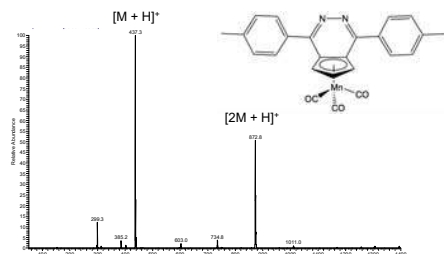


Cyclopentadienyl Pyridazines and Oxazines and Their Applications in Energy and Advanced Electronics

Introduction/Background

Heterocycles and their derivatives have long been of interest for use in advanced electronic applications. Due to their unique properties including environmental stability, high processibility, and low production cost, organic-based electronic materials are an attractive alternative to conventional inorganic semiconductors. The growing interest and demand for alternative energy and next generation electronic devices has led to the incorporation of aromatic heterocycles into field-effect transistors (FETs), organic light-emitting diodes (OLEDs), and organic photovoltaic (OPV) cells. Two such classes of heterocycles, pyridazines and oxazines (6 membered aromatic rings containing two adjacent nitrogen atoms or an adjacent nitrogen and oxygen), represent alluring building blocks for electronic materials due to their ease of synthesis and stability. However, very little is known about the materials properties of pyridazines and oxazines or the feasibility of incorporating them into electronic devices. Our current investigation focuses on the off-metal and transition metal chemistry of Cp pyridazines and oxazines, namely, the formation of a fused-ring complexes bound η^5 (*eta*-5) to a metal through the Cp moiety. By including a transition metal into the pyridazines and oxazines, we hope to create hybrid materials which blend the synthetic versatility of organics with the novel structural and electronic properties that inorganic moieties possess.

DART Analysis of Pyridazine Complexes

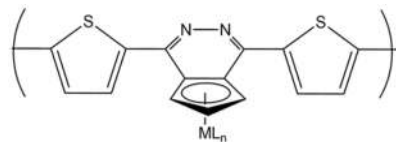


Direct Analysis in Real Time (DART) Mass Spectrometry analysis was shown to be effective for the thallium, manganese, and rhenium pyridazine complexes. This mild and convenient form of MS is better able to confirm structure and molecular weight versus more traditional methods. High relative abundance of the protonated molecular ion peak and dimer was observed under positive mode.

Smith D. L., et al. Analytical Methods. 2015, 7, 4003-4007

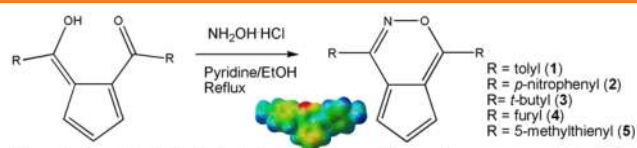
Envisioned Fused Heterocyclic Conducting Polymer

These pyridazine and oxazine complexes will serve as synthetic models and building blocks for future organometallic heterocyclic conducting polymers.



These envisioned polymers could be formed from Suzuki-type coupling reactions with aryl boronic acids and these 1,4-dihaloarylpyridazine and oxazine complexes or by electrochemical polymerization of the thieryl derivatives.

Successful Oxazine Formation

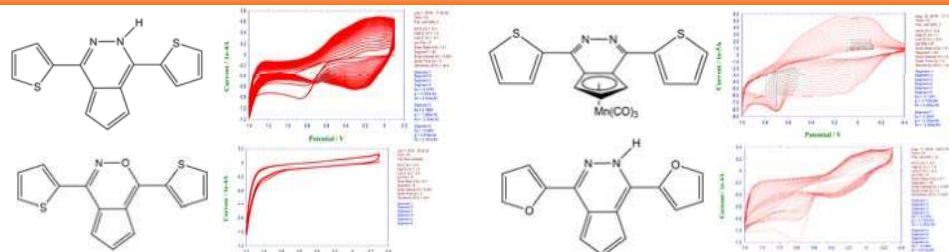


Formation of the 1,2-disubstituted cyclopentadienes (fulvenes) was accomplished by reaction of 3 equivalents of lithium cyclopentadienide and 2 equivalents of the corresponding acid chloride. Ring closure to the oxazine was accomplished by refluxing with hydroxylamine hydrochloride in a pyridine/EtOH mixture, in modest yields (29-46%). X-Ray crystallographic analysis of the tolyl case confirms the desired 5,6-fused oxazine, displaying π -stacking between adjacent layers related by an inversion symmetry element. Natural Bonding Orbitals (NBOs) were calculated for the tolyl case, with the HOMO primarily residing on the Cp portion of the target molecule and the LUMO primarily on the 6-membered oxazine moiety.

Tice, N. C.; Collins, E. M.; Smith, D. L.; Snyder, C. A.; Yan, B.; Stevens, E.; J. of Heterocyclic Chem., 2017, 54, 3235-3240.

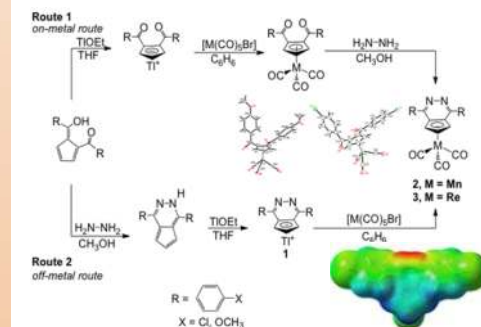
Tice, N. C.; Wild, S.; Olmstead, C.; Stevens, E. D.; Yan, B.; Brooks, H.; Jenkins, J. L. Heterocycles 2019, 98, 1707-1724.

Cyclic Voltammetry Polymerization Trials



Cyclic Voltammetry (CV) trials were performed on a variety of the aryl and thieryl pyridazine and oxazine derivatives. In general, the pyridazines displayed high electrochemical activity and stability. The thieryl and furyl pyridazines were susceptible to electrochemical polymerization on both functionalized and non-functionalized ITO. While, the polymerization of the on-metal pyridazine appeared promising, X-ray Photoelectron Spectroscopy (XPS) confirmed the loss of the manganese during polymerization. In contrast, the oxazine cases showed little electrochemical activity.

Comparison of "On-" vs. "Off-Metal" Routes



Formation of these 5,6-fused ring pyridazines could be accomplished through either a ring-closure reaction on-metal with the corresponding diacyl metallocene (Route 1) or by closure before metallation, followed by complexation with a thallium salt (Route 2). The off-metal synthetic pathway employed (Route 2) did improve upon the isolation of these complexes as compared to previously reported route, with slightly higher yields and better analytical purity.

Tice, N. C.; Snyder, C. A.; et al. Transition Met. Chem. 2012, 37, 141-147.
Snyder, C. A.; Maddox J. B.; Tice, N. C. et al. Transition Met. Chem. 2013, 38, 801-809.

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