, 0.017 mol) in the yield of 1.78 g (36%); m.p. 87° C. Analysis found: C, 48.20; H, 3.08; N, 14.10; Fe, 18.68. $C_{12}H_9N_3O_3Fe$ calcd. C, 48.16; H, 3.01; N, 14.05; Fe, 18.73%.

References

1 A.N. Nesmeyanov, V.N. Babin, N.S. Kochetkova, E.I. Mysov, Yu.A. Belousov and L.A. Fedorov, Dokl. Akad. Nauk SSSR, 200 (1971) 1112.
2 A.N. Nesmeyanov, Yu.A. Belousov, V.N. Babin, N.S. Kochetkova, S.Yu. Silvestrova and E.I. Mysov, Inorg. Chim. Acta, 22 (1977) 173.
3 R.B. King and A. Bond, J. Amer. Chem. Soc., 96 (1974) 1343.
4 A.N. Nesmeyanov, M.I. Rybinskaya, N.S. Kochetkova, V.N. Babin and G.B. Shul'pin, Dokl. Akad. Nauk SSSR, 181 (1968) 1397.
5 A.N. Nesmeyanov, V.N. Babin, N.S. Kochetkova and Yu.S. Nekrasov, Dokl. Akad. Nauk SSSR, 200 (1971) 601.
6 C.W. Rees, R.C. Storr, J. Chem. Soc. (C), (1969) 1478.
7 V.T. Andrianov, Yu.T. Struchkov, M.I. Rybinskaya, L.V. Rybin and N.T. Gubenko, Zh. Strukt. Khim., 13 (1972) 86.
8 F.A. Cotton and P. Lahuerta, Inorg. Chem., 14 (1975) 116.
9 T.N. Sal'nikova, V.T. Andrianov and Yu.T. Struchkov, Koord. Khim., in press.
10 A.N. Nesmeyanov, Yu.A. Belousov, V.N. Babin, G.G. Aleksandrov, M.Yu. Antipin, Yu.T. Struchkov, N.S. Kochetkova and E.B. Zavelovich, Inorg. Chim. Acta, in press.
11 H.D. Murdoch and E.A.C. Lucken, Helv. Chim. Acta, 47 (1964) 1517.
12 A.N. Nesmeyanov, I.I. Kritskaya, Yu.A. Ustynyuk and E.I. Fedin, Dokl. Akad. Nauk SSSR, 176 (1967) 341.
13 M.L. Ziegler, Angew. Chem., 7 (1968) 222.