On the possibility of existence of η^4-π-complexes of corannulene ($C_{20}H_{10}$) and C_{60} fullerene derivatives

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The problem of existence of η^4-π-complexes of transition metal atoms with C_{60} fullerene and its simplest bowl-shaped hydrocarbon precursor, corannulene ($C_{20}H_{10}$), is discussed in the framework of the HF/3-21G and DFT/TZ2P methods. The molecular structures of corannulene and C_{60} fullerene derivatives, namely, $C_{20}H_{14}$, $C_{20}H_{16}$, $C_{60}H_4$, and $C_{60}H_6$ were simulated. These molecules can form stable η^4-π-complexes $C_{20}H_{14}Fe(CO)_3$, $C_{20}H_{16}Fe(CO)_3$, $C_{60}H_4Fe(CO)_3$, and $C_{60}H_6Fe(CO)_3$ in which the Fe atom interacts with C atoms of a fulvene-like or butadiene-like conjugated fragment of the hydrocarbon ligands. The energies of the η^4-π-bonds in the complexes under study were compared with the corresponding bond energies in the classical complexes $C_4H_6Fe(CO)_3$ and $C_5H_6Fe(CO)_3$. The geometric parameters of $C_4H_6Fe(CO)_3$ and $C_5H_6Fe(CO)_3$ obtained from DFT calculations are close to the experimental values. Stabilities of the η^4-π-complexes studied and their η^5-π-analogs were compared.

Key words: fullerene C_{60}, polyhedral carbon clusters, corannulene, η^4-π-complexes, η^5-π-complexes, transition metal carbonyls, fullerene hydrides; nonempirical quantum-chemical calculations, Hartree—Fock—Roothaan method, DFT-PBE approximation.

All polyhedral carbon clusters synthesized to date, *viz.*, fullerenes C_{60}, C_{70}, C_{76}, C_{84}, *etc.* represent systems with conjugated bonds. In principle, they can form chemical compounds with different types of chemical bonds. However, no stable η^n-complexes ($n \geq 3$) of *unsubstituted* fullerenes were synthesized so far. This is, in particular, due to the fact that the formation of such complexes is made difficult by the presence of extended conjugated systems, which results in strong delocalization of the π-electron density and in a decrease in the coefficients at the p_π-AO, which determine the contributions of these AOs to the frontier MOs (FMOs) responsible for π-bonding. This leads to weak overlap of the fullerene FMOs with the AOs of the atom coordinated.[1] In addition, the fullerene FMOs affected by a species coordinated simultaneously to more then two atoms can be poorly transformed to provide bonding with this species. These two factors prevent the formation of stable η^n-π-complexes of *unsubstituted* fullerenes for $n \geq 3$.

The case $n = 5$ has been studied in detail[2—14] taking η^5-π-complexes of C_{20}, C_{40}, C_{60}, and C_{70} fullerenes and their simplest bowl-shaped hydrocarbon precursors ($C_{20}H_{10}$ and $C_{30}H_{10}$) as examples. It was shown that cyclopentadienyl derivatives of these species (for instance, the $^{\bullet}C_{60}R_5$, $^{\bullet}C_{20}H_{10}R_5$, and $^{\bullet}C_{30}H_{10}R_5$ radicals) can form more stable complexes as compared to the initial systems.[2,3] This is due to the fact that attachment of functional groups R to the α-positions relative to the isolated five-membered ring (*pent**) of, *e.g.*, C_{60} fullerene to give a cyclopentadienyl type radical $^{\bullet}C_{60}R_5$ allows one to divide the conjugated system of the polyhedral cluster into two independent subsystems, one of which involves only the π-electrons of the atoms of the *pent** fragment. This favors a substantial increase in the contributions of the $2p_\pi$-orbitals of the *pent** ring atoms to the FMOs. Such polyhedral cyclopentadienyl radicals should be more prone to the formation of η^5-π-complexes than the initial unsubstituted species.

These qualitative estimates were confirmed by the results of quantum-chemical calculations of various *exo*- and *endo*-complexes ($C_{60}R_5Li$, R = H, Cl, Br; $C_{60}H_5XCp$, X = Si, Ge, Sn, Pb, Fe; $2\eta^5$-$Fe@C_{40}H_{10}$; $2\eta^5$-$Fe@C_{40}H_{30}$)[3,6,9—13] and by the synthesis of half-sandwich η^5-π-complexes of a cyclopentadienyl derivative of C_{60} fullerene, $C_{60}Ph_5$, with Li, Tl, and In atoms (see Ref. 4). Complex $C_{60}Ph_5Tl$ was structurally characterized by X-ray diffraction analysis. Further quantum-chemical calculations of this complex revealed closeness of the calculated and experimental geometric parameters.[6]

η^5-π-Complexes of polyhedral molecules can also be stabilized by replacing the C atoms in the α-positions relative to the *pent** face by the atoms of some Group III—V elements.[7,8] Stable complexes can also be formed[9] if the XCp (X = Si, Ge, Sn) species is involved in

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η^5-π-coordination to each of 12 pentagonal faces of C_{60} fullerene, where the fullerene π-system "acts" as a single whole and each pentagonal face represents an analog of Cp radical. The energies of the X—*pent** bonds in the $C_{60}(XCp)_{12}$ complexes are comparable with those of the X—Cp bonds in the classical XCp_2 sandwich systems.

In this work, we discuss the problem of existence of η^4-π-complexes of fullerene derivatives. To this end, we simulated the molecular and electronic structure of some hypothetical complexes formed by the C_{60} fullerene and corannulene ($C_{20}H_{10}$) molecules and representing analogs of classical η^4-π-complexes $C_4H_6Fe(CO)_3$ (**1**) and $C_5H_6Fe(CO)_3$ (**2**), namely, the systems $C_{20}H_{14}Fe(CO)_3$ (**3**), $C_{20}H_{16}Fe(CO)_3$ (**4**), $C_{60}H_4Fe(CO)_3$ (**5**), and $C_{60}H_6Fe(CO)_3$ (**6**) (Figs. 1—3) by the Hartree—Fock (HF) and density functional (DFT) methods.

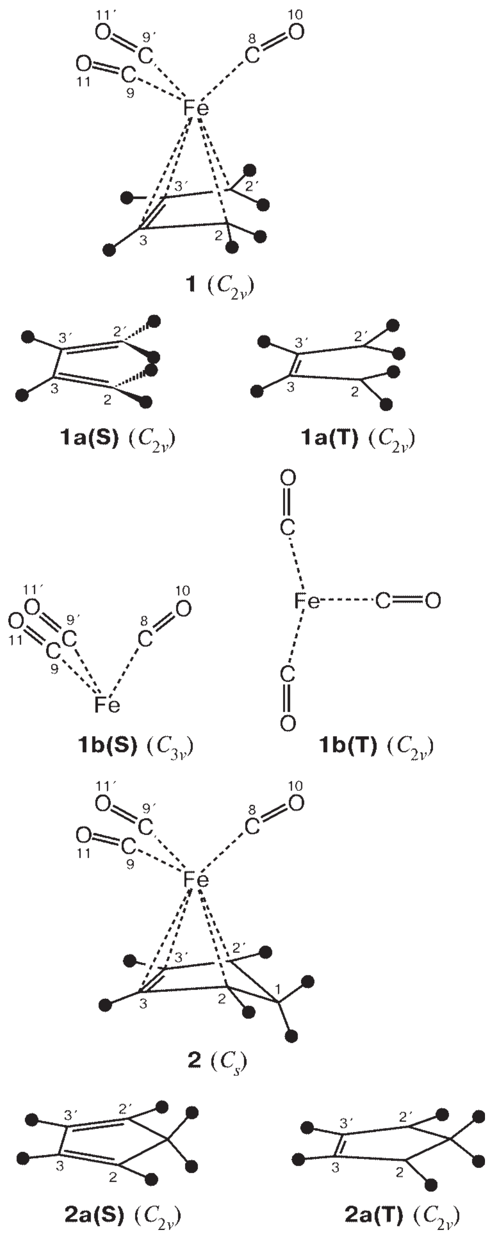
Fragments C_4H_6 (**1a**), $Fe(CO)_3$ (**1b**), and C_5H_6 (**2a**) are constituents of the complexes **1** and **2**. The corannulene and C_{60} fullerene derivatives, *viz.*, molecules $C_{20}H_{14}$ (**3a**), $C_{20}H_{16}$ (**4a**), $C_{60}H_4$ (**5a**), and $C_{60}H_6$ (**6a**) can be considered as ligands in complexes **3**—**6**, respectively. In molecules **3a** and **5a**, four H atoms are attached to the C atoms in the α-positions relative to the five-membered ring (denoted as *pent** in the case of C_{60} fullerene). In molecules **4a** and **6a**, five H atoms are attached to the C atoms that also occupy the α-positions with respect to the five-membered ring, while the sixth H atom is bound to one of the cycle atoms.

In complexes **3**—**6**, the Fe atoms interact with the tetraatomic carbon fragments (*but**) of the five-membered rings, separated out from the corresponding hydrocarbon ligand cages by H atoms.

Calculation Procedure

When carrying out nonempirical quantum-chemical calculations of transition metal complexes, it is strongly recommended to use extended basis sets and the Møller—Plesset perturbation theory.[15,16] However, sometimes satisfactory description of system's geometry cannot be obtained even at this level of theory. Here, we concern with the relative estimates of the energy and structural parameters of the complexes under study taking into account that some of them can contain a large number of atoms (up to 70 atoms and one of them can be the Fe atom). Therefore, we initially restricted ourselves to the 3-21G basis set[17,18] for both C atoms and the Fe atom, thus hoping for a compromise between the accuracy of calculations and the computational cost. Then, we carried out additional HF calculations of relatively small model systems **1** and **2** with an extended (triple zeta valence, TZV) basis set for the Fe atom. More accurate calculations of complexes **1**—**6** and their fragments were carried out by the DFT method using the PBE exchange-correlation functional.[19]

Density functional calculations of the total energies were carried both without (E_{tot}) and with inclusion of zero-point vibrational energy correction ($E_{tot}{}^0$) using the triple zeta basis set augmented with two polarization functions (TZ2P).[20] This allowed comparison of our results with those obtained in the calculations of analogous systems containing second-row and third-row transition metal atoms, though the systems containing the Fe atom could be calculated with the triple zeta (TZ) basis set in order to shorten the computing time.[21] The characters of the stationary points were determined from the number of negative eigenvalues of the Hessian.



1 (C_{2v})

1a(S) (C_{2v}) **1a(T)** (C_{2v})

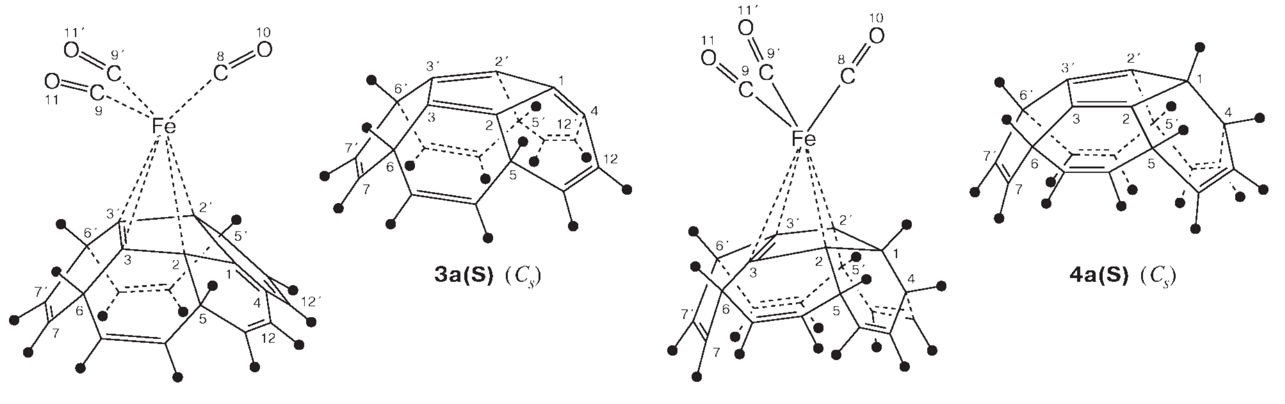
1b(S) (C_{3v}) **1b(T)** (C_{2v})

2 (C_s)

2a(S) (C_{2v}) **2a(T)** (C_{2v})

Fig. 1. Molecular structures of complexes $C_4H_6Fe(CO)_3$ (**1**), $C_5H_6Fe(CO)_3$ (**2**), and their fragments: C_4H_6 (**1a**), $Fe(CO)_3$ (**1b**), and C_5H_6 (**2a**) in the singlet (S) and triplet (T) states.

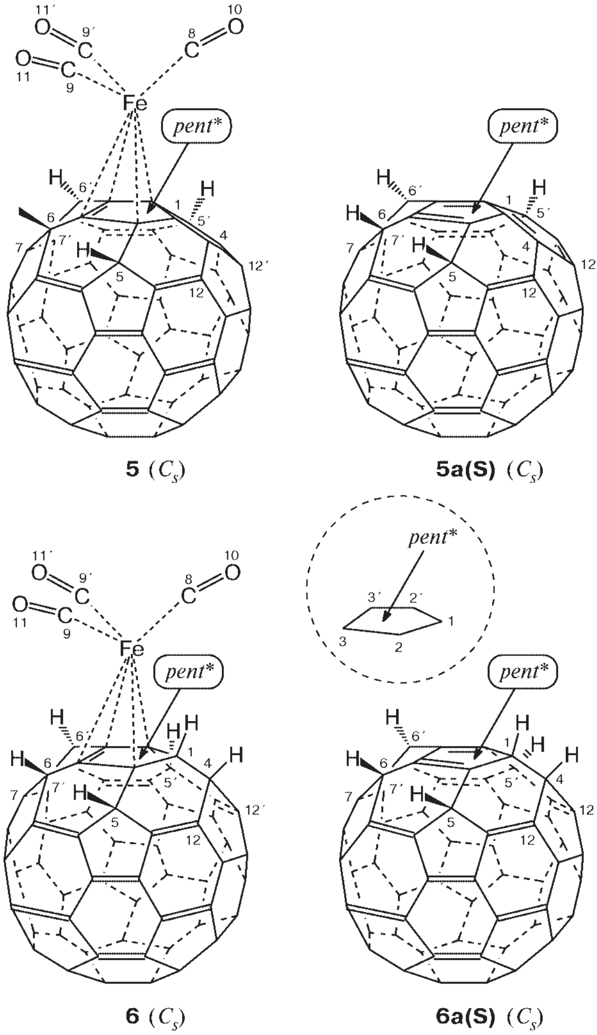
The electron density distribution and the MO structure were, as a rule, analyzed using the MOs and the Mulliken effective atomic charges obtained from HF calculations. Mention may be made that in the PBE approximation the effective charges are defined as the integrals of the electron density over the specified spatial region. In this case, diffuse d-orbitals can contribute



3 (C_s) **3a(S)** (C_s) **4** (C_s) **4a(S)** (C_s)

Fig. 2. Molecular structures of complexes $C_{20}H_{14}Fe(CO)_3$ (**3**) and $C_{20}H_{16}Fe(CO)_3$ (**4**) and their fragments $C_{20}H_{14}$ (**3a**) and $C_{20}H_{16}$ (**4a**) in the singlet (S) state.

largely to the charges on another atoms. Therefore, the atomic charges on Fe obtained from DFT calculations are close to zero.



5 (C_s) **5a(S)** (C_s) **6** (C_s) **6a(S)** (C_s)

Fig. 3. Molecular structures of complexes $C_{60}H_4Fe(CO)_3$ (**5**) and $C_{60}H_6Fe(CO)_3$ (**6**) and their fragments $C_{60}H_4$ (**5a**) and $C_{60}H_6$ (**6a**) in the singlet (S) state.

Calculations were carried out using the GAMESS (US)[22] (on a DEC 3000 AXP-400X workstation), PC GAMESS* (on a PC with Pentium®-III CPU), and GAUSSIAN 94 (for large systems) program packages[23] on a SGI Power Challenge supercomputer server (at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences). Density functional calculations were performed using the PRIRODA program.[24]

Results and Discussion

Complexes $C_4H_6Fe(CO)_3$ (1) and $C_5H_6Fe(CO)_3$ (2) and their fragments C_4H_6 (1a), C_5H_6 (2a), and $Fe(CO)_3$ (1b). The chemical and physicochemical properties of diene complexes with the $Fe(CO)_3$ species have been documented in a number of monographs and reviews (see Refs. 25 and 26 and references cited therein).

The electronic structure of complex **1** was studied by various quantum-chemical methods including the *ab initio* HF method. However, we succeeded only in finding the results of *ab initio* calculations of this system with the 3G basis set[27] using the experimental (non-optimized) geometric parameters obtained from X-ray studies.[28] Therefore, we will first dwell on the results of our HF/3-21G and DFT calculations of complexes **1** and **2**.

In these complexes, the π-system of each hydrocarbon ligand, namely, *cis*-butadiene (**1a**) and cyclopentadiene (**2a**) molecule involves four π-electrons. The molecular structures of **1a** and **2a** in the singlet ground state (**1a(S)** and **2a(S)**, respectively) have a C_{2v} symmetry. Each of them has two double bonds, C(2)—C(3) and C(2´)—C(3´) (see Fig. 1). The structures of the same molecules in the triplet state (**1a(T)** and **2a(T)**, respectively) also have a C_{2v} symmetry. According to calculations, their total energies, E_{tot}, are higher than those of corresponding singlet states by ~40 (HF/3-21G) and ~50 kcal mol^{-1} (DFT) (Table 1). The transition from the singlet ground state to the triplet

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* A. A. Granovsky, this material can be accessed *via* the Internet at URL http://www.classic.chem.msu/gran/gamess/index.html.

Table 1. Energy characteristics of η^4-π-complexes **1—6** and their fragments obtained from DFT calculations with the TZ2P basis set

Complex or fragment	$-E_{\text{tot}}$	$-E_{\text{tot}}{}^0$	ΔE_{S} (δE)	$\Delta E_{\text{S}}{}^0$	$-E_{\text{HOMO}}$	$-E_{\text{LUMO}}$
	au		kcal mol^{-1}		eV	
$C_4H_6Fe(CO)_3$ (**1**)	1768.7302	1768.6187	79.2	76.1	5.8	2.1
$C_4H_6Fe(CO)_3$ (**1´**)	1768.7161	1768.6053	70.3	67.7	5.3	2.3
C_4H_6 (**1a(S)**)	155.8963	155.8135	(0)	(0)	5.7	2.1
C_4H_6 (**1a(T)**)	155.8130	155.7350	(52.2)	(49.2)	3.4 (α), 7.4 (β)	−1.9 (α), 4.3 (β)
$Fe(CO)_3$ (**1b(S)**)	1612.7076	1612.6838	(8.6)	(9.5)	5.5	4.7
$Fe(CO)_3$ (**1b(T)**)	1612.7213	1612.6989	(0)	(0)	5.5 (α), 3.4 (β)	3.9 (α), 4.3 (β)
$C_5H_6Fe(CO)_3$ (**2**)	1806.8196	1806.7016	70.7	67.9	5.6	2.2
C_5H_6 (**2a(S)**)	193.9992	193.9095	—	—	5.2	1.4
$C_{20}H_{14}Fe(CO)_3$ (**3**)	2382.8828	2382.5921	68.3	69.0	4.2	2.6
$C_{20}H_{14}$ (**3a(S)**)	770.0663	769.7983	—	—	4.6	2.9
$C_{20}H_{16}Fe(CO)_3$ (**4**)	2384.0582	2383.7437	51.2	57.0	4.9	2.4
$C_{20}H_{16}$ (**4a(S)**)	771.2594	770.9690	—	—	4.6	1.4
$C_{60}H_4Fe(CO)_3$ (**5**)	3900.5195	—	69.0	—	5.0	3.7
$C_{60}H_4$ (**5a(S)**)	2287.7018	—	—	—	5.5	4.0
$C_{60}H_6Fe(CO)_3$ (**6**)	3901.6862	—	39.3	—	5.2	3.7
$C_{60}H_6$ (**6a(S)**)	2288.9160	—	—	—	5.4	3.5

Note. E_{tot} is the total energy, $E_{\text{tot}}{}^0$ is total energy calculated with inclusion of zero-point vibrational energy correction, ΔE_{S} is the dissociation energy of complex **n** (**n** = **1—6**) into fragments **na(S)** and **1b(S)** (see Eq. (1)), $\Delta E_{\text{S}}{}^0$ denotes the dissociation energy calculated with inclusion of zero-point vibrational energy correction (see Eq. (3)), δE is the energy difference between the lowest triplet and singlet states (figures in parentheses), E_{HOMO} and E_{LUMO} are the energies of the highest occupied and lowest unoccupied MOs, respectively, and α and β are the spin projections.

state is accompanied by significant changes in the molecular geometry: the C(2)—C(3) and C(2´)—C(3´) double terminal bonds become ordinary bonds, while the C(3)—C(3´) ordinary bond becomes a double bond. DFT calculations substantially smooth this effect (Table 2). The carbon skeleton of structure **2a(T)** remains planar.

According to HF/3-21G-calculations, two orbitals in each of the molecules **1a(S)** and **2a(S)**, namely, ψ_{12} and ψ_{15} in the former and ψ_{17} and ψ_{18} in the latter molecule are suitable for η^4-bonding with the $Fe(CO)_3$ species (**1b**). They are characterized by relatively high populations of the C(2), C(2´), C(3), and C(3´) atoms of the butadiene fragment. The major contributions to these orbitals come from the p_z-AOs (Table 3). In the triplet states of molecules **1a** and **2a** (**1a(T)** and **2a(T)**, respectively) the spin population is completely determined by the p_z-orbitals and mainly localized on the C(2) and C(2´) atoms (0.91 au for **1a(T)** and 0.89 au **2a(T)**). Therefore, both molecules **1a** and **2a** in the triplet states can form η^4-bonds and the C(2)—Fe and C(2´)—Fe bonds must be stronger than the C(3)—Fe and C(3´)—Fe bonds. A feature of the results obtained from DFT calculations is that the spin populations of the C(3) and C(3´) atoms in the triplet states **1a(T)** and **2a(T)** are also relatively high, which should lead to equalization of the Fe—C(2) and Fe—C(3) bond lengths.

The $Fe(CO)_3$ species (**1b**) has a triplet ground state. This corresponds to a T-shaped structure **1b(T)** with C_{2v} symmetry (see Fig. 1). The energy characteristics and geometric parameters of the triplet and singlet states of the species **1b** having a structure with C_{3v} symmetry are listed in Tables 1 and 2. In both cases, the bonding between the Fe atom and the C atoms of carbonyl groups involves three MOs. The corresponding bond orders do not exceed 0.548 au for **1b(T)** and equal 0.442 au for **1b(S)**. In the triplet state **1b(T)**, two unpaired electrons occupy the $3d_{xz}$- and $3d_{xy}$-orbitals of the Fe atom. The corresponding spin populations for each of these orbitals are 0.91 au (DFT calculations, Table 4).

According to HF/3-21G calculations, the Fe atom of the group $Fe(CO)_3$ interacts with the butadiene fragments of complexes **1** and **2** involving three MOs (see Table 3) composed mainly of the $3d_{xz}$- and $3d_{yz}$-orbitals of the Fe atom and of the $2p_\pi$-orbitals of C atoms of the butadiene fragments. Complexes **1** and **2** are characterized by transfer of the electron density (of the order of 1 e) from the Fe atom to C atoms of the C(2)—C(3)—C(3´)—C(2´) fragment.

Similarly to triplet states **1a(T)** and **2a(T)**, the bond length distribution in the diene fragments of singlet complexes **1** and **2**, obtained from HF/3-21G calculations is inconsistent with the experimental data[26] and the results of DFT calculations. In addition, the Fe—C(2) bond was found to be shorter than the Fe—C(3) bond, whereas the reverse is observed in the experiment. Hartree—Fock calculations using extended basis sets (6-31G and 6-31G*;

Table 2. Bond lengths (*d*) in η^4-π-complexes **1—6** and their fragments and the C(3)—C(2′)—C(2)—C(1) torsion

Complex or fragment								*d*/Å
	Fe—C(1)	Fe—C(2)	Fe—C(3)	Fe—C(8)	Fe—C(9)	C(8)—O	C(9)—O	C(1)—C(2)
$C_4H_6Fe(CO)_3$ (**1**)		2.119 [2.14]	2.068 [2.06]	1.774 [1.74]	1.777 [1.77]	1.159 [1.13]	1.160 [1.13]	—
$C_4H_6Fe(CO)_3$ (**1′**)		2.161	2.075	1.756	1.779	1.163	1.161	—
C_4H_6 (**1a(S)**)	—	—	—	—	—	—	—	—
C_4H_6 (**1a(T)**)	—	—	—	—	—	—	—	—
$Fe(CO)_3$ (**1b(S)**)	—	—	—	1.710	1.774	1.165	1.165	—
$Fe(CO)_3$ (**1b(T)**)	—	—	—	1.788	1.838	1.163	1.158	—
$C_5H_6Fe(CO)_3$ (**2**)	2.681	2.129	2.064	1.779	1.776	1.160	1.161	1.522
C_5H_6 (**2a(S)**)	—	—	—	—	—	—	—	1.500
$C_{20}H_{14}Fe(CO)_3$ (**3**)	2.532	2.215	2.101	1.801	1.767	1.158	1.162	1.436
$C_{20}H_{14}$ (**3a(S)**)	—	—	—	—	—	—	—	1.443
$C_{20}H_{16}Fe(CO)_3$ (**4**)	2.646	2.218	2.082	1.787	1.768	1.161	1.162	1.530
$C_{20}H_{16}$ (**4a(S)**)	—	—	—	—	—	—	—	1.510
$C_{60}H_4Fe(CO)_3$ (**5**)	2.423	2.212	2.114	1.802	1.772	1.154	1.158	1.445
$C_{60}H_4$ (**5a(S)**)	—	—	—	—	—	—	—	1.459
$C_{60}H_6Fe(CO)_3$ (**6**)	2.658	2.382	2.090	1.805	1.760	1.159	1.162	1.551
$C_{60}H_6$ (**6a(S)**)	—	—	—	—	—	—	—	1.522

Note. The atomic numbering schemes are shown in Figs. 1—3. The experimental values taken from Ref. 28 are given

Table 3. Contributions (populations) of X atoms (ρ[X]) to the HOMOs, responsible for the bonding interaction Fe—*but** and the MO energies calculated with respect to the HOMO energy level (*E*(MO)) in complexes **1—6** and their fragments obtained from RHF/3-21G calculations

Complex or fragment	MO	−*E*(MO)	ρ[Fe]	ρ[C(2)], ρ[C(2′)]	ρ[C(3)], ρ[C(3′)]
		au			
1	30	0.5237	0.53	0.23	0.28
1	45	0.3296	0.34	0.65	0.13
1	47	0.2743	0.49	0.44	0.24
1a(S)	12	0.4445	—	0.37	0.03
1a(S)	15	0.3257	—	0.64	0.31
2	36	0.6697	0.40	0.27	0.31
2	50	0.6602	0.36	0.64	0.15
2	51	0.2462	0.57	0.41	0.17
2a(S)	17	0.4143	—	0.22	0.60
2a(S)	18	0.3118	—	0.65	0.35
3	99	0.3220	0.27	0.53	0.10
3	100	0.3049	0.24	0.12	0.31
3	101	0.1940	0.21	0.18	0.04
3a(S)	61	0.4214	—	0.13	0.21
3a(S)	66	0.2823	—	0.59	0.29
3a(S)	67	0.2794	—	0.00	0.25
4	91	0.4360	0.37	0.14	0.20
4	92	0.4345	0.40	0.16	0.14
4	102	0.2307	0.49	0.38	0.17
4a(S)	62	0.3891	—	0.17	0.43
4a(S)	68	0.2823	—	0.56	0.30
5	204	0.3640	0.31	0.57	0.11
5	205	0.3662	0.12	0.04	0.16
5	216	0.2236	0.08	0.10	0.03
5a(S)	176	0.3315	—	0.54	0.28
5a(S)	182	0.2891	—	0.00	0.06
6	203	0.4311	0.18	0.06	0.32
6	210	0.3326	0.22	0.48	0.09
6	217	0.2547	0.39	0.44	0.16
6a(S)	177	0.3260	—	0.19	0.46
6a(S)	177	0.2921	—	0.04	0.02

up to the use of the TZV basis set for the Fe atom) lead to analogous results. The maximum deviation of the Fe—C(*but**) and C—C bond lengths from the experimental values in complex **1** (see Table 2) is 0.25 and 0.08 Å (HF), respectively, and does not exceed 0.03 Å for all the bonds in the case of DFT calculations.

The energy (Δ*E*) of the bond between the Fe atom and the butadiene fragment in complexes **1—6** was estimated as the energy of dissociation into singlet (ΔE_S)

$$\Delta E_S(\mathbf{n}) = E_{tot}(\mathbf{na(S)}) + E_{tot}(\mathbf{1b(S)}) - E_{tot}(\mathbf{n}) \quad (1)$$

or triplet (ΔE_T) fragments:

$$\Delta E_T(\mathbf{n}) = E_{tot}(\mathbf{na(T)}) + E_{tot}(\mathbf{1b(T)}) - E_{tot}(\mathbf{n}), \quad (2)$$

$\mathbf{n} = \mathbf{1}$—$\mathbf{6}$.

angles (τ) calculated by the DFT/TZ2P method

C(2)—C(3)	C(3)—C(3´)	C(1)—C(4)	C(2)—C(5)	C(3)—C(6)	C(6)—C(7)	C(7)—C(7´)	τ /deg
1.428	1.417	—	—	—	—	—	—
[1.46]	[1.45]						
1.418	1.430	—	—	—	—	—	—
1.343	1.463	—	—	—	—	—	—
1.443	1.368	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
1.432	1.427	—	—	—	—	—	146
1.355	1.463	—	—	—	—	—	
1.430	1.420	1.361	1.498	1.490	1.520	1.342	158
1.370	1.453	1.370	1.485	1.487	1.519	1.342	174
1.423	1.404	1.550	1.504	1.495	1.528	1.343	159
1.351	1.452	1.550	1.487	1.490	1.520	1.342	−173
1.436	1.423	1.376	1.517	1.507	1.535	1.380	167
1.372	1.469	1.371	1.507	1.504	1.522	1.380	178
1.423	1.428	1.549	1.535	1.511	1.526	1.376	179
1.356	1.464	1.552	1.502	1.503	1.530	1.381	−168

in brackets.

Table 4. Effective atomic charges (q_X) and spin populations (in brackets) calculated by the DFT/TZ2P method

Structure	q_{Fe}	$q_{C(1)}$	$q_{C(2)}$	$q_{C(3)}$	$q_{C(8)}$	$q_{C(9)}$	$q_{O(10)}$	$q_{O(11)}$
	au							
$C_4H_6Fe(CO)_3$ (**1**)	0.01	—	−0.08	−0.03	0.08	0.09	−0.12	−0.13
C_4H_6 (**1a(S)**)	—	—	−0.09	−0.04	—	—	—	—
C_4H_6 (**1a(T)**)	—	—	−0.07 [0.64]	−0.05 [0.25]	—	—	—	—
$Fe(CO)_3$ (**1b(S)**)	0.15	—	—	—	0.09	0.05	−0.11	−0.11
$Fe(CO)_3$ (**1b(T)**)	0.11 [1.83]	—	—	—	0.05 [−0.02]	0.07 [0.07]	−0.12 [−0.04]	−0.09 [0.04]
$C_5H_6Fe(CO)_3$ (**2**)	0.00	−0.07	−0.04	−0.04	0.09	0.09	−0.12	−0.12
C_5H_6 (**2a(S)**)	—	−0.07	−0.05	−0.06	—	—	—	—
C_5H_6 (**2a(T)**)	—	−0.08 [0.08]	−0.02 [0.61]	−0.06 [0.23]	—	—	—	—
$C_{20}H_{14}Fe(CO)_3$ (**3**)	−0.00	0.00	0.01	0.00	0.09	0.09	−0.11	−0.12
$C_{20}H_{14}$ (**3a(S)**)	—	−0.01	−0.02	−0.02	—	—	—	—
$C_{20}H_{16}Fe(CO)_3$ (**4**)	−0.01	−0.03	+0.00	−0.00	0.08	0.08	−0.13	−0.13
$C_{20}H_{16}$ (**4a(S)**)	—	−0.03	−0.01	−0.01	—	—	—	—
$C_{60}H_4Fe(CO)_3$ (**5**)	0.01	0.01	0.03	0.01	0.09	0.10	−0.10	−0.10
$C_{60}H_4$ (**5a(S)**)	—	−0.01	−0.02	−0.01	—	—	—	—
$C_{60}H_6Fe(CO)_3$ (**6**)	0.00	−0.03	0.03	−0.01	0.07	0.07	−0.13	−0.13
$C_{60}H_6$ (**6a(S)**)	—	−0.02	0.00	−0.01	—	—	—	—

When performing density functional calculations with inclusion of zero-point vibrational energy correction (the corresponding parameters are labeled by superscript "0"), the $\Delta E_S{}^0$ and $\Delta E_T{}^0$ values for the Fe—*but** bond were estimated by the formulae:

$$\Delta E_S{}^0(\mathbf{n}) = E_{tot}{}^0(\mathbf{na(S)}) + E_{tot}{}^0(\mathbf{1b(S)}) - E_{tot}{}^0(\mathbf{n}), \qquad (3)$$

$$\Delta E_T{}^0(\mathbf{n}) = E_{tot}{}^0(\mathbf{na(T)}) + E_{tot}{}^0(\mathbf{1b(T)}) - E_{tot}{}^0(\mathbf{n}). \qquad (4)$$

The results of calculations for complexes **1** and **2** are listed in Table 5.

Analysis of the results obtained shows that, first, decomposition of each complex (**1** and **2**) into triplet fragments requires a considerable expenditure of energy and therefore there is no point in performing analogous estimation for large systems **3—6**; second, the energies of the bond between the Fe atom and the butadiene fragment

Table 5. Energies of the Fe—*but** bond in complexes **1** and **2** calculated using Eqs. (1)—(4)

Complex	Method	ΔE_S(**n**)	ΔE_S^0(**n**)	ΔE_T(**n**)	ΔE_T^0(**n**)
		kcal mol^{-1}			
$C_4H_6Fe(CO)_3$ (**1**)	HF/3-21G	78.3	—	108.2	—
	DFT-PBE	79.2	76.1	122.8	115.9
$C_5H_6Fe(CO)_3$ (**2**)	HF/3-21G	66.7	—	99.9	—
	DFT-PBE	70.7	67.9	119.0	113.7

calculated by both methods using Eq. (1) are nearly equal (the difference is less than 4 kcal mol^{-1}); and third, the inclusion of zero-point vibrational energy correction reduces these energies by ~4 kcal mol^{-1}.

Taking into account that the fragment **1b** has a triplet ground state, the formula for calculating the ΔE value has the form:

$$\Delta E(\mathbf{n}) = E_{\text{tot}}(\mathbf{na(S)}) + E_{\text{tot}}(\mathbf{1b(T)}) - E_{\text{tot}}(\mathbf{n}). \quad (5)$$

Applying formula (5) to complexes **1** and **2**, we get the following estimates of the energy of the bond between the Fe atom and the butadiene fragment in these systems (ΔE/kcal mol^{-1}): 88.8 (HF/3-21G) and 87.8 (DFT) for complex **1** and 77.2 (HF/3-21G) and 76.5 (DFT) for complex **2**. As can be seen, the bond energies ΔE(**n**) calculated by both methods differ by at most 1.0 kcal mol^{-1}.

This allows one to some extent "rehabilitate" the HF/3-21G method when studying the problem of stability of transition metal complexes and serves as empirical substantiation of the possibility of using this approximation when estimating the stability of the molecules of hypothetical chemical compounds. In the text below the geometric parameters were calculated only by the DFT method, while the HF/3-21G method was used for the analysis of the chemical bonds.

It should be noted that complex **1** has a rotamer **1´**, which can be obtained from **1** by rotating the $Fe(CO)_3$ group by 180° with respect to the symmetry axis. The energy of **1´** is 25 (HF) and 10 kcal mol^{-1} (DFT) higher than that of **1**, while the degree of transfer of electron density from the Fe atom to the C(2)—C(3)—C(3´)—C(2´) fragment is somewhat lower (by 0.11 au according to HF calculations). The C(3)—C(3´) bond in the butadiene fragment of complex **1´** is longer than the corresponding bond in complex **1** and even longer than the C(2)—C(3) bond (DFT calculations). Judging from the lengths and orders of the Fe—C(2) and Fe—C(3) bonds, they are weaker than corresponding bonds in complex **1** (see Table 2). This isomer should also have analogs for all other complexes (**2—6**); however, no consideration of such systems was made in this work.

Hydrocarbon ligands $C_{20}H_{14}$ (3a) and $C_{60}H_4$ (5a) in complexes 3 and 5. The optimized energy, geometric, and charge characteristics of the species **3a** and **5a** and the spin populations in the singlet states are listed in Tables 1—4.

In Figure 2 we present the molecular structures of **3a** and **5a** in the singlet states (**3a(S)** and **5a(S)**, respectively). The structures of **3a** and **5a** in the triplet states differ from those shown in Fig. 2 in distribution of simple and double bonds in the five-membered rings separated by CH groups (two double bonds, C(2)—C(3) and C(2´)—C(3´), for **3a(S)** and **5a(S)** and one double bond for the triplet states **3a(T)** and **5a(T)**). In addition, structures **3a(S)** and **5a(S)** contain nonplanar fulvene-like fragments C(4)—C(1)—C(2)—C(3)—C(3´)—C(2´) in which the angles between the C(1)—C(4) bond and the plane passing through the atoms of the *but** fragment are equal to 31° (**3a(S)**) and 24° (**5a(S)**). In the triplet states, the C(1)—C(4) bond is appreciably lengthened (see Table 2).

Analysis of the MO structure of systems **3a(S)** and **5a(S)** performed by the HF method showed that the set of FMOs includes two orbitals for which the populations of the atoms of the *but** fragments in the above-mentioned quasi-fulvene moieties are rather high and nearly completely determined by the contributions of p_z-AOs (see Table 3). For molecule **3a(S)**, these are the ψ_{66} orbital (the populations of the C(2) and C(2´) atoms are 0.59 au and those of the C(3) and C(3´) atoms are 0.29 au) and the ψ_{67}-HOMO (with highly populated atoms C(1) and C(4) and relatively high population of the C(3) and C(3´) atoms, see Table 3). Considering the HOMO, it should be noted that the populations of the C(1) and C(4) atoms have small contributions of the p_z-AO due to the large deviation of the line of the C(1)—C(4) bond from the plane passing through the atoms of the *but** fragment (by 36°). This indicates incomplete separation of the π-system of the butadiene fragment. Analogously, the orbitals ψ_{176} and ψ_{182}-HOMO of molecule **5a(S)** are characterized by high population of the C atoms of the *but** fragment. Based on comparison of the FMOs of molecules **3a** and **5a** with those of molecules **1a** and **2a** and on the analysis of spin population distribution in the corresponding triplet states, one can suggest that molecules **3a** and **5a** can form η^4-π-complexes with transition metals.

From the data listed in Table 3 it follows that, unlike molecules **1a** and **2a**, no complete separation of the π-system of the *but** fragment from the overall π-system occurs in molecules **3a** and **5a** (there is a small contribution of π-orbitals of the C(1) and C(4) atoms). Because of this, below we will also consider the molecules characterized by complete separation of the π-system of the *but** fragment.

Hydrocarbon ligands $C_{20}H_{16}$ (4a) and $C_{60}H_6$ (6a) in complexes 4 and 6. Molecules **4a** and **6a** differ from **3a** and **5a**, respectively, in two H atoms attached to the C(1) and C(4) atoms (see Fig. 2). Because of this, the C(1)—C(4) double bond becomes ordinary, these atoms are no longer involved in the conjugated system, and the

π-system of the *but** fragment becomes completely separated. Molecules **4a** and **6a** have singlet ground states. Their geometry is described by structures **4a(S)** and **6a(S)**, respectively (see Figs. 2 and 3 and Tables 1 and 2). Two MOs (ψ_{62} and ψ_{68}-HOMO) of molecule **4a**, suitable for η^4-bonding are characterized by rather high populations of the C(2) and C(3) atoms. For molecule **6a**, an analogous role is played by the ψ_{177} and ψ_{182} orbitals (see Table 3). However, the ψ_{182} orbital has small contributions of p_z-orbitals of the atoms of the *but** fragment. Therefore, molecule **6a** can serve a ligand in complex **6**; however, the type of the Fe—*but** bond is intermediate between η^2 and η^4.

Complex $C_{20}H_{14}Fe(CO)_3$ (3). The effective atomic number of the Fe atom in this complex is 18 (eight electrons of the Fe atom, six electrons from three lone electron pairs (LEP) of C atoms of the carbonyl groups, and four electrons from the $C_{20}H_{14}$ fragment). Therefore, in accordance with the effective atomic number rule complex **3** should be stable. By performing full optimization of the geometry of this system by the HF/3-21G and DFT methods we located local minima of the total energy corresponding to structures with C_s symmetry (see Fig. 3). The energy and charge characteristics of complex **3** obtained from DFT calculations are listed in Table 1 while the calculated geometric parameters are listed in Table 2. The distances from the C(2), C(2´), C(3), and C(3´) atoms of the *but** fragment to the Fe atom lie between 2.101 and 2.215 Å (see Fig. 2, Table 2). The overall order of the η^4-bond calculated by the HF/3-21G method is 1.456 au. This indicates that the η^4-bond in complex **3** is rather strong. The Fe—CO bonds were found to be much shorter and their lengths are close to experimental values for complex **1**.

The formation of complex **3** is accompanied by significant changes in the geometry of the constituent fragment **3a**: the angle of folding of the *pent** ring along the C(2)—C(2´) line increases from 5 to 34° and the C(2)—C(2´)—C(1)—C(4)—C(12)—C(12´) fragment becomes nearly planar (the C(2)—C(1)—C(4)—C(12´) torsion angle increases to 170°), while the C(3)—C(3´) bond becomes a double bond; the bonds of the C(2)—C(3) type are appreciably lengthened.

Bonding between the Fe atom and the *but** fragment in complex **3** occurs involving mainly three upper occupied orbitals, namely, ψ_{99}, ψ_{100}, and ψ_{101}-HOMO. They represent bonding orbitals toward the Fe atom and the atoms of the butadiene fragment. The populations of the Fe, C(2), and C(3) atoms and those of the corresponding symmetrical atoms with respect to the symmetry plane are listed in Table 3. The HOMO is a bonding orbital toward the C(1) and C(4) atoms (the populations of these atoms are 0.52 and 0.26 au, respectively) and an antibonding orbital toward the C(1)—Fe and C(4)—Fe bonds. The effective atomic charge of Fe is 1.25 au; this charge is nearly completely (1.17 au) transferred to the fragment **3a**.

The energy of the Fe—*but** bond in complex **3** estimated as the energy of dissociation into singlet fragments **3a(S)** and **1b(S)** using Eq. (1) is 68 kcal mol^{-1} (DFT calculations). The inclusion of zero-point vibrational energy correction increases this value by 1 kcal mol^{-1}.

Complex $C_{20}H_{16}Fe(CO)_3$ (4). Complex **4** has a structure with C_s symmetry (see Fig. 2). Three orbitals of this complex (ψ_{91}, ψ_{92} and ψ_{102}-HOMO, see Table 3) have considerable contributions of the orbitals of the Fe atom and C atoms of the *but** fragment. This results in the formation of the η^4-bond with a rather high energy (51 kcal mol^{-1} according to DFT calculations). Nevertheless, this is ~20 kcal mol^{-1} lower than the energy of analogous bond in complex **3**. The overall order of the η^4-bond also was found to be somewhat lower, namely, 1.404 au (HF/3-21G). Thus, a greater extent of separation of the conjugated system of the *but** fragment from the overall conjugated system of the corannulene molecule did not lead to strengthening of the η^4-bond.

Upon the formation of η^4-π-complex, the *pent** ring undergoes a large deformation. The angle of folding along the C(2)—C(2´) line increases from −7 to 33° (in molecule **4a**, the C(1) atom lies above the plane of the face containing the atoms of the *but** fragment) and the C(3)—C(3´) bond is shortened (even to a greater extent than in complex **1**). In complex **4**, the C(2)—C(2´)—C(3)—C(3´)—C(6)—C(6´) fragment containing the C(3)—C(3´) double bond becomes planar. Flexibility of the corannulene fragment allows its deformation to such extent that the H atom at the C(1) atom produces no steric hindrances to the bonding with the $Fe(CO)_3$ group. The effective charges on the Fe atom (1.15 au) and on the corannulene fragment (1.02 au) are smaller than the corresponding parameters of complex **3** (HF calculations). Similarly to calculations of complexes **1—3**, the DFT method leads to shorter Fe—CO bonds compared to the bond lengths obtained from HF calculations, shorter Fe—C(3) bonds compared to the Fe—C(2) bonds, and to more equalized bond lengths in the *but** fragment.

Complex $C_{60}H_4Fe(CO)_3$ (5). Optimization of the geometry complex **5** led to a structure with C_s symmetry (see Fig. 3). Since the C_{60} fullerene cage is more rigid than that of the corannulene molecule, the formation of η^4-complex is accompanied by less significant changes in the structure of molecule **5a**. The quasi-fulvene fragment of molecule **5a** has a nonplanar structure: the C(1)—C(4) bond deviates from the plane passing through the atoms of the *but** fragment by 31°. Upon the formation of complex **5** the C(2)—C(2´)—C(1)—C(4)—C(12)—C(12´) fragment remains nonplanar in contrast to the corresponding fragment in complex **3**.

The Fe—*but** bonding in complex **5** is due to the interaction between the LEP of the Fe atom of the $Fe(CO)_3$ species and the π-MOs ψ_{176} and ψ_{182}-HOMO of molecule **5a**, which results in the formation of three bonding MOs, namely, ψ_{204}, ψ_{205}, and ψ_{216}-HOMO (see Table 3). The η^4-bond energy estimated using Eq. (1) is 69 kcal mol^{-1} (DFT). Thus, the DFT method gives for complex **5** nearly the same value of the energy of the η^4-bond as for complex **3**. It should be noted that the HF method substantially overestimates this value.

Complex $C_{60}H_6Fe(CO)_3$ (6). Optimization of the geometry of complex **6** led to a structure with C_s symmetry (see Fig. 3). In this complex, the bonding between the Fe atom and the *but** fragment involves three MOs (ψ_{203}, ψ_{210}, and ψ_{217}-HOMO) and is due to the interaction between the LEP of the Fe atom of the $Fe(CO)_3$ species and two π-MOs of molecule **6a(S)** (see Table 3). The energy of this bond is relatively low (39 kcal mol^{-1} according to DFT calculations). This is lower than in analogous complex with corannulene and can be explained, first, by the fact that one of the two π-MOs (ψ_{182}) of molecule **6a** is characterized by very small contributions of the p_z-orbitals of the atoms of the *but** fragment and therefore the Fe—*but** bond is intermediate between η^4- and η^2-bonds (somewhat closer to η^2). Second, structure **6a** is more rigid compared to analogous derivative **4a** of corannulene molecule, which produces steric hindrances to the interaction the atom Fe and the nearest H atom (at the C(1) atom). The Fe—H distance (C(1)) is 2.395 Å (HF) and 2.609 Å (DFT).

According to HF calculations, in all complexes **1—6** the bonds between the Fe atom and the C(2) and C(2´) terminal atoms of butadiene fragments are shorter and, judging from their orders, stronger than the Fe—C(3) and Fe—C(3´) bonds. The overall orders of the Fe—*but** bond in complexes **1** and **2** (1.786 and 1.810 au, respectively) are much larger than those in complexes **3—6**; however, the energies of this bond are no higher than in other complexes (see Table 1).

Comparison of the energies of the η^4-π-bonds in complexes **1—6**, obtained from HF calculations with the energies of η^5-π-bonds in ferrocene molecule (110 kcal mol^{-1}) and η^5-π-$C_{60}H_5$FeCp (117 kcal mol^{-1})[12] and η^5-π-$C_{40}H_5$FeCp (116 kcal mol^{-1})[13] complexes (estimations were performed using the same method) shows that the η^4-π-bonds should be weaker than the η^5-π-bonds.

From the results of our HF and DFT calculations it follows that break of the overall conjugated system in the C_{60} fullerene molecule (or in its simplest bowl-shaped precursor, corannulene molecule) caused by the attachment of four H atoms (or other univalent groups) to the C atoms in the α-positions relative to the same five-membered ring favors the formation of more stable complexes with the $Fe(CO)_3$-type species.

Comparison of the results of HF/3-21G and DFT/TZ2P calculations of the classical complexes **1** and **2** shows that both methods give close values of the energies of η^4-π-bonds. However, the DFT method is characterized by much better reproduction of the geometric characteristics of the systems under study. Mention may be made that both methods also give reasonable values of the energies of the Fe—*but** bond in hypothetical complexes **3—6** (except for complex **5**).

In addition, the energies of η^4-π-bonds in the complexes of corannulene derivatives, **3** and **5**, are close to the energies of corresponding bonds in the complexes of fullerene derivatives, **4** and **6**. Hence, bowl-shaped molecules of the corannulene type and their corresponding derivatives can be considered as convenient models for prediction of the relative stability of different fullerene π-complexes.

Summing up, it should be mentioned our attempts at locating local energy minima for the η^4-π-complexes of unsubstituted C_{60} fullerene and corannulene molecule with the same species $Fe(CO)_3$ failed due to divergence of the self-consistency procedure at various realistic initial approximations for the molecular geometry. Probably, due to the presence of extended conjugated systems the η^4-π-complexes of corannulene and fullerene molecules are much less stable than, *e.g.*, complexes **3** and **5** in which the H atoms separate the conjugated butadiene-like subsystem, or are unstable at all.

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