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Fluorination of [60]fullerene by alkali metal hexafluoroplatinates

Alexey B. Kornev,[a] Pavel A. Troshin,*[a] Alexander S. Peregudov,[b] Zinaida E. Klinkina,[c] Natalya V. Polyakova[c] and Rimma N. Lyubovskaya[a]

[a] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 496 515 5420; e-mail: troshin@cat.icp.ac.ru*
[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation*
[c] *Research Institute of Electrocarbon Products, 142490 Moscow, Russian Federation*

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A comparative study of the fluorinating activity of M_2PtF_6 (M = K, Rb or Cs) in reactions with C_{60} was performed; Rb_2PtF_6 and Cs_2PtF_6 gave much higher yields of fluorofullerene ($C_{60}F_{18}$) than commonly used K_2PtF_6.

The fullerene chemistry resulted in discovering unusual reactions and compounds.[1] Fluorofullerene $C_{60}F_{18}$ can be considered as one of the most exciting fullerene derivatives.[2] On the one hand, it has all 18 fluorine atoms attached to one hemisphere of the fullerene cage, which makes it looking like a tortoise shell.[3] On the other hand, the reactions of $C_{60}F_{18}$ with carbanionic nucleophiles yield trannulenes, aromatic compounds that possess an 18-membered annulene ring with the exclusively *trans* configuration of all unsaturated bonds (Figure 1).[4] Well-known planar aromatics such as benzene or 18-annulene have all π-orbitals overlapped above and below the ring plane. In contrast, the π orbitals of the trannulene ring are overlapped almost in a plane; therefore, they represent the first example of in-plane aromatic compounds.[5] All trannulenes have intense absorption at 500–850 nm, which results in a green colour; it is surprising for fullerene derivatives because most of them are red to brown.

The only drawback is the low availability of $C_{60}F_{18}$. The first method for its production is the fluorination of C_{60} by K_2PtF_6 to give a mixture of products that contain predominantly $C_{60}F_{18}$ and $C_{60}F_{36}$.[2] The maximal yield of HPLC-isolated $C_{60}F_{18}$ from the fluorination products of C_{60} by K_2PtF_6 was reported to be 35–40%.[6]

Potassium hexafluoroplatinate (K_2PtF_6) is an expensive reagent, therefore, it was suggested to use a K_2NiF_6–MnF_3 mixture for the synthesis of $C_{60}F_{18}$ in ~14% yield.[6] Recently, we used CoF_3/KHF_2 or CoF_3/RbF mixtures for the synthesis of $C_{60}F_{18}$ in 18–23% yield.[7] We also separated fluorofullerene mixtures by column chromatography instead of time-consuming HPLC. To prevent hydrolysis of fluorinated fullerenes, we used silica dried at 650 °C as a stationary phase.[†]

Previously, we found that fluorinating power of the complex fluorides such as $M_xM'F_y$ (where M is an alkali metal cation) can be decreased going from Li and Na to Rb and Cs complex fluorides. Particularly, Cs_3PbF_7 is much less reactive than Li_3PbF_7.[8] If this order of reactivity is true for hexafluoroplatinates, Rb_2PtF_6 and Cs_2PtF_6 should be less active and, therefore, give higher yields of $C_{60}F_{18}$ than K_2PtF_6. The aim of this study was to test this hypothesis.

[†] See ref. 7 for the detailed description of the fluorination and isolation procedures.

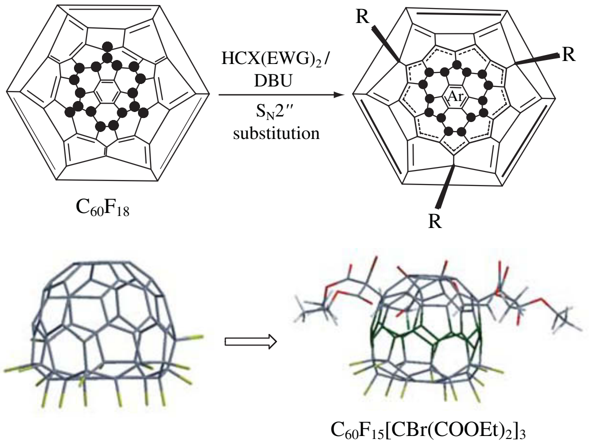

Figure 1 The Schlegel diagrams and molecular structures of $C_{60}F_{18}$ and trannulene $C_{60}F_{15}[CBr(COOEt)_2]_3$. The scheme demonstrates conversion of $C_{60}F_{18}$ to $C_{60}F_{15}R_3$. The EWG denotes electron-withdrawing group such as COOR, $PO(OR)_2$ *etc.*; X = halogen, alkyl, NO_2, CN or COOR.

Indeed, the experimental data given in Table 1 demonstrate that Rb_2PtF_6 and Cs_2PtF_6 give considerably higher yields of $C_{60}F_{18}$ than K_2PtF_6. However, the typical product yields in our experiments with K_2PtF_6 are substantially lower than those reported previously for HPLC-isolated $C_{60}F_{18}$. The explanation of this discrepancy is in partial degradation of the fluorinated fullerenes at the silica gel column, which results in the formation of polar products, which were isolated but could not be confidently identified using ^{19}F NMR spectroscopy. Thus, we proved that the isolation of $C_{60}F_{18}$ by column chromatography significantly reduces its yield in comparison with the HPLC separation procedure. However, it is still the most efficient method for the bulk isolation of $C_{60}F_{18}$ since it allows one to separate up to 1 g of the crude product mixture at one column within 1 h to give 200–300 mg of pure $C_{60}F_{18}$. It is necessary to spend at least a week with HPLC processing of the crude material to obtain the same amount of $C_{60}F_{18}$.

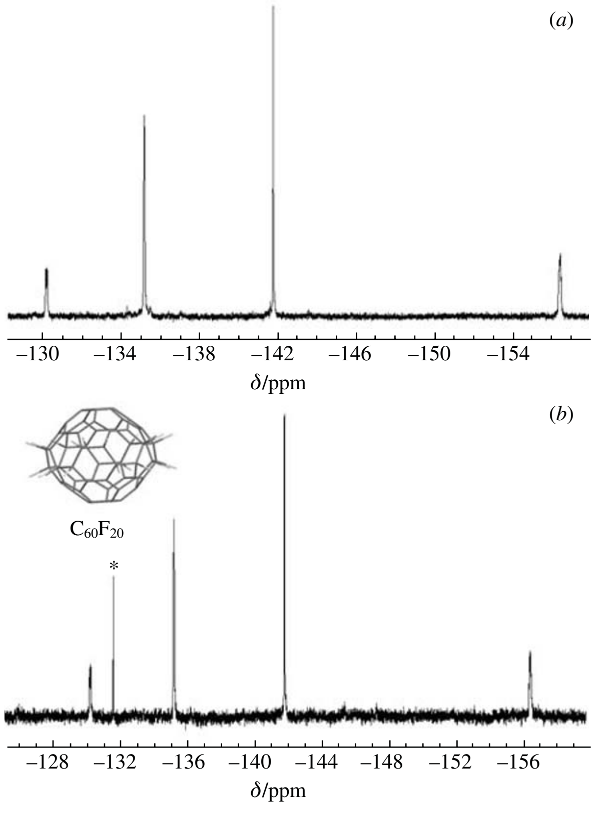

Figure 2 (*a*) The ^{19}F NMR spectra of $C_{60}F_{18}$ and (*b*) $C_{60}F_{18}$ with *ca.* 6% of $C_{60}F_{20}$. Inset shows the molecular structure of $C_{60}F_{20}$.

Table 1 Preparation of fluorofullerenes in reactions with M_2PtF_6.

C_{60}/ mg	Fluorinating agent/g	Recovered C_{60}/mg (%)	$C_{60}F_{36}$/ mg (%)	$C_{60}F_8$ + $C_{60}F_4$/mg	$C_{60}F_{18}$/ mg (%)^a
K_2PtF_6					
500	3	—	90/ 9.2	22	136/18.5
400	4	—	135/17.3	6	122/20.7
300	5.4	—	196/33.5	—	42/ 9.5
Rb_2PtF_6					
153	1.67	30.5/20	—	—	61/33.8
Cs_2PtF_6					
171	2.14	40/23	—	27	65/33.6

^{a}Yields based on C_{60} consumed.

Thus, we showed that Rb_2PtF_6 and Cs_2PtF_6 are more potent fluorinating reagents than K_2PtF_6 with respect to the production of $C_{60}F_{18}$. The purity of the isolated $C_{60}F_{18}$ was checked by ^{19}F NMR spectroscopy. The fluorofullerene samples prepared using Rb_2PtF_6 contain substantial amounts of impurity $C_{60}F_{20}$ (*ca.* 6%, Figure 2). In contrast, the fluorination by K_2PtF_6 and Cs_2PtF_6 produced just trace amounts of this fluorofullerene. The molecule of $C_{60}F_{20}$ is also quite exotic because all of the 20 fluorine atoms occupy equivalent positions at the equator of the fullerene cage. The shape of the $C_{60}F_{20}$ molecule is reflected in its name 'Saturnene'. Only few milligrams of $C_{60}F_{20}$ were isolated previously from grams of the crude product of fluorination of C_{60} with KF/MnF_3.[9] The yield of $C_{60}F_{20}$ formed in the reaction of C_{60} with Rb_2PtF_6 is about 2%, which is much higher than that in the original procedure. However, we achieved *ca.* 4% yield of $C_{60}F_{20}$ in the reaction of C_{60} with MnF_3/MnF_2.

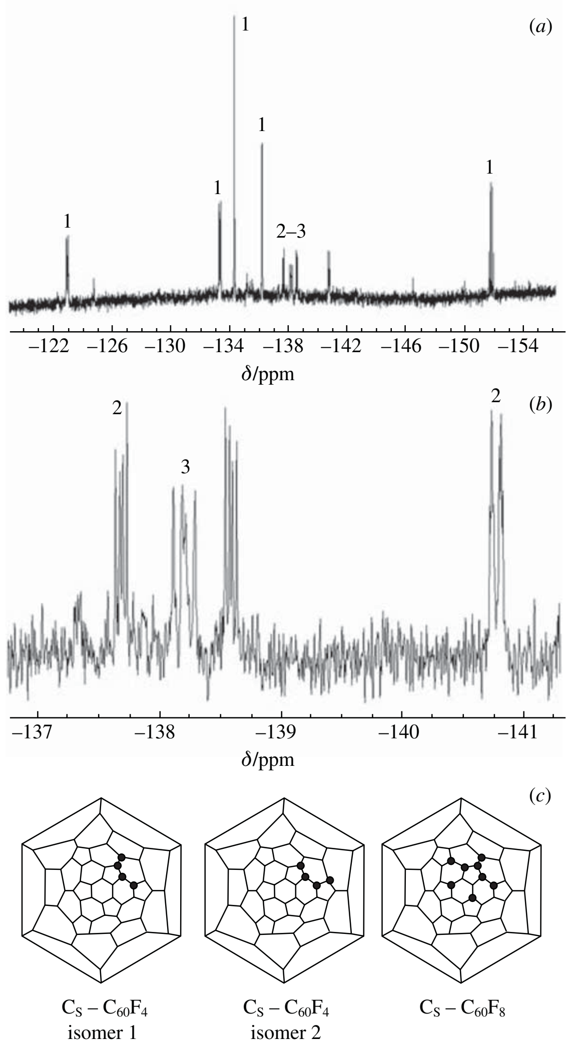

Figure 3 (*a*) The ^{19}F NMR spectrum of $C_{60}F_8$–$C_{60}F_4$ mixture, (*b*) the part of the spectrum with the signals of two isomers of $C_{60}F_4$ and (*c*) Schlegel diagrams for the conjectured structures of $C_{60}F_8$ and two isomers of $C_{60}F_4$.

The careful examination of all fractions of fluorinated products isolated by column chromatography allowed us to observe pure $C_{60}F_2O$ samples and the fractions represented by a mixture of $C_{60}F_8$ (signals marked with 1 in Figure 3) and $C_{60}F_4$ (signals 2 and 3 in Figure 3). The formation of these compounds was observed for all of the tested fluorinating reagents. Fluorofullerene $C_{60}F_8$ is an interesting compound, which was isolated previously in a 1–3 mg quantity and characterised by ^{19}F NMR and EI MS.[10] The structure of this fluorinated fullerene most likely corresponds to the Schlegel diagram shown in Figure 3.[11] Thus, $C_{60}F_8$ is the only known lower fluorinated fullerene that is not a precursor of $C_{60}F_{18}$; its addition pathway is very similar to $C_{60}Cl_6$ and $C_{60}Br_6$.

Two minor components in the $C_{60}F_8$ sample are responsible for the presence of four quartets in the ^{19}F NMR spectrum. Two of these signals correspond to the previously isolated isomer of $C_{60}F_4$ (isomer 1, NMR signals marked with 2); two other quartets can be tentatively assigned to another possible and still unknown C_s-symmetrical isomer of $C_{60}F_4$ (isomer 2, Figure 3).

Note that even HPLC separation sometimes cannot resolve two or even more components; for example it was observed for $C_{60}F_6$ and $C_{60}F_7CF_3$.[10] The isolation of pure $C_{60}F_{18}$ and samples with high contents of $C_{60}F_8$, $C_{60}F_{20}$ and $C_{60}F_4$ points at the high potential of conventional column chromatography in the fluorine chemistry of [60]fullerene. Rb_2PtF_6 and Cs_2PtF_6 improve considerably the yields of $C_{60}F_{18}$ and open wide opportunities for the chemistry of trannulene compounds derived from this fluorofullerene.

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