Palladium Catalysis

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Palladium(I) Dimer Enabled Extremely Rapid and Chemoselective Alkylation of Aryl Bromides over Triflates and Chlorides in Air

*Indrek Kalvet, Theresa Sperger, Thomas Scattolin, Guillaume Magnin, and Franziska Schoenebeck**

Abstract: *Disclosed herein is the first general chemo- and site-selective alkylation of C–Br bonds in the presence of COTf, C–Cl and other potentially reactive functional groups, using the air-, moisture-, and thermally stable dinuclear Pd^{I} catalyst, [Pd(μ-I)PtBu$_3$]$_2$. The bromo-selectivity is independent of the substrate and the relative positioning of the competing reaction sites, and as such fully predictable. Primary and secondary alkyl chains were introduced with extremely high speed (< 5 min reaction time) at room temperature and under open-flask reaction conditions.*

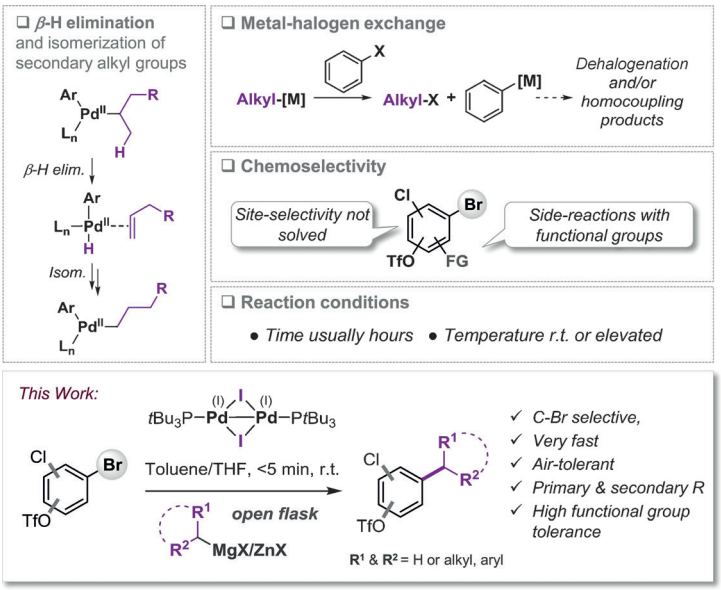

Figure 1. Key challenges in Pd-catalyzed alkylation reactions.

Csp^2–Csp^3 cross-coupling reactions are key transformations to access valuable feedstock material for synthesis, materials, as well as for the pharmaceutical and agrochemical arenas. Consequently, there has been a tremendous interest in devising efficient methodologies to achieve this feat.[1] While remarkable progress has been made with transition-metal catalysis,[2] Pd-based methodology frequently offers superior generality and mildness—a prerequisite to access richly functionalized building blocks for further synthetic transformations.[3] Among the key challenges in Pd-catalyzed alkylations is the possibility for β-hydride elimination from [Pd^{II}]-alkyl intermediates and isomerization of the coupling partner, resulting in product mixtures (Figure 1).[2a] Additionally, the nucleophilic/basic organometallic cross-coupling partners that are generally employed (i.e. RMgX or RZnX) are frequently unstable and may be incompatible with additional functionalities in the substrate, particularly under prolonged reaction times and/or elevated temperatures.

While impressive progress has been made in minimizing side-reactions,[4] as well as addressing the handling and preparation of the cross-coupling partner,[5] to date, no general and chemoselective alkylation of poly-(pseudo)halogenated arenes has been accomplished.[6] This situation may be of little surprise, as even the more facile Csp^2–Csp^2 coupling has until our recent report[8] been a long-standing challenge; the overall site-selectivity in typical Pd^0-based methodology is substrate-, ligand-, and condition dependent.[7]

We recently disclosed that the application of the air-, moisture- and thermally stable iodide-bridged dinuclear Pd^{I} catalyst **1** allows for a substrate-independent, chemoselective arylation of poly(pseudo)-halogenated arenes.[8] Encouraged by these findings, this report discloses our efforts to address the greater challenge of site-selective alkylation, which would be highly desired in the context of synthetic diversity and to allow orthogonal, programmable, and sequential synthetic approaches.[9]

Owing to their relative mildness, alkylzinc reagents are the preferred coupling partners in Pd-catalyzed alkylations of aryl (pseudo)halides.[2a] In this context, the commercially available NHC (N-heterocyclic carbene)-based and biaryl phosphine-based Pd-precatalysts developed by the groups of Organ and Buchwald have been applied in versatile alkylations of aryl bromides, chlorides or triflates at room temper-

[*] M. Sc. I. Kalvet, M. Sc. T. Sperger, M. Sc. T. Scattolin, M. Sc. G. Magnin, 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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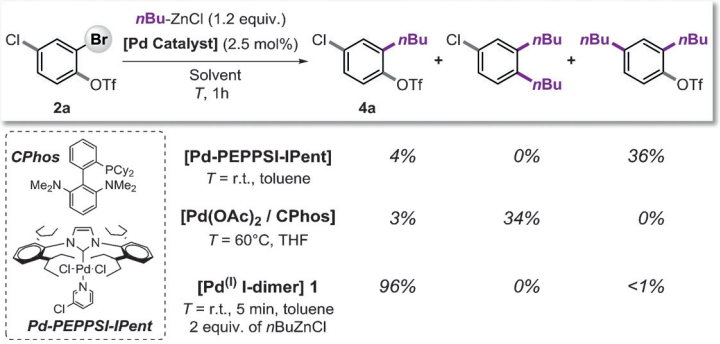
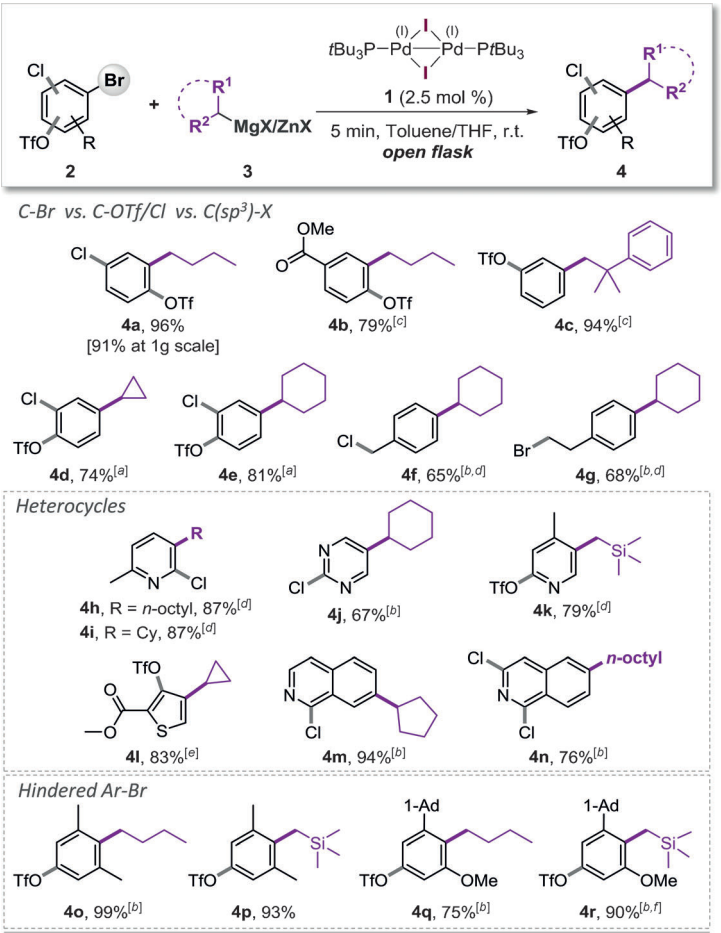


Figure 2. Site-selectivity of Negishi alkylation with commercially available Pd (pre-)catalysts[10] including **1**.

ature or 60 °C in 0.5–2 hours.[4c,e,f] As there has not been any report of a chemoselective alkylation method, we initially assessed the performance of these highly successful catalyst systems and conditions for their potential to site-selectively alkylate substrate **2a**, which displays competing C–Br, C–Cl and C–OTf sites, with *n*-butylzinc chloride (Figure 2). Both catalyst systems were unselective and generated bis-alkylated products in mixtures with starting material. Interestingly, while the biarylphosphine (CPhos) system predominantly gave rise to the product resulting from C–OTf and C–Br alkylation, the NHC (IPent) system showed simultaneous C–Br and C–Cl alkylation instead.[10] Both ligands are generally presumed to form a low coordinate "Pd^0L_1" active species, and would therefore be expected to result in analogous site-selectivities.[11] This may hint toward mixtures of different reactive species, for example, through coordination of the nucleophilic coupling partner to the Pd^0 species to generate anionic Pd^0LX^-,[12] which likely displays different selectivity.[7e,g] Indeed, the majority of Csp^2–Csp^2 Kumada and Negishi couplings resulted in predominant coupling at C–OTf over C–Br.[7a]

We envisioned that a coupling concept based on Pd^I could be advantageous in this context.[13] If the alkyl coupling partner was incorporated as the bridging unit via iodide/alkyl exchange in the dinuclear entity, the resulting transient alkyl-bridged Pd^I dimer might selectively react and also allow us to circumvent the intermediacy of [Pd^{II}]-alkyl species and potential side reactions. Thus, we tested the air-stable Pd^I dimer **1** (2.5 mol %) in the coupling of substrate **2a** with *n*-butylzinc chloride at room temperature in toluene.[14] The reaction was extremely rapid, having reached full conversion of **2a** in less than 5 min reaction time (see Figure 2. To our delight, the reaction proved to be completely selective and yielded the product resulting from C–Br alkylation in 96 % yield. Both the C–Cl and C–OTf sites remained untouched. To the best of our knowledge, this is the first example of a selective Negishi alkylation that does not react with the C–OTf site.[6] Importantly, the transformation was also tolerant to air, yielding the same reaction outcome under inert and open-flask conditions.[15]

Encouraged by this exceptional selectivity along with high practicality, we subsequently explored the generality of the observed C–Br coupling preference. We observed exclusive alkylation of the C–Br bond, independent of its relative positioning to the competing reaction sites or the nature of the alkylating reagent (i.e. primary vs. secondary alkylzinc, see Scheme 1). Selective functionalization of bromide occurred in *ortho*, *meta*, and *para* positions to C–OTf, and also in the presence of C–Cl (**4a**–**4e**, Scheme 1), allowing the isolation of the corresponding Csp^2–Csp^3 coupled products in high yields. The C–Br coupling also proved to be equally selective and efficient for more hindered C–Br sites (entries **4o**–**4r**), as well as for pharmaceutically and agrochemically relevant heterocycles. Selection for C–Br occurred in all cases, leaving the more activated C–OTf and C–Cl sites untouched (entries **4h**–**4n**). To our delight, the alkylation of aromatic Csp^2–Br bonds over competing Csp^3–halogen sites was also effective (entries **4f** and **4g**). For some substrates



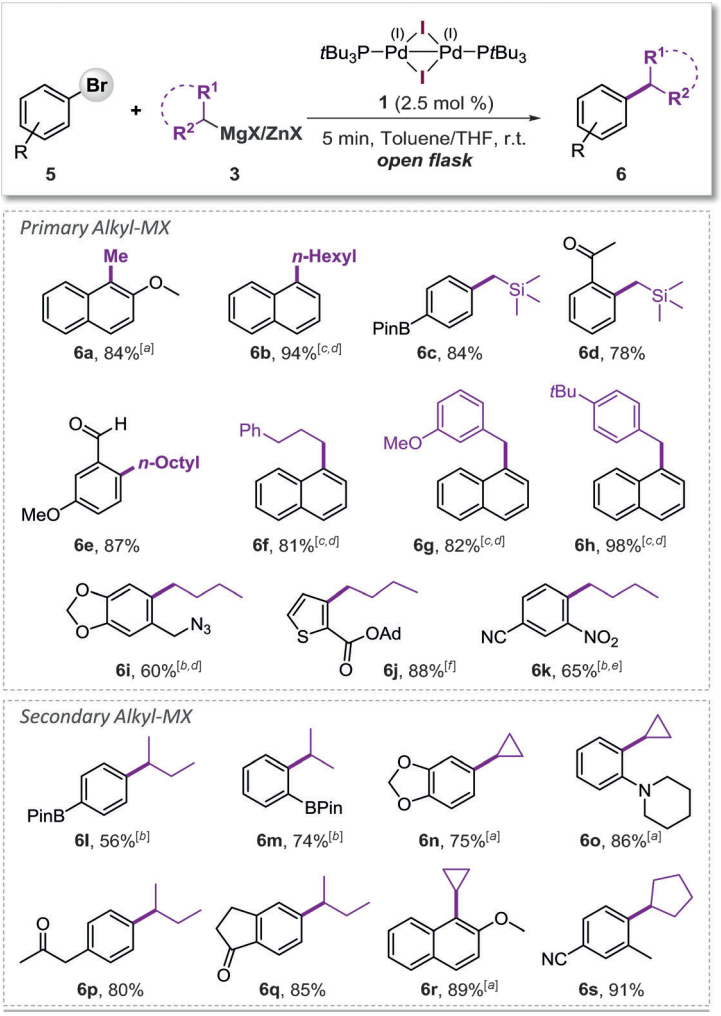
Scheme 1. Demonstration of site-selective alkylation of C–Br bonds. Reaction conditions: **2** (0.4 mmol), **3** (0.8 mmol in THF, prepared from 0.8 mmol of R-MgX and 0.84 mmol of $ZnCl_2$), **1** (0.01 mmol), toluene (1.5 mL), open flask, RT, 5 min. [a] Using R-MgX as **3**. [b] **3** was added drop-wise.[16] [c] 0.6 mmol of **3**. [d] 0.72 mmol of **3**. [e] 1.2 mmol of **3**. [f] 1.0 mmol of **3**.

(e.g. more sterically hindered examples or those bearing highly reactive functional groups), a slower addition (over a 3–5 min interval) of the organometallic coupling partner proved advantageous to achieve higher yields, regardless of whether the reaction was performed in the presence or absence of air.

With these excellent selectivities proven, we subsequently tested this methodology for its potential in large-scale applications. Addition of *n*-butylzinc chloride to 1 g of 2-bromo-4-chlorophenyl triflate (**2a**), along with 1 mol% of the Pd^{I} catalyst **1** under otherwise identical open-flask reaction conditions, yielded the C–Br coupling product (**4a**) in 91% yield in 5 min. Thus, these coupling reactions are also equally selective and rapid under reduced catalyst loadings and significantly larger scales. As such, our methodology allows for fully predictable, robust and substrate-independent C–Br alkylation under highly practical conditions.

Having demonstrated the exclusive bromo-selectivity in competition with C–OTf and C–Cl sites, we next investigated the general synthetic applicability of this methodology for less activated arenes containing only a single coupling site along with additional functional groups (Scheme 2). Heterocycles as well as electrophilic functional groups (i.e. aldehyde **6e**, nitriles **6k** and **6s**, ketones **6d**, **6p**, **6q**, ester **6j**) are well tolerated. The reaction could also be performed in the presence of nitro (**6k**), azido (**6i**) functionalities.[17] Also boronic acid esters (i.e. BPin, **6c**, **6l**, and **6m**), which can enable further orthogonal coupling reactions and hence molecular diversity.

In terms of the scope of organometallic reagents a variety of alkylzinc, as well as some alkylmagnesium coupling partners could be utilized. Alkyl groups, both with and without β-hydrogen atoms, all proved compatible and underwent smooth Csp^2–Csp^3 couplings (Scheme 2). Methylation (**6a**) proceeded most efficiently under Kumada conditions. A range of secondary alkyl zinc and magnesium reagents could also be coupled efficiently. The desired products were obtained in good yields for both acyclic (*i*-Pr, *sec*-butyl) as well as cyclic (cyclopropyl, -pentyl, and -hexyl) alkyl groups. Products arising from isomerization of the secondary alkyl moiety were detected either in trace amounts (≤3% with **6m**) or not at all (**6l**, **6p,q**), and as such are competitive with the current state-of-the-art.[4a–f]



Scheme 2. Scope of C–Br alkylation and functional group tolerance. Reaction conditions: **2** (0.4 mmol), R-ZnX **3** (0.8 mmol in THF, prepared from 0.8 mmol of R-MgX and 0.84 mmol of $ZnCl_2$), **1** (0.01 mmol), toluene (1.5 mL), open flask, RT, 5 min.[18] [a] Using R-MgX as **3**. [b] **3** was added drop-wise. [c] Alkyl-ZnX was prepared from Alkyl-X using Mg, LiCl and $ZnCl_2$. See Supporting Information for details. [d] 0.6 mmol of **3**. [e] 0.72 mmol of **3**. [f] 1.2 mmol of **3**.

To shed light on the potential mechanism of the transformation and the origins of exclusive bromo-selectivity, we conducted computational studies and examined the predicted site-selectivity for C–Br versus C–Cl versus C–OTf as a function of active species.[19] The dinuclear Pd^{I} dimers may either react directly with aryl halides or act as a precursor for monophosphine Pd^{0}. In short, the precise mode of reactivity is highly dependent on whether the coupling partner can function as a bridging unit in the dinuclear entity.[13,20] For related dinuclear Ni^{I} complexes, there has been very recent evidence that carbon-based bridges may in fact be possible.[21] We calculated the predicted selectivities for an *n*-propyl-bridged Pd^{I} dimer, which indicated a clear C–Br addition preference. Both C–Cl and C–OTf are predicted to be significantly disfavored (by $\Delta\Delta G^{\ddagger} = 5.8$ and 2.8 kcal mol^{-1}). Alternatively, $Pd^{0}PtBu_3$ may be active and our computations suggest preferential C–Br addition (by $\Delta\Delta G^{\ddagger} = 4.4$ and 8.3 kcal mol^{-1} for Cl and OTf). Overall, these data suggest that both Pd^{0}-based and Pd^{I}–Pd^{I}-based reactivities are consistent with the observed C–Br selectivity. The NHC and CPhos systems (as presented in Figure 2) are also generally presumed to form mono-ligated active Pd^{0} species.[11] We also calculated the predicted selectivities for these cases. Interestingly, these $Pd^{0}L_1$ species also show a clear preference for oxidative addition at C–Br (by $\Delta\Delta G^{\ddagger} = 5.6$ and 7.8 kcal mol^{-1}, respectively, for C–Cl and C–OTf with L = IPent, and 3.0 and 9.5 kcal mol^{-1} with L = CPhos). These data contrast the observed lack of selectivities and point toward more complex reactivity scenarios. For example, there could be alternative reactive species, or oxidative addition may not be

the selectivity-determining step for these systems. Overall, however, on the basis of the collected data neither Pd^0 nor Pd^I–Pd^I catalysis can be excluded in our case. Our future studies are directed at gaining detailed mechanistic insight on these and related processes.

In conclusion, a predictable, chemoselective alkylation of C–Br sites in the presence of C–OTf, C–Cl, and additional functional groups was developed. The method is characterized by high speed ($\leq$5 min reaction time) and operational simplicity, being fully compatible with oxygen (open-flask conditions) and employing an air-, moisture, and thermally stable dinuclear Pd^I catalyst. Primary and secondary alkyl groups were introduced for a wide range of substrates, tolerating steric bulk and numerous functional groups, including cyano, aldehyde, azide, nitro, ester, methoxy, BPin, and silyl groups, as well as benzylic chlorides, alkyl bromides, and heterocycles. Potential for large-scale applications was also showcased.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: homogeneous catalysis · chemoselectivity · Csp^2–Csp^3 coupling · dimers · palladium

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[15] **Safety note:** organometallic reagents are often moisture sensitive and may react violently in air. All necessary safety precautions must be considered when operating under open-flask conditions.
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Communications

Palladium Catalysis

I. Kalvet, T. Sperger, T. Scattolin,
G. Magnin,
F. Schoenebeck* _____ ▮▮▮▮–▮▮▮▮

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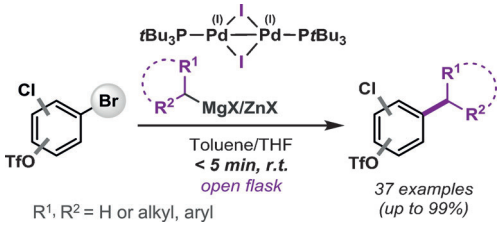

Pick me! A method for cross-coupling bromo groups with Grignard or organozinc reagents mediated by a dinuclear Pd^{I} catalyst was developed. The reactions were highly selective for C–Br and were tolerant of both C–OTf and C–Cl functionalities. The transformations proceeded under open-flask conditions at room temperature, and were complete within 5 min.

