

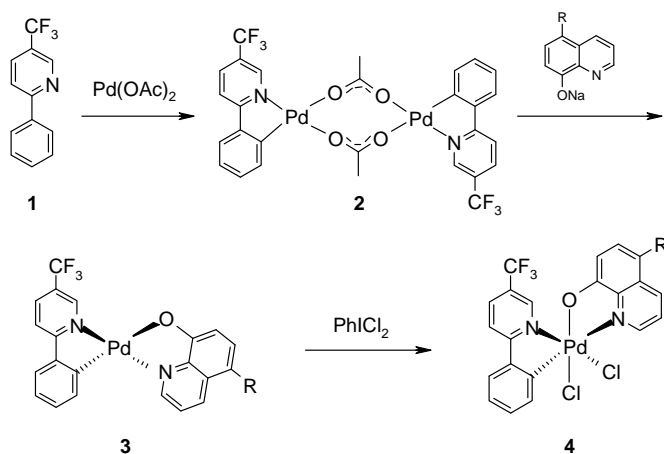
# Reductive Elimination Reactions of Pd(IV) Complexes Containing Pd-O and Pd-C Bonds

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The recently discovered Pd(IV)/Pd(II) and Pd(III)/Pd(II) catalytic cycles provide a convenient way for C–O bond formation through C–H activation, followed by introduction of acetoxy or alkoxy groups [1]. However, so far the C–H to C–O transformation using Pd(IV)/Pd(II) catalytic cycle has not been used for the introduction of aryloxy groups. The prerequisite for the development of such a transformation is in-depth mechanistic studies of the C–O bond forming reductive elimination from Pd(IV) complexes.

To study the formation of diarylether bond, we designed Pd(IV) complexes **4** (Scheme 1) with 2-phenylpyridine and 8-hydroxyquinoline ligands. These complexes contain Pd–C(Ar) and Pd–OAr bonds and may undergo reductive elimination to form diarylethers Ar(C)–OAr. For the convenient reaction monitoring by <sup>19</sup>F NMR, the trifluoromethyl group was incorporated in the 2-phenylpyridine ligand. To evaluate the C–O bond formation in the complexes with different O atom nucleophilicity electronically diverse substituents at the C-5 were introduced in the 8-hydroxyquinoline ligands.

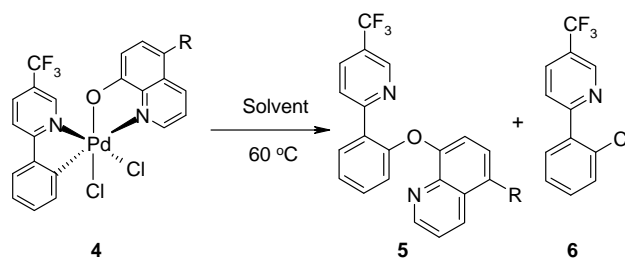


R = -H, -F, -Cl, -Br, -Me, -*t*Bu, -CHO, -COOMe, -NO<sub>2</sub>, -Ph, -C<sub>6</sub>H<sub>4</sub>-*p*-NO<sub>2</sub>

Scheme 1. Synthesis of Pd(IV) complexes

Synthesis of the designed complexes **4** was started with cyclopalladation of 2-phenyl-5-trifluoromethyl pyridine **1** to give complex **2** that was treated with sodium salts of 5-substituted 8-hydroxyquinoline derivatives. Resulting Pd(II) complexes **3** were oxidized with PhICl<sub>2</sub> to give the desired Pd(IV) complexes **4** (Scheme 1).

In the present research, the rates of the thermal reductive elimination reactions of Pd(IV) complexes **4** are reported to produce diaryl ethers **5** (Scheme 2).



Solvent = MeCN, CHCl<sub>3</sub>, acetone, benzene, nitrobenzene

Scheme 2. Reductive elimination reactions of the Pd(IV) complexes

The competitive formation of the side product aryl chloride **6** was also observed, because the use of PhICl<sub>2</sub> as an oxidant resulted in the formation of two Pd–Cl bonds. Thereby the efficiency of the formation of diaryl ethers was controlled to a great extent by comparative rates of C–O vs. C–Cl bond forming reactions. Reaction rates were also studied in solvents of different polarity.

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## REFERENCES

- [1] Dick, A.R.; Hull, K.L.; Sanford, M.S. *J. Am. Chem. Soc.* **2004**, *126*, 2300–2301.