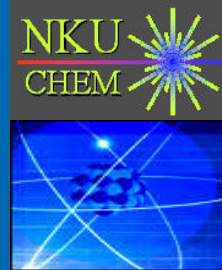


Continued synthesis of a new isocyanide ligand for efficient photo induced charge transfer processes within an octahedral W(0) compound

Rebecca A. Seger, Lindsay Whitehead, Keith A. Walters

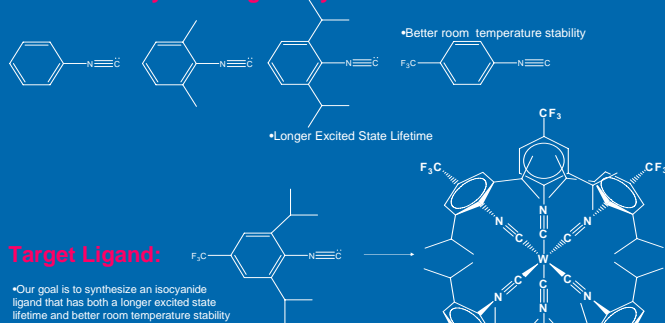
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Abstract: Certain tungsten compounds, when excited by a photon of light energy, have been found to be extremely efficient electron donors in redox reactions. To date however, such tungsten compounds have been inefficient, decomposing quickly at room 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.

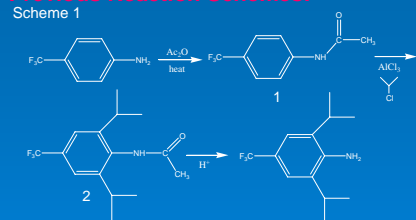
Previous Isocyanide Ligand Syntheses



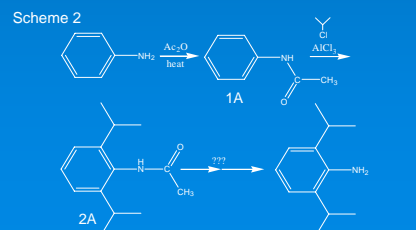
Target Ligand:

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

Previous Reaction Schemes:

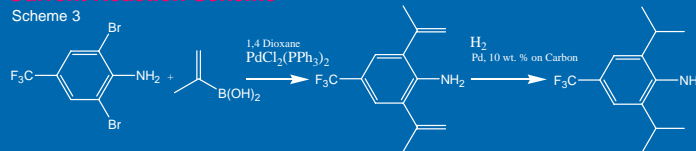


Issues: After several attempts, product 2 was never synthesized. We believe the trifluoromethyl group *para* to the coordination site deactivates the Friedel Crafts alkylation. ¹H NMR spectra indicated that only starting material existed whenever product 2 was synthesized

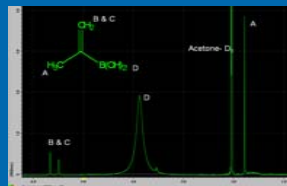
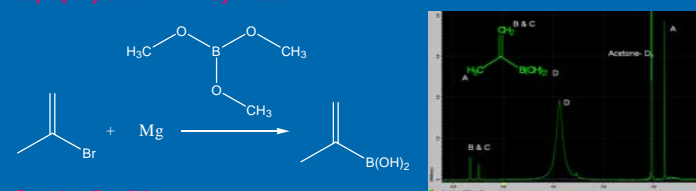


Issues: As with product 2, product 2A was never synthesized. ¹H NMR spectra showed starting material as the final product for all syntheses of product 2.

Current Reaction Scheme



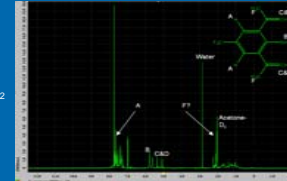
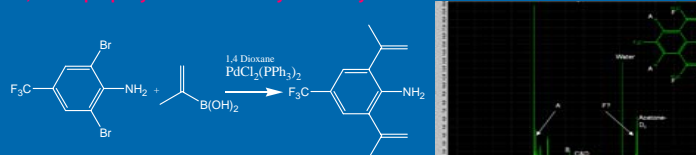
Isopropenylboronic Acid Synthesis



Reaction Conditions

The isopropenylboronic acid had to be synthesized first. 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 Na₂SO₄. The solvent was removed using a rotary evaporator, and a white solid was produced.

2,6-diisopropenyl-4-trifluoromethylaniline Synthesis



Reaction Conditions

This reaction is done under an inert atmosphere in a 3-neck round bottom flask equipped with a pressure equalizing addition funnel and a reflux condenser. The 2,6-dibromo-4-trifluoromethylaniline, palladium catalyst and 1,4 dioxane are added straight to the flask while a solution of 2M K₂CO₃, isopropenylboronic acid and ethanol is added dropwise via the addition funnel.

Issues

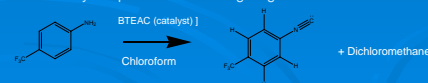
The intended color of the reaction mixture (based on literature) is green. Each synthesis produced a green product, but if the reaction mixture was refluxed for more than 6 hours, the reaction mixture would turn brown. Yields for each reaction are very low. It's suspected that the intended product has not been made.

Next Steps:

The next step in this synthesis, once 2,6-diisopropenyl-4-trifluoromethylaniline is synthesized is a hydrogenation of 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. The reaction mixture is extracted using diethyl ether and then dried with anhydrous sodium sulfate before the solvent is removed to yield the final product, an expected green oil, the target molecule.

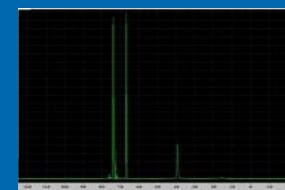
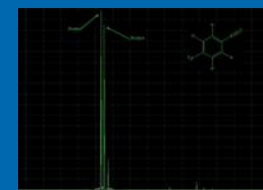
Test Amine to Isocyanide Reaction

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 we try the protocol on the target ligand. The basic chemical scheme is below.

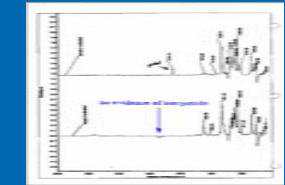
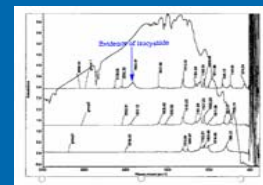


Reaction Conditions

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.



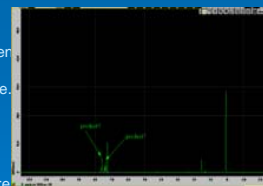
In the NMR graphs above, the graph to the left shows evidence of the desired isocyanide ligand. This is concluded since there are two strong peaks in the area the isocyanide is believed to be and there is no starting material present. The graph on the above right shows no evidence of isocyanide, and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



In the IR spectroscopic graphs above, the graph to the left shows evidence of the desired isocyanide ligand. There are three different samples tested in this IR. The top sample shows the desired product while the bottom two samples do not. This is concluded since there is a peak in the desired area to prove existence of the isocyanide. The graph on the above right shows product in the top IR, but no product in the bottom sample.

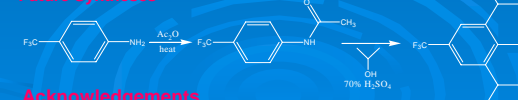
Amine to Tungsten Reaction

The purpose of performing an Amine to Tungsten reaction is to attach the isocyanide ligand to an octahedral Tungsten complex. This research is still inconclusive, although there is evidence of the desired product.



The NMR graph to the left is the most promising thus far. It is obvious that the isocyanide has reacted with the tungsten, although it isn't definite that the tungsten-isocyanide complex was made. Research will continue to prove that the Tungsten complex exists in samples.

Future Synthesis



Acknowledgements

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