The Activation of CO by B$_2$(NHC$^R$)$_2$: HOMO-LUMO Swap Without Photoinduction

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Abstract

Recently, Braunschweig et al. found that diboryne (B≡B) stabilized by N-heterocyclic carbenes (B$_2$(NHC$^R$)$_2$) can bind and activate CO molecules to forge C−C bonds. Here we theoretically explored the bonding nature of B$_2$(NHC$^R$)$_2$ and its activation mechanism for CO using the block-localized wavefunction (BLW) method which is a variant of ab initio valence bond (VB) theory. We first confirmed that the third excited state ($^1\Sigma^+_g$) of a triple bond of B$_2$ is preferred to bind two NHC$^R$ molecules due to strong electrostatic attraction and charge transfer from NHC$^R$ to B$_2$. Then, we showed that the strong steric repulsion between the HOMO of CO and one of the two degenerate π orbitals (also HOMOs) of B$_2$(NHC$^R$)$_2$ leads to the HOMO-LUMO swap in the latter. As a consequence, both HOMO and HOMO-1 of B$_2$(NHC$^R$)$_2$ can effectively interact with the two π* antibonding orbitals (LUMO and LUMO+1) of CO, resulting in the substantial activation of CO.

Reference and notes