Physical Chemistry

On the possibility of existence of η^5-π-complexes of C_{60} fullerene: π-complexes with silicon

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Qualitative estimates of possibility of the formation of fullerene η^5-π-complexes have been carried out by the MNDO/PM3 method. It was shown, as exemplified by the C_{60} cluster, that the introduction of five univalent functional groups R (R = H, Cl, Br) to α-positions of a separate pentagon of C_{60} with the formation of $[R_5C_{60}]^-$ anions results in a pronounced increase in the π-electron density on the atoms of this five-membered cycle and more favorable conditions for the formation of π-bonds with the η^5-ligand. The nature of the interaction between the atoms of the separate cycle in $[R_5C_{60}]^-$ anion and η^5-ligand was analyzed by the example of hypothetical sandwich systems $R_5C_{60}SiCp$. Half-sandwich complexes $R_5C_{60}SiX$ (X = H, Cl) were also investigated. The local energy minima were found on the potential energy surfaces (PES) of systems $R_5C_{60}SiCp$ and $R_5C_{60}SiX$ with C_{5v} symmetry. These systems transform barrirlessly into η^5-π-complexes with the angular structure if the symmetry restrictions are removed. The most favorable conditions for η^5-π-complexes of R_5C_{60} to form are realized for R = H. The results obtained were compared to those of semiempirical and nonempirical calculations of bis (cyclopentadienyl) silicon.

Key words: fullerene, π-complexes, silicon, MNDO/PM3 method.

The polyhedral carbon clusters (fullerenes) are, in principle, capable of forming compounds with various (from η^1 to η^6) types of ligand coordination.[1-2] However, stable complexes of C_{60} identified to date are either compounds with σ-bonding at the vertices of a truncated icosahedron or η^2-π-olefinic complexes. Stable C_{60} derivatives of other types, as well as those of fullerenes with a larger number of atoms, have not yet been obtained. The capability of fullerene C_{60} to form η^5- and η^6-complexes became the subject of discussion in a number of papers.[3-6]

On the basis of the data reported in Refs. 4—6, one can draw the conclusion that the π-electrons in fullerene C_{60} are strongly delocalized. Because of this, the coefficients at the p_z-AOs in the MOs of this cluster for the atoms of a separate pentagonal (or hexagonal) face are significantly less than those in the case of cyclopentadienyl anion or benzene. In addition, simple estimates show that these values (in contrast to the coefficients at the corresponding p_z-AOs of the atoms participating in the (6,6)-type bonds) change little when they are subjected to relatively strong perturbations (the Cou-

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lomb and resonance integrals) of the atoms of the five-membered or six-membered cycles. Therefore, the formation of η^5- or η^6-complexes with C_{60} and all the more with higher fullerenes is unlikely.

The corannulene molecule, $C_{20}H_{10}$, is the simplest hydrocarbon system whose carbon framework coincides with a representative fragment of C_{60}. The following conclusions were drawn[4] on the basis of a comparison of the structure of the MOs of this molecule and that of the MOs of the $[C_{20}H_{15}]^-$ anion formed from corannulene after addition of five H atoms to the five C atoms framing the five-membered cycle: 1) η^5-π-complexes of fullerene C_{60} (if they exist) must be much less stable as compared to their classical analogs, bis(cyclopentadienyls) of transition metals; 2) to stabilize an η^5-π-complex with (5,6)-fullerene (this cluster is only built of five- and six-membered cycles), one must attach five univalent groups to the positions framing one of the five-membered cycles (α-positions). These conclusions, confirmed later by the example of bowl-shaped hydrocarbon molecules, precursors of C_{60} and C_{70},[5] are in agreement with the hypothesis on the methods of stabilization of C_{60} η^5-π-complexes proposed independently by V. I. Sokolov and V. V. Bashilov.

Previously,[4] estimating the relative stability of η^5-π-$C_{60}MCp^+$ complexes (M = Fe, Ru, Os) by the EHT method,[7] we made a number of assumptions on their structure, based on similarity of the structure of fullerene π-complexes and those of corresponding classical sandwich systems. In this work, the discussion about the problem of stabilization of η^5-π-complexes of fullerene C_{60} (or its derivatives) has been continued. Silicon π-complexes (η^5-$C_{60}SiCp^+$, η^5-$R_5C_{60}SiCp$, and η^5-$R_5C_{60}SiX$) were chosen as objects for the investigation. The geometry of the systems investigated was optimized by the MNDO/PM3 method[9] using the MOPAC and GAMESS[10] program packages on a DEC Alpha AXP 3000-400 workstation. Notice that complexes $Si(C_5Me)_2$, stable under normal conditions, were obtained as long ago as 1986, and their structure was characterized by X-ray analysis (in the crystal) and electron diffraction (see Ref. 8 and references cited therein).

Results and Discussion

Anions $[R_5C_{60}]^-$ (1) with C_{5v} symmetry [R = H (1a), Cl (1b), Br (1c)]. The structure of anions (1) is shown in Fig. 1 where the symmetry axis of the C_{5v} group coincides with the z coordinate axis. The Schlegel diagram of the anion **1** is shown in Fig. 2.

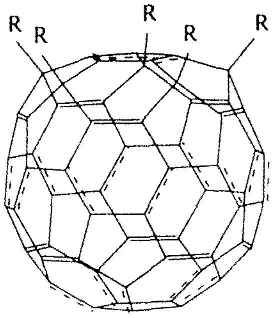


Fig. 1. The structure of $[R_5C_{60}]^-$ anions with C_{5v} symmetry: R = H (**1a**), R = Cl (**1b**), R = Br (**1c**). See geometric parameters in Table 2.

Optimization of the geometry of anions **1a**, **1b**, and **1c** was performed over all geometric parameters with allowance for the C_{5v} symmetry. It was established that there is a local minimum on the potential energy surface (PES) of each anion with the C_{5v} symmetry. The values of the corresponding heats of formation ($\Delta_f H°$), energies of HOMO and LUMO, and effective charges on the atoms are listed in Table 1; the geometric characteristics and the bond orders (the Wiberg indices,[11] W) are given in Table 2 and Table 3, respectively.

Each of the anions **1a—c** has a closed electron shell, fairly high ionization potential determined according to the Koopman's theorem, and a relatively wide energy gap between the HOMO and the LUMO, which points to the kinetic stability of these systems. An analysis of the electron density distribution (see Table 1) shows that the sum of the effective charges on the atoms of a separate pentagon in the anions **1a—c** is close to −1.0 au.

In all the cases considered, the HOMO energy level is doubly degenerate and belongs to the e_1 irreducible representation. The contributions of p_z-AOs of atoms of the upper framed pentagon (the z axis is perpendicular to its plane) dominate in these two MOs, *i.e.*, the HOMOs are π-orbitals. The energy of π-MO with the a_1 symmetry, which is localized on the upper pentagon,

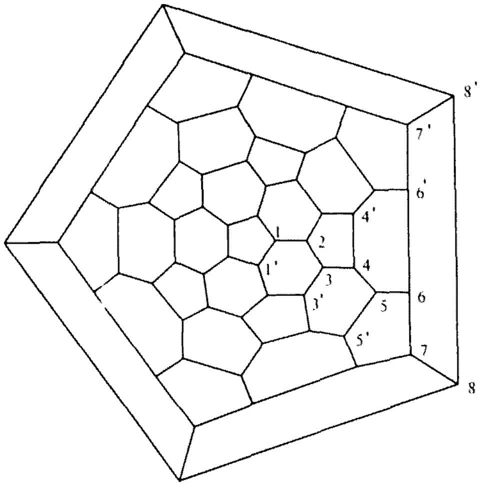


Fig. 2. The Schlegel diagram of anions **1a—c**: the atoms of eight nonequivalent types are enumerated (the numbers of equivalent atoms differ in primes); functional groups R are connected to the atoms of second type.

Table 1. Heats of formation ($\Delta_f H°$), energies of the highest occupied and lowest unoccupied levels (E_{HOMO}, E_{LUMO}) , and effective charges for fullerene derivatives with C_{5v} symmetry (see the numbering of atoms in Fig. 2), calculated by the MNDO/PM3 method

System	$\Delta_f H°$ /kcal mol^{-1}	Energy/eV*		q/au				
		$-E_{HOMO}$	$-E_{LUMO}$	C(1)	C(2)	R	Si	Cp, [X]
$C_{60}(I_h)$	811.7	9.481^5	2.887^3	0.00	0.00	—	—	—
$[H_5C_{60}]^-$	642.5	4.488^2	-0.382^2	−0.20	0.14	0.08	—	—
$[Cl_5C_{60}]^-$	616.0	5.458^2	0.168^2	−0.17	0.17	−0.04	—	—
$[Br_5C_{60}]^-$	662.2	5.707^2	0.308^2	−0.14	0.17	−0.11	—	—
$[Br_5C_{60}Br_5]^{2-}$	558.2	3.776^2	-2.360^1	−0.14	0.19	−0.16	—	—
$SiCp_2$	94.3	8.218^2	0.732^1	—	—	—	0.43	−0.22
$[C_{60}SiCp]^+$	1025.0	11.829^1	5.691^1	0.05	0.03	—	0.62	0.14
$[C_{60}SiCp]^-$	814.3	3.562^1		Distribution of charges with C_s symmetry				
$H_5C_{60}SiCp$	758.8	8.799^2	2.177^2	−0.13	0.11	0.10	0.46	−0.15
$Cl_5C_{60}SiCp$	745.1	9.134^2	2.510^2	−0.13	0.13	0.01	0.50	−0.06
$Br_5C_{60}SiCp$	793.8	9.182^2	2.579^2	−0.12	0.13	−0.05	0.51	−0.05
$[C_{60}SiH]^+$	1044.6	11.674^1	6.309^1	−0.03	0.03	—	0.85	[−0.26]
$[C_{60}SiH]^\cdot$	871.9	5.324	3.214	Distribution of charges with C_s symmetry				
$H_5C_{60}SiH$	762.7	7.792^1	2.292^2	−0.06	0.10	0.10	0.22	[−0.25]
$Cl_5C_{60}SiH$	751.4	8.144^1	2.633^2	−0.07	0.11	0.03	0.35	[−0.23]
$Br_5C_{60}SiH$	800.7	8.192^1	2.700^2	−0.06	0.11	−0.03	0.37	[−0.22]
$[C_{60}SiCl]^+$	973.3	11.960^1	6.062^1	−0.05	0.03	—	0.87	[−0.26]
$[C_{60}SiCl]^-$	748.9	3.749^1	2.298^1	Distribution of charges with C_s symmetry				
$H_5C_{60}SiCl$	697.7	8.690^1	2.297^2	−0.11	0.11	0.10	0.50	[−0.34]
$Cl_5C_{60}SiCl$	685.5	9.011^1	2.620^2	−0.11	0.12	0.02	0.59	[−0.28]
$Br_5C_{60}SiCl$	734.5	9.048^1	2.685^2	−0.10	0.12	−0.03	0.61	[−0.26]

* The upper index means the level degeneracy.

Table 2. Bond lengths (*d*) in the fullerene derivatives with C_{5v} symmetry calculated by the MNDO/PM3 method (see the numbering of atoms in Fig. 2)

System	d/Å					
	1—1′	1—2	2—3	3—3′	3—4	4—4′
$C_{60}(I_h)$	1.456	1.386	1.456	1.386	1.456	1.456
$[H_5C_{60}]^-$	1.414	1.487	1.529	1.372	1.442	1.453
$[Cl_5C_{60}]^-$	1.416	1.479	1.527	1.371	1.443	1.454
$[Br_5C_{60}]^-$	1.419	1.46[illegible]	1.511	1.372	1.445	1.455
$[C_{60}SiCp]^+$	1.464	1.388	1.456	1.385	1.458	1.457
$H_5C_{60}SiCp$	1.431	1.493	1.527	1.370	1.443	1.453
$Cl_5C_{60}SiCp$	1.428	1.488	1.525	1.360	1.444	1.453
$Br_5C_{60}SiCp$	1.430	1.473	1.509	1.371	1.445	1.455
$[C_{60}SiH]^+$	1.465	1.390	1.457	1.384	1.457	1.457
$H_5C_{60}SiH$	1.435	1.494	1.527	1.369	1.443	1.452
$Cl_5C_{60}SiH$	1.433	1.490	1.525	1.369	1.444	1.453
$Br_5C_{60}SiH$	1.435	1.475	1.510	1.372	1.445	1.455
$[C_{60}SiCl]^+$	1.464	1.390	1.455	1.386	1.458	1.457
$H_5C_{60}SiCl$	1.433	1.494	1.527	1.369	1.443	1.452
$Cl_5C_{60}SiCl$	1.430	1.489	1.525	1.369	1.443	1.453
$Br_5C_{60}SiCl$	1.432	1.474	1.509	1.371	1.445	1.455

Note. The nonreduced bond lengths in the fullerene fragment of $C_{60}R_5^-$ anions and complexes R_5C_{60}—SiX (X = H, Cl, Cp) with an accuracy of 0.001 Å for all R and X studied are: *d*(4—5) = 1.387, *d*(5—5′) = 1.446, *d*(5—6) = 1.459, *d*(6—6′7) = 1.382, *d*(6—7) = 1.457, *d*(7—8) = 1.385, *d*(8—8′) = 1.457; those for $[C_{60}$—SiX$]^+$ (X = H, Cl, Cp) cations are: *d*(4—5) = 1.384, *d*(5—5′) = 1.458, *d*(5—6) = 1.458, *d*(6—6′) = 1.384, *d*(6—7) = 1.458, *d*(7—8) = 1.384, *d*(8—8′) = 1.458.

differs from the HOMO energy less than in separated Cp^-. Therefore, this π-MO can also take part in stabilization of η^5-π-complexes; however, its contribution to the bonding must be appreciably less than that of the HOMO.

The values of maximum moduli [*m(*pent)] of the coefficients at the p_z-AOs of the C atoms of the pentagonal face in HOMO of fullerene C_{60} (or anions **1a—c**) and analogous value for the Cp^- anion are given in Table 4. It follows from these data that the value of *m*(pent) increases on going from C_{60} to anions **1a—c**. This quantity has its maximum value in **1a** which is close to *m*(Cp^-). Thus, the MOs capable of forming η^5-π-complexes of fullerene are available in the anions **1a—c** (or in the corresponding radicals). The most favorable situation is realized in the case of anion **1a**.

The introduction of functional groups leads to a pronounced shortening of the C(1)—C(1′) bond length as compared to the analogous bond length in C_{60} (see Table 2) and to an increase in the corresponding Wiberg index (see Table 3). The nature of substituents R merely affects the geometric characteristics of their closest environment (see Tables 2 and 3); the structure of the rest of the fullerene remains virtually unchanged.

Bis(cyclopentadienyl)silicon with D_{5d} symmetry. The structure of the frontier MOs of anions **1** described above allows one to qualitatively estimate the capability of such systems to form η^5-π-complexes. Before we begin discussing this question, let us consider the MOs of bis(cyclopentadienyl)silicon, $SiCp_2$. The PES of this

Table 3. The Wiberg indices (*W*) for the fullerene derivatives with C_{5v} symmetry (see the numbering of atoms in Fig. 2) calculated by the MNDO/PM3 method

System	*W*/au							
	1—1′	1—2	2—3	3—3′	3—4	4—4′	4—5	5—5′
$C_{60}(I_h)$	1.120	1.477	1.120	1.477	1.120	1.120	1.477	1.477
$[H_5C_{60}]^-$	1.359	0.980	0.960	1.600	1.172	1.102	1.449	1.163
$[Cl_5C_{60}]^-$	1.350	0.993	0.956	1.610	1.167	1.101	1.457	1.157
$[Br_5C_{60}]^-$	1.333	1.024	0.971	1.600	1.165	1.101	1.459	1.155
$[C_{60}SiCp]^+$	1.093	1.455	1.122	1.486	1.115	1.113	1.497	1.111
$H_5C_{60}SiCp$	1.277	0.974	0.965	1.618	1.165	1.103	1.460	1.156
$Cl_5C_{60}SiCp$	1.288	0.977	0.961	1.618	1.164	1.101	1.464	1.153
$Br_5C_{60}SiCp$	1.281	0.998	0.975	1.606	1.162	1.100	1.466	1.151
$[C_{60}SiH]^+$	1.092	1.431	1.127	1.476	1.113	1.113	1.498	1.110
$H_5C_{60}SiH$	1.271	0.973	0.965	1.618	1.165	1.103	1.461	1.156
$Cl_5C_{60}SiH$	1.279	0.975	0.961	1.618	1.164	1.100	1.464	1.153
$Br_5C_{60}SiH$	1.273	0.993	0.975	1.606	1.162	1.100	1.466	1.152
$[C_{60}SiCl]^+$	1.093	1.443	1.127	1.478	1.112	1.114	1.499	1.109
$H_5C_{60}SiCl$	1.278	0.973	0.965	1.618	1.165	1.103	1.461	1.156
$Cl_5C_{60}SiCl$	1.288	0.976	0.961	1.618	1.164	1.100	1.464	1.153
$Br_5C_{60}SiCl$	1.282	0.995	0.975	1.606	1.162	1.100	1.466	1.151

Note. The nonreduced Wiberg indices for the bonds in the fullerene fragment of $C_{60}R_5^-$ anions and complexes R_5C_{60}—SiX (X = H, Cl, Cp) with an accuracy of 0.003 au for all R and X studied are: *W*(5—6) = 1.104, *W*(6—6′) = 1.497, *W*(6—7) = 1.119, *W*(7—8) = 1.484, *W*(8—8′) = 1.119; those for $[C_{60}$—SiX$]^+$ (X = H, Cl, Cp) cations are: *W*(5—6) = 1.095, *W*(6—6′) = 1.503, *W*(6—7) = 1.122, *W*(7—8) = 1.476, *W*(8—8′) = 1.120.

molecule has been fragmentarily investigated previously both by semiempirical (MNDO)[8,12] and nonemipirical quantum-chemical methods (using various basis sets, with allowance for correlation corrections[8,14]). A number of local minima was found on the PES of $SiCp_2$. The structures with D_{5d}, D_{5h}, C_2, C_s, C_{2v}, and C_{2h} symmetry correspond to these minima.

It was established that the most symmetric conformers D_{5d} and D_{5h} differ slightly in energy from other conformers. However, the conclusion about the structure of the complex with the minimum energy depends on the calculation procedure. It should be noted that two conformers exist in the crystal in a 1 : 2 ratio: a complex with D_{5d} symmetry and an angular sandwich.[8,14]

Analyzing the MOs of the $SiCp_2$ complex, let us restrict (for clarity) our consideration to bis(cyclopentadienyl)silicon with D_{5d} symmetry that we calculated using the MNDO/PM3 method. To elucidate the nature of the Si—Cp bond, let us take five π-electrons from each Cp-ring and four electrons of the Si atom at a time. Fourteen electrons occupy seven MOs (Scheme 1). The highest occupied energy level (e_{1g}) is doubly degenerate. The corresponding MOs contain no AOs of the Si atom and therefore they are nonbonding MOs (these are the MOs of the Cp-rings). The next a_{1g}*-MO, with a lower energy, is the antibonding AO relative to the Si—Cp interaction and has a large coefficient (0.789) at the s-AO of the Si atom; therefore, it can be considered as an orbital of the lone electron pair of the Si atom. The third of highest occupied levels belongs to the e_{1u} irreducible representation; the corresponding MOs are occupied by four electrons and are the bonding AO.

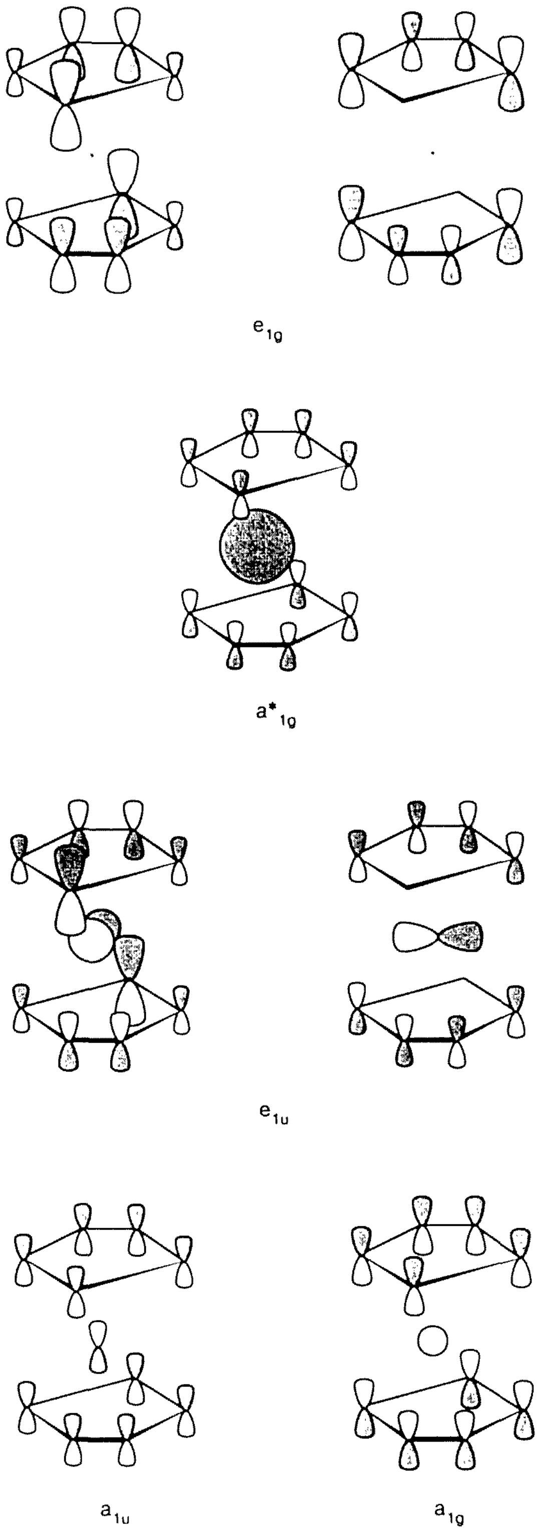
Table 4. Maximum moduli of the coefficients at the p_z-AOs of the C atoms in the HOMOs of the Cp-ring [*m*(Cp)] and the upper pentagonal face of fullerene [*m*(pent)]

System	*m*(Cp)	*m*(pent)
Cp^-	0.63	—
C_{60}	—	0.16
$[H_5C_{60}]^-$	—	0.59
$[Cl_5C_{60}]^-$	—	0.58
$[Br_5C_{60}]^-$	—	0.55

Apart from these orbitals, there are two additional bonding MOs (a_{1g} and a_{1u}) whose energies are 5.7 and 6.4 eV less than the energy of the HOMO. (The structure of the five highest occupied MOs of $SiCp_2$, described above, coincides with that found previously by the MNDO method;[8] however, the last two MOs (a_{1g} and a_{1u}) have not been reported and discussed in this work.) Thus, there are four bonding MOs in the $SiCp_2$ complex belonging to the a_{1g}, a_{1u}, and e_{1u} representations and occupied by eight electrons (see Scheme 1). Taking into account the symmetry of the complex, it is believed that the Si atom is bonded to each of its ligands by two multi-center (generalized) chemical bonds.

The e_{1u} MOs in complexes MCp_2 (D_{5d}) with transition metals M (in contrast to $SiCp_2$ (D_{5d})) contain the AOs of the central atom. These AOs (d_{xz}- and d_{yz}-) overlap with π-orbitals of Cp-rings so that the e_{1u} MOs

Scheme 1



become bonding orbitals. This is the fundamental distinction of the complexes with non-transitional elements from the complexes with transition metals: the central atom of the latter is bonded to each of its ligands by a triple generalized chemical bond.[15]

Sandwich complexes $R_5C_{60}SiCp$ (2), R = H (2a), Cl (2b), Br (2c), $[C_{60}SiCp]^+$ (2d), and $[C_{60}SiCp]^-$ (2e) with C_{5v} symmetry. The results of calculations for these systems are given in Tables 1—3 and in Table 5. It was established that there are local minima on the potential energy surfaces of complexes **2a—c** (Fig. 3) and **2d—e** with C_{5v} symmetry. However, all these critical points, except for that corresponding to complex **2d**, were found to be the saddle points after removal of the symmetry restrictions from the SiCp fragment and upper hemisphere of fullerene. Thus, symmetric complexes **2a—c** barrierlessly transform into η^5-π-complexes with angular structure with an insignificant decrease in the energy (by 1.5 kcal mol^{-1}). Thus, it is believed that the coordination of the SiCp fragment at the pentagonal face in these systems is non-rigid. The symmetric complex **2e** barrierlessly transforms into complex $[\eta^1$-C_{60}-$(\eta^5$-$SiCp)]^-$ whose enthalpy of formation $\Delta_f H°$ is 799.3 kcal mol^{-1}, *i.e.*, the energy decreases by 15.0 kcal mol^{-1}.

Let us consider a qualitative picture of the SiCp bonding to R_5C_{60} by the example of symmetric complexes, taking into account five electrons of R_5C_{60}, five π-electrons of Cp, and four valent electrons of the Si atom. These fourteen electrons of each of complexes **2a—c** occupy seven MOs analogous to those shown in Scheme 1 for $SiCp_2$ and belonging to the a_1 and e_1 irreducible representations of C_{5v} group. However, considering separately the fragment consisting of the five-membered cycle of fullerene C_{60} and SiCp, we can classify its MOs as the orbitals with approximate D_{5d} symmetry. Thus, each of complexes **2a—c** has four bonding MOs with the $\sim a_{1g}$, $\sim a_{1u}$, and $\sim e_{1u}$ symmetry occupied with eight electrons, and it is believed that the

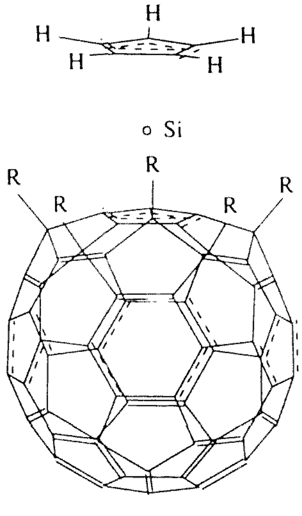


Fig. 3. The structure of η^5-π-complexes $R_5C_{60}SiCp$ with C_{5v} symmetry: R = H (**2a**), R = Cl (**2b**), R = Br (**2c**). See geometric parameters in Table 2.

Table 5. The bond lengths (d/Å), the Wiberg indices (W/au), the valence (V) of the Si atom, and the angle of deviation of the C—H bond from the Cp-ring plane (φ_H) in π-complexes, calculated by the MNDO/PM3 method

Complex	Si—C(Cp)		Si—C(1)		Si—Cp		Si—C_{60}		V_{Si}	φ_H /deg
	d	W	d	W	d	W	d	W		
$SiCp^+$	2.309	0.370	—	—	1.806	1.850	—	—	1.853	6.1
$SiCp^\cdot$	2.270	0.316	—	—	1.916	1.580	—	—	2.431	5.3
$Si—Cp_2$	2.401	0.229	—	—	2.072	1.145	—	—	2.272	4.6
$[C_{60}SiCp]^+$	2.328	0.335	2.569	0.079	1.983	1.675	2.247	0.395	2.138	6.5
$H_5C_{60}SiCp$	2.384	0.251	2.434	0.200	2.050	1.240	2.107	1.015	2.274	4.9
$Cl_5C_{60}SiCp$	2.366	0.280	2.472	0.161	2.030	1.400	2.153	0.805	2.235	5.0
$Br_5C_{60}SiCp$	2.358	0.289	2.483	0.150	2.022	1.440	2.164	0.750	2.229	5.0
$H_5C_{60}SiH$	—	—	2.332	0.302	—	—	1.987	1.510	2.433	—
$Cl_5C_{60}SiH$	—	—	2.360	0.266	—	—	2.021	1.330	2.288	—
$Br_5C_{60}SiH$	—	—	2.367	0.256	—	—	2.028	1.280	2.256	—
$[C_{60}SiCl]^+$	—	—	2.549	0.089	—	—	2.224	0.445	1.847	—
$H_5C_{60}SiCl$	—	—	2.401	0.247	—	—	2.069	1.235	2.347	—
$Cl_5C_{60}SiCl$	—	—	2.437	0.204	—	—	2.111	1.020	2.157	—
$Br_5C_{60}SiCl$	—	—	2.455	0.194	—	—	2.120	0.970	2.140	—

Si atom (as well as in the case of $SiCp_2$) is bonded to each of its ligands by two generalized chemical bonds.

The distinction from the complex $SiCp_2$ lies in the fact that the normalized bonding MOs with the a_1 symmetry in complexes **2a—c** have appreciably lesser coefficients at the AOs of all atoms and therefore they are weakly bonding orbitals. The bonding is predominantly reallized by two ~e_{1u} MOs. In fact, the values of the Wiberg indices W(Si—C_{60}) of complexes **2a—c** are changed from 0.750 to 1.015 which is appreciably larger than that of complex **2d**. The value of W(Si—C_{60}) for complex **2a** is close to the corresponding value for $SiCp_2$ (see Table 5). Analogously to complexes $SiCp_2$, the ~e_{1u} MOs in complexes η^5-π-$R_5C_{60}MCp$ with transition metals M (in contrast to complexes **2a—c**) must become bonding orbitals which will result in strengthening of the Si—C_{60} bond.

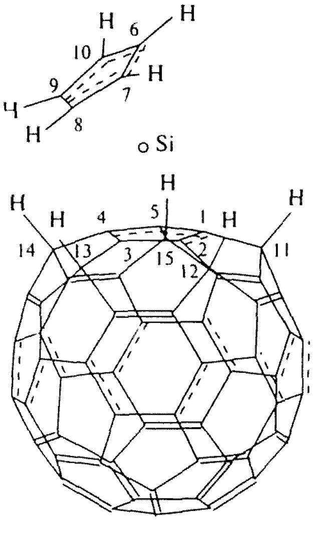


Fig. 4. The structure of η^5-π-complexes $H_5C_{60}SiCp$ with angular configuration. See geometric parameters in Table 6.

Let us discuss some details of the molecular and electronic structure of complexes **2a—2d**. It follows from Table 5 that the Si—C(1) distances in complexes **2a—c** are appreciably shorter than that in **2d** (but they are somewhat longer than that in $SiCp_2$), and the hydrogen atoms of the cyclopentadienyl ligand are deviated upward by an angle $\varphi_H \le 6.5°$. The Wiberg indices also point to the fact that the degree of the Si—C_{60} bonding increases on going from **2d** to **2a—c** (see Table 5). Actually, the Si—C_{60} distances are shortened, and the corresponding Wiberg indices increase in the same sequence as the maximum moduli of the coefficients at the p_z-AOs of the atoms of the upper pentagon in the HOMOs of anions **1a—c** (see m(pent) in Table 4). This confirms the previously made assumption[3,4] on the possibility of stabilizing the η^5-π-bonding of the C_{60} carbon framework by introduction of five functional groups R to α-positions relative to the common pentagon.

The Si—C_{60} bond strength estimated from the heat of reaction

$$[C_{60}SiCp]^+ \rightarrow C_{60} + SiCp^+ \quad (-24.1 \text{ kcal mol}^{-1}).$$

is not high. At the same time, the heats of reactions*

$$H_5C_{60}SiCp \rightarrow [H_5C_{60}]^\cdot + [SiCp]^\cdot \quad (-71.3 \text{ kcal mol}^{-1})$$
$$H_5C_{60}SiCp \rightarrow [H_5C_{60}]^- + [SiCp]^+ \quad (-121.1 \text{ kcal mol}^{-1})$$

are relatively high. This points to the fact that the Si—C_{60} bond strength increases significantly with introducing the functional groups R to α-positions.

Complex $H_5C_{60}SiCp$ (2a′) with C_s symmetry. A more detailed investigation of the PES of complex $H_5C_{60}SiCp$ with full optimization of the geometry of the SiCp fragment and upper hemisphere of fullerene led to another sandwich-type structure of **2a′** (Fig. 4) with angular configuration, which is characterized by the

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* The results of PM3-calculations, $\Delta_f H°(H_5C_{60}^\cdot)$ = 725.0 kcal mol^{-1} [16] and $\Delta_f H°(SiCp^\cdot)$ = 237.4 kcal mol^{-1}, were used.

angles α = 174.1° and β = 153.8° (α is the angle between the line segment, connecting the Si atom to the center of the upper pentagon, and the z axis; β is the angle between the line segments, connecting the Si atom to the centers of Cp and the upper pentagon). This structure has a local minimum on the PES, a symmetry close to C_s, a closed electron shell and $\Delta_f H°$ = 757.5 kcal mol^{-1} (1.3 kcal mol^{-1} lower than $\Delta_f H°$ of **2a**). It should be noted that the configuration of the sandwich complex $SiCp_2$ with the angular geometry (MNDO/PM3-calculations) is 1.1 kcal mol^{-1} more stable than the form with D_{5d} symmetry.

The lengths of some bonds and their Wiberg indices in the structure **2a'** (Table 6) differ considerably from the analogous values in the configuration **2a**. The Si—C_{60} bond is characterized by a total value of W(Si—C_{60}) = 0.992 which is somewhat lower as compared to that of the symmetric sandwich **2a** (see Table 5) while the total value of W(Si—Cp) = 1.240 remained unchanged. The valence of the Si atom is 2.250, which is somewhat lower than in the structure **2a**. The distinction in the electronic structure of configurations **2a'** and **2a** lies in the fact that the hybridization of the Si atom in **2a'** is close to sp^2. The presence on the lone electron pair of the Si atom at one of the sp^2-AOs results in the angular geometry.

Table 6. The bond lengths (d) and the Wiberg indices (W) in the complex **2a'**, mostly differing from the corresponding values in complex **2a** (see the numbering of atoms in Fig. 4)

Bond	d/Å	W/au
C(1)—C(2)	1.422	1.328
C(2)—C(3)	1.432	1.262
C(3)—C(4)	1.441	1.208
C(4)—C(5)	1.434	1.252
C(5)—C(1)	1.422	1.325
C(1)—C(11)	1.492	0.975
C(2)—C(12)	1.493	0.965
C(3)—C(13)	1.493	0.973
C(4)—C(14)	1.493	0.973
C(5)—C(15)	1.492	0.974
C(1)—Si	2.565	0.117
C(2)—Si	2.498	0.165
C(3)—Si	2.357	0.262
C(4)—Si	2.344	0.272
C(5)—Si	2.477	0.176
C(6)—Si	2.497	0.154
C(7)—Si	2.435	0.215
C(8)—Si	2.319	0.315
C(9)—Si	2.310	0.320
C(10)—Si	2.415	0.236

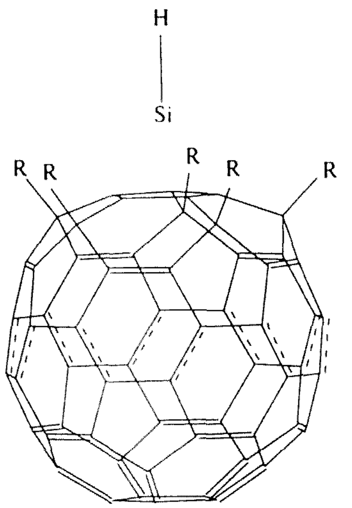

Fig. 5. The structure of η^5-π-complexes $R_5C_{60}SiH$: R = H (**3a**), R = Cl (**3b**), R = Br (**3c**), and that of $R_5C_{60}SiCl$: R = H (**4a**), R = Cl (**4b**), and R = Br (**4c**) with C_{5v} symmetry. See geometric parameters in Table 2.

Half-sandwich complexes $R_5C_{60}SiX$ with C_{5v} symmetry. The calculations have shown that there are local minima on the potential energy surfaces of complexes **3a—c**, **4a—c** (Fig. 5), and $[C_{60}SiX]^+$ (**3d**) with C_{5v} symmetry. Corresponding values of $\Delta_f H°$ are given in Table 1. Complementary investigations with full optimization of the geometry of the SiX fragment and upper hemisphere of fullerene point to the fact that all these configurations correspond to the saddle points and barrierlessly transform into η^5-π-complexes with angular geometry. The decrease in the energy is 13.3 kcal mol^{-1} for the angular configuration of the complex $C_{60}SiH^+$. The Si atom remains on the z axis, β = 109°. There is an isomer of this complex, (η^2-π-C_{60})—SiH^+. Its energy is 15.4 kcal mol^{-1} lower than that of the isomer with the C_{5v} symmetry, and the main geometric characteristics are: α = 160.2°, β = 111.1°, d(Si—C(3)) = d(Si—C(4)) = 2.299 Å, and W(Si—C(3)) = 0.266.

The energies of all angular isomers of compounds **3a—c** and **4a—c** coincide with those of symmetric complexes with an accuracy of 1.5 kcal mol^{-1}; therefore, let us consider for clarity the characteristics of the latter. The geometric parameters of structures **3a—c** and **4a—c** are listed in Tables 2 and 5, whence it follows that the Si—C(1) distances in these complexes are shorter than those in sandwich-type **2a—c** (with the same Rs). However, these values slightly exceed the Si—C bond lengths in $SiCp_2$. The Si—C_{60} distance in complexes **3** is shorter than that in complexes **4** with the same Rs. The data of Table 3 show that the Wiberg indices change analogously. Thus, the Si—C_{60} bond in the complex **3a** appears to be the strongest.

The Si atom in structures **3a—c** and **4a—c** has three generalized chemical bonds with the pentagonal face of fullerene (one orbital with a_1 symmetry and two orbitals with e_1 symmetry). The lone electron pair of the Si atom occupies an antibonding a_1*-MO, in this case its hybrid sp-AO is directed towards fullerene. The second sp-AO participates in the bond with the X atom. The a_1 MO has small coefficients at the AO of the Si atom and therefore makes a small contribution to the $Si-C_{60}$ bonding. The maximum Wiberg index $W(Si-C_{60})$ is 1.5, which corresponds to complex **3a**. The triple generalized chemical bond in the half-sandwiches with nontransitional elements is much weaker than the same bond in the analogous complexes with transitional metals since the bonding MOs with e_1 symmetry in the latter, along with p_x- and p_y-AOs of the central atom, contain the d_{xz}- and d_{yz}-AOs which overlap with the p_z-AOs of the C atoms of the pentagonal face.

Dianion $[Br_5C_{60}Br_5]^{2-}$ (1d) with D_{5d} symmetry. The above procedure of increasing the η^5-π-interaction between the C_{60} framework and the SiCp-type ligands can be extended to the case of two such ligands. The corresponding pentagons are located at the opposite faces of a truncated icosahedron of C_{60}. Thus, for instance, the dianion **1d** is obtained from the structure **1c** by adding five more bromine atoms to α-positions relative to the lower pentagonal face of fullerene.

A local minimum was found from optimization of the geometry on the PES of complex **1d** with D_{5d} symmetry whose energetic characteristics are given in Table 1. The geometric parameters of the upper halves of complexes **1d** and **1c** nearly coincide. The effective charge of −0.70 au is concentrated at each separated face, as in the case of one separate face. Therefore, one can draw a conclusion on the possible existence of η^5-π-complexes of the $CpSi[R_5C_{60}R_5]SiCp$ type on the basis of an analysis of the nature of chemical bonds in the $R_5C_{60}SiCp$ compounds. It is likely that a complex with R = H must be the most stable.

Thus, a qualitative picture of the electronic structure of complexes **2**, **3**, and **4**, established by the MNDO/PM3 method, consists in the following:

1. The introduction of five functional groups R to α-positions relative to the separate pentagonal face of fullerene C_{60} with the formation of $[R_5C_{60}]^-$ anions (R = H, Cl, Br) with C_{5v} symmetry increases the π-electron densities on the C atoms of this face; the maximum effect is achieved at R = H; the distribution of π-electron density on the framed pentagon is close to that of the Cp^- anion. This must favor the formation of η^5-π-complexes.
2. There are local minima on the potential energy surfaces of the model sandwich η^5-$R_5C_{60}SiCp$ [R = H, Cl, Br] systems corresponding to the angular structure of these complexes with non-rigid coordination of the SiCp group. The main characteristics of the $Si-C_{60}$ bond (the length, the Wiberg index, the energy) of these complexes with C_{5v} symmetry are close to analogous values for $SiCp_2$.
3. The Si—Cp bond strength in the half-sandwich complexes $R_5C_{60}SiX$ (X = H, Cl) is higher than that in the sandwich complexes.
4. The existence of local minima on the potential energy surfaces of the η^5-π-complexes $R_5C_{60}SiCp$ in question does not generally point to the existence of analogous η^5-π-complexes with the atoms of transition metals. However, the presence of d_{xz}- and d_{yz}-AOs in the atoms of transition metals makes the hypothesis of stability of the η^5-π-$R_5C_{60}MCp$ compounds reasonably realistic.

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