Reviews

Chemistry of fullerenes, novel allotropic modifications of carbon*

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The currently available data on the structure and reactivity of fullerenes, including the formation of metal complexes (including optically active ones) with fullerenes as ligands, are briefly surveyed. The properties and reactions of fullerenyl radicals and endohedral complexes are considered.

Key words: fullerenes, addition reactions, fulleroids, metal complexes, fullerenyl radicals, endohedral complexes.

This work covers only the chemical aspects of the many-sided problem of fullerenes. The main concepts of reactivity and some topical lines of development are demonstrated. Since the results of studies of fullerenes have been described in detail in the literature (see reviews[2—6]), a brief selective review of recent results is given here; attention is focused on the results obtained at the Institute of Organoelement Compounds of the RAS.

Fullerenes represent a family of individual polyhedral molecules consisting only of carbon atoms. In this respect, the closed fullerene structure differs basically from other forms of carbon, which are infinitely extended systems (diamond, graphite, carbyne, nanotubes, helical nets, *etc.*). The fullerene family can be considered as an allotropic modification of elemental carbon.

Several years after the stability of C_{60}, the first member of the fullerene family, had been predicted theoretically,[7,8] it was actually discovered* (together with C_{70}) in carbon vapor obtained by laser-induced vaporization of graphite.[9] This method allowed the preparation of only very small amounts of the material, which sufficed most of all for spectroscopic studies. Later, a method for preparative-scale synthesis of large amounts of fullerenes based on vaporization of graphite electrodes in an electric arc in a helium atmosphere was proposed.[10]

Fullerenes constitute an object presenting interest for various fields of science: chemistry, physics, materials science, geology, astronomy, and biology. All the fields of science except for astronomy and some branches of physics require substantial amounts of both initial fullerenes and their derivatives. It was not until the preparative method for the synthesis of fullerenes was discovered[10] that development of the studies of fullerenes in the above-mentioned fields, including the prospects for their practical use, became possible.

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* The review is based on the report of the same name delivered at the XVI Mendeleev Congress (May 28, 1998, St. Petersburg).[1]

* Eleven years after the discovery of fullerenes, R. F. Curl, H. W. Kroto, and R. E. Smalley were awarded the Nobel Prize in Chemistry of 1996.

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Below, the main landmarks of the chemical history of fullerenes are presented, as the author sees them (primary attention is paid to stereochemistry and organometallic chemistry):

- 1970 — prediction of the stability of the truncated icosahedron C_{60}[7].
- 1973 — the same, based on Huckel calculations[8].
- 1985 — discovery of C_{60} and C_{70} molecules in the mass spectra of graphite vapor;[9] the discovery of the endohedral complex La@C_{60} by the same method[11];
- 1990 — discovery of the preparative method for the synthesis of large amounts of fullerenes by vaporization of graphite electrodes in an electric arc[10];
- 1991 — the first X-ray diffraction proof of the icosahedral structure of C_{60} in relation to its derivative (osmate ester)[12];
- 1991 — preparation of the first organometallic (platinum) complex of fullerene (π-olefinic type)[13];
- 1992 — discovery of fulleroids in a study of the reaction of C_{60} with diazo compounds[14];
- 1992 — preparation of the first optically active *organic* derivative of fullerene[15];
- 1993 — preparation of the first optically active *organometallic* derivative of fullerene[16];
- 1993 — preparation of an optically active fullerene, C_{76}, with a chiral skeleton[17];
- 1993 — preparation of endohedral helium complexes by direct insertion of a helium atom into the carbon cage[18];
- 1995 — synthesis of dimeric azafullerene[19];
- 1996 — preparation of an η^5-complex of a partially saturated fullerene[20];
- 1998 — extraction of the stable "small" fullerene C_{36} from fullerene soot.[21]

Although fullerene molecules consist only of carbon atoms and, therefore, they seemingly should be subjects of inorganic chemistry, nevertheless, the presence of a system of conjugated and strained double bonds is the crucial factor governing the chemical behavior of these species. Fullerenes behave as electron-withdrawing polyalkenes and mainly comply with the paradigms of organic chemistry. Thus, the nature of the chemical bonds appears to be more significant in a certain sense than the material of which the molecule is built.

Each carbon atom of fullerene (*i.e.*, each vertex of the polyhedron) is linked to three neighboring vertices. This means that it forms two single bonds and one double bond. A C_{60} molecule has two types of bonds, *viz.*, a (6,6) bond shared by two hexagons (behaves as a double bond) and a (6,5) bond shared by a hexagon and a pentagon (behaves as a single bond). Thus, the whole surface of any fullerene is coated by a system of conjugated double bonds, which are strained because the surface is not planar. In fullerenes of lower symmetry than C_{60} (group $\mathbf{I_h}$), the double bonds differ, depending on their positions, in the degree of strain and in reactivity. By now, only the chemistry of the next fullerene, C_{70} (group $\mathbf{D_{5h}}$), has been studied to some extent. Higher fullerenes are still relatively unavailable in a pure state. A fullerene with a chiral skeleton (group $\mathbf{D_2}$), which, by the way, was obtained in an enantiomerically pure state,[17] appeared for the first time among the C_{76} isomers. In a recent study,[21] preparation of a fairly stable lower fullerene, C_{36}, has been reported. It is remarkable that the isomer with $\mathbf{D_{6h}}$ symmetry actually proved to be the most stable, as was predicted in 1992 by E. Gal'pern, I. Stankevich, *et al.*[22]

Fullerenes are unique in that they represent a soluble form of carbon. This provides, for example, the opportunity to prepare carbon films in solutions. Being hydrophobic, fullerenes are soluble in hydrocarbons, especially in aromatic ones, and in carbon disulfide. The maximum solubility of C_{60} in most hydrocarbon solvents[23] is observed at $\sim$315 K. It is worth noting, however, that stable colloid solutions of C_{60} in water can also be obtained.[24,25]

Fullerenes can undergo only addition reactions but not substitution, because there is nothing to be substituted in the initial fullerenes. Since they are strong electron acceptors, they add nucleophiles, including electrons, and homolytic reagents (halogens), including free radicals, to give rather stable (on the ESR time scale) spin adducts. Fullerenes tend to form complexes with incomplete charge transfer, in which they usually function as the acceptors.[26]

It is well known that fullerenes readily accept electrons but release them with difficulty. The radical anions and anions derived from fullerenes have been studied in detail. However, by treating fullerene with relatively strong oxidants, it is also possible to generate the $C_{60}^{\cdot +}$ radical cation. Recently, it was found[27] that oxidation of C_{60} with oleum under certain conditions can lead not only to the formation of $C_{60}^{\cdot +}$ but also to partial dimerization to give $C_{120}^{\cdot +}$. As a further development of this work, oxidation of the preliminarily prepared C_{120} and "dimer ether" $C_{120}O$ by the same reagent was carried out; this gave two ESR-active species, a cation and a dication.[28] The $C_{60}^{\cdot +}$ radical cation has also been detected in the reaction of fullerene with chlorine dioxide.[29]

The organic chemistry of fullerenes is largely based on [n+2] cycloaddition reactions; some examples of this type of reactions are presented below. When $n = 4$, this is the Diels—Alder reaction,[30—32] when $n = 3$, these are reactions with heteroatomic dipoles (see, for example, Refs. 33—35), and for $n = 2$, reactions with double or triple bonds have been reported.[36—37] The formation of the osmate ester[12] is also an example of [3+2] cycloaddition. The Diels—Alder reaction has been repeatedly used in recent years to construct fairly complex systems incorporating the fullerene fragment.[38]

The reaction with diazo compounds is fairly important in fullerene chemistry.[14] It is during the study of this reaction that it was found (to revise the initial conclusion)[39] that a (6,6) double bond adds a carbene fragment to give methanofullerenes containing a fused three-membered ring, whereas a (6,5) bond cleaves to give a new structure with a bridging carbon atom, which was called *fulleroid*. (Methanoannulenes, previously studied by Vogel,[40] represent a structural prototype of the fulleroid fragment.) The mechanism of this reaction has not been definitively established, although it was shown for unsubstituted diazomethane that the first step of the reaction affords pyrazoline,[41] *i.e.*, [3+2] cycloaddition takes place. The subsequent decomposition of the primary product yields methanofullerene and fulleroid. The major products of the reaction of C_{60} with azides are azafulleroids[42]; no intermediates were detected. The researchers were able to convert azafulleroid with a specially selected substituent into azafullerene $(C_{59}N)_2$, which is stabilized by dimerization because the corresponding monomer is a free radical.[19]

The problem of selective preparation of monosubstituted derivatives is an important general challenge in fullerene chemistry. Since the molecule contains a large number of sites with approximately equal reactivities, the reactions often give product mixtures that are difficult to separate. An interesting and promising study in this respect[43] describes a method for the addition of cyanide anion to one double bond in C_{60} followed by the addition of an electrophilic partner.

The presence of double bonds is the prerequisite for the formation of π-complexes with transition metals. The structure of fullerenes permits them to function as ligands with haptic numbers[44] of 1 to 6; nevertheless, of the whole theoretically possible set, only traditional olefinic η^2-complexes are known to date. The addition of outer metal fragments generally decreases the symmetry of the initial fullerene core; the chiral isomers of the bis-osmate derivatives of the double bonds of C_{60} were obtained in an optically active state.[45] Analysis of the point groups of symmetry of the hypothetical derivatives that should be formed upon consecutive η^6- and/or η^5-coordination revealed[46] one chiral combination for bis-(η^6,η^6)-C_{60} and several chiral combinations for various bis-complexes of C_{70} (Fig. 1). Recently, preparation of η^5-metal complexes was reported[20]; however, for this purpose, it was necessary to destroy the common π-electron system of C_{60} by "fencing" one pentagon by five aryl groups, which brought it closer in character to an isolated cyclopentadienyl.*

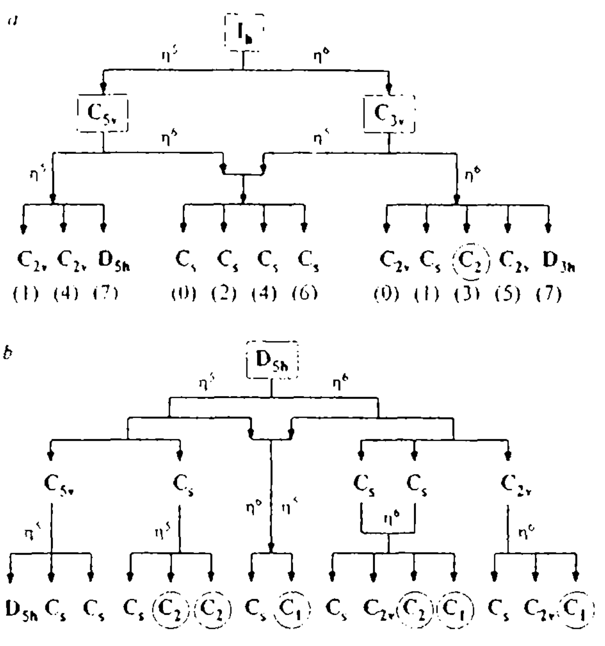

Fig. 1. Point groups of symmetry for mono- and dimetal complexes of fullerenes coordinated in the η^5- and/or η^6-fashion: (*a*) C_{60}, (*b*) C_{70}. Chiral combinations are marked by circles. The digit in parentheses means the number of edges corresponding to the shortest route between the coordinated faces.

Among the problems of organometallic chemistry of fullerenes, the following aspects should be noted: (a) synthesis and study of properties of π-complexes of C_{60} and C_{70} with platinum group metals, especially with palladium, platinum, rhodium, iridium; (b) synthesis of optically active organometallic derivatives of fullerenes; (c) preparation of compounds containing metallocene and fullerene fragments within one molecule; (d) study of fullerene spin adducts, relatively stable fullerenyl radicals with a magnetic nucleus in the addend, by ESR spectroscopy; (e) study of the reactivity of the endohedral metallofullerenes. Some results were briefly considered in previous reviews.[47,48]

After it had been found[49] that C_{60} is able to add free alkyl and thiyl radicals to give spin adducts, which can be studied by ESR spectroscopy, it seemed expedient to study heteroorganic radicals with a magnetic nucleus in a key position. This automatically provides an additional characteristic of fullerenyl spin adducts, namely, the hyperfine splitting (HFS) constant; the same information concerning alkyl C-radicals could be obtained only by using[50] high enrichment with the ^{13}C isotope.

We studied the addition of phosphoryl P-radicals and B-radicals using an original method for the generation of these radicals, namely, photolysis of mercury derivatives.[51] The addition of one Pt-centered radical to C_{60} was also studied. During this study, we discovered and described[52] (independently of other researchers dealing with alkylfullerenyl radicals[53]) reversible dimerization of phosphorylfullerenyl radicals, determined the energy of dimerization, and used for the first time fullerene dimers for synthetic purposes.[54]

It is owing to the highly informative content of this approach, which provides an HFS constant *a* for each ESR signal in addition to a g-factor, that we were able to observe several isomeric signals, corresponding to the

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* Previously it was found by calculations[26] that this structure modification should be favorable for η^5-binding.

addition of free radicals to various types of vertices, in the ESR spectra of spin adducts of phosphoryl radicals with C_{70}[55] and to study fullerenyl adducts with B- or Pt-radicals. Boron-centered radicals were prepared by photolysis of 9-boron-mercury derivatives of *m*-carborane[56] or by elimination of a hydrogen atom from the $Me_3N \cdot BH_3$ complex.[57] The spectra of the corresponding spin adducts with fullerene exhibit two hyperfine splitting constants, one of the ^{10}B isotope (15%, s = 3, 7 lines, $a_B = 6.25$ G) and one of the ^{11}B isotope (85%, s = 3/2, 4 lines, $a_B = 18.25$ G). The platinum-centered radical, prepared by photolysis of a mercury—platinum bond[58] (see below), adds to C_{60} with retention of the *cis*-arrangement of phosphine ligands around the metal, which is indicated by the presence of two different HFS constants $a_P = 30.5$ and 3.5 G; the greater value, $a_{Pt} = 52.0$, corresponds to the direct binding of the platinum atom to the fullerene nucleus.

When passing to the organometallic part of the investigation, it should be mentioned first of all that there are two fundamentally different fashions of combination of fullerene and organometallic fragments within one molecule. One is the traditional and well-known fashion according to which the metal is bound directly to the carbon polyhedron, being coordinated to one or several of its atoms. The other way of combination has not yet received adequate attention; this is insertion of an organometallic fragment into an organic addend (see below).

The organometallic chemistry of fullerenes was initiated by the synthesis[13] of the first mono-η^2-platinum complex of C_{60}; later, a similar complex with six platinum fragments was described.[59] Soon after a crystalline palladium mono-η^2-complex, $(Ph_3P)_2Pd(\eta^2\text{-}C_{60})$, was prepared in a pure state; according to X-ray diffraction analysis,[60] the bond lengths and bond angles in this complex are close to those in the platinum complex but the carbon polyhedron is much less distorted. A typical feature of both complexes is that all four atoms in the ligand sphere of the metal are arranged in one plane, unlike those in the ethylene complex $(Ph_3P)_2Pt(C_2H_4)$ but like those in the complex of electron-withdrawing tetrafluoroethylene $(Ph_3P)_2Pt(C_2F_4)$. Due to this fact, the geometries of complexes $L_2M(\eta_2\text{-}C_{60})$ and methanofullerenes are different; however, both belong to the same point group of symmetry, C_{2v}, which does not adequately reflect the situation. In the course of analysis of the structures of fullerene derivatives, a procedure for unambiguous assignment of indices was proposed[61]; it is based[62] on a more detailed definition of groups of symmetry (Framework Group Approach), which provides description of the symmetry of each molecule by its own individual index.

Electrochemical study of the behavior of $(Ph_3P)_2Pd(\eta^2\text{-}C_{60})$ in the presence of an excess of a zerovalent palladium complex or triphenylphosphine[63] evidences in favor of the following equilibrium:

$$2\,(Ph_3P)_2Pd(\eta^2\text{-}C_{60}) \rightleftharpoons [(Ph_3P)_2Pd]_2(\eta^2\text{-}C_{60}) + C_{60}.$$

The fullerene palladium complex $(Ph_3P)_2Pd(C_{60})$ supported on activated carbon exhibits catalytic activity in the selective hydrogenation of a triple bond to a double bond, exceeding the activity of palladium metal supported on carbon.[64] We found a new method for the synthesis of platinum complexes of fullerenes based on platinum-mercury compounds,[58] whose synthesis was developed in our previous studies.[65,66]

$$R\text{—}Hg\text{—}PtL_2\text{—}X + C_n \longrightarrow R\text{—}Hg\text{—}X + L_2Pt(\eta^2\text{-}C_n)$$

These bimetallic compounds proved to be a convenient source of a platinum carbenoid; in particular, they were used[67] to prepare $(Ph_3P)_2Pt(\eta^2\text{-}C_{70})$. Moreover, it was found that even bis(aryl)platinum complexes react with C_{60} with transfer of L_2Pt to fullerene and with the formation of diaryl; the latter points apparently to a homolytic mechanism of the process. On heating, the reaction is completed over a period of several minutes.[68]

$$L_2PtAr_2 + C_n \longrightarrow Ar\text{—}Ar + L_2Pt(\eta^2\text{-}C_n)$$

An interesting atypical behavior of a bimetallic compound in the presence of C_{60} is observed when the mercury atom carries a polyfluoroalkyl group. In this case, photolysis involves homolytic cleavage of only the metal—metal bond and the resulting Pt-centered radical adds to fullerene.[58] This new platinum-fullerenyl radical, which is relatively stable in solution, was comprehensively described by ESR spectroscopy (see above). It is of interest that it still remains the only representative of metal-containing fullerene derivatives in which the metal is bound to the fullerenyl nucleus in the η^1-(σ)-fashion.

Since the symmetry of C_{70} is lower than that of C_{60}, this molecule contains eight types of nonequivalent double bonds. The most strained (6,6) bond at the "sharp" end of the ellipsoid, which is conventionally designated as *a-b*, is the most reactive toward addition reactions, including the addition of η^2-metal-containing fragments.[69] According to the currently available data,[70] the maximum number of metal atoms that can be added to C_{70} is four rather than six as in the case of C_{60}.

We studied the process of formation and properties of the palladium complex $(Ph_3P)_2Pd(\eta^2\text{-}C_{70})$ in detail.[71] It was shown by ^{31}P NMR spectroscopy that this compound was formed as two regioisomers present in a ratio of 86 : 14. As was to be expected, the predominant compound is the *a-b* isomer, in which two phosphorus atoms are nonequivalent and account for an AB-system in the NMR spectrum. However, simultaneously, a singlet due to equivalent phosphorus atoms in the minor *c-c* isomer was observed for the first time (Fig. 2).

The addition of rhodium and iridium hydride derivatives $HM(CO)(PPh_3)_3$ and $HIr(C_8H_{12})(PPh_3)_2$ to C_{60} and C_{70} fullerenes occurs highly regio- and stereospecifically to give only the corresponding η^2-metal complexes formed at the (6,6) bond[72,73] upon replacement of one triphenylphosphine ligand rather than upon

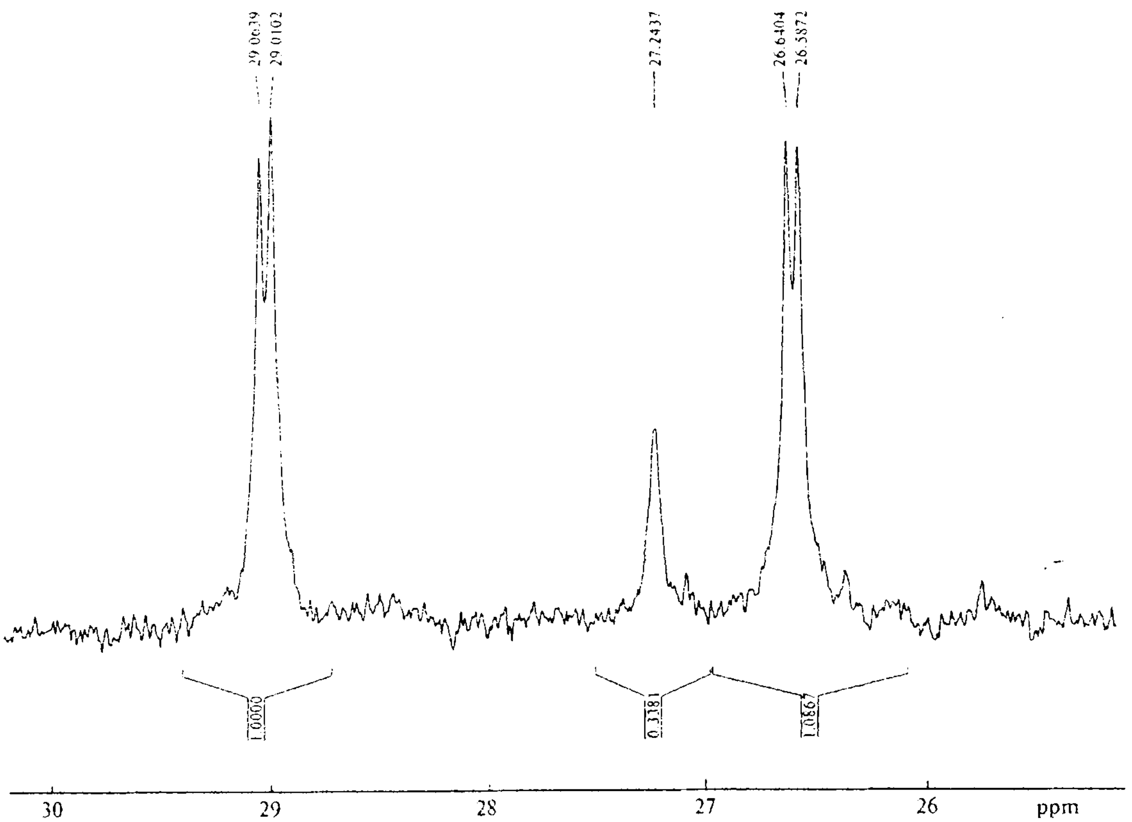

Fig. 2. ^{31}P NMR spectrum of a mixture of two isomers of $(\eta^2-C_{70})Pd(Ph_3P)_2$, $(a-b)/(c-c)$ = 86/14.

the migrational addition of the M—H bond to the polyene system of the fullerene, as occurs when these complexes react with conventional electron-withdrawing olefins like tetrafluoroethylene. The structure, configuration, and site of attachment of a transition metal to the fullerene nucleus for the resulting complexes were proved unambiguously, relying on the data of IR-, ^1H NMR, and ^{31}P NMR spectroscopy. The electrochemical behavior of these fullerene complexes was studied[74]; the procedure for direct generation of these species in an electrochemical cell made it possible to study not only mono- but also dimetal derivatives of both C_{60} and C_{70}. The structures of similar iridium complexes were determined by other researchers.[69] The addition of phosphoryl radicals was also performed and studied using the above-described ESR strategy for complexes of C_{60} with platinum, palladium,[54,75] and iridium.[76]

We prepared the first optically active organometallic complexes of fullerenes by attaching an enantiomeric ligand, (+)- or (−)-3,4-bis[(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane (diop), to a metal. This can be attained by either of the following two methods: ligand exchange in a triphenylphosphine complex or the reaction between fullerene, diop, and the complex $M_2(dba)_3$. The latter method is especially convenient for palladium because its dibenzylideneacetone complex is readily available. First the complex $[(+)\text{-diop}]Pd(\eta^2-C_{60})$ was synthesized[17]; after that, the platinum analog $[(+)\text{-diop}]Pt(\eta^2-C_{60})$ was prepared and its molecular structure was established by X-ray diffraction analysis of the monosolvate with *cis*-cyclooctene.[77] Similar complexes of η^2-C_{70} have also been synthesized. The circular dichroism spectra (Fig. 3) contain many extrema due to the Cotton effect, in particular, in the visible

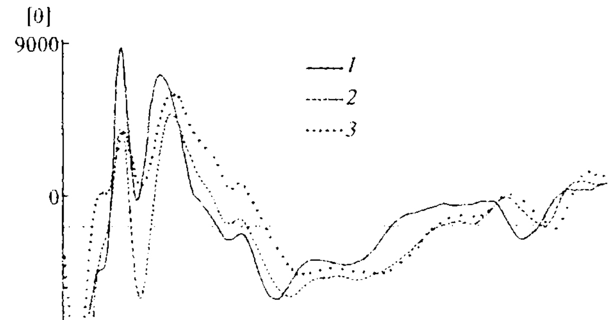

Fig. 3. Circular dichroism spectra of C_{60} enantiomeric complexes: $(\eta^2-C_{60})Pt[(+)\text{-diop}]$ in toluene (*1*); $(\eta^2-C_{60})Pd[(+)\text{-diop}]$ in toluene (*2*); $(\eta^2-C_{60})Pd[(+)\text{-diop}]$ in dimethylformamide (*3*).

region, which correspond to electron transitions in both the fullerene core itself and between fullerene and the metal; this was first reported in a lecture at the 32nd Congress on Coordination Chemistry.[78]

In the case where the addend contains an organometallic moiety, the organometallic and fullerene moieties are linked by covalent bonds *via* a chain of atoms, at least, *via* one atom. The groups that connect or separate two particular moieties in a molecule are generally referred to in the chemical literature as spacers; here, we shall use this term in this particular sense. Apparently, a compound of this type was first prepared in 1994 in our study,[79] in which C_{60} was modified by the Wudl reaction using a diazo compound with an arene(tricarbonyl)chromium substituent, $Ph-C(N_2)-[PhCr(CO)_3]$. Organochromium reaction products comprised one methanofullerene and two fulleroid isomers, which was similar to the products of reaction of diphenyldiazomethane itself with C_{60}. Yet another reaction of this type was successfully performed with mono- and bis-diazoacetylferrocene (preliminary communication[80]).

Combination of an electron-withdrawing fullerene moiety and an electron-donating organometallic moiety within one molecule with a conducting spacer could result in the preparation of a "molecular wire," *i.e.*, intramolecular charge transfer along the chain. This requires that at least two conditions be fulfilled. (1) The oxidation potential of the organometallic moiety should be close to the reduction potential of the fullerene moiety; (2) efficient charge transfer along the spacer should occur. For this purpose, the spacer has to contain apparently a system of conjugated bonds. If the spacer can be reversibly modified in such a way that a system of conjugation could be either formed or destroyed at request, we shall produce a "molecular switch key" (Fig. 4). It is noteworthy that in methanofullerenes, two atoms of the fullerene nucleus have passed into the sp^3-hybridization state and, therefore, a spacer contains at least two atoms not involved in the chain of conjugation.

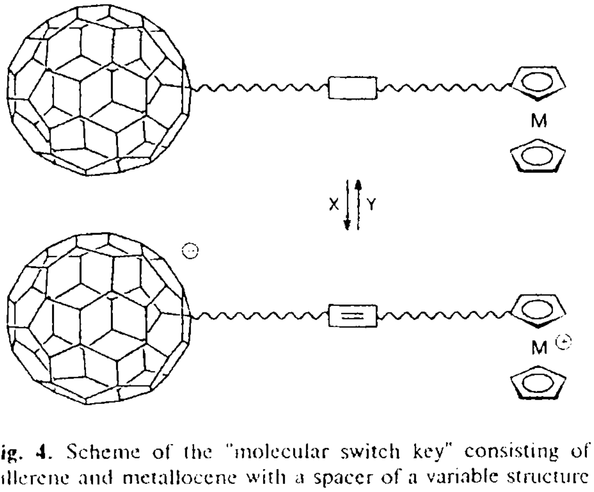

Fig. 4. Scheme of the "molecular switch key" consisting of fullerene and metallocene with a spacer of a variable structure based on reversible introduction of a double bond.

A unique structural feature of fullerenes is the presence of an inner cavity, which is large enough for one or more atoms to fit into. The first example of this type of compounds, which were called *endohedral* complexes, was reported at the same time as fullerenes themselves were discovered[11]; this was the lanthanum complex $La@C_{60}$. Subsequently it was found that two sorts of endohedral complexes exist, namely (*a*) metallofullerenes $M_m@C_n$, which are prepared only by *de novo* synthesis based on vaporization of graphite electrodes filled with a compound of a corresponding metal, and (*b*) compounds of inert gases (from helium to xenon),[81] which can be prepared by insertion of atoms of these gases within an existing carbon cage at high temperatures and pressures. The mechanism of this remarkable process (*b*) is unknown. A recent study aimed at the preparation of He@azafullerene[82] demonstrates that even when there is a relatively large "window" in the carbon cage, a helium atom inserted initially remains in the final product. The insertion of the ^3He isotope, which has a magnetic moment, made it possible to characterize various fullerenes and their derivatives by the chemical shift in the ^3He NMR spectrum[83]; this characteristic proved to be highly sensitive to the structure of the fullerene compound. The chemistry of fullerene endohedral complexes has scarcely been studied.

Endohedral metallofullerenes containing formally neutral lanthanide atoms inside are paramagnetic and can be studied by ESR spectroscopy. In our study,[84] it was found* that $La@C_{82}$ and $Y@C_{82}$ (at least, those mixed with a larger amount of "empty" fullerenes) are inert toward a phosphoryl radical or a bis(triphenylphosphine)platinum fragment, but in a solution in CF_3COOH, their ESR spectra change. More precisely, one of the two multiplets (whose presence is explained by isomerism of the carbon cage of C_{82}) disappears and a doublet appears; this might imply protonation of the carbon cage (Fig. 5). This finding is consistent with the view that the surface is negatively charged due to the partial electron transfer from the metal.[86]

Endohedral complexes of fullerenes can be regarded as a subject for supramolecular chemistry, which considers "host—guest" complexes, the fullerene molecule acting as a sort of host. However, fullerenes can also form complexes in which they act as classical guests. Previously an inclusion complex of C_{60} with γ-cyclodextrin was identified in an aqueous solution and its existence was proved unambiguously by observing induced Cotton effects in circular dichroism spectra.[87] However, the size of the cyclodextrin cavity is rigidly fixed and somewhat too small for fullerenes. There exists a family of syn-

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* This work was carried out in collaboration with the group headed by E. B. Yagubskii (Institute of Problems of Chemical Physics, Chernogolovka), by whom endohedral metallofullerenes were first prepared in Russia.[85]

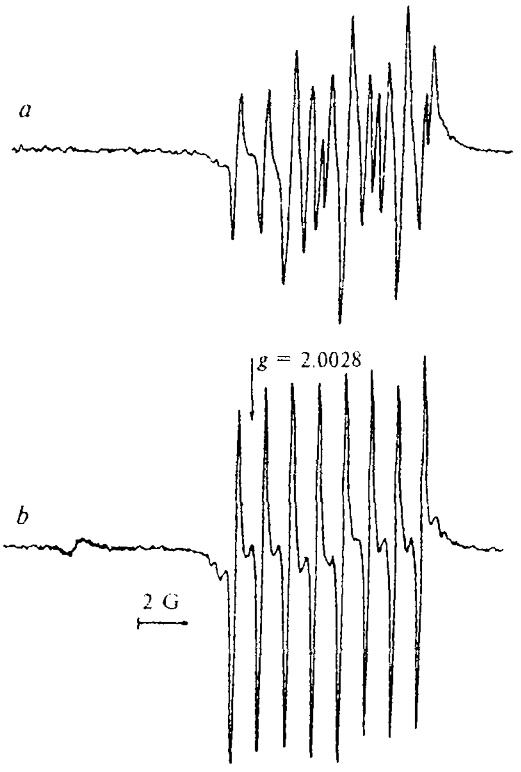

Fig. 5. ESR spectra of the endohedral metal complex La@C_{82} dissolved in toluene (*a*) or CF_3COOH (*b*).

thetic host molecules (although they are optically inactive, unlike natural cyclodextrins) the size of whose cavity can vary, *viz.*, calixarenes. Recently it was shown that [8]calixarenes successfully and selectively include C_{60} with the stoichiometry 1 : 1 and that they can even extract it from fullerene soot.[88,89] A detailed review on this topic has been published.[90]

In recent years, methods for exerting a strong energy impact on a substance, resulting in complete loss of its molecular individuality, have been developed.

The discoverers, or better to say, creators of fullerenes have done and are still doing quite the opposite thing. They were the first to reveal to the full measure the molecular individuality of elementary carbon, which had been shaded by involvement in enormous collections of atoms (graphite, diamond). They demonstrated that the capacity of carbon to form homoatomic molecules is not poorer but richer and more diversified than those of nitrogen, oxygen, fluorine, and silicon. Thus they confirmed once again the validity of the brilliant aphorism of Berthelot stating that chemistry is a science that creates its own subject.

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