SECONDARY INTERACTIONS ORGANIZE HYDROGEN SPLITTING BY FRUSTRATED LEWIS PAIRS

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Recently, there has been considerable interest in the properties of sterically crowded main-group Lewis acid-base pairs. Such systems, termed frustrated pairs, allow remarkable reactions to take place, such as activation of dihydrogen and hydrogenation catalysis without transition metals under mild conditions [1].

Our computational studies on the prototypical (tBu)_3P + B(C_6F_5)_3 + H_2 → [(tBu)_3PH][HB(C_6F_5)_3] reaction showed that a noncovalent preassociation of the base and acid can create a flexible, reactive complex (the frustrated complex) that allows the cooperative interaction of the Lewis centers with the H_2 molecule (see electron density difference map in the Figure) [2].

Investigation of several different pairs revealed [3,4] that not only the equilibrium between covalently quenched and frustrated complexes, but also the flexibility range of the latter plays a determinant role in reactivity. Interpretation of the experimental results requires to account for the interplay between covalent bonding, dispersion and exchange repulsion, which necessitates the use of more recent DFT approaches.

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