Synthesis, spectral characteristics, and crystal structure of the hexanuclear complex $MeSi[\eta^1,\eta^5\text{-}C_5H_4(CO)_2Fe(\eta^1,\eta^5\text{-}C_5H_4)Mn(CO)_3]_3$*

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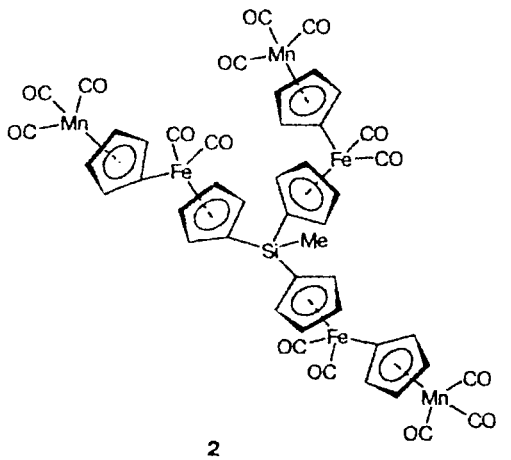
The reaction of $MeSiCl_3$ with 3 equivalents of $LiC_5H_4(CO)_2Fe(\eta^1,\eta^5\text{-}C_5H_4)Mn(CO)_3$ afforded the hexanuclear complex $MeSi[\eta^1,\eta^5\text{-}C_5H_4(CO)_2Fe(\eta^1,\eta^5\text{-}C_5H_4)Mn(CO)_3]_3$. The structure of the resulting complex was established by ^1H and ^{13}C NMR and IR spectroscopy and by X-ray diffraction analysis.

Key words: "ladder" complex, crystal structure.

Previously, we have prepared a series of tri-, tetra-, and pentanuclear complexes, which contain, along with Fe and Mn atoms, atoms of other transition metals (Mo, W, Ti, and Zr), using the binuclear "ladder" complex $Cp(CO)_2Fe(\eta^1,\eta^5\text{-}C_5H_4)Mn(CO)_3$ (**1**), which contains the bridging η^1,η^5-cyclopentadienyl ligand, as the initial "building block."[1,2,3]

In this work, we synthesized the hexanuclear complex $MeSi[\eta^1,\eta^5\text{-}C_5H_4(CO)_2Fe(\eta^1,\eta^5\text{-}C_5H_4)Mn(CO)_3]_3$ (**2**) by the reaction of $MeSiCl_3$ (1 equiv.) with $LiC_5H_4(CO)_2Fe(\eta^1,\eta^5\text{-}C_5H_4)Mn(CO)_3$ (3 equiv.). Complex **2** was obtained as air-stable yellow crystals soluble in organic solvents (ether, THF, benzene, *etc.*; less soluble in hexane).



2

The IR spectrum of complex **2** (a solution in CH_2Cl_2) in the region of CO stretching vibrations is in complete agreement with the spectrum of complex **1**.[4] The spectrum has four bands at 2033, 2004, 1982, and 1918 cm^{-1}, which (by analogy with **1**) can be assigned to vibrations of the CO groups at the Fe atoms (bands at 2033 and 1982 cm^{-1}) and at the Mn atoms (bands at 2004 and 1918 cm^{-1}). The ν(CO) bands in the spectrum of the complex containing 15 carbonyl groups are well interpreted within the framework of the local symmetry of the $Fe(CO)_2$ and $Mn(CO)_3$ fragments (C_{3v}, A_1+E) and are indicative of the absence of vibrational interactions between the carbonyl groups at different metal atoms.

Previously,[4] we have established that ν(CO) frequencies depend on the electronic properties of the adjacent metallocarbonyl fragments. Therefore, the fact that the spectra of complexes **2** and **1** have identical ν(CO) implies that the electronic effect of the binuclear Fe—Mn fragments is not transferred through the Si atom.

The ^1H NMR spectrum has four triplets in the region of δ 4.0—4.4 and a singlet at δ 0.48 corresponding to the protons of the Cp rings and to the protons of the $SiCH_3$ group, respectively.

The structure of complex **2** was established by X-ray diffraction analysis (Fig. 1, projection along the Si—Me bond). The coordination environments about all Fe and Mn atoms are similar ("piano stool"). The central $MeSi(C_5H_4Fe)_3$ fragment has a threefold pseudoaxis. This is manifested in the different values of the angles of rotation of the Cp(Fe) rings (the dihedral angles between the Cp rings, namely, between C(2)—C(6) and C(17)—C(21), C(2)—C(6) and C(32)—C(36), and C(17)—C(21) and C(32)—C(36), are 56.0(3), 66.7(2), and 71.2(2)°, respectively) and in the different deviations of the Si(1) atom from the planes of the Cp(Fe) rings (0.037(6), 0.253(6), and 0.002(5) Å from the planes of the C(2)—C(6), C(17)—C(21), and C(32)—C(36) rings, respectively). The structure of the above-mentioned fragment is similar to that in the complex $MeSi[C_5H_4Fe(CO)_2Et]_3$ (**3**),[5] which, unlike complex **2**,

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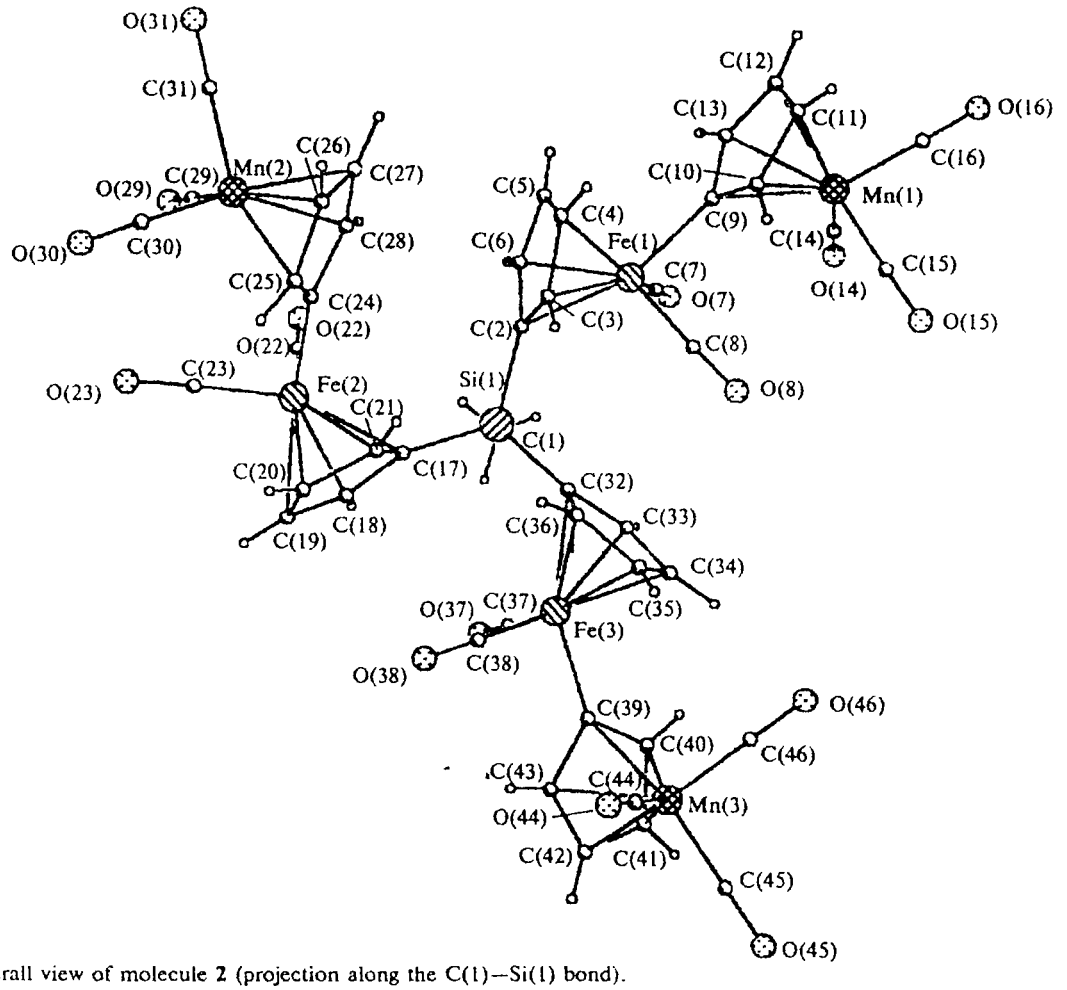


Fig. 1. Overall view of molecule **2** (projection along the C(1)—Si(1) bond).

has the crystallographic threefold axis. In complex **3**, all dihedral angles between the Cp rings and the deviations of the Si atom from all rings are identical (91.5° and 0.018 Å, respectively).

The coordination environments about the Fe atoms in complex **2**, as in **3**, are formed by the η^5-Cp ring and two CO groups. In addition, the carbon atom of the $C_5H_4Mn(CO)_3$ fragment is involved in coordination (in complex **3**, this coordination position is occupied by the carbon atom of the Et group). The $C_5H_4Mn(CO)_3$ fragments have different orientations relative to the Si(1)—Cp(Fe) bond, which leads to loss of the threefold pseudoaxis. The projections of the coordination environments about the Fe atoms onto the plane of the η^5-Cp(Fe) ring are shown in Fig. 2. It can be seen from Fig. 2 that in the polyhedra of the Fe(1) and Fe(3) atoms, the carbon atoms of the Cp(Mn) rings of the $C_5H_4Mn(CO)_3$ fragments (the Cp(Mn) rings are represented by the C(9), C(24), and C(39) atoms in the polyhedra of the Fe(1), Fe(2), and Fe(3) atoms, respectively) are in the transoid configuration relative to the Si—C(η^5-Cp(Fe)) bonds. In the polyhedron of the Fe(2) atom, the above-memtioned atoms are in the cisoid configuration. The torsion angles are as follows: C(9)—Fe(1)—Cn—C(2), 171.5(5)°; C(24)—Fe(2)—Cn—C(17), 70.3(4)°; C(39)—Fe(3)—Cn—C(32), 160.0(6)°; C(9)—Fe(1)—Cn—C(2), 171.5(4)°; C(24)—Fe(2)—Cn—C(17), 70.3(5)°; and C(39)—Fe(3)—Cn—C(32), 160.0(6)°, where Cn is the center of the Cp ring. In complex **3**, the carbon atom of the Et substituent (which occupies the position of the $C_5H_4Mn(CO)_3$ fragment in **2**) is in the transoid orientation with respect to the C(η^5-Cp)—Si bond, as in the polyhedra of the Fe(1) and Fe(3) atoms in complex **2** (the C(η^5-Cp)—Cn—Fe—C(Et) torsion angle in complex **3** is 162.9°).

The coordination environments about the Mn atoms in the cimanthrenyl fragments in molecule **2** are similar. The Mn atom is η^5-coordinated to the Cp(Mn) ring and three CO groups. The projections of the polyhedra $Mn(CO)_3(C_5H_4Fe)$ onto the plane of the cyclopentadienyl ring are shown in Fig. 3. The similarity of the coordination is manifested not only in the eclipsed arrangement of one Mn—C(Cp) bond and one Mn—CO bond and in the transoid arrangement of the other CO

group and the Fe—C(Cp) bond but also in the geometric parameters of this fragment. Thus, the Mn—C(Cp) bonds with the participation of the atoms of the ring directly bonded to the Fe atom (the Mn(1)—C(8), Mn(2)—C(24),

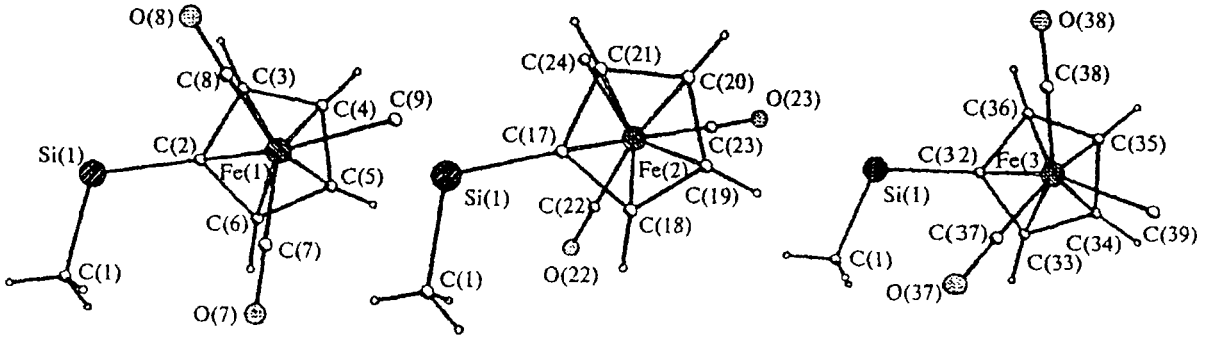


Fig. 2. Projection of the $(Cp)Fe(CO)_2$ fragments onto the plane of the Cp ring of the fragment.

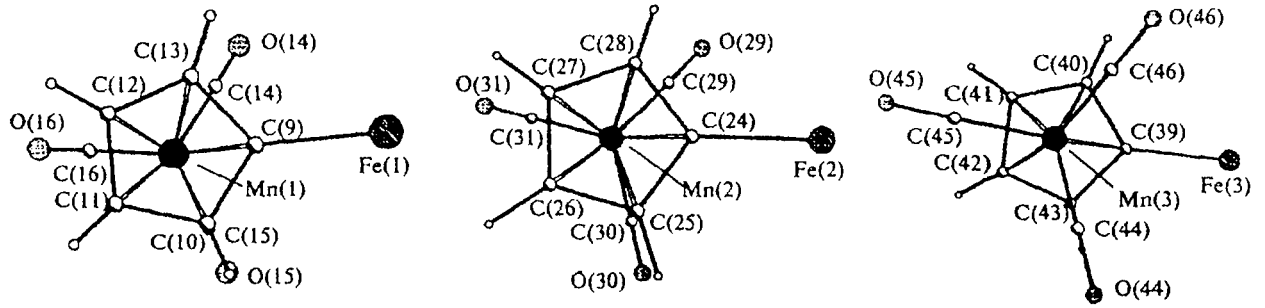
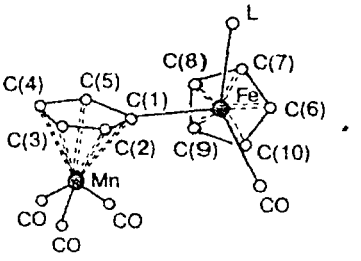


Fig. 3. Projection of the $(Cp)Mn(CO)_3$ fragments onto the plane of the Cp ring of the fragment.

Table 1. Selected geometric parameters and conformational characteristics of the fragment $\{(CO)_3MnC_5H_4Fe(CO)(L)(Cp)\}$



Parameter	2 (L = CO)			4 (L = PPh_3)	1 (L = CO)
	Mn(1)Fe(1)	Mn(2)Fe(2)	Mn(3)Fe(3)		
θ/deg	18.9	36.6	60.1	66	81.3
φ/deg	52.7, 70.1	43.1, 77.0	55.2, 66.9	25.9	1.3
Mn—C(1)/Å	2.196	2.203	2.206	2.25	2.216
Mn—C(2), Mn—C(5)/Å	2.147, 2.145	2.119, 2.139	2.143, 2.135	2.14, 2.16	2.155, 2.144
Mn—C(3), Mn—C(4)/Å	2.118, 2.114	2.116, 2.116	2.113, 2.122	2.16, 2.13	2.129, 2.139
Fe—C(1)/Å	1.992	1.997	1.994	1.99	2.001
Fe—C(6)/Å	2.127	2.127	2.126	2.08	2.092
Fe—C(7), Fe—C(10)/Å	2.109, 2.096	2.106, 2.103	2.096, 2.111	2.10, 2.13	2.091, 2.104
Fe—C(8), Fe—C(9)/Å	2.115, 2.102	2.095, 2.094	2.099, 2.114	2.11, 2.16	2.102, 2.110
Δ_1/Å	0.38	0.19	0.27	0.19	0.25
Δ_2/Å	1.734	1.729	1.734	1.73	1.730
Δ_3/Å	1.776	1.767	1.778	1.80	1.782
Fe—CO/Å	1.754, 1.759	1.753, 1.768	1.745, 1.772	1.70	1.766, 1.744
Mn—CO/Å	1.779, 1.784, 1.790	1.771, 1.774, 1.784	1.775, 1.775, 1.777	1.78, 1.73, 1.70	1.790, 1.792, 1.787

Note. θ is the dihedral angle between the planes of the Cp rings; φ is the torsion angle C(1)CnMnC(O), where Cn is the center of the Cp ring and C(O) is the CO group nearest to the Fe—C(1) bond; Δ_1 is the deviation of the Fe atom from the plane of the Cp ring; Δ_2 is the deviation of the Fe atom from the plane of the coordinated Cp ring; Δ_3 is the deviation of the Mn atom from the plane of the coordinated Cp ring.

Table 2. Atomic coordinates ($\times 10^4$; for hydrogen atoms, $\times 10^3$) and equivalent isotropic (U_{eq}; isotropic U_{iso} for H atoms) temperature factors in the structure of **2**

Atom	x	y	z	U_{eq}/U_{iso}
Fe(1)	14587(1)	13346(1)	6635(1)	31(1)
Fe(2)	15726(1)	9899(1)	7641(1)	38(1)
Fe(3)	15415(1)	12537(1)	9500(1)	35(1)
Mn(1)	13551(1)	15370(1)	5918(1)	37(1)
Mn(2)	14286(1)	9113(1)	6055(1)	46(1)
Mn(3)	14733(1)	13461(1)	11125(1)	40(1)
Si(1)	15757(1)	12065(1)	7849(1)	34(1)
O(7)	16454(4)	14259(3)	6572(3)	92(2)
O(8)	13830(4)	14245(3)	7698(2)	84(2)
O(14)	15648(4)	15987(3)	6230(2)	84(2)
O(15)	12865(3)	15990(3)	7135(2)	69(1)
O(16)	12918(6)	16836(3)	5226(3)	141(3)
O(22)	17299(4)	10201(5)	6777(3)	131(3)
O(23)	15764(4)	8179(3)	7531(2)	76(1)
O(29)	16414(5)	8699(4)	5857(3)	126(2)
O(30)	13774(6)	7572(3)	6597(3)	134(3)
O(31)	13524(4)	8678(3)	4712(2)	81(2)
O(37)	17593(3)	12132(3)	9618(2)	68(1)
O(38)	14743(4)	10993(3)	9914(2)	77(2)
O(44)	12946(4)	12412(3)	11139(2)	85(2)
O(45)	14365(5)	14278(5)	12337(2)	141(3)
O(46)	13594(4)	14684(3)	10329(2)	76(1)
C(1)	17123(5)	12345(5)	7804(4)	58(2)
C(2)	14996(4)	12215(3)	7047(2)	33(1)
C(3)	13896(4)	12278(3)	6907(3)	37(1)
C(4)	13654(5)	12402(3)	6234(3)	43(1)
C(5)	14570(5)	12433(3)	5935(3)	43(2)
C(6)	15382(5)	12308(3)	6425(3)	40(1)
C(7)	15708(5)	13914(3)	6597(3)	52(2)
C(8)	14146(5)	13889(3)	7286(3)	52(2)
C(9)	13781(4)	14080(3)	6017(2)	33(1)
C(10)	12732(4)	14279(3)	6026(3)	43(1)
C(11)	12370(5)	14667(4)	5427(3)	51(2)
C(12)	13198(5)	14703(3)	5049(3)	48(2)
C(13)	14053(5)	14355(3)	5399(2)	37(1)
C(14)	14828(5)	15740(4)	6115(3)	50(2)
C(15)	13150(4)	15748(3)	6668(3)	48(1)
C(16)	13169(7)	16267(4)	5502(3)	75(2)
C(17)	15654(4)	11018(3)	8117(2)	35(1)
C(18)	16460(5)	10531(3)	8440(3)	43(1)
C(19)	16040(5)	9831(4)	8660(3)	50(2)
C(20)	14964(5)	9857(4)	8492(3)	51(2)
C(21)	14737(5)	10583(3)	8169(3)	41(1)
C(22)	16683(5)	10086(5)	7118(3)	70(2)
C(23)	15764(5)	8853(4)	7557(3)	52(2)
C(24)	14646(4)	9939(3)	6879(2)	38(1)
C(25)	13630(5)	9631(4)	6870(3)	51(2)
C(26)	13033(6)	9828(4)	6281(3)	64(2)
C(27)	13675(6)	10272(4)	5903(3)	64(2)
C(28)	14653(6)	10322(3)	6255(3)	52(2)
C(29)	15570(7)	8849(5)	5938(3)	81(2)
C(30)	13996(7)	8169(4)	6376(3)	81(2)
C(31)	13814(5)	8847(4)	5238(3)	56(2)
C(32)	15164(4)	12683(3)	8467(2)	35(1)
C(33)	15556(5)	13406(3)	8772(2)	42(1)
C(34)	14874(5)	13678(3)	9202(3)	49(2)
C(35)	14045(5)	13146(4)	9193(3)	47(2)
C(36)	14216(4)	12545(4)	8739(3)	42(1)
C(37)	16741(5)	12282(3)	9576(2)	43(1)
C(38)	15019(4)	11607(4)	9759(3)	48(1)
C(39)	15687(4)	12888(3)	10429(2)	35(1)
C(40)	16122(4)	13626(3)	10664(2)	40(1)
C(41)	16356(4)	13600(4)	11352(3)	48(2)
C(42)	16048(4)	12848(4)	11565(3)	46(2)
C(43)	15651(4)	12426(4)	11017(3)	41(1)
C(44)	13626(5)	12846(4)	11130(3)	54(2)
C(45)	14497(5)	13952(5)	11861(3)	78(2)
C(46)	14037(5)	14197(4)	10642(3)	51(2)
H(110)	1750(4)	1269(3)	822(3)	53(17)
H(120)	1740(6)	1202(4)	750(4)	90(26)
H(130)	1714(5)	1281(4)	764(3)	79(25)
H(3)	1344(4)	1224(3)	722(3)	55(17)
H(4)	1308(5)	1255(3)	606(3)	59(20)
H(5)	1456(5)	1251(3)	555(3)	55(18)
H(6)	1604(4)	1230(3)	634(3)	47(17)
H(10)	1239(4)	1427(3)	637(2)	24(13)
H(11)	1173(4)	1483(3)	534(2)	40(15)
H(12)	1316(3)	1496(3)	461(2)	30(12)
H(13)	1473(3)	1426(2)	528(2)	11(10)
H(18)	1712(4)	1069(3)	849(2)	36(15)
H(19)	1643(4)	943(3)	886(2)	41(15)
H(20)	1452(5)	956(3)	854(3)	58(19)
H(21)	1414(4)	1070(3)	797(2)	40(16)
H(25)	1338(5)	924(4)	724(3)	72(19)
H(26)	1220(7)	971(5)	611(4)	133(31)
H(27)	1346(4)	1051(3)	547(2)	38(14)
H(28)	1521(4)	1055(3)	614(2)	17(12)
H(33)	1616(4)	1364(3)	874(2)	46(17)
H(34)	1492(4)	1415(3)	946(3)	55(16)
H(35)	1349(4)	1314(3)	942(3)	52(18)
H(36)	1387(3)	1212(3)	866(2)	19(12)
H(40)	1625(4)	1405(3)	1040(2)	29(13)
H(41)	1658(4)	1398(3)	1162(2)	32(14)
H(42)	1607(4)	1269(3)	1197(3)	40(15)
H(43)	1538(4)	1194(3)	1100(2)	27(13)

and Mn(3)—C(39) bonds) are the longest and are equal, on the average, to 2.202 Å. Two Mn—C(Cp) bonds with the participation of the carbon atoms nearest to the C(Fe) atom (*i.e.*, to the C(8), C(24), and C(39) atoms) are somewhat shorter (the average value is 2.138 Å). The Mn—C(Cp) bonds most remote from these atoms are the shortest (on the average, 2.116 Å). The differences between the $(CO)_3Mn(C_5H_4Fe)$ fragments are characterized by the degree of deviation of the Fe atoms from the plane of the Cp(Mn) ring (0.376(2), 0.187(2), and 0.272(3) Å for the Fe(1), Fe(2), and Fe(3) atoms, respectively) and by the slightly different angles of rotation of the CO groups with respect to the Mn—C(Cp) bonds (see Fig. 3).

A comparison of the structural data for compound **2** and the complexes $(CO)_3MnC_5H_4Fe(Cp)(CO)(L)$, where L = PPh_3 (**4**) or CO (**1**),[6] containing identical fragments $\{(CO)_3MnC_5H_4Fe(CO)(Cp)\}$ (the selected characteristics of this fragment in complexes **2**, **4**, and **1** are given in Table 1; the fragments in **2** differ from the fragments in **4** and **1** in that the η^5-Cp(Fe) ring contains

Table 3. Bond lengths (d) in molecule **2**

Bond	d/Å	Bond	d/Å	Bond	d/Å	Bond	d/Å
Fe(1)—C(7)	1.754(7)	Si(1)—C(1)	1.853(7)	Mn(1)—C(14)	1.784(7)	C(10)—C(11)	1.430(8)
Fe(1)—C(8)	1.759(6)	Si(1)—C(17)	1.853(5)	Mn(1)—C(15)	1.790(6)	C(11)—C(12)	1.390(9)
Fe(1)—C(9)	1.992(5)	Si(1)—C(32)	1.867(5)	Mn(1)—C(11)	2.114(6)	C(12)—C(13)	1.393(7)
Fe(1)—C(6)	2.096(6)	O(7)—C(7)	1.138(7)	Mn(1)—C(12)	2.118(5)	C(17)—C(21)	1.413(8)
Fe(1)—C(5)	2.102(5)	O(8)—C(8)	1.147(6)	Mn(1)—C(10)	2.145(6)	C(17)—C(18)	1.441(7)
Fe(1)—C(3)	2.109(5)	O(14)—C(14)	1.148(7)	Mn(1)—C(13)	2.147(5)	C(18)—C(19)	1.390(8)
Fe(1)—C(4)	2.115(6)	O(15)—C(15)	1.139(6)	Mn(1)—C(9)	2.196(5)	C(19)—C(20)	1.411(9)
Fe(1)—C(2)	2.127(5)	O(16)—C(16)	1.142(7)	Mn(2)—C(29)	1.771(8)	C(20)—C(21)	1.407(8)
Fe(2)—C(22)	1.753(7)	O(22)—C(22)	1.132(7)	Mn(2)—C(30)	1.774(8)	C(24)—C(25)	1.418(8)
Fe(2)—C(23)	1.768(7)	O(23)—C(23)	1.135(7)	Mn(2)—C(31)	1.784(7)	C(24)—C(28)	1.435(8)
Fe(2)—C(24)	1.997(5)	O(29)—C(29)	1.156(8)	Mn(2)—C(27)	2.116(6)	C(25)—C(26)	1.411(8)
Fe(2)—C(19)	2.094(5)	O(30)—C(30)	1.149(8)	Mn(2)—C(26)	2.116(6)	C(26)—C(27)	1.410(10)
Fe(2)—C(20)	2.095(6)	O(31)—C(31)	1.144(7)	Mn(2)—C(28)	2.119(6)	C(27)—C(28)	1.403(9)
Fe(2)—C(18)	2.103(6)	O(37)—C(37)	1.133(6)	Mn(2)—C(25)	2.139(6)	C(32)—C(36)	1.424(7)
Fe(2)—C(21)	2.106(6)	O(38)—C(38)	1.148(6)	Mn(2)—C(24)	2.203(5)	C(32)—C(33)	1.436(7)
Fe(2)—C(17)	2.127(5)	O(44)—C(44)	1.149(7)	Mn(3)—C(45)	1.775(7)	C(33)—C(34)	1.392(8)
Fe(3)—C(38)	1.745(6)	O(45)—C(45)	1.149(7)	Mn(3)—C(44)	1.775(7)	C(34)—C(35)	1.401(9)
Fe(3)—C(37)	1.772(7)	O(46)—C(46)	1.157(7)	Mn(3)—C(46)	1.777(6)	C(35)—C(36)	1.408(8)
Fe(3)—C(39)	1.994(5)	C(2)—C(6)	1.425(7)	Mn(3)—C(42)	2.122(6)	C(39)—C(40)	1.428(7)
Fe(3)—C(36)	2.096(5)	C(2)—C(3)	1.437(7)	Mn(3)—C(41)	2.133(6)	C(39)—C(43)	1.438(7)
Fe(3)—C(35)	2.099(6)	C(3)—C(4)	1.401(7)	Mn(3)—C(43)	2.135(6)	C(40)—C(41)	1.415(7)
Fe(3)—C(33)	2.111(5)	C(4)—C(5)	1.397(8)	Mn(3)—C(40)	2.143(5)	C(41)—C(42)	1.408(8)
Fe(3)—C(34)	2.114(5)	C(5)—C(6)	1.402(8)	Mn(3)—C(39)	2.206(5)	C(42)—C(43)	1.386(8)
Fe(3)—C(32)	2.126(5)	C(9)—C(10)	1.410(7)	Si(1)—C(2)	1.853(5)		
Mn(1)—C(16)	1.779(7)	C(9)—C(13)	1.427(7)				

the SiMe substituent) demonstrates (Table 1) that the lengths of the Fe—C(1) σ-bonds in all complexes are identical and are close to the standard value for the Fe—σ(Ar) bond (2.008 Å).[7] The above-mentioned redistribution of the Mn—C(Cp) bond lengths depending on the distance to the carbon atom bonded to the Fe atom (the effect of the Fe—C(1) σ-bond) is not observed in molecules **4** and **1**, except for the elongation of the Mn—C(1) bond, which is, as in complex **2**, substantially longer than the remaining Mn—C(Cp) bonds. It should be noted that molecules **1** and **4** differ from complex **2** in the mutual orientation of the Fe—C(1) and Mn—CO bonds. In complex **1**, one CO group is in the eclipsed orientation with respect to the Fe—C(1) bond, in complex **4**, the mutual arrangement is approximately eclipsed (the torsion angles φ are 25.9 and 1.3° in **4** and **1**, respectively), while all fragments in molecule **2**, as mentioned above, are characterized by the transoid arrangement of one CO group and the Fe—C(1) bond (see Fig. 3). The Fe—C(η^5-Cp) bonds in complexes **4** and **1**, which do not contain substituents in the Cp(Fe) rings, are equalized and are close to the standard value (2.080 Å[7]), unlike complex **2** (containing the SiMe substituent at the C(6) atom of the cyclopentadienyl ring) in which the Fe—C(1) bonds are slightly elongated. The average Fe—C(6) bond length (2.127 Å) is slightly larger than the remaining bonds (2.096—2.115 Å; the average value is 2.103 Å).

Unlike the geometric characteristics of the fragment under consideration, which adequately reflect the effect of the substituents in the cyclopentadienyl rings, the changes in the conformational parameters are not governed by a particular correlation. In molecule **1**, which does not contain substituents in the Cp(Fe) ring, the planes of the Cp rings are mutually orthogonal (the dihedral angle θ = 81.3(2)°) and the unusual eclipsed arrangement of the Fe—C(1) bond and one CO group is observed. The C(1)CnMnC(O) torsion angle (φ) is 1.3(2)°. In all other cases, namely, in the presence of the bulky substituent L = PPh_3 and of the unsubstituted Cp ring coordinated to the Fe atom (complex **4**) as well as in the presence of the small substituent L = CO and of the bulky substituent SiMe in the Cp ring coordinated to the Fe atom (complex **2**), the cyclopentadienyl rings are twisted to a lesser degree (θ = 18.9—66°), and the Fe—C(1) bonds are in the staggered orientation with respect to the CO groups (the torsion angle φ = 25.9—77.0°). It is believed that the conformation of the fragment $\{(CO)_3Mn(C_5H_4Fe(CO)(L)C_5H_4)\}$ is governed by steric and packing factors and is determined by the "adjustment" of the cimanthrenyl fragment $(CO)_3Mn(Cp)$ to the real molecular packing in crystals.

Experimental

All operations were carried out under an atmosphere of argon. Complex **1** was prepared according to a known procedure.[8] THF was distilled over sodium benzophenoneketyl immediately before use.

The IR spectra were recorded on a Nicolet Magna IR 750 Fourier-transform IR spectrometer (the resolution was 2 cm^{-1}). The ^1H and ^{13}C NMR spectra (in C_6D_6) were obtained on a Bruker AMX-400 spectrometer (400 MHz for ^1H).

Table 4. Selected bond angles (ω) in molecule **2**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(7)—Fe(1)—C(8)	95.0(3)	C(26)—Mn(2)—C(24)	65.4(2)	C(21)—C(17)—Si(1)	126.9(4)
C(7)—Fe(1)—C(9)	91.3(2)	C(28)—Mn(2)—C(24)	38.7(2)	C(18)—C(17)—Si(1)	127.3(4)
C(8)—Fe(1)—C(9)	88.3(2)	C(25)—Mn(2)—C(24)	38.1(2)	Si(1)—C(17)—Fe(2)	134.1(3)
C(9)—Fe(1)—C(6)	128.7(2)	C(45)—Mn(3)—C(44)	93.3(3)	C(19)—C(18)—C(17)	109.7(5)
C(9)—Fe(1)—C(5)	92.8(2)	C(45)—Mn(3)—C(46)	91.6(3)	C(18)—C(19)—C(20)	108.0(5)
C(9)—Fe(1)—C(3)	119.0(2)	C(44)—Mn(3)—C(46)	92.3(3)	C(21)—C(20)—C(19)	107.3(6)
C(9)—Fe(1)—C(4)	88.4(2)	C(45)—Mn(3)—C(39)	155.6(3)	C(20)—C(21)—C(17)	110.3(6)
C(9)—Fe(1)—C(2)	154.4(2)	C(44)—Mn(3)—C(39)	105.0(3)	O(22)—C(22)—Fe(2)	179.4(7)
C(22)—Fe(2)—C(23)	95.2(3)	C(46)—Mn(3)—C(39)	103.4(2)	O(23)—C(23)—Fe(2)	176.6(6)
C(22)—Fe(2)—C(24)	90.2(3)	C(42)—Mn(3)—C(39)	65.2(2)	C(25)—C(24)—C(28)	104.0(5)
C(23)—Fe(2)—C(24)	89.0(2)	C(41)—Mn(3)—C(39)	65.1(2)	C(25)—C(24)—Fe(2)	125.5(4)
C(24)—Fe(2)—C(19)	146.7(2)	C(43)—Mn(3)—C(39)	38.6(2)	C(28)—C(24)—Fe(2)	130.3(4)
C(24)—Fe(2)—C(20)	107.4(2)	C(40)—Mn(3)—C(39)	38.3(2)	Fe(2)—C(24)—Mn(2)	131.3(3)
C(24)—Fe(2)—C(18)	145.5(2)	C(2)—Si(1)—C(1)	110.7(3)	C(26)—C(25)—C(24)	111.1(6)
C(24)—Fe(2)—C(21)	88.0(2)	C(2)—Si(1)—C(17)	110.2(2)	C(27)—C(26)—C(25)	106.8(6)
C(24)—Fe(2)—C(17)	105.7(2)	C(1)—Si(1)—C(17)	110.8(3)	C(28)—C(27)—C(26)	107.9(6)
C(19)—Fe(2)—C(17)	66.6(2)	C(2)—Si(1)—C(32)	107.9(2)	C(27)—C(28)—C(24)	110.2(6)
C(38)—Fe(3)—C(37)	94.1(3)	C(1)—Si(1)—C(32)	110.9(3)	O(29)—C(29)—Mn(2)	178.0(8)
C(38)—Fe(3)—C(39)	90.2(2)	C(17)—Si(1)—C(32)	106.2(2)	O(30)—C(30)—Mn(2)	177.1(8)
C(37)—Fe(3)—C(39)	84.7(2)	C(6)—C(2)—C(3)	104.3(4)	O(31)—C(31)—Mn(2)	179.1(6)
C(39)—Fe(3)—C(36)	139.4(2)	C(6)—C(2)—Si(1)	127.2(4)	C(36)—C(32)—C(33)	104.7(5)
C(39)—Fe(3)—C(35)	102.0(2)	C(3)—C(2)—Si(1)	128.5(4)	C(36)—C(32)—Si(1)	127.6(4)
C(39)—Fe(3)—C(33)	117.0(2)	Si(1)—C(2)—Fe(1)	124.4(2)	C(33)—C(32)—Si(1)	127.8(4)
C(39)—Fe(3)—C(34)	91.8(2)	C(4)—C(3)—C(2)	109.2(5)	Si(1)—C(32)—Fe(3)	125.5(2)
C(39)—Fe(3)—C(32)	156.1(2)	C(5)—C(4)—C(3)	108.8(5)	C(34)—C(33)—C(32)	109.4(5)
C(16)—Mn(1)—C(14)	91.3(3)	C(4)—C(5)—C(6)	107.1(5)	C(33)—C(34)—C(35)	108.8(5)
C(16)—Mn(1)—C(15)	91.2(3)	C(5)—C(6)—C(2)	110.5(5)	C(34)—C(35)—C(36)	107.1(6)
C(14)—Mn(1)—C(15)	91.6(3)	O(7)—C(7)—Fe(1)	177.6(6)	C(35)—C(36)—C(32)	110.0(5)
C(16)—Mn(1)—C(9)	155.6(2)	O(8)—C(8)—Fe(1)	177.9(6)	O(37)—C(37)—Fe(3)	178.6(5)
C(14)—Mn(1)—C(9)	102.0(2)	C(10)—C(9)—C(13)	105.1(5)	O(38)—C(38)—Fe(3)	178.2(5)
C(15)—Mn(1)—C(9)	108.6(2)	C(10)—C(9)—Fe(1)	126.1(4)	C(40)—C(39)—C(43)	103.4(4)
C(11)—Mn(1)—C(9)	65.1(2)	C(13)—C(9)—Fe(1)	127.2(4)	C(40)—C(39)—Fe(3)	127.3(4)
C(12)—Mn(1)—C(9)	64.6(2)	Fe(1)—C(9)—Mn(1)	136.8(2)	C(43)—C(39)—Fe(3)	128.7(4)
C(10)—Mn(1)—C(9)	37.9(2)	C(9)—C(10)—C(11)	109.5(5)	Fe(3)—C(39)—Mn(3)	133.7(2)
C(13)—Mn(1)—C(9)	38.4(2)	C(12)—C(11)—C(10)	107.0(5)	C(41)—C(40)—C(39)	110.4(5)
C(29)—Mn(2)—C(30)	93.8(4)	C(11)—C(12)—C(13)	108.6(5)	C(42)—C(41)—C(40)	107.3(5)
C(29)—Mn(2)—C(31)	93.0(3)	C(12)—C(13)—C(9)	109.8(5)	C(43)—C(42)—C(41)	107.6(5)
C(30)—Mn(2)—C(31)	93.4(3)	O(14)—C(14)—Mn(1)	178.6(6)	C(42)—C(43)—C(39)	111.3(5)
C(29)—Mn(2)—C(24)	97.5(3)	O(15)—C(15)—Mn(1)	177.9(5)	O(44)—C(44)—Mn(3)	176.2(6)
C(30)—Mn(2)—C(24)	108.3(3)	O(16)—C(16)—Mn(1)	178.9(6)	O(45)—C(45)—Mn(3)	178.5(7)
C(31)—Mn(2)—C(24)	155.1(2)	C(21)—C(17)—C(18)	104.7(5)	O(46)—C(46)—Mn(3)	179.1(5)
C(27)—Mn(2)—C(24)	65.2(2)				

Synthesis of MeSi[η^1,η^5-$C_5H_4(CO)_2Fe(\eta^1,\eta^5$-$C_5H_4)Mn(CO)_3]_3$ (2). A 1.4 *M* solution of Bu^nLi in hexane (2 mmol, 1.4 mL) was added to a solution of complex **1** (0.74 g, 1.9 mmol) in THF (25 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 45 min. Then $MeSiCl_3$ (0.07 mL, 0.6 mmol) was added, and the reaction mixture was stirred at −78 °C for 1 h. Then the reaction mixture was gradually heated with stirring to room temperature. The solvent was evaporated. The residue was chromatographed on a column with Al_2O_3 (a 1 : 1 benzene—hexane mixture as the eluent). Unconsumed complex **1** (0.2 g) was isolated. Elution with benzene gave complex **2** (0.15 g, 21%). Found (%): C, 47.35; H, 2.10; Fe, 14.85; Si, 2.38. $C_{46}H_{27}Fe_3Mn_3O_{15}Si$. Calculated (%): C, 46.84; H, 2.29; Si, 2.37; Fe, 14.24. IR (CH_2Cl_2), ν(CO)/cm^{-1}: 2033, 2004, 1982, 1918. ^{1}H NMR, δ: 0.488 (s, 3 H, CH_3Si); 4.098 (t, 6 H, $H_{\alpha,\alpha'}$, CpFe, $^3J_{HH}$ = 1.9 Hz); 4.325 (t, 6 H, CpMn, $^3J_{HH}$ = 2.04 Hz); 4.3637 (t, 6 H, CpMn, $^3J_{HH}$ = 1.9 Hz); 4.413 (t, 6 H, $H_{\beta,\beta'}$, CpFe, $^3J_{HH}$ = 1.9 Hz).

^{13}C NMR, δ: −5.69 (CH_3Si); 81.12 (C(1), CpMn); 83.80 (C(2, 5), CpFe); 91.70 and 92.86 (C(2, 5) and C(3, 4), CpMn); 95.48 (C(3, 4), CpFe); 97.21 (C(1), CpFe); 214.30 (CO); 227.00 (C(1), CpFe).

X-ray diffraction analysis of compound 2. Single crystals of **2** were prepared from a solution in CH_2Cl_2 at −18 °C. Yellow transparent crystals of **2**, $C_{46}H_{27}Fe_3Mn_3O_{15}Si$ (M = 1180.14), are monoclinic, at 20 °C a = 13.030(3) Å, b = 16.811(3) Å, c = 20.526(4) Å, β = 95.72(3)°, V = 4474, d_{calc} = 1.752 g cm^{-3}, space group $P2_1/n$, Z = 4. The experimental X-ray data (9930 reflections) were collected on an automated four-circle CAD4 Enraf-Nonius diffractometer at room temperature. After averaging of equivalent reflections (absorption was ignored, μ = 9.62 cm^{-1}), 9085 independent reflections were obtained. The structure was solved by the direct method and refined by the full-matrix least-squares method based on F^2_{hkl} with anisotropic thermal parameters for nonhydrogen atoms. The positions of the hydrogen atoms were located from the difference electron density synthesis and refined isotropically. The final values of the *R*

factors were as follows: $wR_2 = 0.1439$ based on all 9075 independent reflections used in the refinement and $R_1 = 0.0407$ based on F_{hkl} for 4632 observed reflections with $I > 2\sigma(I)$. All calculations were carried out using the SHELXTL PLUS 5 program package.[9]

The atomic coordinates are given in Table 2. The bond lengths and selected bond angles are listed in Tables 3 and 4, respectively.

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