

RECENT ACHIEVEMENTS IN CHEMISTRY OF NANOCARBON AND RELATED SPECIES INCLUDING THE NEW PREPARATION OF PALLADIUM CATALYSTS

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Abstract. The description of the whole scheme of the nanocarbon particles is done. The similarity and differences in fullerenes and nanotubes are stressed. The novel method of preparing Pd catalysts for organic reactions is introduced which is also applicable to inorganic substrates such as based on magnetite or tungsten-disulfide nanotubes. The catalysts are active in the cross-coupling reactions. Then we were able to combine studies of fullerenes and cyclopalladation to afford the novel palladium catalyst derived on both fullerene and ferrocene.

Keywords: nanocarbon, fullerenes, palladium heterogeneous catalysts, Suzuki and Heck reactions, novel and universal method for preparing Pd catalysts using stable Pd_2dba_3 complex, nanotubes based on WS_2 .

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1. Introduction

After the prediction of stability of C_{60} (Osawa, 1970; Bochvar & Gal'pern, 1973) this molecule had been unambiguously identified (Kroto *et al.*, 1985), and appeared to be the first one in the family called *fullerenes*. Moreover, fullerenes themselves were only a part of the broad realm of different forms of carbon, Fig.1. All of them, excluding fullerenes, the single molecular form, have been polymeric, extended species like historically known diamond or graphite.

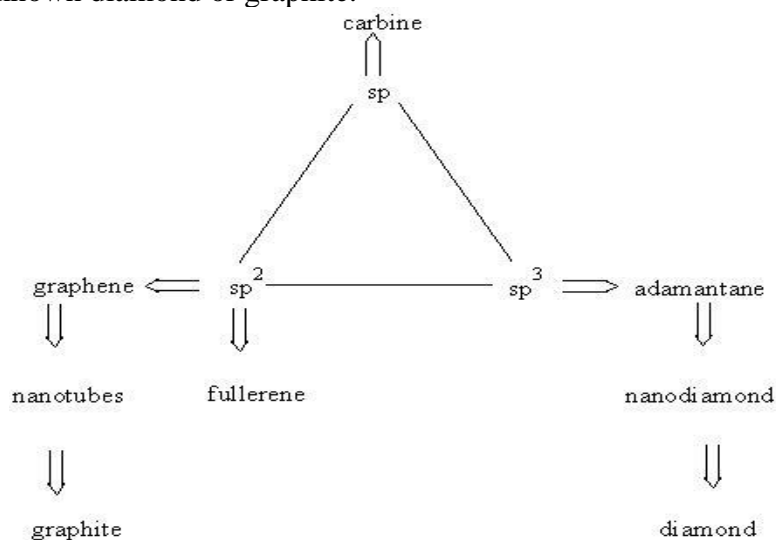


Figure 1. General scheme of (nano)carbon particles with their interactions.

The very important of carbon forms are nanocarbon tubes having the free cylindrical inner part and the strained double bonds like in fullerenes, comparison of these forms is given in Table 1. To make the introduction shorter, one can refer to the recent paper (Sokolov, 2012).

Table 1. Similarity and difference between fullerenes and carbon nanotubes

Fullerenes	Carbon Nanotubes
Individual molecules	Polymeric
Limited solubility	Insoluble <i>per se</i>
Double bonds are strained	Double bonds are strained
Inner cavity is <i>ellipsoidal</i>	Inner cavity is <i>cylindrical or conical</i>
Capable of <i>irreversible</i> introduction of atoms and small molecules into the inner cavity	Capable of <i>reversible</i> introduction of atoms and small molecules into the inner cavity

2. Strained double bonds as reactive centers in fullerenes and carbon nanotubes

Looking at the structures of fullerenes and carbon nanotubes (CNT), it is easy to see that double bonds in both of them are skewed in the same way. Strain of a double bond makes it more reactive as it is known from organic chemistry. One of the early evidence for this similarity was found experimentally from ESR spectra (Gasnov *et al.*, 2007) of radical-adducts [CpM(CO)₃*] as summarized in Table 2.

Table 2. Comparison of the ESR data for chromium and molybdenum radical-adducts of fullerenes and carbon nanotubes. $T = 295$ K.

	"Cr"		"Mo"	
	g-factor	a(53Cr), G	g-factor	a(95Mo), G
C ₆₀	2.0134	13.25	2.029	18.8
C ₇₀	2.0138	13.25	2.029	18.8
CWNT	1.9929	16.5	2.0008	33.0
	1.9938	15.0	2.0148	38.0
			1.9750	*

*non-observable

The coordination of the fullerene double bond with transition metals has been known from the early study (Fagan *et al.*, 1991; Bashilov *et al.*, 1993) of fullerenes, and the analogy was evident for the similar property of nanotubes.

3. The new synthesis of heterogeneous palladium catalysts fixed on polymer supports

3.1. Palladium catalysts based on the carbon supports

We have chosen for palladation the stable reactant of palladium(0), a complex Pd₂(dba)₃ (Sokolov *et al.*, 2008) with an easily removed ligand *dba*-tris(dibenzylideneacetone)dipalladium. Previously, all authors for preparation of the palladium catalysts on any inorganic sorbent used salts of Pd(II), then reduced metal to

Pd(0) in aqueous solvent, washed out thoroughly and dried. Our procedure is one-step, nanopalladium clusters are formed in benzene or toluene and *dba* is liberated in solution. TEM image of CNT with deposited Pd particles is shown on Fig.2 (microdiffraction of Pd particles is in the insert).

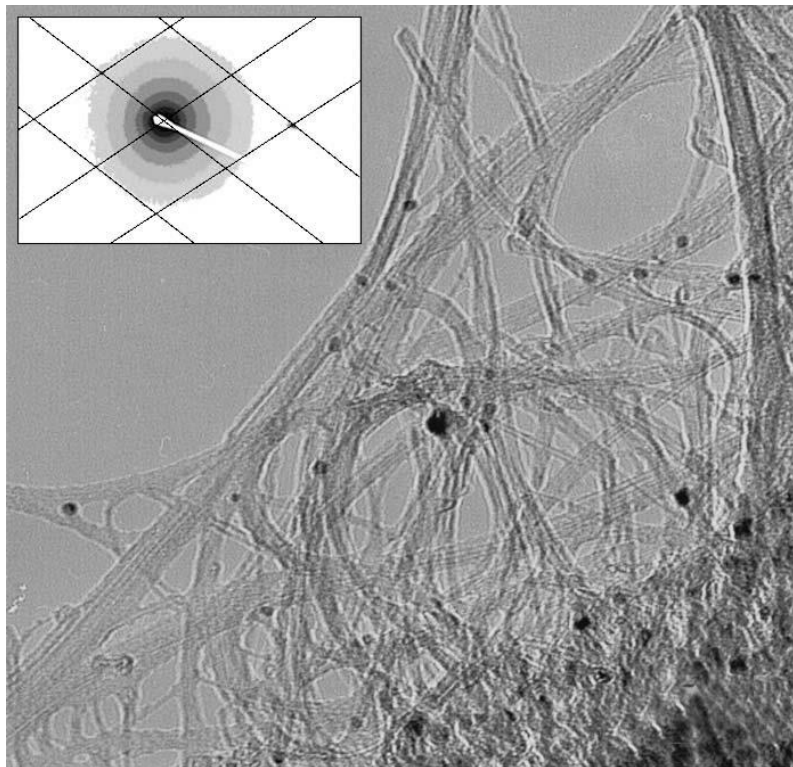


Figure 2. TEM image of CNT with deposited Pd nanoparticles.

Size distribution of Pd particles immobilized on CNT are shown on Figure 3.

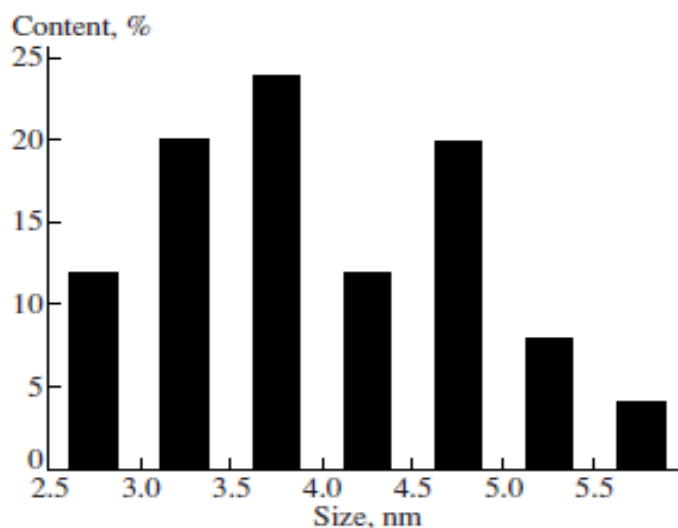
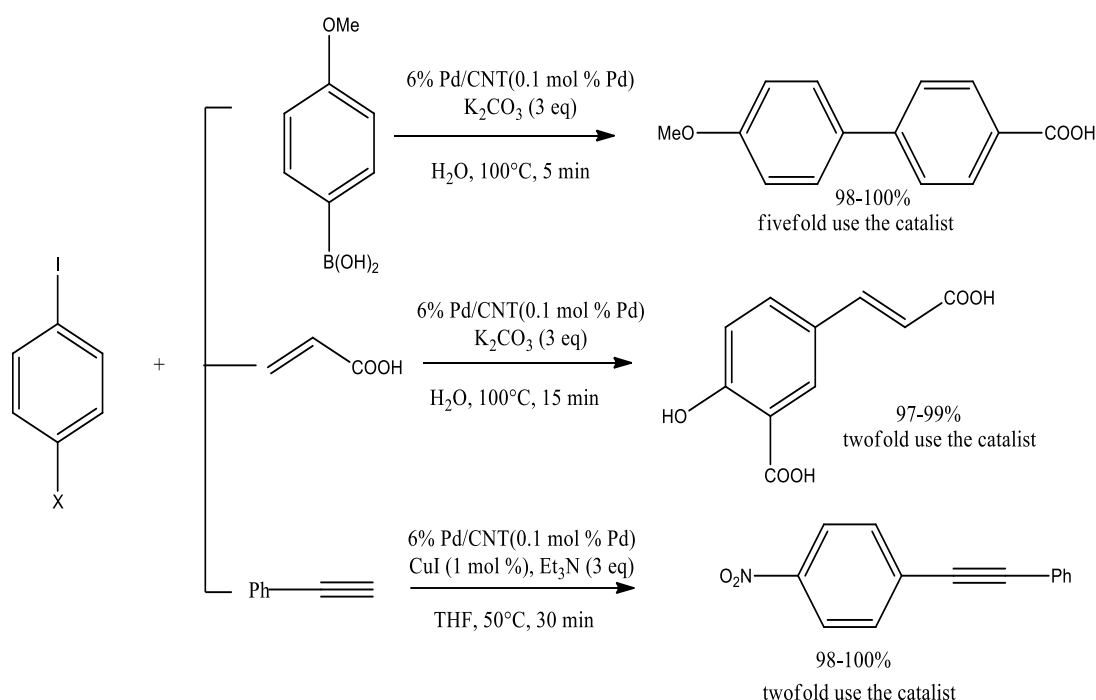


Figure 3. Size distribution of Pd nanoparticles immobilized on CNT.

The typical preparation of the Pd catalyst elaborated for CNT and applicable to other supports as well

27.7 mg (0.047 mmol) of Pd₂(dba)₃ was dissolved in toluene (5 ml). The wine-red solution obtained was filtered through paper filter to remove insoluble particles and magnetically stirred for 30 min. under argon atmosphere at 50 °C in the presence of carbon nanotubes (100 mg). After this, the reaction mixture was cooled to room temperature; black precipitate of Pd/CNT was separated from the straw-colored solution of *dba* by filtering through paper filter, then washed with anhydrous toluene (4 × 20 ml), hexane (4 × 20 ml) and dried. 104 mg of Pd/CNT catalyst containing 6% of palladium was obtained.

This catalyst is very effective in the cross-coupling reactions:



Using nanodiamond (DND) as a carrier to prepare the palladium catalyst, the hydrogenation of the C=C and C≡C bonds of model organic compounds (tolane, unsaturated acid and enamides) was performed (Turova *et al.*, 2011). The activity of the Pd(0)/DND was found to greatly surpass that of palladium loaded on other nanocarbon supports (fullerenes and carbon nanotubes).

The activity of the Pd catalyst supported on graphene shells (Kryukov *et al.*, 2012) is moderate in the Heck reaction (80-100 %) and relatively high in the Suzuki reaction (90%).

To obtain potentially enantioselective catalysts, the single-walled hydroxylated CNT were acylated with optically pure natural α-amino acids followed by palladation with Pd₂(dba)₃. Pd (0) derivatives of L-valine, L-methionine, and L-proline were used as catalysts for the hydrogenation of α-acetamidostyrene, α-phenylcinnamic acid and hydroarylation of norbornene (Abramova *et al.*, 2015). It was detected the high catalytical activity of these catalysts, but all reaction products were racemates. Therefore, the catalysts show no enantioselectivity.

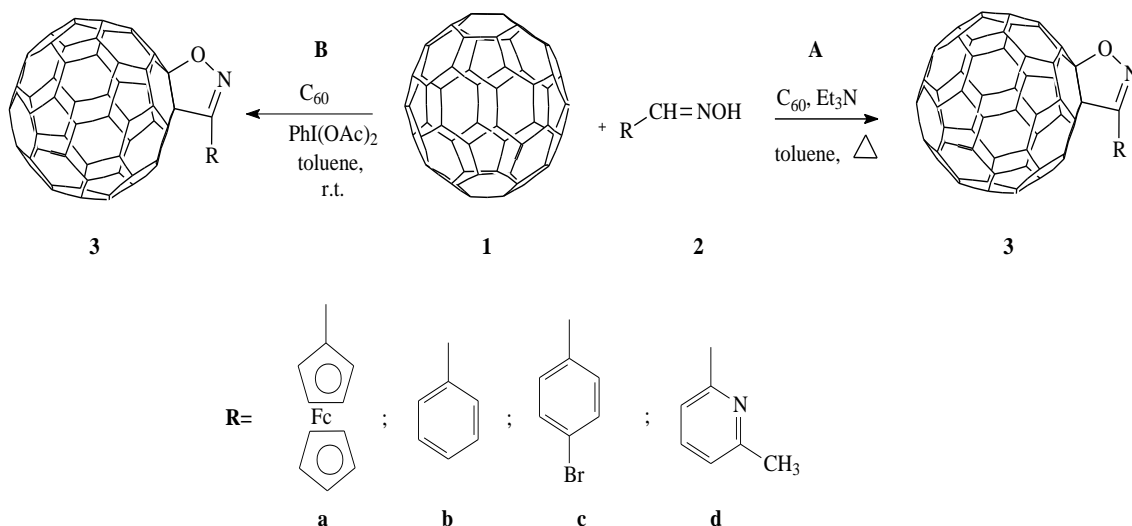
3.2. Palladium catalysts based on the non-carbon supports

The above described straightforward method of using $\text{Pd}_2(\text{dba})_3$ for the Pd nanoclusters formation first suggested for carbon entities appeared to be applicable to the non-carbon objects. Palladium clusters are bonded in different ways. So, insertion into double salts magnetite (LDH)& Fe_3O_4 (Ay *et al.*, 2013) seems to be alike to the reaction with nanodiamonds while the reaction with inorganic nanotubes $(\text{WS}_2)_n$ definitely uses the coordination between sulfur and palladium (Višić *et al.*, 2015). All of them are active catalysts of the Heck and Suzuki processes. Thus, in the case of Pd/(LDH)& Fe_3O_4 products of reactions of cross-coupling were obtained with the yields 100 % (Heck reaction) and 78% (Suzuki reaction). Pd/ $(\text{WS}_2)_n$ gives 91 and 86% respectively. Moreover, the magnetite available as a reagent from Aldrich (Fe_3O_4) is also reacted to $\text{Pd}_2(\text{dba})_3$ to afford the material having Fe (62%) and Pd(2%) which catalyzed Heck reaction in yield close to quantitative and Suzuki reaction about 75% (Sokolov & Abramova, 2015). Probably, the palladium atoms are placed in the defects on crystal lattice.

4. Palladium complexes derived from fullerene derivatives

Among the methods to functionalization fullerenes the most useful is [3+2] cycloaddition (Sidorov *et al.*, 2005). By this way some kinds of condensed heterocycled fullerenes such as fulleropyrrolidines have been synthesized (Prato & Maggini, 1998). In this work, the synthesis of fullerenoisoxazolines has been derived. This structure which contains the nitrogen atom in heterocyclic part and a substituent in position 2 could allow the formation of a palladium 5-membered ring. The following 2-derivatives of fullerenoisoxalidines have been prepared: ferrocenyl, phenyl, 4-bromophenyl, 6-methyl-2-pyridyl.

Earlier was synthesized the ferrocenyfullerenoisoxalidine (Poplawska *et al.*, 2000) but in that paper the conditions were not described in detail. Now we have elaborated the synthesis of fullerenoisoxazolines.



So, at the reaction of oxime **2a** with β -chlorosuccinimide the intermediate nitrilylid is formed, which is condensed with C_{60} in boiling toluene in the inert

atmosphere affords the corresponding cycloadduct **3a**. The product was isolated in pure state after column chromatography on SiO₂, eluent toluene - hexane (1:1), Temp 65°C gave low yield (13%) whereas boiling at 110°C increased the yield to 24%. In the case of aryl oximes the yields of reaction are very small (Table 3).

Table 3. Synthesis of a number of fullerenoisoxazoline derivatives under different conditions.

№	2	R	3	Method A yield [%]	Method B yield [%]
1	2a	Fc	3a	24	-
2	2b	Ph	3b	5	26
3	2c	4-BrPh	3c	10	28
4	2d	6-methyl-2-pyridyl	3d	15	39

Fullerene C₇₀ has three types of nonequivalent bonds "hexagon-hexagon": 1-2, 5-6 and 7-21 (Thilgen *et al.*, 1997), so it can form three possible isomers (Fig. 4). In this case, isomers A and B are mainly formed.

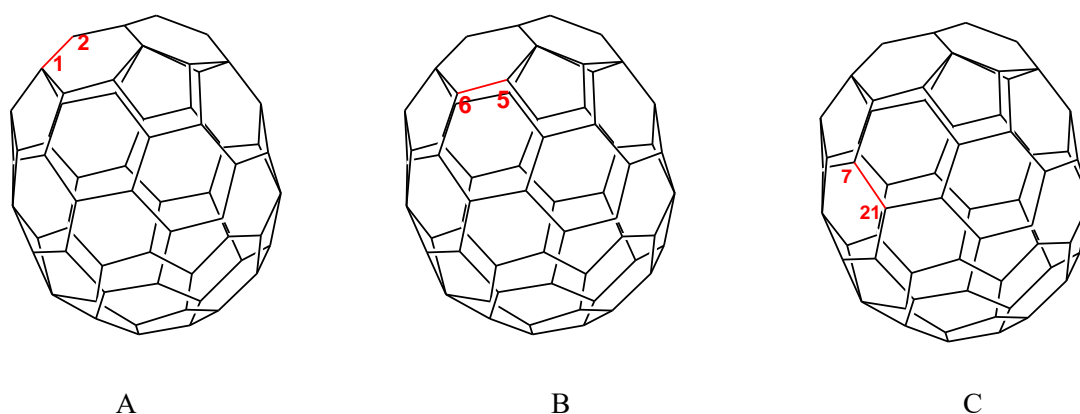


Figure 4. Isomeric A, B, and C products of cycloaddition of C₇₀.

As the result of reaction of ferrocenylalldoxime **2a** with fullerene C₇₀ were obtained all three possible isomers of ferrocenylfullereno[C₇₀]isoxazoline (¹HMR has shown three different Fc protons).

Analysis of that fraction was made by HPLC using UV-detector with a column with inverted phase C18 (Partisil-5 ODS-3), eluent toluene/CH₃CN (3:5 by volume). Per cent content of the isomers was following: 56.98 (A), 32.30 (B), and 1.68 (C), retention time: 8.430, 9.322 and 5.514 min respectively, Fig. 5.

The second method was based on the synthesis of arylfullerenoisoxazolines with (diacetoxy)iodobenzene as oxidant (Yang *et al.*, 2010). Yields of **3b-d** is essentially higher (Table 3), however, the ferrocenyl group did not tolerate that oxidant.

It is known that ferrocenyl group is highly apt to be involved to cyclopalladation reaction (Sokolov, 2018). That is why **3a** seemed to be the best candidate to prepare cyclopalladated derivative in the fullerene series and then apply this in catalysis for making the carbon – carbon bonds.

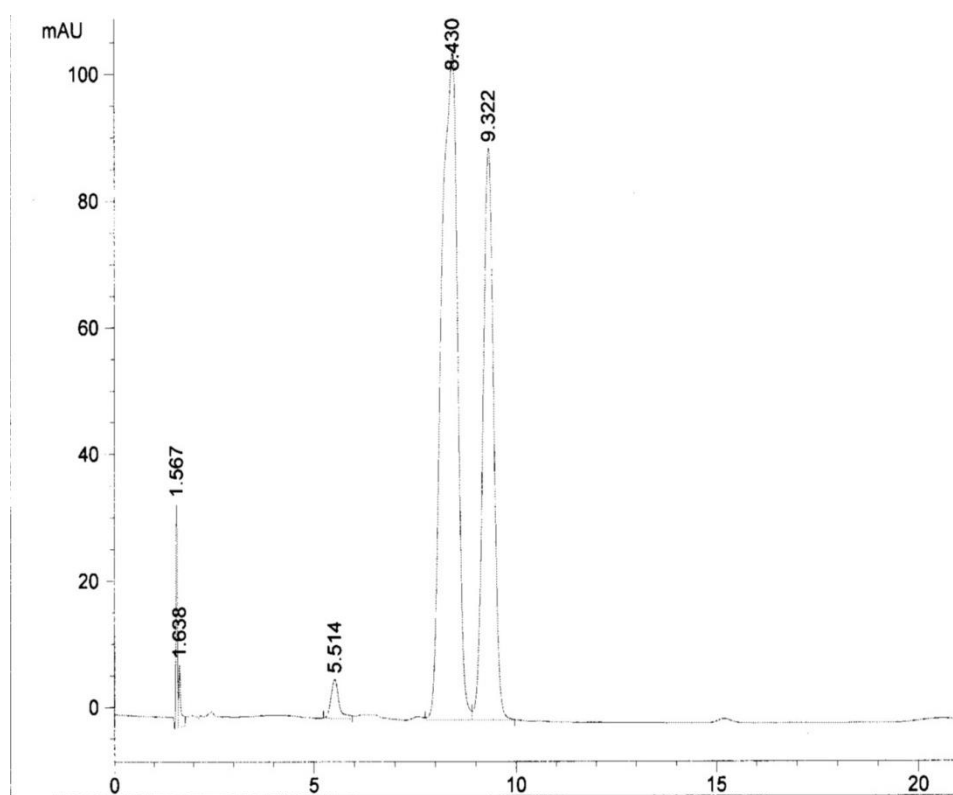
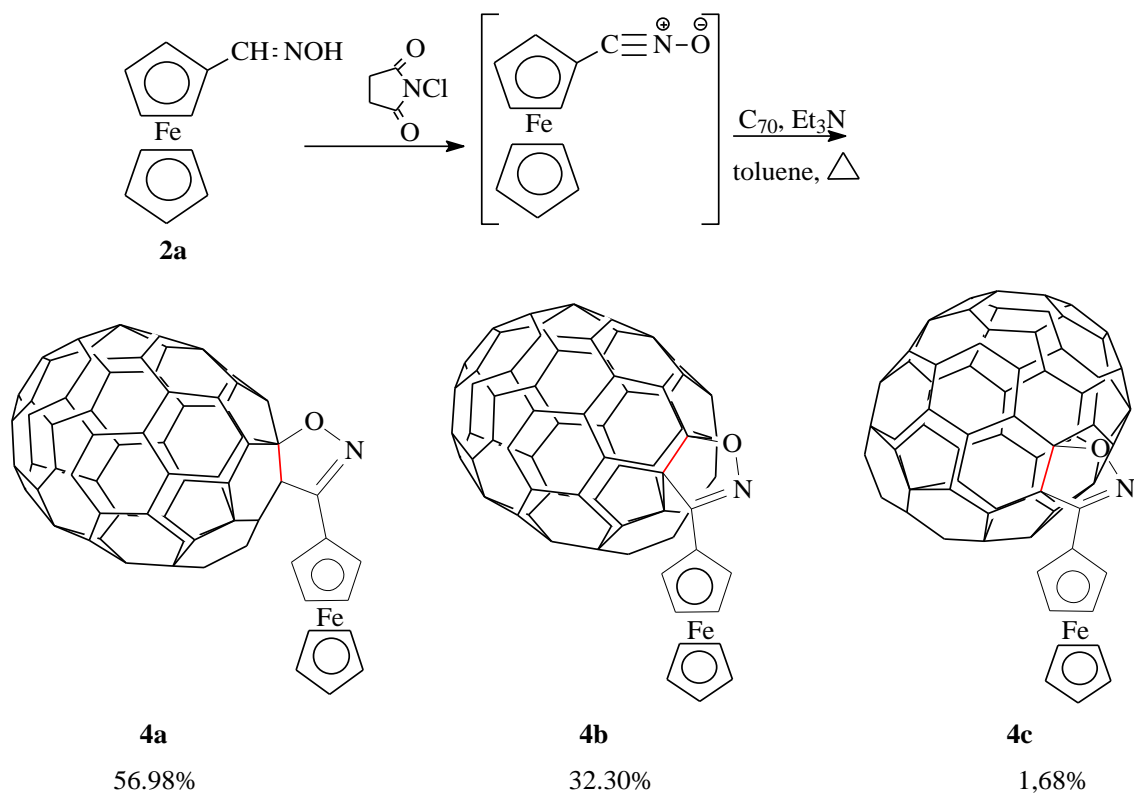
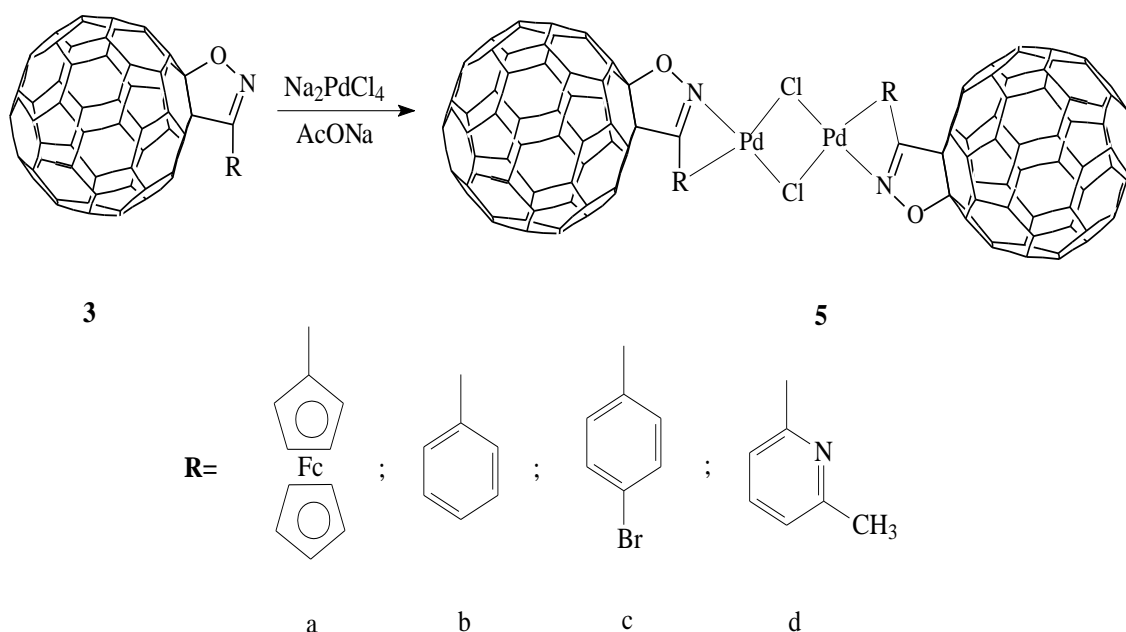


Fig. 5. HPLC data for isomers of ferrocenylfullereno[C_{70}]isoxazoline.

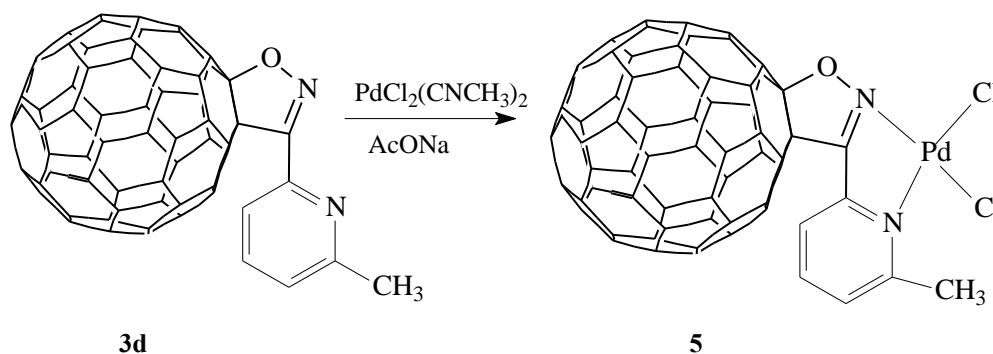
In fact, cyclopalladation of **3** has been carried out by sodium tetrachloropalladate and sodium acetate.



It turned out that only **3a** affords palladium dimer whereas the carbon content in the products from **3b-d** is about 2% and the precipitate isolated is probably Pd black.

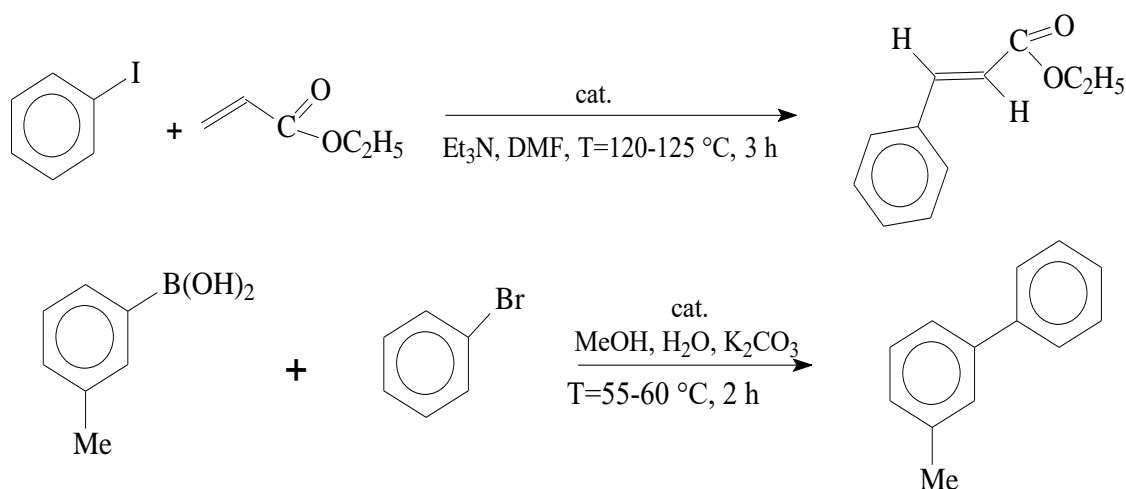
The palladium dimer, di- μ -chloro-bis-[2-ferrocenyl-fullereno[60]isoxazoline]-dipalladium, **5a**, has more complicated composition as supposed. According elemental analysis, it better fits the formula **5a*****6PdCl₂** that could be explained by coordination of palladium with fullereryl double bonds. Attempts to obtain more soluble monomeric derivatives by dissolving **5a** in pyridine-*d*₅ and breakage of the chloride bridges using Na(acac) were completely unsuccessful.

On the other hand, in the case of 6-methyl-2-pyridyl-fullereno[60]isoxazoline, **3d**, the presence of the nitrogen atom in a pyridine group permitting the formation of a 5-membered ring afforded the PdCl₂ complex **6** (see Experimental).



The prepared catalysts were studied in the Suzuki and Heck reactions. Under heterogeneous catalyst **5a** (0.1 mol %) of Heck reaction, namely, cross-coupling of iodobenzene and ethyl acrylate, yield of ethyl-(2E)-3-phenyl acrylate was 98%. Even

after three times of using the conversion was close to 100% according to ^1HMR spectrum. For the pyridine complex **6** yields were 80%.



5. Conclusion

In the last part of this report, we have investigated the possibility to unite the chemistry of fullerenes and organopalladium chemistry to catalyze organic reactions. As it is known from the above text, the only organopalladium fullerenes are direct π -complexes on a double bond of C_{60} or C_{70} . Now we introduced palladium atom into the periphery of a fullerene nucleus. To summarize, we have shown the principal opportunity of the fullereryl palladium derivatives **5a** and **6** as heterogeneous catalysts of the cross-coupling reactions of Heck and Suzuki.

6. Experimental (Sarkisyan, 2017)

6.1. Measurements

NMR ^1H and spectra were obtained using spectrometer «Bruker» 400 HX» (CDCl_3 , internal standard TMS). Mass-spectra of positive ions MALDI were registered on Bruker Autoflex III with nitrogen laser ($\lambda = 337\text{ nm}$), matrix DCNB. The HPLC analysis was performed on Agilent Technologies 1200 Series chromatograph with UV detector using a column with a reversed phase C18 (Partisil-5 ODS-3), eluent toluene/acetonitrile (volumetric ratio 3:5). Determine the percentage of C, H, N were determined by elemental analysis on automatically Vario Micro Cube (Elementar, Germany). Determination of Pd and Fe was performed by x-ray fluorescence method on the VRA-30 (Carl Zeiss Jena; Germany).

6.2. Preparation of the fullerenoisoxazoline derivatives

Method A

To a solution of 0,001 m of oxime **2** in CH_2Cl_2 (30 ml) was added in portions 0,001 m of N-chloro succinimide during 30 min.

In a flask supplied with argon inlet, condenser, and magnetic stirrer was placed 0,0003 m of

fullerene **1** in toluene (250 ml), then added solution of a formed nitroxide and 5 ml of Et₃N.

Reaction was heated on stirring at 110 C and monitored by TLC (Silufol, toluene-hexane 1 : 1). Reaction mixture was evaporated and the product was isolated by column chromatography as described above. Fractions containing the isoxazolines were evaporated, washed out with acetone and dried *in vacuo*.

Method B

In a flask supplied with argon inlet, condenser, and magnetic stirrer was placed 0,0003 m of C₆₀

fullerene **1** in toluene (120 ml), 0.0966 g of diacetyoxyiodobenzene and 0,0003 m of oxime **2**. Further treatment was made as in Method A. Reaction was carried out at room temperature

Ferrocenylfullerenoisoxazoline (3a): received 68,2 mg (yield 24%). ¹H NMR (δ, ppm, CDCl₃): 4,25 (s, 5H, Cp); 4,60 (m, 2H, Cp); 5,28 (m, 2H, Cp). Found (%): C, 88.35; H, 1.29; N, 1.24. C₇₁H₉NOFe. Calc. (%): C, 89.98; H, 0.96; N, 1.48. MALDI-TOF: m/z 947 [M-H]⁺.

Phenylfullerenoisoxazoline (3b): received 63,9 mg (yield 26%). ¹H NMR (δ, ppm, CDCl₃): 7, 58 (m, 3H, Ph); 8,20 (m, 2H, Ph). Found (%): C, 93.36; H, 0.63; N, 1.49. C₆₇H₅NO. Calc. (%): C, 95.83; H, 0.60; N, 1.67.

4-Bromophenylfullerenoisoxazoline (3c): received 76,2 mg (yield 28%). ¹H NMR (δ, ppm, CDCl₃): 7,72 (д, *J* = 8,45 Гц, 2H, Ph), 8,10 (д, *J* = 8,59 Гц, 2H, Ph). Found (%): C, 87.48; H, 0.75; N, 1.34. C₆₇H₄BrNO. Calc. (%): C, 87.60; H, 0.44; N, 1.52.

6-Methyl-2-pyridyl-fullerenoisoxazoline (3d): received 99,8 mg (yield 39%). ¹H NMR (δ, ppm, CDCl₃): 2,40 (s, 3H, CH₃); 7,82 (m, 2H, Py); 8,30 (m, 1H, Py). Found (%): C, 89.43; H, 2.53; N, 2.53. C₆₇H₆N₂O·C₆H₁₄. Calc. (%): C, 93.18; H, 2.14; N, 2.98.

Ferrocenylfullerenof[70]isoxazoline (4):

Isomer **4a**: 56.98%. ¹H NMR (δ, ppm, CDCl₃): 4,14 (s, 5H, Cp); 4,47 (m, 2H, Cp); 5,04 (m, 2H, Cp).

Isomer **4b**: 32.30 %. ¹H NMR (δ, ppm, CDCl₃): 4,42 (s, 5H, Cp); 4,76 (m, 2H, Cp); 5,65 (m, 2H, Cp).

Isomer **4c**: 1.68 %. ¹H NMR (δ, ppm, CDCl₃): 4,07 (s, 5H, Cp); 4,52 (m, 2H, Cp); 5,18 (m, 2H, Cp).

m/z 1068 [M⁺].

Palladation of derivatives of fullerenoisoxazolines

Di-μ-chloro-bis-[2-ferrocenyl-fullerenof[60]isoxazoline]dipalladium (5a):

In a flask, supplied by an argon inlet was prepared the solution of 0.042 mM of **3a** in toluene (150 ml), the same amounts of Na₂PdCl₄ and NaOAc·3H₂O in methanol (30 ml) were added. Reaction mixture has been stirred at room temperature under argon for 3 hr. The dark product was left overnight, then filtered, washed with methanol and dried over P₂O₅. Weight of **5** was 80 mg (86%). Found (%): C, 54,84; H, 0,64; N, 0,55; Fe, 3,8 ± 0,3; Pd, 28,0 ± 2,0. [C₇₁H₈NOFePdCl]₂·6PdCl₂. Calc. (%): C, 52.62; H, 0.50; N, 0.86; Fe, 3.6; Pd, 26.27.

6-Methyl-2-pyridyl-fullerenoisoxazoline-dichloropalladium (6):

In a flask, supplied by an argon inlet was prepared the solution of 0.042 mM of **3d** in toluene (150 ml), the same amounts of PdCl₂(CH₃CN)₂ and NaOAc·3H₂O in

methanol (30 ml) were added. Reaction mixture has been stirred at room temperature under argon for 3 hr. The dark product was left overnight, then filtered, washed with methanol and dried over P₂O₅. Found (%): C, 76.81; H, 1.14; N, 1.52. C₆₇H₆N₂OPdCl₂. Calc. (%): C, 78.34; H, 0.74; N, 1.29; Pd, 9.78.

6.3. Heterogeneous catalysis

Efficacy of the catalysts has been demonstrated on the classical examples for typical representatives of the cross-coupling reactions using arene halides and arylboronic acid (Suzuki) or arene halides and acrylate ester ethyl acrylate (Heck)

Suzuki Reaction. Reaction has been carried out under the same conditions but with different catalysts, **5a** and **6**. In a flask supplied with argon inlet, condenser, and magnetic stirrer was placed bromobenzene (2 mM) and 3-methylphenylboronic acid (3mM) with added K₂CO₃ (4 mM), and warmed at 55 – 60°C for 2 hr. Reaction was monitored by TLC (Silufol, hexane – ethyl acetate 2:1). After the usual work-up the crude product was taken into hexane and poured on thin layer of SiO₂. Finally was obtained 3-methylbiphenyl as 306 mg (91%) with catalyst **5a** or 262 mg (78%) with **6**. ¹H NMR (δ, ppm, CDCl₃): 2.55 (s, 3H, CH₃); 7.29 (m, 1H, Ph); 7.48 (m, 2H, Ph); 7.55 (m, 4H, Ph); 7.70 (m, 2H, Ph).

Heck Reaction. A mixture of iodobenzene (3 mM), ethyl acrylate (7,5 mM), triethylamine (7,5 mM), and dimethylformamide (12 ml) was placed in a three-necked flask and mixed at 120 °C on oil bath for 3 hr. Reaction was catalyzed by palladium derivatives **5a** or **6** (0.15 mol %). After usual workup it was isolated 517 mg (98%) of ethyl-(2E)-3-phenylacrylate (cat. **5a**) or 422 mg (80%) (cat. **6**) of the same product. ¹H NMR (δ, ppm, CDCl₃): 1.35 (t, 3H, CH₃); 4.28 (q, 2H, CH₂); 6.46 (d, 1H, *J*=16.0 Hz, CH=CH); 7.39 (m, 3H, Ph); 7.52 (m, 2H, Ph); 7.71 (d, 1H, *J*=16.0 Hz, CH=CH).

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References

- Abramova, N.V., Turova, O.V., Davidovich, Yu.A. & Sokolov V.I. (2015). Palladium nanocarbon catalysts (Pd/CNT) as potential enantioselective heterogeneous systems. The behavior in the hydrogenation and hydroarylation of unsaturated substrates. *Russ.Chem. Bull. (Int. Ed.)*, 64(1), 216-218.
- Ay, A.N., Abramova, N.V., Konuk, D., Lependina, O.L., Sokolov, V.I. & Zümreoglu-Karan, B. (2013). Magnetically-recoverable Pd-immobilized layered double hydroxide-iron oxide. *Inorg. Chem. Commun.*, 27, 64–68.
- Bashilov, V.V., Petrovskii, P.V., Sokolov, V.I., Lindeman, S.V., Guzey, I.A. & Struchkov, Y.T. (1993). Synthesis, crystal, and molecular structure of the palladium (0) fullerene derivative (h²-C₆₀) Pd(PPh₃)₂. *Organometallics*, 12 (4), 991–992.
- Bochvar, D.A., Gal'pern, E.G. (1973). Carbododecahedron, s-icosahedron, and carbo-s-icosahedron systems. *Dokl. Akad. Nauk SSSR*, 209, 610–612, [*Dokl. Chem. (Engl. Transl)*, 209, 239–241].
- Fagan, P.J., Calabrese, J.C., Malone, B. (1991). The chemical nature of buckminsterfullerene (C₆₀) and the characterization of a platinum derivative, *Science*, 252(5009), 1160-1161.

- Gasanov, R.G., Lobach, A.S., Sokolov, V.I., Demenjev, A.P., Maslakov, K.I. & Obraztsova, E.D. (2007). Organometallic Radical-Adducts of Fullerenes C₆₀, C₇₀ and Single-Walled Carbon Nanotubes Derived from (Cyclopentadienyl)-molybdenumtricarbonyl dimer. *J. Nanoscience and Nanotechnology*, 7(4-5), 1546-1550.
- Kroto, H.W., Curl, R.F. & Smalley, R.E. (1985). C₆₀: buckminsterfullerene, *Nature*, 318, 162–165.
- Kryukov, A.Yu., Davydov, S.Yu., Izvolskii, I.M., Rakov, E.G., Abramova, N.V. & Sokolov, V.I. (2012). Palladium supported on graphene-like carbon: preparation and catalytic properties. *Mendeleev Commun.*, 22, 237-238.
- Osawa, E. (1970). Superaromaticity. *Kagaku*, Kyoto, 25, 854-863.
- Poplawska, M., Byszewski, P., Kowalska, E., Diduszko, R. & Radomska, J. (2000). Preparation and structure of ferrocene derivative C₆₀ adduct. *Synth. Met.*, 109(1-3), 239–244.
- Prato M., Maggini M. (1998). Fulleropyrrolidines: a family of full-fledged fullerene derivatives. *Chem. Res.*, 31(9), 519–526.
- Sarkisyan, K.E. (2017). A.N. Nesmeyanov Institute of Organoelement Compounds RAN, Moscow, Russian Federation. Magister work, Lab. 103.
- Sidorov L.N., Jurovskaja M.A. Borshhevskijj A.Ja., Trushkov, I.V. & Ioffe, I.N. (2005). *Fullerenes*. Moscow, Ehkzamen, 687 (in Russian).
- Sokolov, V.I. (2012). New forms of carbon opening the door to the era of nanochemistry, *Priroda*, 3, 28-33 (in Russian).
- Sokolov, V.I. (2018). Synthesis and Application of N-Cyclopalladated Ferrocene Derivatives. *Chinese Journal of Organic Chemistry*, 38(1), 75-85.
- Sokolov, V.I., Abramova, N.V. (2015). Synthesis of the Efficient Palladium Catalysts for the Cross-coupling Reactions and Hydrogenation by the Direct Loading of Inorganic Supports. 1st International Conference on Chemical Sciences and Technologies, Plenary Lecture, Sarajevo, Bosnia & Herzegovina.
- Sokolov, V.I., Bumagin, N.A., Rakov, E.G., Anoshkin, I.V. & Vinogradov, M.G. (2008). New Synthesis of Palladium Catalyst Immobilized on Carbon Nanotubes and Its Activity in Certain Organic Reactions. *Nanotechnologies in Russia*, 3(9–10), 570–574.
- Thilgen, C., Herrmann, A. & Diederich, F. (1997). The covalent chemistry of higher fullerenes: C₇₀ and beyond. *Angew. Chem. Int. Ed. Engl.*, 36(21), 2268–2280.
- Turova, O.V., Starodubtseva, E.V., Vinogradov, M.G., Sokolov, V.I., Abramova, N.V., Vul, A.Y., Alexenskiy, A.E. (2011). Palladium supported on detonation nanodiamond as a highly effective catalyst of the C=C and C≡C bond hydrogenation. *Catal. Commun.*, 12(7), 577–579.
- Višić, B., Cohen, H., Popovitz-Biro, R. Tenne, R., Sokolov, V.I., Abramova, N.V., Buyanovskaya, A.G., Dzvonkovskii, S.L. & Lependina, O.L. (2015). Direct Synthesis of Palladium Catalyst on Supporting WS₂ Nanotubes and its Reactivity in Cross-Coupling Reactions. *Chem. Asian J.*, 10(10), 2234–2239.
- Yang, H.T., Ruan X.J., Miao, C.B., Sun, X.Q. (2010). An efficient one-step synthesis of fulleroidisoxazolines and fulleropyrazolines mediated by (diacetoxyiodo)benzene. *Tetrahedron Lett.*, 51(46), 6056–6059.