

Early-Transition Metals and Their Multiple Bonds to Ligands: Catalytic Dehydrogenation of Alkanes, Methane Olefination, and Super Bases.

Abstract. Converting natural resources such as methane and ethane, the main components of natural and shale gas, into more value-added materials under mild conditions and using base metals, is one of the main objectives in my research program. I will start by presenting the reactivity of a transient titanium alkylidyne $(\text{PNP})\text{Ti}\equiv\text{C}^t\text{Bu}$ (pincer $\text{PNP} = \text{N}[2\text{-P}(\text{CHMe}_2)_2\text{-4-methylphenyl}]_2^-$), specifically how this species forms and engages in intermolecular C-H activation and functionalization reactions. Such a system can dehydrogenate methane, and react with C2-C8 alkanes selectively by activating the α - and β -positions. In the case of linear alkanes C4-C8, we only observe formation of the terminal olefin adduct. A new catalytic cycle for transfer dehydrogenation of alkanes will be also introduced in addition to unique platforms to form kinetically stable $\text{Ti}=\text{CH}_2$ and $\text{V}=\text{CH}_2$ moieties, some of which are relevant to our proposed catalytic cycle. I will also discuss a new transformation involving the room temperature conversion of methane to an olefin using a titanium alkylidene in cooperation with a redox-active ligand. Learning from our titanium system I will also discuss some progress we have made with other early-transition metals such as scandium and vanadium. In the last component, I will introduce the synthesis and reactivity of group 4 transition metal nitrides and how one can tune the basicity of the nitride ligand by shifting down the group.