

Development of Anions containing Halogen Bonding Sites and their Application for Transition Metal Catalysis

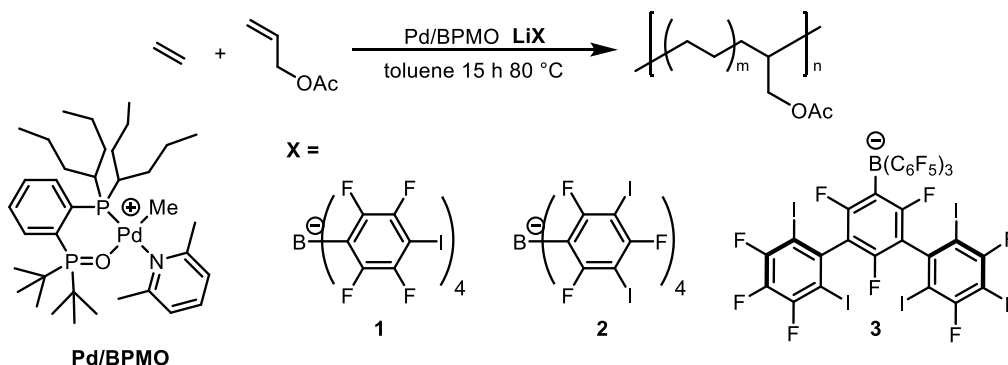
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In recent years, new catalyst designs owing multiple active sites, such as multi-metallic and metal-ligand cooperative catalysts, have been intensively investigated to realize challenging transformations. In contrast, counter anions, coexisting with cationic transition metal complexes, have been much less studied as a candidate for incorporating a catalytic function in transition metal catalysis except for serving as a Brønsted base.^{1, 2} Weakly coordinating anions are often employed as counter anions of cationic metal complexes, but they do not contribute to activating substrates.

We envisioned that a novel type of anion endowed with Lewis acidic property would activate polar functional groups, such as halogens, carbonyls, and nitriles. By combining the anion with a cationic counterpart, the salt would serve as a new class of multi-active site catalyst. As a Lewis acidic property, we chose a halogen bonding, a non-covalent interaction between a σ -hole associated with a carbon-halogen bond and an electron donor. The anions featuring halogen bonding sites can activate substrates electrophilically and serve the captured substrate to transition metal center, closely co-existing via electrostatic attraction.

In this study, we synthesized single-halogen bonding anions bearing C–I bonds at *para*- (**1**) or *meta*-positions (**2**) of highly-fluorinated tetraarylborate and a double-halogen bonding borate **3** consisting of a terphenyl framework. Next, anions **1–3** were applied to the Pd-catalyzed copolymerization of polar monomers and ethylene³ to prove the concept, that the incorporation ratio of polar monomer could be improved by capturing the counter anion. In the presentation, the effect of counter anions in the copolymerization of ethylene and polar monomers such as allyl acetate will be discussed.



- 1) Hamilton, G. L.; Kang, E. J.; Mba, M.; Toste, F. D. *Science* **2007**, 317, 496. 2) Wang, X.; List, B. *Angew. Chem. Int. Ed.* **2008**, 47, 1119. 3) Carrow, B. P.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, 134, 8802.