Ligand Design for Catalysis by Cationic Indium Complexes

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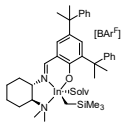
Introduction

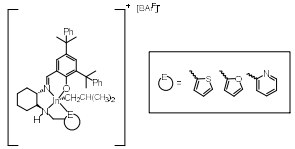
Plastics have numerous applications and are an important part of our everyday life. However, due to their long lifetime they can cause many environmental problems.

Biodegradable plastics are a potentially great solution to many environmental problems, but there has been limited number of ways to produce biodegradable plastics with good functionality.

Cationic indium complexes have been reported to form spiro-ortho esters, which are important monomers for synthesis of valuable biodegradable polymers.

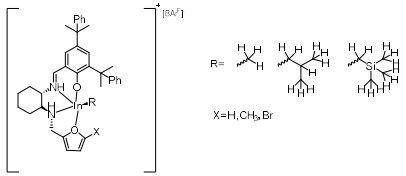


Previously, we reported the use of hemilabile ligands for tuning the stability and reactivity of cationic indium complexes for ring opening polymerization.



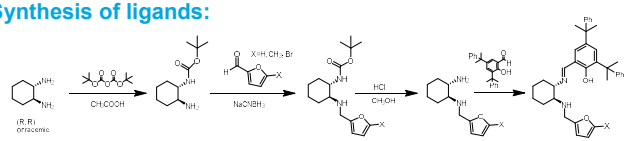
In this project, we are interested in studying the reactivity of cationic indium alkyl complexes with hemilabile ligands in synthesis of spiro-ortho esters.

We study how changing the alkyl ligands and modifying substituents on the hemilabile moiety affects reactivity in synthesis of spiro-ortho esters.



Synthesis pathway

Synthesis of ligands:



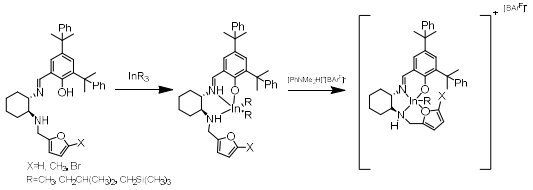
Synthesis of complexes:

Alkyl indium compounds were prepared by a salt metathesis reaction with the corresponding Grignard reagent.

$$InCl_3 + 3\,RMgBr \longrightarrow 3\,MgClBr + InR_3$$

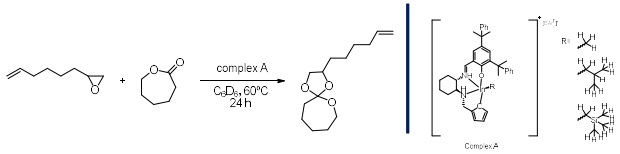
R=$CH_2CH(CH_3)_2$, $CH_2Si(CH_3)_3$

Cationic species were prepared via alkyl abstraction with addition of a Brønsted acid.

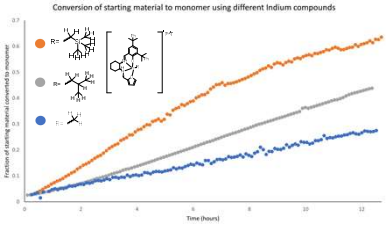


Catalyst Reactivity and Stability

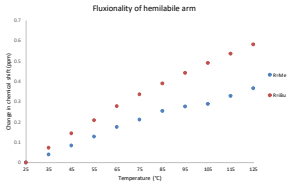
We hypothesized that bulkier alkyl groups around indium can more easily de-coordinate the hemilabile arm and provide an empty coordination spot. To test this, we studied the reactivity of complexes with various alkyl ligands in making spiro-ortho ester.



We found that the bulkier alkyls around Indium increase the reactivity of the catalyst, which agrees with our hypothesis.



VT NMR was used to show the fluxionality nature of the ligand side arm. Through these studies, it was shown that the side arm was more fluxional in case of R= $CH_2CH(CH_3)_2$ than R=CH_3.



For R=$CH_2Si(CH_3)_3$, the catalyst decomposed between 55ºC and 65 ºC. More studies are needed to also consider the polarizability of indium alkyl bonds.

Conclusion

Bulkier alkyl groups seem to facilitate the de-coordination of hemilabile arm and provide an empty coordination spot, therefore increasing reactivity.

The stability and reactivity of the catalyst with R=$CH_2CH(CH_3)_2$ makes it a good choice for alkyl ligand.

Current/ Future Work

We aim to study the effect the synthesized cationic alkyl indium complexes with different substituents on the hemilabile moiety on the reactivity towards synthesis of spiro-ortho esters.

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Reference

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2. Goonesinghe, C.; Roshandel, H.; Diaz, C.; Jung, H.; Nyamayaro, K.; Ezhova, M.; Mehrkhodavandi, P. *Chemical science* **2020**, 11, 6485-6491.