

Activation of H–H and Si–H bonds by boranes

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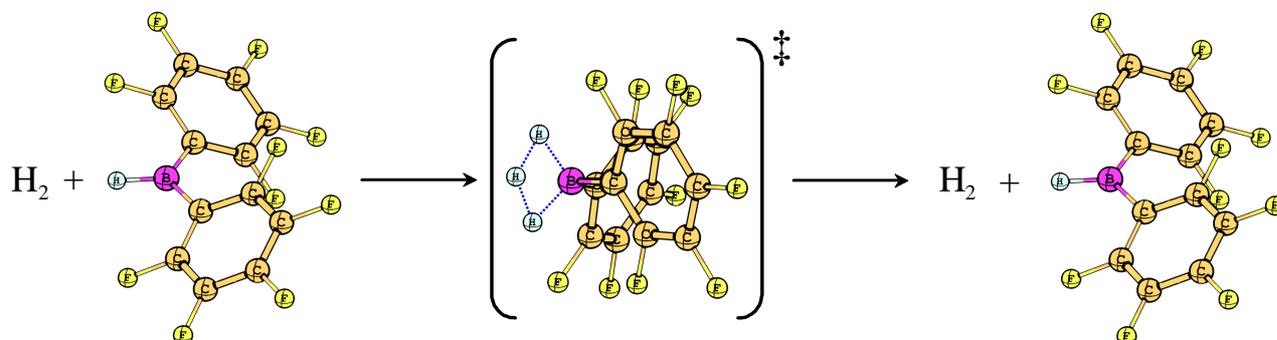
Activation of dihydrogen by non-transition metal systems is a hot research area. Recent progress in this field includes hydrogenation of carbene [1] and H₂ activation by Frustrated Lewis Pairs [2], and an unusual case of H₂ activation in borole [3].

Here we report an H/D exchange between the dihydrogen and silane catalyzed by boranes at room temperature and provide evidence for the activation of H–H and Si–H bonds on a single boron center. Our initial observation was that BAr₃ (Ar = C₆F₅) catalyzes exchange between gaseous H₂ and deuterium-labeled silanes in benzene according to the equation R₃Si–D + H₂ → R₃Si–H + HD (R₃Si = D₂PhSi, DMePhSi, Me₂PhSi, Et₃Si) with an induction period. Our computational study of the mechanism of this reaction discarded as energetically implausible an ionic mechanism via an SiR₃⁺ cation with subsequent hydrogen exchange on silyl center. A weakly bound R₃Si–D···BAr₃ adduct exists, but does not exhibit any reactivity toward H₂. A mechanism based on frustrated Lewis pairs turned out to be impossible too.

In fact, the first stage in the H₂ activation mechanism is an Ar/H exchange to give a secondary borane: R₃SiD + BAr₃ → DBAr₂ + R₃SiAr, which occurs via an R₃Si–H···BAr₃ adduct followed by a σ -bond metathesis ($\Delta^\ddagger G_{298}^\circ \approx 28$ kcal/mol). Subsequently, HBAr₂ undergoes a direct 2+2 σ -bond metathesis ($\Delta^\ddagger G_{298}^\circ \approx 23$ kcal/mol) with dihydrogen. The feasibility of such metathesis was proved experimentally by the direct reaction of BD₃·THF with hydrogen.

A similar σ -bond metathesis DBAr₂ + R₃SiH → HBR₂ + R₃SiD ($\Delta^\ddagger G_{298}^\circ \approx 5$ kcal/mol) eventually accounts for the experimentally observed isotope exchange between H₂ and the deuterium atom in R₃SiD.

In summary, we discovered a new route of H₂ activation and the crucial role of σ -bond metathesis in it.



[1] G. D. Frey, V. Lavallo, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Science*, **2007**, *316*, 439

[2] D. W. Stephan, *Org. Biolog. Chem.* **2008**, *6*, 1535.

[3] C. Fan, L. G. Mercier, W. E. Piers, H. M. Tuononen, M. Parvez, *J. Am. Chem. Soc.*, **2010**, *132*, 9604.

[4] G. I. Nikonov, S. F. Vyboishchikov, O. G. Shirobokov, *J. Am. Chem. Soc.* (short communication) **2012**, *article ASAP*, DOI: 10.1021/ja300365s.