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Preliminary communication

THE CRYSTAL AND MOLECULAR STRUCTURE OF η^5-CYCLOPENTADIENYL-η^1-(2,4-DIPHENYLCYCLOBUT-1-EN-3-ONE)IRON DICARBONYL

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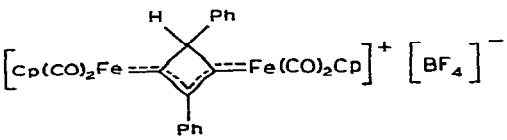
Summary

The X-ray crystal and molecular structure of η^5-cyclopentadienyl-η^1-2,4-diphenylcyclobut-1-en-3-oneiron dicarbonyl (I) was determined (monoclinic crystals, a 9.2371(9), b 26.4502(9), c 8.2450(7) Å, β 115.502(6)°, $Z = 4$, space group $P2_1/c$, 1902 unique reflections, $R = 0.068$). Molecule I contains the η^1-cyclobut-1-en-3-one ligand with three sp^2 and one sp^3 carbon atoms in a four-membered cycle, σ-bonded to the $CpFe(CO)_2$ fragment (bond distance Fe—C 1.935(6) Å).

The new σ-derivative I of the $CpFe(CO)_2$ moiety containing an unusual η^1-cyclobut-1-en-3-one ligand had been prepared earlier [1] by the reaction of 1,3-diphenyl-2,4-bis(η^5-cyclopentadienyl)iron dicarbonyl cyclobutanediylidene tetrafluoroborate (II) with Et_3N in THF. The X-ray crystal and molecular structure



of II had been determined earlier [2]. We now carried out the X-ray study of I and determined its structure unequivocally.

Cell dimensions and intensities of 1902 independent reflections with $I > 2\sigma$ were measured with a Hilger-Watts four-circle diffractometer (Cu-K_α radiation, graphite monochromator, $\theta/2\theta$ scan, $\theta < 63°$). The structure was solved by a standard heavy atom technique and refined by a full-matrix least-squares method in anisotropic approximation for non-hydrogen atoms to $R = 0.068$. All hydrogen atoms were located from difference electron density map and included in the refinement with isotropic thermal parameters.

Compound I forms monoclinic crystals, a 9.2371(9), b 26.4502(9), c

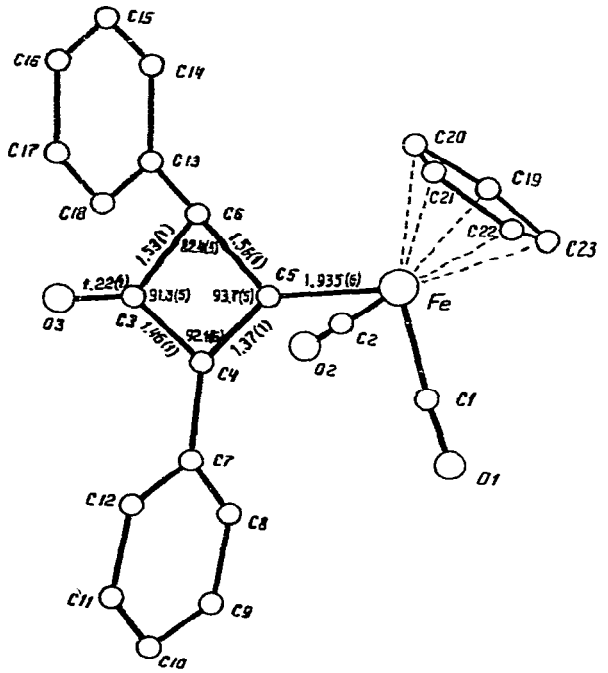


Fig. 1. Molecular geometry of I.

TABLE 1

ATOMIC COORDINATES (X 10^4) FOR THE NON-HYDROGEN ATOMS AND ANISOTROPIC THERMAL PARAMETERS (X 10) IN THE FORM OF $T = \exp(-\frac{1}{4}(B_{11}h^2a^{*2} + \ldots + 2B_{23}klb^*c^*))$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	19(1)	1028.0(4)	173(1)	35.0(5)	28.6(4)	28.7(4)	−0.6(4)	13.2(3)	0.7(4)
O(1)	−3150(8)	584(3)	−1471(9)	47(3)	73(4)	58(3)	−25(3)	16(3)	1(3)
O(2)	1595(8)	349(2)	−1308(8)	57(3)	50(3)	55(3)	18(3)	18(3)	−14(2)
O(3)	−1339(6)	2233(2)	−5228(7)	43(3)	36(2)	39(2)	−5(2)	10(2)	15(2)
C(1)	−1909(10)	746(3)	−895(10)	39(4)	39(4)	39(3)	−3(3)	13(3)	8(3)
C(2)	970(9)	615(3)	−735(9)	42(4)	30(3)	31(3)	3(3)	8(3)	−1(2)
C(3)	−909(8)	1933(2)	−3991(9)	31(3)	25(3)	35(3)	0(2)	13(3)	4(2)
C(4)	−1413(8)	1430(2)	−3730(8)	28(3)	29(3)	27(3)	2(2)	11(2)	2(2)
C(5)	−411(8)	1438(2)	−1928(9)	27(3)	21(3)	30(3)	−1(2)	11(2)	−6(2)
C(6)	364(8)	1952(3)	−2035(9)	37(3)	22(3)	29(3)	0(2)	13(3)	1(2)
C(7)	−2551(8)	1081(3)	−5075(8)	31(3)	34(3)	22(2)	−1(3)	12(2)	−2(2)
C(8)	−2383(10)	559(3)	−4937(9)	50(4)	38(3)	19(3)	−3(3)	7(3)	−2(2)
C(9)	−3377(11)	250(3)	−6273(12)	62(5)	32(4)	49(4)	−7(3)	17(4)	−7(3)
C(10)	−4538(10)	452(3)	−7853(11)	41(4)	53(4)	39(4)	−13(3)	14(3)	−15(3)
C(11)	−4712(9)	960(4)	−8012(10)	32(3)	63(5)	26(3)	−6(3)	7(3)	−2(3)
C(12)	−3734(8)	1282(3)	−6636(10)	28(3)	39(3)	36(3)	−2(3)	8(3)	5(3)
C(13)	2087(8)	1933(3)	−1802(9)	32(3)	28(3)	31(3)	−2(2)	12(2)	2(2)
C(14)	3234(10)	2268(3)	−636(11)	39(4)	38(4)	40(4)	−11(3)	15(3)	−1(3)
C(15)	4765(10)	2263(4)	−471(12)	37(4)	54(4)	41(4)	−11(3)	7(3)	3(3)
C(16)	5220(10)	1931(4)	−1459(14)	30(4)	72(5)	56(5)	0(4)	13(4)	18(4)
C(17)	4120(11)	1597(4)	−2591(12)	43(4)	64(5)	39(4)	9(4)	18(3)	3(3)
C(18)	2554(9)	1602(3)	−2778(10)	36(4)	43(4)	34(3)	−3(3)	14(3)	1(3)
C(19)	1827(11)	960(4)	2811(10)	49(4)	56(5)	26(3)	12(4)	8(3)	1(3)
C(20)	1862(11)	1449(3)	2165(11)	47(2)	47(4)	35(3)	−8(3)	12(3)	−8(3)
C(21)	383(12)	1669(3)	1807(10)	75(5)	27(3)	30(3)	8(4)	20(3)	−3(2)
C(22)	−539(12)	1329(5)	2194(12)	53(5)	82(6)	36(4)	−5(5)	27(4)	−10(4)
C(23)	369(16)	878(4)	2837(12)	93(7)	49(5)	37(4)	−16(5)	35(4)	−7(3)

8.2450(7) Å, β 115.502(6)°, V 1818.2(5) Å^3, Z = 4, space group $P2_1/c$. The molecular structure of I with important geometrical parameters is shown in Fig. 1, positional and anisotropic thermal parameters of non-hydrogen atoms are given in Table 1, bond distances in Table 2, bond angles in Table 3.

According to the present X-ray study the abovementioned reaction product turned out to be η^5-cyclopentadienyl-η^1-2,4-diphenylcyclobut-1-en-3-oneiron dicarbonyl. The $CpFe(CO)_2$ fragment has its usual geometry. The four-membered C(3)—C(6) cycle is slightly bent around the C(3)·····C(5) line with the dihedral angle of 7°. The atoms C(3), C(4), C(5) have the planar trigonal (sp^2) and the atom C(6) tetrahedral (sp^3) coordination. Endocyclic angles are very close to corresponding values in the binuclear cation of II with the similar four-

TABLE 2

BOND DISTANCES (Å) IN THE MOLECULE $CpFe(CO)_2C_4(O)HPh$

Bond	d (Å)	Bond	d (Å)
Fe—C(1)	1.775(9)	C(8)—C(9)	1.36(1)
Fe—C(2)	1.758(8)	C(9)—C(10)	1.39(1)
Fe—C(5)	1.935(6)	C(10)—C(11)	1.35(1)
Fe—C(19)	2.103(8)	C(11)—C(12)	1.40(1)
Fe—C(20)	2.104(9)	C(7)—C(12)	1.39(1)
Fe—C(21)	2.101(8)	C(6)—C(13)	1.52(1)
Fe—C(22)	2.101(11)	C(13)—C(14)	1.40(1)
Fe—C(23)	2.115(10)	C(14)—C(15)	1.36(1)
C(1)—O(1)	1.12(1)	C(15)—C(16)	1.38(1)
C(2)—O(2)	1.14(1)	C(16)—C(17)	1.37(2)
C(3)—O(3)	1.22(1)	C(17)—C(18)	1.39(1)
C(3)—C(4)	1.46(1)	C(13)—C(18)	1.38(1)
C(4)—C(5)	1.37(1)	C(19)—C(20)	1.41(1)
C(5)—C(6)	1.56(1)	C(20)—C(21)	1.40(2)
C(3)—C(6)	1.53(1)	C(21)—C(22)	1.37(2)
C(4)—C(7)	1.48(1)	C(22)—C(23)	1.42(2)
C(7)—C(8)	1.39(1)	C(19)—C(23)	1.37(2)

TABLE 3

BOND ANGLES IN THE MOLECULE $CpFe(CO)_2C_4(O)HPh$

Angle	ω (°)	Angle	ω (°)
C(1)FeC(2)	96.1(4)	C(12)C(7)C(8)	118.3(7)
C(1)FeC(5)	90.9(3)	C(7)C(8)C(9)	121.2(8)
C(2)FeC(5)	85.1(3)	C(8)C(9)C(10)	120.5(9)
FeC(1)O(1)	174.8(8)	C(9)C(10)C(11)	119.0(8)
FeC(2)O(2)	179.4(7)	C(10)C(11)C(12)	121.3(8)
FeC(5)C(4)	138.1(5)	C(11)C(12)C(7)	119.7(7)
FeC(5)C(6)	128.2(5)	C(6)C(13)C(14)	120.6(7)
C(4)C(5)C(6)	93.7(5)	C(6)C(13)C(18)	121.4(7)
C(3)C(4)C(5)	92.1(6)	C(18)C(13)C(14)	117.9(7)
C(3)C(4)C(7)	129.0(6)	C(13)C(14)C(15)	120.7(8)
C(5)C(4)C(7)	138.8(4)	C(14)C(15)C(16)	120.9(9)
C(4)C(3)C(6)	92.3(5)	C(15)C(16)C(17)	119.3(10)
C(4)C(3)O(3)	135.3(7)	C(16)C(17)C(18)	120.1(9)
C(6)C(3)O(3)	132.4(7)	C(17)C(18)C(13)	121.0(8)
C(3)C(6)C(5)	82.4(5)	C(19)C(20)C(21)	106.5(8)
C(3)C(6)C(13)	114.8(6)	C(20)C(21)C(22)	109.1(9)
C(5)C(6)C(13)	116.6(6)	C(21)C(22)C(23)	108.2(10)
C(4)C(7)C(8)	122.8(6)	C(22)C(23)C(19)	106.7(10)
C(4)C(7)C(12)	118.6(6)	C(23)C(19)C(20)	109.5(9)

membered cycle containing three sp^2 and one sp^3 carbon atoms [2]. The interatomic distances C(4)—C(5) of 1.37(1) Å corresponds to the double C=C bond. The distances C(5)—C(6) of 1.56(1) and C(3)—C(6) of 1.53(1) Å are typical for single bonds. The bond distance C(3)—C(4) of 1.46(1) is characteristic for the conjugated system O=C—C=C. The σ Fe—C(5) bond length of 1.935(6) Å is somewhat shorter than most of the known values in the σ-vinyl complexes $CpFe(CO)_2CR{=}CXY$ [3] and is equal within the experimental error to the bond length Fe—C in the cation of II (1.90—1.93 Å), where this bond order is intermediate between 1 and 2 due to delocalisation over the five-centered system.

Two phenyl substituents at C(4) and C(6) form dihedral angles of 30° and 94°, respectively, with the best plane of the four-membered ring and an angle of 67° with one another. Dihedral angles between phenyls and the best plane of the Cp ligand are 66 and 63°.

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References

1 N.E. Kolobova, V.V. Skripkin and T.V. Rosantseva, Izv. Akad. Nauk SSSR, ser. Khim., (1979) 1665.
2 G.G. Alexandrov, V.V. Skripkin, N.E. Kolobova and Yu.T. Struchkov, Koord. Khim., 5 (1979) 453.
3 M.R. Churchill, Perspectives in structural Chemistry, John Wiley, New York, 1970, Vol. 3, p. 128.