

# Simulation of molecular and electronic structure of $\eta^5$ - $\pi$ -complexes of fullerene $I_h$ -C<sub>60</sub> with half-sandwich XCp species (X = Si, Ge, Sn)

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The molecular and electronic structure of hypothetical complexes of unsubstituted fullerene C<sub>60</sub> with  $I_h$  symmetry and its cyclopentadienyl type derivatives were simulated by the MNDO/PM3 method taking the C<sub>60</sub>(XCp)<sub>n</sub> molecules ( $n = 1, 2, 10, 12$ ; X = Si, Ge, Sn) and  $\eta^5$ - $\pi$ -C<sub>60</sub>H<sub>5</sub>XCp (X = Ge, Sn), respectively, as example. The complexes 12 $\eta^5$ - $\pi$ -C<sub>60</sub>(XCp)<sub>12</sub> and  $\eta^5$ - $\pi$ -C<sub>60</sub>H<sub>5</sub>XCp with  $I_h$  and C<sub>5v</sub> symmetry, respectively, were found to be the most stable compounds. The energies of the X—C<sub>60</sub> bonds in these complexes are close to those of X—Cp bonds in bis(cyclopentadienyl) complexes XCp<sub>2</sub> and are substantially higher than the energies of similar bonds in complexes of unsubstituted fullerene  $\eta^1$ -C<sub>60</sub>XCp<sup>•</sup> and  $\eta^5$ - $\pi$ -C<sub>60</sub>XCp<sup>+</sup>. Geometric parameters and spin densities in radicals C<sub>60</sub>XCp<sup>•</sup> and biradicals C<sub>60</sub>(XCp)<sub>2</sub> and C<sub>60</sub>H<sub>10</sub> were calculated.

**Key words:** fullerenes,  $\pi$ -complexes, radicals; silicon, germanium, tin; quantum-chemical calculation, MNDO/PM3 method.

The carbon framework of the polyhedral cluster C<sub>60</sub> with  $I_h$  symmetry ( $I_h$ -C<sub>60</sub>) (as well as the polyhedra of many other fullerenes) consists of five- and six-membered cycles, each of them containing 5 and 6  $\pi$ -electrons, respectively. Because of this, there is a possibility for the cluster  $I_h$ -C<sub>60</sub> to form  $\eta^5$ - $\pi$ - and  $\eta^6$ - $\pi$ -complexes. However, no stable compounds of this type have been synthesized to date, though the fullerene chemistry is progressing very intensively (see, e.g., Ref. 1).

Theoretical estimates of the possibility for  $\eta^5$ - and  $\eta^6$ -complexes of C<sub>60</sub> to exist<sup>2–8</sup> have been carried out first of all taking exohedral and endohedral C<sub>60</sub> complexes with the Li<sup>+</sup> cation as examples (see Ref. 2). It has been shown by the MNDO method that the  $\eta^6$ -coordination of Li<sup>+</sup> to unsubstituted fullerene is more preferable than the  $\eta^5$ -coordination; however, the Li—C<sub>60</sub> bond energy (taking into account the fact that this method overestimates the Li—C bond energy)<sup>9</sup> is low.

The estimates of the stability of hypothetical complexes  $\eta^n$ -C<sub>60</sub>MCp (M = Fe, Ru, Os) and  $\eta^n$ -C<sub>60</sub>CrBz ( $n = 5, 6$ ) obtained from EHT calculations with no geometry optimization show that the M—C<sub>60</sub> bonds in such complexes, if they exist, must be very weak as compared to the M—Cp bonds in the same complexes and in corresponding classical sandwich compounds MCp<sub>2</sub> and MBz<sub>2</sub> with the same metals.<sup>4,5</sup>

Strong delocalization of  $\pi$ -electrons in  $\eta^5$ - and  $\eta^6$ -complexes of unsubstituted fullerenes C<sub>m</sub> ( $m \geq 60$ ) is likely to be the main reason for the relatively low stability of these systems.<sup>5</sup> Previously, we have proposed

three procedures for increasing the stability of  $\eta^5$ -complexes with polyhedral carbon framework.

The first procedure for increasing the strength of the bond between the coordinating atom M and the isolated pentagonal face (*pent\**) of the polyhedral cluster C<sub>60</sub> involves a formal attachment of five univalent functional groups R to the  $\alpha$ -positions relative to the *pent\** face. This procedure was first demonstrated taking bowl-shaped fullerene fragments as an example<sup>6</sup> and then applied to complexes C<sub>60</sub>R<sub>5</sub> (R = H, Cl, Br) with SiCp<sup>•</sup> species (see Ref. 7) and Li atom (see Ref. 8). In this case the  $\pi$ -electron system of the radical C<sub>60</sub>R<sub>5</sub><sup>•</sup> (**1**) formed is divided into two parts consisting of 5 and 50  $\pi$ -electrons. The electron density on the atoms of the isolated *pent\** fragment increases and the net effective charge on the *pent\** face of the C<sub>60</sub>R<sub>5</sub><sup>•</sup> anion amounts to  $-0.98$  au; in addition, the moduli of coefficients at the p<sub>z</sub>-AOs in the near-frontier MOs with a<sub>1</sub> and e<sub>1</sub> symmetry increase. The values of these coefficients are close to those of corresponding coefficients of bonding MOs of the cyclopentadienyl anion C<sub>5</sub>H<sub>5</sub><sup>•</sup> (for this reason, the structure **1** is called a *cyclopentadienyl type* system). This favors the  $\eta^5$ -bonding between the *pent\** face and suitable species (metal atoms or half-sandwiches).

The fruitfulness of these theoretical predictions about the capability of radical **1** to form stable  $\eta^5$ - $\pi$ -complexes has been confirmed experimentally. The first complexes of cyclopentadienyl type fullerene derivatives,  $\eta^5$ - $\pi$ -C<sub>60</sub>R<sub>5</sub>M (**2**) (R = Ph; M = Li, K, Tl, Cu·PEt<sub>3</sub>), were synthesized<sup>10</sup> and the structure of complex with Tl was established by X-ray analysis. The MNDO/PM3 calcu-

lations of complexes **2** ( $R = H, Ph$  and  $M = In, Tl$ ) showed<sup>11</sup> that the  $M-pent^*$  bond at  $R = H$  is stronger than at  $R = Ph$  and that the calculated geometric parameters of complex **2** ( $R = Ph, M = Tl$ ) are close to the experimental values.

The expediency of introducing functional groups to the  $\alpha$ -positions relative to the isolated five-membered cycle of cluster  $C_{60}$  was also confirmed taking corannulene\* derivatives of the type  $C_{20}H_{10}R_5SiCp$  ( $R = H, Cl, Br$ )<sup>12</sup> and fullerene  $C_{70}$  derivatives of the types  $\eta^5-\pi-C_{70}R_5Li$  and  $2\eta^5-\pi-C_{70}R_{10}Li_2$  ( $R = H, Cl, Br$ )<sup>13</sup> as examples.

The second procedure of stabilization of  $\eta^5-\pi$ -complexes with polyhedral carbon framework consists in formal replacement of carbon atoms at the  $\alpha$ -positions by such heteroatoms of Group III–V elements of the Periodic system<sup>13–15</sup> that form ordinary bonds with neighboring carbon atoms. This also results in an increase in the electron density on the  $pent^*$  faces (formally, the  $\pi$ -electron system is divided into two parts, one of which consists of five electrons). It is noteworthy that no considerable gain can be obtained when using any of these procedures of stabilization of the  $X-C_{60}$  bond in the case of  $\eta^6$ -complexes.

The third possible procedure of stabilization of  $C_{60}$  complexes with species  $\eta^n-\pi$ -coordinated ( $n = 5, 6$ ) to the polyhedral framework involves an increase in the number of faces to which coordination occurs. Such an approach was theoretically substantiated<sup>16</sup> by molecular dynamics *ab initio* calculations of a hypothetical complex  $12\eta^5-\pi-C_{60}Li_{12}$  (**3**) with the  $I_h$  symmetry, in which the Li atoms are coordinated to each of 12 pentagonal faces of fullerene  $C_{60}$ . The stability of this system was also confirmed by MNDO calculations.<sup>17</sup> In addition, the calculations of  $C_{60}Li_n$  complexes (for  $n$  varied from 1 to 14)<sup>17</sup> showed that at  $n \leq 9$  the Li atoms are coordinated preferably to hexagonal faces, whereas at  $n > 9$  coordination to pentagonal faces occurs.

Analogous conclusions were drawn from the results of *ab initio* MO LCAO SCF calculations of  $C_{60}Li_n$  systems ( $n = 1, 2, 3, 4, 5, 6, 12$ ) using the STO-3G and 6-31G basis sets.<sup>18</sup> It was established that the average energy of abstraction of one Li atom increases in the series of clusters studied as  $n$  increases; however, attachment to three pentagonal faces is possible if  $n$  is 3, 4, or 5. Mention should also be made of the local density functional calculations of compounds  $C_{60}Li_{12}$  and  $C_{60}Li_{32}$ <sup>19</sup> in which the possibility of both the  $\eta^5-\pi$ -coordination of Li atoms to each of 12 pentagonal faces and the  $\eta^6-\pi$ -coordination to each of 20 hexagonal faces was demonstrated. Mass spectra of complexes  $C_{60}Li_n$  were obtained;<sup>17</sup> however, the structures of these systems were not established.

In our opinion, the stability of complex **3** is explained by the fact that the formation of bonds with Li

atoms occurs involving the entire  $\pi$ -system of the  $C_{60}$  molecule (the number of  $\pi$ -MOs that effectively interact with lithium AOs increases and the contributions from Li and C AOs to each bonding  $\pi$ -MO become close in magnitude as in the case of  $CpLi$ ). The possibility of existence of compounds  $C_{60}X_{12}$  with  $I_h$  symmetry was also confirmed by the MNDO/PM3 method taking the system  $C_{60}In_{12}$  as an example.<sup>15</sup>

Analysis of the energies of the  $Li-pent^*$  bond in complexes of  $C_{60}Li^+$  fullerene (**4**) and its cyclopentadienyl type derivatives  $\eta^5-C_{60}R_5Li$  (**5**) and in cluster **3** shows that for structures **5** and **3** these energies are comparable and appreciably higher than that for complex **4**.

Previously, bis(cyclopentadienyl)  $\pi$ -complexes of Group IV elements of the Periodic system  $XCp_2$  ( $X = Si, Ge, Sn$ ) were synthesized and studied.<sup>20–25</sup> Though these complexes are less stable as compared to the classical transition-metal complexes  $MCp_2$ , it was proved that they may have structures belonging to both symmetric ( $D_{5d}, D_{5h}$ ) and bent types. For instance, both structures of the  $\pi$ -complex  $Si(C_5Me_5)_2$  were studied by X-ray analysis<sup>25</sup> and electron diffraction<sup>21</sup> (see also references cited therein). Both semiempirical and *ab initio* calculations show that the total energies of symmetric and bent sandwich complexes differ insignificantly.

It is of interest to estimate the possibility of existence of similar sandwich structures in which one of the  $Cp$  ligands is replaced by fullerene  $C_{60}$ . In this work, the geometry and electronic structure of hypothetical  $n\eta^5-\pi$ -complexes of unsubstituted fullerene  $C_{60}$  with  $XCp$  species ( $X = Si, Ge, Sn; n = 1, 2, 10, \text{ and } 12$ ) were simulated. Investigation of hypothetical  $\eta^5-\pi$ -complexes of cyclopentadienyl type fullerene derivatives  $H_5C_{60}XCp$  ( $X = Ge, Sn$ ) was also continued.

### Calculation procedure

The calculations were carried out by the MNDO/PM3 method<sup>26,27</sup> at the RHF level for molecular systems with closed electron shells and at the ROHF level for radicals and triplet states using the GAMESS<sup>28</sup> and MOPAC 5.10 program packages for DEC 3000 Alpha AXP-400X workstation. A comparison of the strength of the  $X-C_{60}$  bond for all  $\eta^5-\pi$ -complexes of fullerene  $C_{60}$  with  $XCp$  species studied was made.

### Results and Discussion

**Half-sandwich and sandwich complexes of cyclopentadienyl radical with atoms  $X = Si, Ge, \text{ and } Sn$ .** These systems were studied in detail by the MNDO method and using different *ab initio* approximations.<sup>20–25</sup> However, for comparison in the framework of the same method, only data of our calculations of  $\pi$ -complexes  $XCp$  with  $C_{5v}$  symmetry and  $XCp_2$  with  $D_{5d}$  and  $C_{2v}$  symmetry (in the latter case the sandwiches have bent structures in

\* The carbon framework of corannulene coincides with a representative fragment of the  $I_h-C_{60}$  cluster.

**Table 1.** Energy characteristics and geometric parameters of the cyclopentadienyl radical complexes with atoms X (X = Si, Ge, Sn): the heats of formation ( $\Delta H_f$ ), the energies of abstraction of XCp species ( $\Delta(XCp)$ ), the energies of highest occupied ( $E_{HOMO}$ ) and lowest unoccupied ( $E_{LUMO}$ ) MOs, the  $\delta$  values ( $\delta = E_{HOMO} - E_{LUMO}$ ), the effective charges ( $q$ ), distances ( $d$ ), and the angles of deviation of the C—H bond out of the Cp ring plane ( $\varphi$ ) calculated by the MNDO/PM3 method

| Com-<br>pound     | Symmetry | $\Delta H_f$ | $\Delta(XCp)$          | $E_{HOMO}^a$        | $E_{LUMO}^a$       | $\delta$ | $q/au$ |      | $d/\text{\AA}^b$   |                    |       | $\varphi/\text{deg}$ |
|-------------------|----------|--------------|------------------------|---------------------|--------------------|----------|--------|------|--------------------|--------------------|-------|----------------------|
|                   |          |              | $[\Delta(XCp^+)]$      |                     |                    |          | Cp     | X    | C—C                | C—X                | X—Cp  |                      |
|                   |          |              | kcal mol <sup>-1</sup> | eV                  |                    |          |        |      |                    |                    |       |                      |
| Cp <sup>-</sup>   | $D_{5d}$ | 15.9         | —                      | -2.33 <sup>1</sup>  | 8.05 <sup>2</sup>  | 10.4     | -1.00  | —    | —                  | —                  | —     |                      |
| Cp <sup>·</sup>   | $C_s$    | 61.2         | —                      | -5.00 <sup>1</sup>  | 0.43 <sup>1</sup>  | 5.4      | 0.00   | —    | 1.459 <sup>2</sup> | —                  | —     | 0.0                  |
|                   |          |              |                        |                     |                    |          |        |      | 1.376 <sup>2</sup> |                    |       |                      |
|                   |          |              |                        |                     |                    |          |        |      | 1.480 <sup>1</sup> |                    |       |                      |
| SiCp <sup>+</sup> | $C_{5v}$ | 237.4        | [100.3]                | -14.59 <sup>2</sup> | -5.75 <sup>2</sup> | 8.8      | 0.15   | 0.85 | 1.436              | 2.429              | 1.959 | 7.1                  |
| SiCp <sup>·</sup> | $C_s$    | 98.3         | 71.3                   | -3.16 <sup>1</sup>  | -1.79 <sup>1</sup> | 1.4      | -0.12  | 0.12 | 1.445 <sup>2</sup> | 2.255 <sup>1</sup> | 1.9   | —                    |
|                   |          |              |                        |                     |                    |          |        |      | 1.407 <sup>2</sup> | 2.390 <sup>2</sup> |       |                      |
|                   |          |              |                        |                     |                    |          |        |      | 1.451 <sup>1</sup> | 2.400 <sup>2</sup> |       |                      |
| GeCp <sup>+</sup> | $C_{5v}$ | 213.2        | [70.6]                 | -13.83 <sup>2</sup> | -5.54 <sup>2</sup> | 8.3      | -0.09  | 1.09 | 1.430              | 2.416              | 2.088 | 7.6                  |
| GeCp <sup>·</sup> | $C_s$    | 76.2         | 74.5                   | -2.83 <sup>1</sup>  | -0.27 <sup>1</sup> | 2.5      | -0.49  | 0.49 | 1.421 <sup>2</sup> | 2.461 <sup>1</sup> | 2.249 | —                    |
|                   |          |              |                        |                     |                    |          |        |      | 1.432 <sup>2</sup> | 2.436 <sup>2</sup> |       |                      |
|                   |          |              |                        |                     |                    |          |        |      | 1.407 <sup>1</sup> | 2.494 <sup>2</sup> |       |                      |
| SnCp <sup>+</sup> | $C_{5v}$ | 229.0        | [73.6]                 | -14.57 <sup>2</sup> | -6.20 <sup>2</sup> | 8.4      | 0.02   | 0.98 | 1.433              | 2.541              | 2.230 | 9.6                  |
| SnCp <sup>·</sup> | $C_s$    | 80.6         | 72.6                   | -3.88 <sup>1</sup>  | -1.60 <sup>1</sup> | 2.3      | -0.16  | 0.16 | 1.437 <sup>2</sup> | 2.531 <sup>1</sup> | —     | —                    |
|                   |          |              |                        |                     |                    |          |        |      | 1.413 <sup>2</sup> | 2.608 <sup>2</sup> |       |                      |
|                   |          |              |                        |                     |                    |          |        |      | 1.445 <sup>1</sup> | 2.598 <sup>2</sup> |       |                      |
| SiCp <sub>2</sub> | $D_{5d}$ | 94.3         | 61.0                   | -8.22 <sup>2</sup>  | -0.73 <sup>2</sup> | 7.5      | -0.21  | 0.43 | 1.426              | 2.402              | 2.072 | 4.6                  |
|                   | $C_{2v}$ | 93.2         | 62.1                   | -8.281              | -0.79              | 7.5      | -0.22  | 0.45 | 1.418 <sup>2</sup> | 2.522 <sup>1</sup> | —     | —                    |
|                   |          |              |                        |                     |                    |          |        |      | 1.428 <sup>2</sup> | 2.448 <sup>2</sup> |       |                      |
|                   |          |              |                        |                     |                    |          |        |      | 1.436 <sup>1</sup> | 2.326 <sup>2</sup> |       |                      |
| GeCp <sub>2</sub> | $D_{5d}$ | 74.9         | 58.3                   | -8.20 <sup>2</sup>  | -0.43 <sup>2</sup> | 7.2      | -0.43  | 0.87 | 1.422              | 2.476              | 2.160 | 5.2                  |
| SnCp <sub>2</sub> | $D_{5d}$ | 97.5         | 40.1                   | -8.54 <sup>2</sup>  | -0.96 <sup>2</sup> | 7.5      | -0.38  | 0.77 | 1.424              | 2.633              | 2.338 | 6.7                  |
|                   | $C_{2v}$ | 94.7         | 42.9                   | -8.62 <sup>1</sup>  | -1.02 <sup>1</sup> | 7.6      | -0.39  | 0.78 | 1.428 <sup>2</sup> | 2.732 <sup>1</sup> | —     | —                    |
|                   |          |              |                        |                     |                    |          |        |      | 1.423 <sup>2</sup> | 2.668 <sup>2</sup> |       |                      |
|                   |          |              |                        |                     |                    |          |        |      | 1.416 <sup>1</sup> | 2.565 <sup>2</sup> |       |                      |

Note. The heats of formation for the atoms and cations calculated by the MNDO/PM3 method are 108.4 (Si), 89.5 (Ge), 72.2 (Sn), 280.7 (Si<sup>+</sup>), 226.8 (Ge<sup>+</sup>), and 245.6 (Sn<sup>+</sup>) kcal mol<sup>-1</sup>.

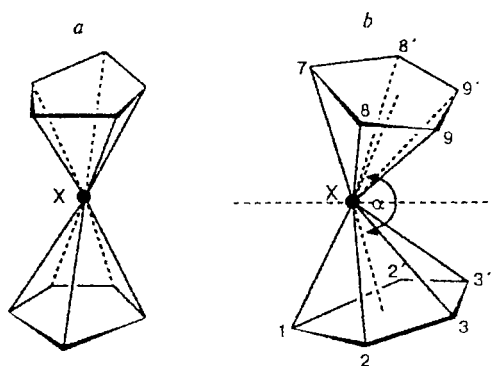
<sup>a</sup> The upper index denotes the level degeneracy.

<sup>b</sup> The upper index denotes the number of identical bonds.

which two parallel edges of the five-membered cycles are brought together; Fig. 1) are listed in Table 1. It should be noted that the energies of bent sandwiches GeCp<sub>2</sub> appeared to be higher than those of their isomers with  $D_{5d}$  symmetry. From the results of calculations it can be concluded that bis(cyclopentadienyl) derivatives of main group elements (Si, Ge, and Sn) are non-rigid systems since the angle  $\alpha$  between the perpendiculars to the planes of Cp ligands can appreciably deviate from 180° and that the heats of formation vary only slightly in this case.

#### Complexes of unsubstituted fullerene C<sub>60</sub>

**Cations  $\eta^5$ -C<sub>60</sub>XCp<sup>+</sup> (X = Si (6a), Ge (6b), Sn (6c); Fig. 2).** The geometric parameters of these cations were optimized assuming that they have  $C_{5v}$  symmetry. Calculations of complex 6a were carried out previously.<sup>7</sup> The structures 6a (6b) with the X—pent\* and X—Cp distances lengthened by 0.2 Å (see Table 1) were used as



**Fig. 1.** Isomers of the sandwich complex XCp<sub>2</sub>: a, isomer with  $D_{5d}$  symmetry; b, bent isomer of the "e—e" (edge-to-edge) type with  $C_{2v}$  symmetry in which the 3—3' edge of the lower Cp ring and the 9—9' edge of the upper Cp ring are brought together;  $\alpha$  is the angle between the perpendiculars to the Cp rings.

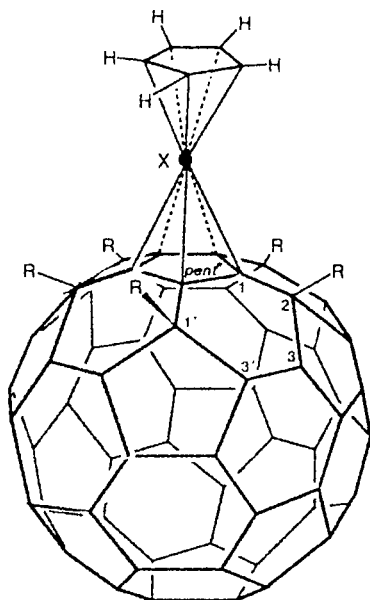


Fig. 2. The structure of complexes  $\eta^5\text{-C}_{60}\text{XCp}^+$  ( $\text{X} = \text{Si}$  (6a), Ge (6b), Sn (6c); with no R) and  $\eta^5\text{-}\pi\text{-H}_5\text{C}_{60}\text{XCp}$  ( $\text{X} = \text{Si}$  (12a), Ge (12b), Sn (12c); R = H) with  $C_{5v}$  symmetry.

**Table 2.** Energy characteristics of complexes of unsubstituted fullerene  $\text{C}_{60}$  with XCp species: the heats of formation ( $\Delta H_f$ ), the energies of abstraction of XCp species ( $\Delta(\text{XCp})$ ), the energies of highest occupied ( $E_{\text{HOMO}}$ ) and lowest unoccupied ( $E_{\text{LUMO}}$ ) MOs, the  $\delta$  values ( $\delta = E_{\text{HOMO}} - E_{\text{LUMO}}$ ), and the effective charges ( $q$ ) calculated by the MNDO/PM3 method

| Compound   | Symmetry | $\Delta H_f$ | $\Delta(\text{XCp})$<br>[ $\Delta(\text{XCp}^+)$ ]<br>kcal mol <sup>-1</sup> | $E_{\text{HOMO}}^a$ | $E_{\text{LUMO}}^a$ | $\delta$ | $q/\text{au}$               |       |       |
|--|----------|--------------|--|---------------------|---------------------|----------|-----------------------------|-------|-------|
|  |          |              |  | eV                  |                     |          | pent*<br>[C(1)]             | Cp    | X     |
| $\text{C}_{60}$                                  | $I_h$    | 811.7        | —  | -9.48 <sup>5</sup>  | -2.89 <sup>3</sup>  | 6.6      | 0.00                        | —     | —     |
| $\text{C}_{60}\text{SiCp}^+$ (6a)                | $C_{5v}$ | 1025.0       | [24.1]   | -11.80 <sup>1</sup> | -5.69 <sup>1</sup>  | 6.1      | -0.24                       | 0.14  | 0.62  |
| $\text{C}_{60}\text{GeCp}^+$ (6b)                | $C_{5v}$ | 1004.6       | [20.3]   | -11.92 <sup>1</sup> | -5.67 <sup>2</sup>  | 6.2      | -0.35                       | -0.16 | 0.95  |
| $\text{C}_{60}\text{SnCp}^+$ (6c)                | $C_{5v}$ | 1030.2       | [10.5]   | -11.88 <sup>1</sup> | -5.67 <sup>2</sup>  | 6.2      | -0.38                       | -0.09 | 0.87  |
| $\text{C}_{60}\text{SiCp}^\cdot$ (7a)            | $C_s$    | 865.7        | 44.3   | -5.24 <sup>1</sup>  | -2.73 <sup>1</sup>  | 2.5      | -0.12                       | 0.05  | 0.33  |
| $\text{C}_{60}\text{GeCp}^\cdot$ (7b)            | $C_s$    | 868.1        | 21.8   | -5.39 <sup>1</sup>  | -3.37 <sup>1</sup>  | 2.0      | -0.09                       | 0.31  | -0.05 |
| $\text{C}_{60}\text{SnCp}^\cdot$ (7c)            | $C_s$    | 871.6        | 20.7   | -5.16 <sup>1</sup>  | -2.71 <sup>1</sup>  | 2.5      | -0.28                       | -0.24 | 0.78  |
| $\text{C}_{60}(\text{SiCp})_2^{2+}$ (8a)         | $D_{5d}$ | 1275.6       | [-13.2]<br>[12.0] <sup>b</sup>   | -13.90 <sup>1</sup> | -7.68 <sup>2</sup>  | 6.2      | -0.18                       | 0.18  | 0.61  |
| $\text{C}_{60}(\text{SiCp})_2^{2+}$ (8b)         | $C_{2v}$ | 1282.7       | [-20.0]<br>[8.4] <sup>b</sup>  | -14.0 <sup>1</sup>  | -8.0 <sup>1</sup>   | 6.0      | -0.20<br>[0.00]             | 0.17  | 0.61  |
| $\text{C}_{60}(\text{SiCp})_2$ (9a)              | $D_{5d}$ | 1127.0       | -118.7   | -5.52 <sup>2</sup>  | -4.95 <sup>1</sup>  | 0.5      | -0.16                       | -0.11 | 0.44  |
| $\text{C}_{60}(\text{SiCp})_2$ (9b)<br>(triplet) | $C_{2h}$ | 920.3        | 43.6<br>44.0 <sup>b</sup>  | -5.06 <sup>1</sup>  | -2.61 <sup>1</sup>  | 2.5      | -0.13                       | 0.05  | 0.33  |
| $\text{C}_{60}(\text{SiCp})_2$ (9c)              | $C_{2v}$ | 918.7        | 45.2   | -7.95 <sup>1</sup>  | -2.62 <sup>1</sup>  | 5.3      | -0.14<br>[-0.16]            | 0.00  | 0.26  |
| $\text{C}_{60}(\text{SiCp})_{10}$ (11a)          | $D_{5d}$ | 1449.8       | 34.5 <sup>b</sup>  | -5.68 <sup>2</sup>  | -3.27 <sup>1</sup>  | 2.4      | -0.39 <sup>d</sup><br>-0.07 | -0.17 | 0.41  |
| $\text{C}_{60}(\text{GeCp})_{10}$ (11b)          | $D_{5d}$ | 1277.2       | 29.7 <sup>b</sup>  | -5.19 <sup>2</sup>  | -3.29 <sup>1</sup>  | 1.9      | -0.36 <sup>d</sup><br>-0.35 | -0.41 | 0.85  |
| $\text{C}_{60}(\text{SnCp})_{10}$ (11c)          | $D_{5d}$ | 1486.2       | 13.2 <sup>b</sup>  | -5.79 <sup>2</sup>  | -3.56 <sup>1</sup>  | 2.2      | -0.30 <sup>d</sup><br>-0.32 | -0.34 | 0.73  |
| $\text{C}_{60}(\text{SiCp})_{12}$ (10a)          | $I_h$    | 1521.9       | 62.3 <sup>c</sup><br>39.1 <sup>b</sup>                                       | -6.29 <sup>3</sup>  | -1.06 <sup>5</sup>  | 5.2      | -0.23                       | -0.20 | 0.43  |
| $\text{C}_{60}(\text{GeCp})_{12}$ (10b)          | $I_h$    | 1290.9       | 69.4 <sup>c</sup><br>38.0 <sup>b</sup>                                       | -6.09 <sup>3</sup>  | -0.68 <sup>5</sup>  | 5.4      | -0.41                       | -0.45 | 0.85  |
| $\text{C}_{60}(\text{SnCp})_{12}$ (10c)          | $I_h$    | 1575.2       | 36.1 <sup>c</sup><br>17.0 <sup>b</sup>                                       | -6.64 <sup>3</sup>  | -1.45 <sup>5</sup>  | 5.2      | -0.35                       | -0.36 | 0.71  |

<sup>a</sup> The upper index denotes the level degeneracy. <sup>b</sup> The average energy of abstraction of one XCp species. <sup>c</sup> The energy of abstraction of one XCp species ( $\Delta E$ ) was determined from the reaction  $\text{C}_{60}(\text{XCp})_{12} \rightarrow \text{C}_{60}(\text{XCp})_{10} + 2 \text{SiCp}^\cdot + 2 \Delta E$ . <sup>d</sup> The charge on the polar face.

initial approximations when calculating cations **6b** (**6c**). The results of calculations for cations **6a–c** are listed in Tables 2 and 3.

These cations have closed electron shells that are characterized by rather large differences  $\delta = E_{\text{LUMO}} - E_{\text{HOMO}}$ , which indicates their potential kinetic stability. However, the energies of the X—pent\* bonds are low so that the existence of such species is improbable. The positive effective charge is localized mainly on the X atom. It should be noted that in the case of low abstraction energies ( $\Delta$ ) of XCp species the X—C<sub>pent\*</sub> and X—pent\* distances are lengthened as compared to analogous distances X—C<sub>Cp</sub> and X—Cp (see Table 3). The Wiberg indices ( $W$ ) of the X—pent\* bond (0.312–0.335) are appreciably smaller than those of the X—Cp bond (1.461–1.675). The X atoms in these cations are divalent. The values of geometric parameters not listed in Table 3 are close to the analogous parameters in the molecule of fullerene  $I_h\text{-C}_{60}$ .

**Radicals  $\text{C}_{60}\text{XCp}^\cdot$**  ( $\text{X} = \text{Si}$  (7a), Ge (7b), Sn (7c); Fig. 3). These systems were calculated with full geometry optimization using the results obtained for the corresponding cations **6a–c** (with X atom on the z axis) as initial approximation. Since the highest occupied

**Table 3.** Distances (*d*), Wiberg indices (*W*), and the angles of deviation of the C—H bond out of the Cp ring plane ( $\phi$ ) in complexes of unsubstituted fullerene calculated by the MNDO/PM3 method

| Compound  | <i>d</i> /Å <sup>a</sup> ( <i>W</i> /au)                       |  |  |  |  |                  |                  |       | $\phi$ /deg |
|---|--|--|--|--|--|------------------|------------------|-------|-------------|
|   | C—C <sub>pent*</sub>   | C—C <sub>Cp</sub>  | C(1)—C(2)  | X—C <sub>pent*</sub><br>[X—C(1)]                               | X—C <sub>Cp</sub>  | X—pent*          | X—Cp             | H...H |             |
| C <sub>60</sub>   | 1.456<br>1.458 <sup>b</sup>                                    | —  | 1.386<br>1.401 <sup>b</sup>                                    | —  | —  | —                | —                | —     | —           |
| C <sub>60</sub> SiCp <sup>+</sup> ( <b>6a</b> )                 | 1.464  | 1.434  | 1.388  | 2.569<br>(0.079)   | 2.328<br>(0.335)   | 2.247<br>(0.395) | 1.983<br>(1.675) | —     | 6.2         |
| C <sub>60</sub> GeCp <sup>+</sup> ( <b>6b</b> )                 | 1.463  | 1.428  | 1.389  | 2.568<br>(0.068)   | 2.434<br>(0.272)   | 2.246<br>(0.339) | 2.109<br>(1.359) | —     | 6.9         |
| C <sub>60</sub> SnCp <sup>+</sup> ( <b>6c</b> )                 | 1.464  | 1.430  | 1.389  | 2.824<br>(0.065)   | 2.568<br>(0.292)   | 2.535<br>(0.312) | 2.259<br>(1.461) | —     | 8.6         |
| C <sub>60</sub> SiCp <sup>·</sup> ( <b>7a</b> )                 | 1.506 <sup>2</sup><br>1.448 <sup>2</sup><br>1.453 <sup>1</sup> | 1.408 <sup>2</sup><br>1.435 <sup>2</sup><br>1.469 <sup>1</sup> | 1.470 <sup>1</sup><br>1.377 <sup>2</sup><br>1.388 <sup>2</sup> | [1.932]  | 2.124 <sup>2</sup><br>2.526 <sup>2</sup><br>2.747 <sup>1</sup> | —                | —                | —     | —           |
| C <sub>60</sub> GeCp <sup>·</sup> ( <b>7b</b> )                 | 1.497 <sup>2</sup><br>1.449 <sup>2</sup><br>1.454 <sup>1</sup> | 1.404 <sup>2</sup><br>1.450 <sup>2</sup><br>1.463 <sup>1</sup> | 1.478 <sup>1</sup><br>1.376 <sup>2</sup><br>1.387 <sup>2</sup> | [1.921]  | 2.029 <sup>2</sup><br>2.525 <sup>2</sup><br>2.800 <sup>1</sup> | —                | —                | —     | —           |
| C <sub>60</sub> SnCp <sup>·</sup> ( <b>7c</b> )                 | 1.501 <sup>2</sup><br>1.450 <sup>2</sup><br>1.452 <sup>1</sup> | 1.411 <sup>2</sup><br>1.432 <sup>2</sup><br>1.447 <sup>1</sup> | 1.467 <sup>1</sup><br>1.378 <sup>2</sup><br>1.387 <sup>2</sup> | [2.276]  | 2.251 <sup>2</sup><br>2.718 <sup>2</sup><br>2.875 <sup>1</sup> | —                | —                | —     | —           |
| C <sub>60</sub> (SiCp) <sub>2</sub> <sup>2+</sup> ( <b>8a</b> ) | 1.463  | 1.435  | 1.387  | 2.607  | 2.319  | 2.291            | 1.972            | —     | 7.0         |
| C <sub>60</sub> (SiCp) <sub>2</sub> <sup>2+</sup> ( <b>8b</b> ) | 1.459 <sup>2</sup><br>1.464 <sup>2</sup><br>1.468 <sup>1</sup> | 1.428 <sup>2</sup><br>1.438 <sup>2</sup><br>1.444 <sup>1</sup> | 1.389  | 2.512 <sup>2</sup><br>2.674 <sup>2</sup><br>2.678 <sup>1</sup> | 2.258 <sup>2</sup><br>2.350 <sup>2</sup><br>2.405 <sup>1</sup> | —                | —                | 7.777 | —           |
| C <sub>60</sub> (SiCp) <sub>2</sub> ( <b>9a</b> )               | 1.457  | 1.429  | 1.412  | 2.462  | 2.376  | 2.128            | 2.041            | —     | 4.7         |
| C <sub>60</sub> (SiCp) <sub>2</sub> ( <b>9b</b> )<br>(triplet)  | 1.506 <sup>2</sup><br>1.448 <sup>2</sup><br>1.453 <sup>1</sup> | 1.408 <sup>2</sup><br>1.435 <sup>2</sup><br>1.468 <sup>1</sup> | 1.471 <sup>1</sup><br>1.377 <sup>2</sup><br>1.388 <sup>2</sup> | [1.929]  | 2.125 <sup>2</sup><br>2.529 <sup>2</sup><br>2.751 <sup>1</sup> | —                | —                | —     | —           |
| C <sub>60</sub> (SiCp) <sub>2</sub> ( <b>9c</b> )               | 1.518 <sup>2</sup><br>1.449 <sup>2</sup><br>1.453 <sup>1</sup> | 1.455 <sup>2</sup><br>1.415 <sup>2</sup><br>1.409 <sup>1</sup> | 1.522  | [1.982]  | 2.078 <sup>2</sup><br>2.312 <sup>2</sup><br>2.652 <sup>1</sup> | —                | —                | 1.635 | —           |
| C <sub>60</sub> (SiCp) <sub>10</sub> ( <b>11a</b> )             | 1.456 <sup>4</sup><br>1.444 <sup>1</sup>                       | 1.449 <sup>2</sup><br>1.408 <sup>2</sup><br>1.423 <sup>1</sup> | 1.421  | 2.294 <sup>1</sup><br>2.378 <sup>2</sup><br>2.643 <sup>2</sup> | 2.172 <sup>1</sup><br>2.377 <sup>2</sup><br>2.595 <sup>2</sup> | —                | —                | 2.582 | —           |
| C <sub>60</sub> (GeCp) <sub>10</sub> ( <b>11b</b> )             | 1.448 <sup>2</sup><br>1.449 <sup>2</sup><br>1.451 <sup>1</sup> | 1.426 <sup>2</sup><br>1.422 <sup>2</sup><br>1.418 <sup>1</sup> | 1.422  | 2.472 <sup>1</sup><br>2.462 <sup>2</sup><br>2.546 <sup>2</sup> | 2.439 <sup>1</sup><br>2.461 <sup>2</sup><br>2.507 <sup>2</sup> | —                | —                | 2.756 | —           |
| C <sub>60</sub> (SnCp) <sub>10</sub> ( <b>11c</b> )             | 1.452 <sup>2</sup><br>1.455 <sup>2</sup><br>1.446 <sup>1</sup> | 1.433 <sup>2</sup><br>1.422 <sup>2</sup><br>1.415 <sup>1</sup> | 1.420  | 2.600 <sup>1</sup><br>2.623 <sup>2</sup><br>2.812 <sup>2</sup> | 2.518 <sup>1</sup><br>2.596 <sup>2</sup><br>2.727 <sup>2</sup> | —                | —                | 2.456 | —           |
| C <sub>60</sub> (SiCp) <sub>12</sub> ( <b>10a</b> )             | 1.447  | 1.426  | 1.435  | 2.427  | 2.400  | 2.070            | 2.072            | 4.082 | 4.4         |
| C <sub>60</sub> (GeCp) <sub>12</sub> ( <b>10b</b> )             | 1.444  | 1.422  | 1.437  | 2.486  | 2.478  | 2.163            | 2.162            | 4.275 | 5.2         |
| C <sub>60</sub> (SnCp) <sub>12</sub> ( <b>10c</b> )             | 1.445  | 1.424  | 1.438  | 2.665  | 2.629  | 2.365            | 2.333            | 4.708 | 6.8         |

<sup>a</sup> The upper index denotes the number of identical bonds.<sup>b</sup> Electron diffraction data.<sup>29</sup>

energy levels in cations **6a–c** are doubly degenerate, the symmetry of radicals **7a–c** can be reduced due to the Jahn–Teller effect. In fact, their optimized structures have C<sub>s</sub> symmetry and radicals **7a–c** are  $\sigma$ -complexes with rather weak X—C(1) bonds (see Tables 2 and 3). The energies of these bonds in radicals **7a–c** are only slightly higher than those in the corresponding cations **6a–c**; the energy gaps  $\delta$  are also narrow, while the spin

populations are localized mainly on the C(2) atom (0.62–0.65 au) and partially on three neighboring atoms and on the X atom (Table 4). All three bonds formed by the C(2) atom and the C(1)—C(1') bond are ordinary bonds, while the C(1')—C(2'), C(1'')—C(2''), and all five C(3)—C(3') bonds are double bonds. The C(1)—C(1') bond is longer than other bonds in the *pent\** fragment. The atom X is  $\pi$ -coordinated to the Cp

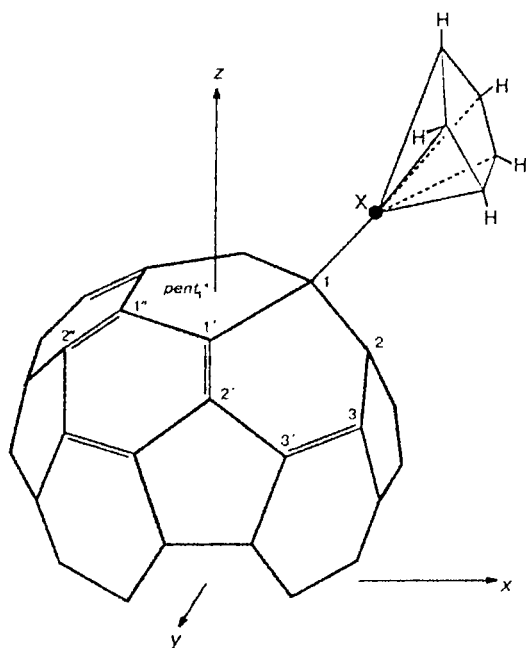


Fig. 3. The fragment of the  $\eta^1$ -structure of radicals  $C_{60}XCp^\cdot$  ( $X = Si$  (7a),  $Ge$  (7b),  $Sn$  (7c)) with  $C_s$  structure (in these systems, the structure of the lower hemisphere is the same as that in fullerene  $C_{60}$  with  $I_h$  symmetry) and the  $2\eta^1$ -structure of biradical (the triplet state)  $C_{60}SiCp_2$  (9b) with  $C_{2h}$  structure, for which the lower half can be completed by inversion ( $i$ ) of the upper half ( $C_2$  axis coincides with the  $y$  axis).

ring; however, the local  $C_{3v}$  symmetry is violated (see Table 3).

Among complexes of  $C_{60}$  with two  $XCp$  groups, only those with  $X = Si$  were calculated. Similar results should also be expected for  $X = Ge$  and  $Sn$ .

**Dication  $C_{60}(SiCp)_2^{2+}$  (8a, Fig. 4)** is a complex in which the  $SiCp$  groups are coordinated to the polar faces

$pent_1^*$  and  $pent_2^*$ . Optimization of its structure assuming that it has  $D_{3d}$  symmetry resulted in a local minimum on the potential energy surface (PES) corresponding to the  $2\eta^5$ - $\pi$ -structure. The geometry of each of its halves (the lower and the upper one) virtually coincides with that of the upper hemisphere of cation 6a with attached  $SiCp$  species (see Table 3 and Fig. 2). The dication 8a has a closed electron shell (for energy parameters, see Table 2); however, the energy of the  $pent-SiCp^+$  bond is negative since the attachment of the second cation to complex 6a is hindered.

**Dication  $C_{60}(SiCp)_2^{2+}$  (8b, Fig. 5)** is an isomer of dication 8a in which the  $SiCp^+$  species are coordinated to two neighboring pentagonal faces  $pent_3^*$  and  $pent_4^*$ . Full geometry optimization performed assuming that the  $SiCp^+$  groups are initially coordinated along the symmetry axes of the isolated  $pent_3$  and  $pent_4$  faces resulted in a local minimum on the PES corresponding to the  $2\eta^5$ - $\pi$ -structure with  $C_{2v}$  symmetry. The heat of formation of isomer 8b is 7.1 kcal mol $^{-1}$  larger than that of structure 8a, which is likely due to the mutual repulsion of two  $SiCp^+$  groups (the effective charges on the Si atom and Cp ring are positive whereas those on the

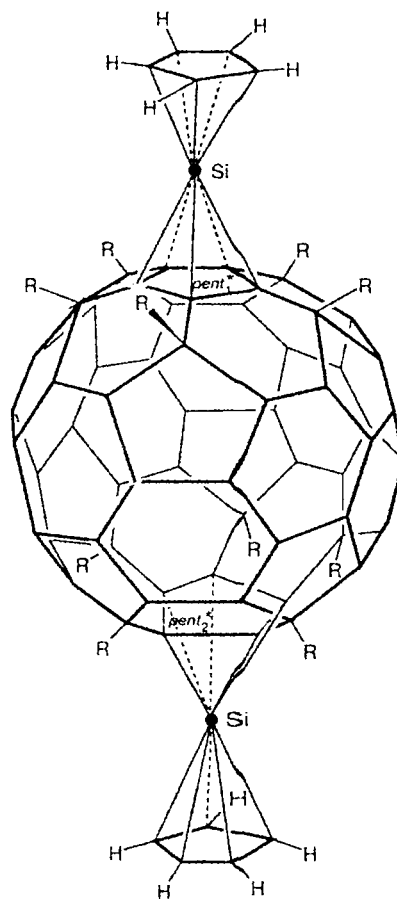


Fig. 4. The structure of dication  $2\eta^5$ - $\pi$ - $C_{60}(SiCp)_2^{2+}$  (8a, with no R), the singlet state of the complex  $2\eta^5$ - $\pi$ - $C_{60}(SiCp)_2$  (9a, with no R), and complex  $2\eta^5$ - $\pi$ - $C_{60}H_{10}(SiCp)_2$  (15,  $R = H$ ).

Table 4. Spin populations ( $\rho$ ) in radicals and biradicals (triplet states) calculated by the MNDO/PM3 method

| Compound                      | $\rho/a.u.$ |       |        |      |      | X    |
|-------------------------------|-------------|-------|--------|------|------|------|
|                               | C(1)        | C(1') | C(1'') | C(2) | C(3) |      |
| $Cp^\cdot$                    | 0.69        | 0.01  | 0.14   | —    | —    | —    |
| $C_{60}H_5^\cdot$             | 0.63        | 0.01  | 0.14   | 0.00 | 0.00 | —    |
| $C_{60}H_{10}$<br>(triplet)   | 0.62        | 0.02  | 0.13   | 0.00 | 0.00 | —    |
| $SiCp^\cdot$                  | 0.00        | 0.02  | 0.03   | —    | —    | 0.89 |
| $GeCp^\cdot$                  | 0.02        | 0.00  | 0.02   | —    | —    | 0.92 |
| $SnCp^\cdot$                  | 0.00        | 0.05  | 0.02   | —    | —    | 0.85 |
| $C_{60}SiCp^\cdot$            | 0.05        | 0.00  | 0.00   | 0.65 | 0.04 | 0.05 |
| $C_{60}GeCp^\cdot$            | 0.04        | 0.01  | 0.00   | 0.62 | 0.02 | 0.05 |
| $C_{60}SnCp^\cdot$            | 0.05        | 0.00  | 0.00   | 0.62 | 0.02 | 0.04 |
| $C_{60}(SiCp)_2$<br>(triplet) | 0.05        | 0.00  | 0.00   | 0.64 | 0.04 | 0.05 |

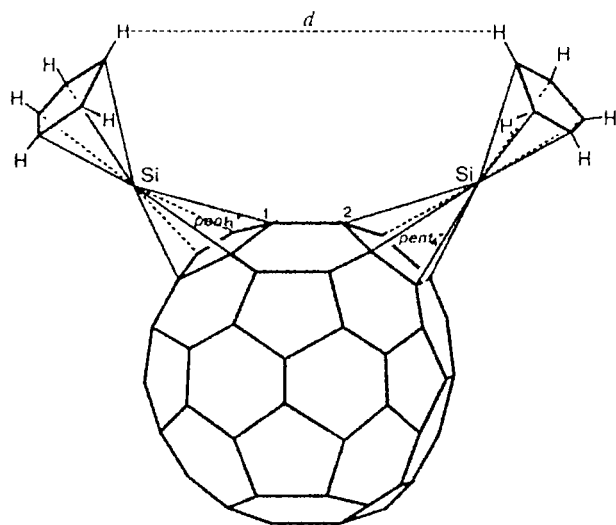
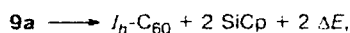


Fig. 5.  $2\eta^5$ -Structure of dication  $C_{60}(SiCp)_2^{2+}$  (**8b**) with  $C_{2v}$  symmetry. Here and in Figs. 6 and 7  $d$  is the H...H distance.

$pent_3^*$  ( $pent_4^*$ ) fragments are negative; the H...H distances are 7.8 Å). The Si—C<sub>pent\*</sub> distances characterizing the multicenter Si— $pent^*$  bond differ appreciably from one another, while the Si—C<sub>Cp</sub> distances characterizing the analogous Si—Cp bond are less different (see Table 3 and Fig. 5).

**Complex  $C_{60}(SiCp)_2$ .** The geometry of the complex was calculated using the structures of dications **8a** and **8b** as initial approximations. Both the triplet and singlet states were calculated for the polar coordination of SiCp species. It was established that the  $2\eta^5$ - $\pi$ -structure **9a** (see Fig. 4) with the  $D_{5d}$  symmetry corresponds to the singlet state. The  $2\eta^1$ -structure **9b** (see Fig. 3) with  $C_{2h}$  symmetry corresponds to the triplet state whose energy is 162 kcal mol<sup>-1</sup> lower than that of the singlet state. The reduced symmetry of complex **9b** is a consequence of the Jahn—Teller effect, since the HOMO level of dication **8a** is doubly degenerate (see Table 2). The geometric parameters of each of the moieties (the upper and the lower one) of compound **9b** coincide with corresponding parameters of the upper moiety of system **7a** (see Table 3 and Fig. 3).

The isomer **9b** is a biradical in which the spin population distribution on each of the  $pent_1^*$  faces is virtually the same as that in radical **7a** (see Table 4). A large amount of energy (118 kcal mol<sup>-1</sup>) is required to form the  $2\eta^5$ - $\pi$ -complex **9a** from radical **7a** and SiCp. The energy of abstraction of one SiCp species from complex **9b** (43.7 kcal mol<sup>-1</sup>) is close to its average value ( $\Delta E = 44.0$  kcal mol<sup>-1</sup>) determined from the reaction



and to the energy of SiCp abstraction from complex **7a** (44.3 kcal mol<sup>-1</sup>).

Having chosen the structure **8b** in which the SiCp species is  $\eta^5$ - $\pi$ -coordinated to neighboring pentagonal faces  $pent_3^*$  and  $pent_4^*$  as initial approximation, we found one more isomer of complex  $C_{60}(SiCp)_2$  which has the  $2\eta^1$ -conformation with  $\sigma$ -coordination of SiCp to two atoms forming the double (in  $C_{60}$ ) C(1)—C(2) bond (**9c**, Fig. 6). The heat of formation of complex **9c** is merely 1.6 kcal mol<sup>-1</sup> lower than that of structure **9b**. For all found isomers of the  $C_{60}(SiCp)_2$  molecule, the energy gaps  $\delta$  are narrow (see Table 2).

**Complexes  $C_{60}(XCp)_2$**  ( $X = Si$  (**10a**), Ge (**10b**), Sn (**10c**); Fig. 7). In these systems, the radicals  $XCp^*$  are coordinated to each of 12 pentagonal faces of fullerene  $C_{60}$ . The geometry of complexes **10a—c** with  $D_{5d}$  symmetry was optimized using the structure of unsubstituted fullerene  $C_{60}$  and the same configurations of half-sandwiches  $XCp$  and  $X-pent^*$  distances as those in the sandwiches  $D_{5d}$ - $XCp_2$  (see Table 1) as initial approximation. The energy minimization resulted in structures **10a—c** with higher  $I_h$  symmetry, and their geometric parameters are listed in Table 3. The calculated clusters have closed electron shells, which undoubtedly is very unusual for such a high degeneracy of the HOMO and LUMO energy levels (see Table 2). The rather large differences  $\delta = E_{HOMO} - E_{LUMO}$  (>5 eV) and high ionization potentials (>6 eV) indicate the kinetic stability of complexes **10a—c**. These values are somewhat lower than those of corresponding bis(cyclopentadienyl) derivatives  $XCp_2$  with  $D_{5d}$  symmetry; however, the energies of the  $X-pent$  bonds are close to those in  $XCp_2$  and are even somewhat higher (see Tables 1 and 2). The ionization potentials and energies of the  $X-pent$  bond in complexes **10a—c** are appreciably higher than those of the unsubstituted fullerene derivatives **7a—c** with one  $XCp$  species. These data are similar to those obtained for the  $LiC_{60}$ ,  $Li_{12}C_{60}$ , and  $LiCp_2$  systems (see above).

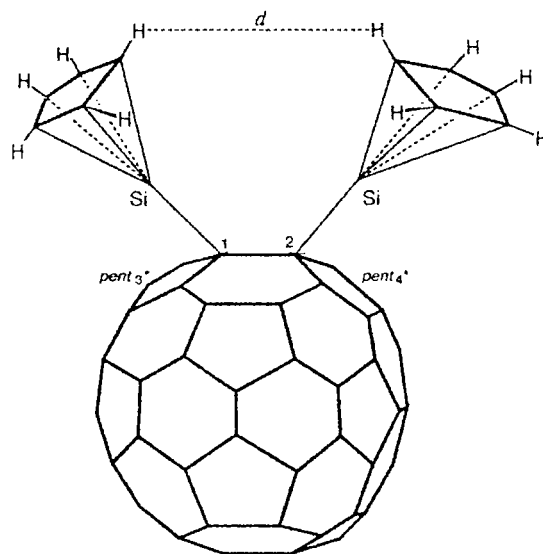


Fig. 6.  $2\eta^1$ -Structure of  $C_{60}(SiCp)_2$  molecule (**9c**) with  $C_{2v}$  symmetry.

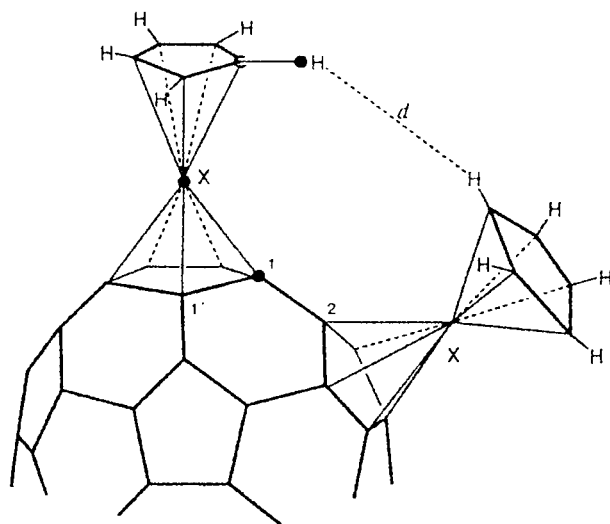


Fig. 7. Fragment of the structure of complexes  $C_{60}(XCp)_{12}$  ( $X = Si$  (10a),  $Ge$  (10b),  $Sn$  (10c)) with  $I_h$  symmetry. Only two XCp ligands are shown; the positions of other ligands are derived by  $D_{5d}$  symmetry operations. The atoms nonequivalent in the symmetry group  $I_h$  are shown by filled circles.

Comparison of geometric parameters of structures 10a–c with analogous parameters of fullerene  $I_h$ - $C_{60}$  shows that the double C(1)–C(2) 6/6-bond (1.386 Å) is lengthened in 10a–c to 1.435–1.438 Å, which is characteristic of ordinary C(1)–C(1') bonds (1.444–1.447 Å). On the contrary, the 5/6-bonds are shortened by 0.01 Å. On the whole, the size of polyhedral fragments of the complexes increases: their diameters lie in the range 7.14–7.15 Å and exceed slightly that of the cluster  $C_{60}$  (7.09 Å). Long H...H distances between the nearest H atoms of neighboring Cp rings (>4 Å) indicate that the introduction of 12 XCp groups produces no steric hindrances. This means that bent attachment of XCp species to pentagonal faces is also possible.

The lengths of the X–*pent* and X–Cp semiaxes are almost equal and close to the corresponding values for the  $XCp_2$  molecule (see Table 3). Like the X atoms in  $XCp_2$ , those in complexes 10a–c are divalent. The effective charges on these atoms in molecules 10a–c are positive and almost the same as those in  $XCp_2$  (the largest and the smallest charges are on the Ge and Si atoms, respectively). The effective charges on each pentagonal face and the Cp ring are virtually independent on X.

To prove that the structures 10a–c correspond to the local minima on corresponding PESs, we performed additional calculations with full optimization of such an initial geometry when the X atoms were displaced with respect to the symmetry axis by 0.02 Å. In all cases the initial symmetric structures were obtained.

**Complexes  $C_{60}(XCp)_{10}$**  ( $X = Si$  (11a),  $Ge$  (11b),  $Sn$  (11c)). Formally, these systems are formed from compounds 10a–c after abstracting two XCp radicals from

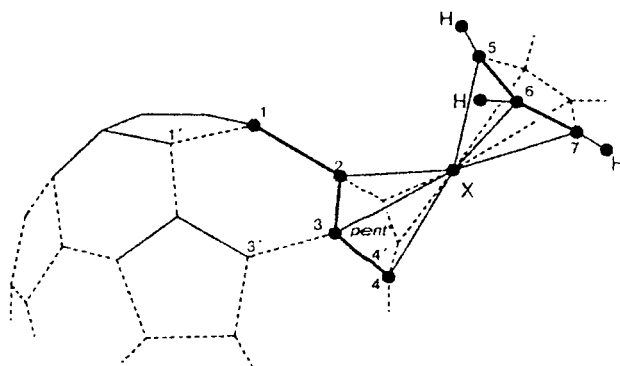


Fig. 8. Fragment of the structure of complexes  $10\eta^5\text{-}\pi\text{-}C_{60}(XCp)_{10}$  with  $D_{5d}$  symmetry ( $X = Si$  (11a),  $Ge$  (11b),  $Sn$  (11c)). Only one XCp ligand is shown. All nonequivalent atoms are shown by filled circles. The molecule is completed by symmetry operations. No coordination of XCp species to the upper and the lower polar pentagons occurs.

the polar five-membered cycles. Minimization of the energy over the geometric parameters was carried out assuming that the  $D_{5d}$  symmetry is conserved. This resulted in a displacement of X atoms relative to the symmetry axes of pentagonal faces (*pent\**), to which they are coordinated, to the polar faces. The *pent\** faces themselves and the carbon skeletons of Cp rings are no longer regular pentagons (see the bond lengths in Table 3) and the angle between the *pent\** and Cp planes differs appreciably from 0° (see Fig. 8). The cyclopentadienyl rings are bent towards polar faces (within free space). In this case the H...H distances between the nearest hydrogen atoms of neighboring Cp rings become appreciably shortened (to 2.6 Å); however, this produces no steric hindrances.

For each X, the average abstraction energies (per XCp group) of systems 11a–c are only slightly lower than those of complexes 10a–c, which is evidence of the potential stability of these systems. The energy gap  $\delta = E_{LUMO} - E_{HOMO}$  (~2 eV) is narrow as compared to those found for complexes 10a–c (5.2–5.5 eV) and  $XCp_2$  (7.7–7.6 eV). The ionization potentials of complexes 11a–c (5.2–5.8 eV) are lower than those of compounds 10a–c (6.1–6.6 eV) and  $XCp_2$  (8.2–8.6 eV).

### Complexes of cyclopentadienyl type fullerene derivatives

**Radical  $C_{60}H_5^\cdot$  and anion  $C_{60}H_5^-$**  were calculated previously<sup>7,30</sup> by the MNDO/PM3 method (see Tables 5 and 6). The spin populations in the radical are localized on the upper pentagonal cycle *pent\** (Fig. 9, see Table 4) which is similar in properties to the Cp radical and thus is capable of forming  $\eta^5\text{-}\pi$ -complexes with XCp species. The negative charge in the  $C_{60}H_5^-$  anion is completely localized on the *pent\** face ( $q = -0.98$  au), which explains its similarity to the  $Cp^-$  anion.



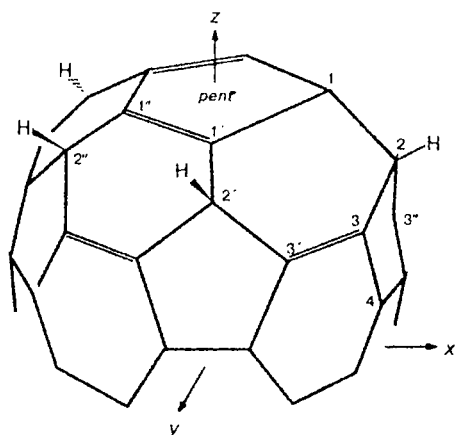


Fig. 9. Fragment of the structure of radical C<sub>60</sub>H<sub>5</sub><sup>•</sup> with C<sub>5v</sub> symmetry (the structure of its lower hemisphere is the same as that in fullerene C<sub>60</sub> with I<sub>h</sub> symmetry) and biradical C<sub>60</sub>H<sub>10</sub> (14) with C<sub>s</sub> $\times$ i symmetry (the lower half is obtained from the upper half by inversion at the fullerene center).

**Complexes H<sub>5</sub>C<sub>60</sub>XCp (12a–c; X = Si, Ge, Sn)** with C<sub>5v</sub> symmetry (see Fig. 2). The case where X = Si has also been considered previously.<sup>7</sup> Minimization of the energy of the systems 12b (12c) over the geometric parameters was first carried out assuming that it has C<sub>5v</sub> symmetry and taking the geometry of the polyhedral fragment in complex 12a and the X–pent\* and X–Cp semiaxes lengthened by 0.2 Å (0.4 Å) as initial approxi-

mations. The results of calculations (see Table 5) indicate that complexes 12a–c have closed electron shells, rather high ionization potentials ( $-E_{\text{HOMO}} = 8.8$  eV, which is somewhat lower than that of I<sub>h</sub>-C<sub>60</sub> but appreciably higher than those of 10a–c), and the energy differences (gaps)  $\delta = E_{\text{LUMO}} - E_{\text{HOMO}}$  of 6.6 eV (like that of I<sub>h</sub>-C<sub>60</sub> but considerably larger than those of molecules 10a–c).

Based on the results mentioned above, it can be argued that complexes 12a–c are kinetically stable systems with energies of the X–C<sub>60</sub> bonds close to those of molecules 10a–c and appreciably higher than the corresponding values for complexes 7a–c of the unsubstituted fullerene C<sub>60</sub>.

The positive effective charges on the atoms X in systems 12a–c are 0.01–0.02 au smaller than those in corresponding complexes XCp<sub>2</sub>, while the negative charges on Cp rings in molecules 12a–c are 0.06–0.07 au smaller than those in XCp<sub>2</sub>. The negative effective charges on C<sub>pent\*</sub> atoms are 0.02 au lower than those on C<sub>Cp</sub> atoms. On the whole, the electron density is transferred from the X atom to the Cp ligand to a greater extent, which corresponds to a stronger X–Cp bond as compared to the X–pent\* bond. This is also evidenced by the geometric parameters of complexes 12a–c (see Table 6): the C<sub>pent\*</sub>–X and pent\*–X bonds are somewhat longer than the C<sub>Cp</sub>–X and Cp–X bonds.

In addition, it is noteworthy that all bonds formed by the C(2) atoms are ordinary (i.e., they are lengthened as compared to the corresponding bonds in the I<sub>h</sub>-C<sub>60</sub> molecule) and that the C–C–H angles are close to

Table 5. Energy characteristics of the complexes of substituted fullerene C<sub>60</sub>H<sub>5</sub> with XCp species: the heats of formation ( $\Delta H_f$ ), the abstraction energies of XCp species ( $\Delta(\text{XCp})$ ), the energies of highest occupied ( $E_{\text{HOMO}}$ ) and lowest unoccupied ( $E_{\text{LUMO}}$ ) MOs, the  $\delta$  values ( $\delta = E_{\text{HOMO}} - E_{\text{LUMO}}$ ), and the effective charges ( $q$ ) calculated by the MNDO/PM3 method

| Compound   | Symmetry        | $\Delta H_f$<br>kcal mol <sup>-1</sup> | $\Delta(\text{XCp})$<br>[ $\Delta(\text{XCp}^+)$ ]<br>kcal mol <sup>-1</sup> | $E_{\text{HOMO}}^a$ | $E_{\text{LUMO}}^a$ | $\delta$<br>eV | $q/\text{au}$ |       |      |
|--|-----------------|--|--|---------------------|---------------------|----------------|---------------|-------|------|
|  |                 |  |  |                     |                     |                | pent*         | Cp    | X    |
| C <sub>60</sub> H <sub>5</sub> <sup>•</sup>              | C <sub>5v</sub> | 642.5                                  | —  | -4.49 <sup>2</sup>  | -0.38 <sup>2</sup>  | 4.1            | -0.98         | —     | —    |
| C <sub>60</sub> H <sub>5</sub> <sup>•</sup>              | C <sub>s</sub>  | 723.6                                  | —  | -6.10 <sup>1</sup>  | -2.37 <sup>1</sup>  | 3.7            | -0.38         | —     | —    |
| H <sub>5</sub> C <sub>60</sub> SiCp (12a)                | C <sub>5v</sub> | 759.8                                  | 62.1<br>[120.1]  | -8.81 <sup>2</sup>  | -2.19 <sup>2</sup>  | 6.6            | -0.67         | -0.14 | 0.45 |
| H <sub>5</sub> C <sub>60</sub> SiCp (13a)                | C <sub>s</sub>  | 757.4                                  | 64.5   | -8.86 <sup>1</sup>  | -2.20 <sup>2</sup>  | 6.7            | -0.69         | -0.14 | 0.45 |
| [H <sub>5</sub> C <sub>60</sub> SiCp] <sup>4-</sup>      | C <sub>5v</sub> | 1018.6                                 | —  | 6.35 <sup>2</sup>   | 8.42 <sup>2</sup>   | 2.0            | -0.66         | -0.66 | 0.16 |
| H <sub>5</sub> C <sub>60</sub> GeCp (12b)                | C <sub>5v</sub> | 739.5                                  | 60.3<br>[116.2]  | -8.82 <sup>2</sup>  | -2.15 <sup>2</sup>  | 6.6            | -0.85         | -0.38 | 0.88 |
| H <sub>5</sub> C <sub>60</sub> GeCp (13b)                | C <sub>s</sub>  | 738.4                                  | 61.4<br>[116.4]  | -8.84 <sup>1</sup>  | -2.15 <sup>2</sup>  | 6.6            | -0.85         | -0.36 | 0.88 |
| H <sub>5</sub> C <sub>60</sub> SnCp (12c)                | C <sub>5v</sub> | 766.1                                  | 38.1   | -8.87 <sup>1</sup>  | -2.18 <sup>2</sup>  | 6.7            | -0.86         | -0.33 | 0.80 |
| H <sub>5</sub> C <sub>60</sub> SnCp (13c)                | C <sub>s</sub>  | 762.8                                  | 41.4<br>[108.3]  | -8.89 <sup>1</sup>  | -2.19 <sup>2</sup>  | 6.7            | -0.87         | -0.34 | 0.82 |
| H <sub>10</sub> C <sub>60</sub> (triplet) (14)           | C <sub>2h</sub> | 638.1                                  | —  | -5.79 <sup>2</sup>  | -1.65 <sup>1</sup>  | 4.1            | -0.39         | —     | —    |
| H <sub>10</sub> C <sub>60</sub> (SiCp) <sub>2</sub> (15) | D <sub>5d</sub> | 710.1                                  | 62.3   | -8.27 <sup>1</sup>  | -1.35 <sup>1</sup>  | 6.9            | -0.66         | -0.17 | 0.45 |

<sup>a</sup> The upper index denotes the level degeneracy.

**Table 6.** Distances (*d*), Wiberg indices (*W*), and angles  $\alpha$  and  $\varphi$  in the complexes of substituted fullerene calculated by the MNDO/PM3 method

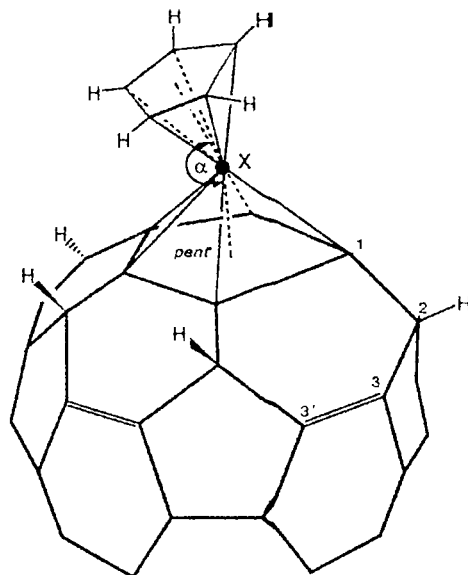
| Compound  | Sym-<br>metry   | <i>d</i> /Å <sup>a</sup> ( <i>W</i> /au) |                    |                    |                      |                    |         |         |            | $\alpha^b$<br>deg | $\varphi^c$<br>deg |
|---|-----------------|--|--------------------|--------------------|----------------------|--------------------|---------|---------|------------|-------------------|--------------------|
|   |                 | C—C <sub>pent*</sub>                     | C—C <sub>Cp</sub>  | C(1)—C(2)          | X—C <sub>pent*</sub> | X—C <sub>Cp</sub>  | X—pent* | X—Cp    | C(3)—C(3') |                   |                    |
| C <sub>60</sub> H <sub>5</sub> <sup>−</sup>                       | C <sub>5v</sub> | 1.414                                    | —                  | 1.487              | —                    | —                  | —       | —       | —          | —                 | —                  |
| C <sub>60</sub> H <sub>5</sub> <sup>·</sup>                       | C <sub>s</sub>  | 1.452 <sup>2</sup>                       | —                  | 1.494 <sup>1</sup> | —                    | —                  | —       | —       | —          | —                 | —                  |
|   |                 | 1.374 <sup>2</sup>                       | —                  | 1.500 <sup>2</sup> | —                    | —                  | —       | —       | —          | —                 | —                  |
|   |                 | 1.475 <sup>1</sup>                       | —                  | 1.499 <sup>2</sup> | —                    | —                  | —       | —       | —          | —                 | —                  |
| H <sub>5</sub> C <sub>60</sub> SiCp ( <b>12a</b> )                | C <sub>5v</sub> | 1.431                                    | 1.428              | 1.493              | 2.434                | 2.384              | 2.107   | 2.050   | 1.368      | 180               | 4.9                |
| H <sub>5</sub> C <sub>60</sub> SiCp ( <b>13a</b> )                | C <sub>s</sub>  | 1.422 <sup>2</sup>                       | 1.420 <sup>2</sup> | 1.492 <sup>1</sup> | 2.568 <sup>1</sup>   | 2.497 <sup>1</sup> | —       | —       | 1.370      | 154               | —                  |
|   |                 | 1.433 <sup>2</sup>                       | 1.431 <sup>2</sup> | 1.493 <sup>4</sup> | 2.498 <sup>2</sup>   | 2.436 <sup>2</sup> | —       | —       | —          | —                 | —                  |
|   |                 | 1.441 <sup>1</sup>                       | 1.436 <sup>1</sup> | —                  | 2.357 <sup>2</sup>   | 2.319 <sup>2</sup> | —       | —       | —          | —                 | —                  |
|   |                 | —  | —                  | —                  | (0.158)              | (0.202)            | (0.790) | (1.010) | —          | —                 | —                  |
| H <sub>5</sub> C <sub>60</sub> GeCp ( <b>12b</b> )                | C <sub>5v</sub> | 1.428                                    | 1.424              | 1.494              | 2.499                | 2.465              | 2.190   | 2.137   | 1.369      | 180               | 5.6                |
| H <sub>5</sub> C <sub>60</sub> GeCp ( <b>13b</b> )                | C <sub>s</sub>  | 1.425 <sup>2</sup>                       | 1.420 <sup>2</sup> | 1.493 <sup>1</sup> | 2.537 <sup>1</sup>   | 2.500 <sup>1</sup> | —       | —       | 1.370      | 146               | —                  |
|   |                 | 1.429 <sup>2</sup>                       | 1.425 <sup>2</sup> | 1.494 <sup>2</sup> | 2.511 <sup>2</sup>   | 2.476 <sup>2</sup> | —       | —       | —          | —                 | —                  |
|   |                 | 1.430 <sup>1</sup>                       | 1.426 <sup>1</sup> | 0.493 <sup>2</sup> | 2.476 <sup>2</sup>   | 2.449 <sup>2</sup> | —       | —       | —          | —                 | —                  |
|   |                 | —  | —                  | —                  | (0.166)              | (0.213)            | (0.831) | (1.068) | —          | —                 | —                  |
| H <sub>5</sub> C <sub>60</sub> SnCp ( <b>12c</b> )                | C <sub>5v</sub> | 1.430                                    | 1.425              | 1.496              | 2.686                | 2.616              | 2.394   | 2.318   | 1.368      | 180               | 7.1                |
| H <sub>5</sub> C <sub>60</sub> SnCp ( <b>13c</b> )                | C <sub>s</sub>  | 1.423 <sup>2</sup>                       | 1.418 <sup>2</sup> | 1.495 <sup>1</sup> | 2.789 <sup>1</sup>   | 2.707 <sup>1</sup> | —       | —       | 1.369      | 138               | —                  |
|   |                 | 1.432 <sup>2</sup>                       | 1.428 <sup>2</sup> | 1.496 <sup>2</sup> | 2.722 <sup>2</sup>   | 2.646 <sup>2</sup> | —       | —       | —          | —                 | —                  |
|   |                 | 1.437 <sup>1</sup>                       | 1.429 <sup>1</sup> | 0.497 <sup>2</sup> | 2.617 <sup>2</sup>   | 2.559 <sup>2</sup> | —       | —       | —          | —                 | —                  |
|   |                 | —  | —                  | —                  | (0.166)              | (0.213)            | (0.831) | (1.068) | —          | —                 | —                  |
| [H <sub>5</sub> C <sub>60</sub> SiCp] <sup>4−</sup>               | C <sub>5v</sub> | 1.456                                    | 1.416              | 1.493              | 2.297                | 2.576              | 1.934   | 2.277   | 1.403      | 180               | —                  |
| H <sub>10</sub> C <sub>60</sub> (triplet) ( <b>14</b> )           | C <sub>2h</sub> | 1.454 <sup>2</sup>                       | —                  | 1.484 <sup>1</sup> | —                    | —                  | —       | —       | —          | —                 | —                  |
|   |                 | 1.374 <sup>2</sup>                       | —                  | 1.493 <sup>2</sup> | —                    | —                  | —       | —       | —          | —                 | —                  |
|   |                 | 1.475 <sup>1</sup>                       | —                  | 1.491 <sup>2</sup> | —                    | —                  | —       | —       | —          | —                 | —                  |
| H <sub>10</sub> C <sub>60</sub> (SiCp) <sub>2</sub> ( <b>15</b> ) | D <sub>5d</sub> | 1.431                                    | 1.427              | 1.494              | 2.427                | 2.389              | 2.100   | 2.058   | 1.366      | 180               | 4.8                |

<sup>a</sup> The upper index denotes the level degeneracy.<sup>b</sup> See Fig. 10.<sup>c</sup> See Table 3.

tetrahedral angles. The C(1)—C(1') and particularly C(3)—C(3') bonds are shortened (the latter bonds become double bonds). The C<sub>pent\*</sub>—X bond lengths in complexes **12a**—**c** and **10a**—**c** nearly coincide.

**Complexes H<sub>5</sub>C<sub>60</sub>XCp (13a—c; X = Si, Ge, Sn)** with C<sub>s</sub> symmetry (Fig. 10). Systems **12a**—**c** can also exist as bent structure isomers. For such systems, full optimization of the geometry also results in local minima corresponding to C<sub>s</sub> symmetry. In this case the heat of formation becomes 1.1—1.3 kcal mol<sup>−1</sup> lower and the angle  $\alpha$  between the perpendiculars to the *pent\** face and Cp ring decreases from 180° to 146—154°. Thus, like the classical sandwiches XCp<sub>2</sub>, the complexes **12a**—**c** are structurally non-rigid systems. For the same X, the geometric parameters of the H<sub>5</sub>C<sub>60</sub> and XCp fragments in compounds **12a**—**c** and **13a**—**c** differ insignificantly (see Table 6). The effective charges on the X atoms of the same type in complexes **10**, **11**, and **12**, and in XCp almost coincide.

**Biradical C<sub>60</sub>H<sub>10</sub> (14, see Fig. 9).** Full optimization of the geometry of the triplet state using the same initial approximation for the upper and lower moieties as that for the upper moiety of C<sub>60</sub>H<sub>5</sub><sup>·</sup> resulted in a local minimum corresponding to C<sub>2h</sub> symmetry (the C<sub>2</sub> axis coincides with  $\gamma$  axis). The geometric and energy parameters of biradical **14** are listed in Tables 6 and 5,



**Fig. 10.** Fragment of the structure of complexes H<sub>5</sub>C<sub>60</sub>XCp (**13a**—**c**) with C<sub>s</sub> symmetry (the symmetry plane passes through the C(1), C(2), and X atoms; the structure of the lower hemisphere is the same as that in fullerene C<sub>60</sub> with I<sub>h</sub> symmetry) and C<sub>60</sub>H<sub>10</sub>(SiCp)<sub>2</sub> (**16**) with C<sub>2h</sub> = C<sub>s</sub> × i symmetry (the lower half is obtained from the upper half by inversion relative at the fullerene center).

respectively. The spin populations on each of the polar faces of radical **14** are the same as in radical C<sub>60</sub>H<sub>5</sub><sup>•</sup> (see Table 4).

**Complex C<sub>60</sub>H<sub>10</sub>(SiCp)<sub>2</sub> (15, see Fig. 4)** has the  $2\eta^5$ - $\pi$ -structure with  $D_{5d}$  symmetry and closed electron shell (see Table 5); the geometry of its lower and upper moieties coincides with that of the upper moiety of the molecule **12a** (see Tables 6 and 3). It is expected that the  $2\eta^5$ - $\pi$ -complex **16** with the  $C_{2h}$  symmetry (see Fig. 10) and bent type of SiCp attachment can be obtained analogously from system **13a**. The heat of formation of this complex, which is isomeric to complex **15**, is somewhat lower than that of **13a**. The energies of SiCp abstraction from molecules **15** and **12a** are equal (see Table 5).

...

The analysis of the results of calculations of complexes C<sub>60</sub>(XCp)<sub>n</sub> ( $n = 1, 2, 10, 12$ ) showed that at  $n = 1$  the XCp species can be  $\eta^5$ - $\pi$ -coordinated to cations and  $\eta^1$ -coordinated to radicals. At  $n = 2$ , the  $2\eta^5$ - $\pi$ -coordination in the molecules is possible only at very large energy consumption required for transition from the triplet ground state with  $2\eta^1$ -structure to the singlet excited state. At  $n = 10$ , the  $10\eta^5$ - $\pi$ -structure with an average energy of SiCp abstraction of 34.5 kcal mol<sup>-1</sup> was found for complex **11a**. At  $n = 12$ , this energy increases to 39.1 kcal mol<sup>-1</sup> and the abstraction energy of one SiCp group is 62.3 kcal mol<sup>-1</sup>.

Thus, according to calculations, all the studied  $12\eta^5$ - $\pi$ -complexes C<sub>60</sub>(XCp)<sub>12</sub> with  $I_h$  symmetry ( $I_h$ -C<sub>60</sub>(XCp)<sub>12</sub>) are the most stable compounds.

The evaluated stability of  $\eta^5$ - $\pi$ -complexes of cyclopentadienyl type fullerene derivative C<sub>60</sub>H<sub>5</sub> with XCp species is as high as that of compounds  $I_h$ -C<sub>60</sub>(XCp)<sub>12</sub> and bis(cyclopentadienyl) complexes XCp<sub>2</sub> and is appreciably higher than that of the corresponding clusters  $\eta^1$ -C<sub>60</sub>XCp and  $\eta^5$ - $\pi$ -C<sub>60</sub>XCp<sup>+</sup>.

On the basis of the results of our calculations one can hypothesize that from the stability of  $\eta^5$ - $\pi$ -complexes of cyclopentadienyl type C<sub>60</sub> fullerene derivatives with XCp species ( $X = \text{Si, Ge, Sn}$ ) it follows that analogous systems with transition metals M can exist. This is possible since despite the fact that the interaction between the M atoms with the fullerene face occurs involving three MOs of the same type (with  $a_1$  and  $e_1$  symmetry), the overlap of  $p_z$ -orbitals of C atoms (the  $z$  axis is perpendicular to the face) with the  $d$ -orbital of the metal atom is appreciably larger than that with  $p_x$ - or  $p_y$ -orbitals of X atoms.

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