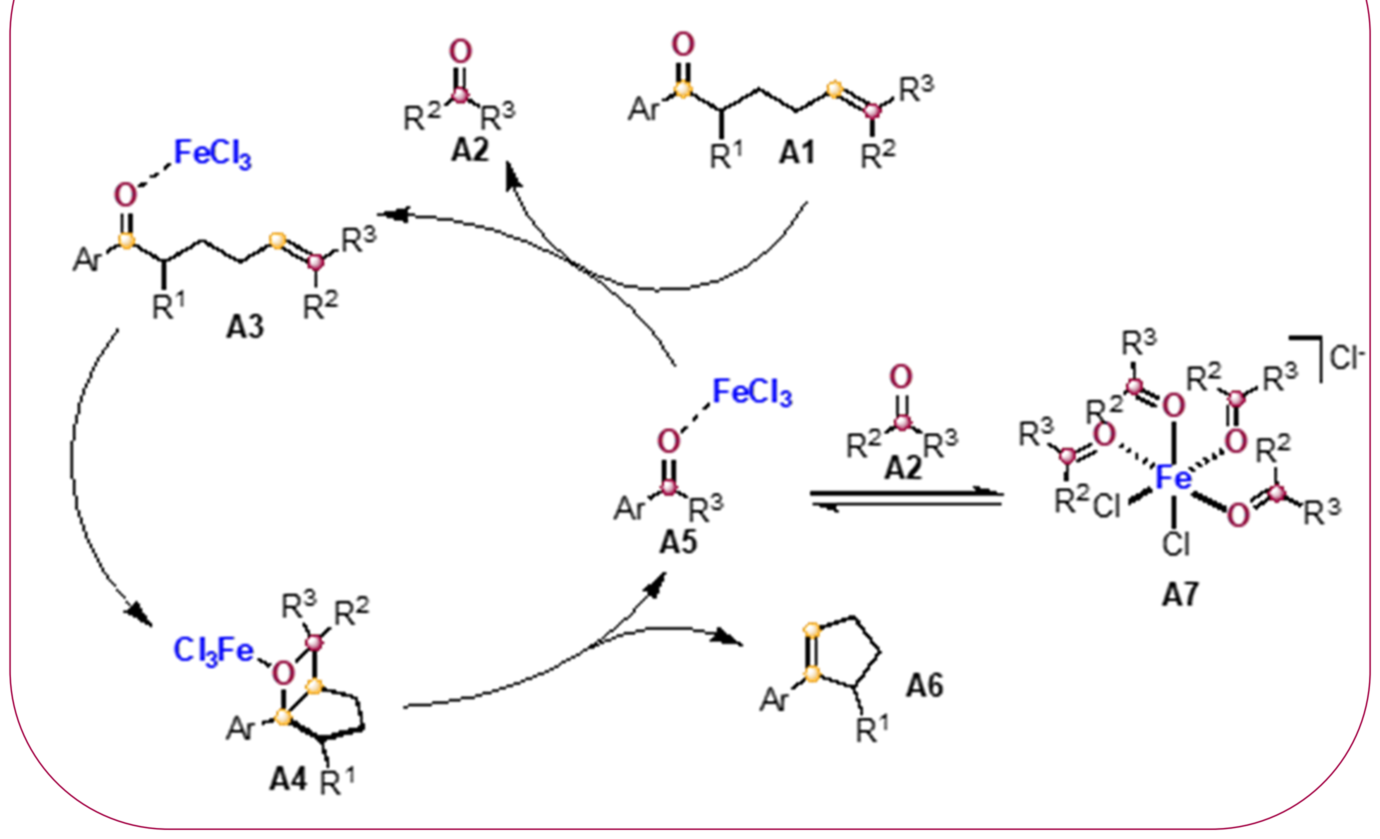
Chlorosilane effect on the efficiency of Metal-Catalyzed Carbonyl-Olefin Metathesis

Sophi Todtz, Cory Schneider, Wiktoria Koza, Clare Anderson, and James J. Devery III Ph.D.
Department of Chemistry and Biochemistry, Loyola University Chicago, Chicago, IL 60660, USA

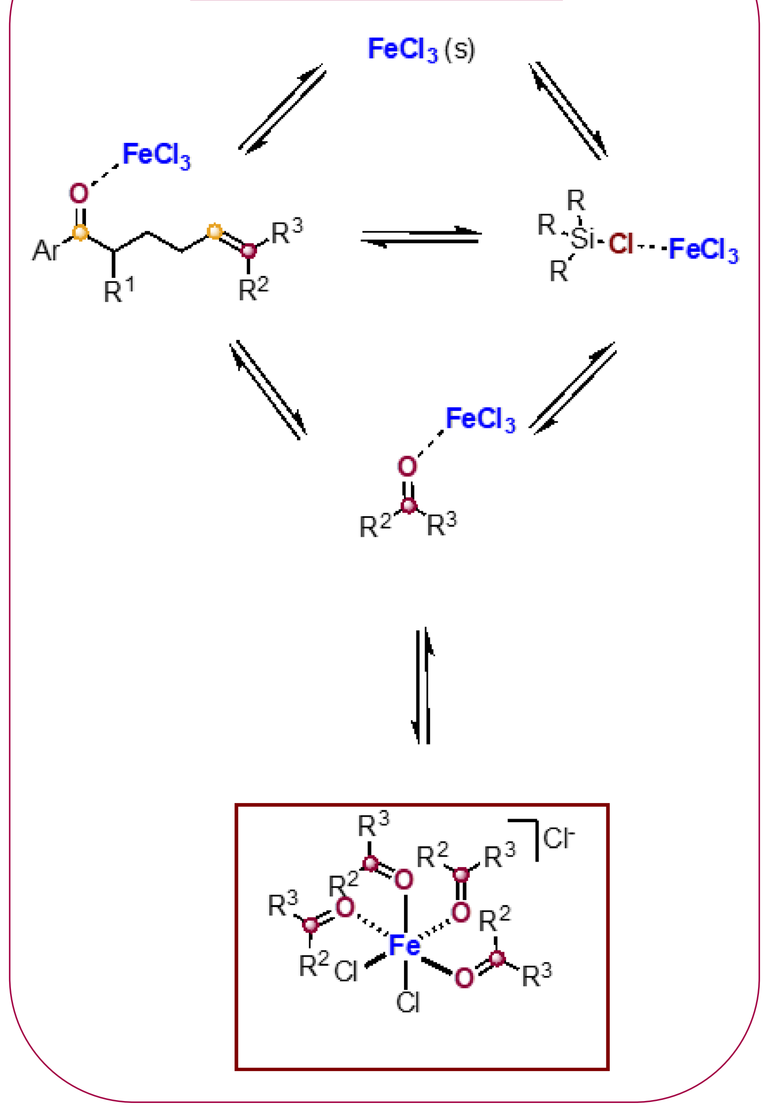
Introduction

Carbonyl-olefin Metathesis (COM) is a reaction in which a carbonyl and an olefin form a new carbon-carbon double bond. This reaction is metal catalyzed and can be very useful in synthetic chemistry. It was previously observed that the use of the Lewis acid, $FeCl_3$, in combination with specific carbonyls creates an excess of byproduct that then coordinates to the metal and forms an aggregate.[1,2] The presence of this aggregate can affect the rate of the COM reaction; therefore, this work investigates how additives, specifically chlorosilane additives, may hinder this change in the rate of reaction and possibly the formation of the aggregate.

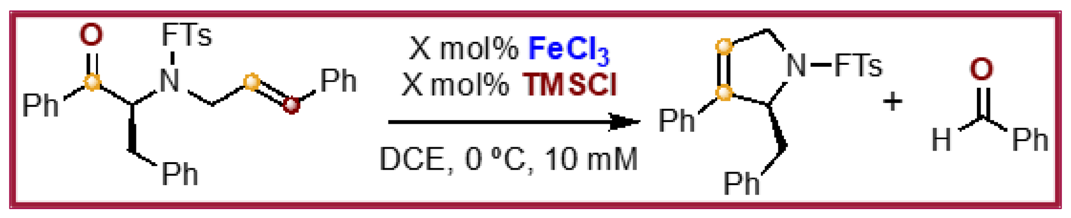
Catalytic Cycle

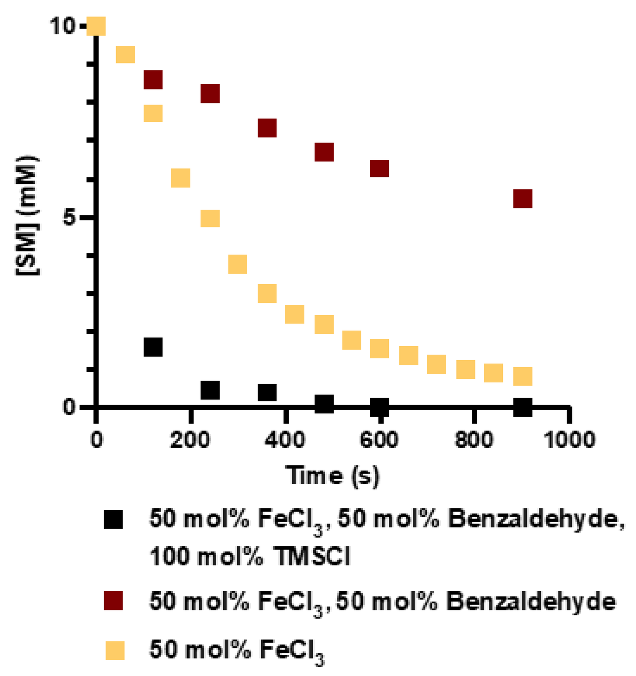


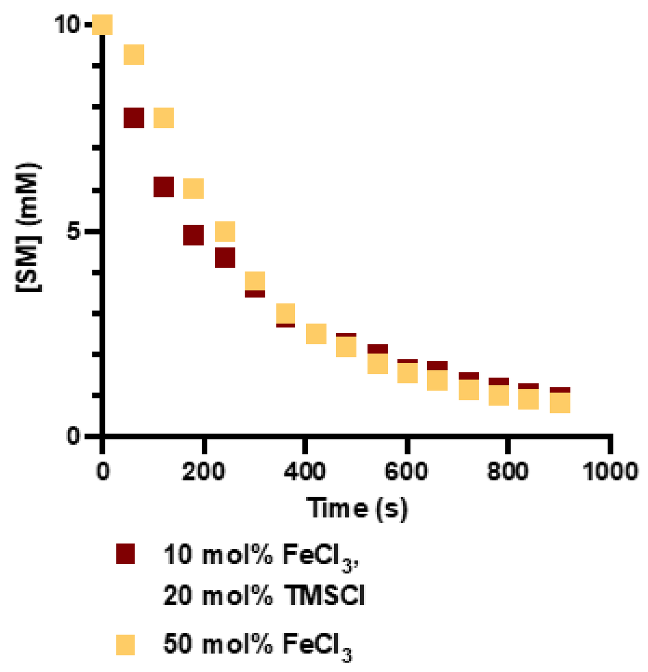
Equilibria



Kinetics





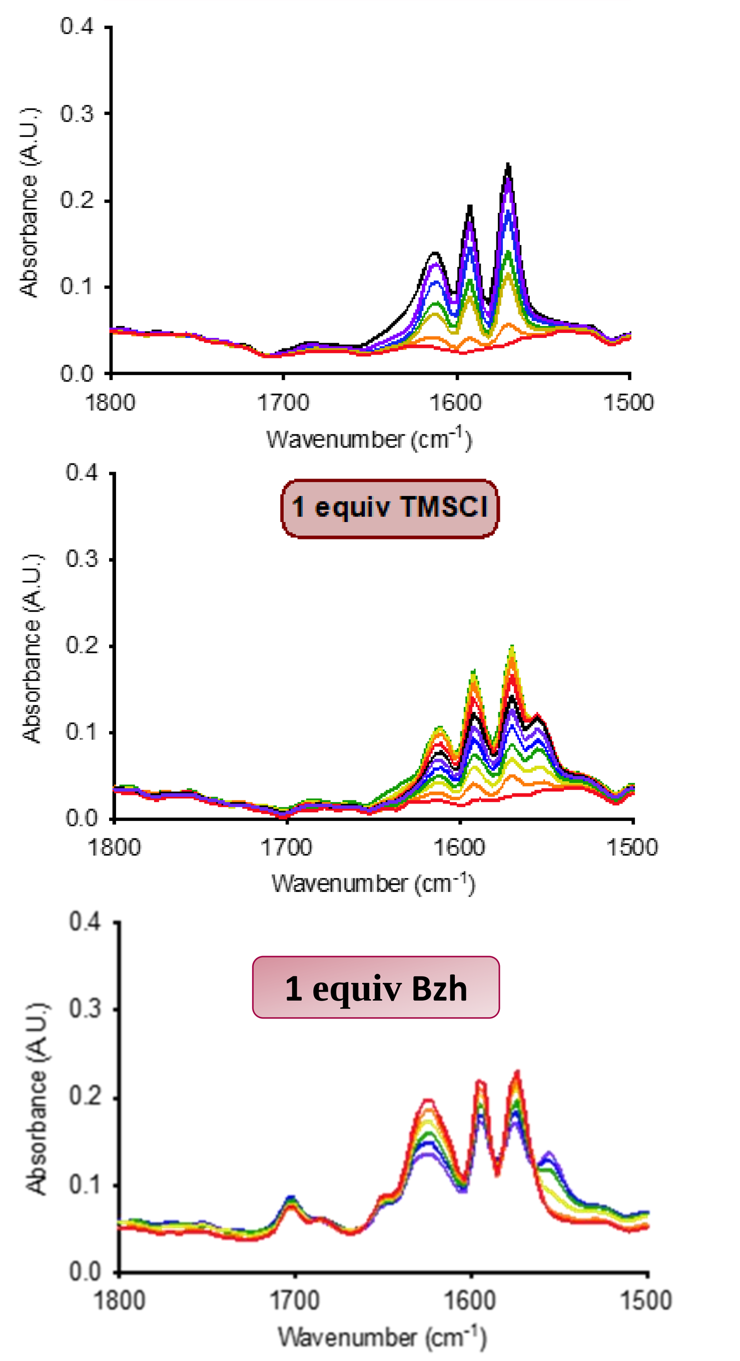


- When carbonyl, TMSCl, and $FeCl_3$ are present reaction is drastically faster

References

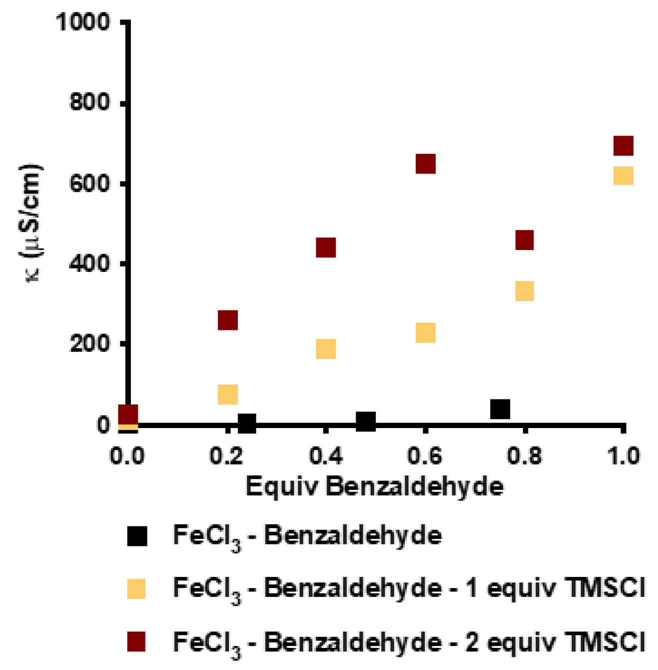
1. Ludwig, J. R.; Schindler, C. S. Lewis Acid Catalyzed Carbonyl-Olefin Metathesis. Synlett 2017, 28 (13), 1501–1509. https://doi.org/10.1055/s-0036-1588827.
2. Hanson, C. S.; Psaltakis, M. C.; Cortes, J. J.; Siddiqi, S. S.; Devery, J. J. Investigation of Lewis Acid-Carbonyl Solution Interactions via Infrared-Monitored Titration. J. Org. Chem. 2020, 85 (2), 820–832. https://doi.org/10.1021/acs.joc.9b02822.

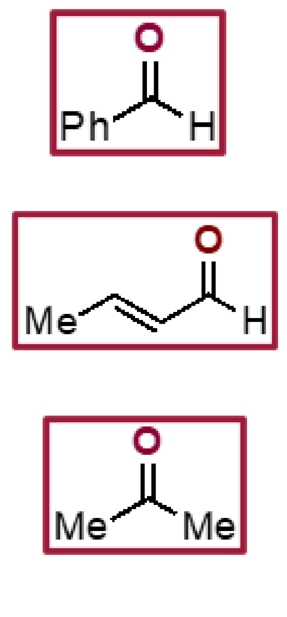
Benzaldehyde IR spectrum

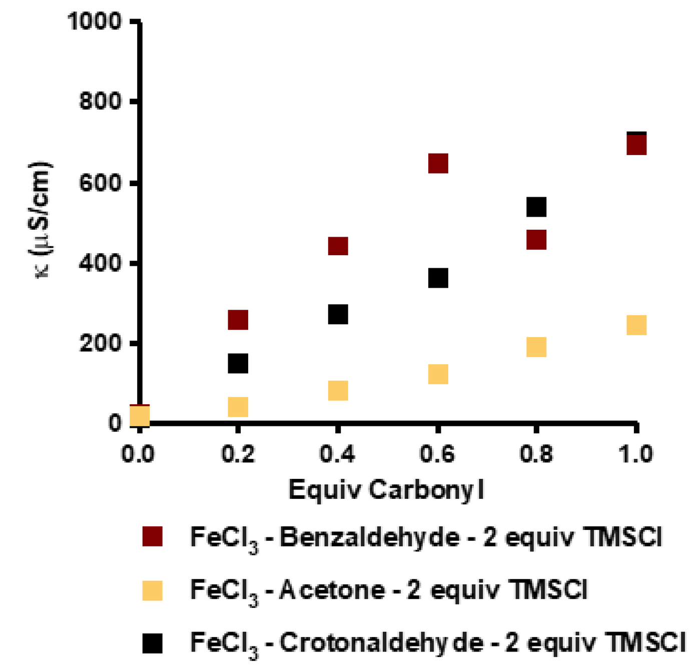


- New peak at 1555 cm^{-1} with TMSCl present

Conductance

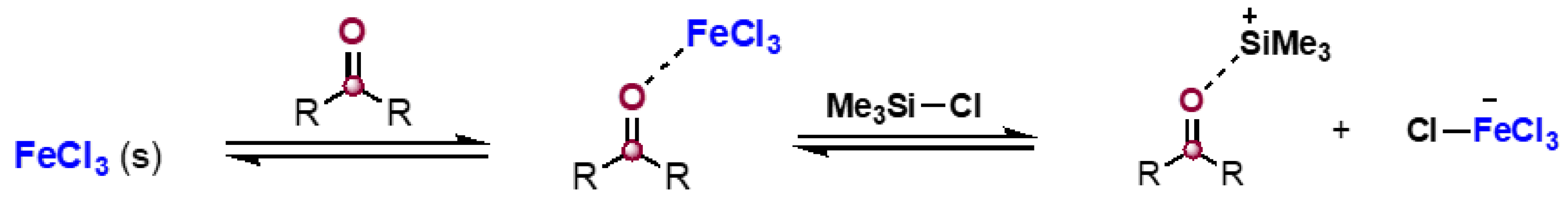


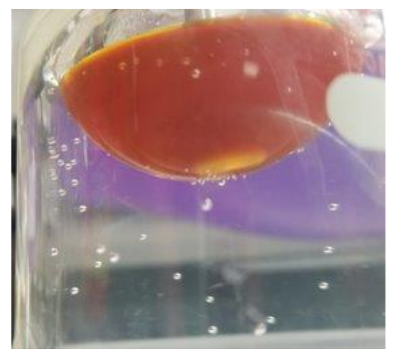




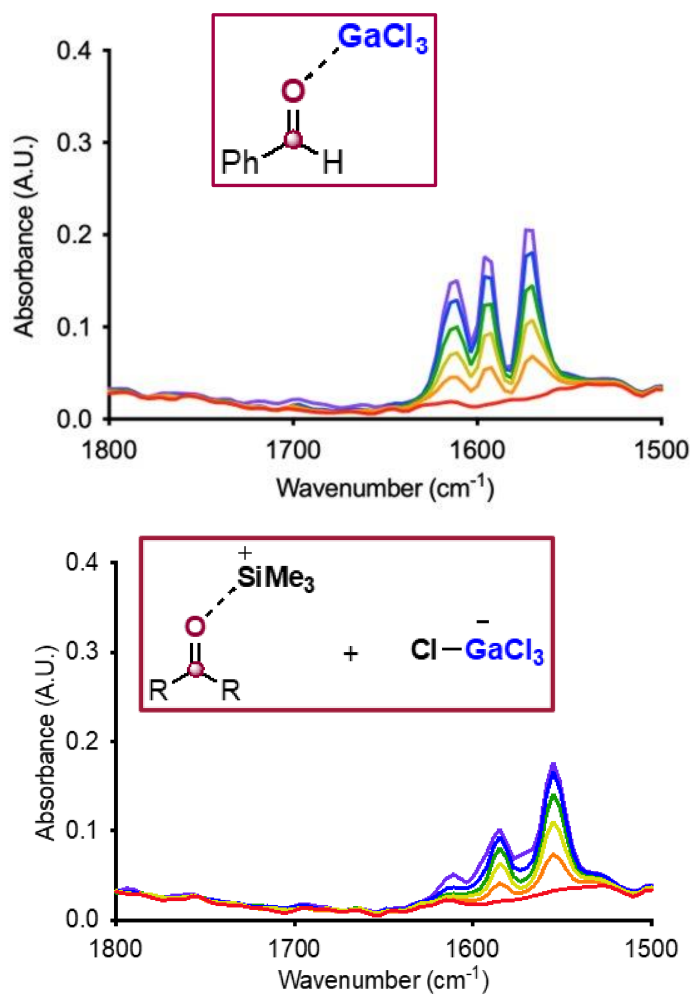
- Conductivity of benzaldehyde increases with equivalents of TMSCl
- Carbonyls with more degrees of unsaturation are more conductive

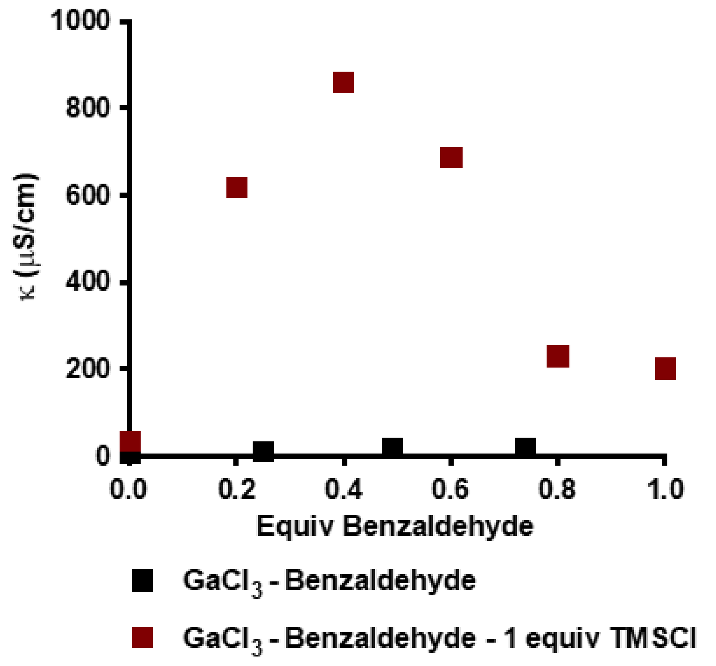
Equilibria with $FeCl_3$





$GaCl_3$ and benzaldehyde IR spectrum and conductance





- Peak present in $GaCl_3$ and TMSCl system at 1555 cm^{-1}
- Large conductivity increase with TMSCl

Equilibria with $GaCl_3$