

Activation of Methyltrioxorhenium for Olefin Metathesis by a Frustrated Lewis PairP. P. Kalapos¹, Y. Stöferle¹, P. Chen^{1*}¹Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir-Prelog-Weg 1-5/10, 8093 Zürich, Switzerland

Methyltrioxorhenium (MTO) supported on Al₂O₃ or SiO₂-Al₂O₃ is an efficient heterogeneous 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(C₆F₅)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(C₆F₅)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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