Synthesis and Complexation of N-Metallocylcic Carbenes

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Key Words:

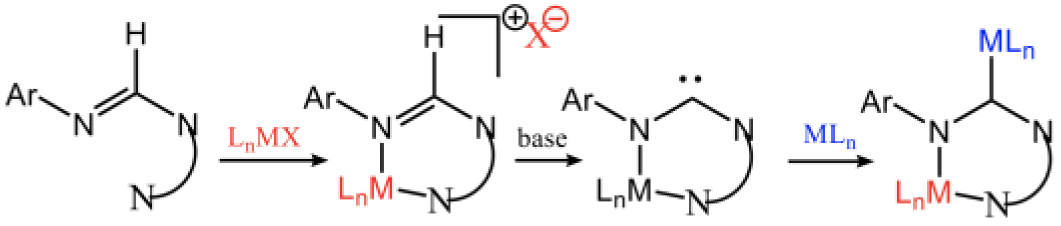
- **Catalysis**: The acceleration of a chemical reaction using a “catalyst”.
- **Organic compound**: A carbon-based molecule.
- **N-Metallocyclic Ring**: A organic ring that includes a nitrogen and metal atom within the ring.
- **Carbene**: a carbon atom with a lone pair of electrons.

ABSTRACT: This project investigated the properties and synthesis of Iridium, Ruthenium, and Rodium bimetal complexes. These complexes are bridged via a Nitrogen-based metallocyclic carbene giving them unique properties to act as a catalyst in a variety of reactions. The applications for these complexes and synthesis pathways have a role to play both within inorganic chemistry and everyday life. Results of the project suggest the synthesis of the N-Metallocyclic Carbene along with direction for the complexation of the second metal to the carbene.

Background: Since the discovery of the first stable variant in the 1990’s, N-heterocyclic carbenes (NHC’s) have become one of the most prolific classes of ligands studied. [1-6] A large variety of NHC’s, with varying steric and electronic properties, have been synthesized and employed in catalysis, both as ligands and as organocatalysts. [7-9] . The electronic properties for a given NHC are fixed, therefore it would be ideal to have a ligand whose electronic properties could be tuned. The synthesis of this tunable NHC is the goal of this project. Many precursors and synthetic pathways have been formed in this pursuit.

Introduction:

In order to produce this tunable catalyst, new ligands with a transition metal incorporated in close proximity to the carbene carbon should facilitate metal-metal communication and should allow for the ligand to be electronically tunable. The synthesis of new N-metallocyclic carbenes (NMC), in a modular fashion comprised of three key components: a formamidine-based chelate, a transition metal, and that metal’s ligands. This modular approach is shown in general in Scheme 1 where the formamidine-based chelate is coordinated to a transition metal resulting in a cationic complex analogous to an azolium salt. Treatment with an appropriate base should result in the formation of the NMC. Coordination of the NMC to a second metal would result in a bimetallic complex.

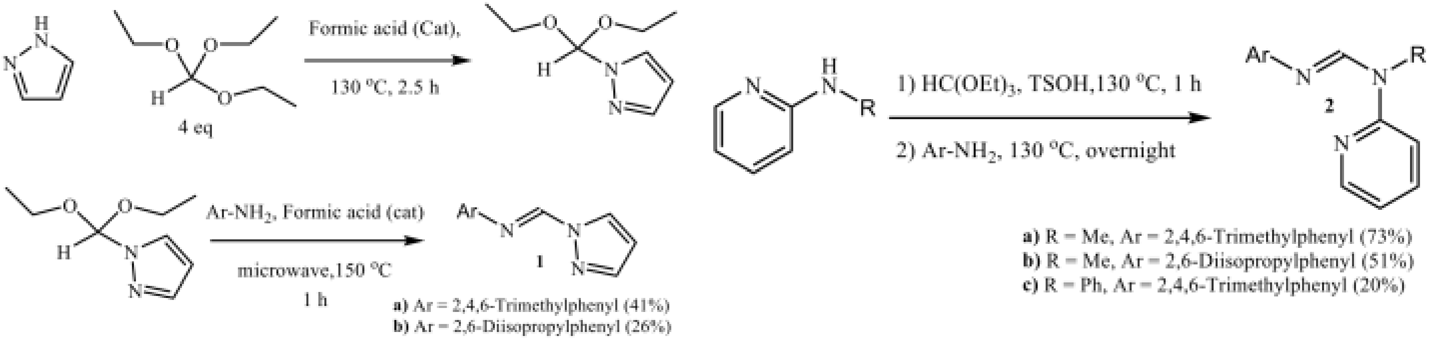


Scheme 1. General mechanism of the synthesis and complexation of the NMC

This synthesis pathway takes three overall steps: formation of pyrazolylformamidine or pyridylformamidine ligand, coordination of the ligand to a transition metal, and lastly, the formation of the carbene and coordination of our second metal. Short summaries of these synthetic attempts will be shown below with supporting information in the associated content.

Formamidine Ligand Synthesis:

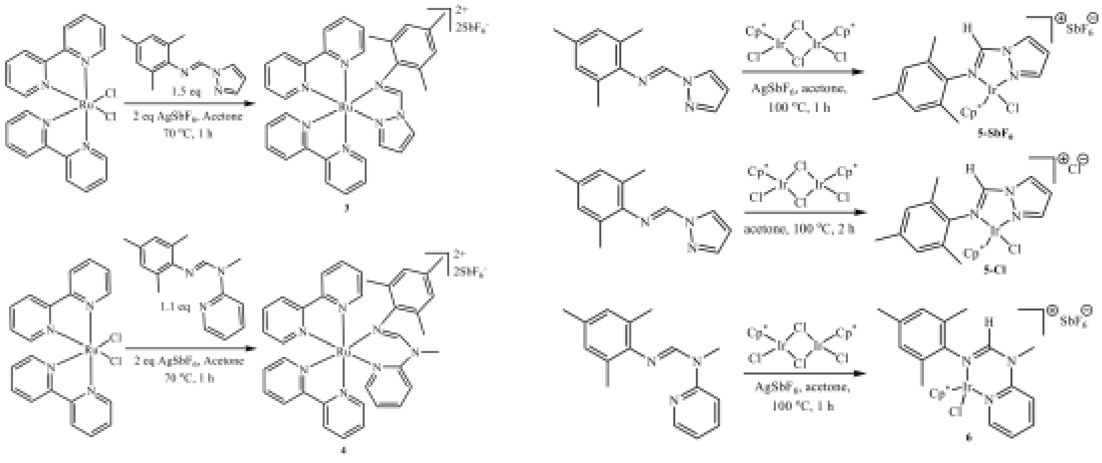
Synthetic strategies for the synthesis of several different formamidine-based chelates developed in our lab are shown in Scheme 2. Both pyrazolylformamidine (**1**) and pyridylformamidine (**2**) ligands have been synthesized with several structural variants. Examples of these two synthetic pathways are shown in Scheme 2.



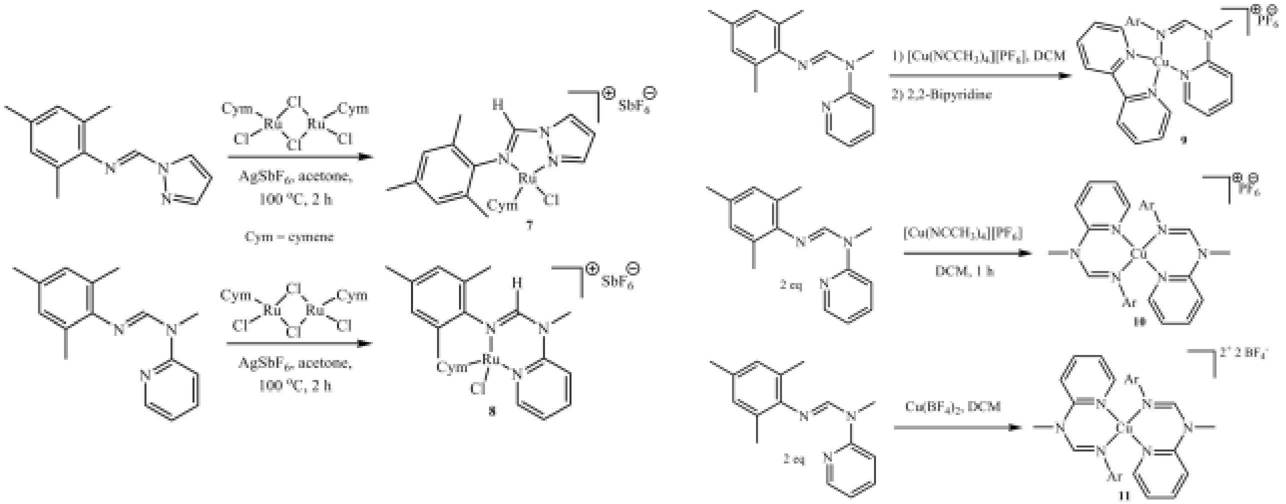
Scheme 2. Mechanisms showing the synthesis of both pyrazolylformamidine(left) and pyridylformamidine(right) based ligands

Precarbene Synthesis:

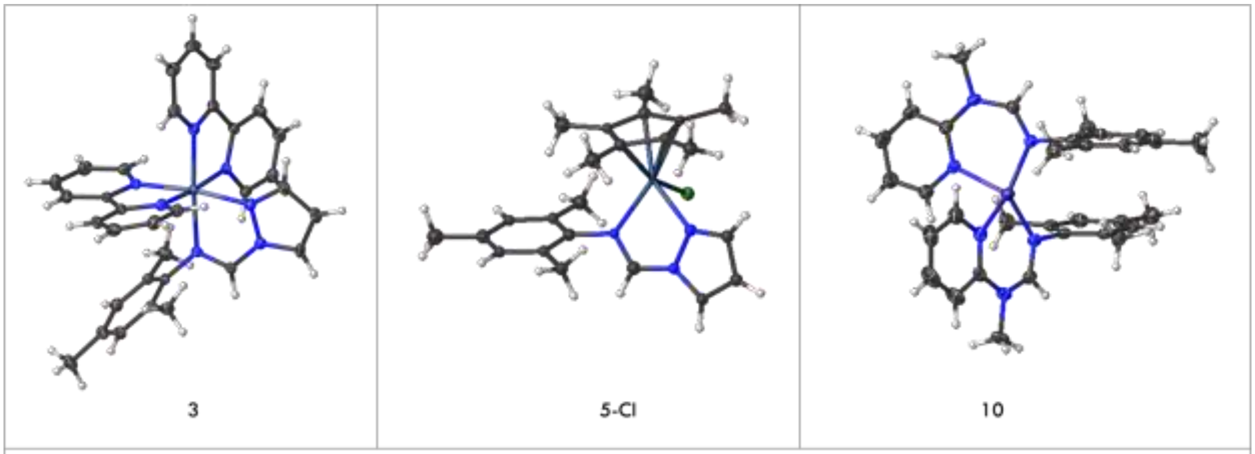
Coordinating the pyrazolyl- and pyridylformamidines described above to a transition metal complex results in the formation of an N-metallocyclic carbene precursor analogous to an azolium salt. The below scheme shows the synthesis of a number of NMC precursors. Five different transition metal complexes have been reacted with the pyrazolylformamidine ligand **1a** and/or the pyridylformamidine ligand **2a** resulting in ten different complexes. Crystal structures have been solved for six of the ten NMC precursors. A few examples are shown below.



Scheme 3a. Mechanisms showing the synthesis of the carbene precursor using a combination of both Ruthenium and Iridium as starting metals along with a mixture of both pyrazolylformamidine and pyridylformamidine ligands.



Scheme 3b. More examples of carbene precursors that have been synthesized using Copper and Ruthenium as base metals along with a mixture of both pyrazolylformamidine and pyridylformamidine ligands.



3

5-Cl

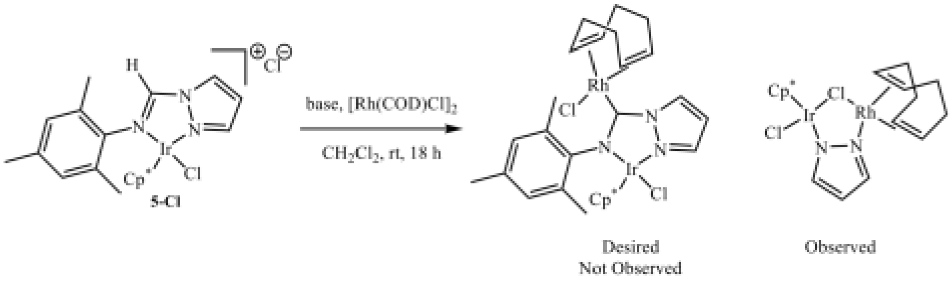
10

Figure 1. Structures of the NMC complexes **5**-SbF$_6$, **5**-Cl, and **10**. Black, blue, green, and white ellipsoids represent C, N, Cl, and H atoms, respectively. The transition metal atoms are represented by purple ellipsoids.

Three of the six crystal structures are shown in Figure 1 as representative examples.

N-Metallocyclic Carbene Synthesis:

We have hypothesized that the NMC precursors can be converted to an NMC via deprotonation with an appropriate base. Being unsure of the long-term stability of the NMC once formed, it seemed best to form it in the presence of a trap like [Rh(COD)Cl]$_2$. Therefore, compound 5, a bright yellow solid, was treated with an appropriate base, either silver oxide or Lithium tert-butoxide, in the presence of the rhodium dimer. The resulting product was a golden solution. This product was dissolved in $CDCl_3$ so a ^{1}H-NMR could be taken. This resulted in a clean single product with a promising set of signals. Unfortunately, crystallization showed the formation of the product shown in which the formamidine had been degraded. Scheme 4 shows this reaction mechanism. It remains possible that the NMC was formed and subsequently decomposed. This process of deprotonating our hydrogen of interest in a [Rh(COD)Cl]$_2$ trap has been attempted with several complexes however similar results have been observed.



Scheme 4. Shows the reaction with compound 5 (an Iridium and pyrazole carbene precursor) going through the complexation of the second metal which in this case is Rhodium. The desired and expected product is displayed on the left side of the reactants so it can be compared to the observed product.

After careful consideration and elucidation of our observed products, it could be understood that the decomposition of the NMC goal product was due to a resonance structure available in the pyrazolylformamidine ligand bridge. Based on this piece of information the goals moving forward will be to synthesize one of the pyridylformamidine carbene precursors and attempt the complexation of Rhodium in an appropriate solvent system.

Associated Content

Synthetic details of select compounds will be described below as they play a large role in the project moving forward. The formation of Compound 5 was done by combining 2 equivalents of our pyrazolylformamidine ligand with one equivalent of Iridium starting material. This was dissolved in dry acetone and reacted at room temperature overnight. The resulting aromatic region of the NMR of reaction ZIB-I-39 is displayed below in Figure 2. This reaction resulted in a 91.5% yield.

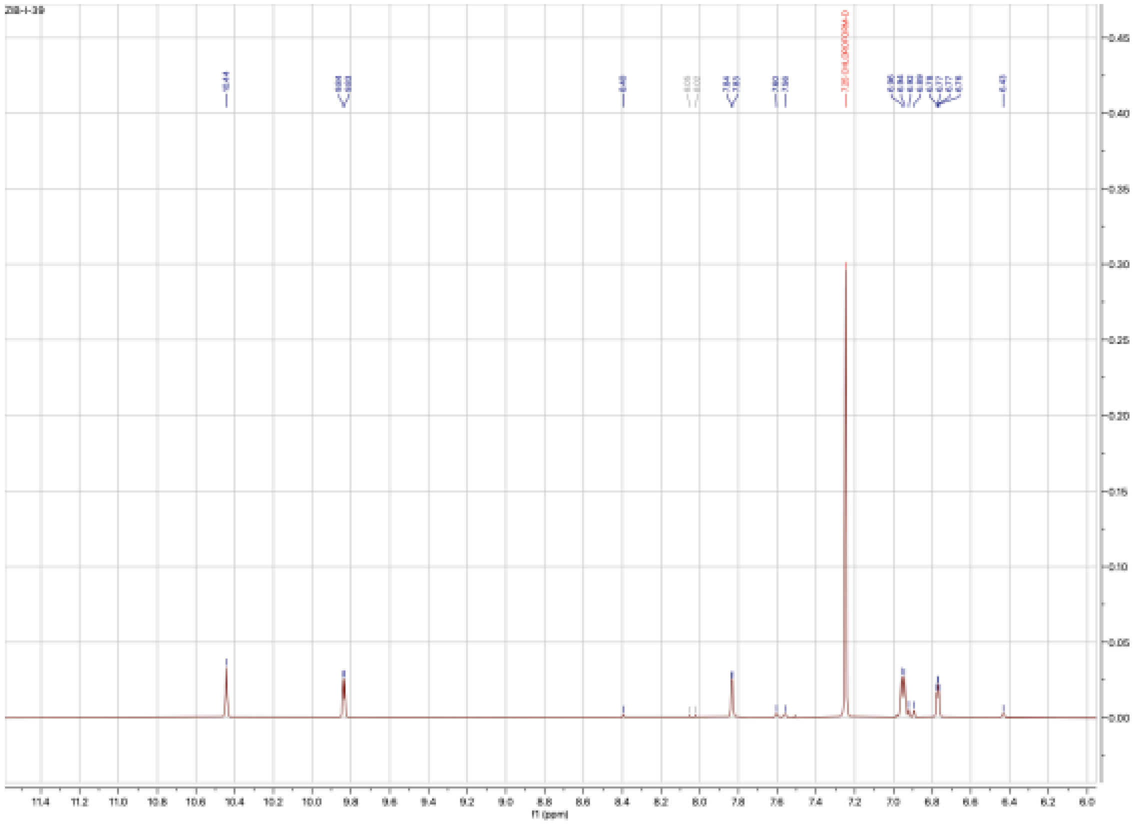


Figure 2. The aromatic region of the NMR taken of ZIB-I-39.

The formation of our new carbene precursor of interest was done in reaction ZIB-I-27. In this reaction, one equivalent of Iridium starting material was combined with two equivalents of our pyridylformamidine ligand along with two equivalents of Silver hexafluoroantimonate. These three compounds were dissolved in dry acetone and reacted at room temperature for one hour. The resulting solution was filtered through celite and ether was added to precipitate the desired product. The resulting aromatic region of the NMR is displayed below in Figure 3. The yield of this reaction was 88.6%

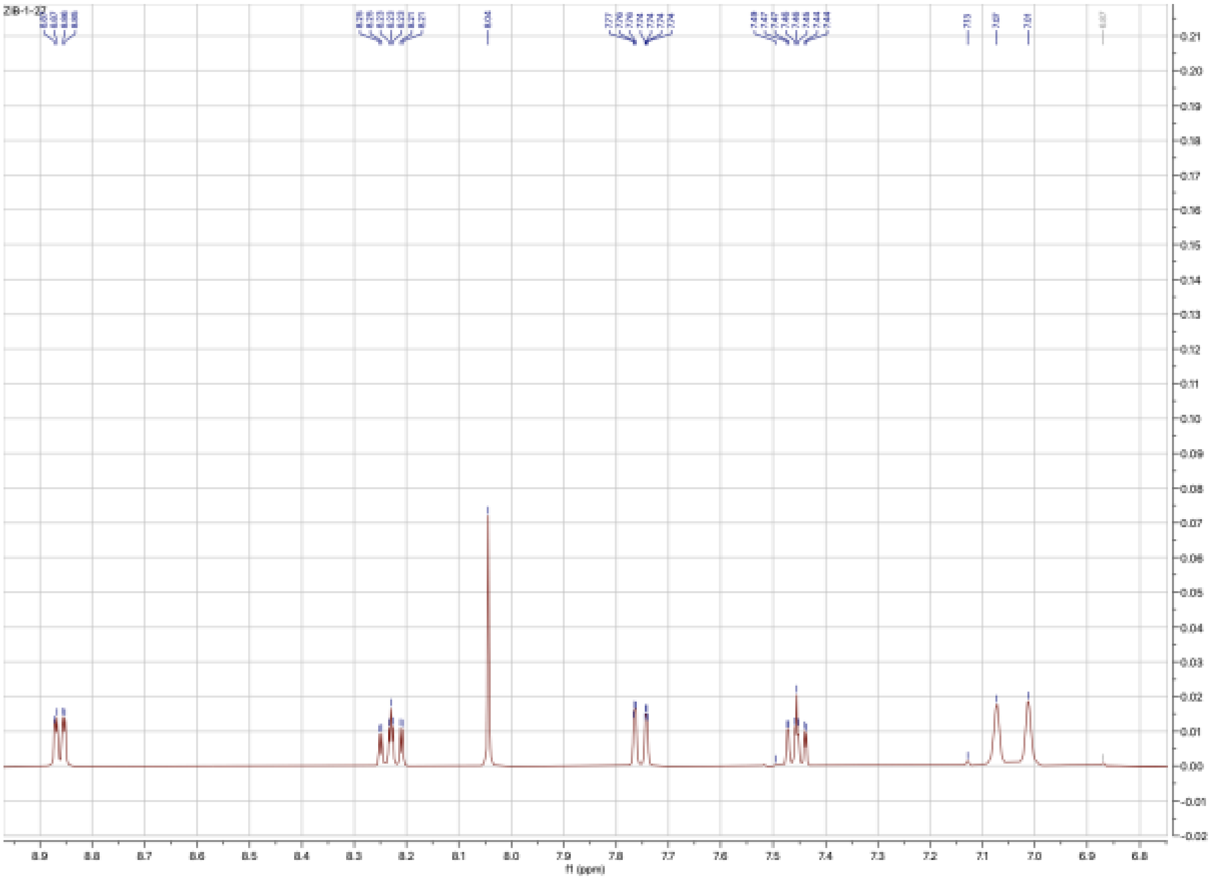


Figure 3. The aromatic region of the NMR taken of ZIB-I-27.

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