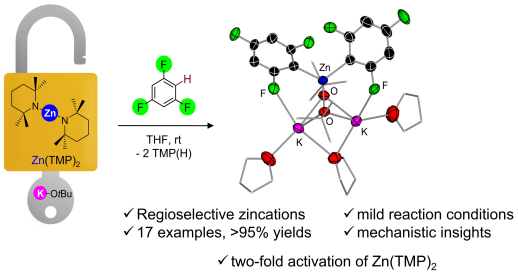
Alkali-Metal-Alkoxide Powered Zincation of Fluoroarenes Employing Zinc Bis-Amide $Zn(TMP)_2$

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The unique activating effects of alkali-metal alkoxides when added to other s-block organometallics is a well-established phenomenon in polar organometallic chemistry.[1] Typified by the LIC-KOR (Lochmann-Schlosser) superbase, combining potassium *tert*-butoxide with *n*-butyllithium greatly enhances the metalation capabilities of this mixture when compared to those of their monometallic counterparts.[2,3] Extending these reactivity enhancement effects beyond group 1 organometallics, our group has recently demonstrated the ability of alkali-metal alkoxides to activate dialky magnesium or zinc reagents towards metal halogen exchange reactions of bromo and iodoarenes. Mechanistic studies indicate that these special behaviors can be attributed to the formation of more reactive mixed-metal mixed-aggregate complexes. [4–6]

Building on this work, we have recently developed a new bimetallic base which allows for the direct zincation of a broad range of aromatic substrates.[7] By combining the Zn amide $Zn(TMP)_2$ (TMP = 2,2,6,6-Tetramethylpiperidide) with two equivalents of KO*t*Bu effective zincation of sensitive substrates such as 1,3,5-trifluorobenzene can be achieved while operating at room temperature (see Figure). Trapping of key reaction intermediates and NMR monitoring of the reactions have uncovered the close interplay between the different components of this bimetallic mixture to facilitate the success of the Zn-H exchange reaction and the stability of the metalated intermediates. Showcasing its metalating power, this bimetallic KO*t*Bu/$Zn(TMP)_2$ partnership, can even effect benzylic zincation of toluene and benzene at room temperature.[7]



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