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

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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.*

Palladium-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 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.

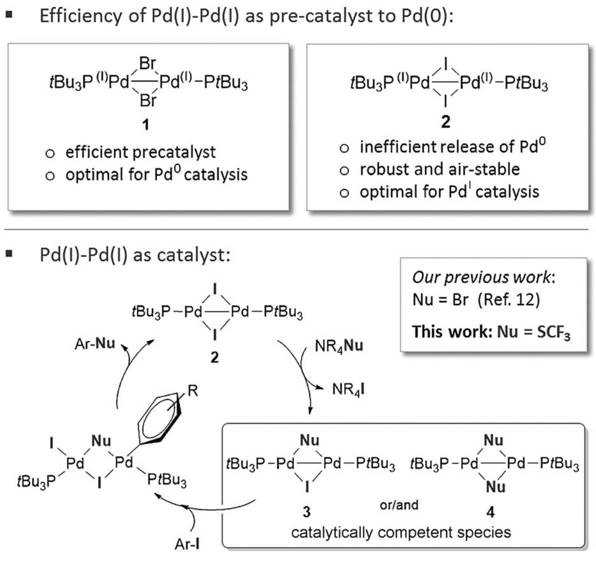

Figure 1. Pd^I-dimer catalysis concept (bottom).

We recently reported our initial success in the area, that is, a Pd^I-dimer-catalyzed I→Br halogen exchange of 9-iodoanthracene with NBu_4Br.[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

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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 $[Pd^0(PtBu_3)_2]$ 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 $(EtO)_3PO$ 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.

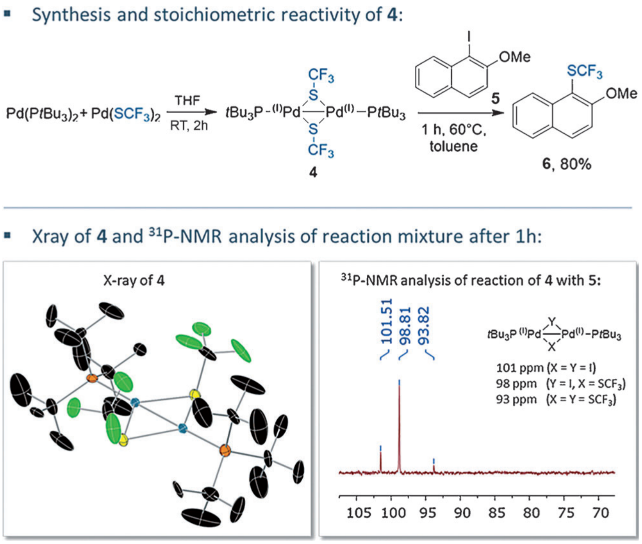


Figure 2. Preparation of the SCF_3-bridged Pd^I dimer **4** and stoichiometric reactivity with **5** (yield relative to **4**, 2 equiv of **6** can form). $(EtO)_3PO$ was used as an internal standard for the ^{31}P NMR analysis. Thermal ellipsoids are shown at 50% probability.

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 $\Delta G^{\neq} = 28.0 \pm 3.9\ \mathrm{kcal\,mol^{-1}}$ for the $ArI \rightarrow ArSCF_3$ 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 $I \rightarrow SCF_3$ 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 $I \rightarrow SCF_3$ exchange reaction is thermodynamically driven, and exergonic overall by $\Delta G_{rxn} \approx -21\ \mathrm{kcal\,mol^{-1}}$ (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 $(Me_4N)SCF_3$,[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

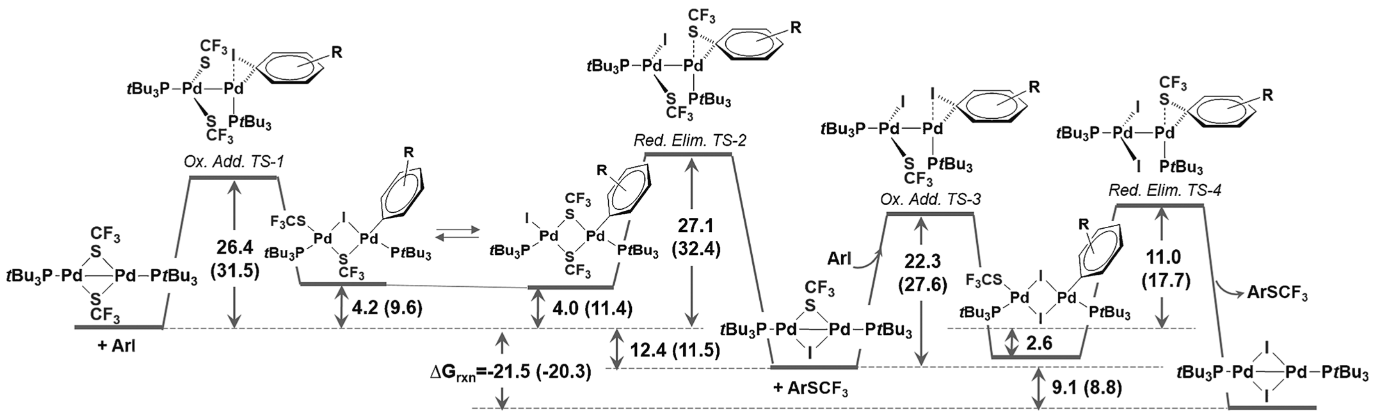
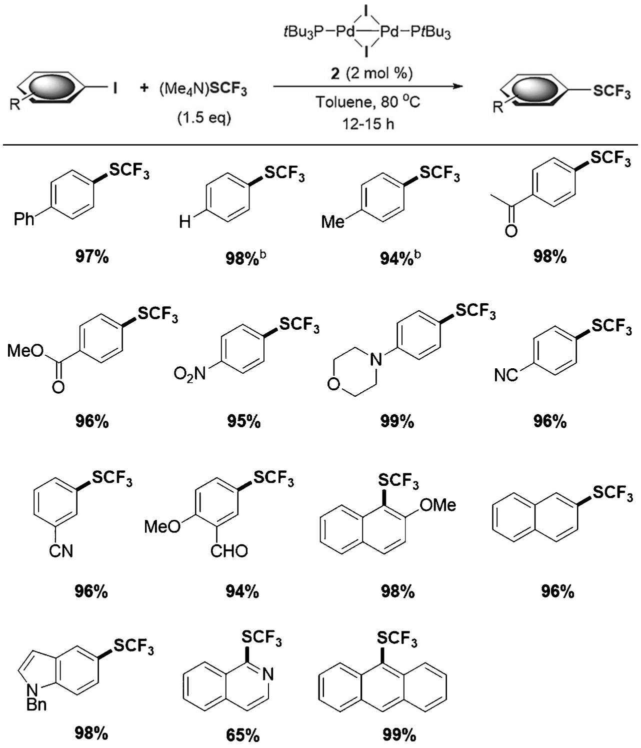


Figure 3. Free-energy path of I→SCF$_3$ exchange between **4** and **7**, calculated at CPCM (toluene) M06L/6-311++G(d,p) [SDD for Pd,I] or CPCM (toluene) M06L/def2TZVP (in parentheses). Geometries were optimized at B3LYP/6-31G(d) [with LANL2DZ for Pd,I]. Values are in kcal mol^{-1} at 298 K.

Table 1: Pd^{I}-catalyzed SCF$_3$ coupling of aryl iodides to ArSCF$_3$.[a]

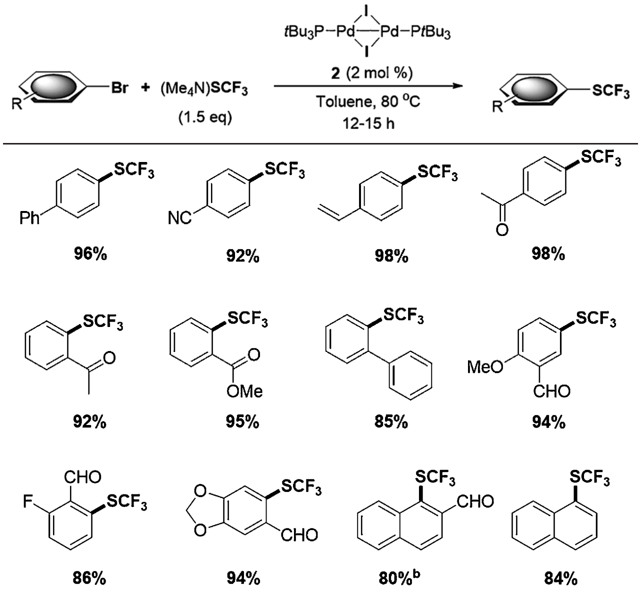


[a] **2** (3.6 mg, 0.004 mmol), ArI (0.2 mmol), (Me$_4$N)SCF$_3$ (52 mg, 0.3 mmol), toluene (1.0 mL). Yield of isolated product given. [b] Yield determined by ^{19}F NMR analysis versus PhCF$_3$ as an internal standard.

than the established metal-catalyzed SCF$_3$-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 SCF$_3$-coupled products were furnished 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.

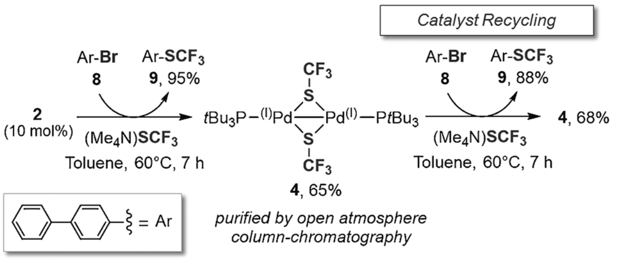
Table 2: Pd^{I}-catalyzed SCF$_3$ coupling of aryl bromides to ArSCF$_3$.[a]



[a] **2** (3.6 mg, 0.004 mmol), ArBr (0.2 mmol), (Me$_4$N)SCF$_3$ (52 mg, 0.3 mmol), toluene (1.0 mL). Yield of isolated product given. [b] 4 mol% catalyst **2** was used.

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 SCF$_3$-coupling of aryl bromides. Although **1** is likely rapidly converted into the brominated analogue of **3** (or to **4**) in the presence of (Me$_4$N)SCF$_3$, mechanistically we cannot rule out that [Pd^{0}] 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 SCF$_3$ 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-methoxybenzaldehyde in 64%, and 1-bromonaphthalene in 69%.[26] This recovery suggests that if [Pd^0] were to be formed during the catalytic transformation, this process would either be reversible or not predominant.

We also recovered the Pd$^{\mathrm{I}}$ catalyst (as the bis-(SCF$_3$) version **4**) from the SCF$_3$-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$^{\mathrm{I}}$ complex to these reaction conditions. Moreover, in analogy to **2**, the SCF$_3$-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−SCF$_3$ 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$^{\mathrm{I}}$ dimer.

In conclusion, we herein demonstrated a highly efficient and operationally simple SCF$_3$-coupling protocol of a range of aryl iodides and bromides enabled by a bench-stable dinuclear Pd$^{\mathrm{I}}$ catalyst and the easily accessible (Me$_4$N)SCF$_3$ 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$^{\mathrm{I}}$ catalyst poses a considerable practical advantage over more sensitive Pd^0- or Ni^0-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$^{\mathrm{I}}$ sites presents a promising advance in this context. Our future research is directed at exploring the full potential of this catalysis concept.

Keywords: cross-coupling · density functional theory calculations · palladium · reaction mechanisms · synthetic methods

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[1] a) *Handbook of Organopalladium Chemistry for Organic Synthesis* (Eds.: E.-I. Negishi, A. de Meijere), Wiley, New York, **2002**; b) *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed. (Eds.: F. Diederich, A. de Meijere), Wiley-VCH, Weinheim, **2004**; c) J. F. Hartwig in *Organotransition Metal Chemistry-From Bonding to Catalysis*, University Science Books, Sausalito, CA, **2010**; d) C. C. Johansson Seechurn, M. O. Kitching, T. J. Colacot, V. Snieckus, *Angew. Chem. Int. Ed.* **2012**, *51*, 5062; *Angew. Chem.* **2012**, *124*, 5150; e) T. Colacot, *New Trends in Cross Coupling: Theory and Applications*, RSC, London, **2014**.

[2] a) Pd^{0}L$_n$ complexes react with oxygen to give the corresponding oxo-complexes which ultimately convert into palladium oxide. Ni^{0}L$_n$ undergo analogous reactions and show greater instability. For early documentation, see: b) G. Wilke, H. Schott, P. Heimbach, *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 92; *Angew. Chem.* **1967**, *79*, 62. On the air-sensitivity of commonly used trialkylphosphine ligands, see: c) D. H. Valentine, J. H. Hillhouse, *Synthesis* **2003**, 2437. For an assessment of oxygen stability of a range of ligands, see: d) T. E. Barder, S. L. Buchwald, *J. Am. Chem. Soc.* **2007**, *129*, 5096.

[3] For examples of air-stable phosphine and phosphine oxide ligands, see: a) G. Y. Li, *Angew. Chem. Int. Ed.* **2001**, *40*, 1513; *Angew. Chem.* **2001**, *113*, 1561; b) L. Ackermann, R. Born, *Angew. Chem. Int. Ed.* **2005**, *44*, 2444; *Angew. Chem.* **2005**, *117*, 2497; c) D. S. Surry, S. L. Buchwald, *Chem. Sci.* **2011**, *2*, 27.

[4] a) J. Dupont, M. Pfeffer, J. Spencer, *Eur. J. Inorg. Chem.* **2001**, 1917; b) D. Zim, S. L. Buchwald, *Org. Lett.* **2003**, *5*, 2413; c) M. G. Organ, S. Avola, I. Dubovyk, N. Hadei, E. Assen, B. Kantchev, C. J. O'Brien, C. Valente, *Chem. Eur. J.* **2006**, *12*, 4749; d) A. Chartoire, M. Lesieur, L. Falivene, A. M. Z. Slawin, L. Cavallo, C. S. J. Cazin, S. P. Nolan, *Chem. Eur. J.* **2012**, *18*, 4517.

[5] Strategies to realize recycability of catalytic systems include: a) employment of polyethylene-bound palladacycles: D. E. Bergbreiter, P. L. Osburn, Y.-S. Liu, *J. Am. Chem. Soc.* **1999**, *121*, 9531; b) the use of metal scavengers, such as Smopex: S. Phillips, P. Kauppinen, *Platinum Met. Rev.* **2010**, *54*, 69; or specialized reactions conditions (biphasic, ionic liquids, supercritical CO$_2$): c) H. Wong, C. J. Pink, F. C. Ferreira, A. G. Livingston, *Green Chem.* **2006**, *8*, 373; d) T. Welton, *Chem. Rev.* **1999**, *99*, 2071; e) P. G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* **1999**, *99*, 475.

[6] For reviews, see: a) T. Murahashi, H. Kurosawa, *Coord. Chem. Rev.* **2002**, *231*, 207; b) H. Kurosawa, *J. Organomet. Chem.* **2004**, *689*, 4511. For other recent examples of alternative Pd$^{\mathrm{I}}$-Pd$^{\mathrm{I}}$ complexes, see: c) F. Proutiere, E. Lyngvi, M. Aufiero, I. A. Sanhueza, F. Schoenebeck, *Organometallics* **2014**, *33*, 6879; d) S. Borjian, M. C. Baird, *Organometallics* **2014**, *33*, 3936; e) D. P. Hruszkewycz, D. Balcells, L. M. Guard, N. Hazari, M. Tilset, *J. Am. Chem. Soc.* **2014**, *136*, 7300; f) S. Oldenhof, M. Lutz, B. de Bruin, J. I. v. d. Vlugt, J. N. H. Reek, *Organometallics* **2014**, *33*, 7293; g) S. Lin, D. E. Herbert, A. Velian, M. W. Day, T. Agapie, *J. Am. Chem. Soc.* **2013**, *135*, 15830; h) C. Jimeno, U. Christmann, E. C. Escudero-Adan, R. Vilar, M. A. Pericas, *Chem. Eur. J.* **2012**, *18*, 16510; i) D. P. Hruszkewycz, J. Wu, N. Hazari, C. D. Incarvito, *J. Am. Chem. Soc.* **2011**, *133*, 3280; j) R. Huacuja, D. J. Graham, C. M. Fafard, C. H. Chen, B. M. Foxman, D. E. Herbert, G. Alliger, C. M. Thomas, O. V. Ozerov, *J. Am. Chem. Soc.* **2011**, *133*, 3820; k) T. Murahashi, K. Takase, M.-A. Oka, S. Ogoshi, *J. Am. Chem. Soc.* **2011**, *133*, 14908; l) C. B. Pamplin, S. J. Rettig, B. O. Patrick, B. R. James, *Inorg. Chem.* **2011**, *50*, 8094; m) U. Christmann, D. A. Pantazis, J. Benet-Buchholz, J. E. McGrady, F. Maseras, R. Vilar, *J. Am. Chem. Soc.* **2006**, *128*, 6376; n) T. E. Barder, *J. Am. Chem. Soc.* **2006**, *128*, 898; o) U. Christmann, R. Vilar, A. J. P. White, D. J. Williams, *Chem. Commun.* **2004**, 1294.

[7] For a commentary, see: R. S. Paton, J. M. Brown, *Angew. Chem. Int. Ed.* **2012**, *51*, 10448; *Angew. Chem.* **2012**, *124*, 10598.

[8] The dimer was first synthesized by: R. Vilar, D. M. P. Mingos, C. J. Cardin, *J. Chem. Soc. Dalton Trans.* **1996**, 4313. An improved synthesis for commercial applications was developed by Colacot and co-workers (Patent): T. J. Colacot, M. W. Hooper, G. A. Grasa (Johnson Matthey), WO2011/12889A1, **2011**.

[9] a) J. P. Stambuli, R. Kuwano, J. F. Hartwig, *Angew. Chem. Int. Ed.* **2002**, *41*, 4746; *Angew. Chem.* **2002**, *114*, 4940; b) M. Prashad, X. Y. Mak, Y. Liu, O. Repic, *J. Org. Chem.* **2003**, *68*, 1163; c) M. W. Hooper, M. Utsunomiya, J. F. Hartwig, *J. Org. Chem.* **2003**, *68*, 2861; d) U. Christmann, R. Vilar, *Angew. Chem. Int. Ed.* **2005**, *44*, 366; *Angew. Chem.* **2005**, *117*, 370; e) T. Hama, D. A. Culkin, J. F. Hartwig, *J. Am. Chem. Soc.* **2006**, *128*, 4976; f) T. J. Colacot, *Platinum Met. Rev.* **2009**, *53*, 183; g) L. L. Hill, J. L. Crowell, S. L. Tutwiler, N. L. Massie, C. Corey Hines, S. T. Griffin, R. D. Rogers, K. H. Shaughnessy, G. A. Grasa, C. C. C. J. Seechurn, H. Li, T. J. Colacot, J. Chou, C. J. Woltermann, *J. Org. Chem.* **2010**, *75*, 6477; h) F. Proutiere, M. Aufiero, F. Schoenebeck, *J. Am. Chem. Soc.* **2012**, *134*, 606; i) P. Mamone, M. F. Grunberg, A. Fromm, B. A. Khan, L. J. Gooßen, *Org. Lett.* **2012**, *14*, 3716.

[10] a) The dimer showed low or no reactivity with small molecules: V. Dura-Vila, D. M. P. Mingos, R. Vilar, A. J. P. White, D. J. Williams, *J. Organomet. Chem.* **2000**, *600*, 198; b) for demonstration that it is an inefficient precatalyst in Suzuki coupling reactions, see: M. Aufiero, F. Proutiere, F. Schoenebeck, *Angew. Chem. Int. Ed.* **2012**, *51*, 7226; *Angew. Chem.* **2012**, *124*, 7338.

[11] We conducted a quantitative study on additive/activity relationships to understand the different activities of Br- versus I-bridged Pd^I dimers. The results will be reported in due course.

[12] a) K. J. Bonney, F. Proutiere, F. Schoenebeck, *Chem. Sci.* **2013**, *4*, 4434; b) I. Kalvet, K. J. Bonney, F. Schoenebeck, *J. Org. Chem.* **2014**, *79*, 12041; c) K. J. Bonney, F. Schoenebeck, *Chem. Soc. Rev.* **2014**, *43*, 6609–6638.

[13] For recent reviews, see: a) G. Landelle, A. Panossian, S. Pazenok, J.-P. Vors, F. R. Leroux, *Beilstein J. Org. Chem.* **2013**, *9*, 2476; b) P. Chen, G. Liu, *Synthesis* **2013**, 2919; c) T. Liang, C. N. Neumann, T. Ritter, *Angew. Chem. Int. Ed.* **2013**, *52*, 8214; *Angew. Chem.* **2013**, *125*, 8372; d) F. Toulgoat, S. Alazet, T. Billard, *Eur. J. Org. Chem.* **2014**, 2415.

[14] For noncatalytic or indirect synthetic methods to generate $ArSCF_3$ from aryl sulfides or disulfides with trifluoromethylation reagents, see: a) V. N. Boiko, G. M. Shchupak, L. M. Yagupolskii, *J. Org. Chem. USSR* **1977**, *13*, 972; b) C. Wakselman, M. Tordeux, *J. Chem. Soc. Chem. Commun.* **1984**, 793; c) T. Umemoto, S. Ishihara, *Tetrahedron Lett.* **1990**, *31*, 3579; d) C. Wakselman, M. Tordeux, J. L. Clavel, B. R. Langlois, *J. Chem. Soc. Chem. Commun.* **1991**, 993; e) N. Roques, *J. Fluorine Chem.* **2001**, *107*, 311; f) G. Blond, T. Billard, B. R. Langlois, *Tetrahedron Lett.* **2001**, *42*, 2473; g) C. Pooput, M. Medebielle, W. R. Dolbier, *Org. Lett.* **2004**, *6*, 301; h) F. Leroux, P. Jeschke, M. Schlosser, *Chem. Rev.* **2005**, *105*, 827. For syntheses in which "SCF_3" functions as nucleophile or electrophile, see: i) T. Billard, B. R. Langlois, *Tetrahedron Lett.* **1996**, *37*, 6865; j) D. J. Adams, A. Goddard, J. H. Clark, D. J. Macquarrie, *Chem. Commun.* **2000**, 987; k) D. J. Adams, J. H. Clark, *J. Org. Chem.* **2000**, *65*, 1456; l) I. Kieltsch, P. Eisenberger, A. Togni, *Angew. Chem. Int. Ed.* **2007**, *46*, 754; *Angew. Chem.* **2007**, *119*, 768; m) S. Capone, I. Kieltsch, O. Flçgel, G. Lelais, A. Togni, D. Seebach, *Helv. Chim. Acta* **2008**, *91*, 2035; n) K. Stanek, R. Koller, A. Togni, *J. Org. Chem.* **2008**, *73*, 7678; o) B. Manteau, S. Pazenok, J.-P. Vors, F. R. Leroux, *J. Fluorine Chem.* **2010**, *131*, 140; p) F. Baert, J. Colomb, T. Billard, *Angew. Chem. Int. Ed.* **2012**, *51*, 10382; *Angew. Chem.* **2012**, *124*, 10528.

[15] a) A. Leo, P. Y. C. Jow, C. Silipo, C. Hansch, *J. Med. Chem.* **1975**, *18*, 865; b) C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165.

[16] Functional groups other than aryl halides may also be cross-coupled to $ArSCF_3$ with metal catalysis. For conversion of aryl boronic acids into $ArSCF_3$, see: a) C. Chen, Y. Xie, L. Chu, R.-W. Wang, X. Zhang, F.-L. Qing, *Angew. Chem. Int. Ed.* **2012**, *51*, 2492; *Angew. Chem.* **2012**, *124*, 2542; b) C.-P. Zhang, D. A. Vicic, *Chem. Asian J.* **2012**, *7*, 1756; c) X. Shao, X. Wang, T. Yang, L. Lu, Q. Shen, *Angew. Chem. Int. Ed.* **2013**, *52*, 3457; *Angew. Chem.* **2013**, *125*, 3541; d) R. Pluta, P. Nikolaienko, M. Rueping, *Angew. Chem. Int. Ed.* **2014**, *53*, 1650; *Angew. Chem.* **2014**, *126*, 1676. For SCF_3-coupling of aryl diazonium salts, see: e) G. Danoun, B. Bayarmagnai, M. F. Gruenberg, L. J. Goossen, *Chem. Sci.* **2014**, *5*, 1312. For examples of metal-catalyzed C-H trifluoromethylthiolation of arenes, see: f) L. D. Tran, I. Popov, O. Daugulis, *J. Am. Chem. Soc.* **2012**, *134*, 18240; g) C. Xu, Q. Shen, *Org. Lett.* **2014**, *16*, 2046.

[17] G. Teverovskiy, D. S. Surry, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2011**, *50*, 7312; *Angew. Chem.* **2011**, *123*, 7450.

[18] C.-P. Zhang, D. A. Vicic, *J. Am. Chem. Soc.* **2012**, *134*, 183.

[19] Our group has recently succeeded in the nickel-catalyzed trifluoromethylthiolation of aryl chlorides. See: G. Yin, I. Kalvet, U. Englert, F. Schoenebeck, *J. Am. Chem. Soc.* **2015**, *137*, 4164–4172.

[20] Z. Weng, W. He, C. Chen, R. Lee, D. Tan, Z. Lai, D. Kong, Y. Yuan, K.-W. Huang, *Angew. Chem. Int. Ed.* **2013**, *52*, 1548; *Angew. Chem.* **2013**, *125*, 1588.

[21] J. Xu, X. Mu, P. Chen, J. Ye, G. Liu, *Org. Lett.* **2014**, *16*, 3942.

[22] Selected X-ray data for **4**: $C_{26}H_{54}F_6P_2Pd_2S_2$, $M = 813.50$, brown rod; space group *Pnma*; $a = 15.016(5)$, $b = 14.811(5)$, $c = 15.214(5)$ Å; $V = 3384(2)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.609\ g\,cm^{-3}$; $T = 100(2)$ K; reflections collected: 33035, independent reflections: 2996 [$R(int) = 0.1112$], $R1 = 0.0884$, $wR2 = 0.2358$. CCDC 995456 contains 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.

[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].

[24] Gaussian 09, Revision D.01, M. J. Frisch et al. (see the Supporting Information for full reference).

[25] $(Me_4N)SCF_3$ was prepared according to the procedure developed by Tyrra and co-workers. See: D. Naumann, B. Hogea, Y. L. Yagupolskii, W. E. Tyrra, *J. Fluorine Chem.* **2003**, *119*, 101. See the Supporting Information for details.

[26] The reaction was performed at 60 °C for 7 h. There was no visible sign of catalyst degradation (as judged by ^{31}P NMR spectroscopic analysis). All phosphine-containing signals observed belonged to the Pd^I dimers. The quantification of Pd^I dimer was performed by ^{19}F NMR spectroscopic analysis versus an internal standard. See the Supporting Information for more details.

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Communications

Cross-Coupling

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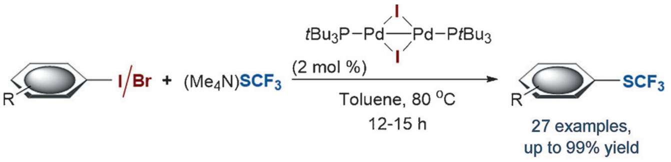
Trifluoromethylthiolation of Aryl Iodides and Bench-Stable and Easy-To-Recover Dinuclear Palladium(I) Catalyst



Pd double team: The cross-coupling enabled by an air-, moisture-, and thermally-stable dinuclear Pd^{I} complex was explored. Highly efficient C–SCF$_3$ coupling of a range of aryl iodides and bromides was achieved and the catalyst was recovered by simple column chromatography, thus highlighting its robustness and the possibility for catalyst recycling. Kinetic and computational data support the feasibility of dinuclear Pd^{I} catalysis.