

# THEORETICAL STUDY OF THE SEMIHYDROGENATION OF ALKYNES CATALYZED BY IMIDAZOLYL AMINO MOLYBDENUM CLUSTER SULFIDES

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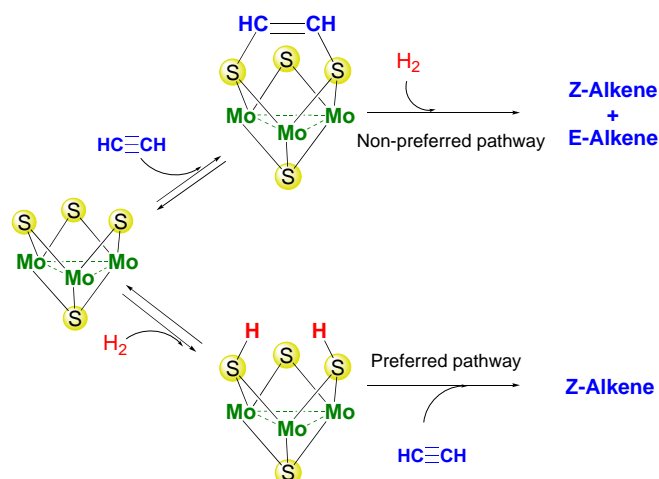
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We have recently reported a novel protocol for the semihydrogenation of alkynes using the cluster  $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{ImNH}_2)_3]^+$  ( $\mathbf{1}^+$ ) and selectively affording the (Z)-alkenes with excellent yields [1]. Mechanistic control experiments suggested a sulfur-based mechanism. While the reaction with diphenylacetylene (dpa) takes place, the presence of a dithiolene  $\text{Mo}_3(\mu_3\text{-S})(\mu\text{-S})(\mu_3\text{-SC(Ph)=C(Ph)S})$  ( $\mathbf{2}^+$ ) adduct formed due to the bridging sulfur atoms of this cluster interacting with dpa was noticed. This adduct disappears with the time, and at the end of the reaction only  $\mathbf{1}^+$  remains.

Herein we report a DFT-based theoretical study on the semihydrogenation of dpa catalyzed by  $\mathbf{1}^+$ . Two pathways have been explored. One of them begins with the formation of  $\mathbf{2}^+$ , followed by its hydrogenation to render an unstable intermediate ( $\mathbf{3}^+$ ) that can afford the Z-alkene. However, isomerization of  $\mathbf{3}^+$  opens additional pathways leading either to the Z- as well as the E-alkene.

The other pathway begins with the hydrogenation of two bridging sulfurs of  $\mathbf{1}^+$  obtaining a hydrogenated cluster  $\mathbf{4}^+$ , as already described by us [2]. Thereafter,  $\mathbf{4}^+$  reacts with dpa in a very smooth way, including intersystem crossings with the triplet electronic state, to render solely the Z-alkene.

Although the formation of  $\mathbf{2}^+$  is preferred over the formation of  $\mathbf{4}^+$ , the large energy needed to follow up from  $\mathbf{2}^+$  prevents this pathway to take place, and the system evolves via the second pathway to selectively render the Z-alkene.



[1] Gutiérrez-Blanco, M., Guillamón, E., Safont, V. S., Algarra, Andrés G., Fernández-Trujillo, M. J., Junge, K., Basallote, M. G., Llusar, R., Beller, M. *Inorganic Chemistry Frontiers*, 2023, **10**, 1786-1794

[2] Guillamón, E., Oliva, M., Andrés, J., Pedrajas, E., Safont, V. S., Algarra, A. G., Basallote, M. G. *ACS Catalysis* 2021, **11**, 608-614