OC54
PUSHING THE LEWIS ACIDITY BOUNDARIES OF BORON COMPOUNDS WITH NON-PLANAR TRIARYLBORANES DERIVED FROM TRIPTYCENES

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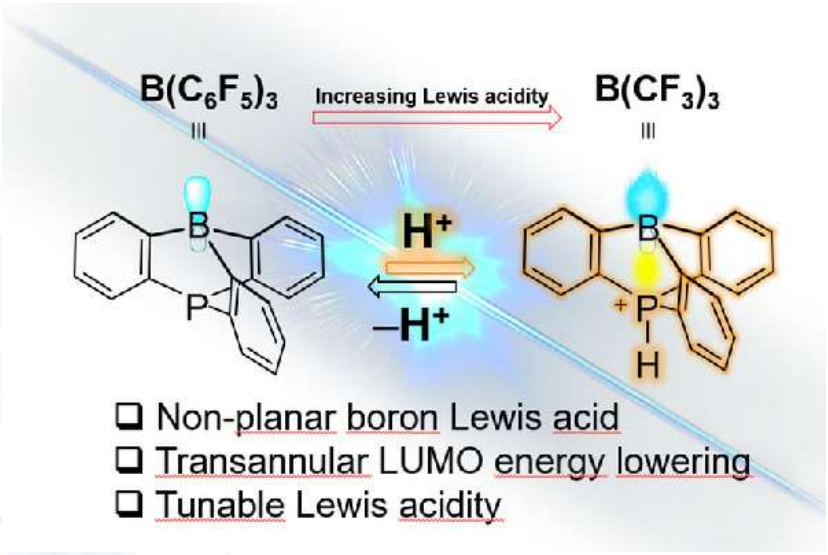
Since the synthesis of $B(C_6F_5)_3$ by Massey in 1963,[1] the main approaches for increasing the acidity strength of boron Lewis acids are to use electron-withdrawing groups (p-$C_6F_4CF_3$, $OC(CF_3)$),[2] cationic substituents (NR_3^+, PR_3^+, SMe_2^+, BR_2^+),[2c] or anti-aromatic borole rings.[3]
We recently showed that bending the planar trigonal boron atom of triphenylborane by connecting its aryl rings with carbon or phosphorus linkers gave access to a series of 9-boratriptycene derivatives with unprecedented structures and reactivities. NMR and X-ray diffraction investigations of the Lewis adducts of these non-planar boron Lewis acids with weak Lewis bases ($OPEt_3$, CH_3CN, EtOAc, Cl^-, Br^-, I^-) revealed particularly strong covalent bond. formation. Experimental and quantum-chemical investigations showed that increasing the pyramidalization of the boron atom and using a cationic phosphonium linker resulted in an exceptional enhancement of Lewis acidity, pushing forward the boundaries of the Lewis acidity scale of trivalent boron Lewis acids. Introduction of a phosphorus and a boron atom at each edge of a triptycene framework, allowed to access new bifunctional Lewis acid-base 9-phospha-10-boratriptycenes featuring promising reactivity for the activation of carbon-halogen bonds.[4] This method will be extended to the design of new main groups Lewis acids by geometricaly constraining the coordination sphere around the group XIII-XV central atom.



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