

Influence of vacuum annealing on concentration of radicals in fullerite, intercalated with molecular oxygen, $(O_2)_x C_{60}$

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We have developed a technique of low temperature intercalation of molecular oxygen into a lattice of fullerite [1]. Molecular oxygen is in singlet state in a lattice of C_{60} and it is not shown in EPR spectrum in any way. Products of thermal decomposition of $(O_2)_x C_{60}$ in vacuum were investigated by EPR spectroscopy. It has been established, that singlet oxygen and C_{60} molecule interaction begins at temperature of about 200°C, that give rise to growth of intensity of EPR signal with $g = 2.0024$.

Table 1. Parameters of EPR signal for investigated samples (30 mg).

Sample	Temperature, \tilde{N}	Peak FWHM, mT	Intensity, $1.4 \cdot 10^{16}$ spin/g	g-factor
purchased fullerite	20	0.10	1.9	2.0025
	150	0.10	1.6	2.0025
	300	0.10	1.1	2.0026
	450	-	less 0.3	
fullerite, intercalated with Ar	20	0.10	0.03	2.0024
	100	0.15	1.3	2.0024
	200	0.14	1.1	2.0024
	300	-	less 0.3	-
	450	-	less 0.3	-
fullerite, intercalated with O_2	20	0.14	2.3	2.0023
	100	0.14	3.0	2.0023
	200	0.24	885	2.0024
	300	0.26	935	2.0024
	450	0.26	385	2.0025

Heating of purchased fullerite in vacuum reduces intensity of EPR signal. For sample, intercalated with Ar, signal's intensity is less, than that for purchased fullerite, and dependence of intensity on heating temperature passes through the maximum at 100° \tilde{N} . The intensity of signal for sample intercalated with O_2 is always higher than such intensity for samples 1 and 2. However, the intensity grows with increase in heating temperature and, hence, with decrease of the oxygen contents in a sample.

Thus, not concentration of oxygen in a sample, but products of oxygen interaction with fullerene determine the intensity of EPR signal. One of the ways to start reaction of interaction of the introduced oxygen with fullerene is heating.

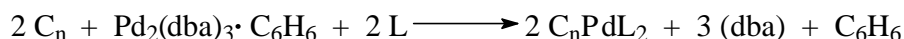
- [1] Y.M. Shulga, V.M. Martynenko, A.F. Shestakov, S.A. Baskakov, A.V. Kulikov, V.N. Vasilets, T.L. Makarova, Y.G. Morozov, *Izv. AN, Ser. khim.*, N 4, 662 (2006).

Synthesis, structure and optical properties of the chiral metal-fullerene C₆₀ and C₇₀ complexes with the optically active ligand (?) -BITIANP

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Over the past decade, considerable progress has been made in the field of η^2 -bonded transition metal complexes with fullerenes. In this work palladium and platinum fullerene complexes with the (-)-2,2'-Bis(diphenylphosphino)-3,3'-bibenzo[*b*]thiophene, (?) -BITIANP have been prepared. The exohedral compounds **1** and **2** that involve Pd have been obtained by direct synthesis from the fullerene, the diphosphine ligand, and Pd₂(dba)₃·C₆H₆.



L = (-)-BITIANP

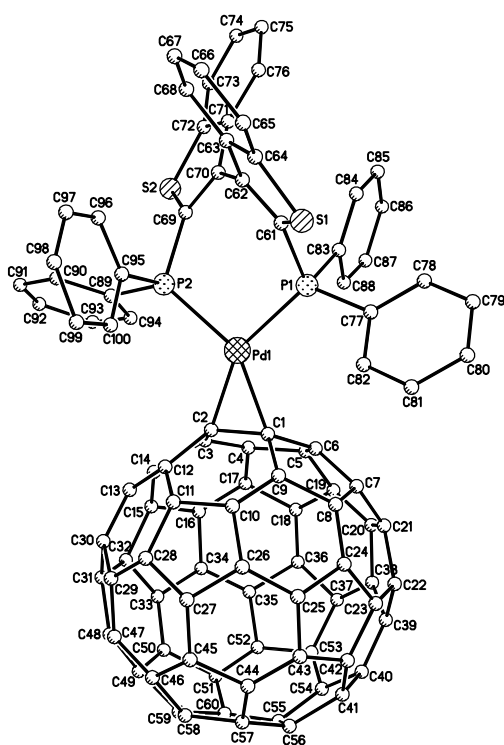
n = 60, **1**; n = 70, **2**

Processes were monitored by ³¹P-{¹H} NMR spectroscopy.

The complexes (η^2 -C₆₀)Pd[(?) -BITIANP], **1**, and (η^2 -C₇₀)Pd[(?) -BITIANP], **2** were isolated as crystalline solids using slow crystallization from toluene and characterized by elemental analysis. Single crystals of **1** were grown and analyzed by X-ray crystallography. Platinum fullerene compound (η^2 -C₆₀)Pt[(?) -BITIANP], **3**, was prepared by exchanging the triphenylphosphine ligand in (η^2 -C₆₀)Pt(PPh₃)₂ for (?) -BITIANP. The obtained complexes **1-3** were characterized by electronic absorption spectroscopy. The (?) -BITIANP is an example of a new class of chiral (C₂) atropisomeric diphosphines characterized by two interconnected five-membered heteroaromatic rings, with hindered rotation around the interanular bond. Circular dichroism spectra were measured in o-dichlorobenzene for compounds **1-3**, and several Cotton effects found which could be attributed to the electronic transitions in the fullerene core.

These compounds **1** and **2** can be useful as the molecular materials for asymmetric homogeneous catalysis.

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New superhard materials on the basis of nanocrystal forms of carbon

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There are various known methods for producing superhard materials (SHM) - synthetic diamonds and cubic boron nitride (cBN). Catalysis synthesis under high pressure - high temperature (HP-HT) conditions, shock wave synthesis and chemical vapor deposition are the main methods for synthesis of SHM.

The idea of the work is the application of nanodiamond and/or carbon nanotubes/nanofibers (NT/NF) for the synthesis of SHM at the HP-HT conditions.

The approach employed was exceptionally fruitful. It is established that hexagonal forms of carbon (graphite) and hexagonal boron nitride (hBN) interact with the nanodiamond and/or NT/NF, therefore there is a transition hexagonal phase into cubic modifications. The synthesis began at temperature 800-1100°N, that it is much less, than at usual synthesis. One of disadvantage in the traditional methods it is big dispersive of particles in the size. In this case the synthesized SHM particles have approximately identical sizes, which strongly depend on parameters of synthesis. Such approach provides great opportunities for creating less expensive production of submicron powders SHM with the strongly determined sizes of particles.

Authors carry out works [1-17] on creation of a complex composite superhard materials “nanodiamond and/or NT/NF- graphite and/or hBN - diamond and/or nBN”.

Such approach in combination with the well known methods provides great opportunities for creating new classes of the less expensive SHM materials with the best properties or less expensive production of the known materials.

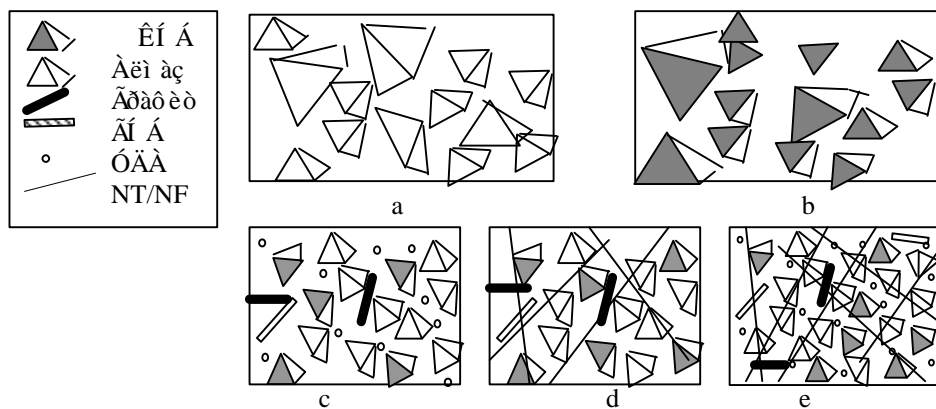


Fig.1. Old (a, b) and new (c, d, e) SHM materials: (ñ) composite SHM materials “nano-diamond- graphite- diamond-hBN- nBN”; a) b) d) composite superhard materials “NT/NF- graphite- diamond- hBN - nBN”; e) composite superhard materials “nano-diamond - NT/NF- graphite- diamond-hBN - nBN”.

- [1] V.V. Filipov, Timoshpolskij V.I., Starchenko I. M et al. Patent ÐÁ. ÁÓ 624. 2002.09.30; 2). Starchenko I.M. et al. Patent RB. U508 2002.03.30; 3). Starchenko I.M. et al. Patent RB U 461. 2002.03.30; 4). Starchenko I.M. et al. Patent RB. U531 2002.06.30; 5). Starchenko I.M. et al. Patent RF 27000 , 2001. 12. 13 ; 6). Starchenko I.M. et al. Patent RF 26999, 2001. 12. 13; 7). Starchenko I.M. et al. Patent RF 27001, 2001.12.13; 8). Starchenko I.M. et al. Patent RB 2187 2005. 7.15; 9). Starchenko I.M. et al. Patent RB 2189 2005. 7.10; 10). Starchenko I.M. et al. Patent RB 2188 2005. 7.15; 11). Starchenko I.M. et al. Patent RB 2484 2005. 7.19; 12). Starchenko I.M. et al. Patent RB 2486 2005. 7.19; 13). Starchenko I.M. et al. Patent RB 2485 2005. 7.19; 14). Starchenko I.M. Patent RB 2566 2005. 8.04; 15). Starchenko I.M. et al. Patent RB 2588 2005. 6.23; 16). Starchenko I.M. et al. Patent RB 2642 2005. 6.23; 17). Starchenko I.M. Patent EA 006011 2002. 4.18.

Interaction of palladium with C₆₀: polymerization and nanoparticles

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Palladium fulleride has been known for a relatively long time. Two and three-dimensional polymeric structures were proposed for Pd_xC₆₀ already in early studies but the exact nature of these polymers remains unclear. For this study palladium fullerides were obtained using reaction of C₆₀ with Pd (DBA) in inert gas and on air. The samples synthesized using various initial Pd:C₆₀ ratios were characterized by XRD, Raman spectroscopy and TEM. The samples were found to be nearly amorphous from XRD with only some broad reflections detected. For Pd_xC₆₀ samples with initial load of reagent corresponding to X=2 and higher, formation of metallic palladium particles was observed. Raman spectra of Pd_xC₆₀ samples showed some close similarity to spectra of C₆₀ polymers obtained at high pressure high temperature conditions. The Raman spectra suggest the formation of chain-like and two-dimensional polymeric structures in Pd_xC₆₀ of various compositions. It is confirmed that Pd_xC₆₀ can be decomposed into pristine C₆₀ and metallic palladium upon heat treatment at moderate temperatures. Thermal decomposition of Pd_xC₆₀ results in the formation of fine 5-10 nm size nanoparticles which can be used for catalytic applications.

Small-angle neutron scattering study of C₆₀/CS₂ solutions

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In recent time, a big interest in fullerene solutions in various organic and non-organic solvents [1,2] has been observed. It is connected with promising medical and biological applications, as well as the procedure of fullerene production. A number of interesting properties of fullerene solutions, like anomalous temperature dependence of C₆₀ solubility [2] or solvatochromism, have been discovered.

In many different solutions fullerenes tend to form clusters. Clusters of C₆₀ have been experimentally observed in non-polar solvents (e.g. benzene, toluene, carbon disulfide), in nitrogen-containing solvents (e.g. pyridine, NMP), fullerene colloids have been detected in water solutions of C₆₀. A phenomenological liquid drop model for fullerene clusters in solutions has been proposed recently [2].

Fullerene solutions in carbon disulfide (CS₂) have been a subject for research since 1993 [3], when for the first time small-angle neutron scattering (SANS) has been successfully applied to C₆₀ solutions. The measured value of radius of gyration R_g of a particle in C₆₀/CS₂ solution is ~15% higher than the calculated R_g for a single C₆₀ molecule in carbon disulfide. At the same time, recent TEM studies of C₆₀/CS₂ [4] have registered formation of large clusters.

In this work, a small-angle neutron scattering study of C₆₀/CS₂ solution is presented. By covering a larger q -range than previous SANS experiments, we investigate cluster state of C₆₀ in the solution and its dependence on the preparation procedure. The effect of larger R_g value is discussed. The proposed descriptions of the effect by C₆₀•[24CS₂] solvate formation, excluded volume effect or the effect of small clusters are considered with respect to the experimental results.

- [1] R.S. Ruoff, D.S. Tse, R. Malhotra et al., *J. Phys. Chem.* **97**, 3379 (1993).
- [2] V.N. Bezmel'nitsyn, A.B. Eletski, M.V. Okun, *Usp. Fiz. Nauk* **168**, 1195 (1998)
- [3] K.A. Affholter, S.J. Henderson, G.D. Wignall et al., *J. Chem. Phys.* **99**, 9224 (1993)
- [4] Alok D. Bokare, A. Patnaik, *J. Chem. Phys.* **119**(8), 4529 (2003).

The first fully regio- and stereoselective [2+3]cycloadditions of azomethine ylides to [70]fullerene

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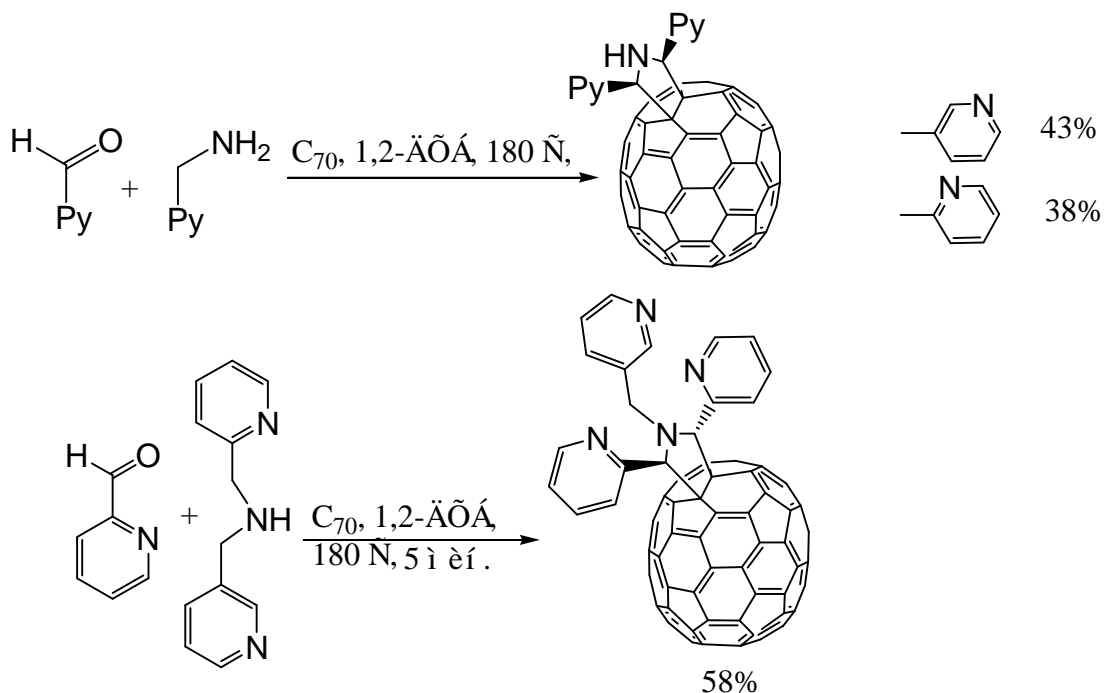
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We have reported recently a new facile method for derivatization of [60]fullerene using picolylamines as reagents for azomethine ylide generation in [2+3]cycloaddition reactions to C₆₀ [1].

In this work we applied this reaction to [70]fullerene and succeeded in preparation and isolation of pure *cis*-2',5'-disubstituted and *trans*-1',2',5'-trisubstituted pyrrolidinofullerenes with moderate to high yields (35-60%). The addition of organic addends occurred only across the most reactive 16, 35-double bond (or 1,2-double bond according to old nomenclature).

Thus, all studied reactions yielded one isomerically pure product while conventional Prato reaction usually gives 6-7 isomeric compounds under the same conditions.



- [1] P.A. Troshin, A.S. Peregudov, D. Muhlbacher, R. N. Lyubovskaya, *Eur. J. Org. Chem.* **14**, 3064-3074 (2005).

Facile derivatization of C₆₀ in Pb(OAc)₄-promoted reactions

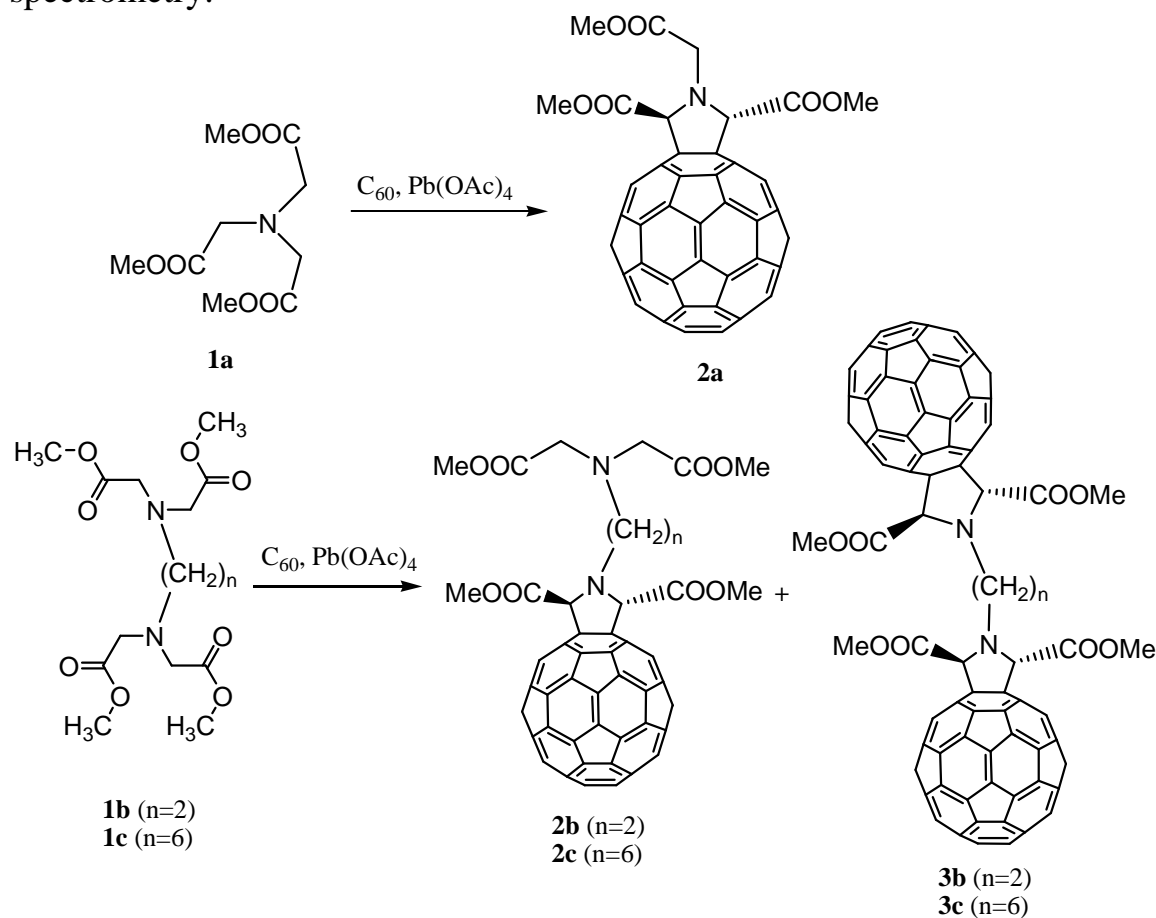
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A family of pyrrolidinofullerenes bearing 3-4 ester functions was easily prepared starting from C₆₀, Pb(OAc)₄ and methyl esters of nityltriacetic, ethylenediaminetetraacetic, and hexamethylenediaminetetraacetic acids. The obtained fullerene derivatives were converted to corresponding water-soluble polycarboxylic acids that can serve as efficient antiviral agents and neuroprotectors *in vivo*.

It was shown that Pb(OAc)₄ promotes also reactions of fullerenes with N-substituted piperazines. In this case, unusual compounds were obtained. They have two nitrogen-containing cycles fused together on the fullerene sphere. These structures were proved by 1D and 2D NMR spectra and mass spectrometry.



Isolation and characterisation of $C_{70}[NR_2]_2O$: the first C_{70} intramolecular ethers bearing two amine groups

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We have reported recently a facile route for preparation of aminated derivatives of [60]fullerene that can be easily converted to water-soluble compounds [1].

In this work we investigated for the first time a photochemical reaction of [70]fullerene with N-substituted piperazines [2]. Compounds possessing composition $C_{70}[NR_2]_2O$ were isolated as major products and fully characterized spectroscopically. These diaminofullerenes have remarkable structure: oxygen atom is inserted between two carbons bearing amine addends (figure 1).

Several by-products with higher number of amine groups were also isolated. Their possible structures were considered on the base of 1D and 2D NMR data.

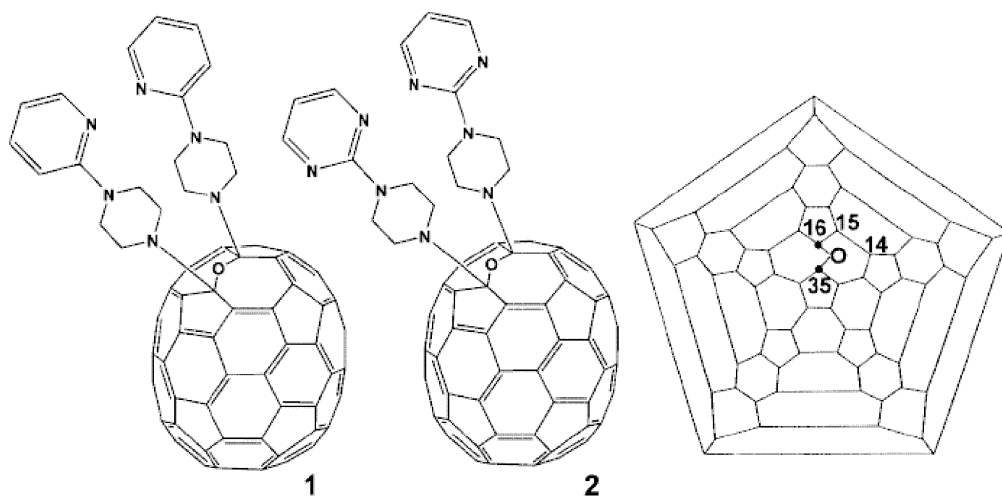


Figure 1. Molecular structures of two isolated diaminofullerenes and a Schlegel diagram illustrating positions of addends

- [1] O.A. Troshina, P.A. Troshin, A.S. Peregudov, V.I. Kozlovskiy, R. N. Lyubovskaya, *Chem. Eur. J.* **12**, 5569-5578 (2006).
- [2] O.A. Troshina, P.A. Troshin, A.S. Peregudov, V.I. Kozlovskiy, R.N. Lyubovskaya, *Eur. J. Org. Chem.* 5243-5248 (2006).

Influence of the metalfragment on the regioselectivity for addition of the radicals CCl_3 and Bu^\dagger to $\text{C}_{60}\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_2$, $\text{C}_{60}\text{Ir}(\text{CO})\text{H}[(+)\text{DIOP}]$, $\text{C}_{60}\text{Os}(\text{CO})(\text{PPh}_3)_2(\text{CNBu}^\dagger)$ and on the stability of the spin-adducts

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It is known that in methano- or in pyrrolidino[60]fullerenes regioselectivity of the radical addition as well as the stability of the spin-adducts (SA) formed are generally determined by the change of the curvature of the fullerene core as a consequence of the methano- or pyrrolidinofragment addition. In the fullerene metallocomplexes, in addition to this factor, the electronic structure of the metalfragment play also an important role.

In this paper we have bring the results of study the electronic influence of the metalfragment on the regioselectivity for addition of radicals CCl_3 (**R1**) and Bu^\dagger (**R2**), which were generated by the abstraction of the Cl or Br atom from the CCl_4 or from BrBu^\dagger by the $\text{Re}(\text{CO})_5$ radicals, to the complexes $\text{C}_{60}\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_2$ (**I**), $\text{C}_{60}\text{Ir}(\text{CO})\text{H}[(+)\text{DIOP}]$ (**II**), $\text{C}_{60}\text{Os}(\text{CO})(\text{PPh}_3)_2(\text{CNBut})$ (**III**) and on the stability of SA.

It was found that the addition of the radicals **R1** and **R2** to complexes **I-III** unlike methano- and pyrrolidinofullerenes, the ESR spectra exhibit signals from some regioisomers which substantial different by the g-factors. The assignment of the individual signals to definite regioisomers were made. The rate constants for the addition of radicals **R1** and **R2** to carbon atoms of individual bonds in **I-III** were determined using the method of competing reactions.

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Catalytic methods for selective functionalization of [60]fullerene

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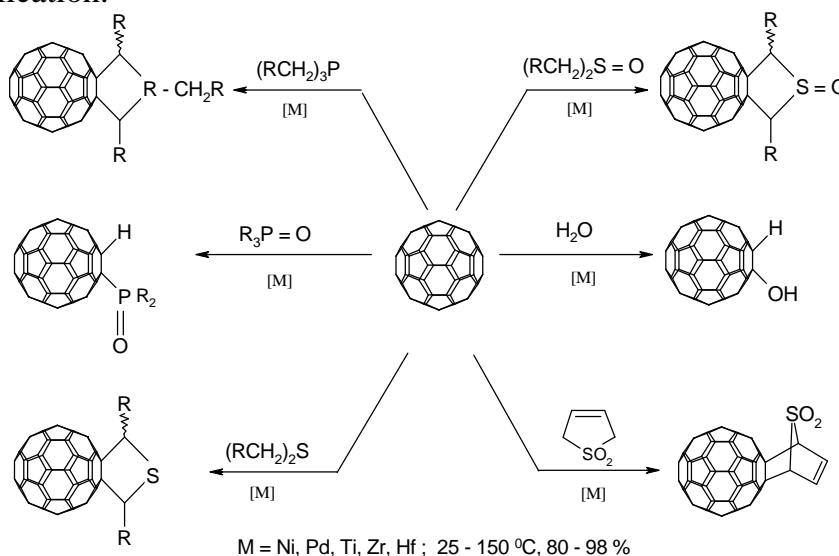
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In the report the new approaches to the selective functionalization of carbon clusters in the presence of catalysts based on Ti, Zr and Hf complexes are presented. This methods are based on discovered by us affinity of metal complex catalysts to activate the subsequent hydrogen transfer from γ -carbon atom associated with heteroatom in various substrates such as cyclic and acyclic amines, esters, thioesters, phosphines, sulfones on fullerene molecule to form fulleroheterocycles. The suggested methods allow to obtain functional substituted fullerenes with high yields and selectivity.

Cycloaddition of tertiary amines, phosphines, ethers, sulfides, sulfoxides and sulfones to [60]fullerene assisted by catalysts based on Ni, Pd, Ti, Zr or Hf complexes was stated to produce fulleropyrrolidines, fullerophospholanes, fullerotetrahydrofuranes, fullerotetrahydrothiofenes, fullerotetrahydrothiofen-1-ones, and others fulleroheterocycles, respectively, in 80-98% yield and with selectivity more than 95%.

Hydroamination, hydrothiolation, hydroalkoxylation and hydrophosphination of fullerene with primary and secondary amines, alcohols and thiols, trialkylphosphine oxides and small molecules (H_2O , NH_3 , H_2S) in the presence metal complex catalysts have been carried out.

High outputs of fulleroheterocycles, availability of initial reagents and simplicity of the realization of these reactions make the methods indicated promising for the practical application.



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The search of new routs of C₆₀F₁₈ fluoride formation

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The goal of the work was the search of new reactions of C₆₀F₁₈ formation within the two known methods of fullerite C₆₀(s) selective fluorination: solid-phase reaction with using binary or complex inorganic fluorides as fluorination reagents and fluorination C₆₀(s) by molecular fluorine in matrices.

For solid-phase fluorination hexafluoronickelat (III) of potassium, K₃NiF₆, was used. The choice of this reagent was based on the data of K₂NiF₆(s) thermal decomposition, which occurs with atomic fluorine evolution in two steps. During the first low-temperature step (550–700K) K₃NiF₆(s) is formed, and then under high temperatures 750–850K (second step) this product dissociates. It was assumed that the solid-phase reaction {C₆₀ + K₃NiF₆} will be occurred under rather high temperatures sufficient for distillation of C₆₀F₁₈ fluoride from mixture of fluorination products.

The fluorination of fullerite by molecular fluorine was done in combined matrix {2KF + Pt(sponge)}. The choice of this matrix was based on C₆₀F₁₈ formation in solid-phase fluorination of fullerite by hexafluoroplatinat (IV) of potassium, K₂PtF₆. The concentration of fullerite in initial mixtures of C₆₀ and matrix was not more than 5-7% mol. The temperature of fluorination was varied in interval 700–750K.

Reactions of fluorination were occurred *in situ* in mass-spectrometer. The ion source was specially reequipped for fluorine inlet. Under these conditions volatile products were fixed directly during fluorination. Besides, fluorination was fulfilled in special setup with flow type reactor to search of conditions for obtaining of preparative quantities of product.

Mixtures of products were analyzed by high efficiency liquid chromatography and mass-spectrometry under electron impact ionization and matrix assistant laser desorption ionization (MALDI). Besides the main product C₆₀F₁₈, trifluoromethyl derivatives were found under fluorination of fullerite by molecular fluorine in combined matrix {2KF + Pt(sponge)}. This result is rather unusual because earlier CF₃-derivatives were fixed only in mixtures of products of solid-phase fluorination.

- [1] N.S. Chilingarov, A.V. Nikitin, J.V. Rau, I.V. Golyshevsky, A.V. Kepman, F.M. Spiridonov, L.N. Sidorov, *J. of Fluorine Chemistry* **113**, 219 (2002).