Catalytic Application of Lewis Acidic Weakly Coordinating Anions

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Complexes consisting of transition metal cations and ion-separated anions play a crucial role as catalysts in organic transformations. Anions are inherently nucleophilic, and the counter anion occasionally activates substrates by its Brønsted basic character in transition metal catalysis.[1,2] If a molecule that exhibits both Lewis acidity and anionic character can be realized, a new mechanism of substrate activation would be achieved. However, Lewis acidic anions[3] have never been employed in transition metal catalysis due to their instability.

Here, we synthesized stable Lewis acidic anion **BBcat**, which is applicable to the transition metal catalysts and photocatalysts. Anion **BBcat** has weak-coordination ability to transition metals in the same manner as a common weakly-coordinating anion **BArF**. The ion pair of cationic **Ir/PHOX** complex and **BBcat** exhibited an 8.2-fold higher reaction rate than **BArF** complex in the hydrogen isotope exchange of acetophenone derivatives bearing additional Lewis basic functionalities on the phenyl group. This enhanced activity was attributed to the substrate capture by the acidic sites on **BBcat** and proximity by electrostatic interaction between the ion pair without occupying the coordination site on Ir.

The counter-anion strategy using stable Lewis acidic anion **BBcat** was further expanded to photocatalysts. In CH_2Cl_2, excited **Ru(bpy)$_3$(BBcat)$_2$** was quenched with the addition of (*E*)-4-styrylpyridine while **Ru(bpy)$_3$(BArF)$_2$** was not. This clear difference between **BBcat** and **BArF** was not observed with (*E*)-stilbene. These results evidenced that coordination of the pyridine moiety to **BBcat** allows approach of the resulting substrate/anion complex to the cationic **Ru(bpy)$_3$** through electrostatic interaction, and thus resulting in facile energy transfer from excited **Ru(bpy)$_3$** to the Lewis basic substrate.

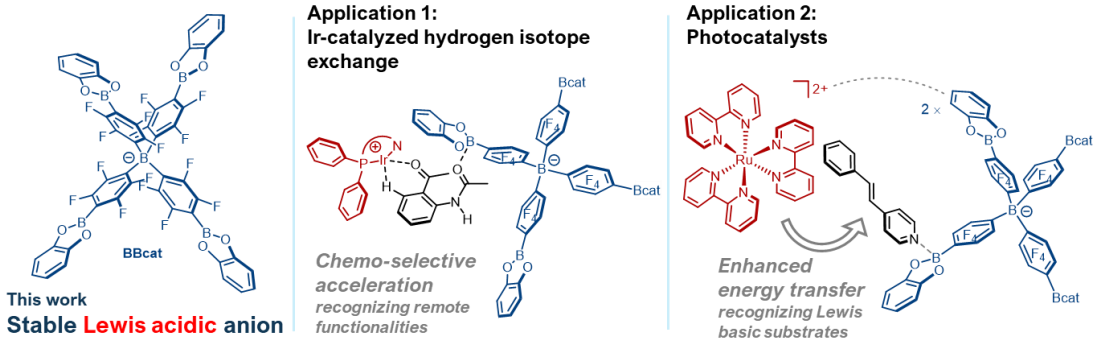

Figure. Stable Lewis acidic anion **BBcat** and its application to catalytic reactions

1. For TM catalysts a) D. Zuccaccia *et al*., *Chem. Eur. J.* **2014**, *20*, 14594. b) F. D. Toste *et al*., *Science* **2007**, *317*, 496. c) B. List *et al*., *JACS* **2007**, *129*, 11336. 2. For photocatalysts a) R. R. Knowles *et al*., *JACS* **2019**, *141*, 13253. b) B. List *et al*., *Science* **2023**, *379*, 494. 3) a) L. Greb *et al*., *JACS* **2019**, *141*, 18009. b) L. Greb *et al*., *ACIE* **2022**, *62*, e202202176.