

A NEW TRIANIONIC ONO³⁻ Pincer-TYPE LIGAND AND ITS APPLICATION IN GENERATING HIGHLY NUCLEOPHILIC M-C BONDS: AN INORGANIC ENAMINE.

Adam S. Veige, Matthew E. O'Reilly, Ion Ghiviriga, Khalil A. Abboud, Department of Chemistry, Center for Catalysis, University of Florida, Gainesville, FL, 32611.

Appending an amine to a C=C double bond drastically increases the nucleophilicity of the β -carbon atom of the alkene and are known as enamines. In this presentation we present the synthesis and characterization of a new CF₃-ONO³⁻ (**1**) trianionic pincer-type ligand that is rationally designed to mimic enamines within a metal coordination sphere. Presented is a synthetic strategy to create enhanced nucleophilic tungsten-alkylidene and -alkylidyne complexes. Specifically, we present the synthesis and characterization of the new CF₃-ONO³⁻ trianionic pincer tungsten alkylidene [CF₃-ONO]W=CH(Et)(O^tBu) (**2**) and alkylidyne {MePPh₃}{[CF₃-ONO]W \equiv C(Et)(O^tBu)} (**3**) complexes. Exhibiting unique nucleophilic reactivity, adding MeOTf to **3** alkylates the alkylidyne to yield [CF₃-ONO]W=C(Me)(Et)(O^tBu) (**4**), but the bulkier Me₃SiOTf silylates the *tert*-butoxide, which subsequently undergoes isobutylene expulsion to form [CF₃-ONO]W=CH(Et)(OSiMe₃) (**5**). A DFT calculation performed on a model complex of **3**, namely [CF₃-ONO]W \equiv C(Et)(O^tBu) (**3'**) reveals the amide participates in an enamine-type bonding combination. For complex **2**, the Lewis acids MeOTf, Me₃SiOTf, and B(C₆F₅)₃ catalyze isobutylene expulsion to yield the tungsten-oxo complex [CF₃-ONO]W(O)(ⁿPr) (**6**).