**Transition Metal-Catalyzed C-H, C-C, and C-Si Bond Activation and Its Application to Material Science**

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Transition metal catalyzed activation of unreactive bond such as C-H and C-C bond is one of challenging topics in synthetic organic chemistry. We developed catalytic C-H bond activation such as hydroacylation, in which aldehyde can be catalytically transformed into ketone.1, 2 Reaction of aldehyde with 1-alkene or alkyne affords corresponding ketones in high yield under cooperative catalyst mixture of rhodium(I) complex and 2-amino-3-picoline.3 The reaction is atom-economical and environmentally benign since no waste is procuced. This protocol can be applied to the C-C bond cleavage of aliphatic ketone4 and further C-C multiple bond cleavage.5 This homogeneous catalyst system can be recycled using mixed solvent system.6 Catalysts are soluble in the solvent during the reaction at high temperature, while the catalyst mixture was recovered on cooling as a self-assembling after the reaction. Another interesting unreactive bond cleavage is that of C-Si bond. In this reaction C-Si bond is cleaved by catalyst mixture of rhodium(I) or iridium(I) with HCl. Vinylsilane reacts with alcohol to give silyl ether compound with evolution of ethylene gas under these catalyst mixture.7 This C-Si bond cleavage catalysis is further applied to immobilize organic molecules onto silica or glass surface through formation of siloxane bond since surface is covered with Si-OH group in this material.8 Another interesting substrate for C-Si bond cleavage is methallylsilane, which can be activated by acid such as Sc(OTf)3, which can be used for immobilizing various organic molecules under very mild condition.9 Even enzymecan be immobilized onto silica efficiently through the reaction of lysine residue of Glucose Oxidase enzyme with N-hydroxysuccinimidyl group attached to silica surface, prepared by one-step catalytic immobilization of N-hydroxysuccinimidyl ester bearing methallylsilyl group onto silica.10 Efficient one-pot covalent-bonding immobilization of GOx onto silica was recently achieved.

References

1. Park, Y. J.; Park, J.-W.; Jun, C.-H. *Acc. Chem. Res.* **2008**, *41*, 222.
2. Kim, D. -S.; Park, W. -J.; Jun, C. –H. *Chem. Rev.* **2017**, DOI:10.1021.
3. Jun, C.-H,; Lee, D.-Y.; Lee, H.; Hong, J. -B. *Angew. Chem. Int. Ed.* **2000**, *39*, 3070.
4. Jun, C.-H.; Lee, H. *J. Am. Chem. Soc.* **1999**, *121*, 880.
5. Lee, D.-Y.; Hong, B.-S.; Cho, E.-G.; Lee, H.; Jun, C.-H. *J. Am Chem. Soc.* **2003**, *125*, 6372.
6. Chang, D.-H.; Lee, D.-Y.; Hong, B. -S.; Jun, C.-H. *J. Am. Chem. Soc.* **2004**, *126*, 424.
7. Park, J.-W.; Jun, C. -H. *Org. Lett.* **2007**, *9*, 4073.
8. Park, J.-W.; Jun, C. -H. *J. Am. Chem. Soc.* **2010**, *132*, 7268.
9. Yeon, Y.-R.; Park, Y. J.; Lee, J.-S.; Park, J.-W.; Kang. S.-G.; Jun, C.-H. *Angew. Chem. Int. Ed.* **2008**, *47*, 109.
10. Y.-K. Shim, J.-W. Park, B.-H. Kim and C.-H. Jun, *Chem. Commun*. **2013**, *49*, 11170.