**Cross-Coupling**

# Trifluoromethylthiolation of Aryl Iodides and Bromides Enabled by a Bench-Stable and Easy-To-Recover Dinuclear Palladium(I) Catalyst**

*Guoyin Yin, Indrek Kalvet, and Franziska Schoenebeck*

***Abstract:*** *While palladium catalysis is ubiquitous in modern chemical research, the recovery of the active transition-metal complex under routine laboratory applications is frequently challenging. Described herein is the concept of alternative cross-coupling cycles with a more robust (air-, moisture-, and thermally-stable) dinuclear $Pd^I$ complex, thus avoiding the handling of sensitive $Pd^0$ species or ligands. Highly efficient C–SCF$_3$ coupling of a range of aryl iodides and bromides was achieved, and the recovery of the $Pd^I$ complex was accomplished via simple open-atmosphere column chromatography. Kinetic and computational data support the feasibility of dinuclear $Pd^I$ catalysis. A novel SCF$_3$-bridged $Pd^I$ dimer was isolated, characterized by X-ray crystallography, and verified to be a competent catalytic intermediate.*

**P**alladium-catalyzed coupling reactions belong to the most utilized synthetic tools in modern academic and industrial research.[1] These transformations generally proceed via the oxidation states (0) and (II) of mononuclear palladium complexes. However, many palladium(0) catalysts and popular ligands are not air-stable,[2,3] thus requiring their handling and storage under inert conditions. A common approach to increasing the operational simplicity is the employment of air-stable precursors [e.g., palladium(II) pre-catalysts[4]] which release the catalytically active components in situ. While these developments have found widespread applications, the recovery of the sensitive in situ generated palladium species after reaction completion is less straightforward.[5] Consequently, under routine laboratory applications, most employed catalysts are simply disposed of.

We envisioned that utilizing the more robust +1 oxidation state of palladium directly as a catalyst through alternative dinuclear coupling cycles would be advantageous in terms of operational simplicity, convenience, and sustainability, since the stable catalytic entity should easily be recoverable without the need for special precautions or technology. In the d$^9$ configuration, palladium favors a dimeric appearance, featuring distinct Pd–Pd bonds.[6] Little is understood about

the reactivities at such dinuclear palladium(I) sites, and the role of such dimers in catalysis has generally been ascribed to being off-cycle precursors to the actual catalytically active palladium(0) species.[7] Indeed, the Pd$^I$ dimer **1**[8] has found use as efficient pre-catalyst in cross-coupling reactions (Figure 1).[9] By contrast, the iodinated analogue **2** does not

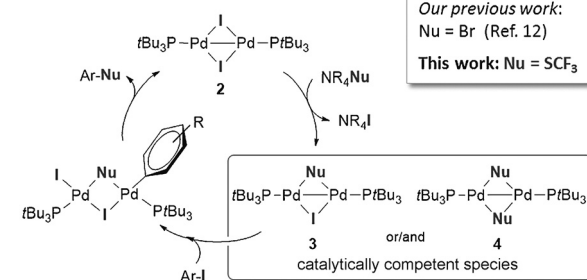■  Efficiency of Pd(I)-Pd(I) as pre-catalyst to Pd(0):
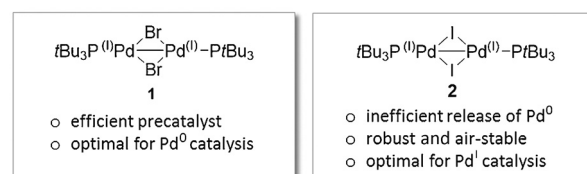


■  Pd(I)-Pd(I) as catalyst:



***Figure 1.*** Pd$^I$-dimer catalysis concept (bottom).

act as an efficient reservoir for Pd$^0$.[10] Its dinuclear Pd–Pd core remains intact in the presence of a variety of nucleophiles, bases, and reaction conditions.[11] Notably, we found **2** to be completely stable to oxygen as a solid; it has been stored in our labs on the bench for over three months without any observed decay to date. We envisioned that these stability features make **2** an attractive candidate for exploring dinuclear Pd$^I$ catalysis.

We recently reported our initial success in the area, that is, a Pd$^I$-dimer-catalyzed I→Br halogen exchange of 9-iodo-anthracene with NBu$_4$Br.[12] Our detailed mechanistic study of this halogen exchange process supported the mechanism presented in Figure 1. Notably, typical Pd$^0$ catalysis did not trigger this halogen exchange under analogous reaction conditions, thus highlighting the potential for distinct reactivities at such dinuclear Pd$^I$–Pd$^I$ sites. While this study was a proof-of-concept, the halogen exchange had not shown a wide substrate scope. We hypothesized that this was because of inefficient I–Br exchange at Pd$^I$ (i.e., conversion of **2** into **3** in Figure 1), and hence the limited formation of the reactive

[*]  Dr. G. Yin, I. Kalvet, Prof. Dr. F. Schoenebeck
    Institute of Organic Chemistry, RWTH Aachen University
    Landoltweg 1, 52074 Aachen (Germany)
    E-mail: franziska.schoenebeck@rwth-aachen.de
    Homepage: http://www.schoenebeck.oc.rwth-aachen.de/

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species **3**. Thus, we subsequently shifted our attention towards nucleophiles that would present a greater driving force, and focused on the Pd$^I$–Pd$^I$-catalyzed conversion of aryl halides into ArSCF$_3$ with [SCF$_3$]$^-$ as nucleophile.

Trifluoromethylthiolation has received considerable attention[13, 14] owing to the importance of ArSCF$_3$ compounds in pharmaceutical and agrochemical research as a result of their remarkable lipophilicity properties.[15] The direct metal-catalyzed functionalization of aryl halides to ArSCF$_3$ constitutes an attractive strategy in this context. However, only three catalytic protocols to functionalize aryl halides have been realized to date.[16] Buchwald and co-workers made a seminal contribution in developing a Pd$^0$-catalyzed Ar–SCF$_3$ bond-formation of aryl bromides.[17] While there have been no other reports of successful Pd-catalyzed SCF$_3$ couplings of alternative aryl halides, Vicic and Zhang developed a [Ni(cod)$_2$]/bipyridine-catalyzed protocol to convert certain aryl iodides and bromides into ArSCF$_3$.[18,19] While electron-rich aryl iodides showed good conversions, interestingly, the more electron-deficient ArI analogues gave less than 50% yield of ArSCF$_3$. Alternative methods to functionalize aryl iodides require either stoichiometric amounts of a copper salt[20] or, under copper catalysis, *ortho*-directing groups to be present.[21]

Our previous fundamental mechanistic studies in the area of Pd$^I$ dimer reactivity suggested that the key requirements for successful catalysis at Pd$^I$–Pd$^I$ sites are that firstly the nucleophile of interest must be capable of replacing the bridging iodines at Pd$^I$–Pd$^I$, and secondly the same nucleophile also needs to be able to stabilize the resulting dinuclear Pd$^I$ framework.[12] To date, there is no SCF$_3$-derived Pd$^I$ dimer known. Thus, we initially set out to synthesize the SCF$_3$-bridged Pd$^I$ dimer **4** by comproportionation of [Pd$^0$(P$t$Bu$_3$)$_2$] and [Pd$^{II}$(SCF$_3$)$_2$] (Figure 2). $^{31}$P NMR spectroscopic analysis indicated that conversion into a single phosphine-containing

species had taken place at room temperature in THF within one hour, as judged by the observation of a single resonance at $\delta = 93.82$ ppm [relative to (EtO)$_3$PO as internal standard]. X-ray crystallographic analysis confirmed that the SCF$_3$-bridged Pd$^I$ dimer **4** had formed (Figure 2).[22] This novel complex features an interesting *cis* arrangement of the SCF$_3$ units and a Pd–Pd bond length of 2.57 Å, which is in line with distances previously reported for Pd–Pd single bonds.[6,23] In analogy to its iodine-bridged counterpart, **4** is completely stable in air.

To test the potential of **4** in functionalizing aryl iodides, we subsequently studied the stoichiometric reactivity of **4** with the aryl iodide **5** (Figure 2). This reaction resulted in clean conversion of **5** into the ArSCF$_3$ **6** with concomitant formation of **2** ($\delta = 101.5$ ppm) and the mixed Pd$^I$ dimer, featuring an iodine and SCF$_3$ bridge ($\delta = 98.8$ ppm). No signals other than those corresponding to the Pd$^I$ dimers were observed by $^{31}$P NMR spectroscopy. These results suggest that direct reactivity of the SCF$_3$-derived **4** with ArI seemed indeed possible.

To gain additional support we undertook kinetic investigations of the **4**-mediated trifluoromethylthiolation of 9-iodoanthracene (**7**). Under pseudo-first-order conditions (**7** was employed in considerable excess), we determined a first-order kinetic dependence in **4** and an overall activation barrier of $\Delta G^{\ddagger} = 28.0 \pm 3.9$ kcal mol$^{-1}$ for the ArI→ArSCF$_3$ exchange process.

We subsequently examined whether these kinetic data would also be in the range of computationally predicted barriers for a mechanism proceeding by direct oxidative addition of **4** to 9-iodoanthracene. We applied the computational method M06L along with the implicit solvation model CPCM to account for toluene and two different basis sets [def2TZVP and 6-311++G(d,p)/LANL2DZ] for our studies.[24,12b] Figure 3 presents the full free-energy profile of the stoichiometric I→SCF$_3$ exchange. The direct oxidative addition by **4** to **7** was found to be energetically feasible and endergonic, and is in line with the spectroscopic data in Figure 2 which only showed the Pd$^I$ dimers as stable phosphine-containing intermediates. The reductive elimination via TS-2 was calculated to be rate-limiting. Within error limits, the calculated barriers are in reasonable agreement with the experimentally determined barrier. Overall, the I→SCF$_3$ exchange reaction is thermodynamically driven, and exergonic overall by $\Delta G_{rxn} \approx -21$ kcal mol$^{-1}$ (Figure 3).

Encouraged by these mechanistic data, and having established that **4** serves as an efficient trifluoromethylthiolation agent, we subsequently set out to explore the corresponding catalytic transformation. Pleasingly, by using 2 mol% of **2** along with the easily accessible SCF$_3$-source (Me$_4$N)SCF$_3$,[25] a range of aryl iodides were successfully trifluoromethylthiolated in toluene at 80°C. Table 1 summarizes the results. Electron-rich and electron-poor aryl iodides were converted into ArSCF$_3$ in excellent yields. The transformation was found to be compatible with aldehyde, ketone, ester, ether, nitro, cyano, and amine functional groups (Table 1). Pleasingly, two heterocyclic examples were also trifluoromethylthiolated in good yields. As such, our Pd$^I$-catalyzed protocol offers a substantially wider substrate scope

▪ Synthesis and stoichiometric reactivity of **4**:
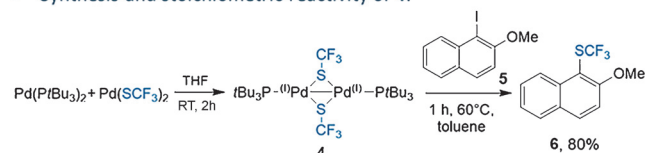
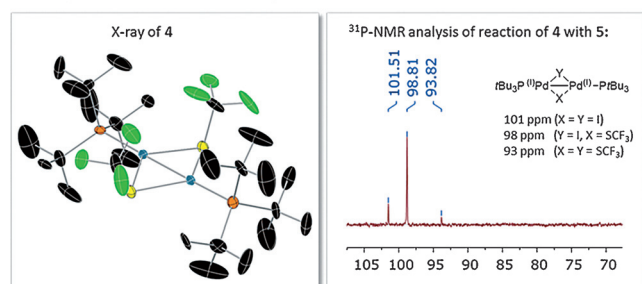▪ Xray of **4** and $^{31}$P-NMR analysis of reaction mixture after 1h:



**Figure 2.** Preparation of the SCF$_3$-bridged Pd$^I$ dimer **4** and stoichiometric reactivity with **5** (yield relative to **4**, 2 equiv of **6** can form). (EtO)$_3$PO was used as an internal standard for the $^{31}$P NMR analysis. Thermal ellipsoids are shown at 50% probability.
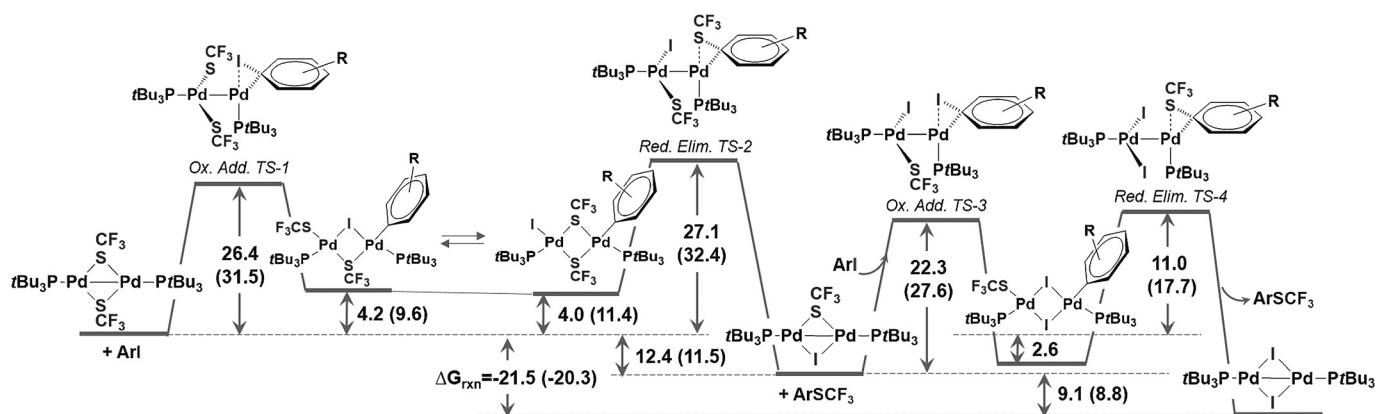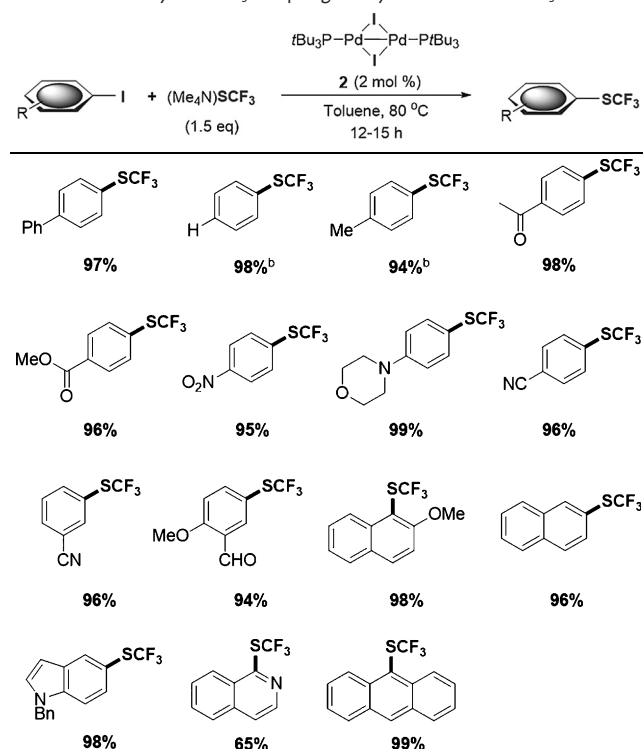
**Figure 3.** Free-energy path of I→SCF₃ exchange between **4** and **7**, calculated at CPCM (toluene) M06L/6-311++G(d,p) [SDD for Pd,I] or CPCM (toluene) M06L/def2TZVP (in parentheses). Geometries were optimized at B3LYP/6-31G(d) [with LANL2DZ for Pd,I]. Values are in kcal mol⁻¹ at 298 K.

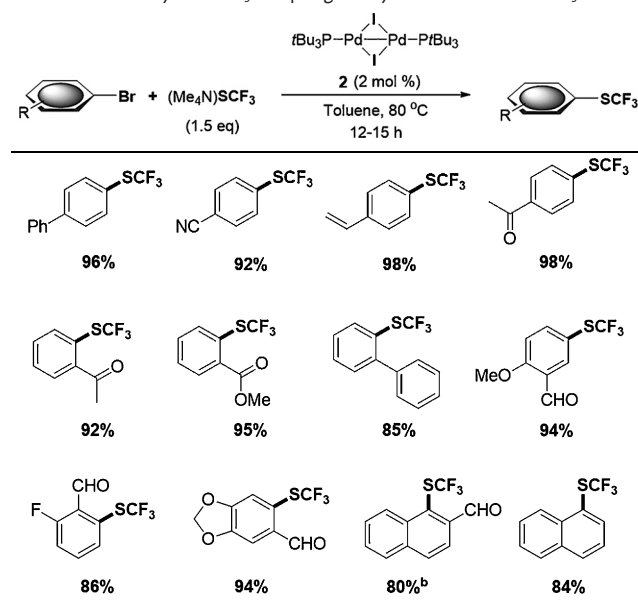**Table 1:** Pd$^I$-catalyzed SCF₃ coupling of aryl iodides to ArSCF₃.[a]



[a] **2** (3.6 mg, 0.004 mmol), ArI (0.2 mmol), (Me₄N)SCF₃ (52 mg, 0.3 mmol), toluene (1.0 mL). Yield of isolated product given. [b] Yield determined by ¹⁹F NMR analysis versus PhCF₃ as an internal standard.

**Table 2:** Pd$^I$-catalyzed SCF₃ coupling of aryl bromides to ArSCF₃.[a]



[a] **2** (3.6 mg, 0.004 mmol), ArBr (0.2 mmol), (Me₄N)SCF₃ (52 mg, 0.3 mmol), toluene (1.0 mL). Yield of isolated product given. [b] 4 mol% catalyst **2** was used.

than the established metal-catalyzed SCF₃-coupling protocols of aryl iodides.

To further test the generality of the coupling enabled by Pd$^I$–Pd$^I$, we embarked on extending our coupling protocol to aryl bromides. Our computational studies predicted roughly 3 kcal mol⁻¹ greater activation energy for the individual coupling steps for the reaction with ArBr (see the Supporting Information for the computed full profile), and catalysis therefore appeared viable. Thus, we subjected a number of aryl bromides to the trifluoromethylthiolation with **2**. Pleasingly, the corresponding SCF₃-coupled products were fur-

nished in very good yields, by using only 2 mol% of the Pd$^I$ dimer (Table 2) and tolerating carbonyl, cyano, ether, and CF functional groups.

If our calculated mechanism in Figure 3 was indeed operative, the more labile **1** would be expected to be generated as a catalytic intermediate in the SCF₃-coupling of aryl bromides. Although **1** is likely rapidly converted into the brominated analogue of **3** (or to **4**) in the presence of (Me₄N)SCF₃, mechanistically we cannot rule out that [Pd⁰] is being released in the catalytic coupling process. However, we succeeded in the recovery of the Pd$^I$–Pd$^I$ catalyst in the form of bridged complex **4** after SCF₃ coupling of a number of aryl bromides. By using a slightly higher catalyst loading (10 mol%), we recovered **4** from the reaction with 4-bromo-1,1′-biphenyl in 76%, with 5-bromo-2-methoxybenz-aldehyde in 64%, and 1-bromonaphthalene in 69%.[26] This

recovery suggests that if [Pd⁰] were to be formed during the catalytic transformation, this process would either be reversible or not predominant.

We also recovered the Pd$^I$ catalyst (as the bis-(SCF₃) version **4**) from the SCF₃-coupling reactions of the iodobenzene (in 88 %), 4-(4-iodophenyl)morpholine (in 84 %), and 3-iodobenzonitrile (in 77 %).[26] These examples are representative of the remarkable persistency of the dinuclear Pd$^I$ complex to these reaction conditions. Moreover, in analogy to **2**, the SCF₃-bridged analogue **4** shows complete air stability and proved to be tolerant to silica, thus allowing the purification of the recovered catalyst by column chromatography under standard laboratory atmosphere. Subsequent reuse of the recovered **4** as the catalyst in another C−SCF₃ coupling of 4-bromo-1,1′-biphenyl gave high conversion into the desired product (88 %) after 7 hours at 60 °C. The catalyst **4** was subsequently recovered in 68 % yield (Scheme 1).
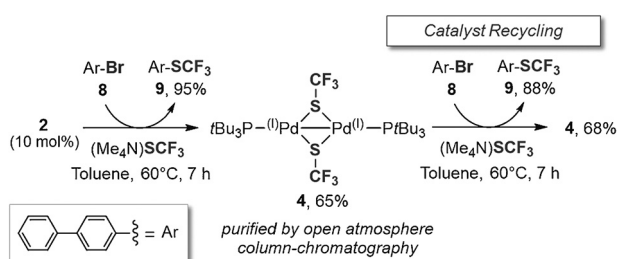


**Scheme 1.** Demonstration of recyclability of the Pd$^I$ dimer.

In conclusion, we herein demonstrated a highly efficient and operationally simple SCF₃-coupling protocol of a range of aryl iodides and bromides enabled by a bench-stable dinuclear Pd$^I$ catalyst and the easily accessible (Me₄N)SCF₃ reagent. The catalyst was shown to be very persistent and was recovered by ordinary column chromatography in an open laboratory atmosphere. The air-stability and straightforward recoverability of the Pd$^I$ catalyst poses a considerable practical advantage over more sensitive Pd⁰- or Ni⁰-catalyzed processes. While a catalyst per definition is not consumed during a reaction, practical obstacles in recoverability frequently still lead to its loss. We envisage that the herein explored alternative coupling concept at dinuclear Pd$^I$ sites presents a promising advance in this context. Our future research is directed at exploring the full potential of this catalysis concept.

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[23] The novel dimer complex **4** has a slightly shorter Pd–Pd distance than the commercial Pd$^I$ dimer **1** (2.62 Å). Also see Ref. [8].

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