

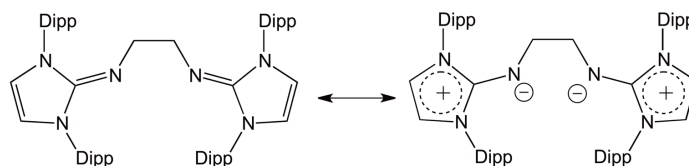
## PRF Grant Number 56702

### Bisguanidine Complexes of Pd(0) and Ni(0) Towards Catalytic Removal of Aryl-heteroatoms From Heavy Crudes

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#### Proposal Overview

We proposed the development of Ni<sup>0</sup> and Pd<sup>0</sup> complexes supported by bulky, neutral bisguanidine-type ligands capable of enhanced electron-donating ability via cation stabilization in the imidazolium ring and concurrent transfer of electron density to exocyclic nitrogen atoms (See Figure 1). These complexes would then be used to perform oxidative additions (OAs) across various otherwise inert sp<sup>2</sup>-heteroatom (N, O or S) bonds found in asphaltenes (or model compounds), and following OA a reductive elimination step would result in the removal of the heteroatom and regenerate the metal complex in catalytic fashion. Our catalyst design proposals were aimed at producing a complex with a particularly electron-rich metal center while also producing a coordinatively unsaturated metal center. The combination of these attributes were thought to, as advised by literature and our inclinations, give the catalyst the best shot at performing an OA, or insertion, across the targeted inert bond. In order to achieve these attributes in the resulting complex, the ligand must have excellent electron-donating ability (electron-rich metal center) and provide steric protection (coordinatively unsaturated metal center). While work on producing and testing the targeted catalysts has continued in the second year of this two-year grant, the majority of the efforts in the second year were spent on evaluating the electronic behavior of the bisguanidine-type ligands upon coordination to a Lewis acid, in this case a proton. This was accomplished via physical observations as well as computational methods.



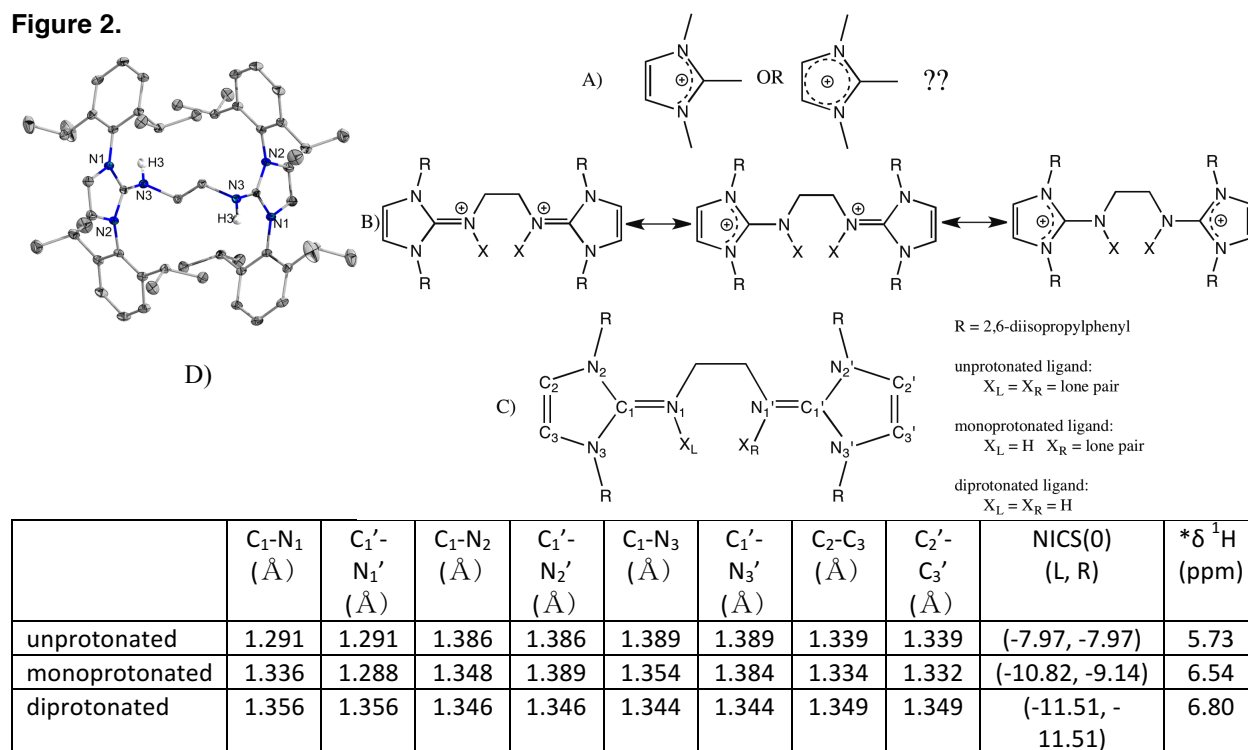
**Figure 1.** Potential resonance contributors for targeted bisguanidine-type ligands, highlighting the ability to transfer electron density to exocyclic coordination sites via stabilization of a positive charge in the imidazolium moiety.

\*\*\*\*It should be noted that while the positive charge is often drawn as seen here in literature, it may be inappropriate to represent the positive charge as being evenly delocalized through the heterocycle. \*\*\*\*

#### Ligand Investigations

In order to gain insight into the electronic behavior of this class of ligands both in the absence of a coordinated Lewis acid and when coordinated to a Lewis acid, crystallographic, spectral and computational evidence was collected and examined in concert. The bidentate ligand seen in Figure 1 [N,N'-bis(1,3-di(2,6-diisopropylphenyl)imidazolin-2-ylidene)-1,2-ethanediamine] was successfully synthesized and crystallographically characterized in the first year of this grant and was chosen for further investigation. The neutral bidentate ligand (EtN<sub>2</sub><sup>IPr</sup>) was further reacted with either 1 or 2 equivalents of a strong acid (triflic acid or *p*-toluenesulfonic acid) in order to produce both the monoprotonated and diprotonated analogs of the ligand (See Figure 2). Both the monoprotonated and diprotonated analogs ([HEtN<sub>2</sub><sup>IPr</sup>][X] or [H<sub>2</sub>EtN<sub>2</sub><sup>IPr</sup>][X]<sub>2</sub> where x= triflate or tosylate) were successfully synthesized and characterized by <sup>1</sup>H NMR and single crystal X-ray diffraction. In addition to cataloguing the bond lengths and proton shifts of interest in all three analogs (unprotonated, monoprotonated and diprotonated) of the ligand, nuclear independent chemical shift [NICS(0)] calculations were also performed (See Figure 2).

Figure 2.



These studies first aimed to see if the correct structural representation of the imidazolium ring could be ascertained (See Figure 2A), and secondly it probed whether or not the imidazole ring was housing the positive charge, a sign that electron density was transferred to the coordinating atom (N<sub>1</sub> or N<sub>1</sub>').

Looking at Figure 1A we see two potential resonance forms, with the latter (full circle dashed line) representing increased delocalization of the positive charge and therefore a stronger driving force for transferring electron density out of the heterocycle relative to the other resonance form. To gain insight into this, two things were looked at, 1) the NICS of both rings in the ligand for every analog, and 2) the proton shift of the chemically equivalent protons bound to carbons C<sub>2</sub> & C<sub>3</sub> or C<sub>2</sub>' & C<sub>3</sub>'. There is a clear trend as you move from unprotonated → monoprotonated → diprotonated both in the <sup>1</sup>H shifts and in the NICS values. While the NICS values of protonated analogs produce values suggestive of aromaticity, the chemical shifts are not quite as convincing. While the protons become more deshielded as you add protons, the values are on the low-end of what one might consider the "aromatic region," and one could argue that the deshielding of the protons is due to the proximity of the protons to the [N<sub>2</sub>C<sub>1</sub>N<sub>3</sub>]<sup>+</sup> moiety. Either way, the evidence is at least clear on the fact that when the N<sub>1</sub> (or N<sub>1</sub>' or both) atom coordinates to a Lewis acid, the bonding clearly changes in the heterocycle. Looking at the second question (is there evidence for positive charge formation in the heterocycle) the evidence is pretty convincing that yes, there is. If you juxtapose the bond lengths of the three C-N bonds in all three analogs a clear pattern emerges, and that is that the C<sub>1</sub>-N<sub>1</sub> bond lengthens upon protonation (decrease in bond order), while the C<sub>1</sub>-N<sub>2</sub> and the C<sub>1</sub>-N<sub>3</sub> bonds shorten (increase in bond order) upon protonation. Both of these observations are consistent with positive charge formation in the heterocycle, and are also consistent with other observations (not discussed here due to space limitations). The conclusions that can clearly be drawn from the data in the table of Figure 2 are that 1) coordination of the N to a Lewis acid precipitates cation formation in the heterocycle and is evidence for electron density buildup at the coordinating N site, and 2) that without further evidence it is likely more appropriate to represent the positive charge in the heterocycle as shown on the left of Figure 2A.