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HEXACARBONYL(TETRAVINYLSILANE)DIIRON

A.S. BATSANOV, Yu.T. STRUCHKOV, G.V. NURTDINOVA, A.A. POGREBNYAK, L.V. RYBIN, V.P. YUR'EV and M.I. RYBINSKAYA *

Nesmeyanov Institute of Organo-Element Compounds of the Academy of Sciences of the U.S.S.R., Vavilova St. 28, Moscow B-334 (U.S.S.R.) and Institute of Chemistry, Bashkir Branch of Academy of Sciences of the U.S.S.R., October Ave. 71, Ufa 54 (U.S.S.R.)

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Summary

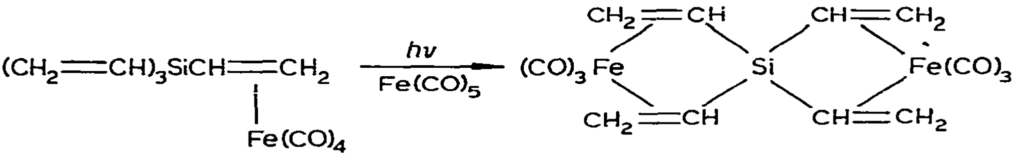
The photochemical reaction of tetracarbonyl(tetravinylsilane)iron with $Fe(CO)_5$ yields hexacarbonyl(tetravinylsilane)diiron, which is characterized by an X-ray structural study.

Introduction

As we have found previously [1], the reaction between equimolar amounts of tetravinylsilane and $Fe(CO)_5$ gives various tetra- and tricarbonyliron complexes. Among them we obtained small amounts of a bis(tricarbonyliron) complex. Herein we report an efficient synthesis of the latter compound and its X-ray structural characterization.

Results and discussion

We have found the complex I to be the only product formed on UV irradiation of a cyclohexane solution of the tetracarbonyl complex II in the presence of $Fe(CO)_5$:



(II) (I)

The photochemical reaction of $(CH_2{=}CH)_4Si$ with $Fe(CO)_5$ also gives I, but in this case the yield is much lower (10—15%). An attempt to obtain I by

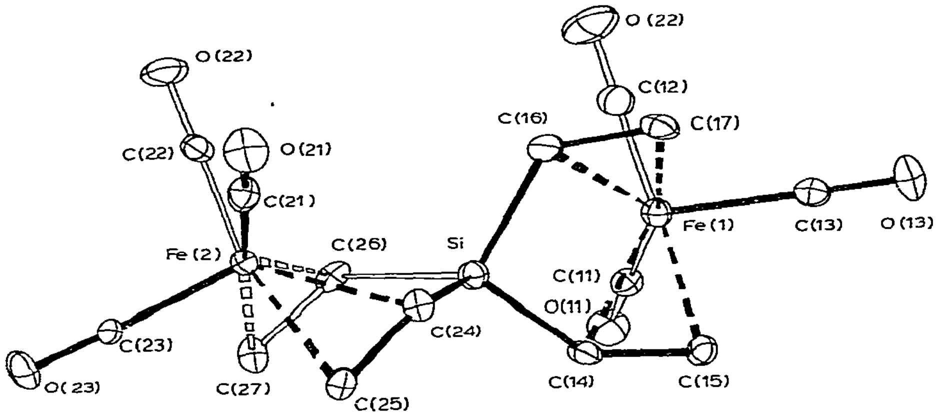


Fig. 1. Molecular structure of I. Moiety 1 is on the right, moiety 2 is on the left. H atoms are omitted.

heating tetravinylsilane with $Fe_3(CO)_{12}$ was unsuccessful.

Complex I is a yellow crystalline substance, air-stable in the solid state but decomposing slowly in solution. According to its ^1H NMR spectrum, all four vinyl groups of the silane moiety in I are coordinated to the metal. The IR spectrum shows four bands of C≡O stretching vibrations in the range common for π-olefinic tricarbonyliron complexes. The mass spectrum exhibits no molecular ion but has peaks with m/e $M - n28$ ($n = 1$—6).

The nature of I as a bis(tricarbonyliron) complex has been established by an X-ray study. The molecule I (see Fig. 1 and bond lengths and angles in Table 1)

TABLE 1

BOND LENGTHS (Å) AND ANGLES (°) [a]

Bond	1	2	Bond	1	2
Fe—C(1)	1.76(1)	1.78(1)	Fe—A(2)	2.05(1)	2.10(1)
Fe—C(2)	1.75(1)	1.75(1)	Si—C(4)	1.85(1)	1.83(1)
Fe—C(3)	1.80(1)	1.80(1)	Si—C(6)	1.83(1)	1.83(1)
Fe—C(4)	2.20(1)	2.17(1)	C(1)—O(1)	1.16(1)	1.13(1)
Fe—C(5)	2.20(1)	2.16(1)	C(2)—O(2)	1.18(1)	1.16(1)
Fe—C(6)	2.19(1)	2.20(1)	C(3)—O(3)	1.14(1)	1.12(1)
Fe—C(7)	2.18(1)	2.21(1)	C(4)—C(5)	1.37(1)	1.39(1)
Fe—A(1)	2.09(1)	2.05(1)	C(6)—C(7)	1.37(2)	1.38(1)
Angle	**1**	**2**	**Angle**	**1**	**2**
C(1)FeC(3)	102.0(5)	97.4(5)	C(1)FeA(2)	151.2(4)	161.7(4)
C(2)FeC(3)	97.9(5)	101.6(5)	C(2)FeA(1)	160.0(4)	147.2(4)
A(1)FeC(3)	102.1(4)	111.1(4)	FeC(1)O(1)	179(1)	179(1)
A(2)FeC(3)	106.7(4)	100.9(4)	FeC(2)O(2)	179(1)	179(1)
C(1)FeC(2)	87.7(5)	86.8(5)	FeC(3)O(3)	178(1)	178(1)
C(1)FeA(1)	87.8(4)	85.9(4)	SiC(4)C(5)	126.6(7)	126.6(7)
C(2)FeA(2)	86.3(4)	88.9(4)	SiC(6)C(7)	125.0(8)	124.8(7)
A(1)FeA(2)	88.3(3)	88.1(3)	C(4)SiC(6)	97.8(4)	97.4(4)
C(14)SiC(24)	122.4(4)		C(16)SiC(24)	115.9(4)	
C(14)SiC(26)	113.0(4)		C(16)SiC(26)	110.8(4)	

[a] A(1) and A(2) are the midpoints of the C(4)—C(5) and C(6)—C(7) bonds, respectively.

TABLE 2

TORSION ANGLES τ (°)

Angle	τ	Angle	τ
C(15)C(14)SiC(16)	49(1)	C(25)C(24)SiC(14)	—74(1)
C(17)C(16)SiC(14)	—49(1)	C(27)C(26)SiC(14)	79(1)
C(25)C(24)SiC(26)	49(1)	C(15)C(14)SiC(26)	166(1)
C(27)C(26)SiC(24)	—51(1)	C(17)C(16)SiC(26)	—168(1)
C(15)C(14)SiC(24)	—78(1)	C(25)C(24)SiC(16)	166(1)
C(17)C(16)SiC(24)	83(1)	C(27)C(26)SiC(16)	—172(1)

consists of two tricarbonyliron moieties linked by a bridging tetravinylsilane ligand which coordinates each iron atom with two C=C bonds. Thus, to our knowledge, I is the second structurally investigated non-conjugated η^4-diene complex of iron in which coordinated double bonds are not incorporated into a cyclic system (the previously studied example being $(CH_2{=}CHCHCH_2OOCC{=}CH_2)Fe(CO)_3$ [2]). Both halves of the molecule I (each one including their common Si atom) have a similar structure; the two halves of the molecule are labelled 1 and 2.

The Fe atoms have a distinct square pyramidal coordination, unlike most non-conjugated diene complexes in which the coordination is intermediate between square pyramidal and trigonal bipyramidal. The apical Fe—C(3) bonds of 1.80(1) Å are longer than the equatorial Fe—CO bonds (average length of 1.76(1) Å). The C(4)=C(5) and C(6)=C(7) double bonds coordinated to the same Fe atom are coplanar within an experimental error. The Fe atoms are displaced from the mean planes of the two double bonds by 1.49 Å in 1 and 1.48 Å in 2, while the C(4)—Si—C(6) moieties are bent in the opposite direction by 38° in 1 and 39° in 2. Thus there is no conjugation between double bonds via the Si atom as well as no bonding Fe—Si interaction (corresponding distances being Fe(1) ... Si 2.853(3) and Fe(2) ... Si 2.855(3) Å). Carbonyl group carbons C(1) and C(2) and the midpoints of the C(4)=C(5) and C(6)=C(7) bonds are coplanar within 0.1 Å, forming the basal plane of a square pyramid. The Fe atoms are situated at 0.4 Å (both in 1 and 2) from the basal planes, while the double bonds are inclined to those planes at the average angle of 77.5°.

Mean Si—C and C=C bond lengths of 1.84(1) and 1.38(1) Å and a Si—C—C angle of 126(1)° are in good agreement with the corresponding values in the free tetravinylsilane molecule measured by electron diffraction in vapour: 1.855(2), 1.355(2) and 124.0(3)°, respectively [4].

Each of the moieties 1 and 2 has an approximate local mirror symmetry plane passing though the Si, Fe, C(3) and O(3) atoms. On the other hand the tetravinylsilane ligand, having in the free state S_4 symmetry with C—C—Si—C torsion angles of —77.5(6)° [4], in I has neither crystallographical nor local symmetry and is chiral, as well as the molecule I as a whole. Torsion angles in I are listed in Table 2.

Experimental

IR spectra were measured with a UR-20 spectrophotometer in cyclohexane solution for C≡O group stretching bands and in KBr pellets for other ranges of the spectra. The ^{1}H NMR spectrum was recorded with a Perkin-Elmer R-12 instrument (60 MHz). Synthesis and isolation of I were carried out under an argon atmosphere. For UV irradiation a mercury vapour lamp PRK-7 was used.

The X-ray experiment was carried out at 20° C with a Syntex P2_1 four circle computer-controlled diffractometer using graphite-monochromated Mo-K_α radiation. All calculations were made with an Eclipse S/200 computer using EXTL programmes modified in our laboratory.

TABLE 3

ATOMIC COORDINATES [a] ($\times 10^4$, FOR $H \times 10^3$) AND ANISOTROPIC THERMAL FACTORS [b]

Atom	x	y	z	Atom	x	y	z
Fe(1)	1415(3)	7240(1)	7639(1)	C(23)	5242(15)	4723(7)	10 540(4)
Fe(2)	3837(2)	4825(1)	9777(1)	C(24)	769(16)	5509(7)	9574(4)
Si	1872(5)	6233(2)	8878(1)	C(25)	1254(17)	5657(6)	10 230(4)
O(11)	4401(13)	8981(6)	7699(4)	C(26)	4657(15)	6109(7)	9104(4)
O(12)	4223(15)	6250(6)	6686(4)	C(27)	5477(15)	6355(7)	9712(5)
O(13)	−1735(14)	8006(7)	6696(3)	H(14)	212	819	880
O(21)	1391(15)	2900(6)	9891(4)	H(15)	−106	868	827
O(22)	6636(14)	3682(6)	8903(3)	H(15′)	−180	737	822
O(23)	6131(14)	4626(6)	11 011(3)	H(16)	249	520	786
C(11)	3217(18)	8291(8)	7678(5)	H(17)	−64	546	727
C(12)	3110(20)	6647(8)	7075(5)	H(17′)	−162	624	789
C(13)	−508(18)	7726(8)	7065(4)	H(24)	−30	491	948
C(14)	1099(19)	7597(6)	8685(4)	H(25)	61	523	1059
C(15)	−709(17)	7913(7)	8379(4)	H(25′)	232	623	1035
C(16)	1389(21)	5662(6)	8068(4)	H(26)	573	586	876
C(17)	−417(19)	5793(7)	7710(4)	H(27)	702	629	984
C(21)	2363(17)	3643(9)	9848(5)	H(27′)	449	661	1009
C(22)	5506(18)	4136(8)	9246(5)				

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Fe(1)	39.2(8)	26.9(5)	24.4(5)	0.6(8)	−0.6(7)	3.5(5)
Fe(2)	28.9(7)	26.6(5)	25.4(5)	−0.2(7)	0.7(7)	2.7(5)
Si	41(2)	30(1)	23(1)	2(1)	−1(1)	5(1)
O(11)	58(6)	51(4)	82(5)	−20(4)	0(5)	−2(4)
O(12)	93(7)	68(5)	68(5)	25(6)	40(5)	−5(4)
O(13)	61(6)	84(6)	54(4)	6(5)	−24(4)	15(4)
O(21)	79(6)	42(4)	98(5)	−34(5)	−6(6)	22(4)
O(22)	69(5)	57(4)	52(4)	15(5)	14(5)	−15(3)
O(23)	80(5)	74(5)	33(3)	7(5)	−21(5)	9(3)
C(11)	46(7)	33(5)	42(5)	5(5)	−2(6)	−1(5)
C(12)	58(8)	33(5)	41(5)	−2(6)	−4(6)	4(5)
C(13)	41(6)	35(5)	32(4)	−3(5)	3(5)	−2(5)
C(14)	52(6)	28(4)	24(4)	−2(6)	−6(5)	−3(3)
C(15)	45(6)	31(5)	24(4)	12(5)	2(4)	5(4)
C(16)	64(7)	19(4)	32(4)	4(6)	−1(6)	8(3)
C(17)	68(8)	24(4)	31(5)	−7(5)	−3(5)	0(4)
C(21)	44(7)	39(5)	46(5)	4(5)	−3(5)	5(5)
C(22)	42(7)	37(5)	32(5)	−2(5)	−5(5)	−3(4)
C(23)	38(6)	28(4)	30(4)	9(5)	−4(4)	5(4)
C(24)	29(6)	36(5)	33(4)	−5(5)	1(4)	7(4)
C(25)	23(5)	45(4)	31(4)	9(5)	11(6)	12(4)
C(26)	29(6)	20(4)	39(5)	−3(4)	9(4)	11(4)
C(27)	28(5)	37(5)	44(5)	−15(4)	−4(5)	13(5)

[a] H atoms have the same numbers as the C atoms to which they are attached.

[b] In the form $T = \exp[-0.025\ (b_{11}h^2a^{*2} + b_{22}k^2b^{*2} + b_{33}l^2c^{*2} + 2b_{12}hka^*b^* + 2b_{13}hla^*c^* + 2b_{23}klb^*c^*)]$.

Crystal data: $C_{14}H_{12}Fe_2O_6Si$, $M = 416.0$, orthorhombic, $a = 6.344(1)$, $b = 12.737(2)$, $c = 20.431(3)$ Å, $V = 1650.8(4)$ Å^3, $D_c = 1.67$ g cm^{-3}, $Z = 4$, space group $P2_12_12_1$.

Intensities of 1639 independent reflections were measured by means of θ—2θ scan technique ($1° \leqslant \theta \leqslant 25°$). 1190 reflections with $I \geqslant 2\sigma$ were used in calculations.

The structure was solved by the direct method using the MULTAN programme and refined by full matrix least squares to $R = 0.076$ with isotropic thermal factors and then to $R = 0.051$ with anisotropic ones. All H atoms were located in the difference synthesis but included in the refinement in fixed calculated positions (C—H 1.0 Å, sp^2 hybridization of C atoms) with $B_{iso} = 6$ Å^2. Finally $R = 0.045$, $R_w = 0.033$ and goodness of fit was 1.50 with the weighting scheme $W = \sigma_F^{-2}$. The absolute configuration of I was not determined. Final atomic coordinates and thermal parameters are given in Table 3.

Synthesis of I

0.304 g (1 mmol) of II and 1 ml of $Fe(CO)_5$, dissolved in 50 ml of cyclohexane, were exposed to UV irradiation for 7.5 hours at room temperature. The reaction mixture was filtered, its volatile components evaporated, and the residue recrystallized from petroleum ether, yielding 0.196 g (46%) of I, m.p. 71—72°C (dec.).

Found: C, 40.36; H, 2.93; Fe, 26.02%. $C_{14}H_{12}Fe_2O_6Si$ calcd.: C, 40.42; H, 2.91; Fe, 26.85%. IR: ν(C≡O) 2048, 2037, 1984, 1970; ν(C=C) 1500 cm^{-1}. ^{1}H NMR: 1.6—3.2 ppm (multiplet, acetone-d_6). Mass spectrum (m/e) 416 — n28 (n = 1—6).

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