

Immobilization of Cationic Molybdenum Alkylidyne Complexes Inside Mesoporous Silica for Selective Ring-Closing Alkyne Metathesis

Vincent Gramm,¹ Michael R. Buchmeiser^{1*}

¹Institute of Polymer Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany

vincent.gramm@ipoc.uni-stuttgart.de

Previous studies have shown that molybdenum alkylidyne complexes directly immobilized on a silica surface have a lower activity than their homogeneous counterparts.¹ The reasons given for this were a changed electronic situation of the complex due to a ligand being substituted for a silica-bound hydroxy group; furthermore, the short distance of the metal center to the surface causes a more rigid system.

We wanted to mitigate both problems by immobilizing the catalyst with a linker, which increases the distance to the silica surface. Additionally, by choosing the right linker, we can tune the electronic properties to the substituted linker, thereby offering access to an electronic situation at the metal that is similar to the one in the homogeneous complex. The immobilization was monitored through ¹⁹F-NMR by quantifying the amount of the free substituted fluorinated alcohol. Alternatively, we also wanted to immobilize a catalyst via electrostatic interactions, this has the advantage that there wouldn't be a change to the known coordination sphere.

The immobilized catalysts were tested for selective ring-closing alkyne metathesis.

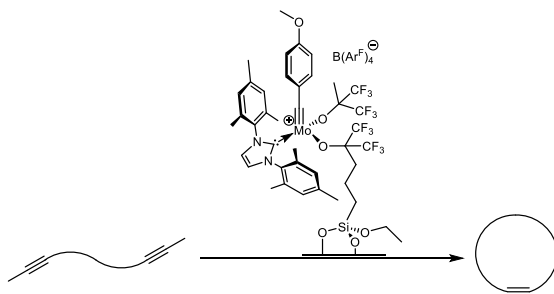


Figure 1: Immobilized catalyst being used for a general ring-closing alkyne metathesis.

[1] D. Estes *et al.*, *J. Am. Chem. Soc.*, 2017, **139**, 17597-17607, DOI: 10.1021/jacs.7b09934