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Modeling of the molecular and electronic structures of some mono- and biosmium complexes of fullerene C_{60}

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The modeling of the molecular and electronic structures of the following mono- and biosmium complexes of fullerene C_{60} was performed by quantum chemical methods (MNDO/PM3 and DFT/PBE): $(\eta^2\text{-}C_{60})[Os(PPh_3)_2(CO)CNMe]$, $(\eta^2,\eta^2\text{-}C_{60})[Os(PPh_3)_2(CO)(CNMe)]_2$, $(\eta^2\text{-}C_{60})[Os(PH_3)_2(CO)H]$, $(\eta^2,\eta^2\text{-}C_{60})[Os(PH_3)_2(CO)H]_2$, $(\eta^2\text{-}C_{60})[Os(PH_3)_2(CO)CNMe]$, $(\eta^2,\eta^2\text{-}C_{60})[Os(PH_3)_2(CO)CNMe]_2$, and $(\eta^5\text{-}C_{60}H_5)[Os(C_5H_5)]$, $(\eta^5,\eta^5\text{-}C_{60}H_{10})[Os(C_5H_5)]_2$. The osmium atoms in the first six complexes are η^2-coordinated by fullerene C_{60}. In the last two complexes, the η^5-coordination mode is observed. The structures of the radical anions of these complexes were calculated. The energies of the frontier orbitals were evaluated. The acceptor properties of the complexes are discussed. The electron affinities were estimated in two ways: from the energy of the lowest unoccupied molecular orbital (LUMO) and as the energy difference between the neutral molecule and its radical anion.

Key words: fullerene, metal fullerene complex, ionization potential, electron affinity, MNDO/PM3 method, density functional theory (DFT), PBE functional.

In recent years, considerable attention has been given to the design and construction of apparatus to produce energy from light (see, for example, the studies[1,2]). The photoinduced electron transfer from semiconducting polymers to different types of acceptors (for example, to derivatives of fullerenes C_{60}, C_{70}, *etc.*) provides the basis for these photovoltaic devices. The targeted selection of the donor and acceptor components of these devices requires a knowledge of their electronic structures (electron-donating and electron-withdrawing properties, energies of frontier orbitals, charge states of atoms, *etc.*). The electron affinities (EA) and ionization potentials (IP) are the fundamental characteristics of the electronic structure of molecules. These values can be estimated by both experimental and theoretical methods. For fullerene C_{60}, the EA and IP values are 2.67 and 7.57 eV, respectively. In the case of higher fullerenes, the EA values may be larger than 3.0 eV.[3]

The acceptor ability of fullerene derivatives used as components of solar photoelements is one of important parameters determining the efficiency of the photoinduced electron transfer from the donor (conjugated polymer) to the acceptor. The acceptor properties of organic fullerene derivatives (for example, such as methanofullerenes and pyrrolidinofullerenes) were systematically investigated and discussed in a number of publications (see, for example, the studies[4,5] and references therein). However, the acceptor properties of transition metal fullerene complexes have not been studied systematically in spite of the fact that, for example, the electron affinity of the molecular system can be *a priori* estimated by different quantum chemical methods. Exohedral transition metal fullerene complexes are of interest of their own as a new type of components for solar photoelements.

Hence, we studied the donor-acceptor properties of some mono- and biosmium complexes of fullerene C_{60}, both synthesized and model, by quantum chemical methods:

$(\eta^2\text{-}C_{60})[Os(PPh_3)_2(CO)(CNMe)]$ (**1**),
$(\eta^2,\eta^2\text{-}C_{60})[Os(PPh_3)_2(CO)(CNMe)]_2$ (**2**),
$(\eta^2\text{-}C_{60})[Os(PH_3)_2(CO)H]$ (**3**),
$(\eta^2,\eta^2\text{-}C_{60})[Os(PH_3)_2(CO)H]_2$ (**4**),
$(\eta^2\text{-}C_{60})[Os(PH_3)_2(CO)CNMe]$ (**5**),
$(\eta^2,\eta^2\text{-}C_{60})[Os(PH_3)_2(CO)(CNMe)]_2$ (**6**),
$(\eta^5\text{-}C_{60})[Os(C_5H_5)H_5]$ (**7**),
$(\eta^5,\eta^5\text{-}C_{60})[Os(C_5H_5)H_5]_2$ (**8**).

Compounds **1** and **2** are related to the recently synthesized complexes $(\eta^2\text{-}C_{60})Os(PPh_3)_2(CO)(CNBu^t)$ (**1´**) and $(\eta^2,\eta^2\text{-}C_{60})[Os(PPh_3)_2(CO)(CNBu^t)]_2$ (**2´**).[6] Compounds **1** and **2** differ from the latter complexes in that they contain the CNMe group instead of the $CNBu^t$ ligand to simplify calculations. Complexes **3**—**8** are model compounds and are used for the analysis of the influence of the ligand nature and the coordination mode of

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† Deceased.

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the osmium atom by fullerene C_{60} (η^2 or η^5) on their acceptor ability.

Computational methods

Initially, the geometry of the complexes was modeled using the molecular mechanics method. Then the geometric parameters were refined by the semiempirical MNDO/PM3 method. In the last step, the energy-optimized structures of the complexes were determined and the electronic characteristics, the energies of frontier orbitals, and the effective charge distribution were calculated by the density functional theory (DFT) method at the PBE level of theory[7,8] with the use of the PRIRODA program.[9] The character of the stationary points was determined based on the analysis of the eigenvalues of the corresponding Hessians. The calculations were carried out with the mixed atomic basis. For second-row elements, two-exponential basis functions were used. The radical anions of complexes **1**—**8** were calculated without energy optimization, *i.e.*, for the geometry found for the corresponding neutral complexes.

Results and Discussion

Complex **(η^2-C_{60})[Os(PPh_3)$_2$(CO)CNMe] (1)** has a structure shown in Fig. 1. Figure 2 presents the atomic numbering scheme for the fullerene cage; the Os atom is

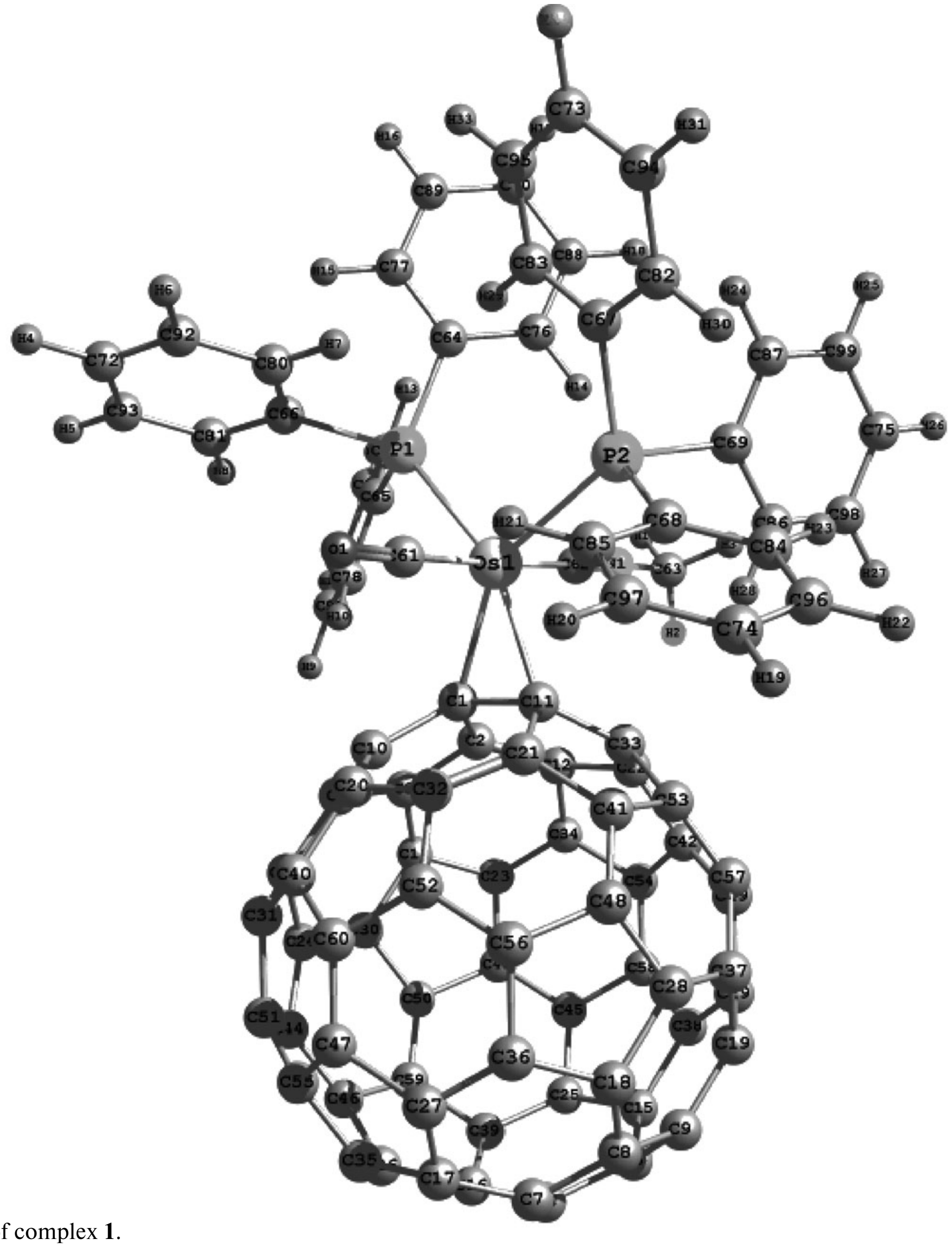

Fig. 1. Structure of complex **1**.

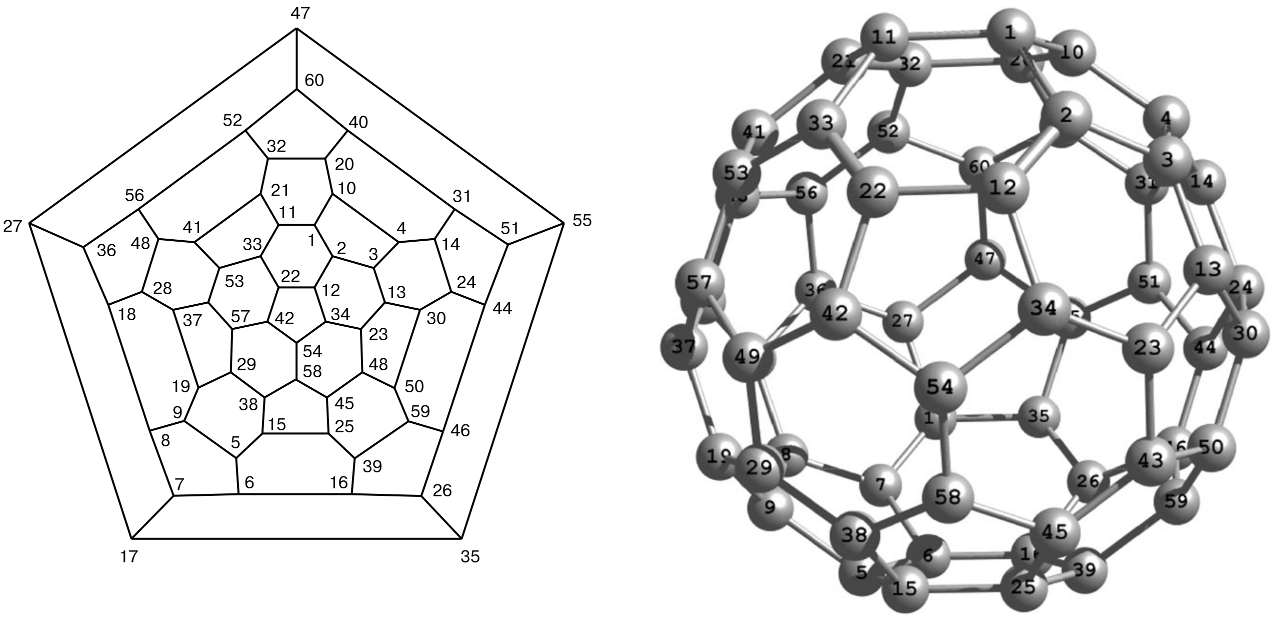

Fig. 2. Atomic numbering scheme in the fullerene moiety of complexes **1** and **2**. The Os atom is attached to the C(1)—C(11) bond.

bound to the atoms 1 and 11 of the fullerene. Table 1 gives selected calculated geometric parameters of complex **1** and (in parentheses) the values determined by X-ray diffraction for complex **1´**.[6]

Both the experimental and calculated P(1)—Os—C(1)—C(11) and P(2)—Os—C(1)—C(11) dihedral angles are close to 180°. This means that the P(1), P(2), Os, C(1), and C(11) atoms lie approximately in one plane.

Table 1. Selected geometric parameters of complex **1** calculated with the mixed/2z basis set

Parameter	Value
Bond	*d*/Å
Os—C(1)	2.22 (2.193)
Os—C(11)	2.23 (2.193)
Os—P(1), Os—P(2)	2.39, 2.40 (2.351, 2.347)
P(1)—C(64), P(1)—C(66), P(1)—C(65)	1.87 (1.898, 2.010)
P(2)—C(61), P(2)—C(69), P(2)—C(68)	1.87 (1.898, 2.010)
C(1)—C(11)	1.54 (1.479)
CO—Os	1.92 (1.898)
C—H	1.09
C—N	1.20 (1.169)
C(1)—C(10)	1.53
Angle	ω/deg
P(1)—Os—C(1)—C(11)	177.4
P(2)—Os—C(1)—C(11)	178.2

Note. The values determined from the X-ray diffraction data for complex **1´** are given in parentheses.

The calculated Os—C(1) and Os—C(11) bond lengths differ from the experimental values by 0.03 and 0.04 Å, respectively, whereas the other bond lengths differ from the experimental values by 0.04—0.06 Å.

However, these differences are not reflected in the topology of complex **1**. The calculated structure of complex **1** provides a qualitatively correct description of the structure of chemical bonds in complex **1´**. It should remember that the calculations were carried out for the individual molecule *in vacuo*, whereas the experimental values were determined for the fragment in the crystal.

Table 2 gives the main energy characteristics of the complexes and their radical anions. The EA values listed in Table 2 were calculated as the total energy differences between the starting molecule and its radical anion. The energy of the lowest unoccupied molecular orbital ($-E_{\mathrm{LUMO}}$) taken with the opposite sign can also serve as an estimate of EA; for complex **1** this value is 3.97 eV.

The EA value for complex **1** calculated by the first method seems to be more realistic. This is evidenced by the fact that the EA value for C_{60} evaluated according to this method with a mixed basis set is 2.85 eV, which is similar to the experimental value (2.72 eV). The EA value estimated from the energy of LUMO (Koopmans´ theorem) is substantially larger (3.33 eV). However, regardless of the method used for the estimation, EA of complex **1** is smaller than EA of fullerene C_{60}. Apparently, this is associated with an increase in the energy of LUMO in going from fullerene to its complex **1** and is indicative of the electron density transfer from the osmium-containing moiety to the fullerene cage.

Charge distribution in complex 1. The effective Mulliken charges on atoms calculated for complex **1** are given in

Table 2. Main energy characteristics of the complexes and their radical anions

Complex M	$-E$(M)	$-E(\mathrm{M}^-)$	EA	$-E_{\mathrm{HOMO}}$	$-E_{\mathrm{LUMO}}$
	a.u.		eV		
1	4691.4819	4691.5793	2.62	5.03	3.97
2	7099.2310	7099.3057	1.90	4.41	3.37
3	3774.8737	3775.000	3.45	5.22	4.48
4	4066.0331	4066.1555	3.32	4.87	4.50
5	3306.8967	3306.9966	2.72	5.37	4.16
6	4330.0697	4330.1527	2.23	4.80	3.69
7	2571.3740	2571.4650	2.47	5.44	4.00
8	2859.0695	2859.0695	1.53	5.00	3.96

Note. E(M) is the total energy of the complex M, $E(\mathrm{M})^-$ is the total energy of the radical anion of the complex M, EA is the electron affinity calculated as the energy difference between the molecule and the radical anion, E_{HOMO} and E_{LUMO} are the energies of the highest occupied and lowest unoccupied molecular orbitals, respectively.

Table 3. Effective Mulliken charges on atoms of the fullerene cage in complex **1**

Atom	Charge/a.u.	Atom	Charge/a.u.
Os	1.70	C(34)	−0.02
P(1)	1.42	C(20)	−0.02
P(2)	1.42	C(4)	−0.02
C(1)	−0.53	C(53)	−0.01
C(11)	−0.50	C(40)	−0.01
C(22)	−0.05	C(52)	−0.01
C(10)	0.04	C(42)	−0.01
C(2)	0.03	C(41)	0.01
C(12)	−0.03	C(21)	0

Table 3. It can be seen that the charges on the Os and P atoms are positive and rather large. Hence, the Os and P atoms are the main sources of the electron density transferred to the fullerene cage.

The charges on the C atoms of the fullerene cage, which are directly bound to the osmium atom (C(1) and C(11)), are negative and their absolute values are substantially larger than the charges on the other C atoms (which are not larger than 0.05 a.u.). However, this charge distribution is nonuniform. The C(2) and C(10) atoms bear a small positive charge, whereas the C(12), C(22), and C(40) atoms have a small negative charge (the atomic numbering scheme is shown in Fig. 2). These carbon atoms are located on the fullerene hemisphere, to which the osmium-containing moiety is attached, and the presence of negative charges on these atoms can facilitate the addition of radical and electrophilic species to this part of complex **1**. The experimental studies[10] showed that the organic and phosphoryl radicals do bind to the osmium-containing hemisphere of complex **1**.

***Complex* $(\eta^2,\eta^2\text{-C}_{60})[\mathrm{Os(PPh_3)_2(CO)(CNMe)}]_2$ (2).** The optimized structure of complex **2** is shown in Fig. 3. In this complex, two $\mathrm{Os(PPh_3)_2(CO)(CNMe)}$ ligands are bound to double bonds of fullerene C_{60} located at the op-

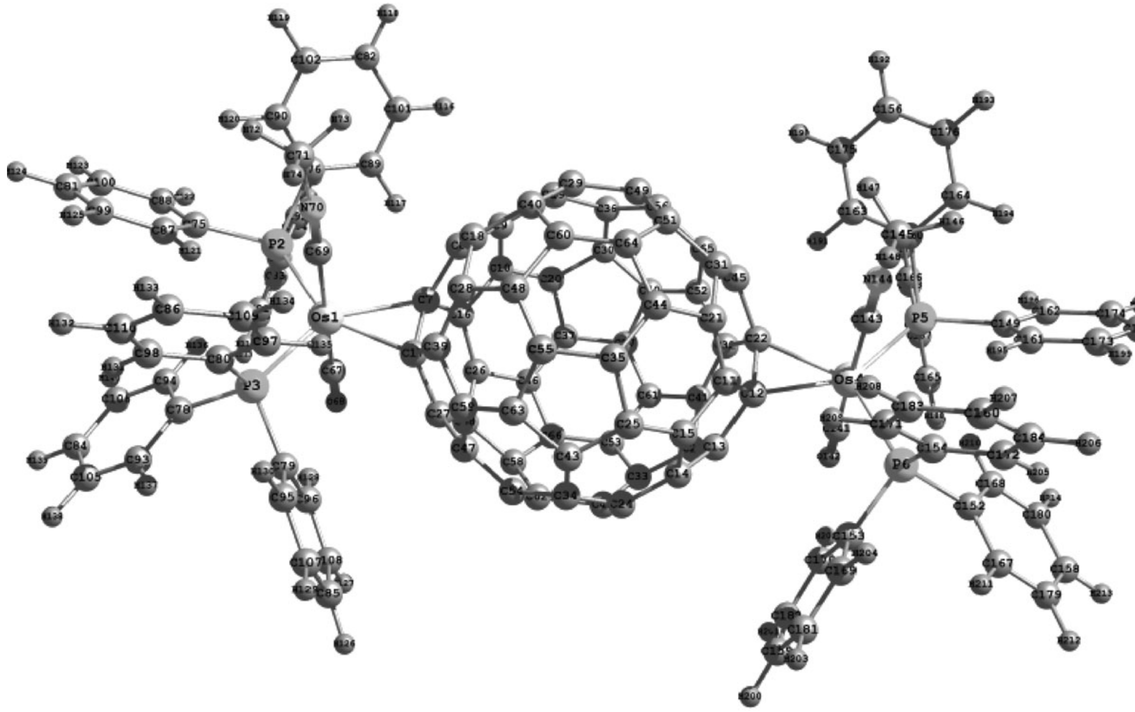

Fig. 3. Structure of the complex $(\eta^2,\eta^2\text{-C}_{60})[\mathrm{Os(PPh_3)_2(CO)(CNMe)}]_2$ (**2**).

posite poles of the carbon cage. According to the accepted classification, complex **2** is the *trans*-**1** isomer. The calculations showed that the addition of the second group has only a slight effect on the geometric parameters and the effective charges on the atoms of the first group. For example, the average Os—C (2.22 Å), Os—P (2.40 Å), C(1)—C(11) (1.53 Å), and P—C_{Ph} (1.87 Å) bond lengths differ only slightly from the corresponding values for complex **1** (see Fig. 3 and Table 1). The average charges on the C(1) and C(11) atoms are –0.50 a.u., and the average charge on the Os atoms is 1.65 a.u. The main energy characteristics of complex **2** are given in Table 2.

Topological model. The regioselectivity of the addition of the second group to monoderivatives of fullerene C_{60} was discussed in a number of publications.[5] The regioselectivity in the nucleophilic and electrophilic biscycloaddition to fullerene C_{60} is often interpreted in terms of the properties of frontier orbitals (HOMO or HOMO–1 and LUMO or LUMO+1) of the corresponding monoadducts.

The probability of cycloaddition of the second group to the free (6,6) bond of fullerene C_{60} depends on a number of factors: the steric size of the first attached group, the electron density distribution in the fullerene cage, the properties of the conjugated system, the free valence indices (in the case of the addition of radicals), *etc.* The addition of each new group at the free (6,6) bond of the fullerene monoderivative leads to a further decrease in the size of its conjugated system and a change in its π-electron energy. This is accompanied by an increase in both the energy gap between the occupied and unoccupied orbitals and the energy of LUMO, resulting in a decrease in EA.

It could be expected that the character of the change in the π-electron energy of the conjugated system of the fullerene upon the addition of other groups to free (6,6) bonds is one of the factors influencing its stability. In this connection, we estimated the relative stability of model π-electron systems, derivatives of fullerene C_{60}, which are derived by the transformation of two independent double bonds, by the Hückel method. The results of these calculations are given in Table 4.

Table 4. Total π-electron energies E_π (expressed in β units = –2.39 eV) of isomers of C_{60} derivatives containing two groups attached at the (6,6) bonds of the fullerene cage

Isomer	E_π	Isomer	E_π
trans-**1**	84.94	*cis*-**1**	85.49
trans-**2**	84.94	*cis*-**2**	84.82
trans-**3**	84.95	*cis*-**3**	84.83
trans-**4**	84.93	*e*	84.97

As can be seen from Table 4, the *cis*-**1** isomer that is formed by the addition of the metal fragment to the monoderivative of C_{60} should be the most stable one. However, the formation of this isomer can be impeded by steric hindrance caused by the first group. The *e* isomer should be the second stable isomer. At least, this isomer should be more stable than the *trans*-**1** isomer.

To confirm this hypothesis, we performed the modeling of the molecular and electronic structure of the *e* isomer of the biosmium complex $(\eta^2,\eta^2\text{-}C_{60})[Os(PPh_3)_2(CO)(CNMe)]_2$. The calculations showed that the energy of the *e* isomer is 1.1 kcal mol^{-1} smaller than that of the *trans*-**1** isomer. However, it is hardly probable that this difference is responsible for the regioselectivity of the addition of the second group, because the direction of the addition is influenced not only by thermodynamic factors but also, to a substantial degree, by kinetic factors.

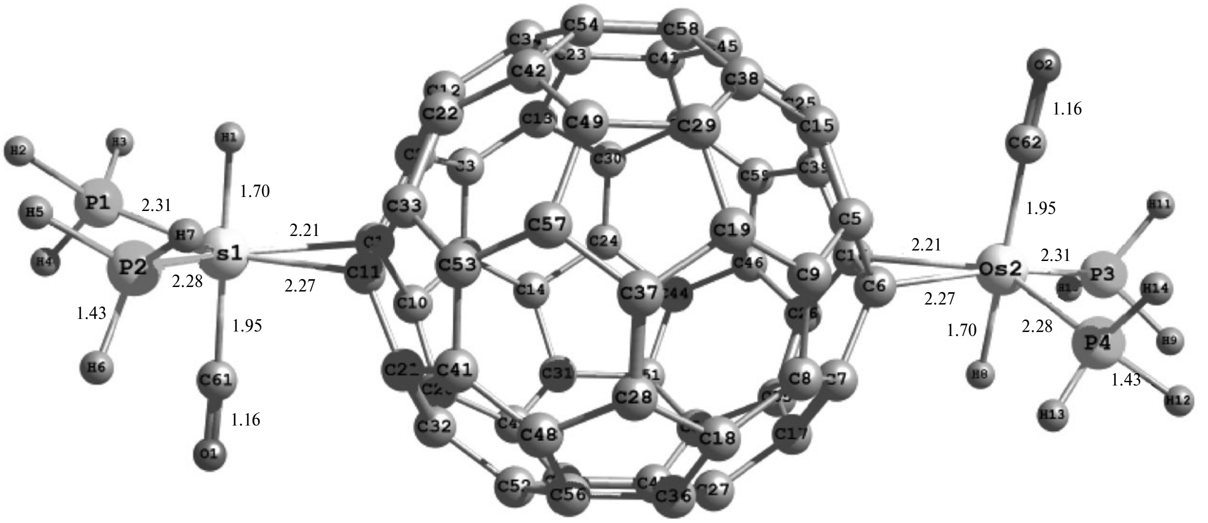

Fig. 4. Structure of the model complex $(\eta^2,\eta^2\text{-}C_{60})[Os(PH_3)_2(CO)H]_2$ (**4**).

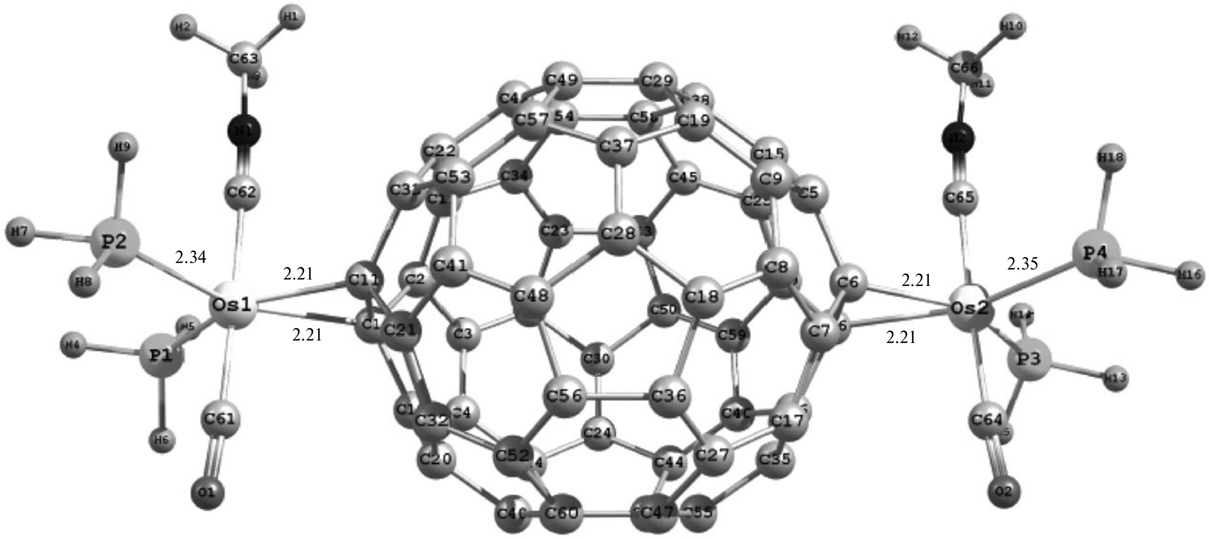

Fig. 5. Structure of the model complex $(\eta^2,\eta^2\text{-}C_{60})[Os(PH_3)_2(CO)(CNMe)]_2$ (**6**).

***Model complexes* 3—6.** In biosmium complexes **4** and **6**, there are two η^2-bonds with fullerene C_{60}. The geometric parameters of complexes **4** and **6** were optimized by the DFT at the PBE level of theory. Selected bond lengths in complexes **4** and **6** are presented in Figs 4 and 5, respectively. The energy characteristics are given in Table 2.

Let us use complex **2** as the reference compound to compare EA. As can be seen from Table 2, among complexes **2**, **4**, and **6** the smallest EA is observed for complex **2**, whereas complex **4** should have the largest EA. Complex **4** is derived from compound **2** by replacing all phenyl groups and the CNMe ligand with hydrogen atoms. In complex **6**, only phenyl groups are replaced, whereas the CNMe group is retained. It should be noted that the EA value of complex **4** is larger than the EA values not only of complex **1** but also of fullerene C_{60}.

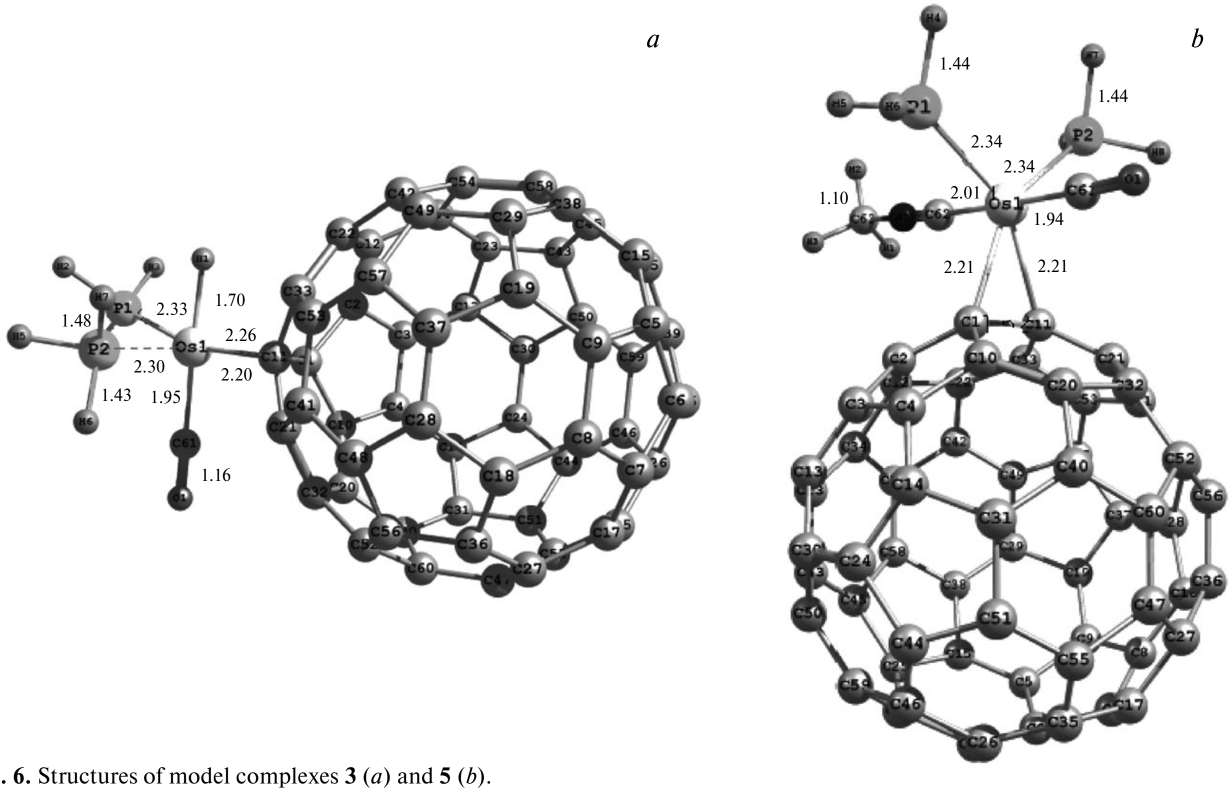

Fig. 6. Structures of model complexes **3** (*a*) and **5** (*b*).

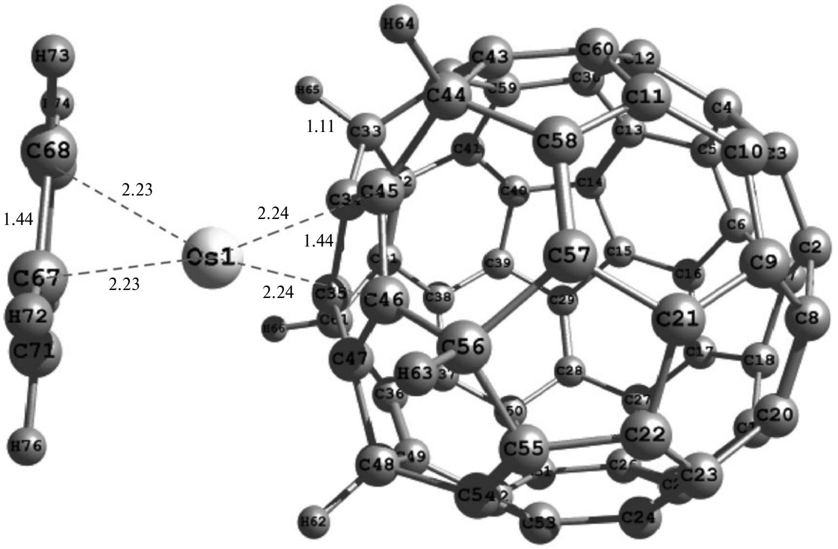

Fig. 7. Structure of complex **7**.

The above-considered data show that a complex having a rather large EA can be prepared by choosing appropriate ligands at the Os atom. It should be noted that the P atoms in complexes **4** and **6** possess negative charges (–0.22 a.u.). The charges on the Os atoms are positive, the charges in complexes **2** and **6** being different by 0.03 a.u., whereas the charge on the Os atom in complex **4** is approximately two times smaller than those in complexes **2** and **6**.

In addition to biosmium complexes **4** and **6**, we investigated their monoosmium analogs, *viz.*, complexes **3** and **5** (Fig. 6). The calculations showed that, as in the case of complexes **1** and **2**, the ligands in the corresponding mono- and bis-complexes **3**, **4** and **5**, **6** have similar structures. The energy parameters of complexes **3** and **5** are given in Table 2. It can be seen that, regardless of the method used for the estimation, the EA values of monoosmium complexes **3** and **5** are larger than EA of the corresponding biosmium derivatives **4** and **6**.

***Complexes* 7 *and* 8.** The Os atoms in complexes **1**—**6** are η^2-coordinated by the fullerene. It is of interest to study the acceptor properties of osmium complexes of fullerene C_{60}, in which the Os—fullerene η^5-bonds are formed. We chose hypothetical complexes **7** and **8** (Figs 7 and 8, respectively) as examples.

In complex **7**, five H atoms are bound to the C atoms of the fullerene in α positions with respect to the five-membered ring of C_{60}, at which the OsC_5H_5 group is co-

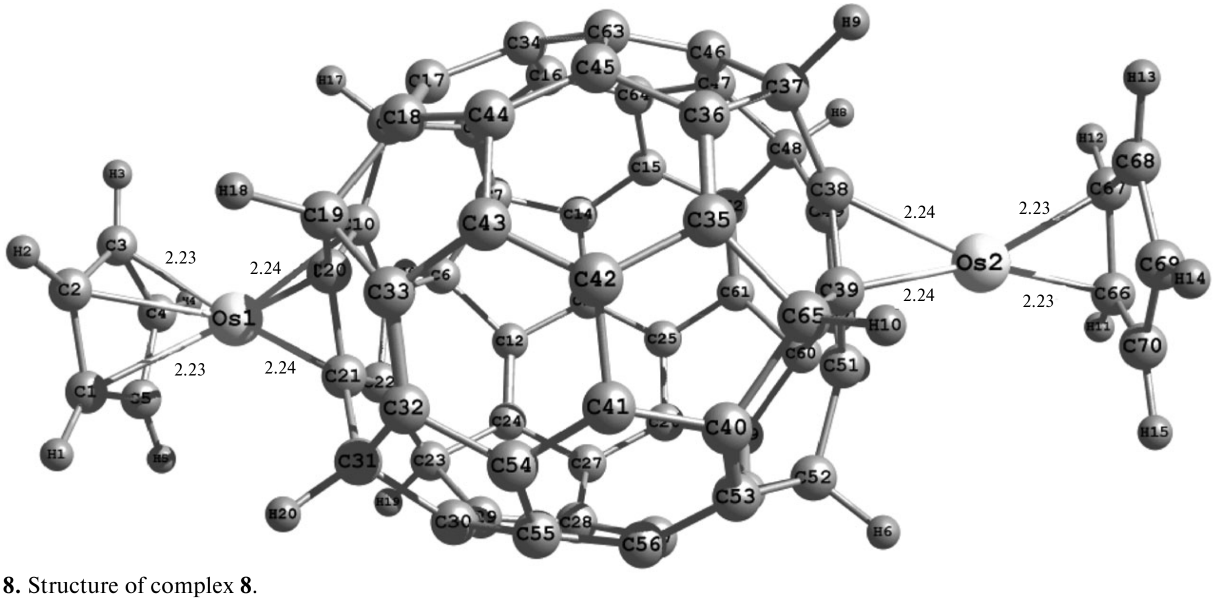

Fig. 8. Structure of complex **8**.

ordinated in the η^5 mode. In complex **8**, there are two such groups, the latter group being coordinated at the opposite (with respect to the former group) pole of the fullerene cage. Complexes **7** and **8** have fivefold symmetry axes.

The calculations performed with the mixed/2z basis set revealed local energy minima corresponding to the structures shown in Figs 7 and 8. The main energy characteristics of complexes **7** and **8** are given in Table 2. As can be seen from this table, EA evalutaed for biosmium complex **8** is 1.53 eV, *i.e.*, it is 1 eV smaller than the corresponding value for monoosmium complex **7**.

The Os atom possesses a positive charge (2.00 a.u). Negative charges are located on the C atoms of the five-membered rings and the sp^3-hybridized C atoms of the fullerene cage bound to the H atoms. Almost no electron density is transferred to the remaining part of the fullerene. The similar electron density distribution is observed in osmocene, in which the negative charge is located on the five-membered rings.

Therefore, in the present study we performed the modeling of the structures and estimated the electron affinities of mono- and biosmium fullerene C_{60} complexes **1—8** with the use of the following two approaches: using Koopmans' theorem (energies of LUMO) and based on the energy difference between the neutral molecule and its radical anion. The drawbacks of Koopmans' theorem, particularly as applied to the estimation of EA, have been discussed in the literature many times. Hence, preference should be given to the second method of estimation. The performed calculations showed that the EA value for monoosmium complex **1** should be in the range of 2.2—2.5 eV, which is comparable with EA of fullerene C_{60}. It was shown that EA decreases in going from monoosmium complex **1** to biosmium complex **2**, which is apparently associated with a decrease in the extension of the conjugated system. Among the η^2-complexes, complex **3**, which is derived from complex **2** by replacing the phenyl groups and the CNMe ligand by hydrogen atoms, should have the largest EA.

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