Exploiting Cobalt(II) Amide Complexes in Deprotonative Metalation of Fluoroaromatic Molecules

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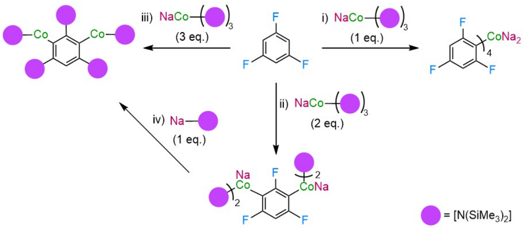
Fluoroaromatic compounds are increasingly heavily employed as scaffolds in agrochemicals and active pharmaceutical ingredients.[1] One of the most powerful methods for the incorporation of these molecules in more complex molecular scaffolds is deprotonative metalation. Typically these reactions have been the exclusive domain of group 1 and group 2 organometallics.[2] On the other hand, earth abundant transition metals such as cobalt have shown excellent potential to selectively functionalise these molecules via C-H and C-F bond activation.[3]

Breaking new ground in this field, in this contribution, by pairing a seemingly toothless cobalt (II) amide with their sodium congener, we report a new bimetallic approach, which enables the regioselective functionalisation of C-H as well as C-F bonds of a wide range of fluoroarenes. While deprotonation of fluoroarenes using conventional lithium bases can be challenging due to the exceptionally fragility of generated intermediates,[4] these cobaltation reactions occur regioselectively at room temperature. Combining the isolation of key metalated intermediates with theoretical calculations, unique mechanistic insights on how the alkali-metal and cobalt can cooperate in a synchronised manner to induce these processes that neither group 1 or cobalt amides are capable of facilitating on their own.



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