Electrocatalytic fluoroalkylation of olefins

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Under electrocatalysis conditions, the perfluoroalkylation of α-methylstyrene by the nickel complex $NiBr_2$bipy proceeds with the formation of dimeric products of addition of perfluoroalkyl radicals to the double bond.

Key words: electrocatalysis, nickel bromide complex with bipyridine, electrolysis, perfluoroalkylation, polyfluoroalkyl halides, α-methylstyrene.

Organofluorine compounds possess unique physical and biological properties, due to which they are widely used in medicine and agricultural chemistry and as various materials.[1—3] However, a few such compounds were found in nature.[4] Synthetic compounds compose the most part of organofluorine products. There are different methods for introducing fluoroalkyl groups into substrates. However, these methods are often poorly selective and have a series of drawbacks (high temperature of synthesis, low yields of final products). It is known that the addition of perfluoroalkyl groups to olefins and acetylenes is one of the most important methods of introduction of perfluoroalkyl groups at the carbon atom.[5,6] Free-radical reactions of addition of polyfluoroalkyl iodides to unsaturated compounds are initiated, as a rule, by high temperatures, ultraviolet irradiation, peroxides, metals, and metal complexes.[7—9] Sulfinatodehalogenating agents, such as dithionites, sodium disulfite, and several others, are often used as radical initiators.[10,11] The electrochemical generation of fluoroalkyl radicals is successfully performed.[12—14] Recent success of electrocatalytic reactions allows one to hope that the use of electrochemical methods of fluoroalkylation of various substrates would contribute to the intensive development of this field of chemistry.[15]

Results and Discussion

With the purpose to search for new routes of electrochemical polyfluoroalkylation of olefins, the electrocatalytic addition of polyfluoroalkyl halides to α-methylstyrene and vinyl acetate in the presence of the organonickel catalysts was studied. No data on styrene are presented because the polymerization product is mainly obtained by electrolysis in this case.

It is known that the nickel complexes are efficient catalysts of reactions of cross-coupling and functionalization of olefins[16] and the organic nickel σ-complexes with the Ni—C bonds are the key intermediates of these processes.[17] The combined electrochemical reduction of $NiBr_2$bipy and polyfluorinated alkyl halides (R^FX, X = I, Br) in the presence of α-methylstyrene affords the product of olefin polyfluoroalkylation. Electrolyses were carried out both in a divided electrolyzer at the Pt cathode and without division of the cathodic and anodic spaces at the Pt cathode and using the Mg anode. During the reaction, the reaction mixture turns dark claret-colored when passing electricity. This color is characteristic of organic nickel σ-complexes with the Ni—C bond. As a result, the final products were isolated as white crystalline compounds. Analysis of the conditions of electrolyses and subsequent isolation of the addition products showed that the electrosynthesis of the fluoroalkylation products of α-methylstyrene in a divided electrolyzer is most efficient.

The obtained addition products, *viz.*, 2,3-dimethyl-1,4-bis(perfluoroalkyl)-2,3-diphenylbutanes **1** and **2** (Scheme 1) were characterized by ^{1}H NMR spectroscopy, IR spectroscopy, X-ray diffraction analysis, and mass spectrometry. Analysis of the spectral characteristics of the compounds obtained made it possible to assign them the dimeric structure of the addition products of polyfluoroalkyl halides to α-methylstyrene. It was also noticed that greenish-blue crystals precipitated from the reaction mixture after standing for 3 days. According to the spectral and cyclic voltammetry data, the crystals corresponded to the starting complex $NiBr_2$bipy.

Electrolysis of 6*H*-perfluorohexyl iodide and vinyl acetate in the presence of catalytic amounts of $NiBr_2$bipy proceeds similarly to form the dimeric addition product, namely, 2,3-diacetoxy-1,4-bis(6*H*-perfluorohexyl)butane (**3**).

It is known that the cyclic voltammograms of the unsaturated complex $NiBr_2$bipy contain two reversible reduction peaks.[18] At the first peak, $NiBr_2$bipy undergoes reversible two-electron reduction to the highly reactive

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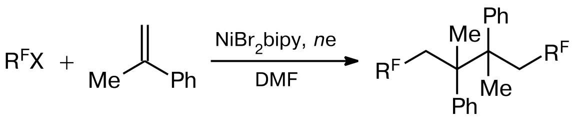
Scheme 1



1,2

$R^F = C_6F_{13}$ (**1**), $H(CF_2)_6$ (**2**)
X = I, Br

complex Ni^{0}bipy (Scheme 2). Upon the addition of polyfluorinated alkyl halide, in particular, perfluorohexyl iodide $C_6F_{13}I$, to this solution, the cathodic current of the first wave increases and reversibility disappears. Based on this fact, we may assume that the complex Ni^{0}bipy rapidly reacts with the substrate in the oxidative addition reaction to form an unstable σ-complex C_6F_{13}NiIbpy, which probably decomposes easily to the polyfluoroalkyl radical and the starting nickel complex through reductive elimination. It is this process which increases the cathodic current of the reduction wave Ni^{II}/Ni^0.

Scheme 2

$$\mathrm{NiBr_2bipy + 2e \rightleftharpoons Ni^0bipy}$$

$$\mathrm{Ni^0bipy + R^FX \longrightarrow R^FNiXbipy}$$

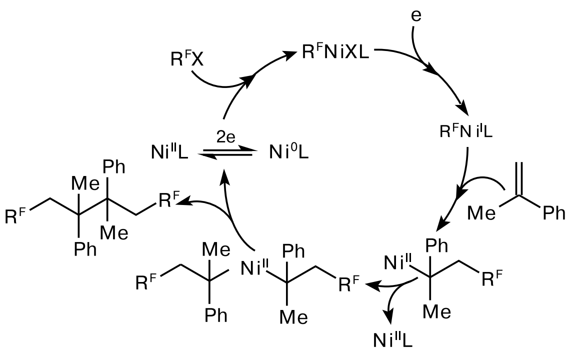
$$\mathrm{R^FNiXbipy \xrightarrow{ne,\ R^FX} R^{F\cdot} + NiX_2bipy}$$

It should be noted that the organic nickel σ-complexes with the Ni—C bonds can add to some olefins in reductive elimination reactions.[18]

Based on the results obtained, we propose the scheme of reactions (Scheme 3) including the steps of oxidative addition and reductive elimination.

The nickel complex in the low oxidation state Ni^{0}bipy is generated during the electrochemical reduction of the complex NiBr$_2$bipy. If the reaction mixture contains polyfluoroalkyl halide ($C_6F_{13}I$, $C_6F_{13}Br$, $C_6HF_{12}Br$), oxidative addition affords the σ-complex R^{F}NiXbipy (X = Br, I), which accepts an electron during electrolysis and transforms into the active complex R^{F}Ni^{I}bipy capable of adding to olefin due to radical decomposition. The complexes formed are, most likely, very unstable and undergo further transformations into the final dimeric addition products. In addition, the starting nickel complex NiBr$_2$bipy is regenerated as a result of this reductive elimination. It was shown for the numerous electrocatalytic reactions involving the NiBr$_2$L complexes and organic halides and studied in detail that the completion step of reductive elimination resulting in the final dimeric product of other cross-coupling product is always nickel-centered.[16] Attempts to isolate intermediates of the catalytic cycle and to model particular steps by the combined use of spectroscopic and electrochemical methods will be made further.

Scheme 3



L = bipy

The reduction of R^{F}X at the electrode is a one-electron process and occurs at more positive potentials (−1.7 V *vs* Ag/AgNO$_3$) than the reduction of olefin. However, in the absence of a nickel catalyst, their combined electrochemical reduction affords no products of addition of the R^F moiety to the double bond.

In the present work, the use of the electrocatalytic approach allowed us for the first time to carry out olefin perfluoroalkylation under mild conditions in 50—70% yield, and the moiety with the long fluoroalkyl radical chain was introduced. Interestingly, the firstly obtained product is not a product of the simple addition of the R^F moiety to olefin, but the dimer of the intermediate adduct, namely, R^F-olefin. Thus, the new scheme of olefin functionalization, which was not described earlier, was accomplished.

Experimental

Preparative electrolyses were carried out using a B5-49 dc source at a current strength of 100 mA h^{-1} in 100-mL three-electrode cell. The potential of the working electrode was detected by a V7-27 dc voltmeter. The working surface of the platinum cylindrical cathode used as a working electrode was 20.0 cm^2. A ceramic plate with the pore size 900 nm was used as a membrane. A platinum grid served as an anode, and the anolyte was a saturated solution of the background used in the catholyte in the corresponding solvent.

^{1}H NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer (400 MHz) relative to the signal of residual protons of the deuterated solvent used as an internal standard.

IR spectra were measured on a Vector-22 spectrometer (Bruker) in the frequency range from 400 to 3600 cm^{-1} in KBr pellets.

Electron ionization (EI) spectra were obtained on a TRACE MS quadrupole mass spectrometer (ThermoQuest). A probe was supplied using the direct injection process (DIP) with water cooling. Peaks of fragmentation ions with the relative intensity less than 5% are not presented.

Dimethylformamide was dried with K_2CO_3 and CaH_2 and distilled from molecular sieves. Benzene was dehydrated by distillation with sodium. Purified anhydrous solvents were stored under a dry argon atmosphere.

The supporting salt Et_4NBF_4 was prepared by mixing an aqueous solution of Et_4NOH (30%) and HBF_4 until the neutral pH value of the indicator. The precipitate formed (Et_4NBF_4) was filtered off, recrystallized twice from ethanol, and dried in a vacuum desiccator at 100 °C for 48 h.

Fluorinated alkyl halides (Close Corporation NPO P&M Invest) and α-methylstyrene (Acros) were used. α-Methylstyrene was purified by fractionation. All syntheses were carried out under a dry argon atmosphere.

Synthesis of 2,3-dimethyl-1,4-bis(perfluoroalkyl)-2,3-diphenylbutanes 1 and 2 (general procedure). The complex $NiBr_2$bipy (1.5 mmol), perfluoroalkyl halide (15 mmol), and α-methylstyrene (15 mmol) in DMF (70 mL) were placed in an electrochemical cell. Electrolysis was carried out with divided anodic and cathodic spaces with magnetic stirring at a continuous argon flow. Electricity (1000 mA h^{-1}) was passed through the electrolyte. After the end of electrolysis, the reaction mixture was washed with water and the organics was extracted with benzene (3×100 mL). The organic layer was dried with $MgSO_4$ for 24 h, the solvent was concentrated, and the white crystals formed were filtered off, washed with diethyl ether, and dried *in vacuo* with an oil pump.

2,3-Dimethyl-1,4-bis(perfluorohexyl)-2,3-diphenylbutane (1). The yield was 4.6 g (70%), m.p. 160—162 °C. ^{1}H NMR (C_6D_6), δ: 1.46 (d, 3 H, CH_3, $^3J_{H,H}$ = 3.3 Hz); 2.25, 3.23 (both m, 2 H, CH_2); 7.07—7.19 (m, 5 H, C_6H_5). IR (KBr), ν/cm^{-1}: 1144, 1208, 1237 (C—F); 1602 (C=C, arom.); 3069 (HC=). MS (EI), m/z (I_{rel} (%)): 437.0 $[1/2\ M]^+$ (100), 418.0 $[1/2\ M - F]^+$ (5), 167.0 $[1/2\ M - C_5F_{11} - H]^+$ (20), 149.1 $[1/2\ M - C_5F_{12}]^+$ (18), 123.0 $[1/2\ M - C_6H_5 - C_4F_{10} - H]^+$ (42), 118.0 $[1/2\ M - C_6F_{13}]^+$ (36), 103 $[1/2\ M - C_6F_{13} - CH_3]^+$ (40), 91.0 $[C_7H_7]^+$ (60), 69.0 $[CF_3]^+$ (20). Found (%): C, 41.28; H, 2.45. $C_{30}H_{20}F_{26}$. Calculated (%): C, 41.19; H, 2.29.

2,3-Dimethyl-1,4-bis(6*H*-perfluorohexyl)-2,3-diphenylbutane (2). The yield was 3.2 g (49.6%), m.p. 156—158 °C. ^{1}H NMR (C_6D_6), δ: 1.36 (d, 3 H, CH_3, $^3J_{H,H}$ = 3.5 Hz); 2.22, 3.15 (both m, 2 H, CH_2); 6.063 (tt, 1 H, $^2J_{H,F}$ = 52.09 Hz, $^3J_{H,F}$ = 5.14 Hz); 7.00—7.20 (m, 5 H, C_6H_5). IR (KBr), ν/cm^{-1}: 1145, 1208, 1238 (C—F); 1600 (C=C, arom.); 3071 (HC=). MS (EI), m/z (I_{rel} (%)): 419.0 $[1/2\ M]^+$ (30), 418.0 $[1/2\ M - H]^+$ (5), 167.0 $[1/2\ M - C_5F_{10} - H]^+$ (15), 148.0 $[1/2\ M - C_5F_{12} - H]^+$ (15), 123.0 $[1/2\ M - C_6H_5 - C_4F_{10} - H]^+$ (35), 118.0 $[1/2\ M - C_6F_{12} - H]^+$ (15), 103 $[1/2\ M - C_6F_{12} - CH_3]^+$ (35), 91.0 $[C_7H_7]^+$ (60), 69.0 $[CF_3]^+$ (20), 51 $[CF_2H]^+$ (100). Found (%): C, 42.58; H, 2.51. $C_{30}H_{22}F_{24}$. Calculated (%): C, 42.96; H, 2.62.

2,3-Diacetoxy-1,4-bis(6*H*-perfluorohexyl)butane (3). The complex $NiBr_2$bipy (0.209 g, 0.56 mmol), 6*H*-perfluorohexyl bromide (2.39 g, 5.6 mmol), and vinyl acetate (0.48 g, 5.6 mmol) in DMF (70 mL) were placed in an electrochemical cell. Electrolysis was carried out without division of the anodic and cathodic spaces with magnetic stirring at a continuous argon flow. Electricity (2 A per mole of the starting 6*H*-perfluorohexyl bromide (300 mA h)) was passed through the electrolyte. After the end of electrolysis, the reaction mixture was washed with water and the organics was extracted with benzene (3×100 mL). The organic layer was dried with $MgSO_4$ for 24 h, and the solvent was concentrated. The residue was purified by chromatography. Compound **3** was obtained in a yield of 0.98 g (51%), colorless liquid. ^{1}H NMR ($(CD_3)_2CO$), δ: 2.03 (s, 3 H, CH_3); 2.12 (s, 3 H, CH_3); 2.63 (m, 2 H, CH_2); 2.80 (m, 2 H, CH_2); 4.39 (2 H, CH); 6.81 (tt, 2 H, $^2J_{H,F}$ = 50.86 Hz, $^3J_{H,F}$ = 4.51 Hz). IR (KBr), ν/cm^{-1}: 1142, 1207, 1235 (C—F); 1760 (C=O). MS (EI), m/z (I_{rel} (%)): 773.93 $[M]^+$ (80). Found (%): C, 30.39; H, 1.35. $C_{20}H_{14}F_{24}O_4$. Calculated (%): C, 31.01; H, 1.81.

X-ray diffraction analyses of compounds 1 and 2 were carried out at the Department of X-ray Diffraction Studies (Collective Use Center of the Russian Foundation for Basic Research) on a Bruker Smart Apex II diffractometer at 20 °C (Mo-K_α radiation, multiscan mode). The structures were solved by a direct method using the SIR program and refined first in the isotropic approximation and then in the anisotropic approximation (SHELXL-97 and WinGX programs). Positions of hydrogen atoms were revealed from difference series of the electron density and refined in the isotropic approximation.

The X-ray diffraction data for compounds **1** and **2** were deposited with the Cambridge Crystallographic Data Centre (CCDC Nos 720 933 and 720 934, respectively) and are available at www.ccdc.cam.ac.uk/data_request/cif.

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