Dinitrogen Functionalization in the Coordination Sphere of Group 6 Metals by Formal 1,3-Hydroboration of a M–N≡N Unit with Piers' Borane $HB(C_6F_5)_2$

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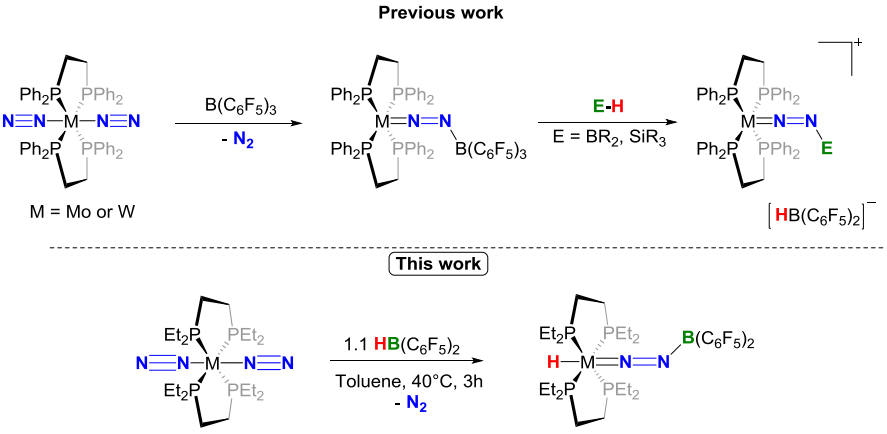
Thanks to the thermodynamic driving force of strong N−B or N−Si bonds formation and the mild hydride donor reactivity of hydro-borane and hydro-silane, the latter appear as attractive substrate for N_2 functionalization. Indeed, hydro-borane and hydro-silane have been shown to perform 1,2-addition on side-on N_2 complexes[1] or N_2-derived nitrides[2] across the reactive M−N bond. In our team, we have shown that it is possible to form N−B or N−Si covalent binding between a N_2 ligand and a hydro-silane or -borane in the coordination sphere of a group 6 metal, with the help of the strongly electrophilic borane $B(C_6F_5)_3$ (Scheme, top).[3] Such an approach was inspired by the Frustrated Lewis Pair (FLP) chemistry. As a continuation of this work, we have recently looked at the reactivity of $HB(C_6F_5)_2$ (also known as Piers' borane) with a family of group 6 phosphine-dinitrogen complexes. The good hydride donor ability as well as its high Lewis acidity have allowed for the first realization of a formal 1,3-addition of a B−H bond across a M−N≡N unit,[4] thus expanding the reactivity map of hydro-boranes with dinitrogen complexes (Scheme, bottom).



Scheme (top) silylation and borylation of a weakly activated N_2 ligand using a hydro-borane or -silane, inspired by the FLP chemistry (bottom) envisioned approach to achieve 1,3-addition of a B−H bond across a M−N≡N arrangement .

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