Synthetic Methods

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Transfer of Aryl Halide to Alkyl Halide: Reductive Elimination of Alkylhalide from Alkylpalladium Halides Containing *syn*-β-Hydrogen Atoms**

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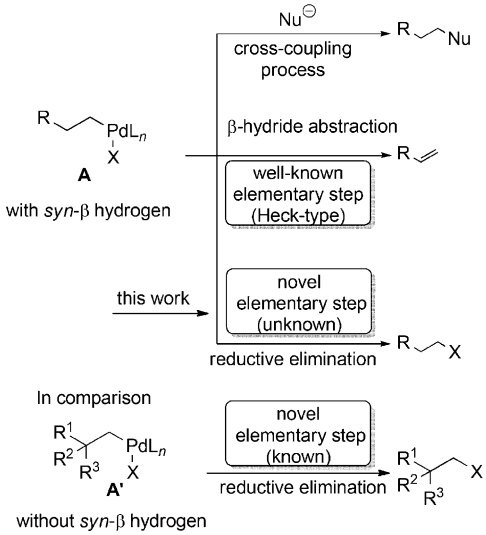
Dedicated to Prof. Tamotsu Takahashi on the occasion of his 60th birthday

Abstract: *β-Hydride abstraction is a well-accepted elementary step for catalytic cycles in organometallic chemistry. It is usually anticipated that alkylpalladium halides containing syn-β-hydrogen atoms will undergo β-hydride abstraction to afford the Heck-type products. However, this study discloses that the above general knowledge is only conditionally correct. Our experimental results demonstrate that the reductive elimination of alkylhalides from alkylpalladium halides containing syn-β-hydrogen atoms may surpass the β-hydride abstraction or even become exclusive in certain cases.*

Alkylpalladium(II) halides (**A**; Scheme 1) containing *syn*-β-hydrogen atoms have recently become synthetically useful for constructing carbon–carbon bonds and carbon–heteroatom bonds through transition-metal-catalyzed cross-coupling reactions.[1] β-Hydride abstraction, a well-accepted elementary step for catalytic cycles in organometallic chemistry, is the major possible competitive reaction, thus resulting in the Heck-type alkene product.[2] Therefore, to suppress β-hydride abstraction and facilitate the following step such as a transmetallation reaction, bulky trialkylphosphine ligands such as $P(t\text{Bu})_2\text{Me}$, PCy_3, and other additives are required.[1c] In contrast, reductive elimination (RE) of alkyl halides from alkylpalladium halide species (**A′**, Scheme 1) has been recently recognized as a novel elementary step for catalytic cycles.[3–8] In all those examples in the literature reporting this RE of **A′**, the alkylpalladium halides do not have *syn*-β-hydrogen atoms.[9] Otherwise, β-hydride abstraction would take place to afford the alkene products.[6c,10] Herein we report the first example of reductive elimination of alkyl halides from alkylpalladium(II) halides containing *syn*-β-hydrogen atoms.



Scheme 1. Elementary steps for catalytic cycles involving alkylpalladium(II) complex **A**, having *syn*-β-hydrogen atoms, and **A′**, lacking *syn*-β-hydrogen atoms. β-hydride abstraction versus reductive elimination.

After screening various reaction conditions with the substrate **1a** and a 3-alkyne (Scheme 2), the base Li*O*t*Bu was found to be most effective. When no Li*O*t*Bu was added, only trace amounts of the product **2a** was formed (see the Supporting Information for details). The role of Li*O*t*Bu is not clear yet, but the base would probably facilitate the regeneration of the active palladium(0) species.[11] During ligand optimization, PPh_3 was found to be the most effective ligand in this reaction. When additional PPh_3 was added, the yield of **2a** decreased. Bulky ligands such as dppf and $P(t\text{Bu})_3$, which were used successfully in the previous reductive elimination of C–I bonds,[6a,c,7] appeared to be ineffective. Other monodentate phosphine ligands such as tri-(2-furyl)phosphine (TFP), *t*BuXPhos, and bidentate phosphine ligands such as dppe and dppp gave much lower yields or no product at all (see the Supporting Information for details).

Solvents were also found to be essential for the success of this reaction (Scheme 2). When the reaction was conducted in polar solvents such as THF and DMF, the reaction became messy, thus affording a mixture of products with 1-phenylpiperidine (deiodination product of **1a**) as the major one. A non-negligible amount of the alkene product **3a** was also

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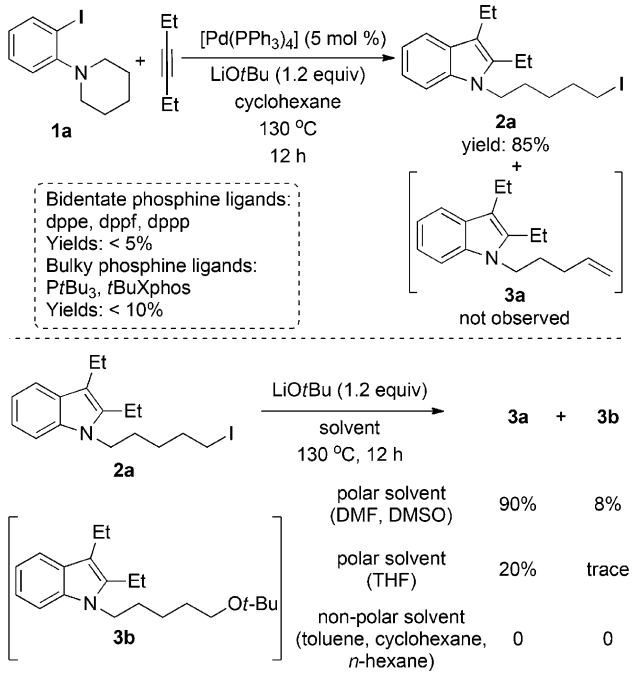


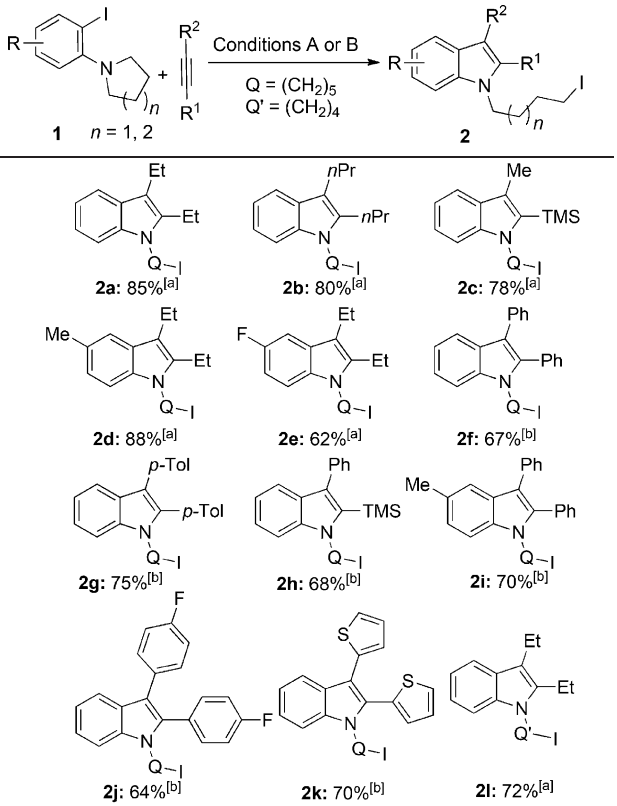
Scheme 2. Ligand effects on the carboiodination reaction and solvent effects on the stability of the product alkyliodide **2a**.

observed in the mixture. Nonpolar solvents such as *n*-hexane, cyclohexane, and toluene generally afforded much cleaner reactions. When the reaction was conducted in toluene, deiodination of **1a** took place, thus affording 1-phenylpiperidine as the side product in a small amount (6% yield), along with 75% yield of the desired product **2a**. Cyclohexane as the solvent was found to be the best for this reaction.[5a] Deiodination of **1a** did not take place in most cases in cyclohexane. Thus, the optimal reaction conditions were found to be **1a** (0.5 mmol), 3-hexyne (0.6 mmol), $[Pd(PPh_3)_4]$ (5 mol%, 0.025 mmol), and LiO*t*Bu (1.2 equiv, 0.6 mmol) in 2 mL of cyclohexane at 130°C for 12 hours. Under these optimized reaction conditions, the alkyliodide indole derivative **2a** was obtained in 85% yield upon isolation.

Furthermore, as mentioned above, the alkene product **3a** appeared and was formed in non-negligible amounts when the reaction was conducted in polar solvents. To know where the **3a** derived from and whether **2a** was stable under the basic reaction conditions, the experiments shown in Scheme 2 were carried out. It was found out that the polarity of solvents remarkably affected the stability of **2a**. In polar solvents such as THF, DMF, and DMSO, **2a** did undergo base-mediated elimination and substitution reactions, thus affording the elimination product alkene **3a** and the substitution product **3b**. Particularly, in DMF and DMSO **2a** underwent elimination and substitution reaction completely. However, in nonpolar solvents such as cyclohexane, *n*-hexane, and toluene, **2a** was stable and remained unchanged in most cases.

The substrate scope of this palladium-catalyzed $C(sp^3)$–I bond formation was investigated under the optimized reaction conditions, and the results are summarized in Table 1. The symmetrical 3-hexyne and 4-octyne afforded their corresponding products (**2a** and **2b**) in excellent yields.

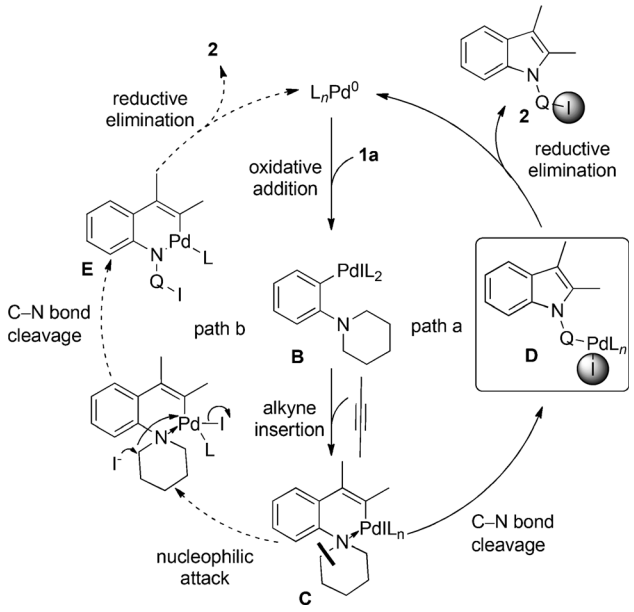
Table 1: Substrate scope.



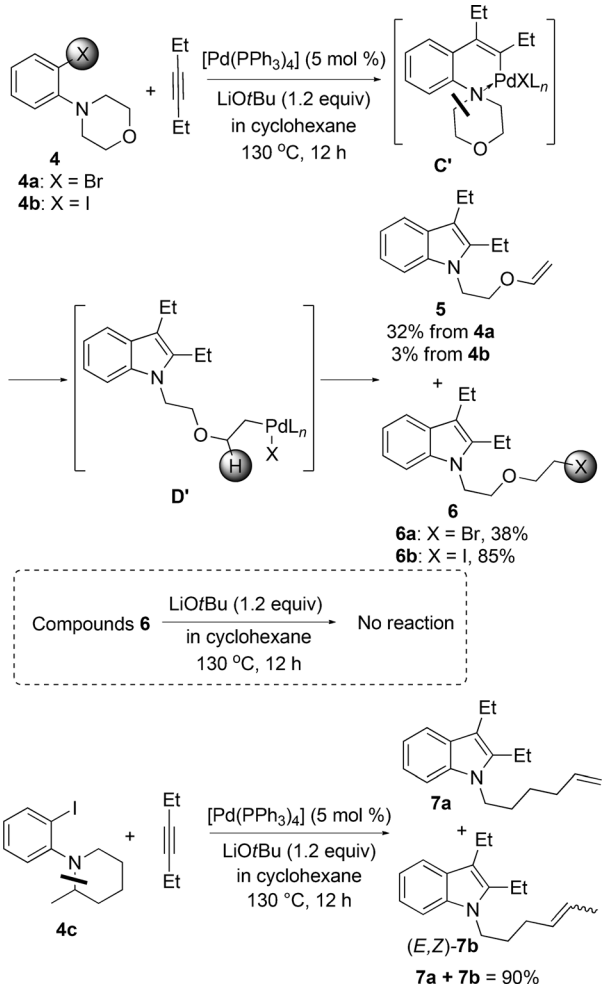
[a] Reaction conditions A: $[Pd(PPh_3)_4]$ (5 mol%), LiO*t*Bu (1.2 equiv) in 2 mL of cyclohexane at 130°C for 12 h. [b] Reaction conditions B: $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%), LiO*t*Bu (1.2 equiv) in 2 mL of cyclohexane at 130°C for 48 h. TMS = trimethylsilyl.

When 1-(trimethysilyl)propyne was used, the product **2c**, bearing a trimethylsily group at the 2-position, was obtained regioselectively. Both electron-donating and electron-withdrawing substituents on the substrate of 2-amino iodobenzene were well tolerated (**2d** and **2e**). However, when **1a** was treated with diphenylacetylene under the above optimized reaction conditions, only trace amounts of the product **2f** could be obtained and the conversion was less than 10%. This result indicated that the reactivity of aliphatic alkynes was different from that of aromatic alkynes for this reaction. Reaction conditions for aromatic alkynes were then screened. The combination of $Pd(OAc)_2$ with PPh_3 as the ligand was found to be effective. Optimal reaction conditions were found to be **1a** (0.5 mmol), diphenylacetylene (0.6 mmol), $Pd(OAc)_2$ (5 mol%, 0.025 mmol), PPh_3 (10 mol%, 0.05 mmol), and LiO*t*Bu (1.2 equiv, 0.6 mmol) in 2 mL of cyclohexane at 130°C for 48 hours (see the Supporting Information for details). The results are given in Table 1. Functionalized alkynes such as the F-substituted one and the thiophene-substituted one, and the five-membered **1b** could also be applied to afford the corresponding products **2j**, **2k**, and **2l** in good yields.

Iodine-transfer reactions involving transition-metal-initiated cyclization of unsaturated alkyl iodides have been reported to proceed by a radical process.[12] In our reaction, addition of TEMPO did not show remarkable effect. In the



Scheme 3. Plausible catalytic cycle.



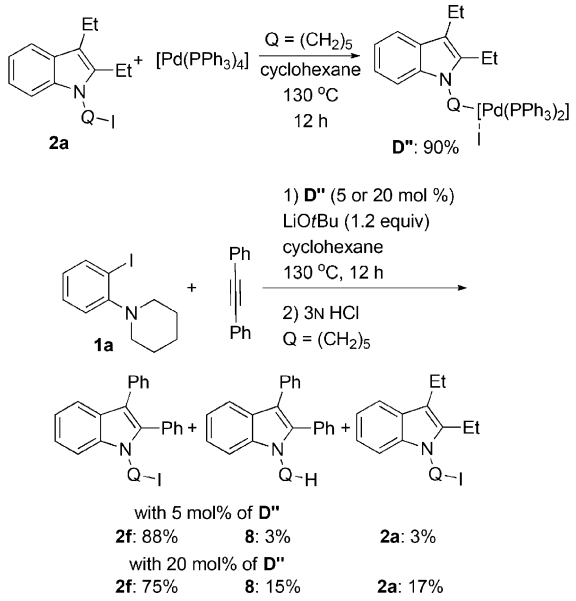
Scheme 4. Palladium-catalyzed reaction of 1-(2-halophenyl)morpholine and 1-(2-iodophenyl)-2-methylpiperidine with 3-hexyne.

presence of 2.0 equivalents of TEMPO, the product **2a** was obtained in 75% yield upon isolation, while **2f** was obtained in 48% yield upon isolation. These results indicate that a radical process can be excluded.

Plausible catalytic cycles are depicted in Scheme 3. The intermediate **C** might be formed from **1a** and an alkyne by oxidative addition followed by alkyne insertion. The intermediate **C** would undergo C–N bond cleavage to generate the intermediate **D** (path a).[13] Formation of the indole moiety could be considered a driving force for this step. Then, the intermediate **D** would undergo reductive elimination to form the alkyliodide product **2** and regenerate the palladium(0) species. Shown in path b is an alternative possibility.[14] Firstly, attack of an iodide anion on the intermediate **C** would generate the six-membered palladacycle **E**. Then **E** would undergo reductive elimination to form the product **2**. However, all our experimental results indicate that path b is unlikely.

Several experiments were carried out to understand the reaction mechanism. First, as given in Scheme 4, the substrate **4a** (X = Br) was used. Both the β-hydride abstraction product **5** and the reductive elimination product **6a** were isolated in 32 and 38% yields, respectively. It has been reported that reductive elimination of alkylbromides could be much slower than that of alkyliodides,[6b,c] thus for the formation of **5**, in addition to the higher acidity of the β-hydrogen atoms in **D′** and the higher stability of the generated vinyl ether moiety in **5**, one the relatively sluggish reductive elimination of the alkylbromide from the intermediate **D′** (X = Br) is important. To further make this point, the corresponding iodo derivative **4b** was applied. Such a reaction would proceed via the intermediate **D′** (X = I), which was expected to show faster reductive elimination of the alkyliodide. As shown in Scheme 4, with **4b** (X = I), the product **6b** was obtained in 85% yield. The product **5** was formed in only 3%. These results demonstrated that reductive elimination of alkyliodides were remarkably easier than that of alkylbromides, which are in good agreement with the literature reports. Furthermore, to make sure whether or not the product **5** was generated from a base-mediated elimination reaction of the alkylhalides **6**, control experiments in which products **6** were heated with the base under the reaction conditions were run (Scheme 4). Results showed that the products **6** were stable under the reaction conditions, thus demonstrating that **5** was not formed by the base-mediated elimination of **6**. The above results show that the products **5** and **6** were formed via the intermediate **D′** and suggest path b would be unlikely, and was further supported by the reaction of **4c** containing a 2-methyl piperidine. As shown in Scheme 4, the ring-opening of **4c** took place highly selectively at the methyl-substituted C–N bond (see the Supporting Information for details).

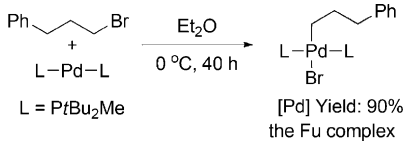
Then, as shown in Scheme 5, the intermediate **D″** was obtained in 90% yield from the reaction between **2a** (substituted with Et groups) and 1 equivalent of $[Pd(PPh_3)_4]$. Characterization of **D″** by using NMR spectroscopy supported its formation. Then the cross-experiment was carried out using **D″** as a catalyst precursor (5 mol%) for the reaction of **1a** with diphenylacetylene. The product **2f**, substituted with phenyl groups was obtained in 88% yield, together with



Scheme 5. Isolation and catalytic application of the alkylpalladium intermediate.

3% of **2a**. When 20 mol% of **D″** was applied, **2f** and **2a** were formed in 75 and 17% yields, respectively. Quench of the reaction mixture with 3N HCl afforded the product **8**, which should be formed from protonolysis of the catalyst residues. These results demonstrate that the alkylpalladium intermediate **D″** is thermally stable,[15] and its reactivity should be initiated by the indicated steps.

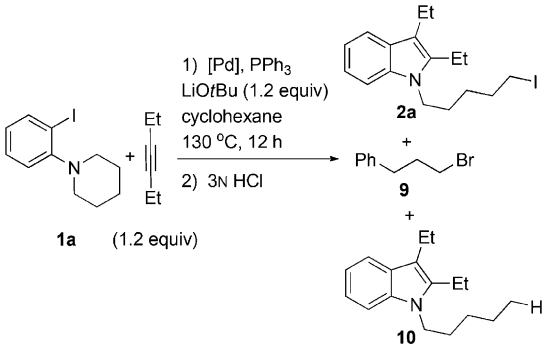
We considered that the alkylpalladium intermediate **D″** to most likely to be the catalyst resting state. We prepared the Fu complex[15a] and used it in our reaction system (Scheme 6).



Scheme 6. Isolation of Fu's alkylpalladium complex (the Fu complex).

Following the reported procedure, the Fu complex was obtained in 90% yield and confirmed by single-crystal X-ray structural analysis. As shown in Table 2, the complex did catalyze the reaction but afforded **2a** in a lower yield (entry 2). When 10 mol% of PPh_3 was added as an additional ligand in the reaction system, the yield of **2a** increased. However, with more PPh_3 ligand (entries 4 and 5), the yields of **2a** decreased. In addition to the formation of **2a**, reasonable amounts of **9** from the complex and **10** from the catalyst resting state were also observed. These results support formation of the alkylpalladium intermediate **D″** as the catalyst resting state. These results again indicated that bulky ligands such as the one ($PtBu_2Me$) in the complex were not good for this reaction.

Table 2: Catalytic application of the Fu complex.



Entry	mol% [Pd]	mol% PPh_3	Yield [%] 2a	9	10
1	0	10	0	0	0
2	5	0	33	2	2
3	5	10	45	3	3
4	5	30	11	2	2
5	5	50	5	2	trace

In summary, we have developed the first example of reductive elimination of alkyl halide from alkylpalladium(II) halides containing *syn*-β-hydrogen atoms. Our experimental results demonstrate that the reductive elimination of alkyl-halides from alkylpalladium halides containing *syn*-β-hydrogen atoms may surpass the β-hydride abstraction or even become exclusive in certain cases. Further detailed investigations into the role of bases and ligand effects will be carried out. This finding is expected to be fundamentally useful for the understanding of elementary reactions in organometallic chemistry, and synthetically useful for further applications of alkylpalladium(II) halide containing *syn*-β-hydrogen atoms.

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