Perfluoroalkylation

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Heterogeneous Platinum-Catalyzed C–H Perfluoroalkylation of Arenes and Heteroarenes**

*Lin He, Kishore Natte, Jabor Rabeah, Christoph Taeschler, Helfried Neumann, Angelika Brückner, and Matthias Beller**

Abstract: *Fluorinated organic compounds are gaining increasing interest for life science applications. The replacement of hydrogen in arenes or heteroarenes by a perfluoroalkyl group has a profound influence on the physical and biological properties of such building blocks. Here, an operationally simple protocol for the direct C–H perfluoroalkylation of (hetero)arenes with R_fI or R_fBr has been developed, using a robust supported platinum catalyst. The ready availability of the starting materials, the excellent substrate tolerance, and the reusability of the catalyst make this method attractive for the synthesis of a variety of perfluoroalkyl-substituted aromatic compounds. Preliminary mechanistic studies revealed the formation of radicals to be crucial in the reaction system.*

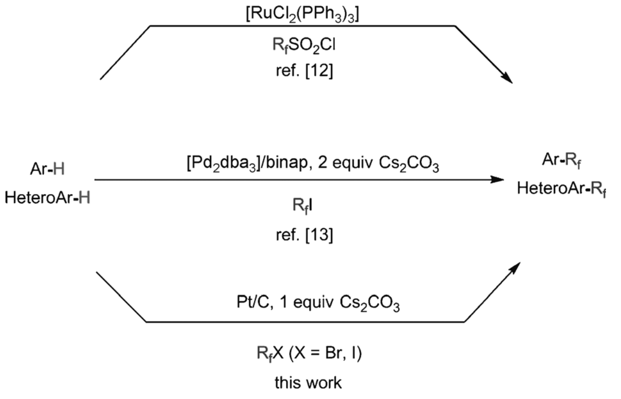
Organofluorine chemistry plays a vital role for the advancement of medicinal, agricultural, and material sciences.[1] The unique behavior of fluorinated compounds is attributed to the high electronegativity of fluorine (4.0), combined with its size, which is close to that of hydrogen.[2] Hence, perfluoroalkyl groups, regarded as a gathering of fluorine atoms, determine the electronic and steric properties of a given molecule in a distinctive manner.[3,4] In the past decades, a number of approaches based on thermal,[5] electrophilic,[6] and photochemical[7] reactions have been reported. Despite impressive achievements, practical issues (harsh reaction conditions), experimental simplicity, and/or the requirement of unwanted stoichiometric reagents[8] (e.g. perfluoro-copper species) are persistent, thus stimulating progress in this area.

For example, transition-metal catalysis has emerged as a powerful tool for perfluoroalkylation reactions. Several reports have demonstrated copper- or palladium-catalyzed reactions for the preparation of perfluoroalkyl (including trifluoromethyl) arenes from aryl halides.[9] In contrast, analogous methods to prepare these compounds from arenes, which are particularly desirable starting materials, are notably lacking.[10] Recently, an elegant indirect strategy was described by the group of Hartwig and involved a one-pot iridium-catalyzed borylation of arenes/copper-reagent-mediated perfluoroalkylation sequence.[11] In addition, a straightforward transformation was developed by Kamigata and co-workers, whereby a wide range of arenes and heteroarenes can be perfluoroalkylated with R_fSO_2Cl in the presence of $[RuCl_2(PPh_3)_3]$.[12] Moreover in 2011, an interesting $[Pd_2dba_3]$/binap-catalyzed reaction for the coupling between R_fI and aromatic compounds was reported by Sanford and co-workers.[13] However, potential drawbacks of all these procedures are the inherent problems associated with homogeneous catalysis because of difficulties in separating and reusing metals and ligands.

An ideal protocol would make use of stable and easily recyclable catalysts for the direct C–H perfluoroalkylation of aromatic compounds. In this respect, heterogeneous catalysis is the preferred choice. Unfortunately, to date, only rare examples of such reactions in the presence of heterogeneous catalysts (performed above 150 °C) with very limited substrate scope have been reported.[14] Thus, the search for alternative materials for this transformation remains a challenging but rewarding task.

Herein, we present a general and versatile heterogeneous platinum-catalyzed system for the coupling of various arenes and heteroarenes with either easily available R_fI or R_fBr (Scheme 1). The good performance of the present catalytic system allowed us also to extend this methodology to the perfluoroalkylation of caffeine as a representative example of nucleobases.

Initially, the catalytic performance for the perfluoroalkylation of benzene with $C_{10}F_{21}I$ was assessed by using several metal-based catalysts. To our delight, in the presence of



Scheme 1. Transition-metal-catalyzed perfluoroalkylation of arenes and heteroarenes. binap = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl.

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[*] Dr. L. He, Dr. K. Natte, Dr. J. Rabeah, Dr. H. Neumann,
Prof. Dr. A. Brückner, Prof. Dr. M. Beller
Leibniz-Institut für Katalyse an der Universität Rostock e.V.
Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)
E-mail: matthias.beller@catalysis.de

Dr. C. Taeschler
Lonza Ltd
Rottenstrasse 6, 3930 Visp (Switzerland)

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Table 1: Perfluoroalkylation of benzene with $C_{10}F_{21}I$ under various conditions.[a]

1

Entry	Catalyst (mol% metal)	Base	T [°C]	t [h]	Con. [%]	Yield [%][b]
1	Pt/C (5)	Cs_2CO_3	100	20	100	96 (90)
2	–	Cs_2CO_3	100	20	–	–
3	C	Cs_2CO_3	100	20	–	–
4	Pd/C (5)	Cs_2CO_3	100	20	63	61
5	Ru/C (5)	Cs_2CO_3	100	20	27	24
6	Ru/Al_2O_3 (5)	Cs_2CO_3	100	20	25	21
7	Rh/C (5)	Cs_2CO_3	100	20	41	39
8	Pt/TiO_2 (5)	Cs_2CO_3	100	20	46	45
9	Pt/Al_2O_3 (5)	Cs_2CO_3	100	20	79	77
10	Pt/ZrO_2 (5)	Cs_2CO_3	100	20	62	61
11	Pt/CeO_2 (5)	Cs_2CO_3	100	20	51	49
12	Pt/C (5)	DBU	100	8	100	56
13	Pt/C (5)	K_3PO_4	100	20	67	60
14	Pt/C (5)	K_2CO_3	100	20	54	49
15	Pt/C (5)	NEt_3	100	20	74	51
16	Pt/C (2.5)	Cs_2CO_3	100	20	67	65
17	Pt/C (2.5)	Cs_2CO_3	120	20	100	93
18	Pt/C (1.8)	Cs_2CO_3	120	20	96	91
19	Pt/C (5)	Cs_2CO_3	80	36	95	92
20[c]	Pt/C (5)	Cs_2CO_3	80	36	91	90
21[d]	Pt/C (5)	Cs_2CO_3	80	36	87	84
22	$PtCl_2$ (5)	Cs_2CO_3	80	36	19	18
23	PtI_2 (5)	Cs_2CO_3	80	36	15	14
24	$[Pt(cod)Cl_2]$ (5)	Cs_2CO_3	80	36	61	42
25[e]	$[Pt_2\{(Me_2SiCH{=}CH_2)_2O\}_3]$ (5)	Cs_2CO_3	80	36	87	60

[a] Reaction conditions: $C_{10}F_{21}I$ (0.2 mmol) and base (1 equiv) in benzene (0.5 mL), under N_2 (10 bar). [b] Yields determined by GC analysis (number within parentheses reflects the yield of the isolated product). [c] Under air. [d] Third run. [e] $[Pt_2\{(Me_2SiCH{=}CH_2)_2O\}_3]$ (Karstedt's catalyst) was supplied by Sigma–Aldrich as 2% Pt complex in xylenes solution. $C_{10}F_{21}I$ (0.2 mmol) and Cs_2CO_3 (1 equiv) were placed in a vial, and xylenes removed under vacuum. Then, benzene (0.5 mL) was added under inert atmosphere. cod = 1,5-cyclooctadiene.

Cs_2CO_3, a commercially available Pt/C catalyst (supplied by Sigma–Aldrich) affords exclusive formation of the perfluoroalkylated product **1** (Table 1, entry 1). Blank experiments without either a catalyst or using the platinum-free carbon gave no conversion (entries 2 and 3). When applying related Pd/C, Ru/C, Ru/Al_2O_3, or Rh/C (provided by Sigma–Aldrich), the desired perfluoroalkyl-substituted benzene was also formed, but in lower yield under the identical reaction conditions (entries 4–7). Other supported platinum systems including Pt/TiO_2, Pt/Al_2O_3, Pt/ZrO_2 and Pt/CeO_2 were also investigated. These catalysts, however, were not found to be particularly active (entries 8–11), thus highlighting the specific high activity of Pt/C with respect to the title reaction.

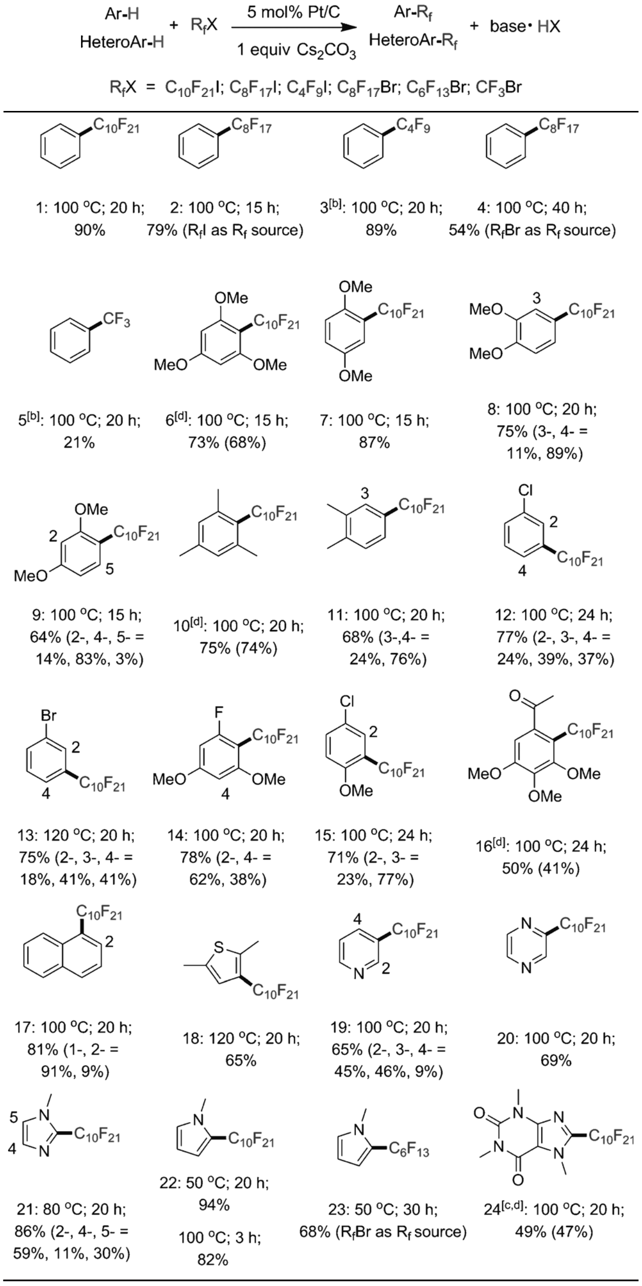
The benefit of Cs_2CO_3 for the perfluoroalkylation of benzene became obvious when compared with other bases. By using DBU (1,8-diazabicycloundec-7-ene), the full conversion of $C_{10}F_{21}I$ was achieved in a shorter time (Table 1, entry 12), but with lower selectivity (some unidentified black tar was formed). When K_3PO_4, K_2CO_3, and NEt_3 were applied, moderate yield of **1** was achieved (entries 13–15). With regard to reaction conditions suitable for practical applications, we conducted experiments in which a reduced amount of platinum was used (entries 16–18). After an optimization, 91% yield of the desired **1** was obtained in the presence of 1.8 mol% of platinum at 120°C. Subsequent attempts at lower temperature showed that an excellent yield can be achieved at 80°C, although a longer reaction time was required (entry 19). Interestingly, when the analogous transformation was conducted in air, similar yield of **1** was detected (entry 20), thus offering practical advantages for an easy work-up.

To verify whether the present system is truly heterogeneous or not, the reaction mixture (for ease of operation, we use 4 mL benzene instead of 0.5 mL in this case) was hot-filtered at around 40% conversion of $C_{10}F_{21}I$ at 80°C. Continued stirring of the filtrate in the presence of additional base did not give any more products. Analysis of the reaction mixture by inductively coupled plasma (ICP) after filtration shows no detectable Pt present in the filtrate. Furthermore, the recovered catalyst could be reused for at least three runs without appreciable loss of the original catalytic activity (Table 1, entry 21). These results, together with much inferior performances of homogeneous Pt^{II} or Pt^{0} catalysts (entries 22–25), strongly suggest the observed catalysis is heterogeneous in nature.

With the objective of extending the scope of the reaction we investigated the reaction of R_fI and R_fBr compounds with (hetero)aromatics under various conditions. $C_{10}F_{21}I$ was used primarily to facilitate the monitoring of reactions by gas chromatographic analysis and the isolation of the desired products. Other shorter chain perfluoroalkyl iodides ($C_8F_{17}I$ and C_4F_9I) were examined to a lesser extent and found to behave similarly to $C_{10}F_{21}I$ (Table 2, entries 2 and 3). In the more challenging reactions employing R_fBr ($C_8F_{17}Br$) as the perfluoroalkyl source, a longer reaction time (compared to that of $C_8F_{17}I$) was required to obtain moderate yields (entry 4). An attempted trifluoromethylation of benzene using CF_3Br resulted in the formation of trifluorotoluene in only 21% yield (entry 5). Nevertheless, these results are still encouraging since the direct perfluoroalkylation of a benzene nucleus with perfluoroalkyl bromide has scarcely described in the literature.

By using the optimized reaction conditions, structurally diverse arenes and heteroarenes were tested. Benzenes bearing either electron-donating or electron-withdrawing substituents underwent perfluoroalkylation in good to excellent yield (Table 2, entries 6–16). In all these cases perfluoroalkylation is preferred at the most electron-rich position. Also naphthalene can be applied as substrate and gave the corresponding perfluoroalkylated naphthalene with excellent selectivity for the kinetically favored 1-position (entry 17). For the reaction of heteroaromatic compounds the present system also shows excellent promise (entries 17–24). Transformation of non-activated thiophene proceeded smoothly to produce the corresponding perfluoroalkylated product at 120°C (entry 18). To our delight, the notoriously difficult pyridine and pyrazine were converted as readily as benzene in

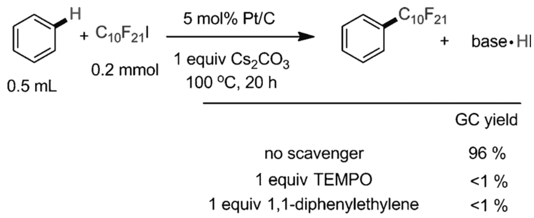
Table 2: Substrate scope of Pt/C-catalyzed perfluoroalkylation.[a]



[a] Reaction conditions: R_fX (0.2 mmol), Pt/C (Pt: 5 mol%) and Cs_2CO_3(1 equiv) in ArH or heteroArH (0.5 mL for liquid substrate; 1 mmol for solid substrate), under N_2 (10 bar). the yield of isolated product. Selectivity for different isomers was determined by GC and ^{19}F NMR spectra of the isolated product. [b] Determined by ^{19}F NMR spectroscopy. [c] In DMSO (0.5 mL) under N_2 (10 bar). [d] Analogous transformations carried out in screw-capped glass vials under air. The values within parentheses refer to yields of the isolated product.

this study (entries 19 and 20). Furthermore, the reaction of *N*-methylimidazole with $C_{10}F_{21}I$ went smoothly under mild reaction conditions (entry 21). Activated *N*-methylpyrrole afforded the 2-perfluoroalkylated product as a single isomer ($C_{10}F_{21}I$ or $C_6F_{13}Br$ as R_f source, 50 °C or 100 °C; entries 22 and 23). Because of the importance of perfluoroalkyl-substituted nucleobases in medicinal chemistry,[15] the reaction of caffeine with $C_{10}F_{21}I$ was conducted. Indeed, 8-perfluorodecyl-caffeine was isolated as a white solid in 49 % yield (entry 24). Notably, when we carried out analogous transformations (entries 6, 10, 16, and 24; in these cases, reaction temperature is below the boiling point of the starting materials or the solvent such as DMSO) in screw-top glass vials under air, moderate to good yields of desired products was obtained.

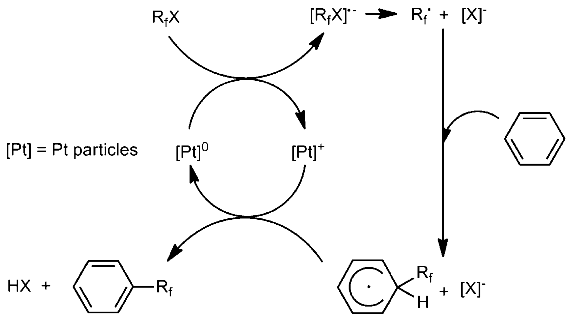
To gain more insight into the present heterogeneous perfluoroalkylation, stoichiometric model reactions and in situ spectroscopic studies were performed. It is well known that such transformations often proceed via radical intermediates.[1g,4c,16] Hence, initially radical scavengers, for example, TEMPO and 1,1-diphenylethylene, were added to the reaction mixture (Scheme 2).[17] Indeed, the desired reactions were completely halted. Interestingly, these results are in particular contrast to homogeneous palladium-catalyzed coupling of perfluoroalkyl iodides with arenes, where were the addition of radical initiators or inhibitors had a negligible effect.[13] Apparently, radical intermediates are involved in our case, which is also supported by the distribution of isomers of perfluoroalkylpyridines (2-, 3-, and 4-substituted = 45 %, 46 %, and 9 %, respectively).[18]



Scheme 2. Radical trapping experiments. TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy.

Furthermore, in situ EPR measurements at 100 °C of the mixture of $C_{10}F_{21}I$, Cs_2CO_3, and Pt/C in activated *N*-methylpyrrole or in mesitylene displayed a resonance characteristic of an organic radical ($g = 2.0030$) centered at 3362 G (see Figure S1 in the Supporting Information). It should be noted that the decrease in signal intensity (as a function of time) reveals the perfluoroalkylation of the activated *N*-methylpyrrole. The obtained EPR results confirm the participation of such organic radicals in the reaction.

Although the precise formation of radicals on the platinum surface remains to be clarified at this stage, it is rationally considered that a perfluoroalkyl halide radical anion is generated from the redox-transfer interaction between R_fX and $[Pt]^0$ species,[19] which converts into a perfluoroalkyl radical upon elimination of X^-. Then, this electron-poor radical adds preferentially to an electron-rich position of the aromatic or heteroaromatic ring. As shown in Scheme 3 in case of benzene, the corresponding cyclohexadienyl radical is formed.[12a] Subsequent H-abstraction affords the perfluoroalkyl-substituted product and HX with regeneration of the $[Pt]^0$ catalyst. To investigate which step is the rate-determining, competitive reactions were carried out with



Scheme 3. Proposed mechanism for the perfluoroalkylation of benzene.

benzene and [D$_6$]benzene. The observed H/D kinetic isotope effect (KIE) value of 1.01 indicates that the latter C—H bond cleavage is fast. Hence, we propose that the heterogeneous platinum catalyst can substantially facilitate the crucial radical-forming step, which is a key factor for the desired perfluoroalkylation.

In conclusion, we have developed an efficient and versatile heterogeneous platinum-catalyzed perfluoroalkylation of arenes and heteroarenes based on commercially available perfluoroalkyl halides. The ready availability of the starting materials, the broad substrate scope, and the reusability of the catalyst make this protocol attractive for a general synthesis of perfluoroalkyl-substituted aromatic compounds.

Experimental Section

General procedure for the perfluoralkylation reaction: A mixture of R$_f$X (0.2 mmol), Pt/C (Pt: 5 mol %), and Cs$_2$CO$_3$ (1 equiv) and either the arenes or heteroarene (0.5 mL for liquid substrate; 1 mmol for solid substrate) were placed in a magnetically stirred Wheaton vial, placed in a sixfold-parallel autoclave (Parr Instruments 4560 series). After replacing the air in the autoclave with nitrogen and increasing the pressure to 10 bar, the reaction mixture was stirred at desired temperature for a given time. At the end of the reaction, the autoclave was cooled to room temperature and the pressure was released carefully. After removing the solids (filtered or centrifuged), the crude reaction mixture was purified by column chromatography on silica gel 60, 0.063–0.2 mm, 70–230 mesh (Merck), or pipette column using FluoroFlash reverse-phase silica gel, thus eluting with a gradient of 4:1 MeOH/H$_2$O (10 mL; MeOH 10 mL and acetone 10 mL). The MeOH and acetone fractions were collected, dried with MgSO$_4$, filtered, and concentrated under vacuum. For some of substrates with a low-boiling point (such as benzene), the mixture was extracted three to five times with CH$_2$Cl$_2$. The combined organic phase was dried with MgSO$_4$, filtered, and concentrated under vacuum to yield the desired product.

Keywords: C—H activation · heterogeneous catalysis · platinum · radicals · synthetic methods

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