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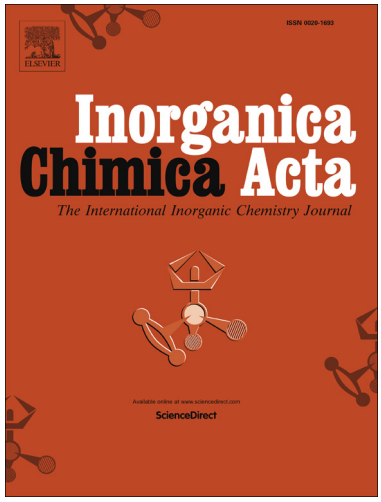


Research paper

# The Interplay of Proton Accepting and Hydride Donor Abilities in the Mechanism of Step-Wise Boron Hydrides Alcoholysis

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# The Interplay of Proton Accepting and Hydride Donor Abilities in the Mechanism of Step-Wise Boron Hydrides Alcoholysis

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**ABSTRACT**. The reaction mechanism for the step-wise alcoholysis of $BH_4^-$, $THF{\cdot}BH_3$, $Me_2NH{\cdot}BH_3$ and $BH_3$ by ROH [ROH = $CH_3OH$, $CF_3CH_2OH$ (TFE) and $(CF_3)_2CHOH$ (HFIP)] was studied computationally. The calculations were performed in gas phase at the DFT/M06/6-311++G(d,p) theory level taking into account non-specific solvent effects by SMD approach. The dihydrogen bonded complexes BH···HOR are the intermediates of this cascade borohydride alcoholysis, which set the proper orientation of the reactants molecules and direct their further activation. The consecutive introduction of RO groups instead of hydride ligands in $[(RO)_nBH_{(4-n)}]^-$ (n = 0–3) decreases the dihydrogen bond strength due to the stabilization of borohydride HOMO orbital and the decrease of molecular electrostatic potential. Nevertheless the B–H bond polarization and thermodynamic hydricity (hydride donor ability) increase with substitution, leading to the decrease of the reaction barrier. The H–H bond formation can be considered as a result of concerted proton and hydride transfer in transition state. For $BH_4^-$

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