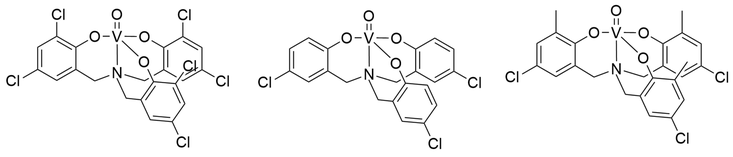
Improved oxovanadium catalysts for aerobic C-C bond cleavage of diols

Therese Chan, Chris Godwin, and R. Tom Baker*

Department of Chemistry and Biomolecular Sciences and CCRI, University of Ottawa

Introduction

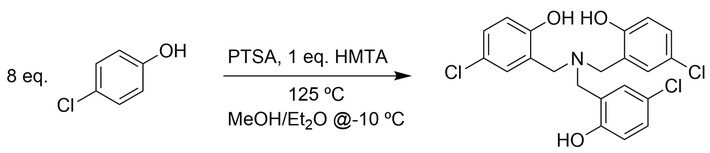
As chemical manufacturers move to develop new processes from renewable resources, new catalysts must be developed that are tailored to conversion of biomass-derived feedstocks to value-added products. In sugar-derived polyalcohols, for example, catalysts that coordinate to hydroxyl groups are believed to allow for selective C-C bond cleavage. Researchers in the Baker lab recently identified oxovanadium triaryloxyamine catalysts that cleave activated diol C-C bonds via a novel 2e- mechanism using the oxygen in air. The main goal of this research project is to make these catalysts more effective by synthesizing new ligands with electron-withdrawing substituents.



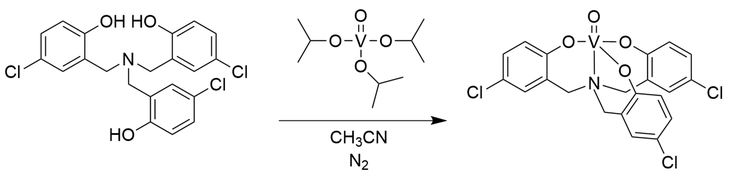
TCC1 **TCC2** **TCC3**

Method

A procedure from the literature was followed as a starting point, making slight variations to synthesize the ligand with the desired substituents. To synthesize the ligand, the procedure involved combining 2.9 equivalents of p-chlorophenol with 1 equivalent of hexamethylenetetramine (HMTA), heating to 110 °C, adding hot ethanol, and stirring overnight. However, this proved to be unsuccessful in synthesizing the para-substituted ligand. An alternate adapted procedure that was used required combining 8 equivalents of p-chlorophenol with 1 equivalent of HMTA and 0.06 equivalents of PTSA to act as a catalyst. This reaction mixture was heated at 125 °C for 18 to 48 hours.



For the synthesis of the catalysts, 1 equivalent of one of the ligands was combined with 1.1 or 1.2 equivalents of vanadium oxytriisopropoxide under nitrogen with 5 or 6 mL of a solvent, with dichloromethane (DCM) and acetonitrile (CH_3CN) being the two main solvents used during different trials.



Catalytic reactions were run at 80 °C using 10 mol% of catalyst. The two initial reactions were performed on hydrobenzoin and pinacol, and the catalysts will be tested with other compounds such as 1,2-cyclohexanediol and 2,3-butanediol which have not reacted using known V catalysts.

Results

The process taken to purify the ligand has improved significantly to make it quite quick and efficient. For instance, past methods included doing a recrystallization and washing with several solvents, but now it has been found that just washing the solid with hot CH_3CN efficiently removes impurities.

Purification of the catalysts has been the most notable hurdle to overcome, preventing further progress with the project as very few catalytic reactions have been conducted thus far with the TCC catalysts. At first, analyzing the NMRs proved to be relatively difficult. It was thought that this was due to the catalyst having poor solubility. The NMR spectra have improved as changes have been made to the procedure for synthesizing and purifying the catalysts and as progress has been made in purifying the ligand.

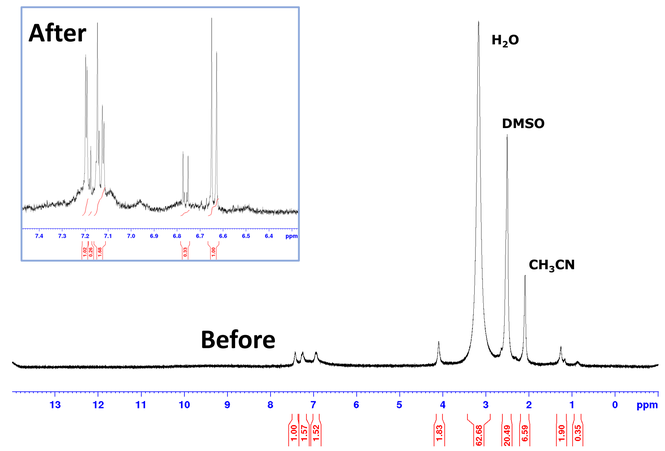


Figure 1. ^{1}H NMR spectra showing improvement in providing clear signals in the aromatic region.

When analyzing NMR spectra, many of the reactions for the catalyst synthesis have shown that anywhere from 25 to 40% of the ligand remained and did not react. In an effort to try and get more ligand to react, an alternate method being tested at the moment is to add the solid ligand to the vanadium in small increments instead of adding the vanadium dropwise into the ligand in solution.

Various methods of purification were tested on the reactions for the synthesis of the batches of catalyst, most with little success. One technique involved adding $NaHCO_3$ and THF and stirring for an hour to allow for the sodium bicarbonate to bind to any unreacted ligand remaining, then trying to do an extraction with the reaction mixture, then heating it under vacuum to remove the water. However, it appears that heating the mixture under vacuum was too much because no vanadium signals could be detected when verifying with NMR. Results from a recent experiment suggest that a hot CH_3CN filtration works to isolate catalyst from the reactions.

Table 1. Catalytic reactions run with the TCC1 and TCC2 catalysts.

Reaction Number	Reaction Description	% Conversion
AM-01-21	Reaction of hydrobenzoin with TCC1	100%
TC-01-023	Reaction of hydrobenzoin with TCC2	100%
AM-01-23	Reaction of pinacol with TCC1	~10%
TC-01-25	Reaction of pinacol with TCC2	~90%

Conclusion

Several ligands with selectively chlorinated triaryloxy groups were synthesized and combined with vanadium to successfully form the desired catalysts. Although purification of these complexes has been problematic and a painstakingly lengthy process with slow progress, preliminary experiments showed promising results for aerobic C-C bond cleavage of several diols. Catalytic reactions are yet to be performed using TCC3, but the catalyst with the para substituted chlorine (TCC2) showed better conversion and yield compared to the same reactions conducted with the 2,4-dichloro substituted catalyst (TCC1). Successful development of these catalysts could allow for routine diol C-C bond cleavage in a more environmentally friendly fashion.

Future Work

Future steps involve:

- Streamlining catalyst purification.
- Further investigate catalyst solubility in other solvents to allow for purification by recrystallization.
- Run additional catalytic reactions to evaluate an extensive range of diol substrates.
- Optimize reaction conditions (such as solvent and temperature) to optimize conversion and yield.

References

Groysman, S., Goldberg, I., Genizi, E., Goldschmidt, Z., and Kol, M. *Adv. Synth. Catal.* **2005**, *347*, 409-415.

Groysman, S., Goldberg, I., Goldschmidt, Z., and Kol, M. *Inorg. Chem.* **2005**, *44*, 5073.

Mba, M., Pontini, M., Lovat, S., Zonta, C. Bernardinelli, G., Kündig, P. E., Licini, G. *Inorg. Chem.* **2008**, *47*, 8616-8618.

Acknowledgements

This project was funded by the Undergraduate Research Opportunity Program (UROP) at the University of Ottawa. Thank you to Prof. R. Tom Baker and the Baker Group for this enriching experience.

uOttawa

CCRI CRIC
Center for Catalysis Research and Innovation
Centre de Recherche et d'Innovation en Catalyse