Brief Communications

η^5—π-Complexes of bowl-shaped precursors of C_{60} fullerene with MCp groups: stability estimates from DFT calculations. Complexes $C_{21}H_9(MCp)_n$ (n = 1—3; M = Fe, Ru)

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Stability of the $C_{21}H_9(MCp)_n$ (n = 1—3; M = Fe, Ru) complexes containing the $C_{21}H_9$ radical, a representative bowl-shaped precursor of C_{60} fullerene, was estimated. The carbon skeleton of the radical comprises three pentagonal faces (pent). DFT calculations of the $C_{21}H_9$ radical and its complexes were carried out with full geometry optimization and the PBE exchange-correlation potential. The energies of the M—pent bonds were found to increase with an increase in n, being only slightly lower than those in the hypothetical icosahedral $12\eta^5$—π-$C_{60}(MCp)_{12}$ complexes and classical sandwich complexes $M(Cp)_2$. The increased stability of the $C_{21}H_9(MCp)_n$ complexes was explained by greater involvement of the conjugated system of the polyhedral skeleton in the interaction.

Key words: C_{60} fullerene, ferrocene, ruthenocene, $n\eta^5$—π-complexes of C_{60}, quantum-chemical calculation, DFT-PBE-method, M—C_{60} bond energy.

The problem of existence of η^5—π-complexes of fullerenes (especially, C_{60} fullerene) and their derivatives with transition-metal atoms has been the subject of intensive research.[1—8] In particular, studies of $CpMC_{60}MCp$ (M = Fe, Si, Ge, Sn) complexes with D_{5d} symmetry and η^5—π-type of coordination of the MCp species to the polar five-membered rings showed that the M—C_{60} bonds in these derivatives of "naked" C_{60} fullerene are much weaker than the M—Cp bonds in the classical sandwich complexes $M(Cp)_2$.[1,7,8] However, the situation changes essentially when fullerene complexes with transition metal atoms contain cyclopentadienyl derivatives of fullerene (*i.e.*, $C_{60}R_5$ radicals with five univalent functional groups R attached to the C atoms of the C_{60} cluster in the α-positions relative to one five-membered ring) instead of "naked" fullerene as ligands.[1—3] Preparation of the η^5—π-$C_{60}Me_5FeCp$ complex, a ferrocene—C_{60} fullerene hybrid,[5] and synthesis of the η^5—$C_{60}Ph_5L$ (L = K, Tl, In) complexes[6] demonstrate the efficiency of this procedure for stabilization of the η^5—bonds of C_{60} fullerene.

In our recent DFT-PBE study[8] we have shown that the stability of icosahedral complexes of C_{60} fullerene with twelve MCp species, namely, $C_{60}(FeCp)_{12}$ (**1a**) and $C_{60}(RuCp)_{12}$ (**1b**), which are also called "coated" C_{60}

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fullerenes,[1,7] is comparable with that of the classical sandwich complexes $M(Cp)_2$. The stability of **1a** and **1b** is estimated from the abstraction energies of one MCp group while that of $M(Cp)_2$ is estimated from the energy of the M—Cp bond. It was hypothesized that the stability of complexes **1a** and **1b** is mainly due to involvement of the entire conjugated system of the C_{60} cluster in the formation of twelve η^5—π-bonds. In this connection a question poses as to can and to which extent successive η^5—π-coordination of the MCp species to the fullerene cage cause additional stabilization of the newly formed complex? Solving this problem is costly even in the case of the C_{60} fullerene. Therefore, in this work we attack this problem taking the η^5—π-complexes $C_{21}H_9(MCp)_n$ (M = Fe, Ru; n = 1—3) of $C_{21}H_9$ radical (**2**) (Fig. 1), a simplest hydrocarbon bowl-shaped precursors of C_{60} fullerene, as examples. The structure of the carbon skeleton of radical **2** coincides with the structure of one of the simplest hydrocarbon bowl-shaped C_{21} fragments of fullerene C_{60}. Cluster C_{21} comprises seven *peri*-condensed rings (four six-membered and three five-membered rings). Each five-membered ring (pent) can be involved in the formation of η^5—π-bonds.

In this work we simulated the structures of the following molecular systems: **2**, $3\eta^5$—π-$C_{21}H_9(FeCp)_3$ (**3a**), $3\eta^5$—π-$C_{21}H_9(RuCp)_3$ (**3b**) (Fig. 2) and their fragments $2\eta^5$—π-$C_{21}H_9(FeCp)_2$ (**4a**), $2\eta^5$—π-$C_{21}H_9(RuCp)_2$ (**4b**) (Fig. 3), η^5—π-$C_{21}H_9FeCp$ (**5a**), and η^5—π-$C_{21}H_9RuCp$ (**5b**) (Fig. 4). The stability of complexes **3a—5a** and **3b—5b** was estimated and the effective atomic charge distributions were determined.

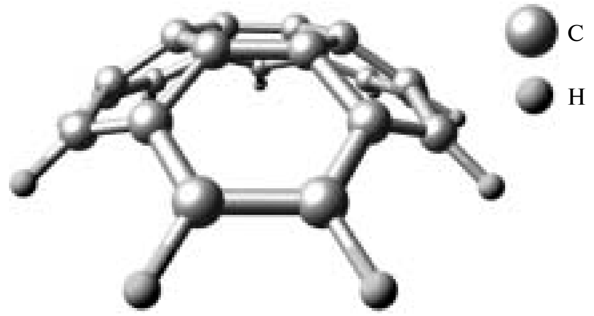

Fig. 1. Geometry of the $C_{21}H_9$ radical (**2**) with C_{3v} symmetry.

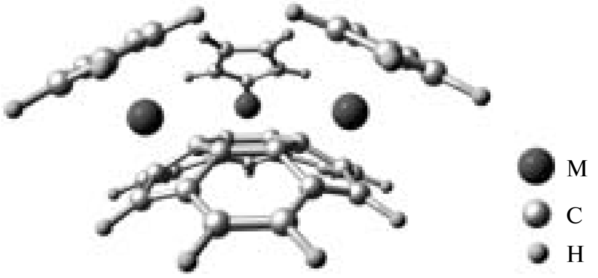

Fig. 2. Geometry of the complexes $3\eta^5$—π-$C_{21}H_9(FeCp)_3$ (**3a**) and $3\eta^5$—π-$C_{21}H_9(RuCp)_3$ (**3b**) with C_{3v} symmetry.

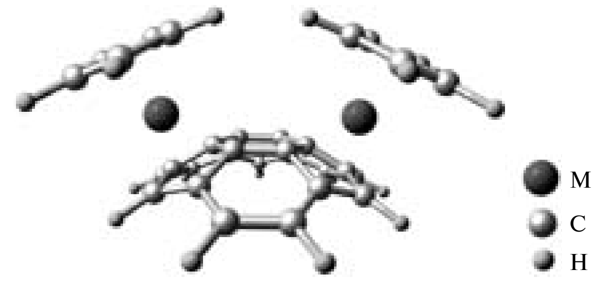

Fig. 3. Geometry of the complexes $2\eta^5$—π-$C_{21}H_9(FeCp)_2$ (**4a**) and $2\eta^5$—π-$C_{21}H_9(RuCp)_2$ (**4b**) with C_s symmetry.

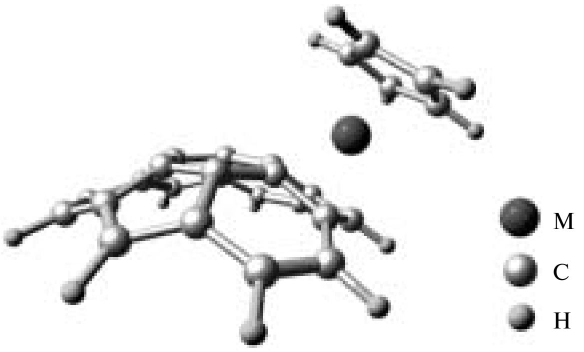

Fig. 4. Geometry of the complexes η^5—π-$C_{21}H_9FeCp$ (**5a**) and η^5—π-$C_{21}H_9RuCp$ (**5b**) with C_s symmetry.

Calculation Procedure

DFT calculations of local energy minima on the potential energy surfaces for systems **2**, **3a—5a**, and **3b—5b** were carried out with full geometry optimization with the PBE exchange-correlation potential,[9] the TZ basis sets for Fe and Ru atoms, and the DZ basis sets for C and H atoms using the PRIRODA program.[10] The total energies of the above-mentioned systems were also estimated with inclusion of zero-point vibrational energy correction. The characters of the stationary points located were determined by analyzing the spectrum of the Hesse matrix. The calculations were carried out with the highest permissible accuracy (10^{-9} for integrals, 10^{-7} for self-consistency procedure, and 10^{-5} for optimization) instead of the default values for the PRIRODA program.

Results and Discussion

Complexes $n\eta^5$—π-$C_{21}H_9(MCp)_n$ (n = 1—3). Table 1 lists the results of calculations of complexes $3\eta^5$—π-$C_{21}H_9(FeCp)_3$ (**3a**), $3\eta^5$—π-$C_{21}H_9(RuCp)_3$ (**3b**), $2\eta^5$—π-$C_{21}H_9(FeCp)_2$ (**4a**), $2\eta^5$—π-$C_{21}H_9(RuCp)_2$ (**4b**), η^5—π-$C_{21}H_9FeCp$ (**5a**) and η^5—π-$C_{21}H_9RuCp$ (**5b**), and radical **2**. The energies of the M—pent bonds, E(M—pent), in complexes **3a—5a** and **3b—5b** were cal-

Table 1. Parameters of the η^5—π-$C_{21}H_9(MCp)_3$ complexes and their fragments*

Complex or fragment	μ	Symmetry	$-E_{tot}$	ZPE	ν /cm^{-1}	E**	E^0**	E_{av}**	E^0_{av}**	Q_M /au
			au			kcal mol^{-1}				
$C_{21}H_9$ (**2**)	2	C_s	804.5754	139.0	82.5	—	—	—	—	—
$C_{21}H_9(FeCp)_3$ (**3a**)	1	C_{3v}	5175.2827	300.0	43.2	101.6	95.2	87.5	84.5	0.99
$C_{21}H_9(FeCp)_2$ (**4a**)	2	C_s	3718.3614	245.2	27.3	87.7	85.7	81.6	79.2	0.96
$C_{21}H_9FeCp$ (**5a**)	1	C_s	2261.4587	192.6	34.3	75.5	66.4	—	—	0.93
$C_{21}H_9(RuCp)_3$ (**3b**)	1	C_{3v}	14714.7624	297.6	27.5	109.2	105.0	92.7	89.8	1.17
$C_{21}H_9(RuCp)_2$ (**4b**)	2	C_s	10078.0071	243.5	14.2	90.2	88.3	84.4	82.1	1.13
$C_{21}H_9RuCp$ (**5b**)	1	C_s	5441.2821	191.7	4.4	78.7	76.0	—	—	1.10

* Notations: μ is multiplicity; E_{tot} is the total energy; ZPE is the zero-point vibrational energy correction; E is the energy of the M—pent bond (superscript "0" denotes calculations with inclusion of zero-point vibrational energy correction, the subscript "av" denotes the average value); ν is the minimum frequency, and Q_M is the Mulliken effective atomic charge of M. The bond energies were calculated using the following values (in kcal mol^{-1}): $E_{tot}(^4FeCp) = -1456.7630$, $E^0_{tot}(^4FeCp) = -1456.6822$, $E_{tot}(^2RuCp) = -4636.5813$, and $E^0_{tot}(^2RuCp) = -4636.5017$ (here the superscripts denote the multiplicity).

** M—pent bond energies.

culated as the energies of abstraction of one MCp group. As can be seen in Table 1, the bond energies E(M—pent) increase with an increase in the number of the coordinated MCp groups and reach their maximum values at $n = 3$. However, these energies are somewhat lower than those of complexes **1a** and **1b** (E(M—pent) = 115.8 and 127.3 kcal mol^{-1}, respectively[8]). For comparison, mention may be made that theoretical estimates of the M—Cp bond energy in the sandwich complexes $Fe(Cp)_2$ and $Ru(Cp)_2$ are 128.7 and 130.2 kcal mol^{-1}, respectively. At the same time, complexes **3a** and **3b** are characterized by much higher E(M—pent) values compared to the "naked" C_{60} fullerene complexes $2\eta^5$—π-$C_{60}(FeCp)_2$ and $2\eta^5$—π-$C_{60}(RuCp)_2$ with D_{5d} symmetry (52.1 and 56.1 kcal mol^{-1}, respectively[3]). The inclusion of zero-point vibrational energy correction causes a decrease in the M—pent bond energy (see the E^0(M—pent) values in Table 1). The average bond energies, E_{av}(M—pent) and $E^0{}_{av}$(M—pent), estimated using the formulas

$$nE_{av}(\text{M—pent}) = E_{tot}(\mathbf{2}) + nE_{tot}(\text{MCp}) - E_{tot}[C_{21}H_9(\text{MCp})_n],$$

$$nE^0{}_{av}(\text{M—pent}) = E^0{}_{tot}(\mathbf{2}) + nE^0{}_{tot}(\text{MCp}) - E^0{}_{tot}[C_{21}H_9(\text{MCp})_n],$$

are also listed in Table 1.

For comparison, the experimental E_{av}(Fe—Cp) value is 73.1 kcal mol^{-1}.[11] In this work we obtained a corresponding theoretical estimate, $E^0{}_{av}$(Fe—Cp) = 99 kcal mol^{-1}, which is somewhat higher than the experimental value. It seems not to be improbable that the E(M—pent) bond energies of the systems under study should also be overestimated. However, we assume that it will have only little effect on the relative stability of complexes **3a—5a** and **3b—5b**.

Thus, the results of our calculations suggest the possibility for complexes $n\eta^5$—π-$C_{21}H_9(MCp)_n$ (n = 1—3, systems **3a—5a** and **3b—5b**) to exist. Their stabilities increase with increasing the number of MCp groups for both M = Fe and Ru. This confirms the assumption that the size of conjugated systems of ligands in η^5—π-complexes of fullerenes has a strong effect on their stability and can serve as additional explanation for increased stability of "coated" fullerenes (*e.g.*, complexes **1a** and **1b**).

In conclusion mention may be made that the calculated average M...C_{Cp} distances in the systems under study are close to the corresponding experimental values in the sandwich compounds $M(Cp)_2$ (2.06 Å for M = Fe and 2.20 Å for M = Ru).[12] The average M...C_{pent} distances are ~0.04 Å longer than these values, which corresponds to a weaker M—pent bond compared to the M—Cp bond.

The Mulliken atomic charges (Q_M) of Fe and Ru in all the systems under study are positive, close to 1 a.u., and increase with increasing the number of MCp groups (see Table 1).

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