

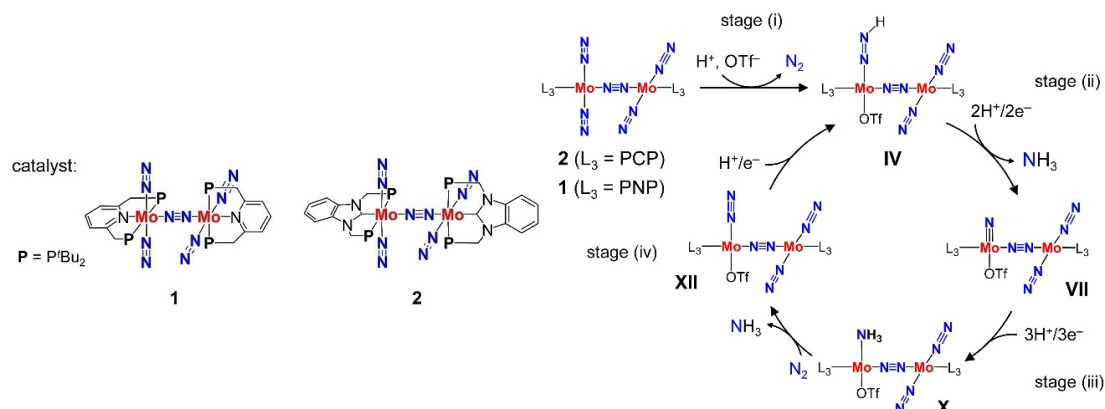
Theoretical Study on Nitrogen Fixation Catalyzed by Dinitrogen-bridged Dimolybdenum Complexes Bearing Pincer-Type Ligands

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Density-functional-theory (DFT) calculations are carried out for the proposal of a theoretically-plausible reaction pathway for nitrogen fixation catalyzed by dinitrogen-bridged dimolybdenum complexes bearing pincer-type PCP and PNP ligands. The free energy profiles of the entire reaction pathway calculated with a dispersion-corrected functional provide a catalytic mechanism energetically more efficient than the previously proposed one.¹ In the newly-proposed mechanism, the dinuclear Mo–N≡N–Mo structure should be maintained during the catalytic cycle.² In spite of the coordination of the triflate (OTf) group with a strong electron-withdrawing ability, dinitrogen coordinated to a Mo^I center has higher reactivity with a proton donor than that coordinated to an electron-rich Mo⁰ center. This result enables us to propose a shortcut pathway, in which the regeneration of the dimolybdenum Mo⁰Mo⁰ complex is not required. Intermetallic electron transfer between two Mo cores induced by protonation effectively enhances the reactivity of coordinate N₂ with a proton donor. Our calculations reveal that the synergy of the Mo cores at the protonation step is essential for the catalytic performance of the dimolybdenum system.



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2) A. Egi, H. Tanaka, A. Konomi, Y. Nishibayashi, K. Yoshizawa, *Eur. J. Inorg. Chem.* **2020**, 1490-1498.