Activation of Methyltrioxorhenium for Olefin Metathesis by a Frustrated Lewis Pair

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Methyltrioxorhenium (MTO) supported on Al_2O_3 or SiO_2-Al_2O_3 is an efficient heterogenous alkene metathesis catalyst that works at room temperature and in the presence of various functional groups.[1] The catalytically active rhenium-methylidene species in MTO based catalysts has not yet been observed. Surface studies revealed that MTO interacts with highly Lewis-acidic tricoordinate aluminum centers on the support surface, and that its methyl group is C–H activated resulting in rhenium-methylidene species.[2] The exact structure of the catalyst resting state and the active species is subject to active scientific debate.[2]

Our group focuses on developing homogeneous model systems for rhenium(VII)-based metathesis catalysts.[3] Previous model systems mainly aimed to mimic the electron deficient nature of the support surface.[4] Here we report on the activation of MTO by 2,6-Lutidine and $B(C_6F_5)_3$, a frustrated Lewis pair (FLP) in solution. The MTO/FLP catalyst is active in ring-opening metathesis polymerization of norbornene, and in the cross-metathesis of internal olefins. ESI-MS and NMR studies found that MTO coordinates to $B(C_6F_5)_3$, and the adduct is activated via the deprotonation of the methyl group by 2,6-lutidine. Moreover, we were able to detect metathesis active rhenium-alkylidenes by ESI-MS experiments during the ring-opening metathesis reaction of rigid cycloalkenes. A rapid second deprotonation of the initially formed methylidene, which yields a rhenium-methylidyne, was identified to be a major catalyst decomposition pathway.

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