

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

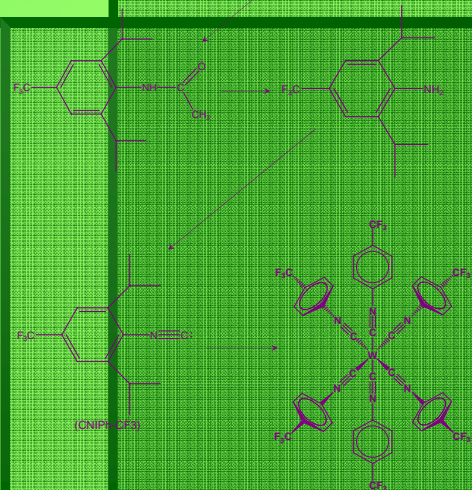
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Abstract: Certain tungsten compounds, when excited by a photon of light energy, have been found to be extremely efficient electron donors in redox reactions. To date however, such tungsten compounds have been inefficient, decomposing quickly at room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

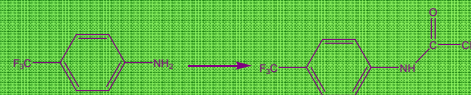
Introduction: Tungsten compounds can undergo a process called photo-induced charge transfer, by which the tungsten molecule is excited by a photon of light energy to its excited state, where it can then be oxidized by a reactant. What makes these tungsten compounds unique is that upon the oxidation of 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. W(O)(NPh-CF₃)₆ is a compound which has never before been made. The isocyanide ligand attached to the tungsten molecule, CNPh-CF₃, has also never before been made, and must first be synthesized. This tungsten compound is expected to be very promising for future sunlight driven redox reactions.

Reaction Schema:



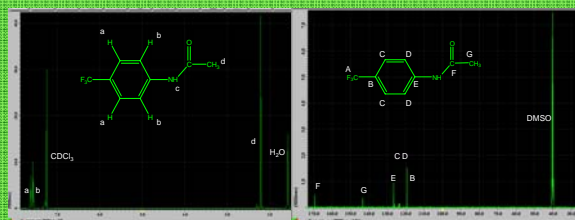
Synthesis of CNPh-CF₃

Step 1- Synthesis of Product 1

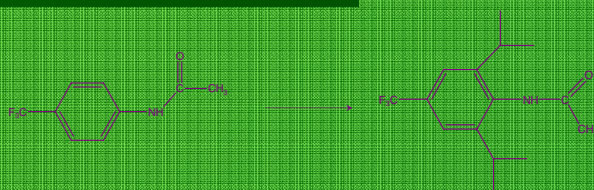


Reaction Conditions: Acylate with acetic anhydride, reflux for 15 minutes, remove reflux condenser, boil for 25 minutes to remove excess acetic anhydride, place in ice bath, collect crystals using suction filtration, recrystallize twice using 50-60 ethanol/water as solvent.

NMR Spectra of Product 1



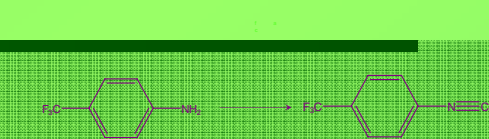
Step 2- Synthesis of Product 2



Reaction Conditions: Reflux WCl₅ (Cat), 3-Chloropropane in an inert atmosphere

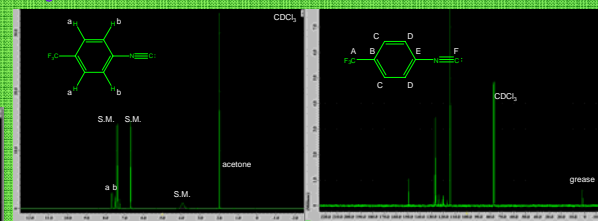
Notes: This reaction was attempted several times each under slightly different circumstances, but with no successful synthesis. TH-NMR analysis for each synthesis indicated that very starting material existed in the final product.

Test Amine to Isocyanide Reaction



Reaction Conditions: NaOH, CHCl₃, Tetraethylammonium chloride hydride, Reflux for 3-4 hours, Solvent: CH₂Cl₂

Next Step: Create an octahedral W(0) compound using this isocyanide ligand



Next Steps:

- Optimize the amine to isocyanide reaction for a better target molecule to starting material ratio in the end product.
- Create an octahedral tungsten molecule using the recently made isocyanide ligand.
- Repeat the synthesis of product 2 for the synthesis of the new isocyanide ligand (CNPh-CF₃).
- Study the photochemistry and electrochemistry of the proposed tungsten compound for insight into their use as efficient reducing agents.

Acknowledgements

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References

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