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Metal complexes of allyl derivatives of C_{60} fullerene: molecular and electronic structure prediction from density functional calculations

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The problem of existence of η^3—π-complexes of C_{60} fullerene with transition metal atoms is discussed. The complexes $C_{60}R_3Co(CO)_3$ (R = H, F, Cl, Br), $C_{60}H_3NiCp$, and $C_{60}H_3Fe(CO)Cp$, where $C_{60}R_3$ is an allyl derivative of C_{60} fullerene, were shown to be sufficiently stable. In these complexes the metal atoms are η^3—π-bound to the fullerene cage. In contrast to this, the metal atoms in the $C_{60}H_3Li$ and $C_{60}H_3FeCp$ complexes are η^5–π-coordinated to the carbon cage. Density functional calculations were carried out with the Perdew—Burke—Ernzerhof exchange-correlation potential (PBE). It was concluded that the type of bonding in the complexes of allyl derivatives of C_{60} fullerene depends on the nature of the species attached. Among the systems studied, the maximum energy of the η^3–π-bond was obtained for the $C_{60}H_3NiCp$ complex. The results obtained can be useful in the design of synthesis of new fullerene derivatives with the η^3—π-coordination of the transition metal atoms to the carbon cage.

Key words: C_{60} fullerene, polyhedral carbon clusters, η^3—π-complexes, η^5—π-complexes, transition metal carbonyls, quantum-chemical calculations, density functional theory, DFT—PBE method.

The problem of existence of η^n—π-complexes of fullerenes with the transition metal atoms ($n > 2$) has been the subject of a considerable literature (see, *e.g.*, Refs. 1—11 and references cited therein). Earlier,[1,2,5,8] we have shown that the C_{60}, C_{70}, and higher fullerenes have strongly delocalized and weakly polarizable π-electron systems, which precludes the formation of sufficiently stable η^n—π-complexes of such fullerenes at $n > 2$. At the same time the attachment of several univalent functional groups (or atoms) to, *e.g.*, C_{60} fullerene results in break of

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the spherical conjugated system comprised of unsaturated C atoms of the polyhedral cage and in a decrease in its extent. This favors the formation of the η^3—π-, η^4—π-, η^5—π-, or η^6—π-complexes of the above-mentioned systems. Under particular conditions it is possible to divide the conjugated system of a fullerene into two or a larger number of independent fragments. The most appropriate way of stabilizing the η^n—π-complexes of fullerenes (*e.g.*, C_{60} fullerene) at $n > 2$ is to attach a number of univalent groups R to the C atoms in the α-positions relative to one five-membered ring. Using five groups R, one can obtain the cyclopentadienyl derivatives $C_{60}R_5$. Attachment of the sixth group R to one of the C atoms of the same ring results in a butadiene derivative $C_{60}R_6$. The butadiene (or fulvene) type derivatives can also be obtained by attaching four univalent groups to the C atoms in the α-positions. This allows one to synthesize analogs of both the classical cyclopentadienyl transition metal complexes[1—3,7—11] and the classical butadiene complexes $Fe(CO)_3C_4H_6$ (see Ref. 6). The efficiency of this procedure was demonstrated experimentally[3,4] by the synthesis of the first η^5-complexes of the cyclopentadienyl derivative of C_{60} fullerene, $C_{60}Ph_5$, with K, Li, and Tl atoms. Besides, the preparation of a ferrocene—C_{60} fullerene hybrid, the $C_{60}Me_5FeCp$ (Cp = C_5H_5) complex with η^5-coordination of the Fe atom to C_{60}, was reported recently.[11]

Attachment of three functional groups to the C atoms in the α-positions relative to three adjacent C atoms of the same five-membered ring in, *e.g.*, the C_{60} or C_{70} fullerenes allows one to separate the allyl fragments of these polyhedral clusters. In this case one should expect the formation of η^3—π-complexes. However, the known $MC_{70}Ar_3$ (M = Li, K, Tl) complexes exhibit the η^5-type of bonding.[7] This was also predicted by the HF/3-21G* calculations of the complex $C_{70}H_3K$. At the same time it was pointed out[7] that the type of bonding in the metal complexes of allyl derivatives of fullerenes can be strongly dependent on the nature of the species attached. Recently,[11] the synthesis of the $C_{70}Me_3FeCp$ molecule, ($C_{70}Me_3$ is the allyl derivative of C_{70} fullerene) was reported. However, this compounds was found to be yet another example of the η^5-bonding between the Fe atom and the carbon cage.[11] It should be noted that no η^3-complexes of fullerenes have been prepared as yet.

In this work we studied the problem of existence of η^3—π-complexes of allyl derivatives of C_{60} fullerene taking the complexes $Co(CO)_3C_{60}R_3$ (R = H (**1**), F (**2**), Cl (**3**), Br (**4**), Fig. 1), $C_{60}H_3NiCp$ (**5**, Fig. 2), $C_{60}H_3Fe(CO)Cp$ (**6**, Fig. 3), $C_{60}H_3Li$ (**7**, Fig. 4), and $C_{60}H_3FeCp$ (**8**, Fig. 5) as examples. Compounds **1—6** are analogs of the classical allyl η^3-complexes $Co(CO)_3C_3H_5$ (**9**, Fig. 6), η^3-$NiCpC_3H_5$ (**5a**, see Fig. 2), and η^3-$Fe(CO)CpC_3H_5$ (**6a**, see Fig. 3).

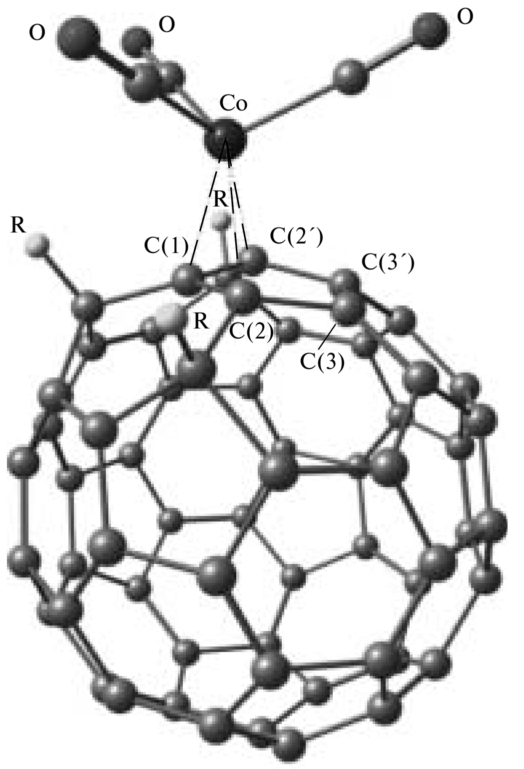


Fig. 1. Structure of the complexes η^3-$Co(CO)_3C_{60}R_3$ (R = H (**1**), F (**2**), Cl (**3**), Br (**4**)).

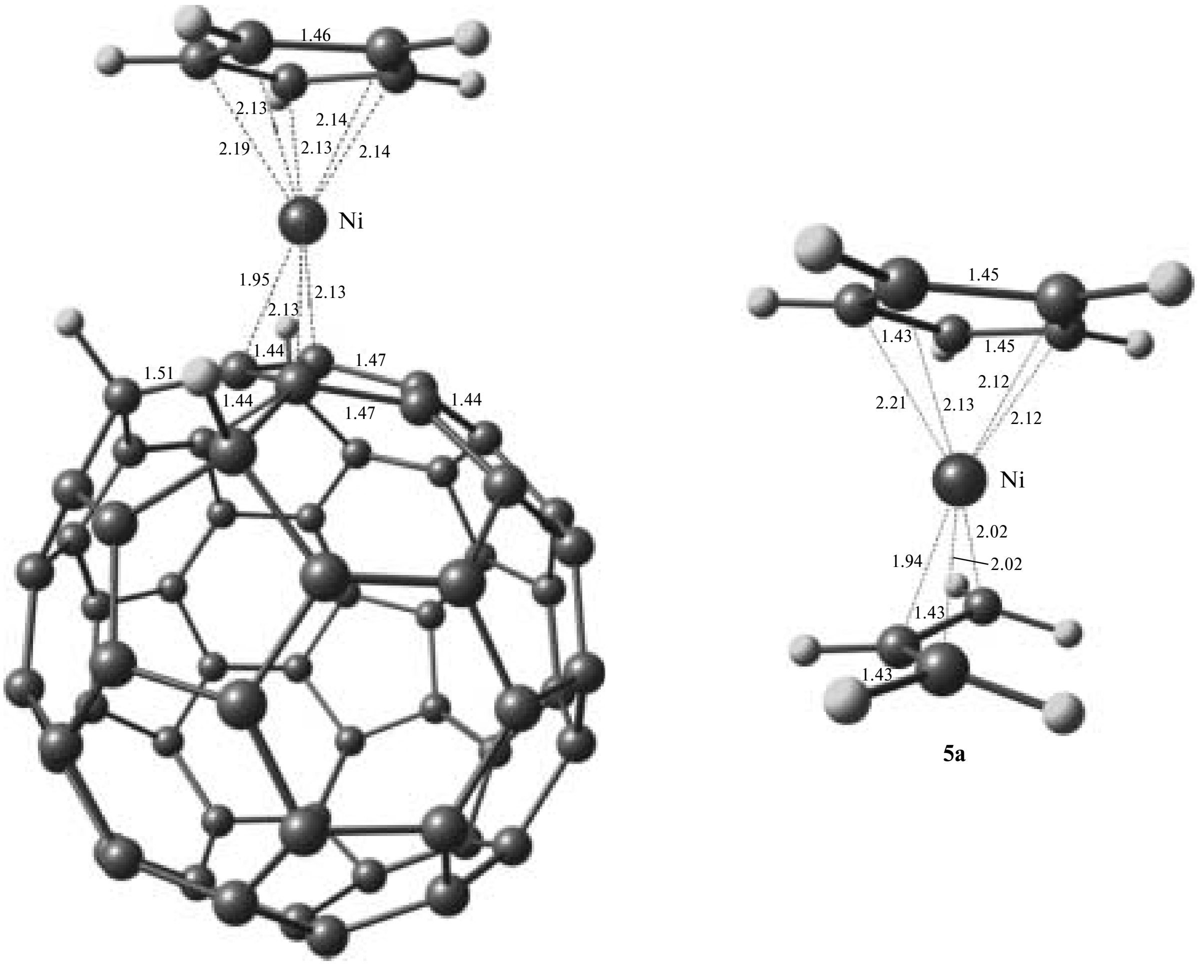
Calculation Procedure

DFT calculations of the complexes and their fragments were carried out using the Perdew—Burke—Ernzerhof exchange-correlation potential (DFT—PBE).[12] The total energies were calculated both without and with inclusion of zero-point vibrational energy correction. The basis sets employed were TZ for the transition metal atoms and DZ for the other atoms.[13] The characters of the stationary points located were determined using the number of negative eigenvalues of the Hesse matrix.

Calculations were carried out using the PRIRODA program (Version 1.10),[14] the suitability of which was preliminarily evaluated taking the classical sandwich transition metal complexes and the C_{60} fullerene as examples.

Results and Discussion

Complex $Co(CO)_3C_3H_5$ (9, see Fig. 6) was first synthesized in 1960.[15] Its structure was determined by gas-phase electron diffraction technique.[16] Complex **9** has a C_s symmetry. The Co atom is bound to three C atoms of the allyl fragment, the distance to the central carbon (1.985 Å) being shorter than the distances to the terminal C atoms of the allyl ligand (2.101 Å). Complex **9** is a closed-shell species. The energy characteristics of com-



5

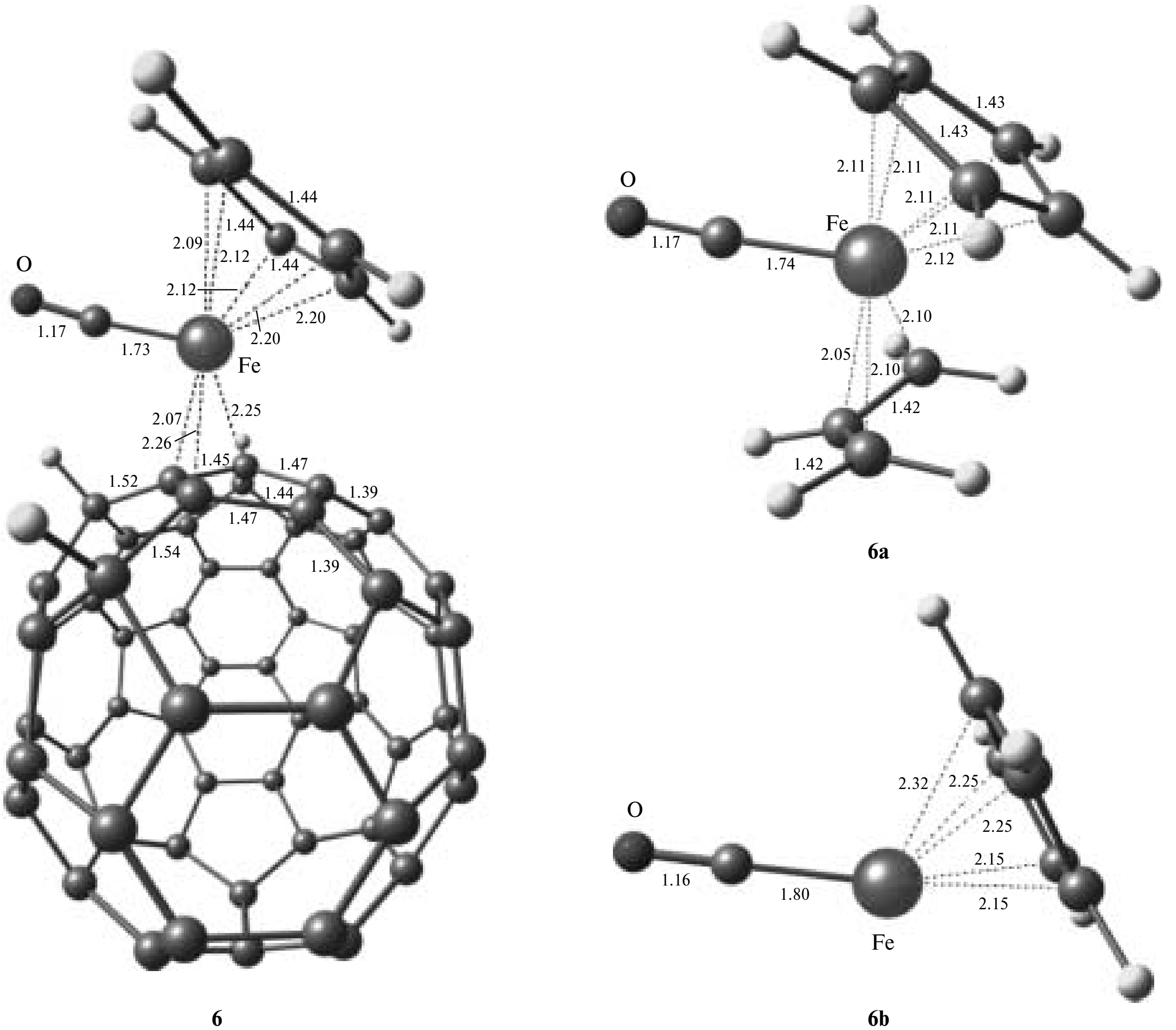
5a

Fig. 2. Structure of the complex η^3-H_3C_{60}NiCp (**5**) and its classical analog η^3-C_3H_5NiCp (**5a**). Here and in Figs. 3—6 shown are the bond lengths (in Å).

plex **9** and its fragments calculated in this work are listed in Tables 1 and 2, respectively, while Table 3 presents selected geometric parameters and their experimental values.[17] A number of geometric parameters of complex **9** and its fragments are shown in Fig. 6. As can be seen from Table 2, the calculated and experimental values differ insignificantly. This can be treated as a substantiation of the possibility of using the DFT-PBE approximation for simulating the geometry and electronic structure of the allyl derivatives of C_{60} fullerene and corresponding complexes with $Co(CO)_3$ species.

The energy of the Co—C_3H_5 bond in complex **9** calculated as the difference between the total energy of the complex and the sum of the total energies of the $^\bullet Co(CO)_3$ and $^\bullet C_3H_5$ radicals is 68.7 kcal mol^{-1} (65.2 kcal mol^{-1} with inclusion of zero-point vibrational energy correction). The corresponding values obtained from the calculations with the TZ basis set for all atoms are 63.3 and 59.4 kcal mol^{-1}. The spin density in the $^\bullet C_3H_5$ radical is localized on the terminal C atoms.

Complexes η^3-$Co(CO)_3C_{60}R_3$ (R = H, F, Cl, Br) (1—4, see Fig. 1). Tables 1—3 list the results of calculations of the energy characteristics and geometric parameters of complexes **1—4**, the corresponding allyl radicals $^\bullet C_{60}R_3$ (R = H, F, Cl, Br) (**1a—4a**), and the species $^\bullet C_3H_5$ (**9a**) and $^\bullet Co(CO)_3$ (**9b**). As follows from Table 3, the bonds in the C(2)—C(1)—C(2´) fragments of the radicals **1a—4a** are about 0.03 Å longer than in the allyl radical (the atomic numbering scheme is shown in Fig. 1). The spin density in the radicals **1a—4a** (0.22, 0.21, 0.20, and 0.19 au, respectively) is mainly localized on the C(2) and C(2´) atoms corresponding to the terminal C atoms of the C_3H_5 species. These values are nearly halved as compared to the spin density on the atoms in the allyl radical, so one would expect weaker Co—C_{60} bonds in the complexes **1—4** (see below). Analysis of the geometry of complexes **1—4** reveals a local retention of the structure similar to that of complex **9**. It should be noted that the Co—C(1) bond length is virtually independent of the nature of the R atom and is close to the corresponding value for com-



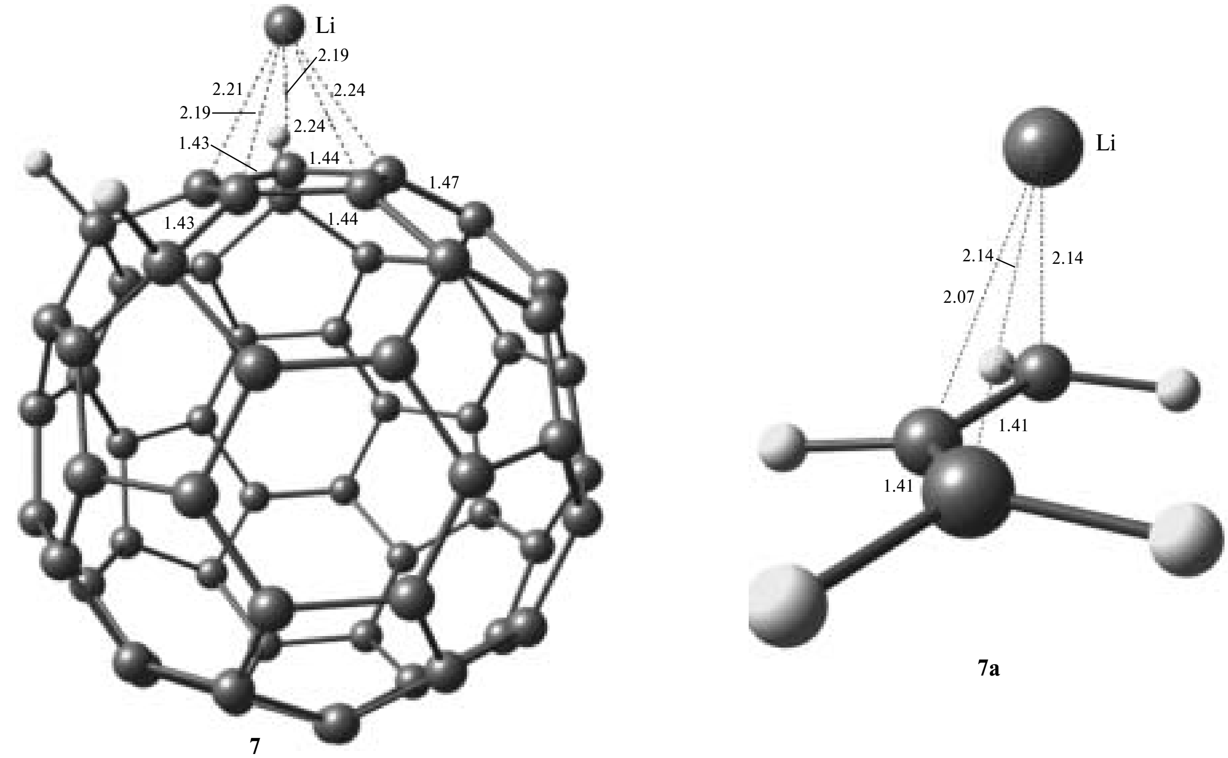
6 **6a** **6b**

Fig. 3. Structure of the complex η^3-$C_{60}H_3Fe(CO)Cp$ (**6**), its classical analog η^3-$Fe(CO)CpC_3H_5$ (**6a**), and the radical $Fe(CO)Cp^{\bullet}$ (**6b**).

plex **9** (see Table 3). However, the distance from the Co atom to the other two C atoms of the allyl fragment of fullerene, C(2) and C(2´), increases by ~0.1 Å. This seems to be mainly due to the decrease in the C(2)—C(1)—C(2´) bond angle down to 109° (*cf.* 116° for **9**) and to the distortion (loss of coplanarity) of that five-membered ring in complexes **1—4** the atoms of which are involved in the interaction with the Co atom (the C(1)—C(2)—C(2´)—C(3) dihedral angle is ~165°). In addition, the carbon—carbon bonds in the allyl fragment of the polyhedral cage are longer than the corresponding bonds in radical **9a**.

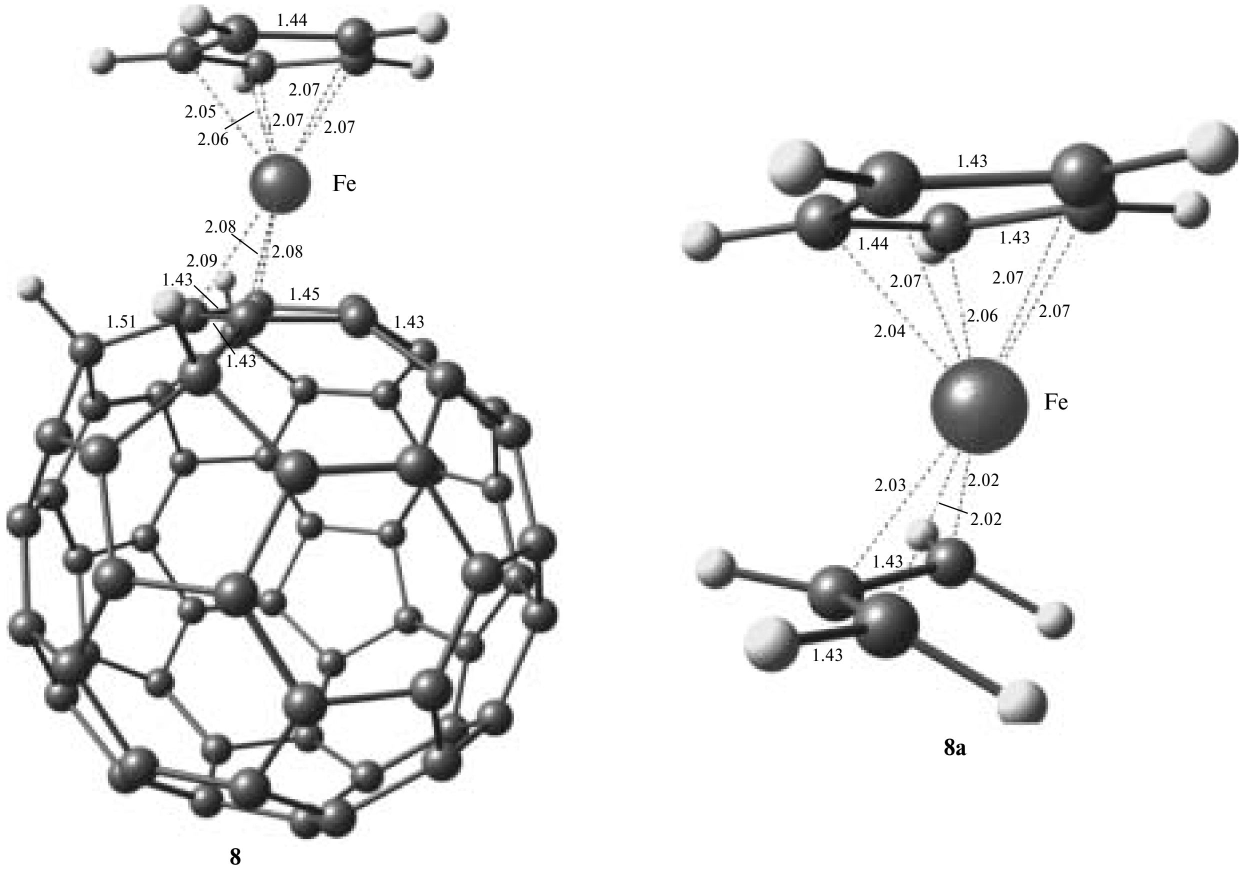
The relative stability of complexes **1—4** was estimated in terms of the Co—C_{60} bond energies denoted as Δ and calculated as the differences between the sums of the total energies of the radicals $^{\bullet}Co(CO)_3$ and $^{\bullet}C_{60}R_3$ and the total energies of the complexes $Co(CO)_3C_{60}R_3$. As can be seen in Table 1, the Δ values increase in the order **4** < **3** < **1** < **2** and lie between 45.4 and 57.0 kcal mol^{-1}. The inclusion of zero-point vibrational energy correction leads to a decrease in the M—C_{60} bond energies of all the complexes **1—4** by at most 2 kcal mol^{-1} (see the Δ_0 values in Table 1). For comparison, mention may be made that the experimental bond energy in the stable butadiene-irontricarbonyl, $Fe(CO)_3C_4H_6$, is nearly 51 kcal mol^{-1}.[17] The results obtained suggest that complexes **1—4** can exist but must be less stable than complex **9**.

It is of interest to compare the estimates of the stability of the η^3—π-complexes of cobalt carbonyl (see above) with the corresponding estimates for the complexes of allyl derivatives of C_{60} fullerene with other metals. To this end, the complexes $C_{60}H_3NiCp$ (**5**), $C_{60}H_3Fe(CO)Cp$ (**6**), $C_{60}H_3Li$ (**7**), and $C_{60}H_3FeCp$ (**8**) were chosen. The main energy characteristics and geometric parameters of



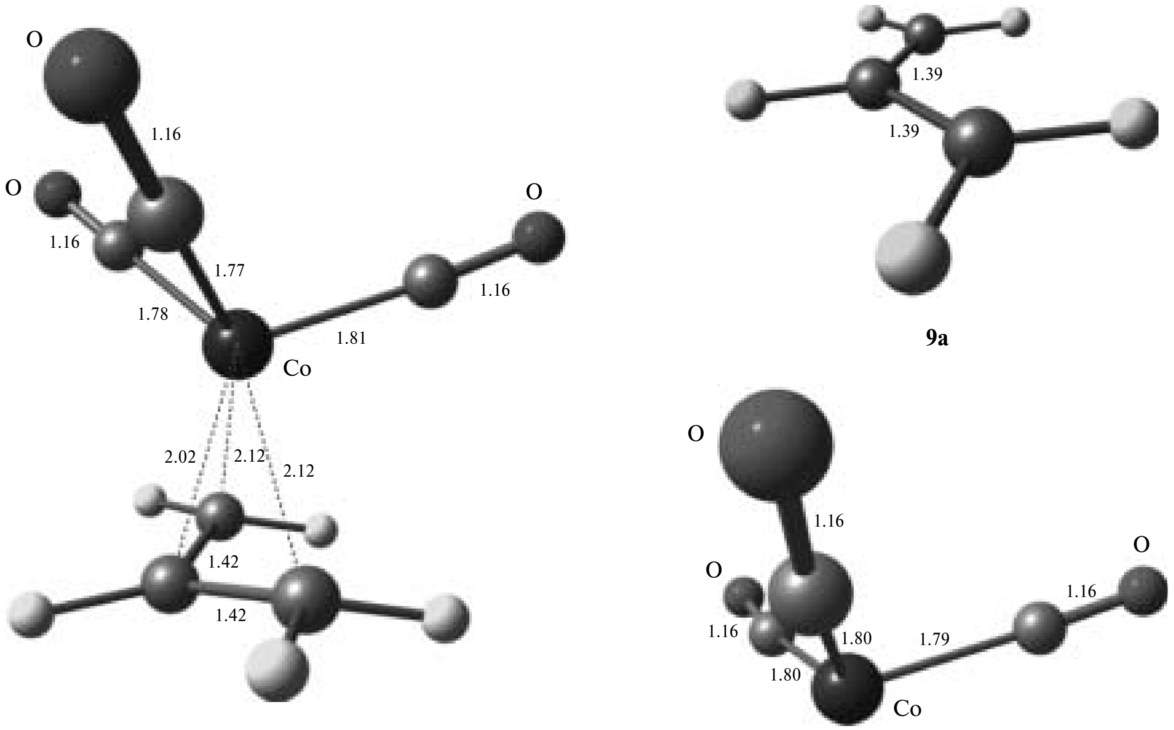
7 **7a**

Fig. 4. Structure of the complex η^5-$H_3C_{60}Li$ (**7**) and its classical analog η^3-C_3H_5Li (**7a**).



8 **8a**

Fig. 5. Structure of the complex η^5-$H_3C_{60}FeCp$ (**8**) and its classical analog η^3-C_3H_5FeCp (**8a**).



9 **9a** **9b**

Fig. 6. Structure of the complex η^3-$C_3H_5Co(CO)_3$ (**9**) and its fragments $C_3H_5^{\bullet}$ (**9a**, allyl radical) and $Co(CO)_3^{\bullet}$ (**9b**).

these complexes and their fragments are presented in Figs. 2—5 and Tables 1—3. Without dwelling on details of these calculations, it should be noted that only two complexes, **5** and **6**, have the structure with the η^3—π-type of bonding. The C_{60}—M bond energy is 77.7 kcal mol^{-1} for **5** (M = Ni) and only 44.0 kcal mol^{-1} for **6** (M = Fe).

Table 1. Energy characteristics[a] of the complexes $R_3C_{60}ML$ and C_3H_5ML obtained from DFT—PBE calculations with the TZ(M) and DZ(C,O,H) basis sets

Complex	$-E_{tot}$	$-E_{HOMO}$	$-E_{LUMO}$	ZPE	Δ	Δ_0
	au			kcal mol^{-1}		
(η^3-$C_{60}H_3$)Co(CO)$_3$ (**1**)	4007.7638	0.2179	0.1662	272.3	53.0	51.0
(η^3-$C_{60}F_3$)Co(CO)$_3$ (**2**)	4305.0783	0.2335	0.1776	257.3	57.0	55.4
(η^3-$C_{60}Cl_3$)Co(CO)$_3$ (**3**)	5386.0774	0.2260	0.1798	254.0	48.2	46.7
(η^3-$C_{60}Br_3$)Co(CO)$_3$ (**4**)	11727.4429	0.2237	0.1808	252.3	45.4	44.0
(η^3-$C_{60}H_3$)NiCp (**5**)	3986.9901	0.1944	0.1608	308.7	77.7	74.6
(η^3-C_3H_5)NiCp (**5a**)	1818.6079	0.1559	0.0827	95.3	85.7	81.3
(η^3-$C_{60}H_3$)Fe(CO)Cp (**6**)	3855.5829	0.2086	0.1575	315.5	44.0	[b]
(η^3-C_3H_5)Fe(CO)Cp (**6a**)	1687.2101	0.1646	0.0656	102.0	57.9	[b]
η^5-Li$C_{60}H_3$ (**7**)[c]	2293.0377	0.1944	0.1585	257.4	62.6	60.9
C_3H_5Li (**7a**)[c]	124.6255	0.1466	0.0531	42.7	51.8	50.0
(η^5-$C_{60}H_3$)FeCp (**8**)	3742.3888	0.1911	0.1680	309.3	108.1	105.0
(η^3-C_3H_5)FeCp (**8a**)	1573.9680	0.1426	0.1111	95.2	91.8	88.2
(η^3-C_3H_5)Co(CO)$_3$ (**9**)	1839.3939	0.2022	0.0903	59.3	68.7	65.2

[a] E_{tot} is the total energy, Δ (Δ_0) is the energy of the ML—C_{60} or ML—C_3H_5 bond calculated without (with) inclusion of zero-point vibrational energy correction, ZPE is the zero-point vibrational energy correction, and E_{HOMO} and E_{LUMO} are the energies of the highest occupied and lowest unoccupied MOs, respectively, at the multiplicity $m = 1$.

[b] In this case attempts to calculate the total energy of the radical Fe(CO)Cp with inclusion of zero-point vibrational energy correction failed due to divergence of the self-consistency procedure.

[c] E_{tot}(Li) = −7.4619 au.

Table 2. Energy characteristics[a] of the fragments of the complexes $C_{60}ML$ and C_3H_5ML obtained from DFT-PBE calculations with the TZ(M) and DZ(C,O,H) basis sets

Radical	*m*	$-E_{tot}$	$-E_{HOMO}$	$-E_{LUMO}$	ZPE /kcal mol^{-1}	Radical	*m*	$-E_{tot}$	$-E_{HOMO}$	$-E_{LUMO}$	ZPE /kcal mol^{-1}
		au						au			
$C_{60}H_3$ (**1a**)	2	2285.4760	0.2265	0.1691	255.7	NiCp (**5b**)	4	1701.3647	0.2043	0.0106	51.6
$C_{60}F_3$ (**2a**)	2	2582.7842	0.2436	0.1871	241.2	Fe(CO)Cp (**6b**)	4	1570.0368	0.1766	0.0560	[b]
$C_{60}Cl_3$ (**3a**)	2	3563.7973	0.2408	0.1844	237.9	FeCp (**8b**)	4	1456.7630	0.1182	0.1069	50.8
$C_{60}Br_3$ (**4a**)	2	10005.1671	0.2385	0.1828	235.3	C_3H_5 (**9a**)	2	117.0811	0.2647	0.0047	40.9
NiCp (**5a**)	2	1701.3903	0.1258	0.0956	49.9	$Co(CO)_3$ (**9b**)	2	1722.2033	0.2077	0.1322	14.6

[a] For notations, see Table 1.

[b] In this case attempts to calculate the total energy of the radical Fe(CO)Cp with inclusion of zero-point vibrational energy correction failed due to divergence of the self-consistency procedure.

Table 3. Bond lengths (*d*) in the complexes of $C_{60}R_3$ (R = H, F, Cl, Br) and C_3H_5 with the $Co(CO)_3$ species calculated by the DFT—PBE method (the experimental values[17] are given in parentheses)[a]

Complex or fragment	*d*/Å						
	C(1)—C(2), C(1)—C(2´)	C(2)—C(3), C(2´)—C(3´)	C(3)—C(3´)	M—C(1)	M—C(2), M—C(2´)	M—CO [b]	M—CO [b]
(η^3-$C_{60}H_3$)$Co(CO)_3$ (**1**)	1.44	1.43	1.44	2.00	2.24	1.84	1.78
(η^3-$C_{60}F_3$)$Co(CO)_3$ (**2**)	1.45	1.48	1.44	1.96	2.21	1.84	1.79
(η^3-$C_{60}Cl_3$)$Co(CO)_3$ (**3**)	1.46	1.48	1.44	1.99	2.23	1.85	1.79
(η^3-$C_{60}Br_3$)$Co(CO)_3$ (**4**)	1.46	1.48	1.44	1.20	2.23	1.85	1.79
(η^3-C_3H_5)$Co(CO)_3$ (**9**)	1.42 (1.39)	—	—	2.02 (1.99)	2.12 (2.10)	1.77 (1.80)	1.81 (1.80)

[a] The atomic numbering scheme is shown in Fig. 1.

[b] Two bonds of this length.

These values are somewhat lower than the M—All bond energies in the corresponding classical sandwich systems **5a** and **6a** (see Table 1). Complex **5** was found to be more stable than the complexes **1**—**4** and **6**. The adiabatic ionization potential and electron affnity calculated for **5** are 6.79 and 2.99 eV, respectively. From Table 1 it also follows that complexes **7** and **8** must be more stable than their classical analogs **7a** and **8a**. Comparison of the energy characteristics of the complexes **6** and **8** shows that the η^5-bond Fe—C_{60} in the latter is much stronger than the η^3-bond Fe—C_{60} in the former.

In conclusion mention may be made that the Mulliken atomic charges of the metals lie between 0.42 au (complex **1**) and 1.03 au (complexes **5** and **8**).

Thus, the results of our calculations confirm that the type of bonding in the metal complexes of allyl derivatives of C_{60} fullerene strongly depends on the nature of the groups attached. Among the η^3—π-complexes of allyl derivatives of C_{60} fullerene, complex **5** is most likely to be synthesized.

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