

The Activation of CO by $B_2(NHC^R)_2$: HOMO-LUMO Swap Without Photoinduction

Huaiyu Zhang^a, Zexing Cao^b, Wei Wu^b, Yirong Mo^{b,c,*}

^a, Institute of Computational Quantum Chemistry, College of Chemistry and
Material Science, Hebei Normal University, Shijiazhuang, China

^b, Department of Chemistry, Xiamen University, Xiamen, China.

^c, Department of Chemistry, Western Michigan University, Michigan, USA.

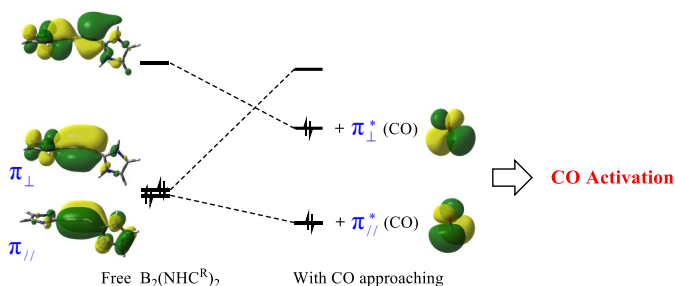
* Yirong.mo@wmich.edu



photo of Yirong Mo
presenting author

Abstract

Recently, Braunschweig et al. found that diboryne ($B\equiv B$) 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^* anti-bonding orbitals (LUMO and LUMO+1) of CO, resulting in the substantial activation of CO.



Reference and notes

[1] H. Braunschweig, *et al. Science* 2012, 336, 1420-1422.

[2] Y. Mo, L. Song, Y. Lin *J. Phys. Chem. A* 2007, 111, 8291-8301.

[3] H. Zhang, Z. Cao, W. Wu, Y. Mo, to be published.