

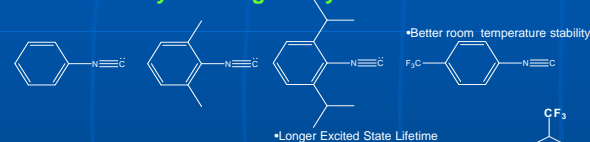
SYNTHESIS OF A NEW ISOCYANIDE LIGAND FOR EFFICIENT PHOTO INDUCED CHARGE TRANSFER PROCESSES WITHIN AN OCTAHEDRAL W(O) COMPOUND

Rebecca A. Seger, Danielle Mazor, Lindsay Whitehead, Faculty Mentor: Keith A. Walters
 Department of Chemistry, Northern Kentucky University, Highland Heights, KY 41099

Abstract: Certain tungsten compounds, when excited by a photon of light energy, have been found to be extremely efficient electron donors in redox reactions. To date however, such tungsten compounds have been inefficient, decomposing quickly at room temperature. The purpose of this research project is to refine the process of amine to isocyanide conversion and then synthesize a more robust tungsten complex which could be used in the treatment of waste water or other chemical reactions that would be driven by sunlight alone.

Introduction: Tungsten compounds can undergo a process called photo-induced charge transfer, by which the tungsten molecule is excited by a photon of light energy to its excited state, where it can then be oxidized by a reactant. What makes these tungsten compounds unique is that upon the oxidation of the compound itself, the energy of the now positively charged compounds ground state nearly equals the energy of the ground state of the uncharged tungsten compound. This similarity in ground states means that nearly all of the energy in the excited state of the tungsten compound is now available for use, making it an extremely rare and efficient compound for photo-induced charge transfer.

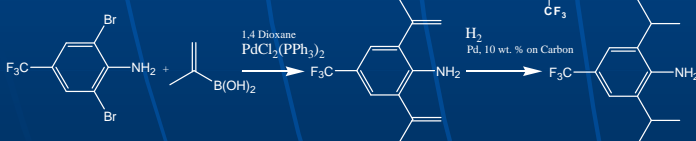
Previous Isocyanide Ligand Syntheses



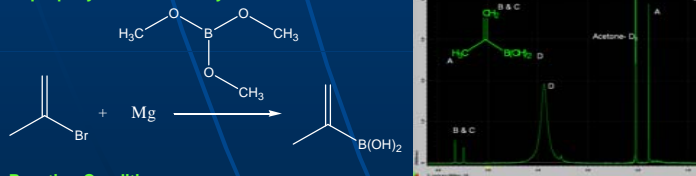
Target Ligand:

*Our goal is to synthesize an isocyanide ligand that has both a longer excited state lifetime and better room temperature stability

Current Reaction Schemes



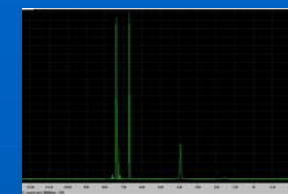
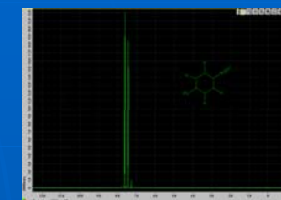
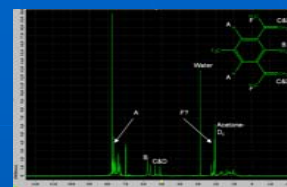
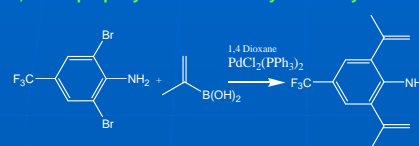
Isopropenylboronic Acid Synthesis



Reaction Conditions

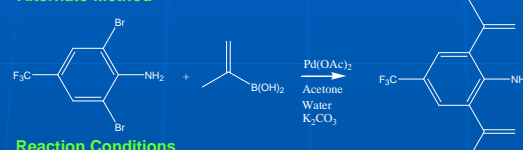
Isopropenylboronic acid was first synthesized. In initial reactions, a Grignard reagent was produced with 2-bromopropene, magnesium metal, and heat. Once the Grignard reagent was stirred for an hour, trimethyl borate was added to the reaction mixture. The reaction mixture was allowed to stir overnight, and then was extracted using diethyl ether and dried with anhydrous Na_2SO_4 . The solvent was removed using a rotary evaporator, and a white solid was produced. In later reactions, the Grignard reagent was purchased to ensure a complete reaction.

2,6-diisopropenyl-4-trifluoromethylaniline Synthesis



In the NMR graphs above, the graph to the left shows evidence of the desired isocyanide ligand. This is concluded since there are two strong peaks in the area the isocyanide is believed to be and there is no starting material present. The graph on the above right shows no evidence of isocyanide, and only starting material.

Alternate Method

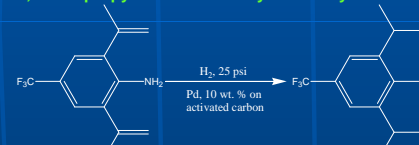


Reaction Conditions

2,6-diisopropenyl-4-trifluoromethylaniline is synthesized under an inert atmosphere in a 3-neck round bottom flask equipped with a pressure equalizing addition funnel and a reflux condenser. In the first method, 2,6-dibromo-4-trifluoromethylaniline, palladium catalyst and 1,4 dioxane are added directly to the flask while a solution of 2M K_2CO_3 , isopropenylboronic acid and ethanol is added dropwise via the addition funnel. The alternate method requires that all of the solutions be degassed and combined immediately in the flask.

The intended color of the reaction mixture (based on literature) is green. The alternate synthesis consistently produced a green oil with promising spectroscopic results.

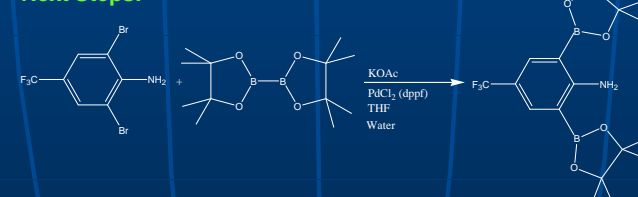
2,6-diisopropenyl-4-trifluoromethylaniline Synthesis



Reaction Conditions

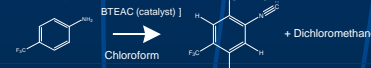
A hydrogenation of 2,6-diisopropenyl-4-trifluoromethylaniline is the product. 2,6-diisopropenyl-4-trifluoromethylaniline is dissolved in methanol and placed into a round bottom flask along with palladium, 10% wt. on activated carbon. The reaction mixture is stirred for 3 days as hydrogen gas is bubbled through it.

Next Steps:



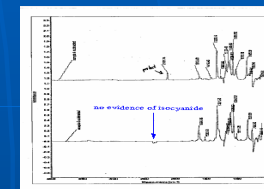
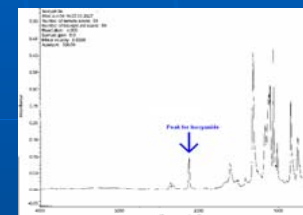
Test Amine to Isocyanide Reaction

The purpose of doing a test amine to isocyanide conversion reaction is to make the isocyanide reaction as efficient as it possibly can be before the protocol is tried on the target ligand. The basic chemical scheme is below.



Reaction Conditions

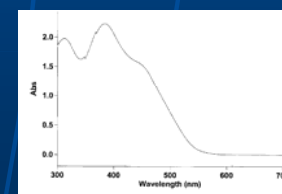
In this scheme, the starting materials are 4-Trifluoromethylaniline, chloroform, and benzyltriethylammonium chloride. Chloroform reacts with benzyltriethylammonium chloride to produce dichlorocarbene and hydrochloric acid. The hydrochloric acid is neutralized by NaOH (which is what the initial reaction is added to). Once the dichlorocarbene is produced, it reacts with the 4-trifluoromethylaniline. This produces the product (C8H4F3N) and methylene chloride. The limiting reagent of the experiment is the 4-trifluoromethylaniline.



In the IR spectroscopic graphs above, the graph to the left shows evidence of the desired isocyanide ligand. The peaks for isocyanide in an IR tend to be present above 2000 but below 2200. This peak is around 2100. So it is concluded that there is isocyanide in this sample. The graph on the above right shows product in the top IR, but no product in the bottom sample.

Isocyanide Ligand to Tungsten Complex Reaction

The purpose of performing an isocyanide ligand to tungsten complex reaction is to attach the isocyanide ligand to an octahedral Tungsten complex. This research is still inconclusive. Although, there is a completed tungsten complex that can aid in the testing process since it can be a bases for comparison there is still no conclusive evidence that the tungsten complex has recently been made.



Though no completed tungsten complex have been made here in this research project, previous research has made the complex. Tests have been performed and shows what is to be expected in future testing. To the left is an absorbance spectrum of the previously made complex.

Acknowledgements

We would like to thank Dr. Noel A.P. Kane-Maguire from Furman University and Northern Kentucky University's Department of Chemistry for their support. We would also like to thank CINSAM and Northern Kentucky University's Research Foundation for their financial support.

References

1. Keith Walters, Senior Thesis, 1996, Furman University.
2. Mann, K.R.; Gray, H.B.; Hammond, G.S. *J. Am. Chem. Soc.* **1977**, *99*, 306
3. Graham Dickerson, Senior Thesis, 1993, Furman University.
4. Michael Lube, Senior Thesis, 1992, Furman University.
5. Heather Tolley, Senior Thesis, 1994, Furman University.
6. W.P. Weber, G.W. Gokel, I.K. Ugi, *Angew. Chem., Internat. Edit.* **1972**, *11*, 530.
7. N.J. Coville, M.O. Albers, *Inorg. Chim. Acta* **1982**, *65*, L7