

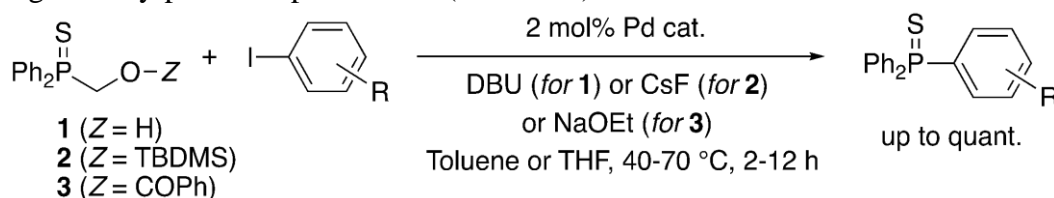
Development of Novel Syntheses of Organophosphorus Compounds: From a Simple P-C Bond Formation to Phosphacycles

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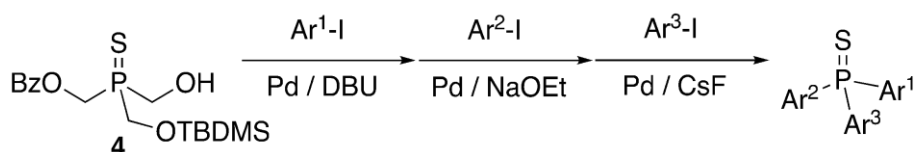
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Organophosphorus compounds play several essential roles in organic chemistry, such as valuable ligands in transition metal catalysis. Although many types of organophosphine derivatives have been synthesized, their syntheses are often troublesome due to a lack of selective P-C bond formation reactions. We have developed quite efficient P-C bond formation procedures via Pd-catalyzed cross-coupling reactions using hydroxymethylphosphine derivatives as stable precursors (Scheme 1). [1,2] In this lecture, the application of the reaction to multiple couplings for the versatile synthesis of organophosphorus compounds will be presented. Synthesis and application of a highly fluorescent phosphacycle, λ^5 -phosphinine, will also be presented.

In addition to a simple one P-C bond formation reaction (Scheme 1), two and/or three substituents on the phosphorus atom can be incorporated by repeating the P-C cross-coupling reactions by using suitably protected precursor **4** (Scheme 2).

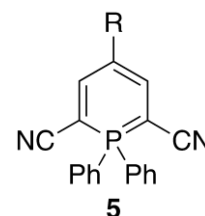


Scheme 1. Pd-catalyzed P-C cross-coupling reactions.



Scheme 2. multiple and selective coupling reactions.

λ^5 -phosphinines are novel fluorescent compounds with a six-membered phosphacycle with phosphorus-ylide in their π -system. We have developed a simple and straightforward synthesis of λ^5 -phosphinines **5** from a suitable phosphonium salt and imines. [3] Further functionalization of the λ^5 -phosphinine-ring allowed fine-tuning of their photophysical properties.



References

- [1] M. Hayashi, T. Matsuura, I. Tanaka, H. Ohta, Y. Watanabe, *Org. Lett.* **2013**, *15*, 628.
 [2] H. Ohta, Q. Xue, M. Hayashi, *Eur. J. Org. Chem.* **2018**, 735.
 [3] N. Hashimoto, R. Umamo, Y. Ochi, K. Shimahara, J. Nakamura, S. Mori, H. Ohta, Y. Watanabe, M. Hayashi, *J. Am. Chem. Soc.* **2018**, *140*, 2046.