1824 Russian Chemical Bulletin, International Edition, Vol. 53, No. 9, pp. 1824—1845, September, 2004

Advances in fullerene chemistry

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The review outlines the key results obtained in experimental and theoretical studies on fullerene chemistry in the Russian Federation and, in particular, at the A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences.*

Key words: fullerenes, polyhedral clusters, organic fullerene derivatives, endohedral fullerenes, physical methods, quantum-chemical methods.

Introduction

Fullerene chemistry is an amazing new branch of science. Fullerenes were discovered in 1985 [1] but the history of fullerene chemistry began in 1990 after the discovery of a method for production of gram amounts of fullerene mixtures containing mostly carbon clusters C_{60} and C_{70} by combustion of graphite rods in an electric arc in inert atmosphere.[2] A short time later, installations for production of fullerene soot were also built in Russia. Pioneering communications on fullerene chemistry were reported in 1992. The prehistory of fullerenes dates back to theoretical prediction of stability of icosahedral C_{60} molecule by researches from Japan (1970)[3] and from the USSR (1973).[4] The A. N. Nesmeyanov Institute of Organoelement Compounds (INEOS), Russian Academy of Sciences, was the first research organization in Russia involved in theoretical and experimental studies of fullerenes.

Historically, the scientific importance of fullerenes is not limited to their own contribution to science. The discovery of fullerenes gave an impetus to self-identification of a new research avenue, namely, nanochemistry and, in a broad sense, nanoscience. The starting point of nanoscience was passage from the C_{60} and C_{70} fullerenes to other carbon clusters, *viz*., higher fullerenes and "nanotubes", which is responsible for the appearance of the prefix "nano".

Fullerenes form a family of structurally similar molecules. They represent the exclusive molecular form of carbon, being different from all other forms of carbon that have polymeric structures. However, the possibility of mutual transformations between different structures makes fullerenes a part of an infinite family of carbon polymorphs, which cannot be studied without using methods of solid state physics, crystallography, and other nonchemical disciplines.

In this review we will not dwell on the basics of fullerene science because various aspects of research in this scientific area and especially those related to fullerene chemistry have been reviewed in domestic scientific journals.[5—9] A review of extensive literature on fullerene chemistry published worldwide is the subject of monographs. Here, the emphasis is placed on the advances in experimental and theoretical fullerene chemistry made by Russian researchers and first of all by those working at the INEOS.

The chemical nature of fullerenes representing a family of highly unsaturated polyhedral carbon clusters allows them to enter addition reactions only. The molecular structure of fullerenes is such that substitution or abstraction reactions cannot proceed without loss of molecular identity, except for the loss of an electron followed by generation of a radical cation and retention of the polyhedral cage.

Electron-acceptor character of fullerenes governs the nature of reactants that can be added. These are mainly electron-releasing species including anions, electrons, and free radicals. The formation of intermolecular complexes is also to a great extent depends upon donor-acceptor interactions with partial charge transfer.

A vital problem of fullerene chemistry is research on the reactivity of strained double bonds, which is complicated by the formation of a system of electrons delocalized over a spheroidal surface. The available information suggests that the members of the fullerene family behave in a similar way in spite of the fact that most studies were carried out with C_{60} and C_{70} fullerenes, the latter being somewhat less accessible and more expensive.

Distinctions between these compounds are associated with molecular symmetry reduction from I_h to D_{5h} on

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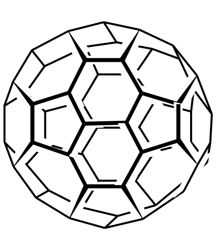
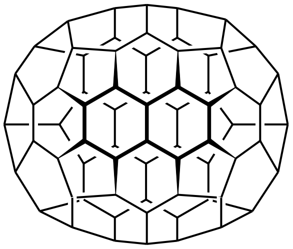
* Devoted to fiftieth anniversary of the A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1749—1770, September, 2004.



C_{60} (I_h)



C_{70} (D_{5h})

going from C_{60} to C_{70}, with replacement of spheroidal shape by ellipsoidal shape, with steric factors, and with the increase in the number of hexagonal faces. On going to higher fullerenes the number of hexagonal faces increases progressively, whereas the number of pentagonal faces always equals twelve, which has a pronounced effect on the shape of a certain molecule. Chemistry of higher fullerenes has virtually not been studied as yet because these compounds are hard to access, except for a few studies on C_{76} and C_{84}. The main difficulty in synthetic fullerene chemistry is the presence of a large number of reactive sites with identical reactivities; because of this, mixtures of products are usually obtained. The synthesis of monoaddition product is a rather complicated task while double and higher addition products are formed as mixtures of isomers possessing nearly identical properties. As a consequence, separation of mixtures of organic fullerene derivatives often requires HPLC.

The inner cavities of ellipsoidal fullerene molecules are large enough to encapsulate one or more atoms, *e.g.*, atoms of inert gases or metals or small molecules. This specific subclass of fullerene derivatives with unique topology is called endohedral fullerene derivatives and denoted as M@C_n. The first representative of this class is La@C_{60} discovered by mass spectrometry.[10]

Because fullerene chemistry emerged less than two decades ago, the first problem of paramount importance is to study the chemical properties and reactivity of the molecules belonging to this new unusual class in every respect including interdisciplinary areas which are also the subject of physics and biology.

The discovery of interesting non-chemical properties (superconductivity, ferromagnetism, photoreactivity, electroluminescence, participation in biochemically active conjugates, *etc.*) of particular fullerene derivatives has initiated interest in the synthesis of related structures. In this connection it is of importance to develop methods of targeted synthesis of fullerene derivatives. As a consequence, methods of separation and analysis of structurally similar compounds, in particular, isomers are much needed.

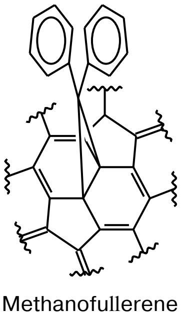
Fullerenes possess strong acceptor properties. Because of this, an important problem in fullerene chemistry is either intramolecular or intermolecular electron density transfer from appropriate donors to fabricate "molecular wires" and "molecular switches"; here, suitable polymeric partners also play an important role. Such fullerene-polymer composites were reported as light-emitting diodes (white light sources).[11] Fullerene complexes with transition metals can exhibit catalytic properties.

Endohedral fullerene derivatives are of paramount interest. These are hard-to-access compounds containing one or more metal (or inert gas) atoms encapsulated in the inner cavity. The hard-to-access and expensive magnetic isotope ^{3}He has found an application in the NMR characterization of fullerene derivatives.

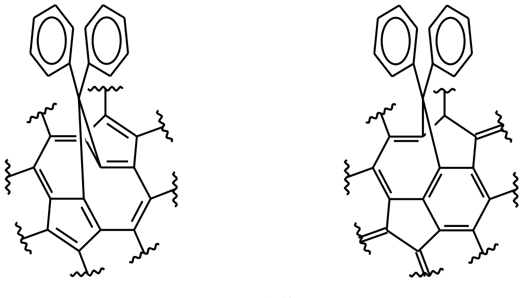
In Russia, the greatest advantages in fullerene chemistry have been achieved in research on the synthesis of fullerene complexes with metals, which is efficiently combined with quantum-chemical and ESR studies; in investigations of intermolecular complexes with electron donors; in development of a new method of isolation of endohedral metallofullerenes; in application of mass spectrometry methods to studies of ion-molecule exchange in the gas phase and to fluorine addition; and in high-predictive-power quantum-chemical studies of fullerene derivatives and heterofullerenes.

Organic fullerene derivatives

Characteristic of fullerenes are [n+2]-cycloaddition reactions (see a review[9]). At $n > 1$, conventional [n+2]-rings are formed, whereas at $n = 1$ a specific behavior typical of the fullerene system only is observed. These products are usually formed from diazo compounds or azides with elimination of a dinitrogen molecule likely *via* two suc-



Methanofullerene

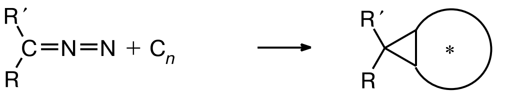


Isomeric fulleroids

cessive reactions, the first reaction being a [3+2]-cycloaddition. The overall reaction can result in not only a product of addition to the double bond connecting two hexagons ((6,6)-bond) but also a product of addition to the ordinary bond between the hexagon and pentagon ((6,5)-bond). The former route leads to the desired three-membered ring (these compounds are called methanofullerenes) while the latter one involves cleavage of the (6,5)-bond with the formation of a monatomic bridge in the nine-membered carbon ring. These structures are called fulleroids;[12] the monatomic bridge in them can be formed by the fragments R´RC or RN (azafulleroids). Yet another synthetic route to methanofullerenes is provided by the Bingel reaction resulting in formal addition of the $C(COOR)_2$ fragment originated from a malonate.[13]

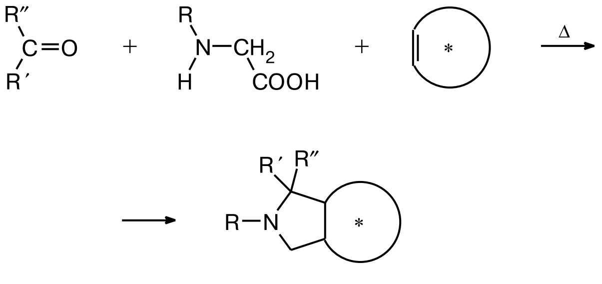
Using an essential modification of the Bingel reaction (replacement of one or both carboxyl groups in the malonic acid molecule by phosphoryl group), a method was developed[14,15] of synthesis of compounds containing one or two phosphoryl groups in the three-membered methanofullerene ring, which can be of interest for biochemical applications. The Wudl reaction involving diazo compounds or azides (Scheme 1) and the Prato reaction (Scheme 2) represent two cycloaddition reactions that are most characteristic of fullerenes.

Scheme 1



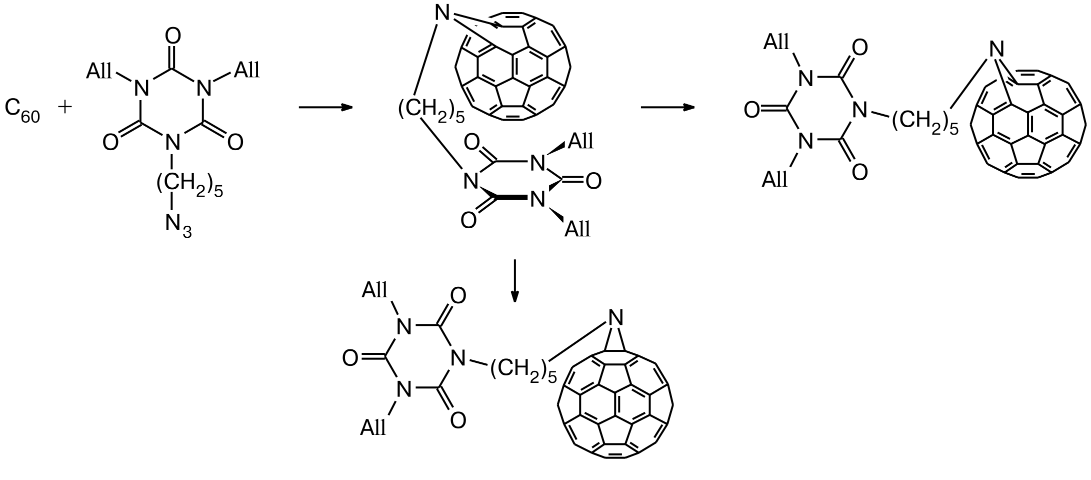
Functionalized 1,3,5-triazine derivatives containing azide group in the side chain react with C_{60} to give some products including azafulleroids and fullerenoaziridines (Scheme 3) and, in particular, an individual bis-azafulleroid isomer with a twelve-membered ring in the cage.[16—18] Particular attention in these studies was paid to the synthesis of fullerene derivatives with higher electron affinities compared to that of the starting C_{60}. This can be controlled electrochemically by the decrease in the reduction potential. Some model compounds containing an isocyanurate group with three acceptor carbonyls were obtained.[19] At the same time an electrochemical method is also developed, which is suitable for the synthesis of fullerene derivatives, in particular, metal complexes *via* nucleophilic reactions of C_{60} or C_{70} dianions with metal halides or malonate structures.[20,21]

Scheme 2



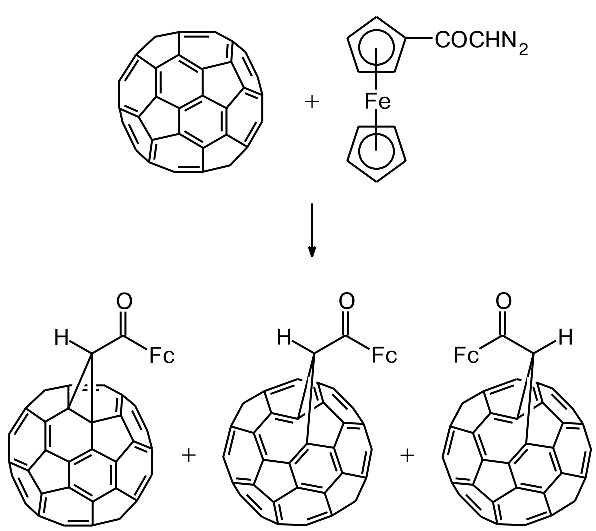
Diazoacetylmetallocenes were used to synthesize methanofullerenes containing organometallic substituents and characterized by intramolecular electron density transfer. It was found that the reaction with diazoacetylferrocene results in a mixture of the desired methanofullerene with fulleroids (Scheme 4) while the reaction with diazoacetylcymantrene affords a mixture of methanofullerene with the dihydrofuran ring condensed with fullerene.[22,23] The reaction involving 1,1´-bis-diazoacetylferrocene leads to a product which, based on the ^{1}H and ^{13}C NMR spectra, was ascribed the structure of an *ansa*-derivative with the ferrocene unit attached to ful-

Scheme 3

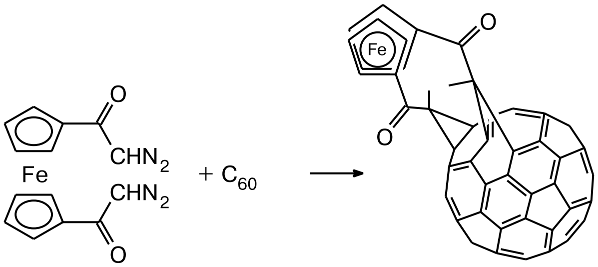


lerene simultaneously at the (6:6) and (6:5) bonds[24] (Scheme 5).

Scheme 4



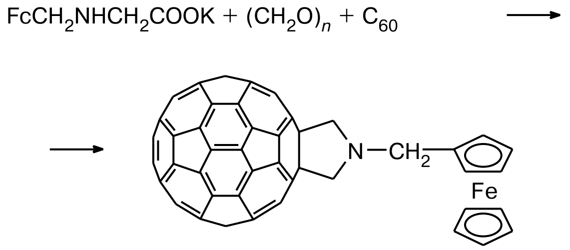
Scheme 5



Monocycloaddition and biscycloaddition of nitrile oxides and nitrile imines were studied by researchers from several groups.[25] The formation of a fulleroid structure as a result of unusual cleavage of an ordinary (6:5)-bond in the course of [3+2]-cycloaddition was reported.[26]

Cycloaddition of *N*-substituted glycines and aldehydes to C_{60} fullerene (Prato reaction[27]) was employed to synthesize fullerenopyrrolidines containing bioactive groups[28] and fullerenopyrrolidines containing various metallocenyl groups in position 2 or the ferrocenylmethyl group in position 3 at the nitrogen atom[29] as substituents (Scheme 6).

Scheme 6



The same reaction was used to obtain a fullerene derivative containing a sterically hindered phenol in the side chain. A feature of the compound is that phenol retained its ability to generate a phenoxyl radical on oxidation.[30]

Double bonds of C_{60} molecules can enter a zirconocene dichloride catalyzed cycloalumination reaction, which was discovered earlier for olefins.[31] In the presence of an excess of triethylaluminum it is possible to add up to twelve Et—Al—CH_2—CH_2 units to C_{60} in high yields. To establish the structure using NMR spectroscopy and mass spectrometry[32] or chemical reactions with aldehydes, nitriles, *etc.*, fused ethylalumacyclopentanes were hydrolyzed (deuterolyzed) to 1-ethyl-2-hydrofullerenes.

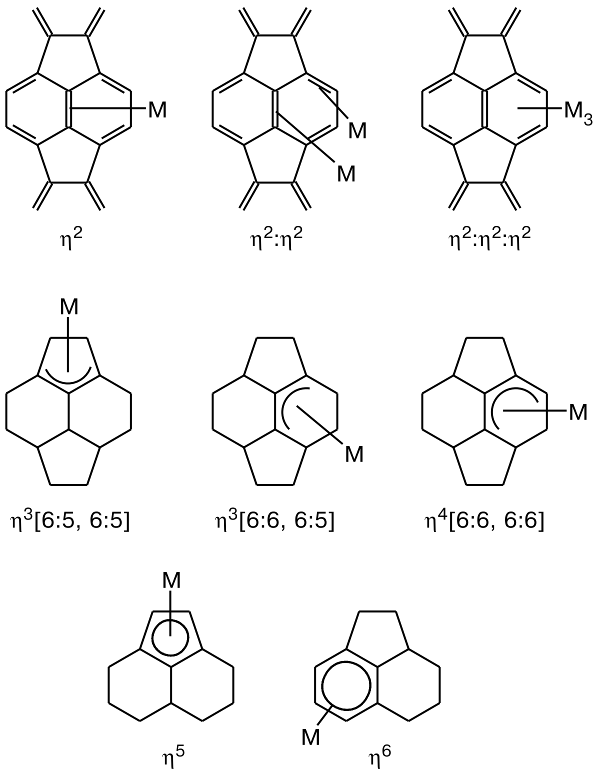
Catalytic hydrogenation of fullerenes with molecular hydrogen usually results in hydrofullerenes with different degrees of saturation with hydrogen. Because of this, indirect methods are employed to obtain hydrofullerenes *via* successive reactions. Conventionally, proton transfer from such donors as dihydroanthracene is used; the major and most stable reaction product is $C_{60}H_{36}$.[33,34] Hydrogen and deuterium were introduced by hydrogenation of polymer metal complexes $C_{60}Pd_x$ or $C_{60}Pt_x$ at a low pressure (20 atm) and on heating to at most 400 °C. All reactions gave mixtures of products with different degrees of hydrogenation (from two to twenty-six atoms[35]). The available data on the methods of synthesis and on investigations of the structure and reactivity of exohedral fullerene hydrides are summarized in a review.[36] The same study also concerns possible fields of practical applications of fullerene hydrides, *e.g.*, hydrogen accumulators, use in catalysis, as components of chemical current sources, *etc.*

Fluorination of fullerenes was studied in detail in close relation to physicochemical (mass spectrometric) studies. Preparative-scale studies succeeded in isolating a few polyfluorinated buckminsterfullerene derivatives; the crystal structures of $C_{60}F_{18}$ and $C_{60}F_{48}$ in the form of solvates with arene hydrocarbons were thoroughly investigated.[37]

The addition of primary and secondary amines (N—H bonds) to the double bond of C_{60} [38] was used to add amino acid molecules to fullerene to obtain bioactive derivatives.[39,40] Further studies failed to establish the chemical structures of the reaction products but acquired a biomedical specialization and allowed not only the physicochemical but also the immunogenic and allergenic properties of these fullerene-amino acid and fullerene-protein conjugates and their interactions with biological objects to be studied[41] and possible applications in medicine to be outlined.

Organometallic *exo*-derivatives of fullerenes

A large number of formally conjugated double bonds in the fullerene structure permits the formation of π-complexes with metals. Fullerenes can act as ligands with different hapticities (from 1 to 6).[42]



However, transition metal complexes are usually characterized by a hapticity of 2, *i.e.*, these are conventional η^2-complexes (or π-olefin complexes). A review[43] concerned with organometallic fullerene complexes summarizes the available data on the methods of synthesis and structure and reactivity investigations of exohedral complexes of C_{60}, C_{79}, *etc.*, fullerenes with transition metal atoms. It was theoretically established[44] that stable η^5-complexes of fullerenes or their bowl-shaped hydrocarbon precursors can be obtained by isolating a pentagon by attaching five groups to it. This complex, which can be called (pentamethylfullereno)ferrocene, was synthesized recently.[45] In the case of C_{70} fullerene three groups are enough to form a π-complex similar to an indenyl complex.[45]

A short time after the synthesis of first fullerene complexes with platinum,[46] a less stable palladium complex $(\eta^2\text{-}C_{60})Pd(PPh_3)_2$ was synthesized and its molecular structure determined (Fig. 1).[47] The equilibrium in solutions (metal—ligand exchange) was studied by electrochemistry and electronic spectroscopy.[48] Two new procedures for the synthesis of complex $(\eta^2\text{-}C_n)Pt(PR_3)_2$ starting from compounds R—Hg—Pt$(PR_3)_2$—R′ containing platinum and mercury[49] or from diarylplatinum complexes $R_2Pt(PR_3)_2$ [50] were proposed (Scheme 7). The first optically active organometallic fullerene derivatives were synthesized, namely, palladium and platinum complexes with enantiomerically pure ligand (+)-DIOP $(\eta^2\text{-}C_{60})$Pd[(+)-DIOP] [51] and $(\eta^2\text{-}C_{60})$Pt[(+)-DIOP],[52] and their circular dichroism spectra were recorded.[53] The platinum complex was structurally characterized by X-ray analysis (Fig. 2).[52]

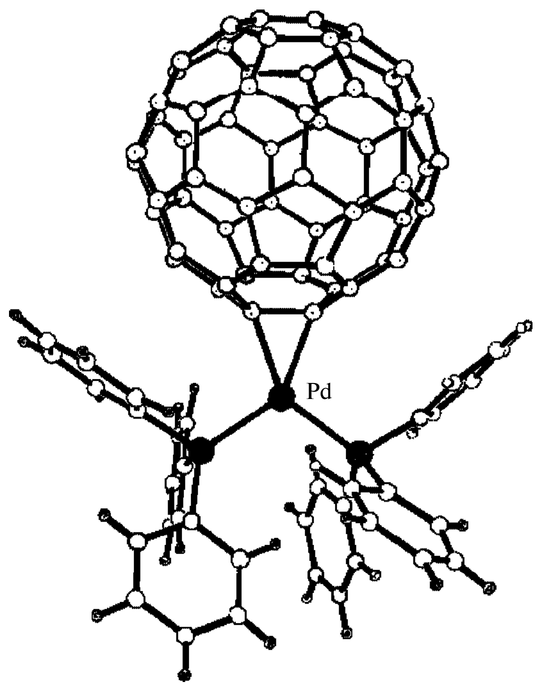


Fig. 1. Structure of complex $(\eta^2\text{-}C_{60})Pd(PPh_3)_2$.

Scheme 7

$$\text{Ar—Hg—Pt(PPh}_3)_2\text{—Hal} + C_n \longrightarrow (\eta^2\text{-}C_n)\text{Pt(PPh}_3)_2$$

$$\text{Ar}_2\text{Pt(PPh}_3)_2 + C_n \longrightarrow (\eta^2\text{-}C_n)\text{Pt(PPh}_3)_2$$

$$(\eta^2\text{-}C_n)\text{Pt(PPh}_3)_2 + \overset{\frown}{\text{P P}} \longrightarrow (\eta^2\text{-}C_n)\text{Pt(}\overset{\frown}{\text{P P}}\text{)}$$

$$\text{Pd}_2\text{(dba)}_3 + C_n + 2\text{ L} \longrightarrow (\eta^2\text{-}C_n)\text{PdL}_2$$

Palladium complexes of C_{60} with bidentate ligands containing metallocene fragments, namely, 1,1′-di(diphenylphosphino)ferrocene and diphenylphosphinocymantrene, were synthesized and thoroughly studied.[54] It was shown that η^2-palladation of C_{70} proceeds at two positions, *a—b* and *c—c*, in a 84 : 16 ratio. η^2-Complexes of C_{60} and C_{70} with rhodium and iridium obtained by the fullerene reactions with $HM(CO)(PPh_3)_3$ (M = Rh, Ir)

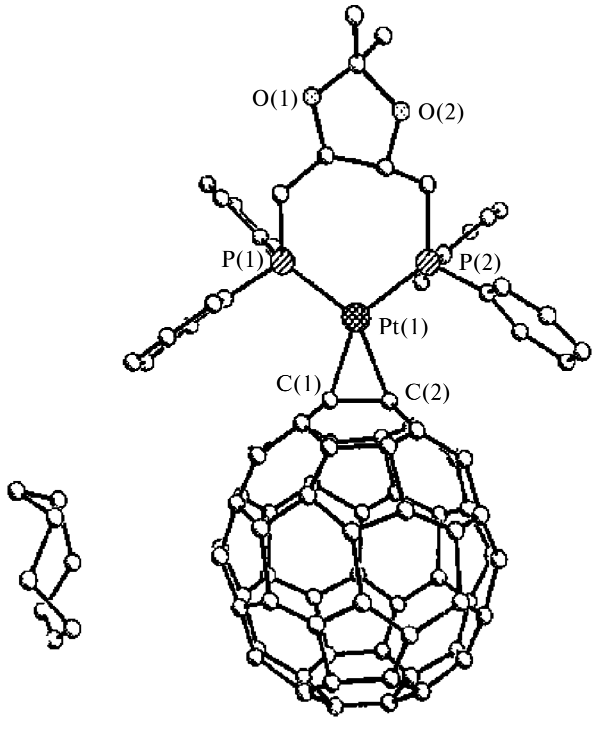


Fig. 2. Structure of complex (η^2-C_{60})Pt[(+)-DIOP].

Bond	*d*/Å	Angle	ω/deg
Pt(1)—C(1)	2.09	C(1)—Pt(1)—C(2)	42.0
Pt(1)—C(2)	2.12	C(1)—Pt(1)—P(1)	104.2
Pt(1)—P(1)	2.28	C(2)—Pt(1)—P(2)	104.4
Pt(1)—P(2)	2.26	P(1)—Pt(1)—P(2)	109.5
C(1)—C(2)	1.51		
C(1)—C(6)	1.44		

followed by loss of one phosphine ligand were studied.[55] A cyclooctadiene complex of iridium similarly reacts with C_{60} to give (η^2-C_{60})IrH(C_8H_{12})(PPh_3). It should be emphasized that the M—H bond is not involved in these reactions with fullerenes in contrast to reactions of conventional olefins. Recently, optically active rhodium and iridium complexes with the (+)-DIOP ligand were also synthesized. The metal atoms in these complexes are in octahedral environment in contrast to the platinum and palladium complexes. These rhodium and iridium complexes can exist as two isomers, which were observed by ^{31}P NMR spectroscopy. Structurally similar bis-derivatives including a mixed rhoduim-iridium complex were also obtained.[56] It is possible to insert a dioxygen molecule into the metal—fullerene bond of an iridium complex of C_{60} fullerene containing also a chelate carborane ligand to give a five-membered ring fused with the fullerene cage; the structures of this compound (Fig. 3) and of compounds listed below were established by X-ray analysis.[57] A η^2-C_{60}-complex of platinum with 1-diphenylphosphino-2-isopropenylcarborane (Scheme 8) and an unusual dimeric platinum complex with bis(diphenylphosphino)methane ligand (Fig. 4) were obtained. Here, the dimeric structure is formed to avoid a high strain in the four-membered ring of the monomeric complex. A titanocene-fullerene complex $Cp_2Ti(\eta^2$-$C_{60})$ (Fig. 5) was also first synthesized by the reaction between C_{60} and bis(trimethylsilyl)acetylene complex of titanocene and structurally characterized.[58]

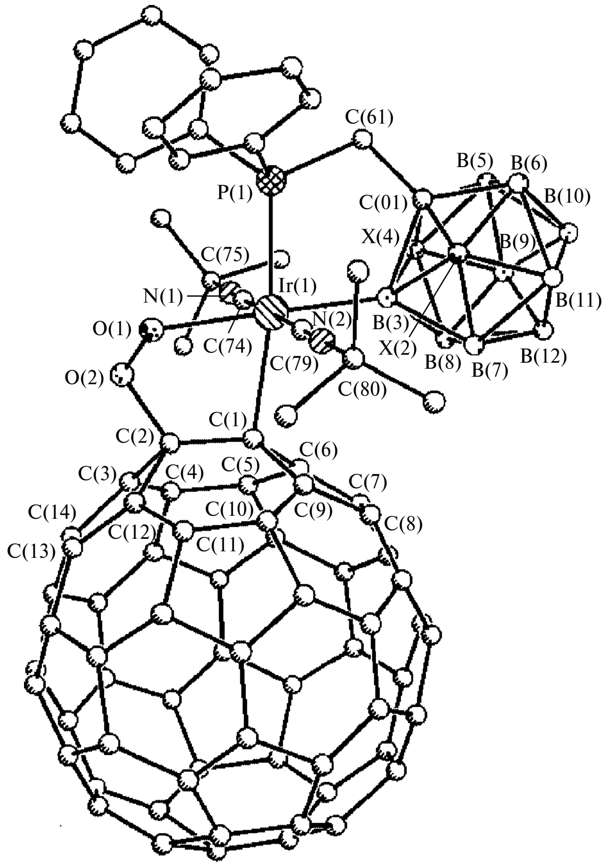
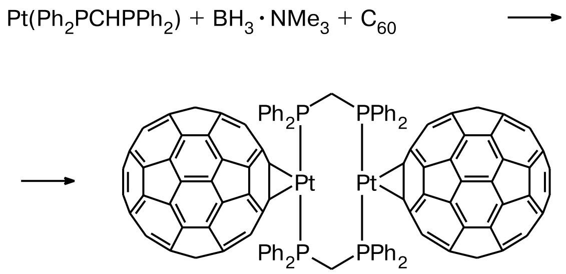


Fig. 3. Structure of iridium complex of C_{60} with inserted dioxygen molecule.

Scheme 8



A procedure for the synthesis of stable different-ligand osmium complexes[59] by introduction of isonitrile ligand instead of one phosphine ligand with simultaneous loss of

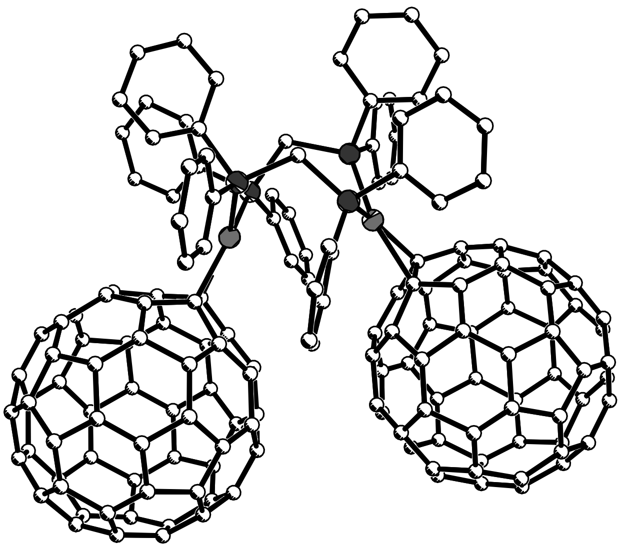
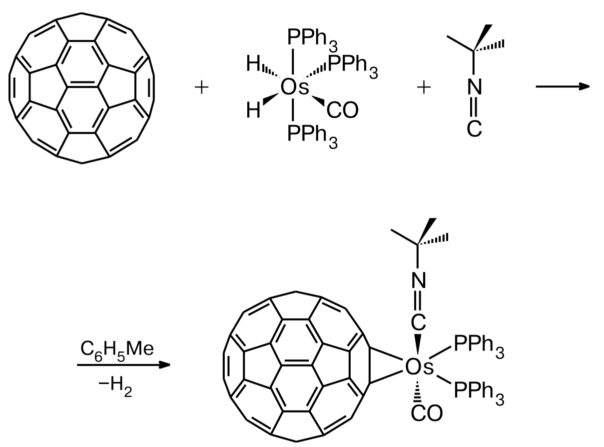


Fig. 4. Dimeric platinum complex of C_{60} with bis(diphenylphosphino)methane ligand.

a hydrogen molecule from the initial Os^{II} dihydride complex (Scheme 9) was developed.

Scheme 9



Fullerene molecular complexes and fullerene salts

Donor-acceptor fullerene complexes in which the fullerene molecules usually act as acceptors have been the subject of intensive research as potential materials possessing unusual optical, conducting, and magnetic properties. The spectrum of possible donor partners is very broad and includes, *e.g.*, so strong donors as tetrathiofulvalenes, aromatic hydrocarbons and their hetero-analogs, (metal)porphyrins, *etc.* (see a review[8]). Charge transfer was indicated by a band in the region 600—1300 nm in the electronic absorption spectra in solution and in the solid phase and by other spectra obtained. The molecular structures and crystal packing of many charge-transfer complexes were studied. An example is provided by the synthesis of, *e.g.*, two molecular complexes with 1,3,5-triphenylbenzene (TPB), namely, TPB • C_{60} and 2TPB • C_{60} • PhCl. The former has a layered structure while in the latter the fullerene molecules form columns along

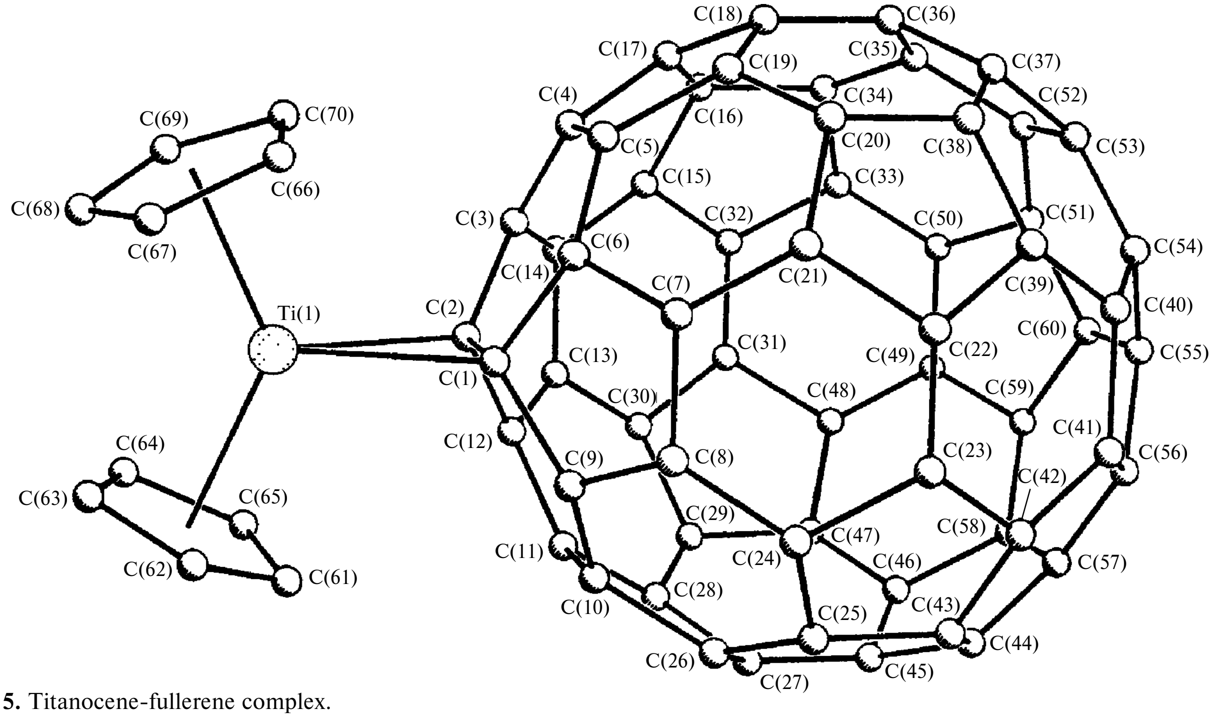


Fig. 5. Titanocene-fullerene complex.

the *a* axis with a shortened distance (10.09 Å) between the centers of the C_{60} molecules. One of the most stable complexes is a complex with anthracene dimer (9,10,9´,10´-"dianthracene") because its concavity geometrically matches the spheroidal shape of the C_{60} (but not C_{70}) molecule and many shortened contacts are thus formed.[60]

Molecular complexes of C_{60} with tetraarylporphyrins and metal porphyrins including dimeric ones (*e.g.*, $C_{60} \cdot (FeTPP)_2O$) were obtained, their molecular structures determined, and ESR spectra studied. New molecular complexes of C_{60} and C_{70} fullerenes with various amines were synthesized. Studies on the supramolecular structures and molecular packing in crystals revealed close-packed double layers, hexagonal layers or quasi-three-dimensional structures. It was shown that structural voids between fullerene molecules in the complexes can be filled with molecules of various size, which stabilizes rotation of the fullerene molecules in the crystal. Inclusion of various donor molecules into voids of the C_{60} crystal lattice allows one to obtain multicomponent compounds containing two donor molecules.[61] An example is provided by a honeycomb structure of a complex of C_{60} fullerene with zinc tetraporphyrinate and pyrazine (Fig. 6). The dependence of the intensity of photo-induced ESR signal on the photon energy was studied taking complexes with tertiary amines as examples. It was found that in most cases direct intermolecular electron transfer from amine to fullerene occurs. Fullerenes also form rather stable crystalline complexes with weaker donors, *e.g.*, heterocyclic molecules S_8 [62] and S_4N_4.[63]

Complete electron transfer results in the formation of salts, transfer of an odd number of electrons leading to radical-ion salts. These salts can also obtained by electrochemical reduction of fullerenes in the presence of an appropriate anion; this approach is exemplified by crystalline salts $(Ph_4P)_2C_{60}Hal$ and $(Ph_4As)_2C_{60}Cl$.[64]

Particularly interesting reversible dimerization of fullerene radical anions was found in bis(arene)chromium fullerides.[65] It was found that cooling of these radical-ion salts results in the formation of a σ-bond between two C_{60} units. Noteworthy is that the phenomenon was observed earlier for alkali metal fullerides.[66] However, it was discussed[66] only from the crystallography and inorganic chemistry viewpoints and no attention was paid to explicit analogy with reversible dimerization of free-radical spin adducts RC_{60} [67] (see below) or information on this process was unavailable. Comparing these facts, it seems undoubtful that the driving force of the process is a trend toward formation of a diamagnetic species and that the role of the charge is insignificant. A C_{70} radical anion in similar bis(arene)chromium salts forms a dimer at room temperature.

Endohedral metallofullerenes

Unique topological structure of endohedral fullerenes and dependence of their properties on the atom encapsulated in the inner cavity are of considerable interest (Fig. 7). Endohedral metallofullerenes (EMFs) are considered candidates for modern technological applications

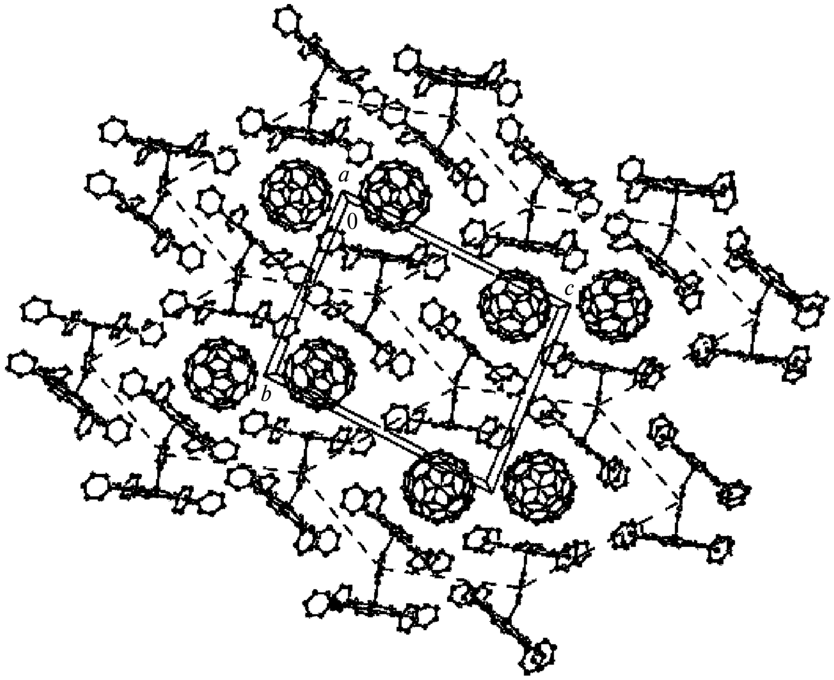


Fig. 6. Supramolecular structure of a C_{60} fullerene complex with zinc tetraphenylporphyrinate and pyrazine.

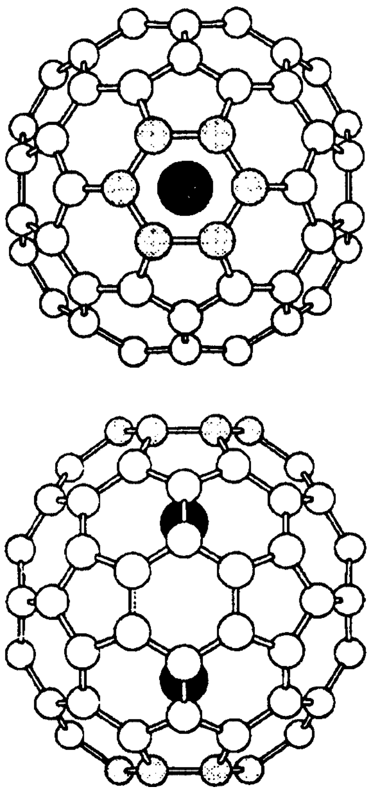


Fig. 7. Schematic view of endohedral fullerene complex.

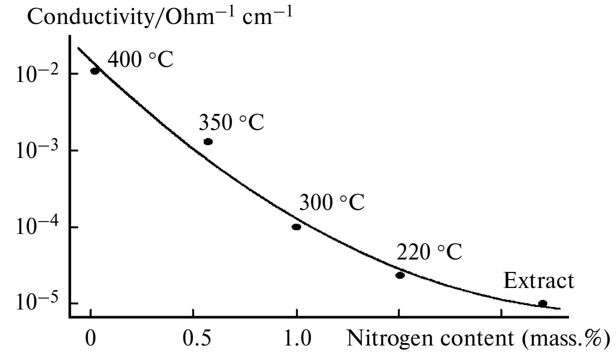


Fig. 8. Conductivity of pure La@C_{82} obtained by sublimation.

as molecular wires, organic ferromagnetics, ESR probes for biomedical research, *etc.* The chemical and physical properties of EMFs are still poorly studied. The main reason is that these compounds are hard to access, which is associated with difficulties in synthetic procedures and isolation of necessary amounts. The synthesis and investigation of endohedral complexes with atoms of inert gases[68] requires specific equipment. Modern methods of synthesis of EMFs (laser-induced and electric arc evaporation of graphite electrodes compounded with rare-earth metals compounds) and traditional methods of isolation of these compounds from soot only allow extracts with very low content of endometallofullerenes (usually, at most 1% of the weight of primary soot) to be obtained. The initially proposed method of synthesis of EMFs[69] was improved by elaborating an isolation technique based on extraction with DMF, which makes the isolation procedure simpler and permits reduction of the loss of EMF.[70] The polar solvent is strongly retained by the compound but it was found that pure EMFs obtained by sublimation under high vacuum have high conductivities[71] (Fig. 8). Reactions of EMFs containing encapsulated yttrium and lanthanum were studied by ESR spectroscopy (this technique uses rather small amounts of compounds) and it was found that these EMFs are inert toward phosphoryl radicals and Pt^0 but one of the two observed multiplets disappears on treatment with CF_3COOH;[72] this is the first observation of different reactivities of two probable EMF isomers.

Physicochemical studies of fullerene derivatives

Electrochemistry and mass spectrometry are important methods of research into fullerenes. The importance of the former is determined by the fact that in all fullerene derivatives the fullerene cage retains its ability to add a number of electrons but the reduction potentials vary depending on the molecular structure, thus providing the possibility of drawing conclusions about electronic effects. Oxidation of the fullerene cage in solution occurs only at very high potentials; however, other (especially, organometallic) groups in the molecule can be oxidized, the magnitude of the potential being affected by the fullerene unit.

Both positive ions (traditional mass spectrometry; determination of ionization potentials) and negative ions (more stable in the case of fullerenes; determination of electron affinities) are formed in the gas phase. This allows not only the weights of the carbon clusters forming but also their thermodynamic characteristics, ionization potentials, and electron affinities to be determined. Studies on the physicochemical properties of higher fullerenes and fluoro derivatives of fullerenes and elaboration of corresponding synthetic procedures have been well documented (see reviews[73,74]).

The thermodynamic characteristics of fullerenes and the most stable fullerene derivatives (fluorides and metallofullerenes) were experimentally studied by mass spectrometry and estimated theoretically. Gas-phase exchange reactions

$$C_n + C_m^{-1} = C_n^{-1} + C_m$$

between various neutral fullerene molecules and monoanions were investigated with the C_{60} buckminsterfullerene used as a reference. The equilibrium constants for these reactions and the relative electron affinities and ionization potentials of higher fullerenes C_{70}, C_{76}, C_{78}, and C_{84} were determined; a gradual increase in the electron affinity and a decrease in the ionization potentials with an increase in the size of the fullerene cage was revealed.[75,76]

A method for generation of thermal negative ions of lower fluoro derivatives of fullerenes was developed.[77] The technique is based on the use of transition metal fluorides. Ion-molecule equilibria involving $C_nF_4^-$, $C_nF_2^-$, and C_nF^- were studied and the Gibbs energies of the fluorine exchange reactions between these anions and C_n^- determined. Steady-state kinetics of a model solid-phase fluorination reaction was investigated. A solution to the system of kinetic equations for the relative concentrations of reaction products was obtained and used to determine conditions for selective formation of compounds with preset compositions.

The electron affinities of some C_{2n} endohedral metallofullerenes containing one or two encapsulated metal atoms (Sc, Y, Gd) and $Sc_xEr_{3-x}@C_{60}$ compounds were determined.[78] Most endohedral molecules were shown to be stronger acceptors than "hollow" fullerenes. These experimental results were complemented by the results of density functional quantum-chemical calculations of the compounds under study. Formation of endohedral complexes of higher fullerenes is governed by the acceptor properties rather than the relative stabilities of the carbon cages in the non-charged state. The molecular and electronic structures of higher fullerenes C_{72}, C_{74}, and C_{82} and the possibility of their stabilization were studied.[79,80]

Methods of direct synthesis of alkali metal fullerides in aromatic hydrocarbons by mechanical activation on prolonged heating were developed. ^{13}C and ^{23}Na NMR studies revealed that the technique leads to essentially the same products (M_3C_{60} and M_6C_{60}; M = Na, K, Rb) as does the vapor phase synthesis.[81] The Gibbs energies of the formation of various K_xC_{60} ($x = 1, 3, 4, 6$) phases were determined.[82] The reaction of C_{60} with metallic lithium was also studied by IR and ESR spectroscopy and by quantum-chemical methods.[83]

A method of synthesis of alkali metal fullerides based on thermal decomposition of azides was elaborated. X-Ray spectral and quantum-chemical studies of the electronic structure of K_xC_{60} were carried out. Joint use of X-ray spectroscopy and quantum-chemical simulation of possible structures of fullerene compounds allowed the main structural motifs in the X-ray amorphous polymer $(C_{60})_n$, hydrofullerene $C_{60}H_{36}$, and fluoride $C_{60}F_{24}$ to be determined.[84,85]

Compounds Pd_xC_{60} and Pt_xC_{60} were obtained. Analysis of the C-Kα-spectra suggested that the chemical bonds formed in these systems are characteristic of π-complexes.[86]

The thermodynamic properties of solid solvates and solubilities of C_{60} and C_{70} fullerenes in aromatic solvents and in water were studied.[87—89] In particular, a number of crystal solvates of C_{60} and C_{70} fullerenes and solvates of a piperazine monoadduct $C_{60}[N_2(C_2H_4)_2]$ with aromatic solvents were investigated. Their compositions, enthalpies, and incongruent melting temperatures were determined by differential scanning calorimetry. The structures of crystal solvates $C_{60}\cdot 2C_6H_4Me$, $C_{60}\cdot 2C_6H_5Br$, $C_{60}\cdot 2(m\text{-}C_6H_4Br_2)$, and $C_{60}\cdot 3(o\text{-}C_6H_4Br_2)$ were established by X-ray diffraction analysis. To correctly interpret the structural data obtained for some compounds, their crystal structures were calculated by the atom-atom potential method. Using a continuum model, qualitative predictions were made of changes in the Gibbs energy of solvation of fullerene molecules depending on the size of the carbon clusters (C_{20}—C_{84}). An explanation for anomalous temperature dependence of the solubility of C_{60} was proposed and then confirmed experimentally. Thermal decomposition of fullerene hydride $C_{60}H_{36}$ and fullerene bromide $C_{60}Br_{24}$ was studied. High-temperature mass spectrometry was employed to investigate sublimation and decomposition of C_{60} fullerene hydrides and deuterides. The temperature dependences of the vapor pressure and enthalpies of sublimation of hydrides $C_{60}H_{36}$ and $C_{60}H_{18}$ were measured. The average C_{60}—X bond dissociation energies in compounds $C_{60}H_{36}$, $C_{60}Cl_2$, and $C_{60}Br_{24}$ were also determined.[90—94]

Selective synthesis of fluorinated fullerenes by direct fluorination with F_2 was reported.[95] The role of transition metal fluorides in the course of selective synthesis was revealed (see also a review[73]).

Numerous studies on the synthesis, chemical structure, and reactivity of paramagnetic fullerene derivatives were carried out by ESR spectroscopy and quantum-chemical methods (see also the Section "Quantum-chemical studies of fullerenes and their derivatives"). Major advances in chemistry of fullerene radicals have been well documented;[96,97] because of this, we will briefly outline some recent results obtained in this field.

ESR spectroscopy was used[98] to study radical adducts of radicals $P(O)(OPr^i{}_2)_2$ (R^1) with fullerene derivatives $C_{60}\{C[P(O)(OEt)_2]_2\}_2$. It was established that the number of stable regioisomers of the phosphorylfullerenyl radicals formed in the addition of phosphoryls to $C_{60}\{C[P(O)(OEt)_2]_2\}_2$ isomers depends on the mutual arrangement of organophosphorus groups and decreases in the order *trans*-2 > *trans*-4 ≈ *trans*-3 > *e*. The rate constant for addition of the R^1 radicals to the *trans*-3 regioisomer was determined. Notations of isomers of C_{60} fullerene derivatives are given in Fig. 9.

The addition of radicals $P(O)Pr^i{}_2$ and Bu^t (R^1) to pyrrolidinofullerenes $C_{60}[CH_2NMeCHX]$ (X = $C_6H_3(CH_2CH_2Cl)_2$; 2,6-$Bu^t{}_2C_6H_2OH$; PhC_6H_4; indol-3-yl) was studied by ESR spectroscopy.[99] The rate constants for addition of the R^1 radicals to these compounds and the rate constants for dimerization of the spin-adducts of the R^1 radicals with these molecules were determined. Pyrrolidinofullerenes were found to be much

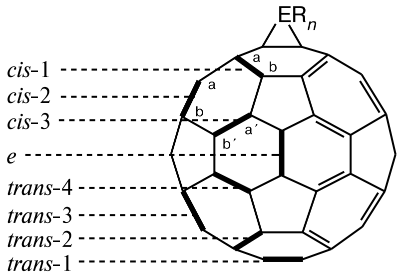


Fig. 9. Notations of *cis*- amd *trans*-isomers of C_{60} fullerene derivatives.

more reactive toward the R^1 radicals than C_{60} fullerene and methanofullerenes $C_{60}CX^1X^2$ ($X^1 = X^2 = CO_2Et$; $X^1 = CO_2Me$, $X^2 = OP(OMe)_2$; $X^1 = X^2 = OP(OEt)_2$).

Exposure of a toluene solution of $C_{60}Ph_5Cl$ to UV radiation leads to the formation of a stable cyclopentadienyl-type fullerenyl radical $^{\bullet}C_{60}Ph_5$.**100** The formation of three isomers of adducts of phosphoryl radicals with $C_{60}Ph_5Cl$ was detected on UV irradition of a toluene solution of $C_{60}Ph_5Cl$ containing $Hg[P(O)(OPr^i)_2]_2$. Density functional (B3LYP) quantum-chemical calculations of all possible radical adducts of phosphoryl radicals with $C_{60}Ph_5Cl$ were carried out. The results obtained were used to evaluate the enthalpies of formation and the hyperfine coupling constants. A $^{\bullet}C_{60}Ph_5C[P(O)(OPr^i)_2]—^{\bullet}C_{60}Ph_5C[P(O)(OPr^i)_2]$ biradical with a 10.5 Å separation between radical centers was also detected.

Y@C_{82} and La@C_{82} solutions and powders were oxidized with oleum and the ESR spectra of oxidation products were studied.**101** In accord with the oxidation conditions and the order of appearance the spectra were ascribed to radical cations M@$C_{82}{}^{n+}$ (n = 2, 4), dimers $M^{3+}{}_2$@$C_{164}{}^+$, and poly(endometallofullerenes).

The rate constants for addition of radicals $Me_2{}^{\bullet}CCN$ ($3.0 \cdot 10^6$ L mol^{-1} s^{-1}), $Me_2{}^{\bullet}CPh$ ($8.1 \cdot 10^5$ L mol^{-1} s^{-1}), and $CCl_3CH_2{}^{\bullet}CHPh$ ($8.5 \cdot 10^5$ L mol^{-1} s^{-1}) to C_{60} fullerene at 20 °C were determined**102** by ESR spectroscopy (spin trap technique). The rate constants for addition of radicals $O^{\bullet}P(OPr^i{}_2)$, $^{\bullet}Bu^t$, and $Me(CH_2)_3{}^{\bullet}CH_2$ to methano[60]fullerenes $C_{60}CX^1X^2$ ($X^1 = X^2 = CO_2Et$; $X^1 = CO_2Me$, $X^2 = OP(OMe)_2$; $X^1 = X^2 = OP(OEt)_2$) were also determined.**103** Methano[60]fullerenes were shown to be somewhat more reactive toward these radicals compared to C_{60} fullerene. This can be explained by an increase in the degree of pyramidality of the carbon atoms participating in the *cis*-2 and *cis*-3 bonds in methano[60]fullerenes compared to C_{60} fullerene.

Destruction of a $(C_{60})_n$ polymer and C_{120} and $C_{120}O$ dimers was studied by ESR and IR spectroscopy at different temperatures. The formation of C_{60} fullerene was revealed. The polymer was found to be more stable than the dimers. Spectral features of three-dimensional, hyper-cross-linked polymers obtained by liquid-phase polymerization were discussed.**104**

Quantum-chemical studies of fullerenes and their derivatives

Modern quantum chemistry methods are widely used in solving various chemical problems in order to not only interpret the experimental data but also estimate the possibility of existence of new chemical compounds and predict their physicochemical properties. Solution to these problems is of particular importance for fullerene chemistry because it allows one to *a priori* evaluate the stability of fullerene isomers or derivatives and to choose those compounds that seem to be best candidates for synthetic applications.

To analyze quantum-chemical studies on the theory of chemical structure of fullerenes and their derivatives, it is convenient to divide the polyhedral structures formed by these species into four groups:

(1) pure polyhedral carbon clusters;

(2) heteroatomic fullerenes (*i.e.*, fullerenes containing heteroatoms in the polyhedral cage);

(3) fullerene *exo*-derivatives (they contain a number of radicals or functional groups attached to carbon atoms from the outside of the polyhedral cage); and

(4) endofullerenes (they contain one or more atoms or other species with more complex structure and composition encapsulated into the polyhedral cage).

In turn, fullerene *exo*-derivatives can be divided into six classes depending on the type of chemical bonding between the species attached and the corresponding carbon atoms of the fullerene cage.

1. Carbon clusters. Pioneering quantum-chemical calculations of polyhedral carbon clusters (fullerenes C_{20}, C_{24}, and C_{60}) were carried out in the late 1960s and early 1970s at the INEOS.**4,105** These studies and the discovery of a linear form of carbon, carbyne,**106** should be considered as a basis for formulation of a more general problem of existence of crystalline forms of carbon different from graphite, diamond, and carbyne (see a review**107**).

In the early 1990s Russian researchers continued their studies on prediction of novel polyhedral forms of carbon. In particular, the topological structure of a family of flattened polyhedral carbon clusters C_n (n = 72—96) was simulated.**108** The electronic structure of all the clusters considered was studied in the π-electron approximation. The geometries of the (D_{6h})-C_{96} and (D_{6d})-C_{96} clusters were calculated by the MNDO, AM1, and PM3 semi-empirical quantum-chemical methods.**109** A new structure of a C_{84} fullerene isomer was proposed in 1992.**110** A number of structures of giant dumb-bell-shaped and toroidal carbon clusters were reported; the one-electron energy levels of C_n clusters (n = 432, 450, 480, 490, 500)

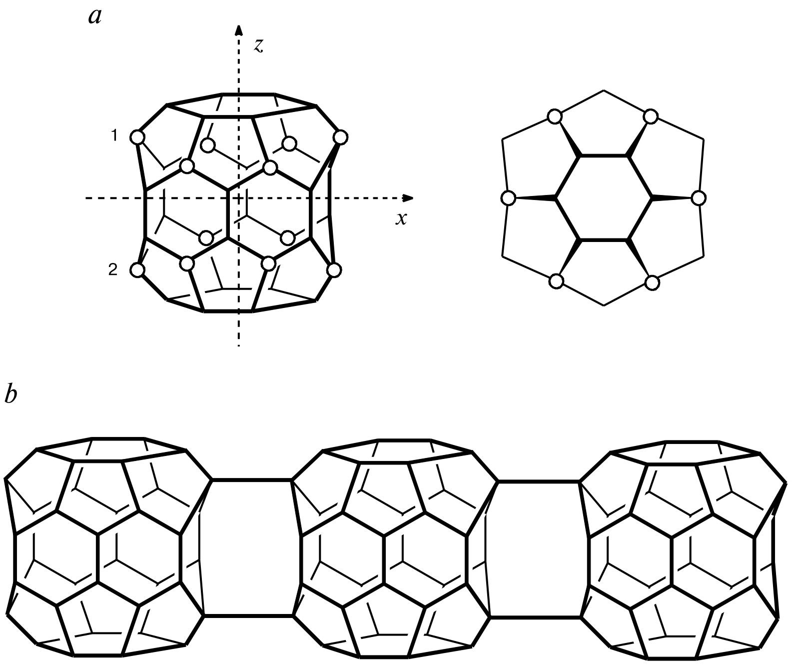


Fig. 10. Tentative structures of C_{36} fullerene (*a*) and $(C_{36})_3$ linear trimer (*b*).

were calculated in the π-electron approximation.[111,112] Dumb-bell-shaped clusters were considered as models for fragments of bamboo-shaped graphite.

The possibility for a (D_{6h})-C_{36} polyhedral carbon cluster (Fig. 10) to exist was considered and it was shown that this fullerene must be a stable species.[113] Recently, the synthesis of this compound was reported.[114]

Cluster (D_{6h})-C_{36} is the first member of a homologous series of C_{36+12n} fullerenes ($n = 0, 1, 2, ...$). At $n > 2$, such fullerenes have a barrel shape and are therefore called barrelenes; they can be considered as precursors of tubular forms of graphite.[115] The structures of five barrelenes ($n = 0, 1, 2, 3, 4$) were calculated by the PM3 method. The results of these studies and of calculations using extended Hückel theory suggested that barrelenes can form η^6-π-complexes with MCp (M = Fe, Ru, Os) species coordinated to the upper and lower hexagonal faces. It was also shown that the (D_{6h})-C_{36} cluster is prone to form oligomers and that the crystal structures based on this cluster must possess a semiconductor-type conductivity.[116]

PM3 quantum-chemical calculations of C_{60} oligomers of different structure were reported. The main structural motifs in the samples studied were determined by joint use of the results of X-ray spectral studies of amorphous $(C_{60})_n$ polymer and the results of quantum-chemical calculations of various C_{60} oligomers.[117]

Among carbon clusters, of great interest are the so-called onion structures. They comprise a number of nested fullerenes of different size.[118] The topological classification of such systems[119] is based on generalization of the concept of molecular topological form introduced earlier.[120] PM3 calculations of a two-layer endohedral cluster $C_{20}@C_{60}$ were also carried out.

The existence of methanofullerenes (compounds $C_{60}CR_2$ in which the CR_2 group is attached to atoms of a double bond of C_{60} fullerene to give a three-membered ring) suggests the possibility for novel forms of molecular carbon (fullerene—carbyne hybrids) to exist. Such carbon clusters comprise linear carbon chains C_n with a cumulated system of double bonds and C_{60} fullerenes η^2-bonded to the terminal chain atoms. *Ab initio* Hartree—Fock calculations of some structurally similar model systems showed that they (*e.g.*, $C_{60}C_nC_{60}$ clusters, Fig. 11) must be rather stable.[121] Up to six cumulene-type carbon chains oriented along the directions of the Cartesian coordinates passing through the midpoints of six double bonds forming an octahedral configuration can be bonded to C_{60} fullerene. This permits the existence of quasi-linear, quasi-two-dimensional, and three-dimensional structures including dendrimers built of covalently bonded alternating fullerenes and linear carbon chains.

Another type of stable carbon structures can be comprised of, *e.g.*, dodecahedral C_{20} and cubic C_8 fullerenes.

A polyhedral cluster C_{20} is the smallest among the 5,6-fullerenes. It has a strained structure, being a highly reactive species. Recently, theoretical proofs of the possibility for a crystalline form of carbon (CFC) with a simple cubic lattice (**1**) comprising covalently bonded C_{20} fullerenes[122] and for more dense CFC phases, orthorhombic (**2**) and tetragonal (**3**),[123] to exist were reported. The unit cell of the crystal of **1** contains eight sp^2-hybridized C atoms while the other carbon atoms are sp^3-hybrid-

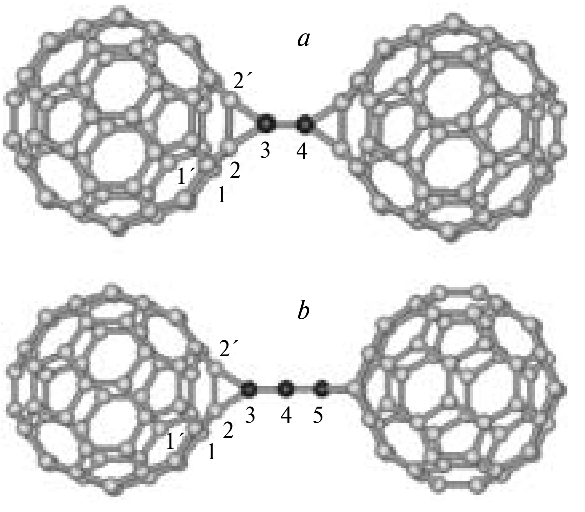


Fig. 11. Tentative structures of carbon clusters comprised of two fullerenes linked by linear chains of carbon atoms C_n with cumulated type of bonds: $n = 2$ (*a*) and 3 (*b*).

ized. In more stable structures **2** and **3** only four atoms in the unit cell are sp^2-hybridized. Voids in the structure of CFC-**1** [124] are large enough to be filled with cubic C_8 clusters, thus resulting in a new crystalline form of carbon, $[C_{20}C_8]_n$ (CFC-**4)** with a cubic lattice built of sp^3-hybridized atoms in contrast to the CFC **1—3**. The geometric parameters of the repeating unit of CFC-**4** were determined using the results of DFT-PBE calculations of $C_8@(C_{20})_8$ cluster (Fig. 12) and $C_8@(C_{20}H_{13})_8$ molecule in which the C_{20} (or $C_{20}H_{13}$) monomers occupy vertices of a cube and each of them is linked to three adjacent monomers by four-membered rings that are formed as a result of [2+2] cycloaddition to two double bonds of adjacent fullerene molecules. Each atom in the C_8 cluster is bound to one of the eight C_{20} ($C_{20}H_{13}$) clusters.

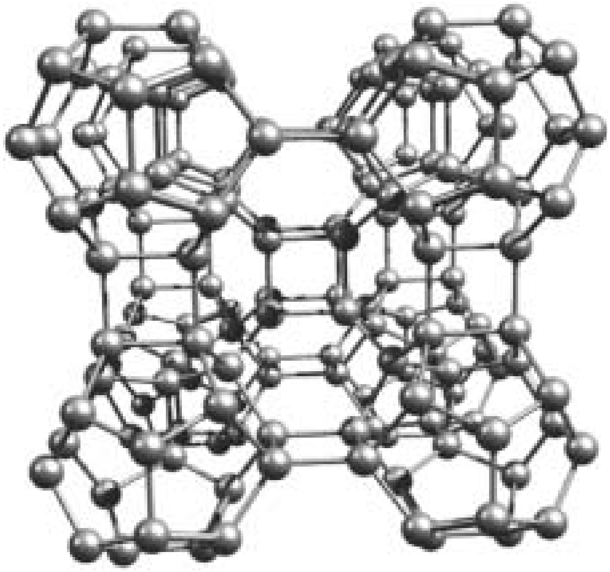


Fig. 12. DFT/PBE calculated structure of $C_8@(C_{20})_8$ cluster.

Fullerenes are unsaturated systems comprising atoms located on curved surfaces. This causes some deviation from sp^2-hybridization and an increase in contributions of p-orbitals. As a result, these systems can be weak radicals in character. A corresponding quantum-chemical study was carried out in the AM1 approximation in the framework of spin-polarized Hartree—Fock method taking C_{60} and Si_{60} fullerenes as examples.[125] Based on the results of calculations, C_{60} fullerene was found to be a much weaker polyradical compared to Si_{60}. This was thought to be the reason for difficulties in the synthesis of silicon fullerene analogs.[125]

2. Heterofullerenes. Pioneering quantum-chemical calculations of heterofullerenes were carried out in the early 1970s at the INEOS. The stability of dodecahedral isomers B_2C_{18} was studied using extended Hückel theory and CNDO/2 method.[126] Recently,[127] *ab initio* Hartree—Fock calculations of all possible dodecahedral isomers B_2C_{18} were carried out. It was found that replacement of two carbon atoms in the C_{20} cluster by boron atoms leads to stable closed-shell polyhedral molecules.

The synthesis of polyhedral carbon clusters gave an impetus to theoretical studies of the possibility for polyhedral structures comprised of atoms of other Group IV elements of the periodic table or for binary clusters built of atoms of Group III and V elements to exist. For instance, the synthesis of the so-called metal-carbohedrenes M_8C_{12} (M = Ti, V) was reported in 1992 (see a review[128]). The problem of existence of heterofullerenes and possible properties of these compounds have been the subject of many theoretical studies reported by the Russian and foreign researchers. Here, we will discuss the results of some studies carried out by Russian researchers working in the field, which were not reported earlier (see, *e.g.*, Ref. 5).

The topological approach using group representation theory was employed[129] in a qualitative study of the electronic structure of dodecahedral clusters X_8Y_{12}. Analytical expressions for one-electron energy levels were derived.

MNDO calculations of the molecular and electronic structures of $X_{12}Y_{12}$ and $X_{16}Y_{16}$ (X = B, Al; Y = N, P) polyhedral clusters were reported.[130,131] It was assumed that the σ-skeletons of these molecules comprise only four-membered and six-membered rings and each atom X (Y) is adjacent to atom Y (X) only.

The molecular and electronic structures of heterofullerenes $C_{n-k}X_k$ (X = B, N, O; $n = 60, 70$; $k = 1, 2$) were studied using extended Hückel theory with allowance for corrections to the π-electron energy due to the inclusion of steric interactions (see a review[132]).

Recently, a variety of polyhedral and tubular structures containing carbon, boron, and nitrogen atoms simultaneously or comprised of boron and nitrogen atoms only were synthesized (see Ref. 133). It should be noted that boron carbonitrides are of considerable interest for molecular electronics. The conducting properties of these systems are strongly dependent on the mutual arrangement of carbon atoms and pairs of B, N atoms.[134—137]

Fullerenes in which a few pairs of C—C bonds are replaced by B—N bonds can form stable dimers and oligomers linked by donor-acceptor B—N bonds. Analysis of the results of quantum-chemical calculations of various conjugated hydrocarbon molecules, polyhedral carbon clusters, and their C—B—N-analogs in which some (possibly, all) C—C bonds are replaced by B—N bonds showed that the total energies of the last-mentioned systems usually are much lower than those of the initial hydrocarbon molecules or carbon clusters. A theoretical explanation for this fact was reported.[138] Using the variational principle, an inequality was derived relating the total energies of the carbon cluster and its B—N—C-analog, from which it follows that the energy of the C—B—N-system containing no B—B and B—N bonds is lower than the energy of the corresponding homoatomic cluster.

3. Fullerene exo-derivatives. Fullerene *exo*-derivatives can have a very large number of isomers (*e.g.*, 21330558 for $C_{60}X_8$ isomers[73]). Usually, isolation of such isomers (most of them are unstable) and description of their molecular and electronic structures by experimental methods is a very complicated task. If the number of isomers is small, this problem can be solved using modern high-level quantum-chemical methods. Otherwise, the approach is of low efficiency because of great computational difficulties. In this case simplified (semiempirical) schemes of structure simulation and stability evaluation of isomers are often appropriate. This can be exemplified by a scheme developed (see Ref. 132 and references cited therein) and employed to evaluate the stability of different isomers of C_{60} and C_{70} fullerene derivatives (fulleroids with simple and coordinated addends). In particular, $C_{60}X_2$ and $C_{70}X_2$ derivatives with different species X (X = $(Bu^tC_5H_4N)_2OsO_4$, $(R_3P)_2M$, M = Pt, Pd, *etc.*) and heterofullerenes $C_{n-k}X_k$ (X = B, N, O) were studied. The method is based on joint use of the π-electron approximation and the inclusion of steric interaction energy.

C_{60} fullerene fluorides have been the subject of numerous quantum-chemical studies,[73] most of which were closely related to certain experiments. For instance, quantum-chemical PM3 calculations of some isomers of $C_{60}F_{24}$ fluoride were used to simulate X-ray spectra, which were then compared with experimental spectra. This enabled the determination of the most preferable structure of the major isomer containing in the sample studied.[139,140]

The synthesis of fullerene derivatives containing transition metal atoms bonded to the carbon cage atoms was first reported in 1991.[46] However, it should be noted that the metal atoms in both the $(Ph_3P)_2Pt(\eta^2\text{-}C_{60})$ complex described in the study[46] and its analogs synthesized more recently were only η^2-bonded to the fullerene carbon cage. Naturally, this brought up another point: what are the reasons precluding formation of η^n-complexes of fullerene with transition metals at $n > 2$. This problem was analyzed by quantum chemistry methods taking various model compounds as examples. These were hydrocarbon bowl-shaped precursors (corannulene $C_{20}H_{10}$, a $C_{30}H_{10}$ molecule whose carbon core matches the hemisphere of C_{60} fullerene, and some other compounds) and small clusters. The results obtained showed that the main reasons precluding the formation of η^n-complexes of "naked" fullerene with transition metal atoms at $n > 2$ are a too extended conjugated system of fullerene and a low polarizability of the fullerene fragments comprising three and more atoms under the action of the attacking species. It was shown that violation of the fullerene conjugated system by, *e.g.*, modifying it by either adding radicals to some carbon atoms or replacing certain carbon atoms by heteroatoms can change the local structure of the frontier orbitals and cause a substantial stabilization of complexes with the transition metal atoms coordinated to three or more carbon atoms. The most pronounced effect is attained when the conjugated system can be divided into two or more independent fragments (Fig. 13).

For instance, the addition of five radicals to carbon atoms in the α-positions relative to the same pentagon results in a cyclopentadienyl-type radical. This makes the formation of η^5-complexes of fullerene with MCp species (Fig. 14) possible.[44,142,143] As mentioned above, these systems and, in particular, the so-called ferrocene—fullerene hybrid[45,144] were obtained very recently. It was also theoretically shown that the addition of four or three radicals to carbon atoms in the α-positions relative to the same five-membered or six-membered ring can favor the formation of η^4- or η^3-complexes of fullerene with transition metals.[145—147]

Now we briefly outline similar results obtained for both C_{60} and C_{70} fullerenes and some bowl-shaped hydrocarbon fullerene precursors, which appeared to be convenient models for analyzing the nature of chemical bonding between fullerenes and transition metal atoms.

MNDO/PM3 or *ab initio* MO LCAO SCF methods were employed[148—150] to evaluate the stabilities and to calculate the molecular and electronic structures of half-sandwich and sandwich species based on the $C_{20}H_{15}^{\bullet}$ and $C_{60}H_5^{\bullet}$ derivatives of the corannulene $C_{20}H_{10}$ and fullerene (I_h)-C_{60} molecules containing one or two cyclopentadiene fragments, respectively. These were η^5-π-MCpC$_{20}$H$_{15}$, η^5-π-MCpC$_{20}$H$_{15}^+$, η^5-π-MCpC$_{60}$H$_5$, η^5-π-MCpC$_{60}$H$_5^+$, $2\eta^5$-π-M(C$_{20}$H$_{15}$)$_2$, $2\eta^5$-π-M(C$_{60}$H$_5$)$_2$ (M = Si, Ge, Sn, Pb; MNDO/PM3) and η^5-π-C$_{60}$H$_5$XC+p, η^5-π-C$_{60}$XCp$^+$ (X = Fe, Si; *ab initio*, HF, with STO-3G and STO-3-21G basis sets). In these complexes the M and X atoms are η^5-π-coordinated to the five-membered rings (*pent**) of the cyclopentadienyl

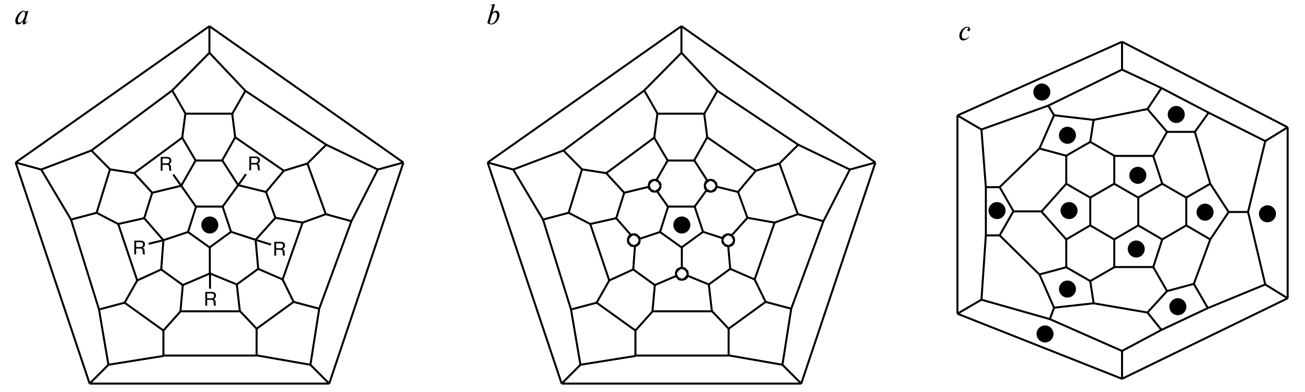


Fig. 13. Three ways of stabilization of η^5-complexes of polyhedral structures with XCp (X = Si, Ge, Sn, Fe, Ru, *etc.*) species (full circles denote the XCp groups): addition of five radicals R to the atoms in α-positions relative to the five-membered ring (*a*); replacement of the atoms in α-positions relative to the five-membered ring (light circles) by heteroatoms (B, N, Si, Ge, *etc.*) (*b*); and an increase in the number of groups XCp (greater extent of involvement of the five-membered rings in the conjugated system of the carbon cage in bonding with XCp species) (*c*).

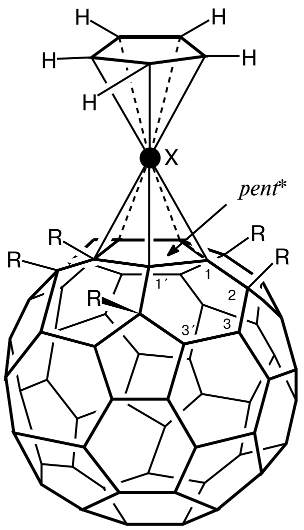


Fig. 14. Structure of complex η^5-FeCpC$_{60}$H$_5$ (fullerene—ferrocene hybrid).

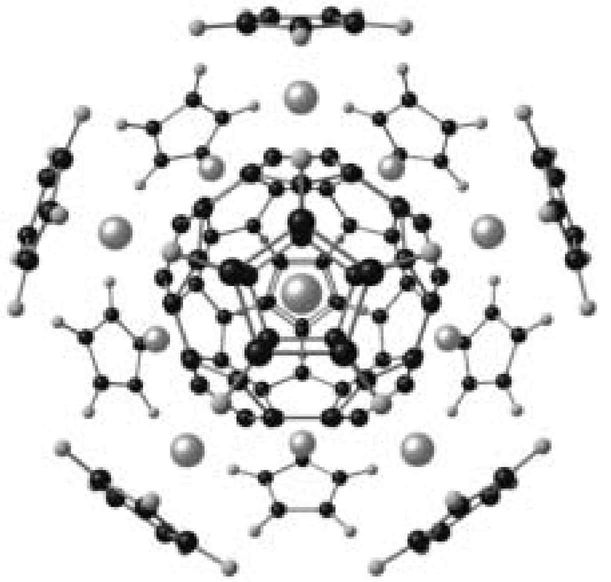


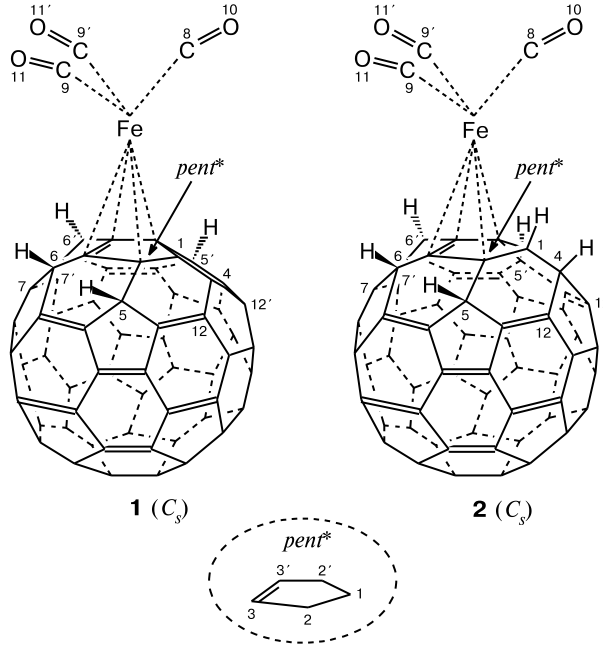
Fig. 15. Structure of "coated" fullerene 12η^5-π-C$_{60}$(MCp)$_{12}$ (M = Fe, Ru, Os).

fragments of the compounds under study. It was theoretically proved that complexes 2η^5-π-M(C$_{60}$H$_{10}$)$_2$ and 2η^5-π-M(C$_{20}$H$_{15}$)$_2$ (M = Si, Ge, Sn, Pb) similar to classical sandwich complexes must be stable, the existence of the complexes containing Si and Ge atoms being the most probable.[151,152]

The molecular and electronic structure of the C$_{60}$H$_5$$^\bullet$ and $^\bullet$H$_5$C$_{60}$H$_5$$^\bullet$ derivatives of C$_{60}$ fullerene was simulated by the DFT-PBE method. The possibility of existence of a "coated" C$_{60}$ fullerene 12η^5-π-C$_{60}$(MCp)$_{12}$ containing twelve MCp (M = Si, Fe, Ru) groups was theoretically proved. In these complexes each MCp species is η^5-π-coordinated to the atoms of a five-membered ring of C$_{60}$ fullerene (Fig. 15). The energies of the M—C$_{60}$ bonds in these compounds are comparable with the energies of the M—Cp bonds in the corresponding sandwich complexes M(Cp)$_2$.[153,154]

The possibility of formation of η^4-π-complexes of C$_{60}$ with a Fe(CO)$_3$ species was analyzed theoretically using the DFT-PBE approach. It was found that attachment of four (or six) hydrogen atoms to C$_{60}$ to give "butadiene"- or "fulvalene"-type derivatives of C$_{60}$ fullerene, respectively (Fig. 16), favors stabilization of η^4-π-complexes of this type of C$_{60}$ derivatives with Fe(CO)$_3$ unit.[155]

DFT-PBE calculations of allyl-type derivatives of C$_{60}$ fullerene and their complexes were performed. It was shown that complexes C$_{60}$R$_3$Co(CO)$_3$ (R = H, F, Cl, Br),



1 (C_s) **2** (C_s)

Fig. 16. Tentative structure of complex η^5-π-$C_{60}Fe(CO)_3$.

$C_{60}H_3NiC_5H_5$, and $C_{60}H_3Fe(CO)C_5H_5$ (in which $C_{60}R_3$ ligands are allyl-type derivatives of C_{60} fullerene) must be rather stable species. Here, the metal atoms are η^3-π-bonded to the fullerene carbon cage. At the same time the metal atoms in the $C_{60}H_3Li$ and $C_{60}H_3FeC_5H_5$ complexes are η^5-bonded to the carbon atoms of C_{60} [147,156] (Fig. 17) (see also Ref. 157).

The local geometry and electronic structure of η^5-fullerene complexes was simulated using not only corannulenes but also other bowl-shaped hydrocarbon precursors of fullerene, *e.g.*, $C_{21}H_9$ and $C_{30}H_{10}$ containing one or more unsaturated five-membered rings. In particular, the effect of the size of the conjugated system on the relative stability of complexes formed by successive attachment of FeCp groups η^5-π-bonded to the carbon cage of the $C_{21}H_8$ radical was studied taking complexes of this radical as examples.[158]

Quantum-chemical calculations of η^5-π-complexes of cyclopentadienyl derivatives of corannulene $C_{20}H_{15}$ with MCp species (M = Fe, Ni, Ru, Co, V) showed that the bowl-shaped hydrocarbon fullerene precursors are convenient for simulation of the local geometry and for stability evaluation of various fullerene *exo*-derivatives.[159,160]

Note that the possibility of existence of (i) polyhapto-bonded fullerene *exo*-complexes with the Fe atom and (ii) *exo*- and *endo*-complexes of C_{60} fullerene with Li atoms was also studied.[161,162]

Fullerenopyrrolidine is a product of a particular case of the Prato reaction (see above). It was synthesized from *N*-methylglycine, C_{60} fullerene, and 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde. Quantum-chemical calculations of this species were carried out[30] and the effective charge distribution, the HOMO and LUMO energies, and the orbital structures determined. Based on analysis of the

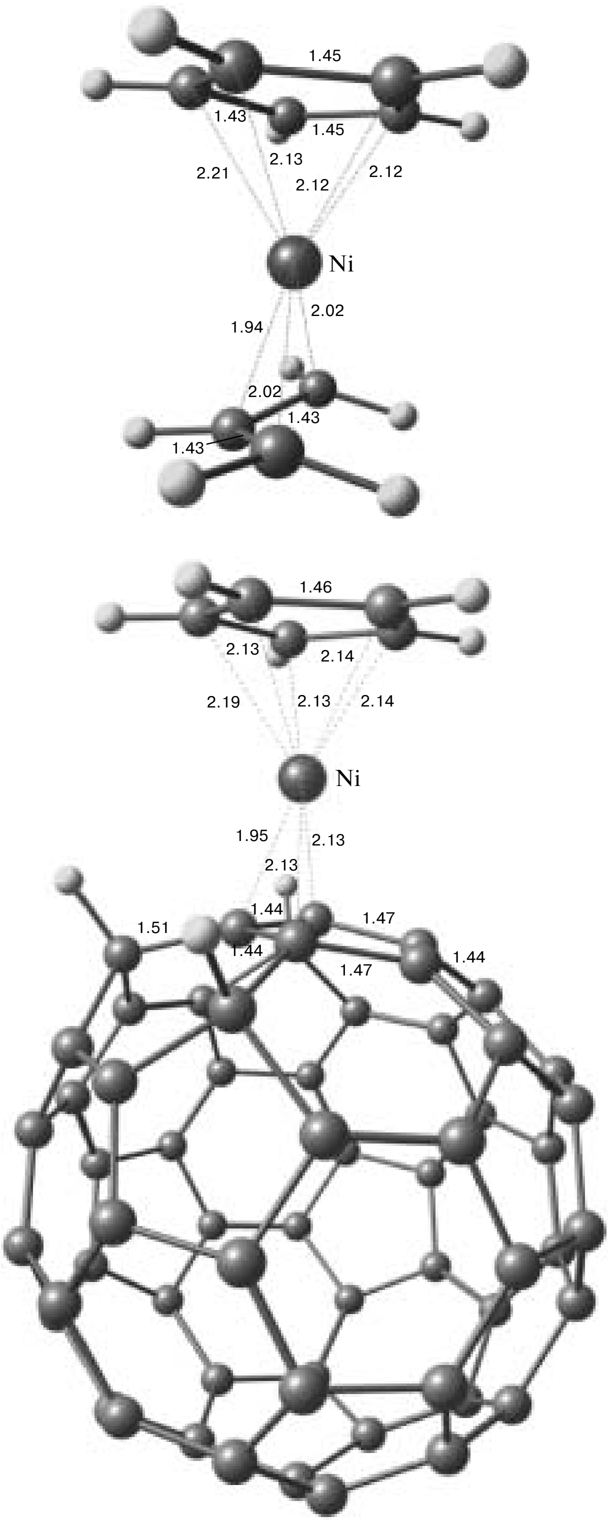
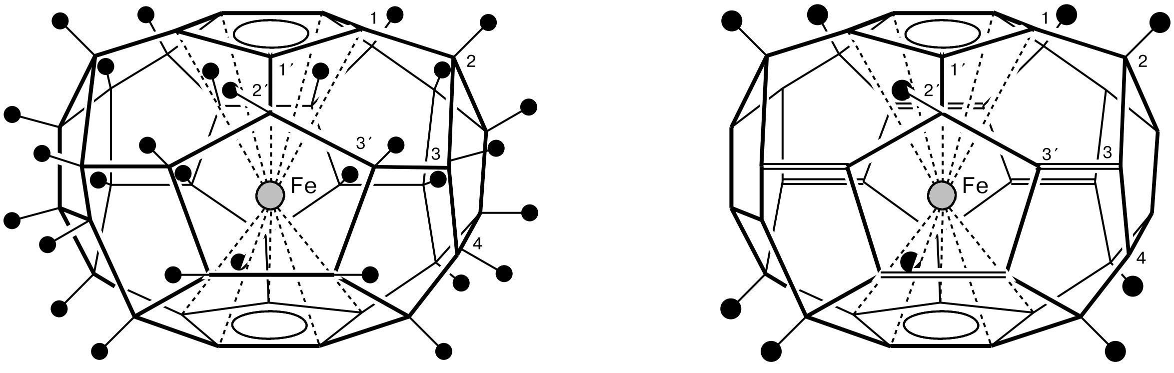


Fig. 17. DFT/PBE calculated of complex η^3-π-C_{60}NiCp.



2η5-Fe@C40H30 2η5-Fe@C40H10

Fig. 18. Endohedral analogs of ferrocene molecule.

ESR data and on the results of quantum-chemical calculations, it was concluded that this compound must be highly reactive in deactivation of various radical species.

The redox properties of mono-substituted *N*-methyl[60]fullerenopyrrolidines were studied using cyclic voltammetry and electrolysis combined with ESR spectroscopy and semiempirical PM3 quantum-chemical calculations.

The polyhedral carbon cage structures of methanofullerenes $C_{61}X_2$ (X = H, COOEt, and some other radicals) were analyzed by the *ab initio* Hartree—Fock and semiempirical PM3 methods.[163] Particular attention was paid to analysis of the character of changes in the bond lengths depending on the electronegativities of addends.

4. Endofullerenes. This class of compounds is of particular interest for the development of the theory of chemical bonding, because these are unique molecules with the topological type of bonding: usually, the encapsulated atom is not bonded to the cage. In addition, endofullerenes can also be useful from the practical viewpoint as, *e.g.*, potential magnetics.[164] It should be noted that pioneering quantum-chemical calculations of endohedral fullerene complexes were carried out at the INEOS for $M@C_{24}$ (M = Li, Na) systems.[165]

Density functional PBE calculations were employed to calculate[78] a number of endohedral complexes of higher fullerenes, namely, $Sc@C_{78}$, $Y@C_{78}$, $Y_2@C_{78}$, *etc.* The relative stability of endohedral derivatives of the C_{76}, C_{74}, and C_{72} fullerenes was studied. Analysis of the results obtained in calculations of neutral and charged forms of some higher fullerenes and their endohedral complexes suggested that the carbon cage makes the major contribution to the electron affinity of endohedral complexes.

The possibility of existence of endohedral analogs of the ferrocene molecule in which the metal (iron) atom is encapsulated into the carbon cage and chemically bonded to it was studied.[166] Complexes (D_{5d})-2η^5-π-$Fe@C_{40}H_{30}$ and (D_{5d})-2η^5-π-$Fe@C_{40}H_{10}$ were shown to be stable (Fig. 18).

The possibility for endohedral polyhapto-complexes of C_{60} fullerene with iron and chromium atoms to exist was considered taking $M_n@C_{60}$ complexes and their *exo*-analogs as examples.[167,168] Conclusions about the relative stability of this type of systems and the geometries of the species under study were based on the results of the MM^+ and modified INDO calculations.

The molecular and electronic structures of endohedral fullerenes $X@C_n$ (X = He, Ne, Ar; *n* = 20, 24, 30, 32, 40, 50, 60) were reported.[169,170] Based on the results of B3LYP/6-3-11G* calculations, it was concluded that the encapsulated atoms in these systems are located at the centers of the carbon polyhedra and have a little effect on the cage structures.

Conclusion

Russian researchers are involved in studies on most of topical avenues in fullerene chemistry. However, the efficiency of their investigations is markedly lowered by the lack of modern equipment, especially, HPLC instruments. This makes separation of chemically similar compounds, to say nothing of isomers a hard to solve problem. Another type of precision equipment, *e.g.*, MALDI TOF and ESI mass spectrometers are also often unavailable. Unfortunately, so important branch of synthetic chemistry as organic synthesis is developed inadequately. Research on azafullerenes and high-hapticity metal complexes (analogs of ferrocene and bis(benzene)chromium) marks time. Only a few studies on fullerene-containing polymers have been reported. The synthesis of endometallofullerenes is still a stubborn problem. Finding fields of practical application of fullerenes requires intensive development of methods for the synthesis of fullerene derivatives and effective interdisciplinary research collaboration, first of all with specialists in materials science, electrochemistry, polymers, and medicine.

The authors express their gratitude to R. N. Lyubovskaya, Yu. N. Novikov, A. L. Chistyakov, and E. B. Yagubskii for kindly submission of materials.

The work was financially supported by the Russian Federation Ministry of Science and Education, Russian Foundation for Basic Research (Project Nos 01-03-07005 and 03-03-32695), Presidium of the Russian Academy of Sciences in the framework of the Research Program "Low-Dimensional Quantum Structures", and the Chemistry and Materials Science Branch of the Russian Academy of Sciences.

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Received March 30, *2004*