Fullerenes coordinated to transition metals: Synthetic and stereochemical study

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Abstract. Fullerenes may serve as ligands of different hapticity for metals. Symmetry groups and chirality conditions are examined for C_{60} and C_{70} bonded to one or two metals in η^5 and/or η^6 fashion. Palladium and platinum η^2 complexes of C_{60} and C_{70} are described (novel synthesis, NMR spectra, electrochemistry) as well as first optically active organometallic fullerene derivatives, Pd and Pt complexes with (+) DIOP ligand, characterised by CD spectra with many Cotton effects. Homolytic additions of the P-, B-, Pt-centered free radicals afford spin-adducts of C_{60} studied in detail by EPR spectroscopy. A Pt-fullerenyl radical is the first η^1-metalfullerene species reported. Unique application of the fullerenylradical dimer for synthetic purpose is described. Selective protonation of endohedral metallofullerenes $M@C_{82}$ (one of two isomers) in CF_3COOH was revealed by EPR spectra.

INTRODUCTION

Discovery of fullerenes [1] was one of the greatest achievements in natural sciences of modern time relating to different branches such as chemistry, physics, biology, material science, geology etc. One cannot.help.noting about a very interesting pre-history, the most successful predictions by quantum-chemical calculations [2,3] of unusual stability of C_{60}. However, during the first period, 1985-1991, fullerenes had been things for physicists, mostly spectroscopists. For synthetic chemical work only discovery of a bulk fullerene preparation procedure by Kraetschmer, Huffman and their co-workers [4] had a decisive and crucial significance. After that fullerenes, C_{60} at first, and later C_{70} became things for chemists because they are in need of some real amount of substance (as well as material scientists or biologists by the way). more than to observe spectroscopic lines Therefore all fullerene chemists are to be greatly indebted to the Kraetschmer-Huffman team.

Fullerenes are ambiguous objects to be classified. They have to belong to inorganic chemistry being made of pure carbon. They have to belong to organic chemistry as unsaturated species that behave like strained polyalkenes. At any rate their metal complexes are doubtless objects of coordination chemistry. Studies in organic chemistry of fullerenes had been pioneered by Fred Wudl [5], Joel Hawkins [6] and other workers since 1991. Organometallic chemistry of fullerenes was initiated by a well-known work of Fagan, Calabrese, and Malone [7] . It is now possible to summarize main features of fullerene reactivity due to the intensive work of many research groups as follows:

Fullerenes are alkenes with strained double bonds, (6:6) being more reactive than (6:5). They are strong electron acceptors with the tendency for adding nucleophiles including electrons (up to 6) and free radicals. Three-dimensional structure permits to have several remote reaction sites. Carbenoids are capable of adding on both (6:6) and (6:5) double bonds with the formation of three-membered fused ring in the former case or bridged-open structures, fulleroids, in the latter.
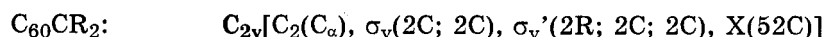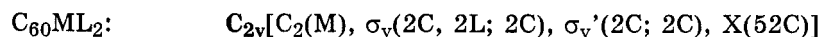
Our previous activity was mostly in the area of organometallic stereochemistry, more precisely, in optically active organometallics. And when five years ago we turned to the fullerene chemistry we became interested primarily in the following topics close to our background: *(i)* fullerenes as ligands of various hapticity for metals and chirality conditions for some metal complexes; *(ii)* synthesis, molecular structure, and reactivity of C_{60} and C_{70} coordinated to the platinum group metals; *(iii)* optically active organometallic fullerene derivatives; *(iv)* attachment of organometallic moieties to the fullerene core through some spacers; *(v)* formation and reactivity of Z-fullerenyl free radicals wherein group Z is linked to fullerene through a magnetic nucleus to be studied by EPR spectroscopy; and, very recently, *(vi)* reactivity of endohedral metal complexes.

FULLERENES AS LIGANDS FOR METALS.
SYMMETRY AND CHIRALITY

From a viewpoint of coordination chemistry fullerenes are very interesting objects. They might be ligated to metal in all conceivable ways that is different hapticity is possible in principle, from η^1 to η^6 as we showed in 1992 [8]. However, nearly all fullerene metal complexes synthesized till present are η^2 complexes. The only η^1-bonded species known is a platinated free radical *(vide infra)*. There are just few examples when two [9] or three [10] metal atoms are coordinated to the same hexagonal face but they can be described as η^2:η^2 and η^2:η^2:η^2 complexes. Finally it was necessary to partly violate the fullerene structure in order to synthesize the first η^5 metal complex related to fullerene as reported recently by Sawamura et al. [11].

η^2 η^2:η^2 η^2:η^2:η^2

$\eta^3[6:5, 6:5]$ $\eta^3[6:6, 6:5]$ $\eta^4[6:6, 6:6]$ η^5 η^6
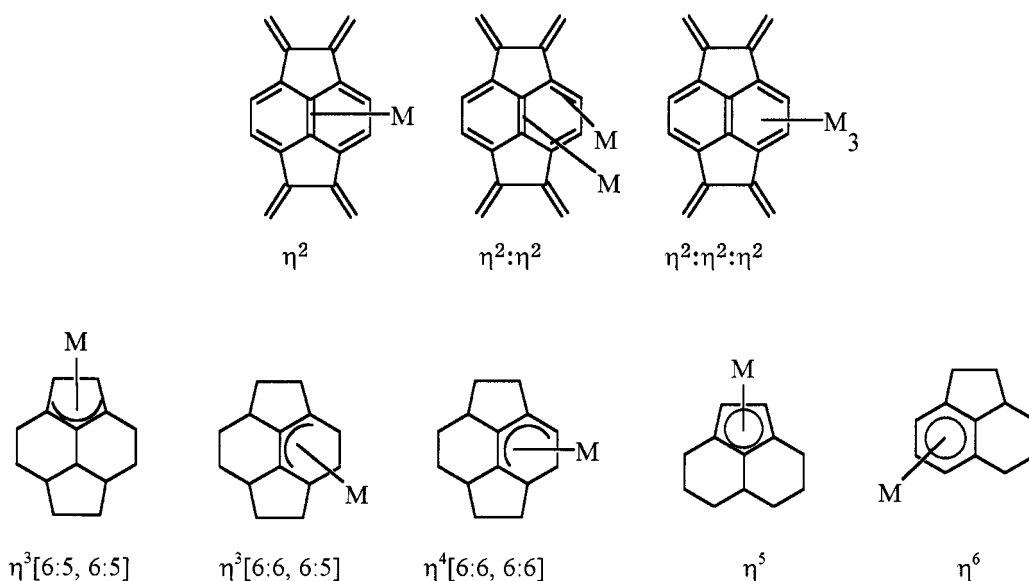
Geometries of η^2 metal complexes and of methanofullerenes are similar except one noticeable difference. An atom added has a square-planar environment in the former case but a tetrahedral one in the latter. Like their prototypes, molecules A_2MB_2, they belong to the same symmetry group C_{2v}. In order to overcome this obvious drawback of the point group nomenclature for simple molecules, Pople had proposed some years ago [12] the Framework Group Approach in which each structure is given its own unique index. Application of this approach to fullerenes [13] will be here exemplified as follows:

$C_{60}ML_2$: $C_{2v}[C_2(M), \sigma_v(2C, 2L; 2C), \sigma_v'(2C; 2C), X(52C)]$

$C_{60}CR_2$: $C_{2v}[C_2(C_\alpha), \sigma_v(2C; 2C), \sigma_v'(2R; 2C; 2C), X(52C)]$

First members of the fullerene family have high symmetry: C_{60} I_h, C_{70} D_{5h}. Chiral cages appear starting from C_{76} which had been resolved and studied as enantiomers by Hawkins [14]. All mono-metal complexes of C_{60} and C_{70} are achiral independent on the way of coordination. In 1992 we have shown that C_{60} doubly bonded to metal in η^6-fashion will be chiral if the hexagons involved are separated by 3 edges [15]. Later on the complete analysis has been published [16] of all possible combinations for double η^5 and/or η^6 metal complexes in C_{60} and C_{70}. It turned out that whereas for C_{60} the chiral combination of two edges is unique, for C_{70} one-third of all possible pairwise combinations are chiral. Between them are not only η^6,η^6 as for C_{60} but η^6,η^5 and η^5,η^5 as well.

PALLADIUM COMPLEXES

In 1993 we reported [17] the synthesis and X-ray study of $C_{60}Pd(PPh_3)_2$. Molecular structure is similar to that of the platinum analogue. Elongation of the C1-C2 bond is less compared with the platinum case (1.447 *vs* 1.502 A) that reflect less strong the fullerene - metal bonding. The coordination sphere of the metal is not a tetrahedron but planar square as in metal complexes with tetra(fluoro *or* cyano)ethylene that correlates with strong electron-withdrawing character of fullerene. Use of combination $Pd_2(dba)_3$ + 2L as reagents in the synthesis of C_nPdL_2 permits to involve different (at least) phosphine ligands without preliminary preparation of their Pd(0) complexes.

Electrochemical study (by cyclic voltammetry) of this complex in acetonitrile in the presence of $Pd(PPh_3)_4$ in excess revealed the disappearance of some reductive waves characteristic of free C_{60} [18] (Table 1).

TABLE 1. Comparison of Reduction Potentials of free C_{60} and $C_{60}Pd(PPh_3)_2$

	$- E_{1/2}$ (red)					
C_{60}	0.34		0.78		1.30	1.78	2.30
$C_{60}Pd(PPh_3)_2$	0.34	0.57	0.78	0.99	1.27	1.47	
$C_{60}Pd(PPh_3)_2$ + $Pd(PPh_3)_4$		0.57	0.81	0.99	1.25	1.48	

Exactly the same picture was obtained for $C_{70}Pd(PPh_3)_2$, first reductive potential for this complex being 0.70 v [19] (for C_{70} itself 0.48 v). This can be explained by the existence of the equilibrium

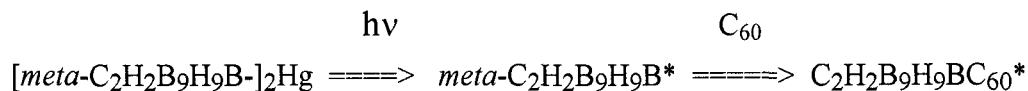$$2 C_nPd(PPh_3)_2 \Longleftrightarrow C_n[Pd(PPh_3)_2]_2 + C_n$$
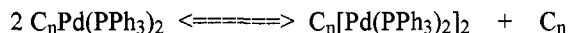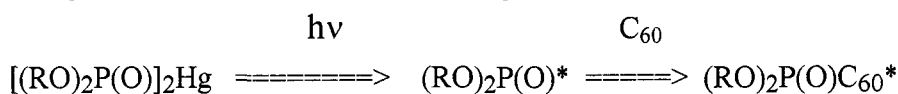
PLATINUM COMPLEXES

We found and developed an alternative method for preparing the platinum - fullerene complexes starting with Pt(II) derivatives as a source of the L_2Pt moiety. First we used mercuryplatinum compounds whose synthesis had been derived by us previously [20]. They appeared to be able to transfer L_2Pt onto a fullerenyl [6:6] double bond in a moderate fast reaction and high yield at room temperature [21]. This procedure ensures the absence of free phosphine ligand in the reaction mixture.

$$R\text{-}Hg\text{-}Pt(PPh_3)_2\text{-}Br + C_{60} \Longrightarrow C_{60}Pt(PPh_3)_2 + R\text{-}Hg\text{-}Br$$
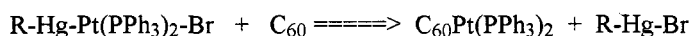
The reaction is slower when R is perfluoroalkyl group but in that case the completely different process may occur under photolytic conditions *(vide infra)*. Furthermore it turned out that even diarylbis(triphenylphosphine)platinum reacts slowly (during several days) with C_{60} to give the same $C_{60}PtL_2$ in fair yield and diaryl identified by chromatography and NMR spectroscopy for Ar = phenyl, p-tolyl. The reaction is complete after 15 min. when carried out at $100°C$ in toluene in sealed tube and the yield of $C_{60}PtL_2$ is nearly quantitative [22].

HOMOLYTIC PHOSPHORYLATION AND EPR STUDY OF PHOSPHORYLFULLERENYL RADICALS

After Krusic and coworkers [23] had demonstrated the high ability of C_{60} to add free radicals we began investigation of the radicals Z wherein unpaired electron is centered on a nucleus with non-zero magnetic moment such as ^{31}P, ^{10}B-^{11}B, ^{195}Pt etc in order to gain some additional information from hyperfine splitting (hfs) constants a in EPR spectra of newly formed Z-fullerenyl radicals. We introduced a very convenient procedure for generating phosphoryl and carboranyl radicals by photolysis of the corresponding mercuric derivatives with a mercury lamp [24, 25].

$$[(RO)_2P(O)]_2Hg \xrightarrow{h\nu} (RO)_2P(O)^* \xrightarrow{C_{60}} (RO)_2P(O)C_{60}^*$$

$$[meta\text{-}C_2H_2B_9H_9B\text{-}]_2Hg \xrightarrow{h\nu} meta\text{-}C_2H_2B_9H_9B^* \xrightarrow{C_{60}} C_2H_2B_9H_9BC_{60}^*$$

EPR signal of phosphorylfullerenyl radical is registered as a doublet with $a(P)$ 63.5 G due to coupling to ^{31}P (100%, spin 1/2). Beautiful picture is observed for carboranylfullerenyl radical (Fig.1) where couplings to both boron isotopes are clearly seen: ^{10}B (15%, spin 3), $a(B)$ 6.25 G (7 lines) and ^{11}B (85%, spin 3/2), $a(B)$ 18.25 G (4 lines). More details about EPR results can be found in a review [25].
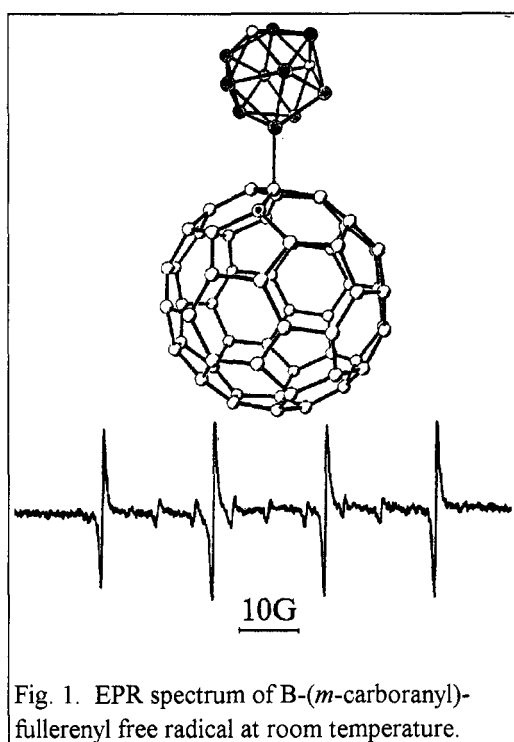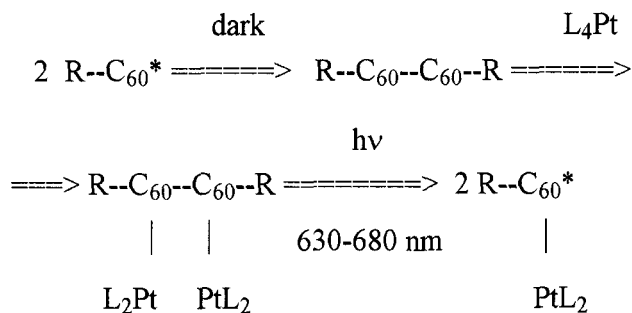
Now I would like to stress that we have independently uncovered the reversible dimerization of the phosphorylfullerenyl radical, determined the dimerization constant, 1.9 $L(mol.s)^{-1}$, enthalpy of activation, $\Delta H = 13$ kcal.mol^{-1}, and at the first time used the fullerene-fullerene dimer in preparative synthesis [26] .

When $C_{60}Pt(PPh_3)_2$ was exposed to phosphoryl radicals under the usual conditions EPR signals of several P-fullerenyl radicals were observable during several minutes after that only one survived which was identical with the parent $*C_{60}P(O)(OR)_2$ by g-factor and hfs constant a. This evidenced that preferential attack was directed on the metal followed by fast demetalation.

In order to circumvent this obstacle we have designed the indirect way, namely, η^2-platination of the dimer and then irradiation with *visible* light which is able to cleave the weaker fullerene-fullerene bond but not Hg-P bond. Dimer is diamagnetic and does not exhibit any EPR signal. They arise only after the dissociation into paramagnetic monomers.
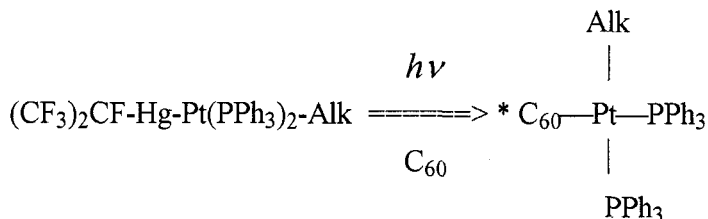

Fig. 1. EPR spectrum of B-(*m*-carboranyl)-fullerenyl free radical at room temperature.

10G

$$2\ R\text{--}C_{60}* \xrightarrow{\text{dark}} R\text{--}C_{60}\text{--}C_{60}\text{--}R \xrightarrow{L_4Pt}$$

$$\xrightarrow{} R\text{--}C_{60}\text{--}C_{60}\text{--}R \xrightarrow[630\text{-}680\ nm]{h\nu} 2\ R\text{--}C_{60}*$$

$$\underset{L_2Pt\quad PtL_2}{|\quad|} \qquad\qquad \underset{PtL_2}{|}$$

When the mercury lamp was switched off the EPR signal disappeared rapidly because of dimerization. Platination of the dimer was carried out using L_4Pt or a mercuryplatinum derivative. Then the source of visible light was switched on and new signals appeared immediately. They were five. One of them had g-factor 2.0023 and $a(P) = 63.5$ G and was identified as a parent P-fullerenyl radical without platinum. It probably stemmed from incomplete metalation of the dimer. Four doublets can be assigned to regioisomers with different distance between the platinum and phosphorus sites.

In addition, we were able to prepare a Pt-fullerenyl radical with platinum as the key atom. When a perfluoroalkyl mercuryplatinum derivative *(vide supra)* reacts with C_{60} under UV irradiation then only metal-metal bond is selectively cleaved in a homolytic way. The platinum-centered free radical formed adds immediately to fullerene. Novel platinumfullerenyl radical is relatively stable and observable at room temperature by EPR spectroscopy [21]. Its structure follows from hyperfine splitting due to one platinum (^{195}Pt), $a(Pt)$ 52.0 G, and two non-equivalent phosphorus (^{31}P), $a(P1)$ 30.5 G, $a(P2)$ 3.5 G,

nuclei that points to *cis*-arrangement of two phosphine ligands in this species. Surprisingly, this radical seems to be the first representative of $\eta^1(\sigma)$-Pt-fullerenyl compounds and may be of monohapto-metallofullerenes at all.

$$(CF_3)_2CF\text{-Hg-Pt}(PPh_3)_2\text{-Alk} \xrightarrow[\substack{hv \\ C_{60}}]{} *\ C_{60}\text{---}\overset{\displaystyle Alk}{\underset{\displaystyle PPh_3}{\overset{|}{\underset{|}{Pt}}}}\text{---}PPh_3$$

η^2-METAL COMPLEXES OF C_{70}

The second member of the fullerene family, C_{70}, has lower symmetry $\mathbf{D_{5h}}$. So there are different types of vertices and edges and regiochemistry of C_{70} is more rich and complicated than that of C_{60}. We used successfully the transfer of L_2Pt from a mercuryplatinum compound *(vide supra)* to [6:6] bond in the preparation of η^2-$C_{70}Pt(PPh_3)_2$. It is generally accepted mostly due to the work of Alan Balch [27] that preferable reaction site in C_{70} is the most strained *a-b* bond near the pole of ellipsoid. It is confirmed now because two phosphorus atoms in the platinum complex are non-equivalent and exhibit AB system in ^{31}P NMR: $\delta(P_a)$ 25.5, $\delta(P_b)$ 22.9, $J(P_a,P_b) = 24.5$ Hz. However, analytically pure $C_{70}Pd(PPh_3)_2$ {$C_{106}H_{30}P_2Pd\cdot C_7H_8$, Found (Calcd) %: C 86.88. H 2.32 (2.45), P 3.91 (3.97)} according to ^{31}P{^{1}H} NMR (1,2-dichlorobenzene, δ, ppm) consists of two regioisomers [18]: isomer *a-b* : $\delta(P_a)$ 29.06, $\delta(P_b)$ 26.6, $J(P_a,P_b) = 9.4$ Hz and isomer *c-c* : $\delta(P_c)$ 27.24. Ratio *(a-b)/(c-c)* is 86/14.

OPTICALLY ACTIVE METAL FULLERENE COMPLEXES

First *optically active organic* fullerene derivative was reported in 1992 by Vasella, Diederich and coworkers [28]. They created chiral environment near C_{60} by using covalently linked sugar moiety and observed in the circular dichroism (CD) spectra many Cotton effects due to the electronic transitions in C_{60} itself. We reported the synthesis of first *optically active organometallic* fullerene in 1993 with palladium as metal and (+)DIOP {(+)-2,3-isopropylidene-2,3-*trans*-1,4-bis(diphenylphosphino)-butane} as ligand and chirality source [29]. Later on we have prepared the platinum analogue and solved its molecular structure by X-ray study of a single crystal of its solvate with *cis*-cyclooctene [30] shown on Fig. 2. Selected bond lengths and valent angles are listed in Table 2. CD spectra of these two compounds in toluene and dimethylformamide are shown on Fig. 3. Major part of the Cotton effects are close to those observed in work [28]. Some are different perhaps due to the interaction between the C_{60} chromophore and the metal.

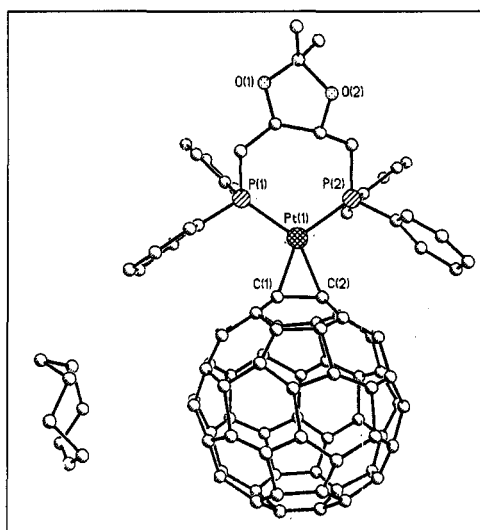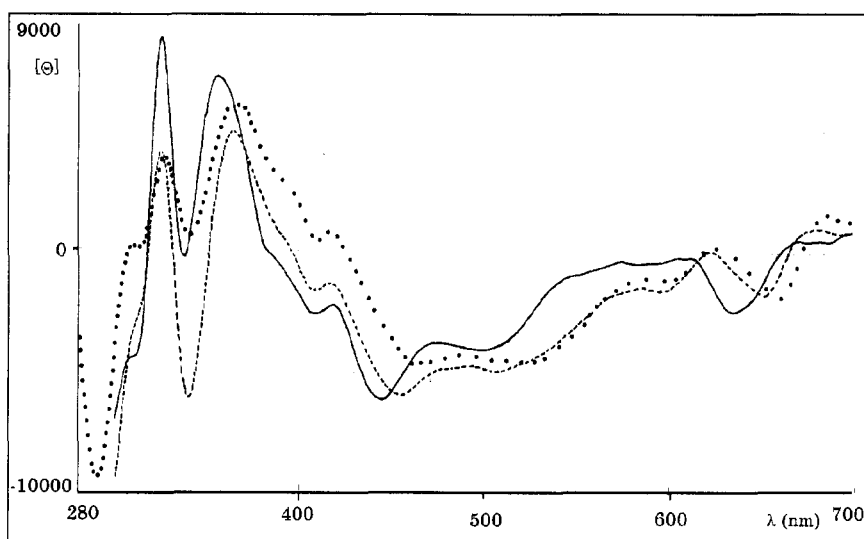Fig.2. X-Ray Structure of $C_{60}Pt[(+)DIOP]$

TABLE 2. Selected Bond Lengths and Valent Angles in $C_{60}Pt[(+)DIOP]$

bond	Å	angle	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		

Fig. 3. CD spectra of the enantiomeric platinum and palladium C_{60} derivatives

——————— $(C_{60})Pt[+DIOP]$ in toluene

·················· $(C_{60})Pd[+DIOP]$ in toluene

•••••••••• $(C_{60})Pd[+DIOP]$ in dimethylformamide

$(C_{70})Pt[(+)DIOP]$ has been synthesized as well and has displayed a similar CD spectrum with Cotton effects at 312 (+), 335 (-), 386 (+), 496 (+) nm in toluene, optical rotation: $[\alpha]_{365}$ - 3,92°.

FULLERENES WITH PENDANT ORGANOMETALLIC GROUPS

Fullerene and organometallic fragment can be united within one molecule and interaction between these parts may be of interest in terms of mutual influence, electron transfer etc. Synthetic pathways to these molecules have not been elaborated. Our design was based on the Wudl reaction [31] with organometallic diazo compounds as reactants few of which had been known previously. The corresponding diazo derivative of arenechromiumtricarbonyl series had been synthesized as follows:
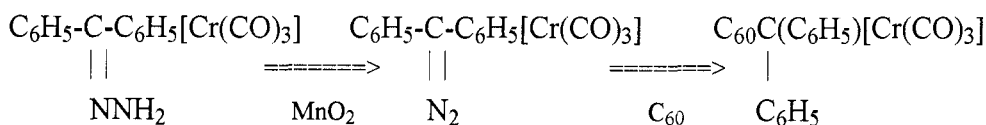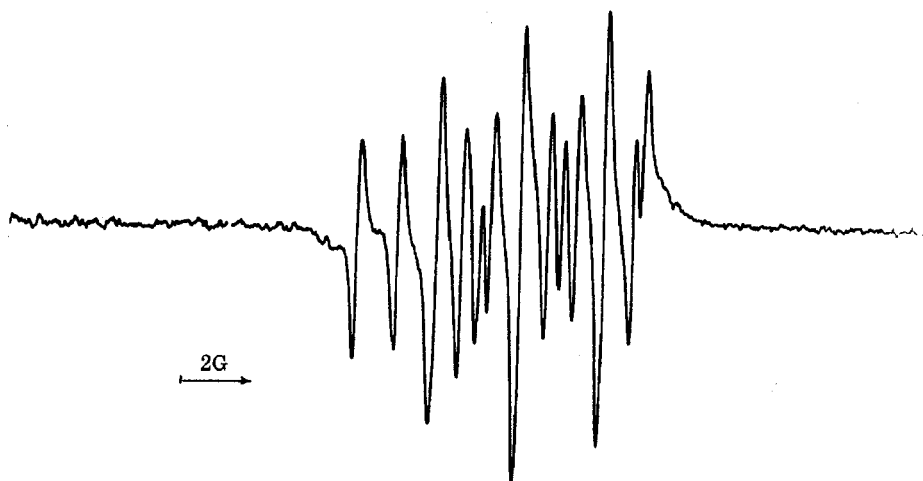
Product of the thermal reaction with C_{60} was a mixture of (6,6)methanofullerene and (6,5)fulleroid [32] in accordance with Wudl's result for corresponding demetallo-analogue. Thermal isomerization, however, was hindered by steric or electronic factors. The ferrocene-containing diazo compound, Fc-CO-CHN$_2$, displays similar reactivity vs C_{60}.

REACTIVITY OF ENDOHEDRAL METALLOFULLERENES

Absolutely new structural type is endohedral complexes of fullerenes. This unique opportunity for topological bond is provided by the hollow structure of fullerenes whose surface divides the space in the inner and the outer parts. Even in the case of strong interaction between the encapsulated atom and the shell that atom is not able to go out without breaking the surface. It is generally accepted that electron density is substabtially transferred from the atom to the carbon shell [33]. Let us note that (apart from helium atom [34]) only metals of Group 3 have been encapsulated thus far. As a consequence of this electron transfer, the character of the fullerene surface has to be changed. It has to be apt now to undergo electrophilic attack not nucleophilic as "empty" fullerenes. Chemical reactivity of endohedral metallofullerenes (EMF) is not explored except a couple of reactions [35] because they are hardly accessible. Luckily endohedral metallofullerenes are paramagnetic due to the lanthanoid atom inside. So it is possible to work using EPR spectroscopy for which tiny amounts of substance are sufficient.

We have observed for La@C_{82} and Y@C_{82} EPR spectra identical to those published in the literature [36]. Each of them consists of two well-resolved close multiplets of 8 lines for La and of 2 lines for Y in the accordance with their spins of 7/2 and 1/2 correspondingly. EPR spectra did not change at all when samples were treated in solution with L$_4$Pt or phosphoryl radicals under conditions described. That means that EMF are not reactive vs nucleophilic and free radical reactants (or at least they are much less reactive than empty fullerenes and cannot compete with them present in the mixture). However, there was a remarkable change in EPR spectra when CF$_3$COOH was added to toluene in ampoule. One of two octets (or doublets) disappeared while another one survived. Instead a new signal arose (Fig. 4) that might be a component of a new doublet due to hfs to one proton covalently bound to the cage. La@C_{82} and Y@C_{82} behave similarly. Two isomers are supposed to be cage isomers. In any case, ability of CF$_3$COOH to distiguish between two isomers of the EMF's seems extraordinary but not impossible.
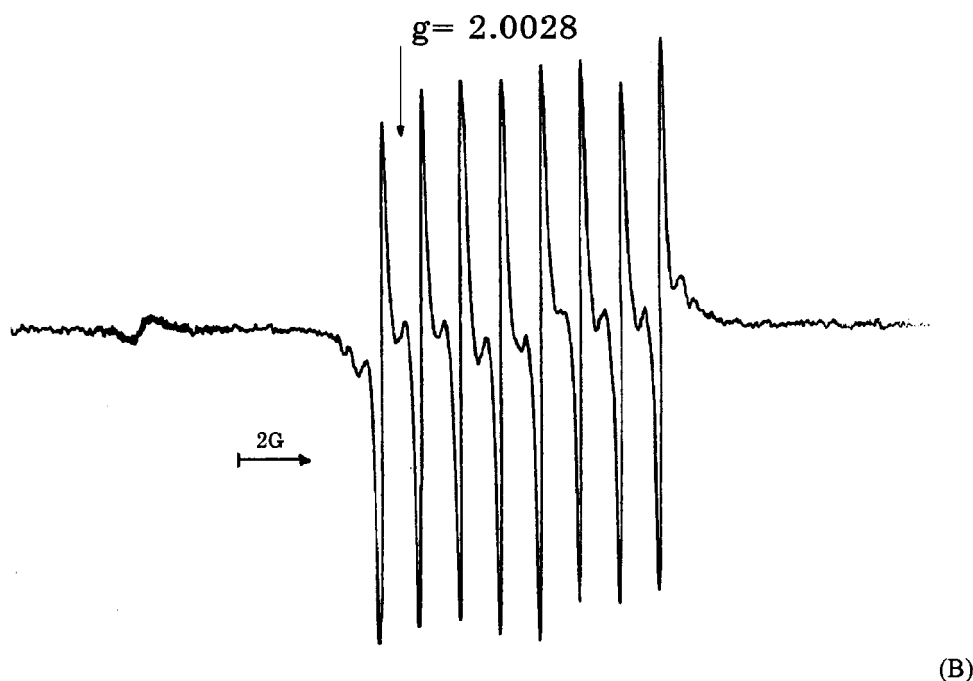

2G

(A)

$g = 2.0028$

2G

(B)

Fig. 4. EPR spectra of La@C$_{82}$ in toluene: (A) before adding CF$_3$COOH, (B) after adding

References

1. H.W.Kroto, J.R.Heath, S.C.O'Brien, R.F.Curl, and R.E.Smalley, *Nature*, 318, 162 (1985).
2. E.Osawa, *Kagaku (Kyoto)*, 25, 854 (1970).
3. D.A.Bochvar and E.G.Gal'pern, *Dokl. Akad. Nauk SSSR*, 209, 610 (1973).
4. W.Kraetschmer,L.D.Lamb, K.Fostiropoulos, and D.R.Huffman, *Nature*, 347, 354 (1990).
5. F.Wudl, *Acc. Chem. Res.*, 25, 157 (1992).
6. J.M.Hawkins, *Acc. Chem. Res.*, 25, 150 (1992).
7. P.J.Fagan, J.C.Calabrese, and B.Malone, *Science*, 252, 1160 (1992).
8. V.I.Sokolov, *Dokl. Akad. Nauk*, 326, 647 (1992).
9. M.Rasinkangas, T.T.Pakkanen, T.A.Pakkanen, M.Ahlgren, and J.Rowinen, *J. Amer. Chem. Soc.*, 115, 4901 (1993).
10. H-F.Hsu and J.R.Shapley, *J. Amer. Chem. Soc.*,118, 9192 (1996).
11. M.Sawamura, H.Iikura, and E.Nakamura, *J. Amer. Chem. Soc.*, 118, 12850 (1996).

12. J.A.Pople, *J. Amer. Chem. Soc.*, <u>102</u>, 4615 (1980).

13. V.I.Sokolov, *Fullerene Science & Techn.*, <u>5</u>, 281 (1997).

14. (a) J.M.Hawkins and A.Meyer, *Science*, <u>260</u>, 1918 (1993).
    (b) J.M.Hawkins, M.Nambu, and A.Meyer, *J. Amer. Chem. Soc.*, <u>116</u>, 7642 (1994).

15. V.I.Sokolov, (a) 181st Meeting of Electrochemical Society, FUL662, StLouis, 1992;
    (b) *Dokl. Akad. Nauk*, <u>326</u>, 647 (1992).

16. V.I.Sokolov, *Molec. Mater.*, <u>7</u>, 23 (1996).

17. V.V.Bashilov, P.V.Petrovski, V.I.Sokolov, S.V.Lindeman,I.A.Guzei, and Yu.T.Struchkov,
    Organometallics, <u>12</u>, 991 (1993).

18. T.V.Magdesieva, V.V.Bashilov, S.I.Gorelski, V.I.Sokolov, and K.P.Butin, *Izv. Akad. Nauk, Ser.*
    khim., #12, 2153 (1994); *Russ. Chem. Bull.*, <u>43</u>, 2034 (1994) [Engl.]

19. T.V.Magdesieva, V.V.Bashilov, D.N.Kravchuk, P.V.Petrovski, V.I.Sokolov, and K.P.Butin,
    Inorg. Chim. Acta, submitted for publication.

20. (a) V.I.Sokolov, V.V.Bashilov, and O.A.Reutov, *J. Organometal. Chem.*,<u>111</u>, C13 (1976);
    (b) V.V.Bashilov, V.I.Sokolov, and O.A.Reutov, *Izv. Akad. Nauk SSSR, Ser. khim.*, *1982*, 2069
    {*Bull. Acad. Sci. USSR, Div. Chim. Sci.*, <u>31</u>, 1825 (1982) [Engl.]}

21. V.V.Bashilov, B.L.Tumanski, P.V.Petrovski, and V.I.Sokolov, *Izv. Akad. Nauk, Ser. khim.*,
    #5, 1131 (1994); *Russ. Chem. Bull.*, <u>43</u>, 1069 (1994) [Engl.]

22. V.V.Bashilov and V.I.Sokolov, unpublished results.

23. P.J.Krusic, E.Wasserman, B.A.Parkinson, P.N.Keizer, J.R.Morton, and K.F.Preston,
    Science, <u>254</u>, 1183 (1991).

24. B.L.Tumanski, S.P.Solodovnikov, V.V.Bashilov, and V.I.Sokolov, *Izv. RAN, Ser. khim.*, #6, 1457
    (1992); *Russ. Chem. Bull.*, <u>41</u>, 1392 (1992) [Engl.]

25. B.L.Tumanski, *Izv. RAN, Ser. khim.*, #10, 2396 (1996); *Russ.Chem.Bull.*, <u>45</u>, 2280 (1996) Engl

26. B.L.Tumanski, V.V.Bashilov, N.N.Bubnov, S.P.Solodovnikov, and V.I.Sokolov, *Izv. RAN, Ser.*
    khim., #8, 1936 (1992); *Russ. Chem. Bull.*, <u>41</u>, 1521 (1992) [Engl.]

27. A.L.Balch, V.J.Catalano, J.W.Lee, M.M.Olmstead, and S.R.Parkin,
    J. Amer. Chem. Soc., <u>113</u>, 8953 (1991).

28. A.Vasella, P.Uhlmann, C.A.Waldraff, F.Diederich, and C.Thilgen, *Angew. Chem. Intern. Ed.*, <u>31</u>,
    1388 (1992).

29. V.V.Bashilov, P.V.Petrovski, and V.I.Sokolov, *Izv. RAN, Ser. khim.*, #2, 428 (1993);
    Russ. Chem. Bull., *42*, 393 (1993) [Engl.]

30. V.V.Bashilov, P.V.Petrovski, V.I.Sokolov, F.M.Dolgushin, A.I.Yanovsky, and Yu.T.Struchkov,
    Izv. RAN, Ser. khim., #5, 1268 (1996); *Russ. Chem. Bull.*, <u>45</u>, 1207 (1996) [Engl.]

31. M.Eiermann, F.Wudl, M.Prato, and M.Maggini, *J. Amer. Chem. Soc.*, <u>116</u>, 8364 (1994).

32. M.N.Nefedova and V.I.Sokolov, *Izv. RAN, Ser. khim.*, #4, 780 (1995);
    Russ. Chem. Bull., <u>44</u>, 761 (1995) [Engl.]

33. S.Nagase and K. Kobayashi, Chem. Phys. Lett., 214, 57 (1993)

34. M.Saunders, H.Jimenes-Vasquez, R.J.Cross,S.Mroczkowski, D.I.Freedberg, and F.A.L.Anet,
    Nature, <u>367</u>, 256 (1994).

35. T.Akasaka, T.Kato,, K.Kobayashi, S.Nagase, K.Yamamoto, H.Funasaka, and T.Takahashi,
    Tetrahedron, <u>52</u>, 5015 (1996).

36. S.Nagase, K.Kobayashi, and T.Akasaka, *Bull. Chem. Soc. Japan*, <u>69</u>, 2131 (1996).

37. B.L.Tumanski, V.V.Bashilov, S.P.Solodovnikov, V.I.Sokolov, V.P.Bubnov, E.E.Laukhina,
    Ya.I.Estrin, V.K.Kolt'over, and E.B.Yagubski, *Fullerene Science & Techn.*, submitted for
    publication.