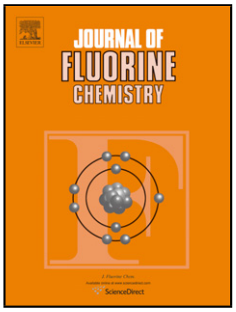

Title: Novel Electrochemical Pathway to Fluoroalkyl
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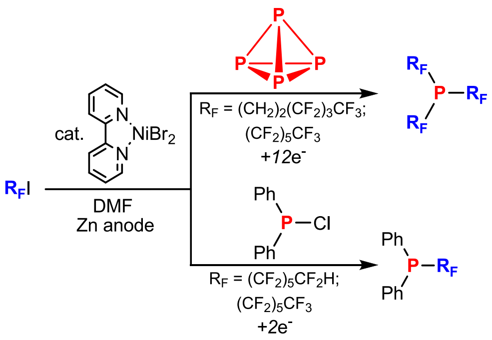
***Graphical Abstract - Pictogram**



The electrochemical joint reduction of fluoroalkyl iodides in presence of 2,2’-bipyridine nickel dibromide with white phosphorous or diphenylchlorophosphine leads effectively to fluoroalkyl phosphines in mild conditions.

- Organofluorine phosphines are obtained from white phosphorous under electrocatalysis
- The procedure is applicable for partly fluorinated and fully fluorinated phosphines
- Electrocatalytic coupling with diphenylchlorophosphine leads to fluorinated product
- Electrochemically generated bypiridine nickel (0) complex serves as catalyst
- Available fluoroalkyl iodides are used as the fluoroalkyl sources

Novel Electrochemical Pathway to Fluoroalkyl Phosphines and Phosphine Oxides

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Abstract

Novel versatile electrocatalytic route for obtaining fluoroalkylated phosphines and phosphine oxides from white phosphorous or diphenylchlorophosphine is discussed. This process occurs under electrochemical generation of nickel complexes in low oxidation state during undivided electrolysis of organofluorine iodides and phosphorous-containing substrate in mild conditions without supporting electrolyte.

Keywords: Electrocatalysis, white phosphorus, nickel complex, fluoroalkyl halides, fluorinated phosphines

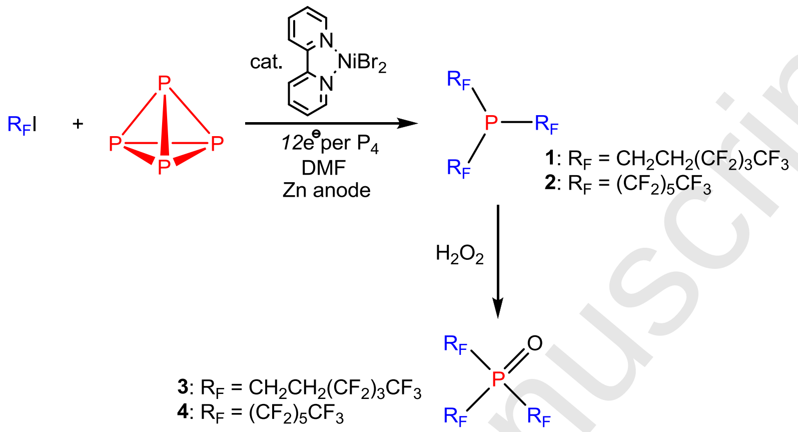
1. Introduction

Among organofluorine compounds, those containing perfluoroalkyl groups (R_F) have became especially important; thus, it is required to develop new approaches to introducing these particular groups. Perfluoroalkylsubstituted phosphines have lately drawn much attention due to their potential applications as ligands in organometallic chemistry [1-8] particularly in fluorous biphase catalysis [9]. Phosphines functionalized with perfluorinated chains are known for their thermomorphic properties with a significant increase in solubility observed on raising the temperature [10-11]. Lastly, fluorine substitution has been successfully employed in phosphorus chemistry to increase bioabsorption and metabolic stability of biologically important compounds. After a pioneer work of Emeleus and Hazeldine [12] reporting the first synthesis of tris(trifluoromethyl)phosphine in 1953 some efforts in the field of perfluoroalkylphosphines have been made. In 1999 Lagow and coworkers reported direct elemental fluorination of trialkylphosphines in the solution phase reactor [13], Caffyn *et al* perfomed the synthesis of tris(perfluoroalkyl)phosphines by the reaction of triphenylphosphite with Ruppert's reagent (R_FSiMe_3) [14]. Alternative synthetic procedure for synthesis of diphenyl(perfluoroalkyl)phosphines was based on the reaction of trimethylsilylphosphines with corresponding perfluoroalkyl iodides [15]. Recently published comprehensive review on fluoroalkyl-containing phosphines has only short column devoted to direct synthesis of R_FI with elemental phosphorus and majority of methods have obvious drawbacks [16]. Partially fluorinated phosphines with "fluorous ponyltails" ($-(CH_2)_n-R_F$) recently have gained much attention [9]. First report on the synthesis of $P(CH_2CH_2(CF_2)_5CF_3)_3$ published in 1985 was based on utilizing PCl_3 and $IZnCH_2CH_2R_{F6}$ [17]. Further developments in this field were made by using Grignard reagents [18] of fluoroalkyl halides. Gladysz and co-workers reported procedure from gaseous PH_3, fluorinated olefins and radical initiators [19]. The synthesis of $(R_F)_3P$ by means of reduction of the difuorophosphoranes $(R_F)_3PF_2$ with the $NaBH_4$ is known [20-21]. Apparently, this method is not suitable for long-chain Rf phosphines, as only experiments with phosphoranes of C_2 and C_4 and their products were described in the patent. Although the higher perfluoroalkyl derivatives were included in the general patent formula, the authors specify that the C1-C4 derivatives are preferred. Initial perfluoroalkyl phosphoranes are produced by electrochemical fluorination of corresponding trialkylphosphines (49-74%) or phosphine oxides (24-46% yield) in anhydrous hydrogen fluoride, and as can be expected, the yield of tris(perfuoroalkyl)difuorophosphoranes diminishes with increasing number of CH2 groups in the aliphatic chain of the starting trialkylphosphine due to adverse degradation processes [22-24]. Although growing interest in a last few decades resulted in number of publications on the synthesis of tertiary fluoroalkylphosphines the convenient route for obtaining these compounds is a question of a great demand.

The interest in the direct synthesis of organophosphorus compounds from elemental phosphorus, escaping the traditional stages of its chlorination, stems from the increasing needs to reorient the chemical technology towards the strategic target of combining increased ecological safety with low-waste production. In this context, a replacement of the current process for the preparation of organophosphorus compounds using phosphorus chloride and oxychloride is of paramount importance. We previously described the convenient electrochemical pathway to triarylphosphines from white phosphorous [25-30]. However, this approach was unsuccessful in case of alkylphosphines. Furthermore, just recently we developed the electrocatalytic fluoroalkylation of olefins with readily available fluoroalkyl halides as a source of organofluorine moieties [31-33]. The scope of the current contribution is to obtain organofluorine phosphines and phosphine oxides from white phosphorus or diphenylchlorophosphine by means of the electrosynthesis mediated by highly reactive nickel species.

2. Results and Discussion

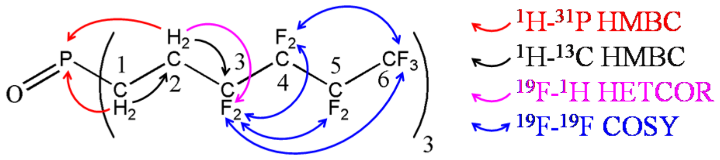
We demonstrate herein the possibility to prepare compounds with P-C bonds directly from white phosphorus and organofluorine halides under the action of electrochemically generated complexes of nickel in low oxidation state or organofluorine σ-complexes, obtained on their basis. For this purpose, electrochemical reduction of solutions of fluoroalkyl iodides in DMF in the presence of tetraphosphorus emulsion and (bpy)NiBr$_2$ complex as a catalyst were performed (Scheme 1).



Scheme 1. Electroreductive preparation of fluoroalkyl derivatives of white phosphorous. The reaction proceeds in undivided electrochemical cell equipped with Pt-cathode and sacrificial Zn-anode without any supporting electrolyte. Electroconductivity was provided by NiBr$_2$bpy at the beginning of the reaction, and in the initial stage of the process was fair and quickly became very good after dissolving the zinc anode. Tertiary phosphines are observed in all cases as major products in reaction mixture by ^{31}P NMR (more than 90%). E$_p$ reduction for NiBr$_2$bpy is -1.50V, for $C_6F_{13}I$ -1.76V and $C_6H_4F_9I$ -1.80V (GC, DMF, ref.Ag/AgNO3) respectively.

The oxidation of phosphine to phosphine oxide probably proceeds under the action of oxygen trace and at the product isolation stage because no special precautions were taken and nickel compounds are known to promote this reaction.[34-35] It is shown previously that the autocatalytic transformation of phosphines to phosphine oxides under tine influence of Ni° complexes and molecular oxygen at room temperature takes place. To avoid this reaction, syntheses should be carried out in the absence of oxygen at all stages using the so-called argon line and at below -5 °C.

However, we targeted to show the proof-in-principle of organofluorine addition to white phosphorous and it was decided to further oxidize the phosphine to phosphine oxides, which are easy to handle. Whereas compounds **1** and **3** are new, **2** [13,14] and **4** [17,23] were previously reported. The important aspect is that the electrolyses were performed without any supporting electrolyte which simplifies the product isolation and makes this method more convenient. It should be noted that in absence of nickel catalyst and in presence of supporting electrolyte the phosphines can be observed by ^{31}P NMR spectra, however the yields are poor and there are various undesired side products. In this case, ^{31}P NMR spectrum shows phosphines (less than 10%), phosphine oxides, phosphonium salts and therefore electrosynthesis proceeds nonselectively. The structure of product **3** was fully characterized by variety of NMR correlation methods. Starting from phosphorus the molecule structure up to C_3 carbon can be directly established by 2D ^{1}H-^{31}P HMBC and ^{1}H-^{13}C HSQC/HMBC, connectivities (Fig. 1). Unfortunately due to large quantity of vicinal fluorine atoms with strong spin-spin couplings to more remote fluorine bearing carbons (C_4-C_6) their intensities are dramatically diminished and therefore no signals were assigned in ^{13}C NMR spectra for these carbons (ESI). Proton-fluorine and fluorine-fluorine correlation NMR experiments were particularly helpful in this case and allowed to us follow along the perfluorinated chain and thus establish the whole molecule structure. This conclusion in additionally supported by agreement of the calculated (GIAO B3LYP/6-31G(d)//B3LYP/6-31G(d), (see supporting information)) *versus* experimental ^{19}F chemical shifts (R^2 = 0.96). Moreover, comparison of experimental ^{1}H CSs with calculated for two main conformers of **3** (“disk” and “pyramid” like) let us suggest that this molecule in solution prefer the “disk”-like structure (Fig. 1).



tris(1H,1H,2H,2H-perfluorohexyl)phosphine oxide

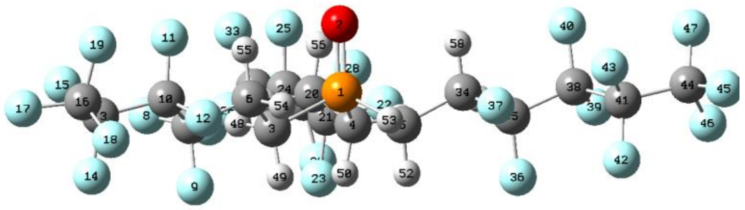
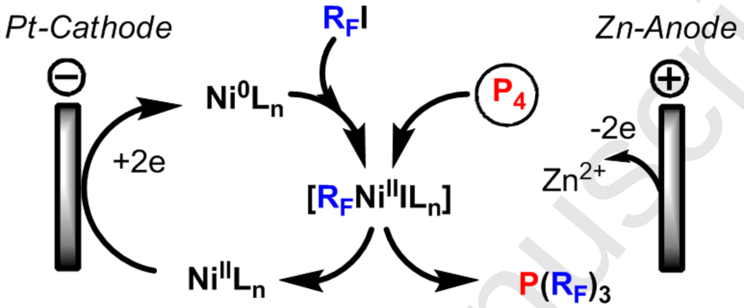


Figure 1. Principal ^{1}H-^{31}P/^{13}C HMBC, ^{1}H-^{19}F HETCOR and ^{19}F-^{19}F COSY connectivity’s for compound **3** (top). Main conformation of **3** (bottom).

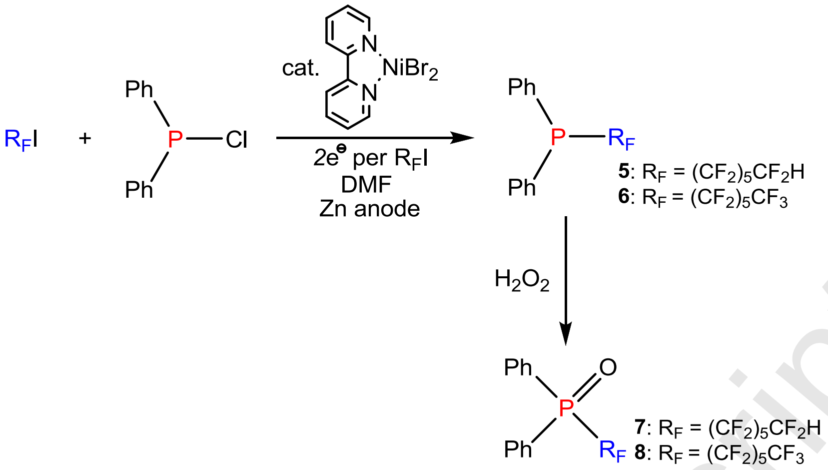
We suppose that white phosphorus can be involved in the reaction with perfluoroalkyl under conditions of cyclic regeneration of metallocomplex catalyst at the electrode. By analogy with the white phosphorus functionalization process by Grignard reagents, it is proposed that a key stage of the reaction consists in the interaction of organonickel compound, $[R_FNi^{II}XL_n]$, with white phosphorus according to the following sequence (Scheme 2). In course of the reaction several processes may occur. First of all, the tetraphosphorous molecule reacts with organofluorine sigma-complex of nickel similarly as for aryl-nickel complexes [28-29,35]. Another one is abovementioned Grignard-type functionalization. Moreover, the anode material is also important due to the possible formation of the corresponding intermediate metal phosphides with various reactivity and due to the favorable transmetallation at several stages. A variety of intermediates with P-R_F bond are formed during the synthesis. However the main feature is that the total process selectively yields to the full disclosure of all P-P bonds and result to the final product with three P-C bonds.



Scheme 2. Proposed reaction sequence.

The process scheme is given in general terms on the basis of detailed mechanism studies of the of activation and transformation of white phosphorus in systems containing Ni(0)L generated electrochemically, alkyl (or aryl) halide, sacrificial anode (Zn, Mg, Al), highly reactive σ-organonickel complexes in electrocatalytic processes, described earlier [29,30,36-38]. In order to confirm the white phosphorus pathway, the organonickel compound RNiXL formation and the functionalization of white phosphorus by this nickel complex were separated. The mechanism of P_4 functionalization is still not completely understood. Interestingly, the electrolysis of perfluoroalkyl halide in the presence of white phosphorus and zinc anode (in the absence of nickel complex catalyst) yields no desired fluoroalkyl phosphines or their oxides. So, intermediate organozink, R_FZnI, obtained by R_FX reduction in the presence of Zn^{2+} in these conditions does not allow to break the P-P bonds of white phosphorus or its oligomers selectively. The most part of the white phosphorus is polymerized in low reactive insoluble structures with a high content of phosphorus. Electrolysis in the divided electrolytic cell with the absence of zinc ion generated from the anode does not produce the desired products also.

Earlier we described nickel-catalyzed electrochemical coupling between mono- or di-chlorophenylphosphines and aryl or heteroaryl halides [39]. Aiming to expand the scope of the proposed method we decided to alter the source of phosphorous and therefore examined the electrocatalytic fluoroalkylation with diphenylchlorophosphine (Scheme 3).



Scheme 3. Electrocatalytic fluoroakylation of diphenylchlorophosphine.

The structure of compound **7** was unequivocally established directly starting from one "end" of molecular up to another "end" through variety NMR connectivity's (^{1}H-^{13}C HMBC, ^{1}H-^{31}P HMBC, ^{1}H-^{19}F HETCOR, ^{19}F-^{19}F COSY, ^{1}H-^{19}F HETCOR and finally ^{1}H-^{13}C HMBC). Moreover good correlation of the calculated (GIAO B3LYP/6-31G(d)//B3LYP/6-31G(d), (see supporting information)) *versus* experimental ^{19}F chemical shifts (R^2 = 0.98) additionally supports the above conclusion on the structure.

Compounds **6** and **8** were previously obtained by Rossi *et al.* upon reaction of Ph_2P^- ions and R_FI in HMPA, DMPU or liquid ammonia and under photochemical irradiation [40]. However, the yields of diphenyl(perfluorohexyl)phosphine **6** were low and authors do not provide ^{31}P NMR data for diphenyl(perfluorohexyl)phosphine.

3. Conclusions

Hereby we report one-step versatile and convenient method for obtaining organofluorine derivatives of phosphorous, directly from white phosphorus or diphenylchlorophosphine with good yields. Electrochemically generated nickel (0) complex with 2,2'-bipyridine serves as catalyst. The procedure is applicable either for partly fluorinated as well as fully fluorinated phosphines and phosphine oxides. Moreover, it was possible to avoid the use of hazardous PH_3, air and moisture sensitive organometallic reagents, complicated reactors, high temperatures and pressure. The ability to perform the reaction without any supporting electrolyte greatly simplifies the workup procedure. Further efforts are forwarded to discover the mechanistic details of these intriguing reactions.

4. Experimental

4.1. General consideration

All reactions were carried out under dry argon atmosphere. All solvents employed were purified and dried prior to use. *N*,*N*-Dimethylformamide was purified by double fractionation distillation over melting potash. Organofluorine iodides was purchased from P&M Invest and used without further purification. Preparative electrolyses were performed by means of the direct current source B5-49 in thermostatically controlled cylindrical undivided 80 mL electrolyser (a three-electrode cell). Platinum with surface area of 20 cm^2 was used as a cathode, Zn-rod as an anode. The working electrode potential was determined using reference electrode SCE. Electrolysis was carried out at constant current. The high rate of the catalyst regeneration allows using the constant current density of 5 mA/cm^2, but the cathode potential was controlled and consistent to nickel complex reduction. During electrolysis, the electrolyte was stirred with a magnetic stirrer. Mass spectra were recorded in EI mode using ThermoQuest TRACE MS. (Bpy)NiBr$_2$ was prepared according reported procedure [41].

4.2. NMR experiments

NMR investigation was carried out in the NMR department (A.E.Arbuzov Institute of Organic and Physical Chemistry) of the Federal Collective Spectral Analysis Center for physical and chemical investigations of structure, properties and composition of matter and materials. NMR experiments were carried out with Bruker spectrometers AVANCE-400 (161.9 MHz (^{31}P),400.1 MHz (^{1}H), 376.5 MHz (^{19}F), 100.6 MHz (^{13}C)) equipped with a pulsed gradient unit capable of producing magnetic field pulse gradients in the z-direction of 53.5Gcm^{-1}. Chemical shifts are reported in the δ (ppm) scale relative to the residual ^{1}H and ^{13}C signal of $(CD_3)_2CO$, (C_6D_6) andto external 85% H_3PO_4 for ^{31}Pand C_6F_6 (-164.9 ppm) for ^{19}FNMR spectra. Chemical shifts were calculated within the DFT framework using a hybrid exchange-correlation functional, B3LYP, at the 6-31G(d) level as implemented in Gaussian 98 [33]. Full geometry optimizations were done at the same level of theory. All data were referred to TMS (^{1}H and ^{13}C) and C_6F_6 chemical shifts that were calculated under the same conditions.

4.3. Electrosynthesis of tris(1H,1H,2H,2H-perfluorohexyl)phosphine (**1**).

Electrochemical cell was charged with 0.185 g (1.5 mmol, 1 eq) of P_4, 0.112 g (0.3 mmol, 0.2 eq) of NiBr$_2$bpy, 6.7 g (18 mmol, 12 eq.) of 1H,1H,2H,2H-perfluorohexyl iodide and DMF (50 ml) was added. The amounts of electricity passed through the electrolyte were 2F per one mole of 1H,1H,2H,2H-perfluorohexyl iodide (965mA·h). After completing the electrolysis, the reaction mixture was concentrated on rotary evaporator. The orange oily residue showed a major product of $P(CH_2CH_2(CF_2)_3CF_3)_3$ by ^{1}H NMR and ^{31}P NMR. ^{1}H NMR: (400 MHz,

$(CD_3)_2CO$)δ= 1.72 (m, 6H), 2.24 (m, 6H) and $^{31}P\{^1H\}$ (161.94 MHz, $(CD_3)_2CO$)δ= -23.5 (s). EIMS, *m/z*: 772 $[M]^+$, 753, 653, 603, 539, 456. The residue was used without further purification for the next step of synthesis.

*4.4. Synthesis of tris(1H,1H,2H,2H-perfluorohexyl)phosphine oxide (***3***).*

The residue after synthesis of compound **1** was transferred into 100 ml round-bottom flask and treated with an excess of 10% hydrogen peroxide. After 2 hours the mixture was washed with hexane (3x40 ml), the organic layer was separated, dried over $MgSO_4$and the solvent was removed. The oily solid residue was washed with cold diethyl either (20 ml) on a frit to give $O{=}P(CH_2CH_2(CF_2)_3CF_3)_3$ as a white solid (3.02 g, 64% based on white phosphorous, 21% current efficiency). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ= 2.33 (m, 6H), 2.64 (m, 6H); $^{31}P\{^1H\}$ NMR (161.94 MHz, $(CD_3)_2CO$) δ= 44.02 (s). ^{13}C NMR (100.6 MHz, $(CD_3)_2CO$): δ = 19.75 (d, $^2J_{PC}$ = 67.5 Hz, C^1), 24.37 (t, $^3J_{CF}$ = 22.5 Hz, C^2), 120 (C^3). ^{19}F NMR (376.5 MHz, $(CD_3)_2CO$): δ = -81.98 (t, 3F, $^4J_{FF}$ = 9.63 Hz, CF_3), -115.37 (s, 2F, at C^3), -124.66 (s, 2F, at C^4), -126.68 (t, 2F, $^4J_{FF}$ = 10.48 Hz, at C^5). EIMS, *m/z*: 788 $[M]^+$, 769, 669, 555, 472. Anal.calcd. for $C_{18}H_{12}F_{27}OP$: C, 27.43; H, 1.53; P, 3.93; found: C, 27.94; H, 1.72; P, 3.57.

*4.5. Electrosynthesis of tris(perfluorohexyl)phosphine (***2***).*

Electrochemical cell was charged with 0.185 g (1.5 mmol, 1 eq) of P_4, 0.112 g (0.3 mmol, 0.2 eq) of $NiBr_2$bpy,8.03 g (18 mmol, 12 eq.) of perfluorohexyl iodide and DMF (50 ml) was added. The amounts of electricity passed through the electrolyte were 2F per one mole of perfluorohexyl iodide (965mA·h). After completing the electrolysis, the reaction mixture was concentrated on rotary evaporator. The vinous oily residue showed a major product of $P(CF_2(CF_2)_4CF_3)_3$ by ^{19}F NMR and ^{31}P NMR. ^{19}F NMR (376.5 MHz, $(CD_3)_2CO$): δ: -81.05 (s, CF_3); -114.25 (d, $^2J_{PF}$ = 61.2 Hz,2F, at C^1); -122.23 (s, 2F, at C^2); -123.30 (s, 2F, at C^3); -124.21 (s, 2F, at C^4); -126.01 (s, 2F, at C^5) and $^{31}P\{^1H\}$ (161.94 MHz, $(CD_3)_2CO$)δ= 26.6 (br s) [lit.[13,14] 27.9 (br)]. EIMS, *m/z*: 988 $[M]^+$. The residue was used without further purification for the next step of synthesis.

*4.6. Synthesis of tris(perfluorohexyl)phosphine oxide (***4***).*

The residue after synthesis of compound **2** was transferred into 100 ml round-bottom flask and treated with an excess of 10% hydrogen peroxide. After 2 hours the mixture was washed with hexane (3x40 ml), the organic layer was separated, dried over $MgSO_4$and the solvent was removed. The oily solid residue was washed with cold diethyl either (20 ml) on a frit to give 3.36 g (56% based on white phosphorous, 18% current efficiency) $O{=}P(C_6F_{13})_3$.$^{31}P\{^1H\}$

NMR (161.94 MHz, $(CD_3)_2CO$) δ= 22.5(m), [lit.[17,23]25.6]. ^{19}F NMR (376.5 MHz, $(CD_3)_2CO$): δ = -81.67 (t, 3F, $^4J_{FF}$ = 8.7 Hz, CF_3), -114.12 (d, 2F, $^2J_{PF}$ = 59.9 Hz, at C^1), -122.31 (s, 2F, at C^2), -123.38 (s, 2F, at C^3), -124.01 (s, 2F, at C^4), -126.71 (2F, at C^5). EIMS, *m/z*: 1004 $[M]^+$. Anal.calcd. for $C_{18}F_{39}OP$: C, 21.51; P, 3.09; found: C, 21.38; P, 3.15.

*4.7. Electrosynthesis of diphenyl(6H-perfluorohexyl)phosphine (**5**).*

Electrochemical cell was charged with 0.617 g (2.8 mmol, 1 eq) of diphenylchlorophosphine, 0.21 g (0.56 mmol, 0.2 eq) of $NiBr_2bpy$, 1.197g (2.8 mmol, 1 eq.) of 6H-perfluorohexyl iodide and DMF (50 ml) was added. The amounts of electricity passed through the electrolyte were 2F per one mole of 6H-perfluorohexyl iodide (150 mA·h). After completing the electrolysis, the reaction mixture was concentrated on rotary evaporator. The brown oily residue showed a major product of $Ph_2P(C_6F_{12}H)$ by ^{1}H NMR and ^{31}P NMR. ^{1}H NMR: (400 MHz, C_6D_6)δ= 5.52 (tt, 1H, $^2J_{HF}$=51.6 Hz, $^3J_{HF}$=5.32 Hz), 7.28-745 (m, 10H), 7.61-7.75 (m, 4H) and $^{31}P\{^1H\}$ NMR (161.94 MHz, C_6D_6) δ= 1.9 (t, $^2J_{PF}$=83.4 Hz). EIMS, *m/z*: 486 $[M]^+$, 185, 183, 108, 51. The residue was used without further purification.

*4.8. Synthesis of diphenyl(6H-perfluorohexyl)phosphine oxide (**7**).*

The residue after synthesis of compound **5** was transferred into 100 ml round-bottom flask and treated with an excess of 10% hydrogen peroxide. After 2 hours the mixture was washed with hexafluorobenzene (3x30 ml), the organic layer was separated, dried over $MgSO_4$and the solvent was removed. The oily solid residue was washed with cold diethyl either (10 ml) on a frit to give $O{=}PPh_2(C_6F_{12}H)$ as a white solid (0.98 g, 71% based on diphenylchlorophosphine, 69.8% current efficiency). The product has minor phosphine impurity by ^{31}P NMR (10 %) which can be removed by column chromatography on silica gel (Et_2O:CH_2Cl_2, 8:2).^{1}H NMR (400 MHz, C_6D_6) δ= 5.08 (tt, 1H, $^2J_{HF}$=50.86 Hz, $^3J_{HF}$=5.78 Hz, H^6), 8.04 (m, 4H), 7.95 (m, 4H), 6.9-7.75 (m, 2H); $^{31}P\{^1H\}$ NMR (161.94 MHz, C_6D_6) δ= 23.4 (t, $^2J_{PF}$=69.24 Hz). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 108.59 (tt, $^2J_{FC}$=253.62 Hz,$^3J_{FC}$=32.80 Hz, C^6), 131.58 (s, Ph), 133.14 (d, $^2J_{CP}$=9.56 Hz,C_{ipso}at Ph). ^{19}F NMR (376.5 MHz, C_6D_6): δ = -108.44 (dt, $^3J_{FF}$ = 13.17 Hz, $^3J_{PF}$ = 54.83 Hz, 2F at C^2), -118.08 (dt, $^3J_{FF}$ = 14.36 Hz, $^2J_{PF}$ = 68.56 Hz, 2F at C^1), -121.50 (t, $^4J_{FF}$ = 10.73 Hz, 2F at C^3), -123.18 (s, 2F at C^4), -129.40 (s, 2F at C^5), -136.84 (s, 2F at C^6). EIMS, *m/z*: 502 $[M]^+$, 201, 200, 51. Anal.calcd. for $C_{18}H_{11}F_{12}OP$: C, 43.05; H, 2.21; P, 6.17; found: C, 43.51; H, 2.46; P, 6.34.

*4.9. Electrosynthesis of diphenyl(perfluorohexyl)phosphine (**6**).*

Electrochemical cell was charged with 0.617 g (2.8 mmol, 1 eq) of diphenylchlorophosphine, 0.21 g (0.56 mmol, 0.2 eq) of $NiBr_2bpy$, 1.25 g (2.8 mmol, 1 eq.) of perfluorohexyl iodide and DMF (50 ml) was added. The amounts of electricity passed through the electrolyte were 2F per one mole of perfluorohexyl iodide (150 mA·h). After completing the electrolysis, the reaction mixture was concentrated on rotary evaporator. The residue was washed with a saturated ammonium chloride solution (3x50) and extracted with hexafluorobenzene (3x50). The organic layer was separated, dried over $MgSO_4$ and the solvent was removed. The brown oily residue showed a major product of $Ph_2P(C_6F_{13})$ by ^{1}H NMR and ^{31}P NMR. ^{1}H NMR: (400 MHz, C_6D_6)δ= 8.02 (4H, m), 7.78 (2H, m), 7.41 (4H, m) and ^{31}P NMR {^{1}H} (161.94 MHz,C_6D_6)δ= 2.83 (br.s). The residue was used without further purification.

*4.10. Synthesis of diphenyl(-perfluorohexyl)phosphine oxide (**8**).*

The residue after synthesis of compound **6** was transferred into 100 ml round-bottom flask and treated with an excess of 10% hydrogen peroxide. After 2 hours the mixture was washed with hexafluorobenzene (3x30 ml), the organic layer was separated, dried over $MgSO_4$and the solvent was removed. The oily solid residue was washed with cold diethyl either (10 ml) on a frit to give $O{=}PPh_2(C_6F_{13})$ as a white solid (1.06 g 73% based on diphenylchlorophosphine, 68.7% current efficiency). The product was purified by column chromatography on silica gel ($Et_2O:CH_2Cl_2$, 8:2).^{1}H NMR (400 MHz, C_6D_6) δ= 8.04 (4H, m), 7.78 (2H, m), 7.14 (4H, m).^{31}P{^{1}H} NMR (161.94 MHz, C_6D_6) δ= 23.78 (t $^2J_{PF}$ = 68.5 Hz) [lit.[42] 24.58 (t $^2J_{PF}$ = 71 Hz)].^{19}F NMR (376.5 MHz, C_6D_6): δ = -81.70 (s, CF_3), -109.71 (d, $^2J_{PF}$ = 60.12 Hz, 2F at C^1), -122.22 (s, 2F at C^2), -123.88 (s, 2F at C^3), -124.54 (s, 2F at C^4), -126.70 (s, 2F at C^5).EIMS, *m/z*: 520 $[M]^+$, 501, 201, 69. Anal.calcd. for $C_{18}H_{10}F_{13}OP$: C, 41.54; H, 1.92; P, 5.96; found: C, 41.05; H, 1. 64; P, 6.13.

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