

Seminario del Prof. Aaron D. Sadow, previsto per lunedì **25
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Rare Earth and Main Group Organometallic Compounds for Catalytic Hydroboration and Hydrosilylation

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Reductive conversions of unsaturated oxygenates typically avoid oxophilic early metal catalysts; however, we sought to explore new transformations and new mechanisms potentially accessible with such metal centers as non-traditional organometallic catalysts. New organometallic and pseudo-organometallic ligands for rare earth, early transition metal, and main group metal centers have been studied to access new catalysts, new transformations, and new mechanisms for hydrosilylations and hydroborations. For example, silazido ligands containing β -SiH groups, which form bridging secondary M–H–Si interactions, are activated for the "direct" hydrosilylation of carbonyl moieties. Catalytic hydrosilylations are mediated by cationic or zwitterionic species containing M $\{\mu$ -HB(C₆F₅)₃} groups, where the nature of the metal center and ancillary ligand affects the reaction pathway. To^MMg $\{\mu$ -HB(C₆F₅)₃} (To^M = tris(4-oxazolanyl)phenylborate) catalyzes hydrosilylation of acrylates via 1,4-addition to give silyl ketene acetals, whereas M = {(Me₂HSi)₃C}₂Ce $\{\mu$ -HB(C₆F₅)₃} catalyzes the addition to give α -silyl esters. A cationic rhodium compound containing HB(C₆F₅)₃ as the counterion catalyzes the partial deoxygenation of esters to ethers. Related oxophilic compounds catalyze hydroborations of carbonyls such as esters to give boron esters, and the mechanism for these reactions varies between metal centers and carbonyl moieties. Silica-supported zirconium catalysts, soluble magnesium catalysts, and rare earth catalysts each show distinct kinetics for these hydroboration reactions.

Tutti gli interessati sono invitati a partecipare.



Prof. Alceo Macchioni