

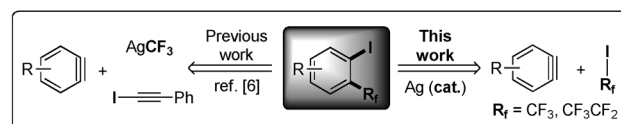
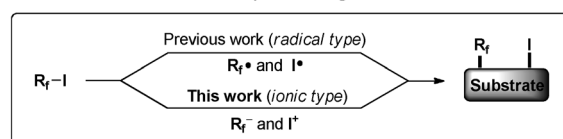
Insertion Reactions

Silver-Catalyzed Formal Insertion of Arynes into R_f-I Bonds**Yuwen Zeng and Jinbo Hu*^[a]

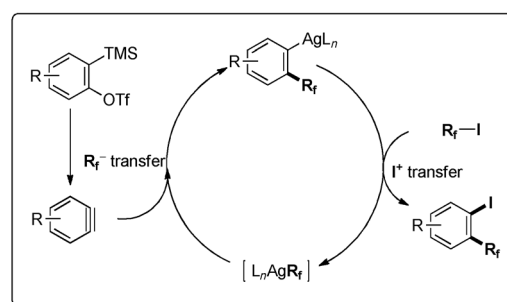
Abstract: An unprecedented silver-catalyzed formal insertion of arynes into R_f-I ($R_f = CF_3, C_2F_5$) bonds has been developed. This protocol provides easy access to various *ortho*-perfluoroalkyl iodoarenes under mild conditions. In this insertion reaction, an ionic atom-transfer reaction of R_fI occurs, and a silver-mediated metathesis process is involved in the efficient transfer of the electropositive iodine atom.

Aromatic compounds bearing perfluoroalkyl (R_f) groups are widely used in the fields of pharmaceuticals, agrochemicals, and materials.^[1] In particular, trifluoromethylated aromatics play important roles in life-science-related applications because the CF_3 group can profoundly change both the biological and physical properties of organic molecules.^[2] As a result, many methods have been developed for introducing CF_3 group(s) onto aromatic rings.^[3] However, although significant progress has been made in the trifluoromethylation of arenes,^[4] to date, little attention has been paid to the introduction of higher R_f groups, such as pentafluoroethyl (C_2F_5) groups, into aromatic compounds.^[3f]

Arynes are highly reactive intermediates and have been widely used in transition-metal-catalyzed coupling reactions.^[5] We have recently reported a silver-mediated trifluoromethylation-iodination of arynes to give the corresponding *ortho*-trifluoromethyl iodoarenes (Scheme 1a).^[6] Although the installation of CF_3 and I groups was rather efficient, an excess amount (3 equiv) of $AgCF_3$ and 1-iodophenylacetylene was required to achieve the optimal yields, with large quantities of silver phenylacetylide being produced as a byproduct. Therefore, a catalytic process for vicinal trifluoromethylation-iodination of arynes by using substoichiometric amounts of silver species is highly desirable. We reasoned that *ortho*-trifluoromethyl iodoarenes and their long-chain R_f analogues could be synthesized by a more atom-economic method, that is, silver-catalyzed insertion of arynes into R_f-I bonds (Scheme 1a).

(a) Synthesis of *o*-perfluoroalkyl iodoarenes(b) Atom transfer reaction of R_fI to a single molecule

(c) Designed catalytic cycle for arynes insertion



Scheme 1. Insertion of arynes into perfluoroalkyl iodides.

Perfluoroalkyl iodides (R_fI) are known as readily available R_f sources. These compounds could serve as both excellent R_f^- and R_f^\bullet precursors in many transformations.^[7-9] For instance, perfluoroalkyl iodides are known to undergo oxidative additions with transition metals, such as Pd ,^[3e,7a] Pt ,^[7a] Zn ,^[3b] Cu ,^[7b] and Ni ,^[7c] to give high-valent perfluoroalkylmetal complexes in cross-coupling reactions. However, in these cases, the electropositive iodine atoms were reduced to iodide anions, which are hard to utilize in the subsequent conversions. In this regard, atom transfer (AT) of R_fI to organic molecules would be an ideal process to achieve complete conversion of R_fI (Scheme 1b). Although the atom-transfer process has great value in synthetic applications, it has previously been restricted to radical additions.^[8] To the best of our knowledge, the ionic atom-transfer reaction of R_fI has never been reported. We envisioned that the insertion of in situ generated arynes into perfluoroalkylmetals (MR_f) would give the corresponding arylmetal intermediates, which would continue to undergo σ -bond metathesis^[10,13] with R_fI to give the desired products and regenerate the MR_f intermediates (Scheme 1c). Herein, we wish to report an unprecedented protocol for a formal insertion^[11] of arynes into R_f-I bonds under silver(I) catalysis, representing probably the first example of ionic atom-/group-transfer reac-

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E-mail: jinbohu@sioc.ac.cn[**] $R_f = CF_3, C_2F_5$ Supporting information for this article is available on the WWW under
<http://dx.doi.org/10.1002/chem.201402846>.

tions of both perfluoroalkyl and iodine groups from R_fI into a single molecule (Scheme 1 a–c).

To test the feasibility of our hypothesis, we carried out the reaction of benzyne (generated in situ from **1a**) with CF_3I by using various metal sources (10 mol%) as catalysts (Table 1).

Table 1. Optimization of the insertion of benzyne into CF_3I .

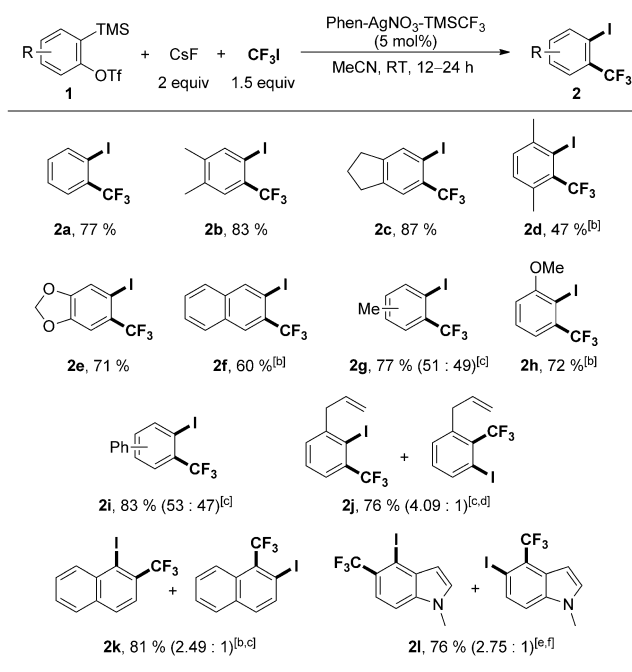
Entry ^[a]	Catalyst	Ligand	CF_3I [equiv] Concentration [(M)]	T [°C]	Yield [%] ^[b]	
					$PhCF_3$	2a
1	none	none	2 (0.4)	50	0	0
2	$ZnCl_2$	none	2 (0.4)	50	0	0
3	$FeBr_2$	none	2 (0.4)	50	0	0
4	$Pd(OAc)_2$	none	2 (0.4)	50	0	0
5	$Ni(acac)_2$	none	2 (0.4)	50	0	0
6	CuI	none	2 (0.4)	50	2	0
7	$AgNO_3$	none	2 (0.4)	50	8	23
8	$AgCF_3$	none	2 (0.4)	50	11	52
9	$AgCF_3$	TMP	2 (0.4)	50	10	43
10	$AgCF_3$	phen	2 (0.4)	50	5	84
11	$AgCF_3$	phen	2 (0.4)	RT	0	88
12	$AgCF_3$	phen	1.5 (0.1)	RT	0	89
13	$AgNO_3 + TMSCF_3$	phen	1.5 (0.1)	RT	0	86
14 ^[c]	$AgNO_3 + TMSCF_3$	phen	1.5 (0.1)	RT	0	88

[a] General conditions: **1a** (0.4 mmol, 1 equiv), CsF (0.8 mmol, 2 equiv), catalyst (10 mol%) in MeCN for 12 h. $AgCF_3$ was prepared before use. acac = acetylacetonate, TMP = 2,2,6,6-tetramethyl-piperidine, phen = 1,10-phenanthroline. [b] Determined by ^{19}F NMR spectroscopy. [c] The catalyst loading was reduced to 5 mol%.

Firstly, we found that no insertion reaction occurred in the absence of a metal catalyst (entry 1). We also tested the reaction in the presence of transition-metal salts, such as $ZnCl_2$, $FeBr_2$, $Pd(OAc)_2$, $Ni(acac)_2$, and CuI ; however, no desired product was detected (entries 2–6). Gratifyingly, when $AgNO_3$ was employed, insertion product **2a** and the undesired protonated product $PhCF_3$ were formed in 23 and 8% yield, respectively (entry 7). Replacing $AgNO_3$ with trifluoromethylsilver ($AgCF_3$)^[12] gave **2a** in 52% yield, along with 11% yield of $PhCF_3$ (entry 8). This finding was in line with our previous study,^[6] in which we discovered that silver(I) species are an appropriate transition metal for the transfer of electropositive iodine atoms. The advantage of silver species comes not only from the moderate nucleophilic reactivity of $ArAg$ species towards R_fI ,^[13] but also from the orthogonal reactivity between R_fAg and ArI .^[6,12d,e] It should be noted that although silver(I) species are widely used as soft Lewis acids and as mild oxidants, their application in catalytic C–X coupling is rare.^[14] To further enhance the efficiency of this insertion reaction, a range of ligands were screened. Although the previously reported hindered monodentate ligand 2,2,6,6-tetramethylpiperidine (TMP) proved to be ineffective (entry 9), 1,10-phenanthroline (phen) gave a much higher yield (entry 10).^[15] This dramatic improvement could be attributed to the high donor ability and strong *trans*

effect of phen, making the aryl group (in $ArAg$) more electro-negative and, thus, accelerating the iodine atom transfer step (Scheme 1 c).^[16] Carrying out the reaction at room temperature (RT) prevented the formation of $PhCF_3$ (entry 11). Reducing the concentration (0.1 M) and quantity of CF_3I (1.5 equiv) did not have a significant effect on the yield of **2a** (entry 12). This result was surprising because in previous studies,^[9a–c] large excess (5–12 equiv) and high concentration (0.8–3.0 M) of CF_3I solutions were needed to achieve favorable yields. Thus, in the present case, gas-injection operations and specific devices, such as Teflon-capped pressure tubes, were not required.^[17] To further simplify the experimental operation, the prepared $AgCF_3$ was exchanged for $AgCF_3$ generated in situ (derived from 1:1 molar ratio of $AgNO_3$ and $TMSCF_3$ in the presence of CsF). Intriguingly, the efficiency of the reaction was not affected (entry 13). Further studies revealed that 5 mol% of phen- $AgNO_3$ - $TMSCF_3$ was sufficient for this insertion reaction (entry 14). Thus, the optimal reaction conditions were found to be as follows: 1.0 equivalent of **1a**, 1.5 equivalents of CF_3I (0.1 M), 2.0 equivalents of CsF , and 5 mol% of phen- $AgNO_3$ - $TMSCF_3$, in acetonitrile at RT.

To explore the scope of the present reaction, we next examined the insertion of various substituted arynes into trifluoromethyl iodide (Scheme 2). In some cases, modifications, such as reducing the reaction temperature and increasing the catalyst loading, were needed to achieve the optimal yields. Moderate to good yields were obtained for both symmetrical (**2a–2f**) and unsymmetrical aryne precursors (**2g–2l**). Functional

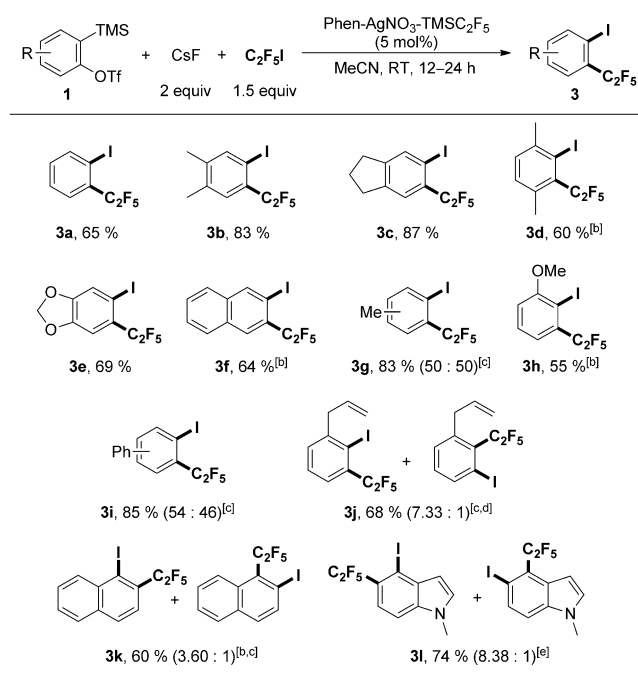


Scheme 2. Scope of silver-catalyzed insertion of arynes into CF_3I .^[a]

[a] The reaction was conducted on a 2 mmol scale under the optimized conditions. Yields are of isolated products. [b] 0.2 equivalents phen- $AgCF_3$. [c] Isolated as a mixture, the ratio of regioisomers was determined by ^{19}F NMR spectroscopy prior to isolation. [d] At 0 °C. [e] 0.1 equivalents phen- $AgCF_3$. [f] Contains \approx 5% impurity.

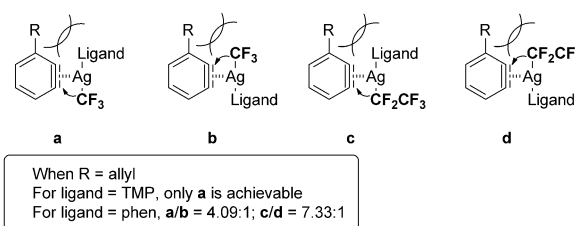
groups, such as acetal, ether, and allyl groups, were compatible with this reaction (**2e**, **2h**, and **2j**). However, the sterically hindered substrate, 3,6-dimethylbenzynes, gave the product **2d** in relatively lower yield. Remarkably, 4,5-indolynes^[18] underwent CF₃–I bond insertion to form **2i** in 76% yield. The indole ring is one of the “privileged structures” in natural products and medicinal agents.^[19] It should be noted that despite the great variety of strategies developed to synthesize C2- and C3-functionalized indoles, methods to synthesize benzenoid-substituted indoles remain limited.^[20]

The scope of silver-catalyzed insertion of arynes into other R_f–I bonds was also studied. To our surprise, although C₂F₅I underwent this insertion reaction smoothly, other R_fI compounds, such as (CF₃)₂CFI and C₄F₉I, failed to give any desired products. When the similar conditions (as those mentioned in Scheme 2) conditions were used for C₂F₅–I bond insertion, similar results were obtained (Scheme 3). It is worth noting that the regiose-



Scheme 3. Scope of silver-catalyzed insertion of arynes into C₂F₅I.^[a]
[a] The reaction was conducted on a 1 mmol scale under the optimized conditions. Yields are of isolated products. [b] 0.2 equivalents phen-AgC₂F₅. [c] Isolated as a mixture, the ratio of regioisomers was determined by ¹⁹F NMR spectroscopy prior to isolation. [d] At 0 °C. [e] 0.1 equivalents phen-AgC₂F₅.

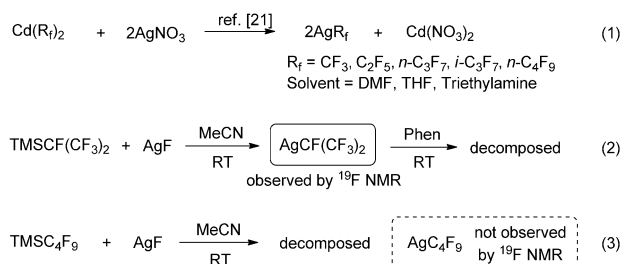
lectivity in **2j** and **3j** was 4.09:1 and 7.33:1, respectively. In contrast, the previously reported trifluoromethylation–iodination of 3-allylbenzynes gave only one isomer.^[6] This difference in regioselectivity can be explained by the repulsion of the *ortho*-substituent group of the arynes by the ligand in the coordinated AgCF₃ species (Scheme 4). This result is consistent with an increase in steric hindrance and rigidity of phen-AgCF₃ towards 3-substituted arynes compared with that of the previously reported TMP-AgCF₃ intermediate (Scheme 4a). Thus, the



Scheme 4. Regioselectivity of 3-substituted arynes.

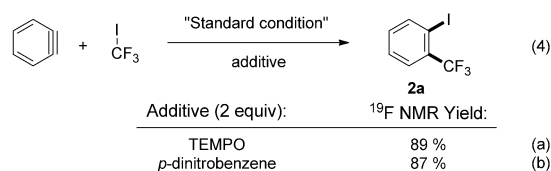
steric effect of the ligands may be arranged as follows: CF₂CF₃ > CF₃ (Scheme 2 and 3, **2j** versus **3j**); CF₃ > phen (Scheme 2, **2j**); phen > TMP (**2j** versus the single isomer that was previously reported^[6]). In addition, an *ortho* donating group on the arynes could serve as a directing group and enhance the regioselectivity of the products. Hence, the reaction of 3-methoxybenzynes gave only **2h** or **3h** without other isomers.

To gain more insights into the different reactivity of perfluoroalkyl iodides, we examined the stability of AgCF(CF₃)₂ and AgC₄F₉, which were prepared from AgF and the corresponding TMSR_f derivatives, in a 1:1 ratio, at room temperature in acetonitrile. Naumann et al. reported the preparation and characterization of AgR_f species by means of ligand-exchange reactions of AgNO₃ and Cd(R_f)₂ in aprotic polar solvents [Eq. (1)].^[21] We found that AgCF(CF₃)₂ was stable in MeCN and existed as an equilibrium between the neutral species AgCF(CF₃)₂·D (D = solvent) and the ate complex [Ag(CF(CF₃)₂)₂][−]. However, when 1,10-phenanthroline was added into this solution, brown sediment was instantly formed and the original fluorine signals disappeared from the ¹⁹F NMR spectrum [Eq. (2)]. In contrast, the reaction of TMSC₄F₉ and AgF gave an unidentified product, which may be generated from the decomposition of the AgC₄F₉ intermediate [Eq. (3)]. Thus, the failure of R_f–I bond insertion reaction (when R_f = CF(CF₃)₂, C₄F₉) may be explained by the low stability of AgR_f, although the origin of this low stability remains unknown.^[22]



To probe whether radical intermediates are involved in this insertion reaction, 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO; 2.0 equiv), an efficient free radical scavenger, was introduced as an additive under the standard conditions [Eq. (4a)]. An identical yield (89%) of **2a** was obtained, suggesting that TEMPO has no significant effect on the reaction efficiency. We also examined the reaction in the presence of an electron-

transfer (ET) scavenger. When 2.0 equivalents of *para*-dinitrobenzene (DNB) was employed as a SET inhibitor, desired product **2a** was formed in 87% yield [Eq. (4b)]. Thus, these observations indicate that a mechanism involving radical or SET pathways is not likely.^[23]



In conclusion, we have developed a silver-catalyzed insertion of arynes into R_f-I bonds under mild conditions. In this reaction, R_fI compounds were transferred to aryne intermediates through an ionic atom-/group-transfer process. This protocol provides not only a quick access to the corresponding *ortho*-perfluoroalkyl iodoarenes, but also a fundamentally new and intriguing pathway for R_fI atom transfer. Further exploration of this new type of insertion reaction and the reactivity of R_fI is in progress.

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Keywords: arynes • insertions • iodination • perfluoroalkyl iodide • perfluoroalkylation

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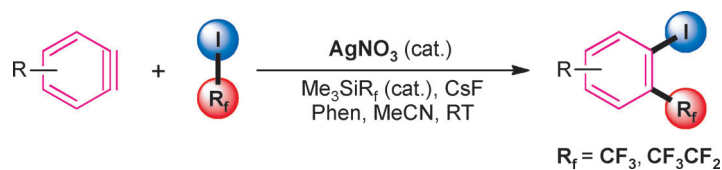
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Insertion Reactions

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 Silver-Catalyzed Formal Insertion of Arynes into R_f-I Bonds

Silver catalysis: Silver nitrate (AgNO₃) catalyzes the vicinal perfluoroalkylation-iodination of arynes with perfluoroalkyl iodides R_fI (R_f = CF₃, C₂F₅), representing

the first example of ionic atom-/group-transfer reactions of both the perfluoroalkyl group and iodine atom from R_fI into a single molecule (see scheme).