



Review

Prospects of synthetic electrochemistry in the development of new methods of electrocatalytic fluoroalkylation



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ABSTRACT

Principal achievements and modern trends in the development of new methods of electrocatalytic fluoroalkylation are analysed and generalised. Possibilities and advantages of the electrochemical preparation of fluoroalkyl compounds are demonstrated. The attention is focused on the fluoroalkylation of olefins, σ -fluoroorganonickel complexes reactivity, aromatic perfluoroalkylation, fluoroalkyl phosphines and phosphine oxides synthesis, ligand directed C–H-fluoroalkylation.

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1. Introduction

The field of fluoroorganic chemistry has grown rapidly in recent years, and nowadays fluorochemicals are utilized for a variety of different applications ranging from pharmaceutical chemistry to materials science [1–9]. As developmental pipelines for new drugs are predicted to contain an even higher percentage of fluorinated molecules, developing better methods to prepare organofluorines are expected to be paramount to the health industry. The reasons why fluorine has become an important functionality in drug design are manifold, but most commonly attributed to polarity effects, chemical and metabolic stability, conformation effects, and

lipophilicity. Fluorinated molecules have established a remarkable record in contemporary medicinal chemistry and that fluorinated compounds will surely play a continuing role in providing lead compounds for therapeutic applications.

Despite the synthetic strategies for selective perfluoroalkylation have expanded significantly over the past decades, there are only a few catalytic methods to incorporate perfluoroalkyl groups into aromatic or olefinic substrates [10–14]. Known methods either require use of harsh reaction conditions or suffer from limited substrate scope. Therefore, synthetic methodology to incorporate fluorine synthons must be improved in order to prepare complicated organofluorine molecules on a practical scale. Metal-catalysed cross-coupling procedures would greatly facilitate the construction of fluoroorganic molecules; however many areas in the field of metal-promoted perfluoroalkylation reactions are still underdeveloped and require further improvements.

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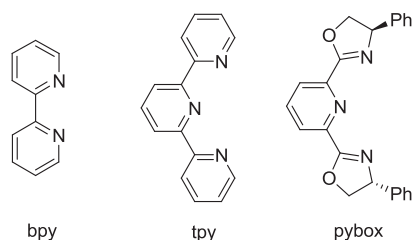
On the other hand transition-metal-catalysed C–C and C–P coupling reactions [15–17] are among the most valuable transformations in organic synthesis, and their importance was recognized by the scientific community with a 2010 Nobel Prize in chemistry [18,19]. These transformations are generally rests on catalytic cycle involving transition metal complexes at various oxidation states. In this context, electrochemistry provides advantageous methods both for synthetic purposes and for mechanistic investigation [20,21]. Electrosynthesis is useful in transition metal catalysis to generate the active catalyst form without specially added reducing or oxidizing agents. Performed in mild conditions it offers more environmentally non-polluting alternatives to traditional organic synthesis. Understanding mechanistic details of catalysed reactions may pave the way to the design of new and improved catalysts. Kinetics and thermodynamics of the electron transfer, bond cleavage, substitution, addition and other reactions can be provided, as well as intermediate species can be detected characterised by various electrochemical techniques with cyclic voltammetry being the most available and favourable one [22–30]. However, although electrochemical methods provide a way of mechanistic studying of reactions, they give no information on the structures of intermediates. Electrochemical methods should be used in combination with spectroscopy techniques like NMR, IR, UV–vis–NIR absorption, EPR or EXAFS to provide detailed characterization of the intermediate species [31,32].

Our group is interested in the development and mechanistic understanding of transition-metal-mediated electrocatalytic reactions, with a particular focus on perfluoroalkylation reactions. We also wish to gain insight into how to develop more examples of catalytic reactions at inexpensive and readily available first-row late metals such as Ni and Co which are particularly attractive for synthetic purposes, due to sufficiently low ionization potential to favour oxidative addition, sufficiently weak metal–carbon bonds, tendency to form square-planar complexes and to reach penta-coordination to allow insertion, sufficiently high electron affinity of Ni^{II} complexes to allow reductive elimination and the ability to accept different oxidation states (0, +1, +2, +3, +4) at different stages of a catalytic cycle [33–36]. Herein, we summarize the advances in electrocatalytic perfluoroalkylation methods which have been shown to be applicable for functionalization of diverse substrates, such as olefins, aryl halides, white phosphorus, chlorophosphines and arenes (ligand directed C–H functionalization), consider the intermediates of catalytic cycles and prospects of this interesting and promising research area. Depending on the substrate nature the microreview is divided into four sections elucidated the features of each reaction type.

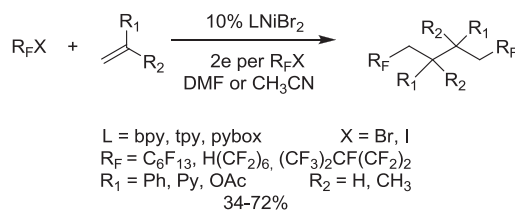
2. Results and discussion

2.1. Nickel-induced fluoroalkylation of olefins

Low valent transition metal complexes such as [Ni(tet a)](ClO₄)₂ [37], (Py)_xCoBr₂ [38], (Py)_xNiBr₂ [39] (tet a = 5,5,7,12,12,14-hexamethyl-1,4,-8, 11-tetra-azacyclotetradecan; Py = pyridine) are known to be efficient catalysts capable of electrochemical



Scheme 1. Ligands selected for catalytic purposes (bpy = 2,2'-bipyridine; tpy = 2,2':6',2''-terpyridine; pybox = (S,S)-2,6-bis(4-phenyl-2-oxazolin-2-yl)-pyridine).



Scheme 2. Electrocatalytic fluoroalkylation of olefins: addition–dimerization reaction.

generating organic radicals in olefin addition chemistry. In efforts to further expand the scope we set out to explore the possibility of using electrochemical methods to add perfluoroalkyl radicals across double bonds to generate new functionalized fluorocarbons.

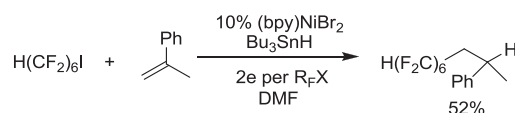
Dibromide nickel complexes LNiBr₂ with α -diimine ligands (Scheme 1) are proved to be efficient catalysts, providing the fluoroalkylation product of styrene derivatives in good or moderate yields (Scheme 2) [40–44].

The reaction results as an addition–dimerization sequence therefore the products bear two olefin and fluoroalkyl moieties and contain two stereocenters. Noteworthy, it was revealed that (bpy)NiBr₂ is the most effective catalyst of the studied reactions [41]. The products obtained have been characterized by NMR spectroscopy and X-ray analysis. Despite two diastereomeric forms could be formed, the X-ray diffraction data reveal only the major meso-forms. Thereat a complex of experimental and computational NMR techniques (including 1D and 2D experiments) was shown to be advantageous both to confirm the dimeric structure and to evaluate the diastereomers ratio (meso to dl), so the factors it depends on have been estimated [41,44]. Interestingly, the branching nature of the fluoroalkyl halides affects the diastereomeric ratio: isopentyl iodide favours dl form formation in comparison with linear perfluorohexyl iodide.

We also have shown the way to control whether addition of perfluoroalkyl radicals occurs with dimer or monomer formation. The use of tributyltin hydride as a hydrogen source prevents the dimerization and gives the monomeric product as described in Scheme 3 [44].

Detailed mechanistic study of the reaction has been performed using cyclic voltammetry and ESR spectroscopy. In DMF solution, for the complex with bpy the first two-electron (Ni^{II}/Ni⁰) reduction wave is reversible, while complexes with tpy and pybox are characterized by two one-electron reversible successive reduction stages (Ni^{II}/Ni^I/Ni⁰). ESR experiments show Ni^I metal-centred species formation upon reduction of the initial complexes [41,44] that is confirmed by the structural, magnetic, and electrochemical studies of isolated complex (tpy)NiBr [45]. The cyclic voltammograms for the reduction of selected Ni complexes in the presence of perfluoroalkyl halides have been used to evaluate the catalytic efficiency and reactivity of the catalysts and to unambiguously demonstrate the Ni^IL complex is the active catalyst form. The latter is proposed to react with R_FX to form a σ -complex LNiR_FBrX.

Organonickel σ -complexes are found to be the key intermediates in transformations of variety of substrates with C–Hal, P–P, P–Cl, C=C and other bonds [27,29,43,46]. These compounds are of special interest, because they are just on the limits of stability. Understanding the structure and properties of intermediate complexes involved in the catalytic cycle may pave the way to the design of new and improved catalysts. The known linear fluoroalkyl complexes of a nickel bipyridine framework (dtbpy)Ni(CF₃)₂,



Scheme 3. Electrocatalytic fluoroalkylation of olefins: monomer synthesis.

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