Halogen Dance Reaction Promoted by Novel Aryltrifluoroborate Catalysts

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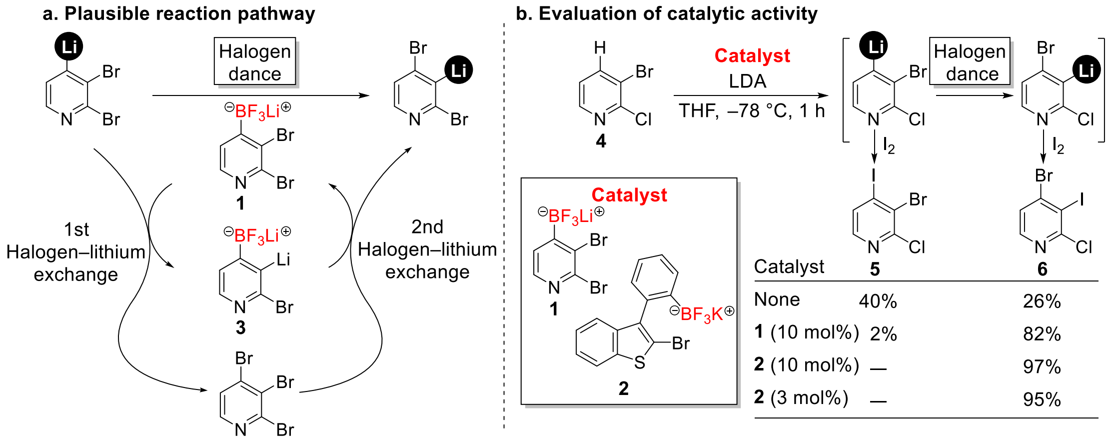
Halogen migration of halogenated arenes, referred to as halogen dance, is of great importance for the synthesis of various arenes with hitherto unachievable substitution patterns.[1] In 2023, our group reported lithium pyridyltrifluoroborate **1** as an effective catalyst for broadening the limited substrate scope of this reaction.[2] In this work, we further explored various arenes as the core structure of the catalyst and found that potassium benzothienyltrifluoroborate **2** showed an extremely high catalytic activity.

First, we designed the catalyst based on the reaction pathway, which suggests that the first halogen–metal exchange generating thermodynamically unfavored organolithium species **3** is the rate-determining step.[2] An appropriate choice of the flamework of catalysts that stabilizes the organolithium species would accelerate this step. The calculated p*K*a values of the conjugate acids of the organolithium species suggested that benzothienyltrifluoroborate **2** would exhibit high catalytic activity. We evaluated the catalytic activity of these catalysts using 3-bromo-2-chloropyridine (**4**) as a model substrate, which is less reactive toward the halogen dance reaction. As a control experiment, a THF solution of 3-bromo-2-chloropyridine (**4**) was treated with LDA at –78 °C for 1 h without a catalyst. Subsequent iodination gave a mixture of iodopyridines **5** and **6** in 40% and 26% yields, respectively. In the presence of lithium pyridyltrifluoroborate **1**, iodopyridine **6** was obtained in 82% yield, exclusively. The use of potassium benzothienyltrifluoroborate **2** resulted in full conversion of the pyridyllithium and improved the yield of iodopyridine **6** in 97% yield. Decreasing the catalytic loadings (3 mol%) gave iodopyridine **6** in comparable yield. We will discuss the effect of counterions on the catalytic activity.



Catalyst	5	6
None	40%	26%
1 (10 mol%)	2%	82%
2 (10 mol%)	—	97%
2 (3 mol%)	—	95%

1) Schnürch, M.; Spina, M.; Khan, A. F.; Mihovilovic, M. D.; Stanetty, P. *Chem. Soc. Rev.* **2007**, *36*, 1046.
2) Inoue, K.; Hirano, K.; Fujioka, S.; Uchiyama, M.; Mori, A.; Okano, K. *ACS Catal.* **2023**, *13,* 3788.