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Volume 52 | Number 1 | 4 January 2016 | Pages 1–216

ChemComm
Chemical Communications
www.rsc.org/chemcomm

ISSN 1359-7345

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# A General and Practical Ni-Catalyzed C-H Perfluoroalkylation of (Hetero)Arenes

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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**A direct perfluoroalkylation of (hetero)arenes using the air- and moisture-stable complex (dppf)Ni(*o*-tol)Cl was developed (23 examples). The novel procedure allows for the synthesis of various fluorinated products and tolerates sensitive functional groups including aldehydes, free amino groups and several heterocycles.**

The introduction of fluorine atoms into a given organic compound significantly changes its chemical and physical properties.[1] Consequently, the performance of perfluoroalkylated chemicals is drastically different compared to their parent hydrocarbons.[2] Owing to their distinctive characteristics, perfluoroalkylated arenes continue to attract the interest of researchers from life and material sciences,[3] and have been used for the preparation of new pharmaceuticals, agrochemicals, and hydrophobic materials.[4] Hence, for the synthesis of this class of compounds, numerous methods were developed including thermolysis,[5] electrolysis,[6] or treatment of arenes with stoichiometric reagents.[7] However, all these approaches suffer from drawbacks such as harsh reaction conditions and/or low atom efficiency. In this respect, the recently disclosed photochemical[8] and Cu-mediated procedures[9] are interesting as they proceed under milder conditions. Despite all these achievements in the past decades, the demand for more practical and convenient procedures still exists. Here, transition-metal catalysis offers interesting possibilities, as shown by the recent perfluoroalkylation of aryl halides or aryl boronic acids.[10] Obviously, C-H functionalizations of (hetero)arenes are more desirable; however, only few reports are known using specific perfluoroalkyl reagents, e.g. $R_FSO_2Na$ and $R_FSO_2Cl$.[11] Particularly, the direct perfluoroalkylation of (hetero)arenes with $R_FI$, which are commercially available, is rare. Notably, Fuchikami and Ojima reported in 1982 the first example of perfluoroalkylation of arenes with $R_FI$.[12] Unfortunately, two equivalents Cu and $R_FI$ were needed in this case. Later on, Loy and Sanford made this transformation catalytic by using a $Pd_2dba_3$/BINAP system.[13] In 2015, our group reported the first heterogeneous catalytic system (Pt/C) for such reactions, which could be recycled to some extent.[14] Despite such recycling possibilities, the search for less expensive and more general catalysts is ongoing. In this regard, the use of non-noble metals, e.g. Ni, Co, Fe, Cu, Mn, is particularly attractive.

Herein, we present the first general and practical Ni-catalyzed protocol for direct C-H perfluoroalkylation of (hetero)arenes in the presence of air-stable pre-catalysts.[15] To date, this kind of catalysis is scarcely known with very limited substrate scope.[16]

In our initial studies, we investigated the perfluorodecylation of benzene. Although nickel is an abundant and inexpensive metal, its use in catalysis is sometimes difficult due to its sensitivity. To avoid reproducibility problems, we used specific metallated precursors, which allow for a more controlled formation of the potentially active nickel(0) species. As shown in Scheme 1, five defined nickel complexes were compared with the in situ system consisting of $NiCl_2 \cdot H_2O$ and dppf as ligand. Although the in situ generated catalyst system showed some conversion (38%), the desired product yield was low (10%). Instead, using the defined (dppf)$NiCl_2$ complex gave the desired product in 21% yield. To our delight, the metallated ((dppf)Ni(*o*-tol)Cl) **Ni2** performed significantly better giving 88% conversion of $C_{10}F_{21}I$ and 60% yield of **2**. Next, related pre-catalysts **Ni3** – **Ni5** which were synthesized from different ligands were tested, but showed no activity at all. Based on these initial tests, the influence of key-reaction parameters on this transformation was studied. As shown in Table 1 a control experiment without any catalyst revealed only traces (2%) of the desired product (Table 1, entry 2), while in the presence of 5 mol% catalyst 68% and 77% yield of **2** was observed at 130 and 150 °C, respectively (Table 1, entries 3 and 4).

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Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

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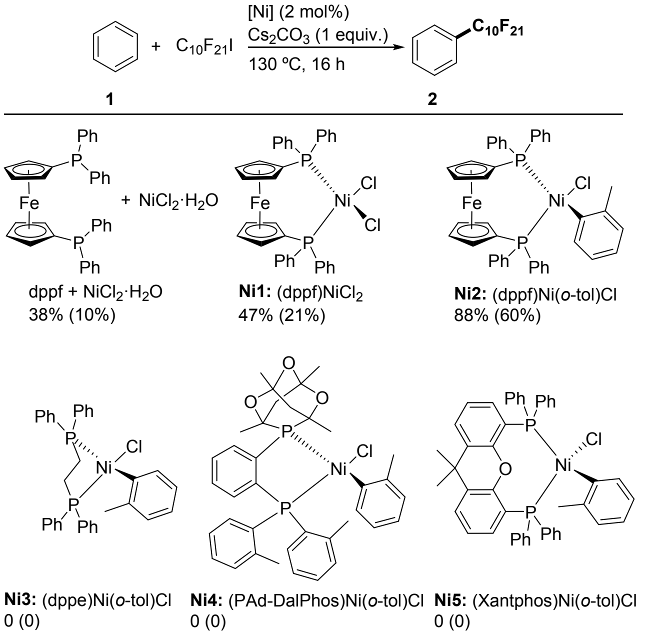
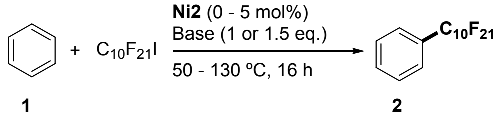


**Scheme 1.** Perfluorodecylation of benzene catalyzed by different Ni pre-catalysts. Reaction conditions: 0.2 mmol $C_{10}F_{21}I$, 0.5 mL benzene, argon atmosphere. Yields and conversions were determined by $^{19}F$ NMR with 1,4-difluorobenzene as standard, the values within parentheses refer to the yields while outsides refer to the conversions.

Meanwhile, experiments in the presence of different bases ($K_3PO_4$, KOAc, CsOPv and NaO*t*Bu) clearly showed the special role of $Cs_2CO_3$ for the perfluoroalkylation of benzene (Table 1, entries 5-8). Attempts to decrease the reaction temperature showed significantly lower product yields at 100 °C (Table 1, entry 9), while at 50 °C no reaction took place. However, using 1,5 equiv. of $Cs_2CO_3$ gave **2** in satisfying 75% already at 100 °C (Table 1, entry 11). Apart from the base, the reaction is also sensitive to the solvent. Although significant conversions could be obtained using NMP, DMF, DMSO or dioxane only low yields of the perfluorinated benzene were observed (Table 1, entries 12-15). Here, in most cases decomposition of the starting material was observed. In NMP and dioxane the corresponding $R_FH$ was generated in significant amounts, too. Interestingly, in the latter solvent an oxidative perfluoroalkylation was observed and the resulting coupling product 5-(perfluorodecyl)-2,3-dihydro-1,4-dioxine could be isolated in up to 29% yield (see SI, table S1). Other tested solvents (acetone, TAA) proved to be even worse (Table 1, entries 16 and 17). With the optimized reaction conditions in hand, the perfluoroalkylation of structurally and electronically diverse arenes and heteroarenes with $C_{10}F_{21}I$, $C_8F_{17}I$, $C_4F_9I$, and more importantly $CF_3Br$ was tested (Scheme 2). Various substrates bearing either electron-donating or electron-withdrawing substituents on the aryl ring were converted to the corresponding products in good to excellent yields. Notably, some nitrile- and carbonyl-substituted arenes as well as heteroarenes provided the desired products only in low yields (see SI). Although there is no clear trend in reactivity with respect to the electronic character of the substrate, regioselectivity-wise perfluoroalkylation occurred in general at the most electron-rich position.

**Table 1.** Ni-catalyzed perfluorodecylation of benzene with $C_{10}F_{21}I$.



| Entry | Catalyst (mol%) | Base (equiv.) | Solvent[a] | T / °C | Conv. (Yield) / % |
|---|---|---|---|---|---|
| 1 | **Ni2** (2) | $Cs_2CO_3$ (1) | None | 130 | 88 (60) |
| 2 | None | $Cs_2CO_3$ (1) | None | 130 | 9 (2) |
| 3 | **Ni2** (5) | $Cs_2CO_3$ (1) | None | 150 | 100 (77) |
| 4 | **Ni2** (5) | $Cs_2CO_3$ (1) | None | 130 | 100 (68) |
| 5 | **Ni2** (2) | $K_3PO_4$ (1) | None | 130 | 0 (0) |
| 6 | **Ni2** (2) | KOAc (1) | None | 130 | 0 (0) |
| 7 | **Ni2** (2) | CsOPv (1) | None | 130 | 0 (0) |
| 8 | **Ni2** (2) | NaO*t*Bu (1) | None | 130 | 0 (0) |
| 9 | **Ni2** (5) | $Cs_2CO_3$ (1) | None | 100 | 55 (36) |
| 10 | **Ni2** (5) | $Cs_2CO_3$ (1) | None | 50 | 0 (0) |
| 11 | **Ni2** (5) | $Cs_2CO_3$ (1.5) | None | 100 | 97 (75) |
| 12 | **Ni2** (5) | $Cs_2CO_3$ (1) | NMP | 100 | 99 (12) |
| 13 | **Ni2** (5) | $Cs_2CO_3$ (1) | Dioxane | 100 | 98 (35) |
| 14 | **Ni2** (5) | $Cs_2CO_3$ (1) | DMSO | 100 | 57 (8) |
| 15 | **Ni2** (5) | $Cs_2CO_3$ (1) | DMF | 100 | 44 (7) |
| 16 | **Ni2** (5) | $Cs_2CO_3$ (1) | Acetone | 100 | 0 (0) |
| 17 | **Ni2** (5) | $Cs_2CO_3$ (1) | TAA | 100 | 0 (0) |

Reaction conditions: 0.2 mmol $C_{10}F_{21}I$, 0.5 mL benzene, argon atmosphere. Yields and conversions were determined by $^{19}F$ NMR with 1,4-difluorobenzene as standard. [a] In the case of using solvent: 10 equiv. benzene, 0.32 mL solvent, NMP = *N*-methyl-2-pyrrolidone, DMSO = dimethyl sulfoxide, TAA = 2-methyl-2-butanol.

Comparing multi-substituted arenes, *meta*-substituted benzenes performed better than *ortho*- and *para*-ones (**4d** – **4i**). From a synthetic point of view, it is interesting that aniline derivatives including primary anilines with free $NH_2$-group underwent smooth transformation to the desired products in 70–96% yields (**4j** – **4n**). Furthermore, various heterocycles based on pyridine (**4o** and **4p**), pyrrole (**4q**), thiophene (**4r**), and imidazole (**4s**) were all successfully perfluoroalkylated to give the products in good to excellent yields. Finally, naphthalene was tested and gave the 1- and 2-perfluoroalkyl isomers in a ratio of 79:21 (**4t**). Notably, in many of the presented examples, the perfluoroalkylation reaction occurred at a specific position with high selectivity. In some cases (**4d**, **4g**, **4m**, **4n**, **4p**, and **4q**), the product were obtained even with >99% selectivity. Furthermore, the other perfluoro sources ($CF_3Br$, $C_4F_9I$ and $C_8F_{17}I$) were also applicable to our general catalytic system (**4u** – **4w**). Notably, trifluoromethylation is also possible using the comparably inexpensive $CF_3Br$. Thus, *N*-methylpyrrole gave under slightly modified conditions 72% yield of **4w**. To get mechanistic insights into this novel general perfluoroalkylation protocol, in situ EPR measurements were performed. In detail, a mixture of $C_{10}F_{21}I$, $Cs_2CO_3$, and the catalyst **Ni2** was investigated in benzene at low temperature

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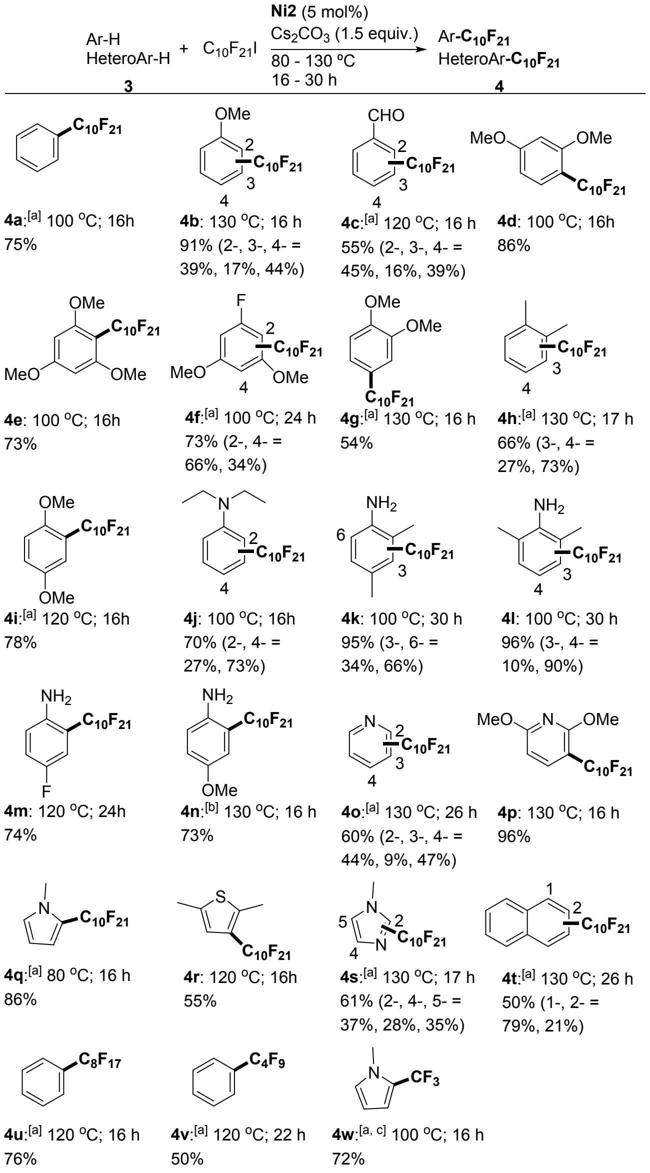
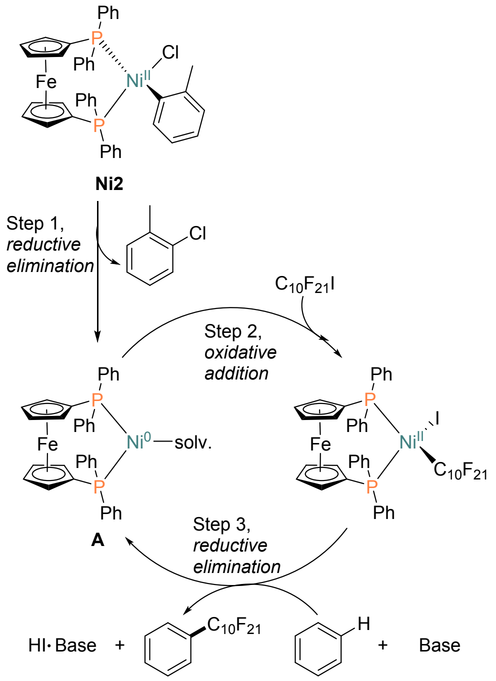
(100 K) and close to the reaction temperature (346 K) (see SI, Figure S1).



**Scheme 2.** Substrate scope of Ni-catalyzed perfluoroalkylation with of (hetero)arenes. Reaction conditions: 0.2 mmol $C_{10}F_{21}I$, 0.5 mL (hetero)arenes (2 mmol for solid substrates), argon atmosphere. Isolated yields, selectivity for different isomers was determined by $^1H$ and $^{19}F$ NMR of the isolated product. [a] Yields determined by $^{19}F$ NMR with 1,4-difluorobenzene as standard. [b] 10 mol% **Ni2**. [c] 0.5 mmol *N*-methylpyrrole, 5 bar $CF_3Br$, 40 bar $N_2$, 10 mol% phenylboronic acid as additive, 1 mL perfluorobenzene, yield was determined respect to *N*-methylpyrrole with the average of two runs.

In agreement with previous observations,[14] an organic radical and a decrease of the signal intensity (as a function of time) were detected which confirmed the participation of organic radicals in this reaction. However, there is no signal split in the obtained EPR spectrum, so it was not possible to resolve the exact structure of the observed radical. The occurrence of radical intermediates was further proven by a typical experiment in the presence of 1 equiv. of TEMPO, which resulted in no product formation and the decomposition of $C_{10}F_{21}I$. On the other hand, in the presence of 1 equiv of BHT product formation still occurred (yield 2: 72%). Further control experiments revealed an extensive period (about 10 h!) for the formation of the active Ni(0) catalyst (see SI, Figure S2). Apparently, reductive elimination in the Ni(II) complex **Ni2** proceeds very slow. To shorten such long reduction period, typical reductants (e.g. phenylboronic acid, ammonium formate, sodium formate) were added to the reaction, which afforded nearly full conversion and more than 40% yield of the desired product within 2 h (see SI, Table S2). Obviously, this opens the possibility for further improved protocols, too.

In order to understand the pre-formation of the catalyst in more detail, control experiments using **Ni2** with base, solvent and perfluorinated substrate at 100 °C for 16 h were performed (see SI, Table S3). Interestingly, among all the tested cases, a signal change in the $^{31}P$ NMR was found only in the presence of **Ni2** and $C_{10}F_{21}I$. Thus, we conclude that **Ni2** can be activated in the presence of $C_{10}F_{21}I$ to form the active catalytic species; however, this needs high temperature and long reaction time. Running the reaction of **Ni2** and $C_{10}F_{21}I$ on a larger scale gave a brown powder, which unfortunately could not structurally resolved due to its extremely low solubility. (see SI) Nevertheless, some product of **2** was obtained from the mixing of this brown powder and benzene at 100 °C for 16 h (see SI).



**Scheme 3**. Activation of pre-catalyst and mechanistic proposal.

Based on the obtained results and former reports on related Ni- and Pd-complexes,[17] we propose the following catalytic cycle (Scheme 3). Initially, **Ni2** undergoes reductive elimination to afford the corresponding Ni(0) intermediate **A**. Typically, this step is rate determining. **A** is highly active and may be stabilized by iodide ions. After oxidative addition with the perfluoroalkyl iodide and subsequent activation of the (hetero)arene, the desired perfluoroalkylated product is obtained. At this point, we do not know how the latter reaction steps proceed and the involvement of radical intermediates vide supra is likely.

In conclusion, we have developed a general and practical Ni-catalyzed perfluoroalkylation of (hetero)arenes using the defined Ni-complex **Ni2**. This kind of catalyst is air- and moisture-stable and thus can be easily handled. The reported protocol allows the effective perfluoroalkylation of various (hetero)arenes in moderate to good yields. Control experiments revealed the importance of the activation of the pre-catalyst as rate determining step. We believe these studies will be also of interest for related Ni-catalyzed coupling processes.

We are grateful for financial support from Lonza, Switzerland, BMBF and the State of Mecklenburg-Western Pommerania, Germany. S.Z. thanks the Chinese Scholarship Council, China.

**Keywords:** Nickel • catalysis • perfluoroalkylation • (hetero)arenes • fluorinated compounds

## Conflicts of interest

There are no conflicts to declare.

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