

Ligand Sphere Effects on Dinitrogen Activation in Bimetallic Complexes

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Dinitrogen fixation is crucial chemical transformation to produce ammonia as a fertilizer and other N-containing compounds. Even though dinitrogen's abundance in the Earth's atmosphere is 80%, splitting dinitrogen under ambient conditions remains a challenge due to its kinetic inertness. The N≡N bond is strong and interactions with reactive atoms such as transition metals tend to be weak. In this work, we rationalize the factors influencing the reactivity of dinuclear end-on bridged (μ - $\eta^1:\eta^1$ -N₂) complexes in different ligand environments. The first bridged dinitrogen complex for dinitrogen activation and metal-nitride complex formation was reported by Cummins. This complex features Mo(III) (d³) supported by three N^RAr ligands (R = Me₃C, Ar = 3,5-C₆H₃Me₂).^[1] Another complex designed as an isovalent analog is reported by Mindiola. It contains V(II) (d³) in a triply coordinated ligand scaffold, [(nacnac)V(Ntoly₂)], but it does not cleave dinitrogen.^[2] Sita's isostructural series of early transition metal complex with a η^5 -cyclopentadienyl (Cp*) and η^2 -amidinate ligand (Am) coordination sphere undergo successful dinitrogen activation to form a bridged diamond core.^[3] Furthermore, we discuss the differences and similarities of these systems with the catalytically active Mo(I) pincer complex reported by Nishibayashi.^[4] We systematically explore the potential energy surfaces and use electronic energy decomposition techniques to rationalize the equilibrium between the μ - $\eta^1:\eta^1$ -N₂ form and the characteristic zig-zag transition state (Fig 1b). We identify multiple competing factors influencing the dinitrogen splitting chemistry and find that two different strategies for successful N₂ activation are realized in the synthetic complexes.

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