

CO が配位した生体模倣型 $[\text{Mo}_3\text{S}_4\text{M}]$ ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}$)クラスター錯体の理論計算
CO-Bound Biomimetic $[\text{Mo}_3\text{S}_4\text{M}]$ ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}$) Clusters: A Computational Study

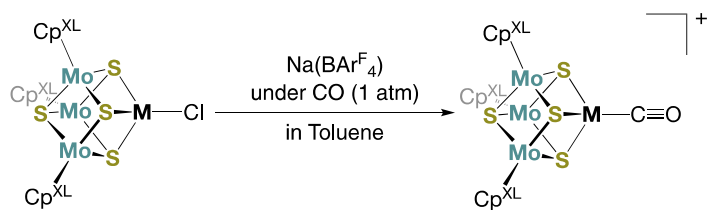
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研究成果概要

Transition metal clusters can be used as catalysts to perform chemically or biologically relevant reactions.^{1,2} Relationships between the electronic structure and reactivity can be established by employing density functional theory (DFT). We have developed $[\text{Mo}_3\text{S}_4\text{M}]$ -type clusters ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}$), consisting bulky cyclopentadienyl ligands (Cp^{XL} , $\text{C}_5\text{Me}_4\text{SiEt}_3$). CO can be coordinated to $[\text{Mo}_3\text{S}_4\text{M}]$ cubes. According to experimental data, $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{M}(\text{CO})]^+$ ($\text{M} = \text{Co}, \text{Ni}$) is stable, while $[\text{Cp}^{\text{XL}}_3\text{Mo}_3\text{S}_4\text{Fe}(\text{CO})]^+$ complex revealed unexpected instability. Their M-CO interactions were analyzed by DFT calculations.

An energy decomposition analysis (EDA) together with the natural orbitals for chemical valence (NOCV) was performed to rationalize the M-CO interactions. The interaction energy



between M and CO follows the order of Fe-CO (-101.1 kcal/mol) > Co-CO (-81.5 kcal/mol) > Ni-CO (-77.3 kcal/mol). In all three cases, orbital interactions become dominant compared to

electrostatic, dispersion, and solvent interactions. According to EDA-NOCV, π back-donation from Co to $\pi^*(\text{CO})$ is stronger than σ CO to $\text{M}(\text{d})$ σ donation for all three systems. These findings give quantitative insights to develop bio-mimetic catalysts for the direct conversion of CO into hydrocarbons.

発表論文(謝辞あり)

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