Electronic Structure of NHC-Silylium Frustrated Radical Pair

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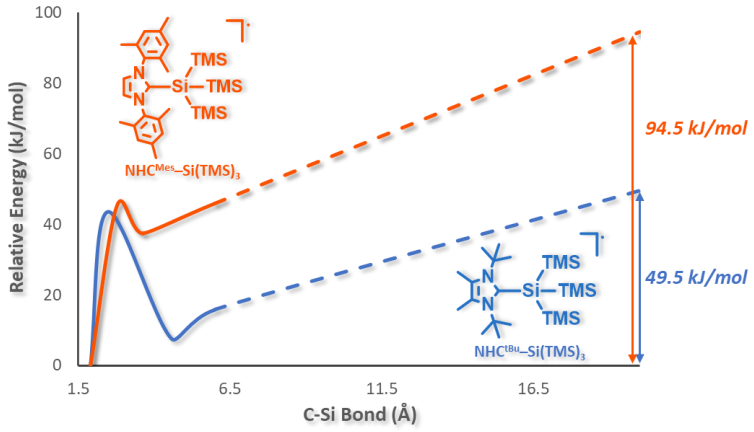
Abstract:
Frustrated Lewis pair catalysts have seen a meteoric rise in popularity as a viable alternative to transition metal-based catalysts in the past couple of decades. However, they are still outshone by the latter due to their limited scope, lower reactivity and lower functional group tolerance. While the popularly accepted reaction mechanism for FLP catalysis involves the transfer of an electron pair from the frustrated Lewis base to another non-frustrated Lewis acid in the reaction mixture, recently it has been shown that some combinations of frustrated Lewis pairs undergo single electron transfer, forming an ionic frustrated radical pair (FRP).[1]
This inspired the design of neutral FRPs to facilitate the cleavage of small-molecules, a daring step towards development of complementary, metal-free catalysts. In this study, we explore the electronic structure and reactivity of NHC-Silylium FRP catalysts theoretically, aided and abetted by experimental results. Attempts were been made to synthesize two NHC-silylium catalysts – NHC^{Mes}–$Si(TMS)_3$ and NHC^{tBu}–$Si(TMS)_3$, however only the former has been isolated and characterized by EPR. The DFT-calculated dissociation energies and dissociation curves were found to be significantly different for the two, rationalizing the experimental observation. A study of the spin densities over the dissociation scans reveals that although the unpaired electron in the FRP is initially located on the carbene C in the FRP, it ends up on the silylium Si upon dissociation. To understand the electron transfer during the dissociation in greater detail, wave-function based methods have been invoked to study model systems.



References:

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