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X-RAY CRYSTAL STRUCTURE OF THE π-ALLYL-σ-CARBAMOYLIRON COMPLEX $(OC)_3FeC(O)N(CH_2Ph)(\eta^3\text{-}CMe{\cdots}CH{\cdots}CHPh)$

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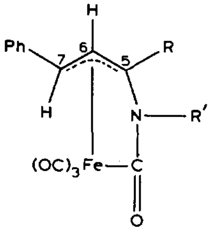
Summary

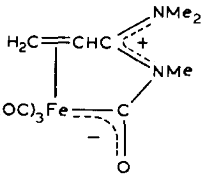
An X-ray structural study of the title complex at −120°C (autodiffractometer, $R = 0.031$ for 3859 reflections) was carried out. The iron atom has a *fac*-octahedral environment with three CO groups and a $\eta^3{:}\eta^1$ chelating organic ligand with bond distances Fe–C(σ) 1.993, Fe–C(allyl) 2.182, 2.097 and 2.159 Å.

Introduction

The α,β-unsaturated iminetetracarbonyliron complexes are of interest due to their tautomerism [1,2]. Depending on the nature of the substituents in the ligating imine



(I : R = Me, R' = CH_2Ph;
II : R = Ph, R' = *cyclo*-C_6H_{11})



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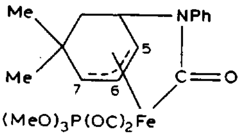

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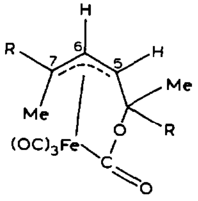
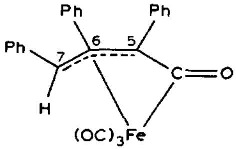


(V : R = H; VI : R = Me)



(VII)

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molecule, isomeric complexes of the type $(OC)_3Fe(\pi$-olefin-σ-carbamoylate), $(OC)_3Fe(\pi$-allyl-σ-carbamoyl) or $(OC)_4Fe(\sigma$-*N*-imine) may be formed. Earlier, we reported the crystal structures of the complexes II [3] and III [4] which have a different coordination around iron. To establish unequivocally the type of coordination in the complex I, we have carried out the determination of its study, which is discussed below.

Results and discussion

The molecular structure of I is shown in Fig. 1; bond lengths and angles are listed in Tables 1–3.

The iron atom is coordinated by the $\eta^3:\eta^1$ chelating organic ligand and three linear carbonyl groups and has a distorted *fac*-octahedral environment (considering π-allyl as a bidentate ligand) and a 18-electron outer shell. The molecular structure of I strongly resembles that of II, and the coordination of the Fe atom is similar to that found in IV [5] and ferralactones V [6] and VI (*cis*- and *trans*-isomers) [8], containing larger chelate cycles.

The Fe–C(3)O(3) bond (*trans* to the Fe–C(4) σ-bond) is, as usual, longer (in this case by 0.04 Å) than the other two Fe–CO bonds (*trans* to the π-allyl group). The

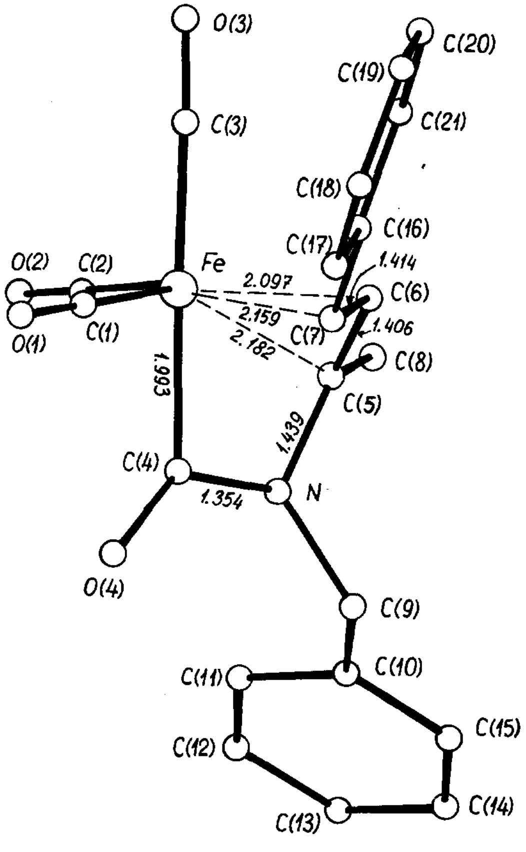

Fig. 1. Molecular structure of I with relevant bond lengths (hydrogen atoms are omitted).

TABLE 1

BOND DISTANCES (Å)

Bond		Bond		Bond	
Fe–C(1)	1.795(2)	N–C(4)	1.354(3)	C(11)–C(12)	1.389(3)
Fe–C(2)	1.797(2)	N–C(5)	1.439(3)	C(12)–C(13)	1.384(4)
Fe–C(3)	1.837(2)	N–C(9)	1.470(3)	C(13)–C(14)	1.377(4)
Fe–C(4)	1.993(2)	C(5)–C(6)	1.406(3)	C(14)–C(15)	1.389(3)
Fe–C(5)	2.182(2)	C(5)–C(8)	1.495(3)	C(16)–C(17)	1.392(3)
Fe–C(6)	2.097(2)	C(6)–C(7)	1.414(3)	C(16)–C(21)	1.394(3)
Fe–C(7)	2.159(2)	C(7)–C(16)	1.481(3)	C(17)–C(18)	1.387(4)
O(1)–C(1)	1.132(3)	C(9)–C(10)	1.509(3)	C(18)–C(19)	1.376(4)
O(2)–C(2)	1.136(3)	C(10)–C(11)	1.387(3)	C(19)–C(20)	1.379(4)
O(3)–C(3)	1.137(3)	C(10)–C(15)	1.392(3)	C(20)–C(21)	1.385(3)
O(4)–C(4)	1.218(3)				

length of the Fe–C(4) σ-bond of 1.993(2) Å is in good agreement with values found in the analogous complexes (1.978(7) in II, 2.02 (1) in IV, 1.985(2) in V, 1.998(3) in *cis*-VI and 2.010(3) Å in *trans*-VI).

The coordination of the Fe atom by the π-allyl ligand is almost symmetrical (Fe–C(5) ≈ Fe–C(7) > Fe–C(6)), although the chelate cycle is severely strained, as indicated by distortion of the intracyclic angles at C(4) (98.5(1)°) and N (108.1(2)°). Surprisingly, in the complexes IV–VI expansion of the chelate cycle by one sp^3

TABLE 2

BOND ANGLES (°)

Angle		Angle		Angle	
C(1)FeC(2)	104.3(1)	C(6)FeC(7)	38.76(8)	FeC(7)C(16)	120.5(2)
C(1)FeC(3)	96.2(1)	FeC(1)O(1)	173.6(2)	C(6)C(7)C(16)	122.7(2)
C(1)FeC(4)	86.65(9)	FeC(2)O(2)	179.3(2)	NC(9)C(10)	114.8(2)
C(1)FeC(5)	145.97(9)	FeC(3)O(3)	177.4(2)	C(9)C(10)C(11)	122.0(2)
C(1)FeC(6)	127.74(9)	FeC(4)O(4)	136.3(2)	C(9)C(10)C(15)	118.3(2)
C(1)FeC(7)	89.03(9)	FeC(4)N	98.5(1)	C(11)C(10)C(15)	119.5(2)
C(2)FeC(3)	92.7(1)	O(4)C(4)N	125.1(2)	C(10)C(11)C(12)	120.0(2)
C(2)FeC(4)	87.22(9)	C(4)NC(5)	108.1(2)	C(11)C(12)C(13)	120.1(2)
C(2)FeC(5)	93.79(9)	C(4)NC(9)	125.8(2)	C(12)C(13)C(14)	120.3(2)
C(2)FeC(6)	127.29(9)	C(5)NC(9)	122.8(2)	C(13)C(14)C(15)	119.9(2)
C(2)FeC(7)	162.67(9)	FeC(5)N	87.9(1)	C(10)C(15)C(14)	120.2(2)
C(3)FeC(4)	177.10(9)	FeC(5)C(6)	67.6(1)	C(7)C(16)C(17)	118.4(2)
C(3)FeC(5)	111.72(9)	FeC(5)C(8)	128.7(2)	C(7)C(16)C(21)	123.3(2)
C(3)FeC(6)	89.74(9)	NC(5)C(6)	118.5(2)	C(17)C(16)C(21)	118.3(2)
C(3)FeC(7)	96.82(9)	NC(5)C(8)	116.7(2)	C(16)C(17)C(18)	120.4(2)
C(4)FeC(5)	65.40(9)	C(6)C(5)C(8)	122.8(2)	C(17)C(18)C(19)	120.6(3)
C(4)FeC(6)	87.99(9)	FeC(6)C(5)	74.1(1)	C(18)C(19)C(20)	119.9(3)
C(4)FeC(7)	82.51(9)	FeC(6)C(7)	73.0(1)	C(19)C(20)C(21)	119.8(2)
C(5)FeC(6)	38.29(8)	C(5)C(6)C(7)	122.1(2)	C(16)C(21)C(20)	121.1(2)
C(5)FeC(7)	69.26(8)	FeC(7)C(6)	68.2(1)		

TABLE 3

SELECTED BOND DISTANCES (Å) AND ANGLES (°) INVOLVING HYDROGEN ATOMS

Bond		Angle	
C(6)–H(6)	0.97(2)	FeC(6)H(6)	116(1)
C(7)–H(7)	0.97(2)	C(5)C(6)H(6)	118(1)
C(Ph)–H	0.86(2) –1.02(2)	C(7)C(6)H(6)	119(1)
Average	0.95(5)	FeC(7)H(7)	105(1)
C(sp^3)–H	0.96(2) –1.01(2)	C(6)C(7)H(7)	118(1)
Average	0.98(2)	C(16)C(7)H(7)	113(1)

carbon atom (which should supposedly relieve the strain) makes the Fe–allyl coordination strongly unsymmetrical, viz. in IV Fe–C(5) 2.115, Fe–C(6) 2.042, Fe–C(7) 2.171 Å, while in V and VI Fe–C(5) $\approx$ Fe–C(6) $<$ Fe–C(7). The same lack of symmetry is observed in complex VII with the chelate cycle contracted by one atom (Fe–C(5), 2.135, Fe–C(6) 2.129, Fe–C(7) 2.168 Å) [7].

The plane of the π-allyl moiety, C(5)C(6)C(7), forms a dihedral angle of 133° with the mean plane through Fe and C(1)O(1) and C(2)O(2) groups, while in sterically unhindered octahedral iron complexes this angle varies from 105 to 117°, averaging 111° [8]. The distances of some other atoms from the π-allyl plane are as follows: Fe 1.702, N −0.37, C(4) 0.52, C(8) 0.00, C(16) 0.19, H(6) 0.17, H(7) −0.52 Å. The out-of-plane displacement of the N and H(7) atoms in the direction opposite to the Fe atom displacement is due to the short non-bonding contacts Fe $\cdots$ N of 2.570(2) and Fe $\cdots$ H(7) of 2.59(2) Å. The C(16)–C(21) phenyl ring is inclined by 19.1, and the C(7)–C(16) bond by 7.4° to the π-allyl plane.

As in II, the coordination of C(4) in I is strictly planar-trigonal, while that of N is nearly planar-trigonal, this atom being 0.15 Å out of the plane through three neighbouring atoms with a sum of the N bond angles of 356.7° vs. 355.8° in II. The torsion angles around the C(4)–N (9°) and N–C(5) (63°) bonds are consistent with their lengths, the value for the former bond (1.354 Å) being close to the standard length of an amide (i.e. conjugated) bond of 1.334 Å [9], and for the latter (1.439 Å) to that of an unconjugated single $>$N–C(sp^2) bond of 1.452 Å [10].

Differences between corresponding geometrical parameters of I and II are small and only the largest of them (Fe–C(5) 2.182(2) Å in I vs. 2.235(7) Å in II, C(4)–N 1.354(3) vs. 1.39(1), N–C(5) 1.439(3) vs. 1.48(1), C(5)–C(6) 1.406(3) vs. 1.35(1) Å, and C(5)C(6)C(7) 122.1(2) vs. 127.0(6)°) are significant and may be attributed to steric effects of replacing Ph and cyclohexyl substituents in II by less bulky Me and benzyl groups in I.

Experimental

Crystal data: $C_{21}H_{17}FeNO_4$, monoclinic, at −120°C $a = 14.28(2)$, $b = 7.016(9)$, $c = 18.34(3)$ Å, $\beta = 98.14(15)°$, $V = 1819(5)$ Å^3, $Z = 4$, $D_{calcd.} = 1.47$ g cm^{-3}, space group $P2_1/c$.

Unit cell parameters and intensities of 3859 independent reflections with $I \geqslant 2\sigma$ ($\theta/2\theta$ scan, $2\theta \leqslant 52°$) were determined with a Syntex P2_1 autodiffractometer at −120°C, using graphite-monochromated Mo-K_α radiation. The structure was solved

TABLE 4

ATOMIC COORDINATES (× 10^4, × 10^5 FOR Fe) AND ANISOTROPIC THERMAL FACTORS IN THE FORM $T = \exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	28532(2)	8004(4)	3639(2)	1.11(1)	1.17(1)	1.46(1)	0.04(1)	0.325(9)	0.07(1)
O(1)	4335(1)	3631(2)	273(1)	2.16(8)	2.39(8)	3.29(9)	−0.82(6)	1.03(7)	0.12(7)
O(2)	1402(1)	1597(3)	−898(1)	2.19(8)	2.89(8)	2.76(8)	0.42(7)	−0.58(7)	0.55(7)
O(3)	3674(1)	−2348(3)	−428(1)	2.60(8)	3.25(9)	2.15(7)	1.25(7)	0.15(6)	−0.79(7)
O(4)	2331(1)	4567(2)	960(1)	2.27(7)	0.94(6)	3.88(9)	−0.02(6)	0.90(7)	−0.11(6)
N	1678(1)	1737(3)	1242(1)	1.44(8)	1.10(7)	2.12(8)	0.02(6)	0.71(7)	−0.23(7)
C(1)	3776(2)	2486(3)	274(1)	1.68(9)	1.87(9)	1.91(9)	0.44(8)	0.52(8)	0.32(8)
C(2)	1967(2)	1282(3)	−412(1)	1.61(9)	1.49(9)	2.3(1)	0.14(8)	0.65(8)	0.18(8)
C(3)	3362(2)	−1170(3)	−111(1)	1.37(9)	2.2(1)	1.41(9)	0.11(8)	−0.14(8)	0.14(8)
C(4)	2257(2)	2844(3)	897(1)	1.32(9)	1.35(9)	2.20(9)	0.04(7)	0.27(8)	0.04(8)
C(5)	1830(1)	−217(3)	1053(1)	1.33(9)	1.18(9)	1.51(9)	−0.06(7)	0.48(7)	0.00(7)
C(6)	2734(2)	−1009(3)	1256(1)	1.65(9)	1.09(9)	1.20(8)	0.02(7)	0.33(7)	0.08(7)
C(7)	3544(2)	135(3)	1459(1)	1.53(9)	1.40(9)	1.15(8)	−0.15(8)	0.24(7)	−0.11(7)
C(8)	966(2)	−1407(3)	838(1)	1.31(9)	1.51(9)	1.98(9)	−0.14(7)	0.28(8)	0.01(8)
C(9)	1238(2)	2289(3)	1889(1)	1.56(9)	1.84(9)	1.66(9)	0.10(8)	0.34(8)	−0.35(8)
C(10)	178(1)	2536(3)	1743(1)	1.49(9)	0.93(8)	1.85(9)	0.13(7)	0.35(8)	−0.38(8)
C(11)	−272(2)	3328(3)	1093(1)	2.1(1)	1.48(9)	1.79(9)	0.20(8)	0.38(8)	−0.13(8)
C(12)	−1241(2)	3649(4)	1004(1)	2.3(1)	2.0(1)	2.3(1)	0.59(9)	−0.43(9)	−0.43(9)
C(13)	−1757(2)	3204(4)	1566(1)	1.4(1)	2.6(1)	3.3(1)	0.32(9)	0.11(9)	−1.3(1)
C(14)	−1317(2)	2395(4)	2208(1)	1.79(9)	2.3(1)	2.7(1)	−0.33(9)	0.94(9)	−0.89(9)
C(15)	−348(2)	2063(3)	2300(1)	1.93(9)	1.54(9)	1.79(9)	−0.02(8)	0.45(8)	−0.30(8)
C(16)	4515(2)	−655(3)	1573(1)	1.45(9)	2.4(1)	0.96(8)	−0.06(8)	0.19(7)	0.17(8)
C(17)	5246(2)	486(4)	1915(1)	1.8(1)	2.9(1)	1.70(9)	−0.54(9)	0.12(8)	0.12(9)
C(18)	6167(2)	−197(5)	2033(1)	1.5(1)	5.3(2)	2.2(1)	−1.1(1)	−0.33(9)	0.7(1)
C(19)	6372(2)	−2004(5)	1811(1)	1.5(1)	5.7(2)	2.0(1)	1.1(1)	0.39(9)	1.2(1)
C(20)	5656(2)	−3160(4)	1476(1)	2.3(1)	4.1(1)	1.7(1)	1.4(1)	0.34(9)	0.53(9)
C(21)	4734(2)	−2489(4)	1359(1)	1.74(9)	2.6(1)	1.60(9)	0.48(9)	−0.02(8)	0.06(9)

TABLE 5

COORDINATES ($\times 10^3$) AND ISOTROPIC THERMAL FACTORS (Å^2) OF HYDROGEN ATOMS [a]

Atom	x	y	z	B
H(6)	281(1)	−236(3)	117(1)	1.1(4)
H(7)	348(1)	128(3)	175(1)	1.4(5)
H(8)	55(2)	−98(3)	40(1)	2.3(5)
H′(8)	56(2)	−144(4)	121(1)	2.9(6)
H″(8)	112(2)	−277(4)	72(1)	2.8(6)
H(9)	155(1)	345(3)	207(1)	1.9(5)
H′(9)	144(1)	136(3)	229(1)	1.2(5)
H(11)	7(2)	366(3)	67(1)	2.3(5)
H(12)	−153(2)	422(3)	57(1)	2.1(5)
H(13)	−246(2)	354(4)	149(1)	2.6(6)
H(14)	−168(2)	207(2)	260(1)	2.6(6)
H(15)	−4(2)	152(3)	276(1)	1.8(5)
H(17)	512(1)	175(3)	203(1)	1.5(5)
H(18)	661(2)	54(3)	225(1)	2.8(6)
H(19)	696(2)	−249(4)	191(1)	3.2(6)
H(20)	583(2)	−448(4)	135(1)	3.9(7)
H(21)	428(1)	−331(3)	117(1)	1.7(5)

[a] Hydrogen atoms have the same numbers as the carbons they are bonded to.

by the heavy atom method (all hydrogen atoms being located in the difference Fourier map) and refined by the full-matrix least-squares technique with weighting scheme $W = \sigma_F^{-2}$. Non-hydrogen atoms were refined with anisotropic thermal factors, H atoms with isotropic ones. The refinement converged at $R = 0.031$ and $R_w = 0.030$. Final atomic parameters are listed in Tables 4 and 5. All calculations were performed with an Eclipse S/200 computer using published programmes [11].

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