

Three-Coordinate Vanadium(II): Synthesis, Characterization, and Reactivity

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With the exception of cyclopentadienyl and bulky phenolate systems, the stabilization of low valent and low coordinate of 3d early metals is not readily accessible due to the inherently electron rich nature of these species to promote intramolecular ligand rearrangements. Herein, we describe the use of nacnac ligand [$\text{nacnac}^- = [\text{Ar}]\text{NC}(\text{Me})\text{CHC}(\text{Me})\text{N}[\text{Ar}]$, $\text{Ar} = 2,6\text{-(CHMe}_2)_2\text{C}_6\text{H}_3$] combined with a hard, bulky, and monoanionic anilide or phenolate ligand to support unsaturated and reactive vanadium(II) fragments. A masked three-coordinate vanadium(II) complex, $(\text{nacnac})\text{V}(\text{Ntol}_2)$ (**1**), is isolated and fully characterized by a range of physical methods. The electron rich vanadium center is masked by an arene interaction from the anilide ligand. Compound **1** is a high spin, $S = 3/2$ species as corroborated by SQuID, HFEPR, and method of Evans. Disruption of the metal-arene interaction unleashes a reactive vanadium(II) center capable of undergoing multi-electron chemistry and leading to activation of a variety of substrates including P_4 to generate a novel early 3d terminal *cyclo*- P_3 fragment. Interestingly, we have successfully isolated a compound, $(\mu\text{-N}_2)[\text{V}(\text{nacnac})(\text{ODiiP})]_2$, featuring an end-on dinitrogen bridged between two vanadium centers. This species is interesting in relation to our recent syntheses of terminal vanadium(V) $\equiv\text{N}$ products. A detailed electronic understanding of these species may potentially illuminate insight into the cleavage of dinitrogen by vanadium.