

Highly Efficient C–SeCF₃ Coupling of Aryl Iodides Enabled by an Air-Stable Dinuclear Pd^I Catalyst**

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Abstract: Building on our recent disclosure of catalysis at dinuclear Pd^I sites, we herein report the application of this concept to the realization of the first catalytic method to convert aryl iodides into the corresponding ArSeCF₃ compounds. Highly efficient C–SeCF₃ coupling of a range of aryl iodides was achieved, enabled by an air-, moisture-, and thermally stable dinuclear Pd^I catalyst. The novel SeCF₃-bridged dinuclear Pd^I complex **3** was isolated, studied for its catalytic competence and shown to be recoverable. Experimental and computational data are presented in support of dinuclear Pd^I catalysis.

While nature makes use of the synergistic interplay of two (or more) metals in many metalloenzymes,^[1] the field of homogeneous cross-coupling catalysis is dominated by the reactivity of mononuclear metal complexes, in particular well-defined Pd⁽⁰⁾ complexes.^[2] Dinuclear Pd^I–Pd^I complexes have been known for the past 70 years,^[3] but their application in catalysis has been primarily limited to being labile off-cycle precursors to the active Pd⁽⁰⁾ complexes.^[4] In contrast our group recently established that more robust dinuclear Pd^I complexes that are less prone to the release of Pd⁽⁰⁾ may function directly as catalysts in cross-coupling of aryl halides by alternative coupling cycles.^[5,6] In this context we recently succeeded in the catalytic I/Br halogen exchange^[5a,b] and the trifluoromethylthiolation of aryl halides,^[5c] employing the iodine-bridged Pd^I-dimer **1**. Notable practical advantages of this concept are the air-stability of **1** and the straightforward recoverability of the dinuclear entity after reaction completion, avoiding the handling of sensitive Pd⁽⁰⁾ complexes or ligands. Building on this work, we herein report the first catalytic method to synthesize ArSeCF₃ compounds.

The embedding of fluorine into organic molecules significantly alters their physical properties. These include conformational, solubility, lipophilicity, and metabolic stabil-

ity which in turn are of relevance to numerous branches of chemistry.^[7] In this context, the trifluoromethylselenide group (SeCF₃) is a promising target for agrochemical and pharmaceutical research as it features several important properties that control membrane permeability and bioavailability.^[8] Although excess selenium is toxic to humans because it replaces sulfur in several metabolic processes without mimicking its function,^[9] at lower (subtoxic) doses selenium is an essential nutrient to humans and other living systems.^[10] Moreover, it has recently stimulated increasing attention because of its therapeutic and preventive effects against several kinds of cancer, in particular prostate and colorectal cancer.^[11] Straightforward access to fluorinated analogues, in particular ArSeCF₃ compounds may hence enable various avenues in chemical and biomedical research.

However, the synthetic access to this class of compounds is limited, relying on indirect synthetic approaches^[12] which often have a small substrate scope or which require the employment of stoichiometric amounts of metal salts.^[13] To date, no direct catalytic route to aryltrifluoromethyl selenides exists. While palladium-catalyzed cross coupling is arguably the method of choice to install carbon–heteroatom bonds in a catalytic fashion, little progress has been made in the Pd-catalyzed synthesis of ArSeR^[14] where R = CF₃ and also more generally (i.e. for R ≠ CF₃). The current state of the art relies on a Stille approach with the use of Bu₃Sn–SePh as coupling partner.^[15] This approach would generate stoichiometric amounts of potentially toxic stannane by-products, thus our objective was instead to develop an operationally simple and general method that minimizes the generation of waste. Ideally, this involves convenient and air-stable reagents.

Following our detailed fundamental studies, we recently succeeded in a highly efficient cross-coupling reaction triggered by a dinuclear Pd^I complex.^[5] Our mechanistic data of this coupling process were consistent with the mechanism presented in Figure 1. Key to effective catalysis is that the

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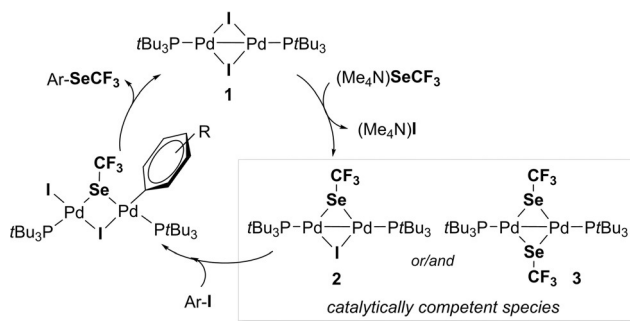
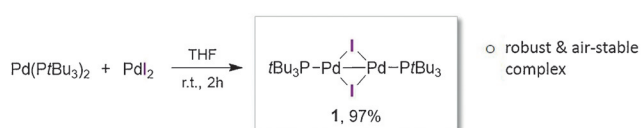


Figure 1. Anticipated Pd^I-dimer catalyzed C–SeCF₃ coupling.

employed nucleophile efficiently displaces the bridging iodine atoms in complex **1**, and also functions as a suitably stabilizing bridge in the dinuclear Pd^I framework (as **2** or **3**, see Figure 1). This catalysis concept does not require the handling of sensitive Pd⁽⁰⁾ catalysts and instead utilizes the robust and bench-stable Pd^I-I dimer **1** (see Figure 1).

However, the previously reported syntheses of **1** are rather cumbersome, involving the reaction of Pd-precursors with organic electrophiles and generating stoichiometric amounts of side-products.^[16,17] We therefore initially set out to develop a facile synthesis for rapid access to catalyst **1** and identified that the direct comproportionation of commercially available Pd^{II}I₂ and [Pd⁽⁰⁾(P(*t*Bu)₃)₂]^[18] in THF for 2 h at room temperature yields the air-stable Pd^I-I dimer catalyst **1** in quantitative yield (Figure 2).

Improved synthesis of Pd^I-I-dimer **1**:



I / SeCF₃ exchange at Pd^I-Pd^I and X-ray structure of **3**:

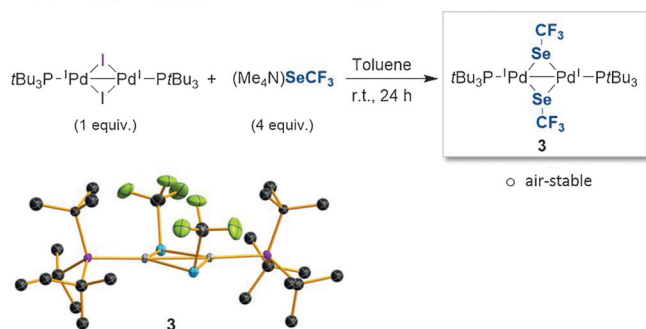


Figure 2. Preparation of Pd^I dimer complexes **1** (top) and **3** (bottom).

With complex **1** in hand, we subsequently examined the feasibility for I→SeCF₃ exchange at the bridging units of the Pd^I-I dimer using a suitable SeCF₃ nucleophile. Tyrra, Naumann et al. developed a facile route to (Me₄N)SeCF₃ and we implemented a modified version of this synthesis for our studies.^[19] Treating a solution of Pd^I-I dimer **1** in toluene with an excess of (Me₄N)SeCF₃ at room temperature pleasingly led to clean replacement of the bridging iodine atoms by SeCF₃, as confirmed by ³¹P and ¹⁹F NMR spectroscopic analyses. Analysis of the mixture after 5 h revealed that two new ³¹P signals at δ = 99.1 and 101.4 ppm had formed in addition to that of Pd^I-I-dimer **1** (δ = 102.3 ppm), in accordance with a potential I/SeCF₃-mixed dimer **2** and fully displaced SeCF₃-dimer **3**.^[20] After 24 h, conversion into a single phosphine-containing species was complete (resonance at δ = 99.1 ppm in the ³¹P NMR spectrum and δ = −24.5 in the ¹⁹F NMR spectrum). Isolation and X-ray crystallographic analysis of this species unambiguously confirmed that the novel doubly SeCF₃-bridged Pd^I-dimer **3** had formed.^[21] The X-ray structure of **3** is illustrated in Figure 2.^[22]

In analogy to the iodinated analogue **1**, Pd^I-SeCF₃ dimer **3** also proved to be stable in air.^[23] It features a distinct Pd–Pd bond of 2.6073(3) Å, and the SeCF₃ groups are oriented in a *syn* fashion.

We subsequently tested for the ability of complex **3** to function as trifluoromethylselenolation agent. To our delight, treating the Pd^I-SeCF₃ dimer **3** with two equivalents of 1-iodo-4-nitrobenzene (**4**) resulted in clean formation of ArSeCF₃ under concomitant formation of Pd^I-I dimer **1** at 60 °C in 2.5 h. The in situ analysis of the reaction mixture by ³¹P NMR spectroscopy showed no sign of Pd⁽⁰⁾- or Pd^{II}-derived species.

Computational studies were next applied to test whether the observed reactivity could be consistent with a mechanism that proceeds by direct oxidative addition of the dimer **3** to **4**. For energy calculations, we employed M06L in combination with the implicit solvation model CPCM to account for toluene and the basis set def2-TZVP.^[5] The geometries were optimized at B3LYP.^[24] Distinct dinuclear oxidative-addition transition states were located, of which the addition of ArI **4** to dimer **3** to is illustrated in Figure 3. The corresponding full

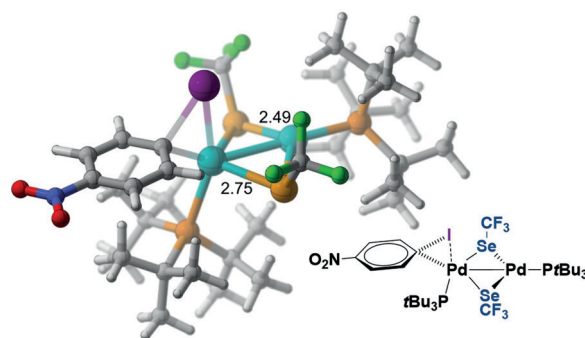


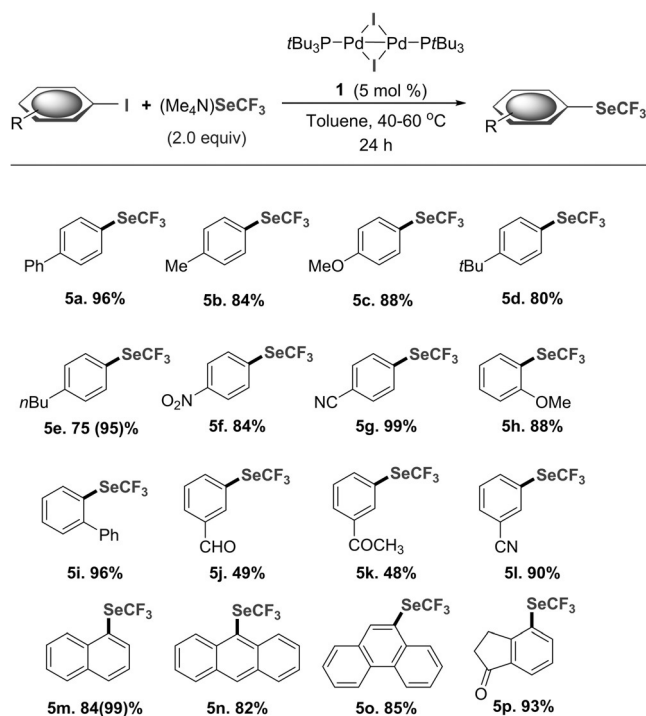
Figure 3. Calculated transition state for the oxidative addition of Pd^I-SeCF₃ dimer **3** (left) to 1-iodo-4-nitrobenzene. The Pd...Pd distance in the transition state is 2.83 Å. (Geometry was optimized at B3LYP/6-31G(d) with LANL2DZ for Pd,I.)

reaction free-energy profile is in the Supporting Information (Figure S1) and is largely analogous to our previously studied reactivity profiles of dinuclear reactivity.^[5] The direct oxidative addition of ArI to **3** was calculated to proceed with a barrier of ΔG[‡] = 31.4 kcal mol^{−1}. The mixed Pd^I-SeCF₃-I dimer **2** is predicted to be more reactive, giving a barrier of ΔG[‡] = 29.0 kcal mol^{−1}.^[25] The overall driving force of the I / SeCF₃ exchange is thermodynamics, as the reaction is exergonic.

As the catalytic trifluoromethylselenolation is, to date, unprecedented, we next set out to investigate the efficiency of C–SeCF₃ bond formation with dinuclear Pd^I catalysis. Given that we had seen clean I/SeCF₃ exchanges at the Pd^I framework in the presence of the external (Me₄N)SeCF₃ nucleophile (see Figure 2), we envisioned that the required regeneration of the active Pd^I-SeCF₃ dimer **3** or the mixed Pd^I-SeCF₃-I dimer **2** under catalytic conditions should also be feasible. Notably, the mixed Pd^I-SeCF₃-I dimer **2**, that was computationally predicted to be more reactive than **3**, would form initially from **1**, requiring only a single I/SeCF₃ exchange

at Pd^I–Pd^I. As such, this concept holds promise to allow for the first direct catalytic C–SeCF₃ bond formation.

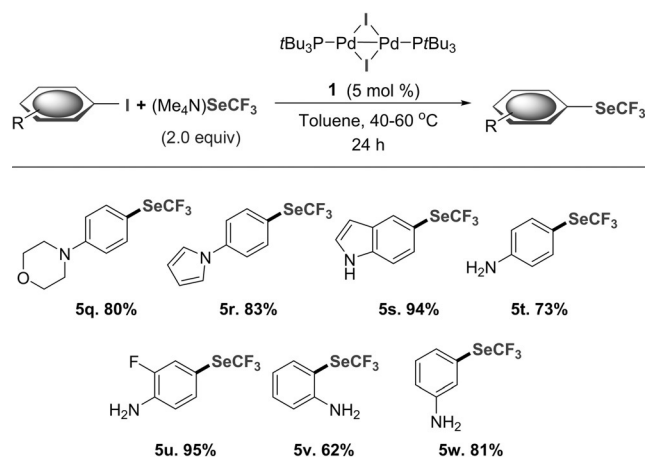
Using 5 mol% of the iodine-bridged Pd^I dimer **1** and (Me₄N)SeCF₃ (2.0 equiv) in toluene at 40–60 °C, we successfully coupled a range of aryl iodides to the corresponding SeCF₃ compounds. Scheme 1 summarizes the results. A number of electron-rich and electron-poor aryl iodides were trifluoromethylselenolated in excellent yields. The method proved to be compatible with nitro (**5f**), cyano (**5g**, **5l**), ether (**5c**, **5h**), aldehyde (**5j**) and ketone (**5k**, **5p**) functional groups as well as polyaromatic substrates (**5m–o**, see Scheme 1).^[26]



Scheme 1. Pd^I-catalyzed SeCF₃ coupling of aryl iodides to Ar–SeCF₃. Pd^I dimer **1** (8.7 mg, 0.01 mmol), ArI (0.2 mmol), (Me₄N)SeCF₃ (89 mg, 0.4 mmol), toluene (1.0 mL), yields are of isolated product. The numbers in parenthesis were determined by ¹⁹F NMR spectroscopy analyses against internal standard (4,4'-difluorobiphenyl).

Given the relevance of nitrogen-containing compounds in pharmaceutical and agrochemical research, we also investigated the functionalization of N-heterocycles and amine derivatives (see Scheme 2). Notably, we found that protecting groups were not required. The C–SeCF₃ coupling proceeded efficiently in the presence of unprotected primary aromatic amines in *ortho*-, *meta*-, or *para*-position (**5t–w**, Scheme 2), heterocyclic (pyrrole, indole) and aliphatic amines (morpholine, **5q**).

This stability in the presence of nucleophilic functional groups is a reflection of the remarkable robustness of the iodine- or SeCF₃-bridged Pd^I–Pd^I frameworks. In line with these stability features, we could recently show that the dinuclear Pd^I entity can be recovered after the reaction by ordinary column chromatography under standard laboratory atmosphere.^[5c] The air stability of the Pd^I dimers considerably



Scheme 2. SeCF₃ coupling of amine-containing and N-heterocyclic aryl iodides. Pd^I dimer **1** (8.7 mg, 0.01 mmol), ArI (0.2 mmol), (Me₄N)SeCF₃ (89 mg, 0.4 mmol), toluene (1.0 mL), yields are of isolated product.

simplifies their handling and no special precautions needed to be taken.

For the trifluoromethylselenolation we were also able to recover considerable amounts of the dinuclear Pd^I catalyst. Applying standard reaction conditions (5 mol% of **1**, 40 °C, 24 h) for the synthesis of **5a**, we isolated Pd^I–SeCF₃ dimer **3** from the reaction in 50 % yield by column chromatography.^[27] Alternatively, for the synthesis of **5m** (Scheme 1), we also applied distillation for purification, and the catalyst appeared unaffected to the heat applied (150 °C), allowing **3** to be recovered and isolated in 60 % yield. This is a potential attractive feature for larger scale applications, for which chromatography is a less-desired purification method. The subsequent recycling of the recovered Pd^I dimer **3** catalyst (5 mol%) in another C–SeCF₃ coupling of aryl iodide was also efficient and the product ArSeCF₃ **5m** was obtained in high yield (93 %).

In conclusion, the first catalytic trifluoromethylselenolation method for aryl iodides has been developed. This transformation is enabled by the benchstable dinuclear Pd^I complex [(PtBu₃)PdI]₂ (**1**), for which an improved synthesis allowing straightforward access was also developed. The method is operationally simple and shows high functional-group tolerance. Even unprotected aromatic amines and heterocycles were well tolerated, highlighting the robustness of the dinuclear Pd^I complexes used. The novel SeCF₃-bridged Pd^I dimer **3** was isolated, characterized, and shown to be a competent trifluoromethylselenolation agent for aryl iodides. Stoichiometric reactivity investigations, NMR spectroscopy and computational studies suggest the feasibility of dinuclear reactivity.^[28] Given the air stability of the dinuclear Pd^I catalyst, its straightforward recoverability, and the minimal waste generated (Me₄NI), we anticipate that the coupling concept presented herein will find widespread applications and may stimulate future developments of bond formations triggered by dinuclear catalysis.

Keywords: cross coupling · DFT calculations ·
dinuclear catalysis · fluorine chemistry · synthetic methods

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- [19] W. Tyrre, D. Naumann, Y. L. Yagupolskii, *J. Fluorine Chem.* **2003**, *123*, 183. We added molecular sieves and performed the synthesis under the exclusion of light. The reagent was obtained in high quality (which is of utmost importance for optimal reactivity).
- [20] The ³¹P NMR shifts are against (OMe)₃P=O as internal standard.

- [21] Selected X-ray data for **3**: $C_{26}H_{54}F_6P_2Pd_2Se_2$, $M_r = 913.35$, monoclinic; space group $I2m$ (no. 12), $a = 13.1716$ (9), $b = 15.5289$ (11), $c = 17.0646$ (17) Å, $\beta = 95.9150$ (10)°, $V = 3471.8$ (5) Å³, $Z = 4$, $T = 100$ K; 23136 reflections measured ($3.554^\circ \leq 2\theta \leq 64.826^\circ$), 5968 unique ($R_{int} = 0.0203$, $R_{sigma} = 0.0192$) which were used in all calculations. The final R_1 was 0.0265 ($I > 2\sigma(I)$) and wR_2 was 0.0624. CCDC 1407567, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [22] The species giving rise to a resonance signal at $\delta = 101.4$ ppm in ^{31}P NMR (and $\delta = -26.2$ ppm in ^{19}F NMR) is likely the mixed Pd^I -I-SeCF₃ dimer **2**. Mixing of dimers **1** and **3** in 1:1 ratio also led to the appearance of **2**.
- [23] After 3 days of exposure to air, **3** was unchanged as a solid or in solution.
- [24] a) Gaussian 09, Revision D.01, Frisch, M. J. et al. (see Supporting Information for full reference and additional computational information); b) E. Lyngvi, I. A. Sanhueza, F. Schoenebeck, *Organometallics* **2015**, *34*, 805; c) K. J. Bonney, F. Schoenebeck, *Chem. Soc. Rev.* **2014**, *43*, 6609; d) A. S.-K. Tsang, I. A. Sanhueza, F. Schoenebeck, *Chem. Eur. J.* **2014**, *20*, 16432.
- [25] Using CPCM (toluene)M06L with 6-311++G(d,p) basis set and SDD (for Pd) as applied in Ref. [5c], gives a barrier of $\Delta G^\ddagger = 27.1$ kcal mol⁻¹ for addition of **3** to ArI and $\Delta G^\ddagger = 24.7$ kcal mol⁻¹ for addition of **2** to ArI.
- [26] Our preliminary studies suggest that aryl bromides may also be reactive, as we successfully converted three aryl bromides into the corresponding ArSeCF₃ compounds **5a** (91 %), **5c** (90 %), and **5m** (95 %) under the standard conditions noted in Scheme 1. See Supporting Information for details.
- [27] Prolonged exposure to excess nucleophile in solution will eventually lead to degradation of the Pd^I dimer. Thus, for optimal catalyst recoveries, monitoring of the reaction progress and its completion will be required.
- [28] While our data suggest the feasibility of direct reactivity at Pd^I - Pd^I , we have not performed rigorous tests to rule out $Pd^{(0)}$ (or alternative species) in the catalysis experiments. The detection of dinuclear Pd^I complex (without any sign of $Pd^{(0)}$) at the end of the reaction suggests that if release of $Pd^{(0)}$ or other species were to happen, this would be either a minor process or reversible.

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