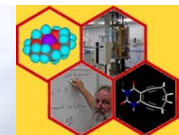


CONTINUED SYNTHESIS OF SYMMETRIC AND ASYMMETRIC LIGATION POINTS FOR ORGANOMETALLIC SUPRAMOLECULAR SYSTEMS

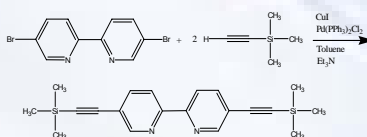
SEAN M. GOINS, JAMES KARETH, AND KEITH A. WALTERS, DEPARTMENT OF CHEMISTRY, NORTHERN KENTUCKY UNIVERSITY, NUNN DRIVE, HIGHLAND HEIGHTS, KY 41099, GOINSS1@NKU.EDU



The goal of this research is to synthesize both symmetric and asymmetric molecules which will serve as the central ligation point of more advanced transition metal/fullerene systems. The symmetric center will allow for rapid production of these systems, while the asymmetric center will allow for the production of more complex systems with differing moieties on each side of the center. A detailed description of the reaction mechanisms involved, as well as refinements to existing methodologies for the Sonogashira and Stille coupling reactions, will be presented. The symmetric center has been completed and utilized in the fullerene systems, while the asymmetric system is still being optimized. With successful isolation of the asymmetric molecule, further research will focus on attachment of fullerenes to this center, as well as their incorporation into other areas of our supramolecular photochemical research.

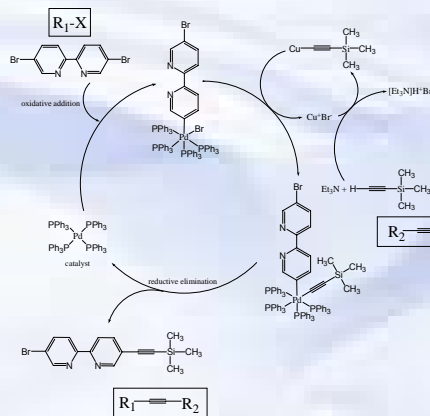
Successful utilization of the starting material 5,5'-dibromo-2,2'-bipyridine includes synthesis of two major products: 5,5'-diethyl TMS-2,2'-bipyridine, our symmetric product, and 5-ethynyl TMS-5'-ethynyl-dimethyl propargylol-2,2'-bipyridine, our asymmetric product. Synthesis of symmetric product is shown below. Synthesis of the asymmetric product is shown to the right.

Synthesis of 5,5'-diethyl TMS-2,2'-bipyridine:

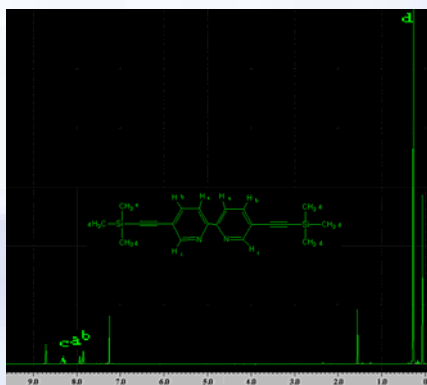


Synthesis of the 5,5'-diethyl TMS-2,2'-bipyridine symmetric product utilizes the Sonogashira Coupling reaction. Two molar equivalents of TMS acetylene are attached to the two electrophilic carbons:

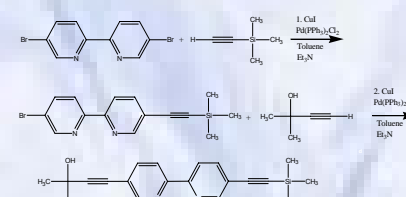
Sonogashira Coupling reaction (first cycle):



Successful synthesis of the symmetric product produces a proton NMR with the TMS peak:

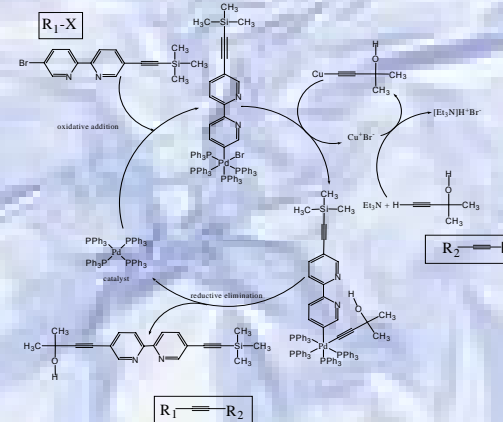


Synthesis of 5-ethynyl TMS-5'-ethynyl-dimethyl propargylol-2,2'-bipyridine:



Synthesis of the asymmetric product involves the addition of 2-methyl-3-buten-2-ol in a second cycle of the Sonogashira Coupling reaction to attack the remaining electrophilic carbon on the intermediate.

Second cycle using 2-methyl-3-buten-2-ol:



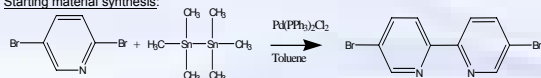
Although NMR data has indicated synthesis of the 5-ethynyl TMS-5'-ethynyl-dimethyl propargylol-2,2'-bipyridine, the asymmetric product, separation of pure product has been difficult. The NMR data indicates synthesis of multiple products. Column chromatography has been used with little success. Future research includes successful separation of pure asymmetric product along with successful utilization of symmetric and asymmetric molecules in fullerene systems.

REFERENCES:

1. Bruce, J.I.; Chambron, J.C.; Kollé, P.; Sauvage, J.P., Synthesis of a linear bis-porphyrin with a Ru(phen)2+ -complexed 2,2'-bipyridine spacer. *J. Chem. Soc., Perkin Trans. 1*, **2002**, 1226-1231.
2. Schubert, U.S.; Eschbaumer, C.; Heller, M., Stille-Type Cross-Coupling – An Efficient Way to Various Symmetrically and Unsymmetrically Substituted Methyl-Bipyridines: Toward New ATRP Catalysts. *Organic Letters*, **2000**, 2 (21), 3373-3376.
3. Opris, D.M.; Franke, P.; Schluter, A.D., Shape-Persistent Macrocycles with Bipyridine Units: Progress in Accessibility and Widening of Applicability. *Eur. J. Org. Chem.*, **2005**, 622-837.
4. Ley, K.D.; Li, Y.; Johnson, J.V.; Powell, D.H.; Schanze, K.S., Synthesis and characterization of π-conjugated oligomers that contain metal-to-ligand charge transfer chromophores. *Chem. Commun.*, **1999**, 1749-1750.
5. Kiyatskaya, S.V.; Tretyakov, E.V.; Vasilevsky, S.F., Synthesis and chemical properties of polyacetylenic derivatives of benzo- and dibenzo- crown ethers. *ARKAT-USA Jour.*, **2003**, 13.
6. Li, J.H.; Liang, Y.; Xie, Y.X., Efficient Palladium-Catalyzed Homocoupling Reaction and Sonogashira Cross-Coupling Reaction of Terminal Alkynes under Aerobic Conditions. *J. Org. Chem.*, **2005**, 70, 4393-4396.
7. Lei, A.; Srivastava, M.; Zhang, X., Transmetalation of Palladium Enolate and Its Application in Palladium-Catalyzed Homocoupling of Alkynes: A Room-Temperature, Highly Efficient Route to Make Diynes. *J. Org. Chem.*, **2002**, 67, 1969-1971.
8. Bianchini, C.; Meli, A.; Vizza, F., Modelling the Hydrodenitrogenation of Aromatic N-Heterocycles in the Homogeneous Phase. *Eur. J. Inorg. Chem.*, **2001**, 43-68.

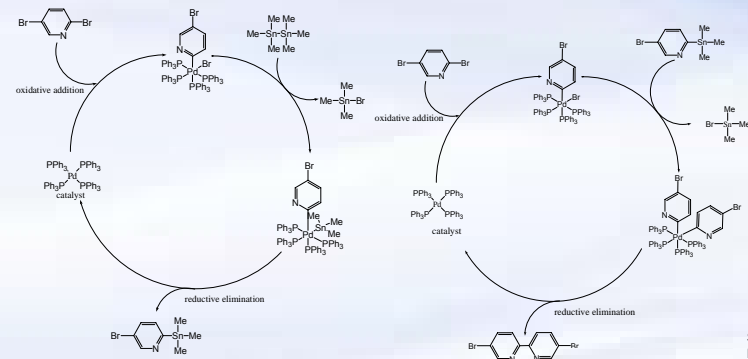
Acknowledgements: Dr. Keith Walters, James Kareth, Joel Deye, Celeste Morris, Rebecca Seger, Craig Girten, Danielle Mazor, and also Northern Kentucky University and CINSAM for financial support.

Starting material synthesis:



In order to understand the function of the "central hub" structure, it is essential to understand how the molecule is constructed. Using 2,5 dibromopyridine, hexamethylditin, and palladium catalyst in a Stille Cross-Coupling reaction, the starting material 5,5'-dibromo-2,2'-bipyridine is produced. This material is used for both the asymmetric and symmetric reactions. The schemes shown represent how this starting material is synthesized.

Stille Cross-Coupling reaction:



The following proton NMR represents a typical successful synthesis of the 5,5'-dibromo-2,2'-bipyridine molecule:

