

Catalytic Approaches to Complex Molecules from Carbohydrate Biomass

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There are a number of interesting known catalysts for the heterolytic activation of silanes, including those based on Ir and B complexes. This presentation will present the state-of-the-art in utilizing these catalysts to activate the C–O bonds of carbohydrates, with a special emphasis on their selective reduction (to C–H bonds). In contrast to traditional methods for the deoxygenation of overly functionalized poly-saccharides, which are eliminative in nature, these catalysts promote stereoselective and stereospecific mechanisms that provide products that maintain a high sp^3 content (and are hence chiral with multiple stereocenters), are functionalized and readily functionalizable, and may thus provide routes to high-value materials from bio-renewables. From a recent study on the readily available C6O6 and C5O5 starting materials (sorbitol, etc) our ability to control the catalytic reactions have enabled the synthesis (in 1 or 2 steps usually) of a number of new C6On and C5On compounds not previously reported in the literature. Given how long synthetic chemists have been making derivatives of glucose and the like, it is noteworthy that one can find derivatives that have not yet been synthesized.

In addition to describing the reaction chemistry, the influence of silane, catalyst, and the substrate will be examined to paint a picture of the underlying mechanisms that control reactivity and selectivity. Key intermediates that have been observed and/or proposed include sila-oxonium ions (R_2O-Si^+), sila-oxocarbenium ions ($C=O-Si^+$), and less exotic Lewis adducts. Several methods have been uncovered to modulate the speciation of the catalysts under reaction conditions and these will be also discussed.