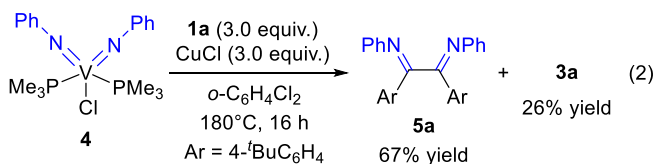
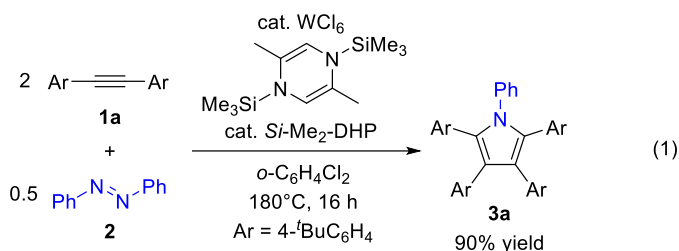


[2+2+1]-Cycloaddition Reaction of Azobenzene and Diarylacetylenes Catalyzed by Early Transition Metal Imido Complexes

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Reactivity of an early transition metal-nitrogen double bond involved in imidometal complexes with unsaturated organic compounds has been extensively investigated as a key step for synthesizing a variety of *N*-containing organic molecules. Catalytic [2+2+1]-cycloaddition reaction of the metal-nitrogen double bond with two equiv. of alkynes is a straightforward method in preparing synthetically valuable multi-substituted pyrrole derivatives. We previously reported that imido complexes of titanium and vanadium served as efficient catalysts to obtain alkyl-substituted pyrroles in one-pot manner; however, these catalysts were ineffective for incorporating diarylacetylenes.¹ Herein, we report that an *in situ*-generated bis(imido)tungsten species from WCl₆ and organosilicon reductant, *Si*-Me₂-DHP, exhibits superior catalytic activity among group 4-6 transition metal imido complexes for the [2+2+1]-cycloaddition of diarylacetylene **1a** with azobenzene (**2**), giving pyrrole **3a** in 90% yield (eq. 1). DFT calculations on the reaction sequences revealed that bis(imido)tungsten species possesses the lowest activation barrier for the rate-determining initial incorporation of **1a** to one of two imido moieties of *in situ*-generated bis(imido)tungsten among the structurally related Mo, Nb, and Ta derivatives. In addition, low catalytic activity of bis(imido)vanadium species for the formation of **3a** is ascribed to the generation of energetically accessible and unreactive (α -diimine)vanadium species; in fact, formation of the α -diimine **5a** from the bis(imido)vanadium complex **4** and **1a** was confirmed by the control experiment (eq. 2). Further details on the difference of W and Ti-catalyzed multi-arylated pyrrole formation are disclosed in this presentation.



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