Physical Chemistry

Sandwich complexes of Si, Ge, Sn, and Pb with cyclopentadienyl type derivatives of corannulene and fullerene C_{60}: stability estimates and molecular and electronic structure prediction by the MNDO/PM3 method

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The ability of cyclopentadienyl type derivatives of corannulene $C_{20}H_{10}$ and fullerene I_h-C_{60} to form η^5-π-complexes and the problem of their existence is discussed. MNDO/PM3 calculations of half-sandwich complexes η^5-π-$MC_{20}H_{15}$, η^5-π-$MC_{20}H_{15}^+$, η^5-π-$MC_{60}H_5$, η^5-π-$MC_{60}H_5^+$ and sandwich complexes $2\eta^5$-π-$M(C_{20}H_{15})_2$, $2\eta^5$-π-$M(C_{20}H_{15})_2$, $2\eta^5$-π-$M(C_{60}H_5)_2$ (M = Si, Ge, Sn, Pb) were performed. For all systems studied, local minima were found on corresponding potential energy surfaces and the heats of formation, geometric parameters, and distributions of effective atomic charges were calculated. Sandwich complexes are most likely to exist with M = Si and Ge. The energy and geometric characteristics of η^5-π-complexes of corannulene were compared with those of η^5-π-complexes of fullerene I_h-C_{60}. It was concluded that the results of quantum-chemical calculations of sandwich type corannulene derivatives can be used for simulation of the geometry and electronic structure of analogous complexes of fullerene I_h-C_{60}.

Key words: corannulene, fullerene C_{60}, sandwich complexes with Si, Ge, Sn, and Pb atoms, radicals, quantum-chemical calculations, MNDO/PM3 method.

Fullerene molecules have polyhedral frameworks and are pericondensed systems built of carbon rings arranged on convex surfaces in the three-dimensional space. The existence of such molecules was predicted in the early 1970's.[1,2] The first synthesis of fullerenes was reported in 1984 [3] and an efficient procedure for their preparation was developed in the early 1990's,[4] which led to intensive development of the chemistry and physics of these new allotropic modifications of carbon (see, *e.g.*, Refs. 5 and 6).

It has been shown that the most stable forms of fullerenes obey the so-called isolated pentagon rule, according to which the five-membered rings in the fullerene molecules built of five- and six-membered rings* are separated and surrounded only by six-membered rings (see Refs. 5 and 6 and references cited therein). Seemingly, such a "privileged" arrangement of the 12 five-membered rings must favor the formation of η^5-π-complexes of unsubstituted fullerenes. However, rather stable compounds belonging to this type have not

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* The number of five-membered rings in the molecules of such fullerenes is 12.

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been synthesized as yet. At the same time, it has been shown theoretically[7—10] and experimentally[11,12] that the existence of η^5-π-complexes is more probable for cyclopentadienyl type derivatives of fullerenes (C_{60}, C_{70}, *etc.*), such as $R_5C_{60}^{\cdot}$ and $R_5C_{70}^{\cdot}$ radicals. In these systems, functional groups R are attached to carbon atoms in the α-positions relative to the same five-membered ring. For instance, the first synthesis of half-sandwich η^5-π-complexes $MC_{60}R_5$ (M = K, Tl, In; R = Ph) was reported.[11] However, fullerene-based sandwich structures have not been obtained to date. Among these systems, of particular interest are those complexes in which each ligand is a cyclopentadienyl type derivative of fullerene C_{60}. Would such systems appear to be stable and would efficient methods for their synthesis be developed, the possibility of obtaining oligomeric (multi-decker) structures of the type $[MR_5C_{60}R_5]_n$, as well as quasi-linear, quasi-two-dimensional, and three-dimensional macromolecular structures, containing η^5-π-bonded (*e.g.*, by metal atoms) polyhedral molecules will appear. It can be expected that such multi-decker, or network, structures will possess unusual magnetic or conducting properties.

It should be noted that fullerene-based multi-decker molecular systems contain a large number of atoms and it is difficult to study them even by semiempirical quantum-chemical methods. In this connection we attempted to assess the stability, bond energies, selected geometric parameters, and electronic structure of sandwich $2\eta^5$-$M(C_{60}R_5)_2$ complexes using calculations of model $2\eta^5$-$M(C_{20}H_{10}R_5)_2$ systems in which the ligands are cyclopentadienyl type ($C_{20}H_{10}R_5^{\cdot}$) derivatives of corannulene $C_{20}H_{10}$ (Cor). Previously,[13] the efficiency of such an approach was demonstrated in our MNDO/PM3 study of η^5-C_{60}SiCp and η^5-CorX$_5$SiCp (X = H, Cl, Br) complexes, whose structure is simpler than that of $2\eta^5$-$M(C_{60}R_5)_2$ complexes. The Cor molecule is the simplest bowl-shaped conjugated unsaturated hydrocarbon precursor of the fullerene C_{60} molecule. Its carbon framework consists of a five-membered ring (*pent**) framed by five six-membered rings. The geometry and electronic structure of Cor and other bowl-shaped precursors of C_{60} have been studied in detail.[14—16] In this work, the possibility of existence of $2\eta^5$-$(MCorH_5)_2$ (M = Si, Ge, Sn, Pb) complexes and their use in simulation of the geometry and electronic structure of $2\eta^5$-$M(C_{60}H_5)_2$ systems are discussed.

Calculation procedure

The calculations were carried out by the MNDO/PM3 method[17,18] using the MOPAC 5.10 and GAMESS [19] program packages. The RHF and ROHF (for radicals) approximations were used. Molecular geometry was optimized by the analytical gradient method. To accelerate the self-consistency procedure, the DIRSCF and SHIFT procedures incorporated into the GAMESS program package were used.

Results and Discussion

Half-sandwich complexes of cyclopentadienyl type corannulene derivative, the $C_{20}H_{15}^{\cdot}$ radical. The topological structure of the corannulene molecule $C_{20}H_{10}$ is represented as the Schlegel diagram in Fig. 1, *a*, in which the numbering of carbon atoms and α-positions relative to the *pent** cycle are also indicated.

The structure of the cyclopentadienyl type Cor derivative, the $C_{20}H_{15}^{\cdot}$ radical (**1**, Fig. 2), was calculated earlier.[13] The results of these calculations are listed in Tables 1 and 2. Graphic images of the structures of half-sandwich $MC_{20}H_{15}$ complexes ($[\mathbf{1}—M]^{\cdot}$) and $MC_{20}H_{15}^+$ cations ($[\mathbf{1}—M]^+$) are shown in Figs. 3 and 4. Radicals were studied without symmetry restrictions and cationic complexes were calculated assuming that they have C_{5v} symmetry. For all systems considered, local minima were found on corresponding potential energy surfaces (PES). The heats of formation, energies of frontier orbitals, energies of the **1**—M (for radicals) and **1**—M$^+$

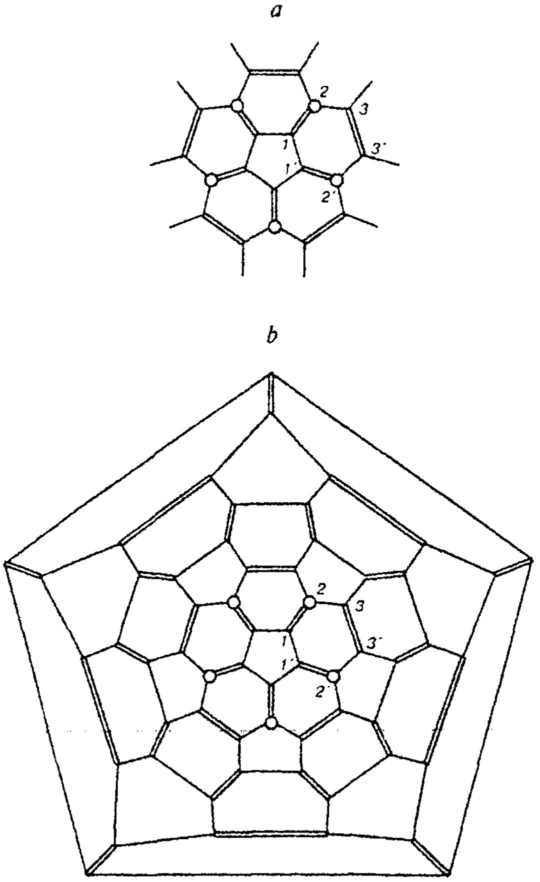

Fig. 1. Schlegel diagrams of corannulene (*a*) and fullerene molecules (*b*); the α-positions relative to the central pentagon (*pent**) are denoted by open circles. Hereafter the atoms equivalent under C_{5v} symmetry differ in the number of primes.

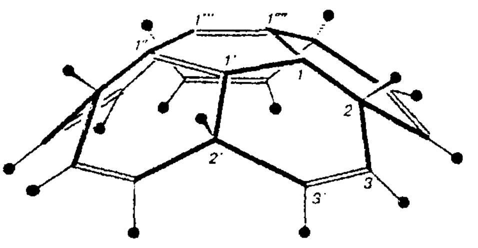

Fig. 2. Structure of corannulene derivative, the CorH$_5^\cdot$ radical (**1**) with C_s symmetry (the symmetry plane passes through atoms *1*, *2*, and the midpoint of the *1''*—*1'''* bond). Hereafter the filled circles denote H atoms.

(for cations) bonds, and charges on the atoms are listed in Table 1. The geometric characteristics of the complexes studied and corresponding Wiberg indices (*W*) are listed in Table 2.

From the data listed in Table 1 it follows that the energy of dissociation ($\Delta_{1^\cdot-M}$) of the [**1**—M]$^\cdot$ radicals into the **1**$^\cdot$ and M species decreases in the series Si > Ge > Sn > Pb and its maximum and minimum values are respectively 72.1 kcal mol^{-1} (M = Si) and 24.3 kcal mol^{-1} (M = Pb). The energy of dissociation ($\Delta_{1^\cdot-M^+}$) of cationic [**1**—M]$^+$ complexes into the **1**$^\cdot$ radical and M$^+$ cation is also maximum at M = Si (105.6 kcal mol^{-1}) and minimum at M = Pb (44 kcal mol^{-1}). In all cases, positive charges are localized on M atoms. Charges in the cations vary from 0.75 au (M = Si) to 1.04 au (M = Ge); among radicals, the largest positive charge (0.46 au) is also localized on the Ge atom.

From the data listed in Table 2 it can be seen that the distance from the M atom to the plane of the five-membered ring in radical **1**$^\cdot$ monotonically increases as the atomic number of M increases. In the [**1**—M]$^\cdot$ radicals, it varies from 2.1 to 2.5 Å, while in the cations it varies from 1.95 to 2.51 Å.

Radicals have C_s symmetry. The M atoms are in the symmetry plane and (at M = Si, Ge, Sn) are shifted toward the C(1) atom of the five-membered ring lying in the same plane (see Fig. 3). Conjugation in the five-membered *pent** ring is violated, *viz*., the C(1)—C(1') and C(1''')—C(1'''') bonds are ordinary (the atoms equivalent under C_{5v} symmetry differ in the number of primes). The *pent** ring is nonplanar: the folding angle along the C(1')—C(1'''') line is about 10°. The M...C distances are varied in the intervals 2.00—2.70 Å (M = Si), 2.45—2.50 Å (M = Ge), 2.45—2.80 Å (M = Sn), and 2.81—

Table 1. Energy characteristics of radical [**1**—M]$^\cdot$ and cationic [**1**—M]$^+$ complexes of $C_{20}H_{15}^\cdot$ radical (**1**) with M = Si, Ge, Sn, Pb: heats of formation (ΔH_f), dissociation energies of **1**—M and **1**—M$^+$ bonds (Δ_{1-M} and Δ_{1-M^+}, respectively), energies of the highest occupied (E_{HOMO}) and lowest unoccupied (E_{LUMO}) MOs, and effective atomic charges (q) calculated by the MNDO/PM3 method

Radical or ion	Symmetry	ΔH_f [a]	Δ_{1-M} (Δ_{1-M^+})	E_{HOMO} [b]	E_{LUMO} [b]	q/au			
		kcal mol^{-1}		eV		C(1) (C(1')) [C(1'')]	C(2) (C(2')) [C(2'')]	C(3)	M
1$^\cdot$	C_s	151.4	—	-5.0^1	0.2^1	0.02 (−0.15) [−0.06]	0.05 (0.08) [0.06]	−0.14	—
1$^-$	C_{5v}	101.8	—	-2.8^2	4.6^2	−0.20	0.11	−0.14	—
[**1**—Si]$^\cdot$	C_s	187.7	72.1	-3.9^1	1.4^1	−0.19 (−0.10) [−0.08]	0.09 (0.08) [0.07]	−0.13	0.08
[**1**—Ge]$^\cdot$	C_s	172.5	68.4	-2.8^1	-0.2^1	−0.12 (−0.23) [−0.15]	0.09 (0.10) [0.09]	−0.14	0.46
[**1**—Sn]$^\cdot$	C_s	179.5	44.1	-3.9^1	-1.5^1	−0.11 (−0.13) [−0.09]	0.08	−0.14	0.10
[**1**—Pb]$^\cdot$	C_s	173.7	24.3	-4.4^1	-1.9^1	−0.11 (−0.13) [−0.12]	0.08	−0.14	0.18
[**1**—Si]$^+$	C_{5v}	326.5	(105.6)	-12.9^2	-5.3^2	−0.10	0.07	−0.13	0.75
[**1**—Ge]$^+$	C_{5v}	304.6	(83.6)	-12.5^2	-5.1^2	−0.15	0.08	−0.13	1.04
[**1**—Sn]$^+$	C_{5v}	322.2	(74.8)	-12.8^2	-5.7^2	−0.13	0.09	−0.13	0.88
[**1**—Pb]$^+$	C_{5v}	325.0	(44.3)	-12.4^2	-6.3^2	−0.11	0.07	−0.13	0.85

[a] Heats of formation of atoms and their cations calculated by the MNDO/PM3 method (kcal mol^{-1}): 108.4 (Si), 89.5 (Ge), 72.2 (Sn), 46.6 (Pb), 280.7 (Si$^+$), 226.8 (Ge$^+$), 245.6 (Sn$^+$), 217.9 (Pb$^+$).

[b] Here and in Tables 3 and 5 the upper indices mean the level degeneracy.

Table 2. Interatomic distances (d/Å), Wiberg indices (W/au), and valences of M atoms (V(M)/au) for radical **1**$^{\cdot}$, anion **1**$^{-}$, and half-sandwich complexes of radical **1**$^{\cdot}$ calculated by the MNDO/PM3 method

Radical or ion	C(1)—C(1′) (C(1′)—C(1″)) [C(1″)—C(1‴)]		C(1)—C(2) (C(1′)—C(2′)) [C(1″)—C(2″)]		C(2)—C(3) (C(2′)—C(3′)) [C(2″)—C(3″)]		C(3)—C(3′)		C(1)—M (C(1′)—M) [C(1″)—M]		V(M)	**1**—M	
	d	W *	d	W *	d	W *	d	W *	d	W *		d	W *
1$^{\cdot}$	1.444 (1.368) [1.463]	—	1.468 (1.477) [1.475]	—	1.504	—	1.338	—	—	—	—	—	—
1^{-}	1.408	1.359	1.473	0.991	1.506	0.973	1.338	1.940	—	—	—	—	—
[**1**—Si]$^{\cdot}$	1.466 (1.435) [1.386]	—	1.484 (1.486) [1.476]	—	1.501 1.505 1.500	—	1.337	—	1.981 (2.208) [2.668]	—	—	2.1	—
[**1**—Ge]$^{\cdot}$	1.421 (1.434) [1.401]	—	1.477 (1.482) [1.478]	—	1.505	—	1.337	—	2.471 (2.440) [2.516]	—	—	2.2	—
[**1**—Sn]$^{\cdot}$	1.442 (1.440) [1.393]	—	1.485 (1.488) [1.479]	—	1.502 (1.504) [1.505]	—	1.336	—	2.454 (2.536) [2.798]	—	—	2.4	—
[**1**—Pb]$^{\cdot}$	1.424 (1.437) [1.409]	1.280 (1.190) [1.384]	1.483 (1.484) [1.481]	0.984 (0.981) [0.984]	1.505 (1.506) [1.505]	0.976	1.337	0.943	2.83 (2.81) [2.88]	0.16 (0.33) [0.17]	2.017	2.5	1.16
[**1**—Si]$^{+}$	1.436	1.212	1.482	0.973	1.504	0.975	1.337	1.945	2.308	0.385	1.966	1.958	1.925
[**1**—Ge]$^{+}$	1.431	1.242	1.483	0.974	1.504	0.976	1.336	1.945	2.421	0.315	1.614	2.092	1.575
[**1**—Sn]$^{+}$	1.436	1.224	1.487	0.970	1.503	0.976	1.335	1.945	2.556	0.356	1.819	2.245	1.780
[**1**—Pb]$^{+}$	1.433	1.233	1.486	0.976	1.503	0.976	1.335	1.945	2.792	0.353	1.829	2.512	1.765

* No procedures for calculating the Wiberg indices in the course of semiempirical calculations are incorporated in the GAMESS program package.

2.88 Å (M = Pb). (For comparison, the sum of the atomic radii of C and M is 2.11, 2.16, 2.35, and 2.52 Å with M = Si, Ge, Sn, and Pb, respectively.[20]) It should be noted that with M = Si, Ge, and Sn the M...C(1), M...C(1′), and M...C(1⁗) distances are approximately equal, whereas the M...C(1″) and M...C(1‴) distances are much longer (see Table 2). Hence, the Si, Ge, and Sn atoms are coordinated to the atoms of the *pent** face according to the η^3-type (see Fig. 3). Approximate equality of the Pb...C_{pent*} distances makes it possible to conclude that the Pb...*pent** interaction belongs to the η^5-type (see Fig. 4), though, strictly speaking, the [**1**—Pb]$^{\cdot}$ radical has no C_{5v} symmetry.

Sandwich complexes 1—M—1. These systems were investigated assuming that they have D_{5h} symmetry; in this case the five-membered *pent** rings should lie in parallel planes (Fig. 5), which corresponds to the available experimental data on the derivatives of cene

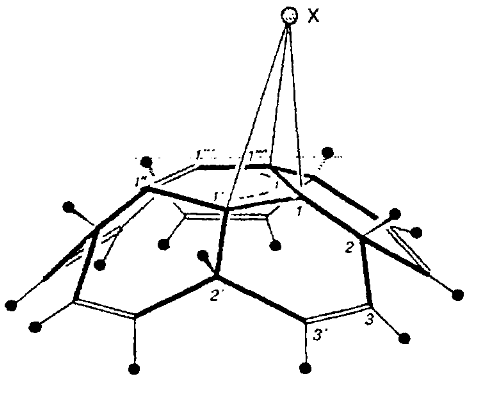

Fig. 3. Structure of radical complexes η^3-X—CorH$_5^{\cdot}$ ([**1**—X]$^{\cdot}$; X = Si, Ge, Sn) with C_s symmetry.

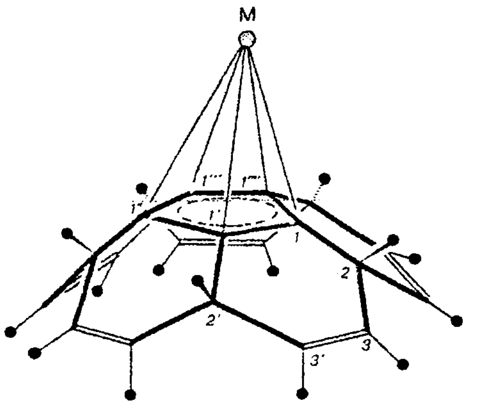

Fig. 4. Structure of radical complex η^5-Pb—CorH$_5^{\cdot}$ ([**1**—Pb]$^{\cdot}$) and cationic η^5-M—CorH$_5^{+}$ ([**1**—M]$^{+}$; M = Si, Ge, Sn, Pb) complexes with C_{5v} symmetry.

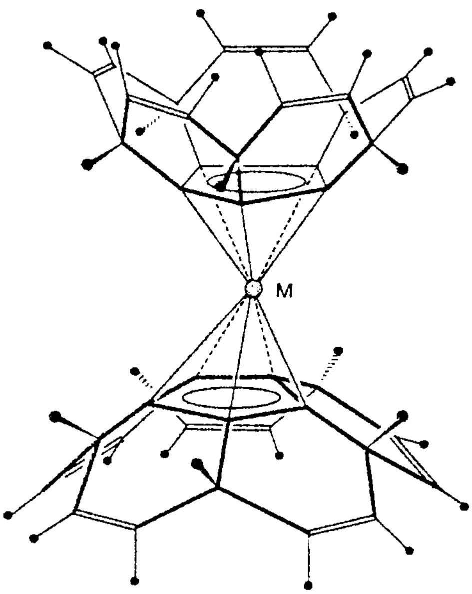

Fig. 5. Structure of $2\eta^5$-M(CorH$_5$)$_2$ (**1**—M—**1**; M = Si, Ge, Sn, Pb) complexes with D_{5h} symmetry.

type compounds of Si, Ge, and Sn with bulky substituents.[21]

The results of calculations for the **1**—M—**1** complexes are listed in Tables 3 and 4. From the data in Table 3 it follows that the energy of dissociation (Δ_{1-M}) of the **1**—M—**1** complex into the [**1**—M]$^{\cdot}$ and **1**$^{\cdot}$ radicals is maximum at M = Si (53 kcal mol^{-1}) and minimum at M = Pb (21 kcal mol^{-1}). The bond energy Δ_{1-M} monotonically decreases in the series Si > Ge > Sn > Pb. For the most stable complexes, $2\eta^5$-π-Si(C$_{20}$H$_{15}$)$_2$ and $2\eta^5$-π-Ge(C$_{20}$H$_{15}$)$_2$, it is 7—8 kcal mol^{-1} lower than the energies of the M—Cp bonds in the sandwich complexes SiCp$_2$ and GeCp$_2$ (62 and 58 kcal mol^{-1}, respectively[10]). The energies of heterolytic dissociation of the **1**—(M—**1**) bond with the formation of the **1**$^-$ anion and [**1**—M]$^+$ cation change in parallel with the above homolytic bond dissociation energies; however, the former are 80—100 kcal mol^{-1} higher. From the data in Table 3 it also follows that the energies of the highest occupied molecular orbitals (HOMOs) lie in the range from −8.0 to −7.7 eV and are virtually independent of the nature of the central atom (these orbitals are mainly composed of ligand orbitals). Charges on the M atoms lie in the range from

Table 3. Energy characteristics of sandwich L—M—L (L = **1**, **2**; M = Si, Ge, Sn, Pb) complexes with D_{5h} symmetry: heats of formation (ΔH_f), homolytic and heterolytic dissociation energies of the L—M bond (Δ_{L-M} and $\Delta_{L^--M^+}$, respectively), energies of the highest occupied (E_{HOMO}) and lowest unoccupied (E_{LUMO}) MOs, and effective atomic charges (q) calculated by the MNDO/PM3 method

Complex	ΔH_f	Δ_{L-M} (Δ_{1-M^+})	E_{HOMO}	E_{LUMO}	q/au			
	kcal mol^{-1}		eV		C(1)	C(2)	C(3)	M
1—Si—**1**	285.9	53.2 (142.4)	−7.7^2	−0.7^2	−0.12	0.09	−0.14	0.41
1—Ge—**1**	272.8	51.1 (133.6)	−7.8^2	−0.1^2	−0.16	0.09	−0.14	0.81
1—Sn—**1**	297.8	43.1 (126.2)	−8.0^2	−0.9^2	−0.16	0.09	−0.14	0.79
1—Pb—**1**	304.4	20.7 (122.4)	−7.8^2	−1.9^2	−0.15	0.09	−0.14	0.72
2—Si—**2**	1425.9	57.3 (128.8)	−9.1^2	−2.4^2	−0.13	0.11	−0.06	0.47
2—Ge—**2**	1406.5	59.5 (124.2)	−9.0^2	−2.3^2	−0.17	0.12	−0.06	0.90
2—Sn—**2**	1437.2	36.8 (112.3)	−9.1^2	−2.4^2	−0.17	0.12	−0.06	0.83
2—Pb—**2**	1443.1	23.3 (107.9)	−9.1^2	−3.2^2	−0.16	0.11	−0.06	0.81

Table 4. Interatomic distances (d/Å), Wiberg indices (W/au), valences of M atoms (V(M)/au), and the C(1)—C(2)—H angle (φ/deg) in L—M—L (L = **1**, **2**) complexes calculated by the MNDO/PM3 method

Complex	C(1)—C(1′)		C(1)—C(2)		C(2)—C(3)		C(3)—C(3′)		C(1)—M		V(M)	C(2)—H,	L—M		φ
	d	W *	d	W *	d	W *	d	W *	d	W *		d	d	W *	
1—Si—**1**	1.425	1.267	1.479	0.982	1.505	0.976	1.337	1.943	2.409	0.228	2.314	1.119	2.082	1.140	110.7
1—Ge—**1**	1.422	1.265	1.480	0.985	1.504	0.976	1.337	1.943	2.485	0.216	2.237	1.119	2.171	1.080	110.8
1—Sn—**1**	1.424	1.284	1.483	0.979	1.503	0.977	1.336	1.943	2.662	0.190	1.923	1.120	2.371	0.950	110.8
1—Pb—**1**	1.423	1.285	1.483	0.981	1.503	0.977	1.336	1.943	2.865	0.195	1.996	1.120	2.597	0.975	110.8
2—Si—**2**	1.432	—	1.493	—	1.527	—	1.369	—	2.414	—	—	1.112	2.085	—	113.0
2—Ge—**2**	1.429	—	1.494	—	1.527	—	1.369	—	2.488	—	—	1.112	2.264	—	113.0
2—Sn—**2**	1.431	—	1.497	—	1.526	—	1.368	—	2.667	—	—	1.112	2.372	—	113.1
2—Pb—**2**	1.431	—	1.497	—	1.526	—	1.368	—	2.890	—	—	1.112	2.622	—	113.1

* No procedures for calculating the Wiberg indices in the course of semiempirical calculations are incorporated in the GAMESS program package.

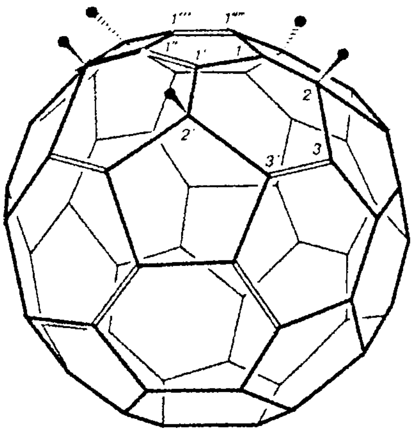

Fig. 6. Structure of fullerene derivative, the $C_{60}H_5{}^{\cdot}$ radical (**2**) with C_s symmetry (the symmetry plane passes through atoms *1*, *2*, and the midpoint of the *1''—1'''* bond).

0.41 to 0.81 au. It should be also noted that the distances between the M atom and the planes of the five-membered *pent** rings in **1** become slightly longer on going from half-sandwich [**1**—M]$^{\cdot}$ complexes to sandwich systems, which corresponds to a decrease in the **1**—(M—**1**) bond energy in the sandwich complexes (see Table 1).

The aforesaid makes it possible to conclude that, among the sandwich complexes considered, the **1**—Si—**1** and **1**—Ge—**1** systems are most likely to exist.

Half-sandwich complexes of cyclopentadienyl type derivative of fullerene I_h-C_{60}, $C_{60}H_5{}^{\cdot}$. The topological structure of fullerene I_h-C_{60} is shown as the Schlegel diagram in Fig. 1, *b* and the structure of its cyclopentadienyl type derivative, the $C_{60}H_5{}^{\cdot}$ radical (**2**), is shown in Fig. 6, in which the numbering of carbon atoms is also indicated. Calculations of half-sandwich $MC_{60}H_5{}^{\cdot}$ ([**2**—M]$^{\cdot}$) complexes and $MC_{60}H_5{}^{+}$ ([**2**—M]$^{+}$) cations have led to structures in which the type of coordination of the M atom to the *pent** face virtually coincides with that shown in Figs. 3 and 4 for the half-sandwich [**1**—M]$^{\cdot}$ and [**1**—M]$^{+}$ systems. Namely, the M atoms in the [**2**—M]$^{\cdot}$ (M = Si, Ge, Sn) radicals are coordinated according to the η^3-type, whereas in the [**2**—Pb]$^{\cdot}$ radical and [**2**—M]$^{+}$ cations they are coordinated according to the η^5-type.

Radical complexes were studied without symmetry restrictions. Cationic complexes were calculated assuming that they have C_{5v} symmetry. For all systems considered, local minima were found on corresponding PES. The heats of formation, energies of frontier orbitals, energies of **2**—M and **2**—M^{+} bonds (for radicals and cations, respectively), and effective atomic charges are listed in Table 5. The geometric characteristics of

Table 5. Energy characteristics of radical [**2**—M]$^{\cdot}$ and cationic [**2**—M]$^{+}$ complexes of radical $C_{60}H_5$ (**2**) with M = Si, Ge, Sn, and Pb: heats of formation (ΔH_f), dissociation energies of **2**—M and **2**—M^{+} bonds (Δ_{2-M} and Δ_{2-M^+}, respectively), energies of the highest occupied (E_{HOMO}) and lowest unoccupied (E_{LUMO}) MOs, and effective atomic charges (q) calculated by the MNDO/PM3 method

System	Symmetry	ΔH_f	Δ_{2-M} (Δ_{2-M^+})	E_{HOMO}	E_{LUMO}	q/au			
		kcal mol^{-1}		eV		C(1) (C(1')) [C(1'')]	C(2) (C(2')) [C(2'')]	C(3)	M
2$^{\cdot}$	C_s	723.6	—	-6.1^{1}	-2.4^{2}	0.03 (−0.15) [−0.05]	0.08 (0.11) [0.09]	−0.05	—
2^{-}	C_{5v}	642.5	—	-4.5^{2}	0.4^{2}	−0.20	0.14	−0.05	—
[**2**—Si]$^{\cdot}$	C_s	759.6	72.4	-4.7^{1}	-2.4^{2}	−0.21 (−0.13) [−0.09]	0.11 (0.10) [0.11]	−0.06	0.23
[**2**—Ge]$^{\cdot}$	C_s	741.4	71.8	-3.6^{1}	-2.1^{2}	−0.17 (−0.28) [−0.12]	0.12	−0.06	0.52
[**2**—Sn]$^{\cdot}$	C_s	750.4	45.4	-4.6^{1}	-2.3^{2}	−0.13 (−0.15) [−0.11]	0.11	−0.06	0.21
[**2**—Pb]$^{\cdot}$	C_s	742.8	27.4	-5.1^{1}	-2.7^{1}	−0.11 (−0.15) [−0.12]	0.11	−0.05	0.30
[**2**—Si]$^{+}$	C_{5v}	912.2	(92.2)	-11.4^{1}	-6.2^{2}	−0.11	0.10	−0.06	0.82
[**2**—Ge]$^{+}$	C_{5v}	888.2	(62.2)	-11.3^{1}	-5.6^{2}	−0.15	0.11	−0.06	1.09
[**2**—Sn]$^{+}$	C_{5v}	907.0	(62.2)	-11.5^{1}	-5.8^{2}	−0.14	0.11	−0.06	0.96
[**2**—Pb]$^{+}$	C_{5v}	908.5	(33.0)	-11.3^{1}	-6.8^{2}	−0.12	0.10	−0.06	0.96

Table 6. Interatomic distances (*d*/Å), Wiberg indices (*W*/au), and valences of M atoms (*V*(M)/au) for radical **2**$^{\cdot}$, anion **2**$^{-}$, and half-sandwich complexes of radical **2** calculated by the MNDO/PM3 method

Radical or ion	C(1)—C(1′) (C(1′)—C(1″)) [C(1″)—C(1‴)]		C(1)—C(2) (C(1′)—C(2′)) [C(1″)—C(2″)]		C(2)—C(3) (C(2′)—C(3′)) [C(2″)—C(3″)]		C(3)—C(3′)		C(1)—M (C(1′)—M) [C(1″)—M]		*V*(M)	C(2)—H,	1—M	
	d	*W*^{a}	*d*	*W*^{a}	*d*	*W*^{a}	*d*^{b}	*W*^{a}	*d*	*W*^{a}		*d*^{b}	*d*	*W*^{a}
2$^{\cdot}$	1.453 (1.374) [1.473]	—	1.483 (1.492) [1.490]	—	1.526 (1.529) [1.528]	—	1.371	—	—	—	—	—	—	—
2^{-}	1.414	—	1.487	—	1.529	—	1.372	—	—	—	—	1.111	—	—
[**2**—Si]$^{\cdot}$	1.478 (1.445) [1.392]	—	1.495 (1.501) [1.491]	—	1.512 (1.529) [1.524]	—	1.368^{2} 1.369^{2} 1.370^{1}	—	1.963 (2.211) [2.651]	—	—	1.114^{1} 1.113^{2} 1.112^{2}	2.0	—
[**2**—Ge]$^{\cdot}$	1.436 (1.447) [1.412]	1.25 (1.36) [1.21]	1.500 (1.491) [1.493]	0.97 (0.98) [.97]	1.526 (1.529) [1.530]	0.960	1.369^{2} 1.371^{2} 1.369^{1}	1.612	2.457 (2.506) [2.488]	0.20 (0.17) [0.12]	1.682	1.112	2.2	0.78
[**2**—Sn]$^{\cdot}$	1.446 (1.445) [1.401]	—	1.497 (1.502) [1.493]	—	1.524 (1.528) [1.524]	—	1.368^{4} 1.369^{1}	—	2.470 (2.558) [2.801]	—	—	1.113^{1} 1.112^{4}	2.3	—
[**2**—Pb]$^{\cdot}$	1.449 (1.428) [1.408]	1.30 (1.20) [1.39]	1.500 (1.499) [1.496]	0.97	1.531 (1.529) [1.526]	0.960	1.369^{2} 1.370^{3}	1.619	2.863 (2.883) [2.870]	0.13 (0.29) [0.16]	1.920	1.113	2.6	1.03
[**2**—Si]$^{+}$	1.443	1.218	1.497	0.965	1.526	0.966	1.368		2.320	0.370	1.886	1.113	1.969	1.850
[**2**—Ge]$^{+}$	1.437	1.247	1.497	0.966	1.526	0.966	1.368	1.621	2.428	0.302	1.543	1.113	2.098	1.572
[**2**—Sn]$^{+}$	1.442	1.231	1.501	0.962	1.524	0.966	1.367	1.622	2.566	0.337	1.717	1.113	2.254	1.685
[**2**—Pb]$^{+}$							1.367	1.622	2.779	0.331	1.705			1.657

[a] No procedures for calculating the Wiberg indices in the course of semiempirical calculations are incorporated in the GAMESS program package.

[b] The upper indices mean the multiplicity of the given value.

the complexes studied and corresponding Wiberg indices are listed in Table 6.

From the data in Table 5 it can be seen that in the case of [**2**—M]$^{\cdot}$ radicals, the **2**—M bond energy is maximum at M = Si (72.4 kcal mol^{-1}) and decreases in the series Si > Ge > Sn > Pb ($\Delta_{2-\mathrm{Pb}}$ = 27.4 kcal mol^{-1}). For cationic complexes, the energy of the **2**—M^{+} bond is also maximum at M = Si (92 kcal mol^{-1}) and minimum at M = Pb (33 kcal mol^{-1}). Comparison of the energies of the **2**—M and **1**—M bonds with those of the **2**—M^{+} and **1**—M^{+} bonds shows that, with the same M atoms, these values are rather close.

In all cases, positive charges are localized on M atoms. Charges in the cationic complexes vary from 0.82 au (M = Si) to 1.09 au (M = Ge). Among the [**2**—M]$^{\cdot}$ radicals, the largest positive charge (0.46 au) is also localized on the Ge atom. Thus, the charge distribution on the M atoms in [**1**—M]$^{\cdot}$, [**2**—M]$^{\cdot}$ and [**1**—M]$^{+}$, [**2**—M]$^{+}$ systems appeared to be almost identical.

From the data in Table 2 it follows that the distance from the M atom to the plane of the five-membered *pent** ring in radical **2** monotonically increases as the atomic number of M increases. In the [**2**—M]$^{\cdot}$ radicals, it varies from 2.0 Å (M = Si) to 2.6 Å (M = Pb), whereas in cationic systems these distances are shortened by 0.1—0.2 Å (for comparison, according to the data of X-ray studies,[21,22] the average M...Cp distances in sandwich M(CpR$_5$)$_2$ complexes are 2.11, 2.21, 2.39, and 2.48 Å with M = Si, Ge, Sn, and Pb, respectively).

Radicals have C_s symmetry. The M atoms are in the symmetry plane and (with M = Si, Ge, Sn) are shifted toward the C(1) atom of the five-membered ring lying in the same plane. The M...C distances are in the intervals 1.96—2.65 Å (M = Si), 2.46—2.51 Å (M = Ge), 2.47—2.80 Å (M = Sn), and 2.86—2.88 Å (M = Pb). These bounds are close to the corresponding values for [**1**—M]$^{\cdot}$ radicals.

Thus, the main geometric parameters of [**1**—M]$^{\cdot}$ and [**2**—M]$^{\cdot}$ systems also appear to be close.

Sandwich complexes 2—M—2. These systems were studied assuming that they have D_{5h} symmetry. The results of calculations are listed in Tables 3 and 4 and the structure of complexes is shown in Fig. 7. The energies of dissociation of the **2**—M—**2** complexes into the radical species [**2**—M]$^{\cdot}$ and **2**$^{\cdot}$ are 57.3, 59.5, 36.8, and 23.3 kcal mol^{-1} for M = Si, Ge, Sn, and Pb, respectively (see Table 3). They differ from analogous values for sandwich **1**—M—**1** complexes by 4—8 kcal mol^{-1}, the energies of the **2**—(M—**2**) bonds in the **2**—Si—**2** and **2**—Ge—**2** systems being comparable with those of the Si—Cp and Ge—Cp bonds in SiCp$_2$ and GeCp$_2$ complexes (61 and 58 kcal mol^{-1}, respectively). In addition,

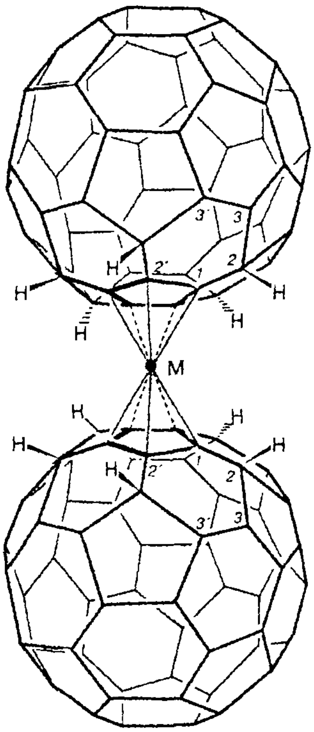

Fig. 7. Structure of $2\eta^5$-$M(C_{60}H_5)_2$ (2—M—2; M = Si, Ge, Sn, Pb) complexes with D_{5h} symmetry.

it should be noted that the energy of dissociation of complex [2—SiCp]$^+$ into the 2$^+$ and SiCp species is 71.3 kcal mol^{-1}, *i.e.*, the [2—SiCp]$^+$ complex must be more stable than the 2—Si—2 and $SiCp_2$ systems.[10] As in the case of **1**—M—**1** complexes, from the results of calculations it follows that the existence of sandwich **2**—Si—**2** and **2**—Ge—**2** complexes is more probable than that of the **2**—Sn—**2** and **2**—Pb—**2** systems.

From the data in Table 3 it can be seen that the HOMO energies are varied in the range 9.0—9.1 eV and are virtually independent of the nature of the central atom. As for the sandwich complexes **1**—M—**1**, the HOMOs of the **2**—M—**2** systems are mainly composed of the ligand orbitals.

Analysis of geometric characteristics of **2**—M—**2** complexes indicates that the distances between the M atom and the plane of the five-membered *pent** ring in fullerene-based sandwich complexes are virtually the same as in the corannulene-based complexes considered above.

Thus, our calculations showed that it is possible to simulate the geometry and electronic structure of η^5-π-complexes of cyclopentadienyl type derivatives of fullerene I_h-C_{60} with Si, Ge, Sn, and Pb atoms using analogous cyclopentadienyl type derivatives of corannulene. However, in this case one should take into account the differences in the first (vertical) ionization potentials of the complexes studied, which are strongly dependent on the ligand nature. In addition, we established that Si- and Ge-containing complexes must be the most stable ones.

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