Pd^{I} Catalysts

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Highly Efficient C–$SeCF_3$ 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 $ArSeCF_3$ compounds. Highly efficient C–$SeCF_3$ coupling of a range of aryl iodides was achieved, enabled by an air-, moisture-, and thermally stable dinuclear Pd^{I} catalyst. The novel $SeCF_3$-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 $ArSeCF_3$ compounds.

The embedding of fluorine into organic molecules significantly alters their physical properties. These include conformational, solubility, lipophilicity, and metabolic stability which in turn are of relevance to numerous branches of chemistry.[7] In this context, the trifluoromethylselenide group ($SeCF_3$) 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 $ArSeCF_3$ 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 $R = CF_3$ and also more generally (i.e. for $R \neq CF_3$). The current state of the art relies on a Stille approach with the use of Bu_3Sn–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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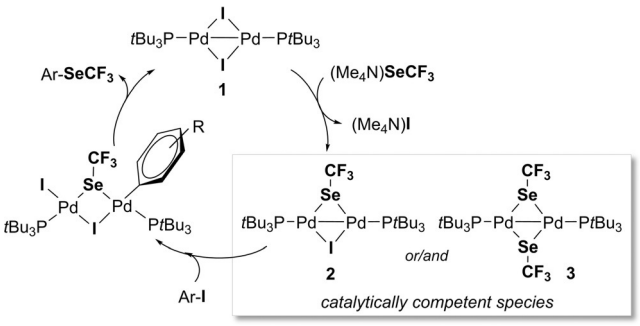


Figure 1. Anticipated Pd^{I}-dimer catalyzed C–$SeCF_3$ coupling.

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 $Pd^{II}I_2$ and $[Pd^{(0)}(PtBu_3)_2]$[18] in THF for 2 h at room temperature yields the air-stable Pd^{I}–I dimer catalyst **1** in quantitative yield (Figure 2).

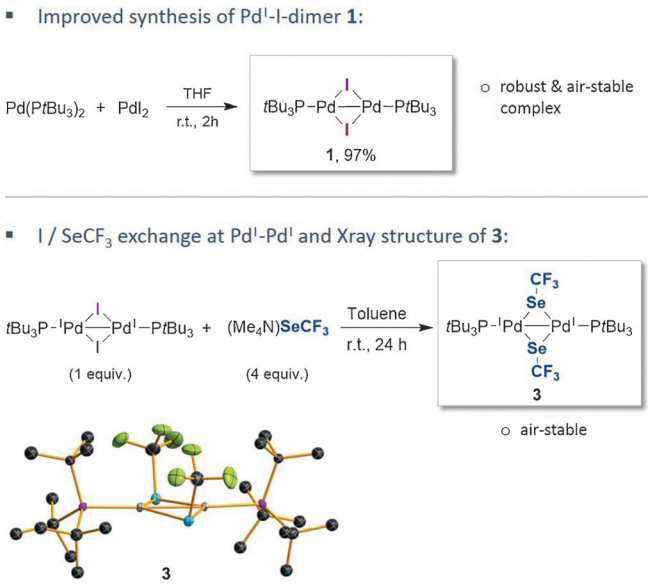


Figure 2. Preparation of Pd^{I} dimer complexes **1** (top) and **3** (bottom).

In analogy to the iodinated analogue **1**, Pd^{I}–$SeCF_3$ dimer **3** also proved to be stable in air.[23] It features a distinct Pd–Pd bond of 2.6073(3) Å, and the $SeCF_3$ 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}–$SeCF_3$ dimer **3** with two equivalents of 1-iodo-4-nitrobenzene (**4**) resulted in clean formation of $ArSeCF_3$ 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 ^{31}P 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

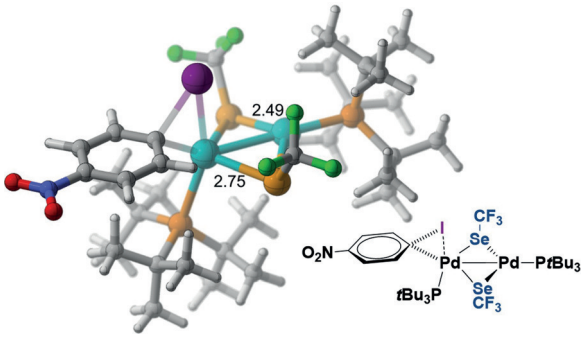


Figure 3. Calculated transition state for the oxidative addition of Pd^{I}–$SeCF_3$ dimer **3** (left) to 1-iodo-4-nitrobenzene. The Pd···Pd distance in the transition state is 2.83 Å. (Geometry was optimized at B3LYP/6-31G(d) with LANL2DZ for Pd,I.)

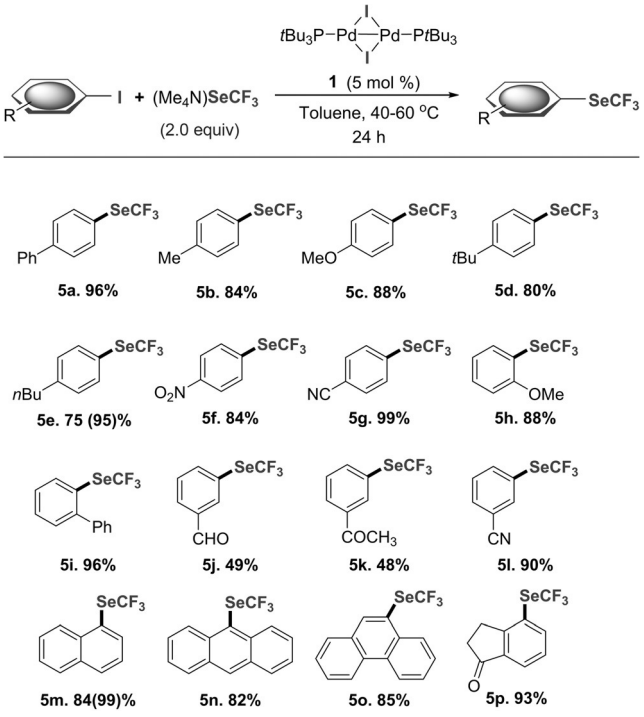
With complex **1** in hand, we subsequently examined the feasibility for I→$SeCF_3$ exchange at the bridging units of the Pd^{I}–I dimer using a suitable $SeCF_3$ nucleophile. Tyrra, Naumann et al. developed a facile route to $(Me_4N)SeCF_3$ and we implemented a modified version of this synthesis for our studies.[19] Treating a solution of Pd^{I}-I dimer **1** in toluene with an excess of $(Me_4N)SeCF_3$ at room temperature pleasingly led to clean replacement of the bridging iodine atoms by $SeCF_3$, as confirmed by ^{31}P and ^{19}F NMR spectroscopic analyses. Analysis of the mixture after 5 h revealed that two new ^{31}P signals at $\delta = 99.1$ and 101.4 ppm had formed in addition to that of Pd^{I}-I-dimer **1** ($\delta = 102.3$ ppm), in accordance with a potential I/$SeCF_3$-mixed dimer **2** and fully displaced $SeCF_3$-dimer **3**.[20] After 24 h, conversion into a single phosphine-containing species was complete (resonance at $\delta = 99.1$ ppm in the ^{31}P NMR spectrum and $\delta = -24.5$ in the ^{19}F NMR spectrum). Isolation and X-ray crystallographic analysis of this species unambiguously confirmed that the novel doubly $SeCF_3$-bridged Pd^{I}-dimer **3** had formed.[21] The X-ray structure of **3** is illustrated in Figure 2.[22]

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 $\Delta G^{\ddagger} = 31.4$ kcal mol^{-1}. The mixed Pd^{I}–$SeCF_3$–I dimer **2** is predicted to be more reactive, giving a barrier of $\Delta G^{\ddagger} = 29.0$ kcal mol^{-1}.[25] The overall driving force of the I/$SeCF_3$ 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–$SeCF_3$ bond formation with dinuclear Pd^{I} catalysis. Given that we had seen clean I/$SeCF_3$ exchanges at the Pd^{I} framework in the presence of the external $(Me_4N)SeCF_3$ nucleophile (see Figure 2), we envisioned that the required regeneration of the active Pd^{I}–$SeCF_3$ dimer **3** or the mixed Pd^{I}–$SeCF_3$–I dimer **2** under catalytic conditions should also be feasible. Notably, the mixed Pd^{I}–$SeCF_3$–I dimer **2**, that was computationally predicted to be more reactive than **3**, would form initially from **1**, requiring only a single I/$SeCF_3$ exchange

at Pd^{I}–Pd^{I}. As such, this concept holds promise to allow for the first direct catalytic C–$SeCF_3$ bond formation.

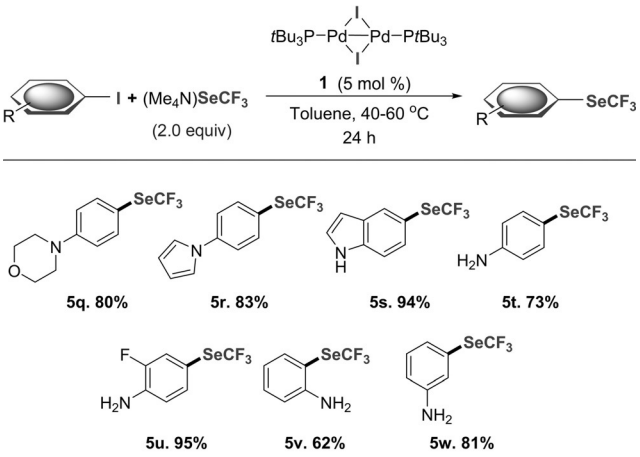
Using 5 mol% of the iodine-bridged Pd^{I} dimer **1** and $(Me_4N)SeCF_3$ (2.0 equiv) in toluene at 40–60 °C, we successfully coupled a range of aryl iodides to the corresponding $SeCF_3$ compounds. Scheme 1 summarizes the results. A number of electron-rich and electron-poor aryl iodides were trifluoromethylselenolated 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 $SeCF_3$ coupling of aryl iodides to Ar-$SeCF_3$. Pd^{I} dimer **1** (8.7 mg, 0.01 mmol), ArI (0.2 mmol), $(Me_4N)SeCF_3$ (89 mg, 0.4 mmol), toluene (1.0 mL), yields are of isolated product. The numbers in parenthesis were determined by ^{19}F 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–$SeCF_3$ 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 $SeCF_3$-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. $SeCF_3$ coupling of amine-containing and N-heterocyclic aryl iodides. Pd^{I} dimer **1** (8.7 mg, 0.01 mmol), ArI (0.2 mmol), $(Me_4N)SeCF_3$ (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}–$SeCF_3$ 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–$SeCF_3$ coupling of aryl iodide was also efficient and the product Ar$SeCF_3$ **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 $[\{(PtBu_3)PdI\}_2]$ (**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 $SeCF_3$-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 (Me_4NI), 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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[20] The ^{31}P 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)°, $V = 3471.8(5)$ Å^3, $Z = 4$, $T = 100$ K; 23136 reflections measured ($3.554° \leq 2\Theta \leq 64.826°$), 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-$SeCF_3$ 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 $ArSeCF_3$ 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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