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ARTICLE

Electrocatalytic Reactivity of Imine/Oxime-type Cobalt Complex for Direct Perfluoroalkylation of Indole and Aniline Derivatives

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Imine/oxime-type cobalt complexes, regarded as simple vitamin B_{12} model complexes, were utilized as catalysts for direct C–H perfluoroalkylations of indole and aniline derivatives with nonafluorobutyl iodide (*n*-C_4F_9I) as the readily available perfluoroalkyl source. The synthetic approach described herein was performed under mild reaction conditions driven by controlled-potential electrolysis at –0.8 V *vs.* Ag/AgCl in organic solvents. The mechanistic investigations suggest that a nonafluoroalkyl radical is mediated by homolytic cleavage of the cobalt(III)–carbon bond in the catalytic cycle. This is the first report concerning a fluoroalkylation reaction of (hetero)aromatics catalyzed by the simple vitamin B_{12} model complex. The convenient electrocatalytic method employing a simple cobalt complex provides a facile synthesis method toward novel fluoroalkylated compounds, demonstrating potential applications in the fields of pharmaneutical chemistry and materials science.

Introduction

Organocobalt(III) complexes featuring a cobalt–carbon bond (Co–C) have attracted much attention in bioinorganic and organometallic chemistry due to the ability to produce carbon-centered radicals from homolytic cleavage of the Co–C bond in a controlled manner by photolysis, electrolysis, or thermolysis.[1-3] Vitamin B_{12} derivatives represent the most familiar biological source of radicals resulting from thermal homolysis; hence, vitamin B_{12}-type alkylcobalt complex is important as the most studied organometallic compound, promoting many bio-molecular transformations under mild conditions.[1, 4-6] Additionally, the imine/oxime-type cobalt complexes such as [Co(III){(C_2C_3)(DO)(DOH)pn}Br_2] (**C1**) and [Co(III){(DO)(DOH)pn}Br_2] (**C2**) (**Figure 1 (a)**), namely Costa-type complexes,[7, 8] are useful models for the vitamin B_{12} family.[9, 10] They contain an analogous square planar monoanionic ligand as the suitable model for the corrin framework and exhibit similar redox behaviors of Co(III)/Co(II) and Co(II)/Co(I) to those in natural vitamin B_{12}.[11-16] Nevertheless, the imine/oxime-type B_{12} models are less studied except for the main application in hydrogen evolution with a proton source.[17-20]

Fluoroalkyl-substituted organic compounds have been found in a range of fields including medicinal chemistry, agrochemistry, and materials science,[21-23] and there is a gradually increasing interest in synthetic methods for fluoroalkylation of organic compounds.[24-26] Compared to fluoroalkyl cation or anion intermediates with poor stabilization, radical methods for fluoroalkylation stand out.[27, 28] Nonetheless, catalytic radical fluoroalkylation assisted by Co–C bond is still less studied.[29-31] Soper's group has reported the (hetero)arene C–H trifluoromethylation activated by the new Co(III)–trifluoromethyl complex in stoichiometric protocols rather than the catalytic method.[29] Togni and co-workers reported a series of perfluoroalkyl cobaloximes and characterized their properities. However, the authors didn't explore the reactivity for fluoroalkylation of (hetero)arenes.[30] In 2019, Cobaloxime-catalyzed C–H monofluoroalkylation of styrenes was performed by Feng *et al*. group under photoinduced conditions.[31] These works promoted us to explore other cobalt-mediated catalytic fluoroalkylations. From the viewpoint of expanding the Co–C chemistry, naturally derived and simple vitamin B_{12} model complexes[9, 10, 32, 33] for fluoroalkylation of non-functionalized substrates have been of interest to us. In 2017, our group developed a Co(III)–C bond-mediated catalytic radical fluoroalkylation of (hetero)arenes under controlled-potential electrolysis catalyzed by a naturally derived vitamin B_{12} model complex, heptamethyl cobyrinate perchlorate [Cob(II)7C_1ester]ClO_4 (**C3**) (**Figure 1 (a)**).[34] This finding encouraged us to design fluoroalkylation of non-functionalized aromatic compounds based on the imine/oxime-type cobalt complexes (**C1** and **C2**) as catalysts due to the economic effect and versatile reactivity of the Co–C bond.

Here we designed fluoroalkylation reactions based on the non-functionalized indole and aniline derivatives as radical acceptors because that indole and aniline moiety are both useful building block for the preparation of functional products,[35-39] along with commercially available *n*-C_4F_9I as the fluoroalkylating reagent. The reactions were mediated by the simple vitamin B_{12} model complex, [Co(III){(C_2C_3)(DO)(DOH)pn}Br_2] (**C1**) as the catalyst through controlled-potential electrolysis under mild reaction conditions

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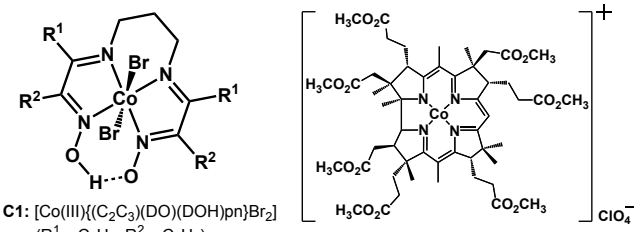
(**Figure 1 (b)**). This is the first example of a Co–C mediated radical perfluoroalkylation of (hetero)arenes catalyzed by simple vitamin B_{12} model complex using an electrochemical approach.

(a) Cobalt catalysts



(b) This work: perfluoroalkylations of indole (or aniline) derivatives

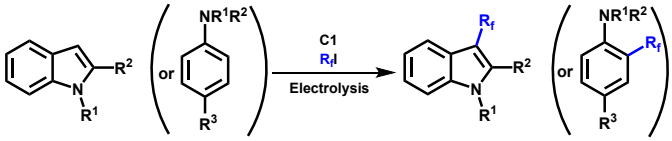


Figure 1. (a) Molecular structures of **C1, C2** and **C3**. (b) This work: method for perfluoroalkylation of indole and aniline derivatives catalyzed by **C1**.

Experimental Section

Materials and measurements. All chemical reagents and solvents used in this study were obtained from commercial sources and used as received unless otherwise stated. The imine/oxime-type cobalt complex, [Co(III){(C_2C_3)(DO)(DOH)pn}Br_2] (**C1**), was prepared according to the literature.[15] ^{1}H NMR and ^{19}F NMR spectra were recorded by using a JEOL JNM-ECZ400 NMR spectrometer at the Centre of Advanced Instrumental Analysis, Kyushu University. The chemical shifts (in ppm) of ^{1}H NMR were referenced relative to tetramethylsilane $(CH_3)_4Si$, with the residual solvent peak of chloroform-d ($CDCl_3$) at 7.26 ppm and methanol-d_4 at 3.31 ppm as an internal standard. The chemical shifts (in ppm) of ^{19}F NMR were referenced relative to hexafluorobenzene (C_6F_6) at –162.90 ppm in $CDCl_3$ and methanol-d_4. ^{13}C NMR spectra were recorded by using a Bruker Avance 500 NMR spectrometer and the chemical shifts (in ppm) were referenced relative to the residual solvent peak of $CDCl_3$ at 77.2 ppm. The coupling constants, J are reported in Hertz (Hz). Multiplicity is abbreviated as follows: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Cyclic voltammetry (CV) was carried out using a BAS ALS-630C electrochemical analyzer at a scan rate of 100 mV s^{-1}. The cell was equipped with three electrodes: an Ag/AgCl (3 M NaCl aq.) reference electrode, a platinum working electrode, and a platinum wire counter electrode. The experiments were performed in different solvents under N_2 atmosphere with tetrabutylammonium perchlorate (TBAP, 0.1 M) as the electrolyte. The concentrations of the analytes were 1×10^{-3} M. The gas chromatography-mass spectra (GC-MS) were obtained using a Shimadzu GCMS-QP2010SE equipped with an Agilent J&W DB-1 column (length: 30 m; ID: 0.25 mm; film: 0.25 µm) and helium as the carrier gas. For the measurement, the injector and detector temperatures were 250 °C, the oven temperature was initially held at 100 °C for 2 min, then increased to 240 °C at the rate of 10 °C / min. A 200 W tungsten lamp with a 420 nm cut-off filter (Sigma Koki, 42L) and a heat cut-off filter (Sigma Koki, 30H) purchased from TechnoSigma were used as the visible light irradiation experiment. Gel permeation chromatography (GPC) was carried out by a Japan Analytical Industry Co. Ltd., LC-908 apparatus equipped with a UV-3702 attachment using three connected columns, JAIGEL-1H, 2H, and 2.5H with a chloroform ($CHCl_3$) eluent. The high-resolution mass spectra (HRMS, EI-MS) were performed with a JEOL JMS-700 instrument. MALDI-TOF-MS spectrum was obtained on Autoflex III (Bruker Daltonics) under the linear/positive mode with dithranol as matrix. All the products were isolated by silica-gel column chromatography (Kanto Chemicals, 60N) and GPC; and then isolated products were identified by GC-MS, HRMS (EI-MS), ^{1}H, ^{19}F and ^{13}C NMR.

X-ray crystal structure analysis. The crystals were mounted on a loop. Diffraction data of crystal samples were collected at 93 K or 123 K using a Rigaku XtaLABmini CCD diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Collected data were integrated, corrected, and scaled using CrysAlisPro.[40] The structures were refined using SHELXT (Sheldrick, 2015)[41] Intrinsic phasing and SHELXL (Sheldrick, 2015).[42] All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and included in the structure factor calculation but were not refined. The program Olex 2 was used as a graphical interface.[43] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. The data can be obtained free of charge on application to CCDC, 12 Union Road, Canbridge CB21EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk). The CCDC numbers for crystal structures of **C1** and **3•C_4F_9** are 1951624, and 1966854, respectively.

General procedure for catalytic perfluoroalkylation reaction under electrochemical conditions.[34] Controlled-potential electrolysis were carried out in dry acetonitrile at –0.8 V *vs.* Ag/AgCl under N_2 atmosphere in an undivided electrolysis cell. The electrolysis cell was equipped with three electrodes; i.e., a platinum mesh cathode (7 mm × 25 mm × 0.07 mm thick), a sacrificial Zn-plate anode (5 mm × 20 mm × 0.1 mm thick), and an Ag/AgCl (3.0 M NaCl aq.) as a reference electrode. For a typical reaction, a 5 mL acetonitrile solution of **C1** (5.0×10^{-4} M) (1 mol%), 1,2-dimethylindole (**1**) (5.0×10^{-2} M), TBAP (n-Bu_4ClO_4) (0.1 M) and decafluorobiphenyl ($C_{12}F_{10}$) as the internal standard was degassed by N_2 gas and stirred at room temperature. N_2 gas was passed over the solution during the measurement to remove O_2 from the reaction system. Fluoroalkylating reagent (n-C_4F_9I, 3 eq. of substrate) dissolved in acetonitrile was taken into a 5 ml diameter syringe pump and then it was connected to a reaction cell. A constant flow (0.5 eq. of substrate per 1 h) of this solution was added into the reaction mixture for about 6 h. After the catalytic reaction, the reaction mixture was passed through a short silica-gel column to remove the catalyst and TBAP, and then analyzed by GC-MS. All the products were purified by silica-gel column chromatography and GPC. The authentic samples were characterized by NMR and mass spectrometry.

Results and Discussion

The structure of **C1** was unambiguously confirmed by X-ray crystallography analysis for the first time (**Figure S1** and **Table S1**). Firstly, the redox behavior of *n*-C_4F_9I was characterized by cyclic voltammetry (CV) at a scan rate of 100 mV s^{-1} by using tetrabutylammonium perchlorate (TBAP, *n*-Bu_4NClO_4) as the supporting electrolyte in acetonitrile (CH_3CN) (**Figure 2 (a)**). As shown in **Figure 2 (a)**, *n*-C_4F_9I can be directly reduced over –1.0 V *vs.* Ag/AgCl in CH_3CN. The result indicated that electrocatalytic potential for fluoroalkylation should be controlled below this value to avoid the reduction of *n*-C_4F_9I. To further confirm the formation of the Co(I) species, the redox behavior of **C1** was investigated under analogous conditions using CV with/without *n*-C_4F_9I in the described solvent (**Figure 2 (b)**). The reduction potentials for Co(III)/Co(II) and Co(II)/Co(I) couples in CH_3CN were observed at –0.15 V and –0.64 V *vs.* Ag/AgCl, respectively. In the presence of *n*-C_4F_9I, a new irreversible reduction peak at –1.10 V *vs.* Ag/AgCl appeared, which was attributed to the one-electron reduction of the Co–C_4F_9 complex.[44] Additionally, the solvent effect is critical for catalytic reactions since the polarity and reagent solubilizing ability of the solvent affect the rate and selectivity of reactions.[45] In other solvents, such as methanol (CH_3OH), dimethyl sulfoxide (DMSO) and 1-propanol, the similar CV results can be observed with slight shift of reduction potentials, exhibiting the solvent effect on the catalytic system (**Figure S2**).

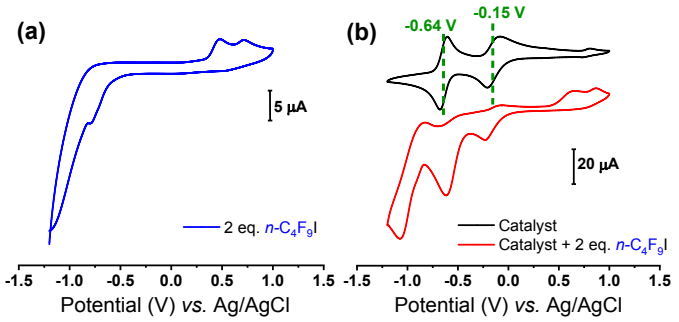
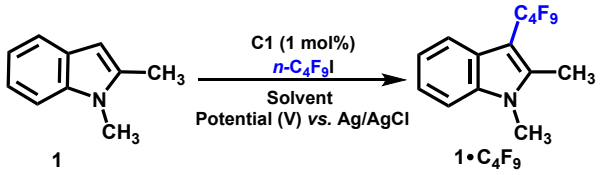


Figure 2. (a) CV of nonafluorobutyl iodide (*n*-C_4F_9I) (2 mM) and (b) [Co(III){(C_2C_3)(DO)(DOH)pn}Br_2] (**C1**) as the catalyst (1 mM) with/without *n*-C_4F_9I (2 mM) in CH_3CN.

Based on our previous work and the CV results,[34] we commenced our investigation of direct perfluoroalkylation of (hetero)arenes at –0.8 V *vs.* Ag/AgCl using 1,2-dimethylindole (**1**) as the model substrate and *n*-C_4F_9I as the perfluoroalkyl source in the presence of **C1** (1 mol%) at room temperature employing an electrochemical approach (**Figure S3**). The results are summarized in **Table 1**. Following a series of examinations using various solvents (**Table 1, entries 1–4**), we found that CH_3CN (**Table 1, entry 4**) was most optimal for this catalytic transformation. It resulted in increased yield of the desired product **1•C_4F_9** to 85% (**Table 1, entry 4**), accompanied by a relatively high turnover number (TON) of 85. Using other solvents led to incomplete conversions and lower yields (**Table 1, entries 1–3**). Moreover, the potential of –0.6 V *vs.* Ag/AgCl was also chosen for the catalytic reaction and resulted in a yield of 81% for **1•C_4F_9** (**Table 1, entry 5**) while more negative potentials such as –0.9 V and –1.2 V *vs.* Ag/AgCl achieved a slightly reduced yield of the desired compound **1•C_4F_9** (**Table 1, entries 6** and **7**) due to by-product formation (**Figure S4**). Only 10% yield of the desired product **1•C_4F_9** was achieved in the absence of the **C1** catalyst (**Table 1, entry 8**). The flow rate of the *n*-C_4F_9I reagent was also measured to check the reactivity. We found that increased speed of *n*-C_4F_9I addition and even adding the same amount of *n*-C_4F_9I at first without the use of the syringe pump both led to a lower yield of **1•C_4F_9** (**Table 1, entries 9** and **10**). In the present study, we also evaluate the reactivity under the dark and visible-light conditions (**Table 1**, **entries 11** and **12**) and found no obvious differences with the previously obtained outcomes. Furthermore, another imine/oxime-type cobalt complex, **C2**, exhibited low reactivity for the described perfluoroalkylation reaction (**Table 1, entry 13**), possibly due to its low solubility in the organic solvent. Additionally, an optimized reaction catalyzed by **C3** was also conducted and afforded 78% yield of **1•C_4F_9** (**Table 1, entry 14**). Although the yield was slightly lower than the result mediated

Table 1. Optimization of the reaction conditions for the perfluoroalkylation of indole derivatives[a]



Entry	Potential (V) *vs.* Ag/AgCl	Solvent[b]	Yield (%)[c]
1	–0.8 V	CH_3OH	58
2	–0.8 V	1-propanol	55
3	–0.8 V	DMSO	30
4	–0.8 V	CH_3CN	85
5	–0.6 V	CH_3CN	81
6	–0.9 V	CH_3CN	69
7	–1.2 V	CH_3CN	70
8[d]	–0.8 V	CH_3CN	10
9[e]	–0.8 V	CH_3CN	64
10[f]	–0.8 V	CH_3CN	50
11[g]	–0.8 V	CH_3CN	76
12[h]	–0.8 V	CH_3CN	75
13[i]	–0.8 V	CH_3CN	44
14[j]	–0.8 V	CH_3CN	78
15[k]	–0.8 V	CH_3CN	0
16[l]	–0.8 V	CH_3CN	0

[a] Reaction conditions: [**C1**] = 5.0×10^{-4} M; [1,2-dimethylindole (**1**)] = 5.0×10^{-2} M; [*n*-C_4F_9I] = 0.5 eq. of substrate per 1 h, 3 eq. in total; [*n*-Bu_4NClO_4] = 0.1 M; Decafluorobiphenyl ($C_{12}F_{10}$) as the internal standard; Reaction time: 6 h. [b] Abbreviations: CH_3OH, methanol; CH_3CN, acetonitrile; DMSO, dimethyl sulfoxide. [c] The yields are based on the initial concentration of 1,2-dimethylindole (**1**) and were determined by gas chromatography-mass spectrometry (GC-MS). [d] In the absence of the **C1** catalyst. [e] [*n*-C_4F_9I] = 1.0 eq. of substrate per 1 h, 3 eq. in total. [f] 3 eq. of *n*-C_4F_9I were added initially without the syringe pump. [g] In the dark. [h] With visible light (≥ 420nm). [i] **C2** as the catalyst. [j] **C3** as the catalyst. [k] In the presence of [TEMPO] (5.0×10^{-2} M) as the radical trapping reagent. [l] In the presence of [PBN] (5.0×10^{-1} M) as the radical trapping reagent.

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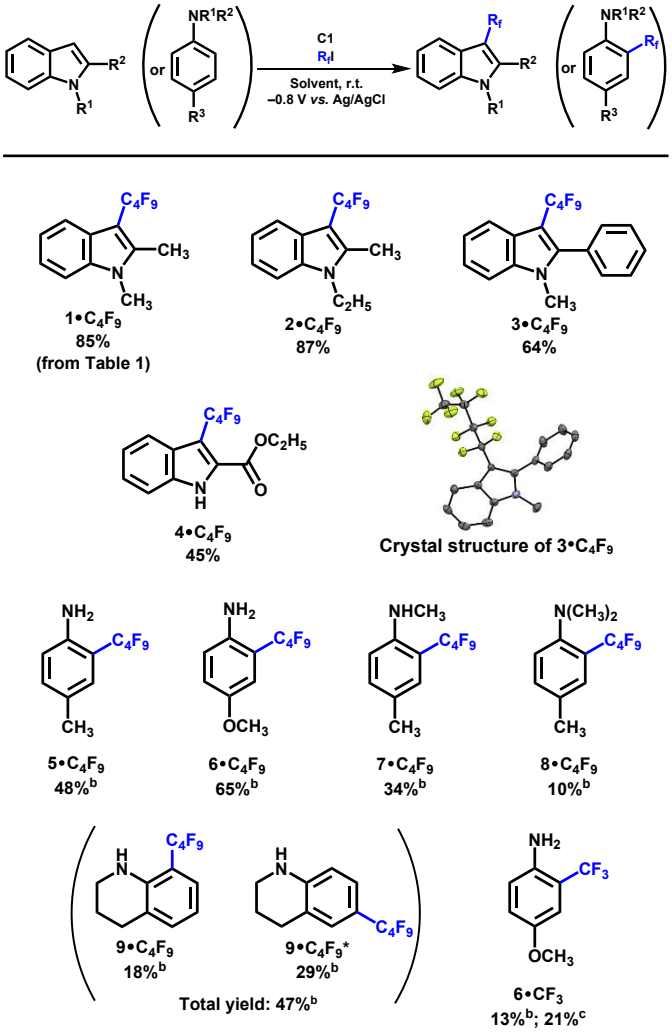
by **C1**, good reactivity of **C3** for the direct C–H perfluoroalkylation of aromatic substrate was demonstrated. Besides, in the presence of 2,2,6,6-trtramethylpiperidine 1-oxyl free radical (TEMPO) and *N-tert*-butyl-α-phenylnitrone (PBN), exhibiting radical scavenging activity, the reaction was inhibited and no formation of the desired product **1•C_4F_9** was observed (**Table 1, entries 15** and **16).** Notably, the adduct of TEMPO and the nonafluorobutyl radical (•C_4F_9) generated *in situ* was detected by GC-MS (**Figure S5**). Similarly, we can also monitor the adducts of PBN and •C_4F_9 by GC-MS (**Figure S6**). These results indicated that some radical intermediates were essential for the formation of the product. Based on these results, the standard conditions were optimized at –0.8 V *vs.* Ag/AgCl for the controlled-potential electrolysis using the substrate (100 eq. to catalyst) with 3 eq. of *n*-C_4F_9I in the presence of the catalyst **C1** (1 mol%) in CH_3CN for 6 h at room temperature (**Table 1, entry 4**).

Utilizing these optimized conditions, the reactions of different non-prefunctionalized indole derivatives, such as 1-ethyl-2-methylindole (**2**), 1-methyl-2-phenylindole (**3**), and ethyl indole-2-carboxylate (**4**), mediated by **C1** with fluoroalkylating reagent (*n*-C_4F_9I) provided perfluoroalkylated products in good to excellent yields (**Table 2**). The obtained yields for **2•C_4F_9** and **3•C_4F_9** were 87% and 64% corresponding to the TON of 87 and 64, respectively. A crystal structure of **3•C_4F_9** was successfully determined (**Figure S7** and **Table S2**). Under the optimized conditions, no formation of any significant amounts of side products was observed. Additionally, the compound **4** could also be performed in the reaction, affording 45% yield of the desired **4•C_4F_9** product. All these transformations exhibited that this method provided a straightforward and versatile route for synthesizing perfluoroalkylated indole derivatives.

To continue investigations in this area, we decided to extend our electrocatalytic protocol to explore the perfluoroalkylation of aniline derivatives. Similarly, various amounts of the catalyst, different solvents and light irradiation were screened to improve the reaction efficiency using *p*-toluidine (**5**) as the model substrate (**Table S3** and **Figure S8**). Finally, –0.8 V *vs.* Ag/AgCl was chosen as the controlled potential for the electrolysis with the aniline substrates with 3 eq. of *n*-C_4F_9I in the presence of **C1** (3 mol%) in DMSO for 6 h under visible-light irradiation. The above standard conditions led to the desired product **5•C_4F_9** in a yield of 48% (**Table 2**). Then, we undertook the perfluoroalkylation reactions of a series of aniline derivatives employing **C1** as the catalyst (**Table 2**). The reaction of *p*-anisidine (**6**) afforded 65% yield of the substitution product **6•C_4F_9.** In addition, *N*-methyl-*p*-toluidine (**7**) was subjected to reaction with *n*-C_4F_9I, providing perfluoroalkylated product **7•C_4F_9** in 34% yield. Furthermore, the fluoroalkylation of *N,N*-dimethyl-*p*-toluidine (**8**) resulted in the formation of **8•C_4F_9** in a low yield of 10%. The disappointing outcome of this reaction was associated with the 8% yield of side product **7•C_4F_9,** possibly resulting from the instability of light-sensitive *N,N*-dimethyl-*p*-toluidine (**8**) under visible-light irradiation. Moreover, special electron-rich aniline of 1,2,3,4-tetrahydroquinoline (**9**) was also amenable to the transformation, affording the desired product **9•C_4F_9** in 18% yield in the presence of another isomer product **9•C_4F_9*** in 29% yield, achieving a total yield of 47%. Additionally, it is also possible to prepare trifluoromethylated aniline derivatives through this method. Herein, 2DMSO•CF_3I was chosen as the trifluoromethylated source[46] and led to corresponding product **6•CF_3** in 21% yield with further optimized conditions. Thus, this general and cost-effective method offers access to highly functionalized fluoroalkylated aniline molecules.

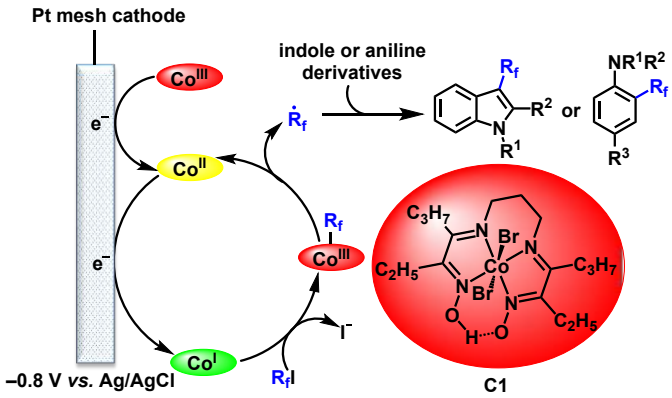
Table 2. Substrate scope of electrochemical fluoroalkylation of various indole and aniline derivatives[a]



[a] Reaction conditions: [**C1**] = 5.0×10^{-4} M (1 mol%); [substrate] = 5.0×10^{-2} M; [*n*-C_4F_9I] = 0.5 eq. of substrate per 1 h, 3 eq. in total; [*n*-Bu_4NClO_4] = 0.1 M; Internal standard: $C_{12}F_{10}$; Reaction time: 6 h; Solvent: CH_3CN; The yields are based on the initial concentration of the indole substrate and were determined by GC-MS. [b] [**C1**] = 1.5×10^{-3} M (3 mol%); Solvent: DMSO; With visible light (≥ 420nm). [c] [**C1**] = 1.0×10^{-3} M (4 mol%); [substrate **6**] = 2.5×10^{-2} M; [2DMSO•CF_3I] = 1.0 eq. of substrate per 1 h, 12 eq. in total; Reaction time: 12 h; Solvent: DMSO; With visible light (≥ 420nm).

According to the above investigations and the previously reported studies,[34, 47] a plausible reaction mechanism is illustrated in **Scheme 1.** Initially, the supernucleophilic Co(I) species was generated under electrolysis at –0.8 V *vs.* Ag/AgCl. Subsequently, the intermediate Co(III)–R_f complex was formed by the reaction of fluoroalkylating iodide and Co(I) with the removal of an iodide ion.[48] The homolytic dissociation of the Co(III)–R_f bond then leads to the formation of the key •R_f species, which reacts with the non-activated indole and aniline derivatives. One-electron oxidation and a proton loss result in the formation of the desired fluoroalkylated product.[49] Isolation of the Co(III)–R_f intermediate was not possible at this stage

due to the low stability at ambient conditions. Therefore, we performed DFT calculation to estimate the bond dissociation energy (BDE) of Co(III)–R_f bond (See Supporting Information **Table S4**).[50] For simplicity, **C2** was used as imine/oxime-type cobalt complex and corrin cobalt complex (**corrin**) was used as a model for vitamin B_{12} derivative (**C3**). The results show that BDEs of **C2**(III)–CF_3 and **C2**(III)–C_4F_9 complexes are 46.0 and 40.0 kcal/mol, respectively. These BDEs agree well with values obtained by **C2**(III)–CH_3 and **corrin**(III)–CH_3 (36.0 and 42.3 kcal/mol). These results supported the fact that Co(III)–R_f complex exhibits similar reactivity as the Co(III)–CH_3 complex. The mass peak corresponding to the **C1** catalyst was detected using matrix-assisted laser desorption/ionization-time of flight-mass spectrometry (MALDI-TOF-MS), indicating the stability of the catalyst during the process (**Figure S9**). Although the catalytic fluoroalkylation reactions using naturally derived vitamin B_{12} derivatives have been previously reported by our group[34] and some perfluoroalkyl cobaloximes have been synthesized and described by the Togni *et al.*,[30] electrocatalytic fluoroalkylation of the indole and aniline derivatives mediated by imine/oxime-type cobalt complexes has not been reported so far.



Scheme 1. Mechanistic study of radical fluoroalkylation mediated by **C1**.

Conclusions

In summary, we have demonstrated the electrocatalytic reactivity of imine/oxime-type cobalt complex as a simple vitamin B_{12} model complex for the direct C–H trifluoromethylation and perfluoroalkylation of (hetero)arenes with an electrochemical approach. The maximum value of TON is up to 87, suggesting the sufficient stability of this catalyst for the fluoroalkylation reactions. The radical trapping studies indicated that the reaction proceeds through a radical pathway mediated by homolytic cleavage of the cobalt(III)–carbon bond. At this stage, cobalt(III)–R_f intermediate was not isolated due to the low stability at ambient temperature. The mechanism study is still under investigation in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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