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Facial Rhenium Tricarbonyl Complexes with Modified DII Ligands

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Abstract

   Over the course of this semester, promising preliminary research into a novel area of inorganic chemistry has been underway. Multiple different bis(arylimino)isoindolines (BAI), a compound made from the disubstitution of diiminoisoindoline with aryl amines to form planar tridentate ligands, were tested to determine if the structure could be forcefully bent to fit a facial binding mode. It was theorized that the bending of the usually planar chelate would cause an electronic change, destabilizing the orbitals. Different synthetic techniques were explored allowing the formation a new BAI, 1,3-bis(3-pyrazolylimino)isoindoline which was characterized via X-ray crystallography, as well as a few previously reported BAIs which were characterized by NMR spectroscopy. Then, attempts were made to complex these BAIs with the rhenium(I) tricarbonyl subunit. Success was found with 1,3-bis(2-pyridylimino)isoindoline (BPI) when 1,3-bis(2-pyridylimino)isoindoline-fac-tricarbonylrhenium(I) ([Re(CO)3(BPI)]) was successfully synthesized and characterized by X-ray crystallography. Results indicate that the azole class of BAIs undergo too much stress when attempting to facially bind to the metal center, causing the cleavage of one of the aryl arms of the chelate. Future work will involve the investigation into BAIs similar to BPI as well as characterization involving DFT and TD-DFT studies.

Introduction

   Ever since the first synthesis of diiminoisoindoline (DII) in the 1950s, multidentate isoindoline derived ligands have been shown to bind strongly to a variety of metal centers.[1–3] The chemistry of DII substituted with primary amines has been extensively explored, and reliable synthetic methods have been developed and reported.[4–6] The first widely accepted and useful synthetic method was developed by Sir Reginald Patrick Linstead and John Arthur Elvidge in 1952. Their method, later known as the Linstead method, involved a reaction at reflux between DII and two equivalents of a primary aryl or alkyl amine.[4,5] Then, in 1976, Walter O. Siegl published his work on finding a synthetic method which accomplished the same goal as Linstead and Elvidge's method, but with a better success rate with aryl amines. The new method involved refluxing phthalonitrile with two equivalents of an aryl amine, with the addition of a catalyst such as anhydrous calcium chloride.[6] The resulting products of either of these methods involving an aryl amine are disubstituted diiminoisoindoline compounds known as bis(arylimino)isoindolines, or BAIs. **Figure 1** shows the layout of both the Linstead method and the Siegl method. These planar tridentate chelates have been shown to avidly bind to a variety of metal centers, and they tend to keep their rigid planar geometry when binding.[1,2]
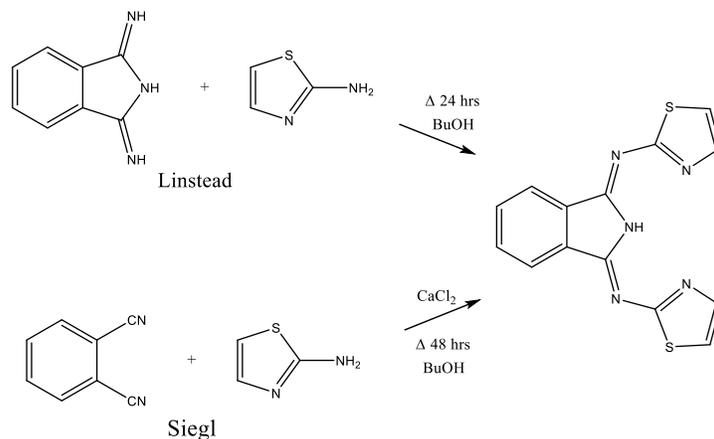
Figure 1: The Linstead method (top) and the Siegl method (bottom) for the synthesis of 1,3-bis(2-thiazolylimino)isoindoline.

Rhenium, the third-row, group seven transition metal, in the +1 oxidation state, has six binding sites and an octahedral geometry. As discussed in any inorganic course, three of the same ligand can bind to an octahedral metal center either in a facial or meridional geometric conformation[7]. A facial conformation occurs when all of the three ligands are adjacent to both of the other two ligands, generally at or close to a 90° angle. A meridional conformation takes place when the ligands and the metal center all in the same plane. This same rule set applies to one tridentate ligand in place of three identical ligands, as well. The rhenium(I) tricarbonyl subunit is particularly interesting, as three carbonyl ligands almost always favor the facial conformation. This in turn guarantees that the remaining three binding sites are also in a facial conformation.

In this study, usually planar tridentate BAIs are first synthesized, and then combined with the facial coordination chemistry of the rhenium(I) tricarbonyl subunit. The BAIs that will be synthesized and used are shown below in **Figure 2**. In order to fit the facial binding sites on the metal center, the BAI must deform and bend out of its electronically preferred planar state. This, in theory, should destabilize the ligand orbitals and opens up the possibilities for these contorted complexes as photosensitizers or dyes in industrial or medicinal applications.[8]
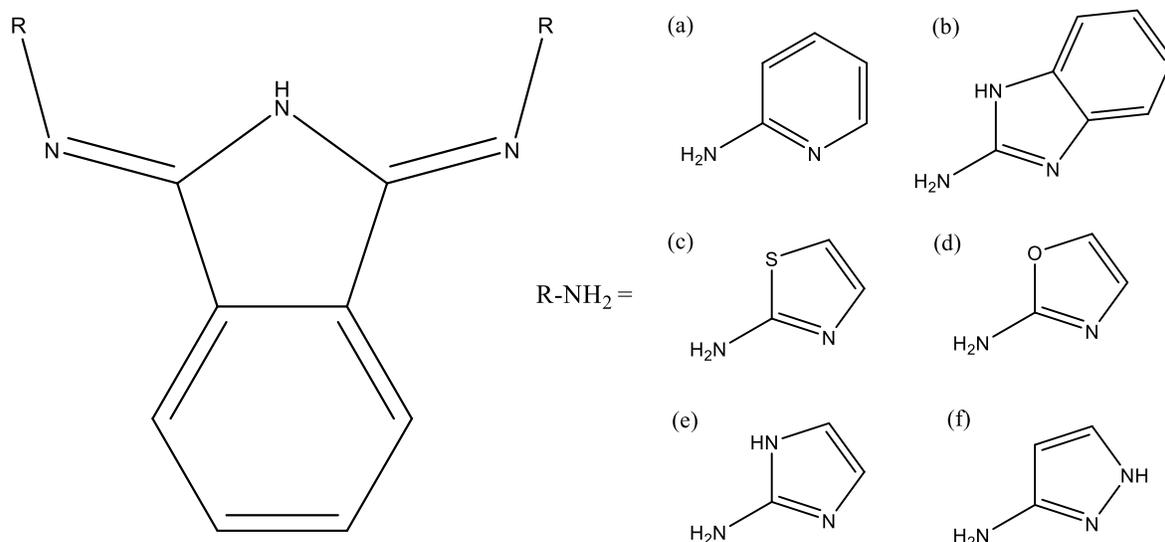
Figure 2: Diiminoisoindoline structure as well as the structure of each of the aryl amines that are to be disubstituted onto the ligand to form BAIs.

Materials and Methods

All reagents were purchased from commercial vendors with the exception of diiminoisoindoline and all were used without further purification. Diiminoisoindoline (DII) was previously synthesized by group members for use in synthesis. Rhenium(I) pentacarbonyl chloride (98%) was provided by Acros Organics. Rhenium(I) pentacarbonyl bromide (98%) was provided by Strem Chemicals. Phthalonitrile (98%) was provided by Alfa Aesar. 2-Aminopyridine (>99.0%) was provided by TCI. 2-Aminobenzimidazole (99.16%) was provided by Chem-Implex International. 3-Aminopyrazole (98%) was provided by Accela. 2-Amino-4-picoline (99%) was provided by Aldrich Chemical Company. 2-Aminoimidazole sulfate was provided with no listed purity by Oakwood Chemical. 2-Aminooxazole was provided with no listed purity by Oakwood Chemical. Synthesis of the BAI ligands follow previously reported methods such as the Siegl method and the Linstead method,[4,6] although simple melt reactions were employed using a sand bath, as well. All synthesis of the rhenium complexes utilized refluxing. All NMR spectra were gathered using a 300 MHz NMR spectrometer, and all crystallographic structures were collected and mounted on a cryoloop with paratone oil and cooled using nitrogen at 100K for analysis using a Bruker Apex Duo X-ray Diffractometer with SADABS and SHELXTL software. Table 1 lists the X-ray data collection and crystal structure parameters for the four compounds elucidated in this report.

Compound	1,3-bis(3-pyrazolylimino)isoindoline	[Re(CO)$_3$(BPI)]	Complex B	Complex P
Emp. form	C$_{31}$H$_{29}$N$_{15}$O	C$_{21}$H$_{12}$N$_5$O$_3$Re	C$_{25}$H$_{17}$Cl$_l$N$_7$O$_5$Re	C$_{19}$H$_{19}$Cl$_l$N$_7$O$_5$Re
Form. weight	627.69	568.56	717.10	647.06
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	P2$_1$/c	P2$_1$/m	P-1	P2$_1$/c
a/ Å	10.2918(2)	6.7522(2)	8.3081(6)	8.7309(6)
b/ Å	18.5703(3)	15.3489(4)	10.7850(8)	14.7224(10)
c/ Å	15.8997(2)	9.0349(3	15.5026(11)	17.5714(12)
α(°)	90	90	76.467(5)	90
β(°)	98.5810(10)	106.1680(10)	87.408(5)	90.138(4)
γ(°)	90	90	72.151(5)	90
Volume (Å^3)	3004.76(9)	899.33(5)	1284.98(17)	2258.6(3)
Z	4	2	2	4
Dc (Mg/m^3)	1.388	2.100	1.853	1.903
μ (mm^{-1})	0.759	13.537	4.883	5.545
F(000)	1312	544	696	1256
Reflections collected	18150	5922	18867	21943
Data/Restraints/Parameters	5250 / 0 / 438	1581 / 12 / 142	4611 / 0 / 356	5653 / 0 / 300
GOF on F^2	1.033	1.011	1.046	1.038
R1 (on F$_o{}^2$, I > 2σ(I))	0.0543	0.0269	0.0511	0.0364
wR2 (on F$_o{}^2$, I > 2σ(I))	0.1483	0.0712	0.0993	0.0734
R1 (all data)	0.0660	0.0270	0.0806	0.0539
wR2 (all data)	0.1583	0.0713	0.1108	0.0799

Table 1: X-ray data collection and crystal structure parameters for 1,3-bis(3-pyrazolylimino)isoindoline, [Re(CO)$_3$(BPI)], Complex B and Complex P.

Synthesis of 1,3-bis(2-benzimidazolylimino)isoindoline (**Scheme 1**): Diiminoisoindoline (0.500 g, 3.44x10^{-3} mol) and 2-aminobenzimidazole (0.923 g, 6.93x10^{-3} mol) were reacted in 25.0 mL of 1-butanol via Linstead's method.[4] Solid product was filtered from solution via vacuum filtration and placed in the oven to dry for three hours. The final product (0.331 g) was obtained in 25.5% yield. ^{1}H NMR (300 MHz, DMSO-d6): δ = 7.30 ppm (t, 4H, C-H), 7.58 ppm (s, 4H, C-H), 7.86 ppm (q, 2H, C-H) 8.06 ppm (q, 2H, C-H), 12.81 ppm (s, 1H, N-H).

Synthesis of 1,3-bis(2-thiazolylimino)isoindoline (**Scheme 2**): Phthalonitrile (0.499 g, 3.89x10^{-3} mol,) and 2-aminothiazole (0.783 g, 7.82x10^{-3} mol) were reacted via melt reaction in a tapered round bottom flask in a sand bath at 180°C. The solids were then dissolved in DMF, and DI water was added to precipitate the product. Solid product was filtered from solution via vacuum filter and left in hood to dry. The final product (0.282 g) was found in 23.4% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.22 ppm (d, 2H, C-H), 7.27 ppm (s, solvent), 7.68 ppm (q, 2H, C-H), 7.79 ppm (d, 2H, C-H), 8.02 ppm (q, 2H, C-H), 13.46 ppm (s, 1H, N-H).

Synthesis of 1,3-bis(3-pyrazolylimino)isoindoline (**Scheme 3**): Phthalonitrile (0.508 g, 3.96×10^{-3} mol) and 3-aminopyrazole (0.690 g, 8.30×10^{-3} mol) were reacted via melt reaction in a round bottom flask in a sand bath at 125°C. The solids were then dissolved in DMF, and DI water was added to precipitate the product. Solid product was filtered from solution via vacuum filter and left in hood to dry. The final product (0.841 g) was obtained in 76.5% yield. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 2.50$ ppm (m, solvent), 3.33 ppm (s, water), 6.34 ppm (s, 2H, C-H), 7.70 ppm (2H, C-H), 7.78 (s, 2H, C-H), 7.94 ppm (m, 2H, C-H), 8.14 ppm (phthalonitrile), 11.90 ppm (s, 1H, N-H), 12.78 ppm (s, 2H, N-H). Crystals of 1,3-bis(3-pyrazolylimino)isoindoline suitable for X-ray diffraction were grown via vapor diffusion with chloroform as the solvent and hexane as the antisolvent.

Synthesis of 1,3-bis(2-pyridylimino)isoindoline (BPI) (**Scheme 4**): Phthalonitrile (1.29 g, 0.0101 mol), 2-aminopyridine (1.99 g, 0.0211 mol), and anhydrous calcium chloride (0.121 g, 0.0010 mol) were added to a flask containing 1-butanol (15.0 mL) that had been degassed with N$_2$. Under N$_2$, the reaction mixture was refluxed for 48 hours. The crude product was filtered from solution via vacuum and then dissolved in 95% ethanol. Cold DI water was added to recrystallize the product and the yellow-green precipitate was collected via vacuum pump in 59% yield. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 2.50$ ppm (m, solvent), 3.33 ppm (s, water), 7.29 ppm (td, 2H, C-H), 7.48 ppm (d, 2H, C-H), 7.77 ppm (q, 2H, C-H), 7.93 ppm (td, 2H, C-H), 8.03 ppm (q, 2H, C-H), 8.74 ppm (m, 2H, C-H), 14.00 ppm (s, 1H, N-H).

Both 1,3-bis(2-oxazolylimino)isoindoline and 1,3-bis(2-imidazolylimino)isoindoline were unable to be synthesized either by the Linstead method or by melt reaction with phthalonitrile.[4]

Synthesis of 1,3-bis(2-pyridylimino)isoindoline-fac-tricarbonylrhenium(I) ([Re(CO)$_3$(BPI)]) (**Scheme 5**): Rhenium(I) pentacarbonyl chloride (0.0515 g, 1.42×10^{-4} mol) and BPI (0.041 g, 1.46×10^{-4} mol) were added to a flask with toluene (4.0 mL). The solution was refluxed for four hours, followed by cooling in an ice bath for one hour. A dark red precipitate formed and was collected via vacuum filtration. The product (0.0328 g) was collected in 51.0% yield. Crystals of [Re(CO)$_3$(BPI)] suitable for X-ray diffraction were grown using vapor diffusion with the solvent as chloroform and the antisolvent as cyclohexane.

Synthesis of 2-aminobenzimidazolium[(1-(2-benzimidazolylimino)-3-oxoisoindoline)-fac-tricarbonylchlororhenate(I)] (Complex B) (**Scheme 6**): 1,3-bis(2-benzimidazolylimino)isoindoline (0.0530 g, 1.40×10^{-4} mol) and rhenium(I) pentacarbonyl chloride (0.0498 g, 1.377×10^{-4} mol) were reacted in 4.0 mL of toluene via 24 hour reflux. A dark red solid (0.0210 g) was filtered from solution via vacuum filtration. The product was obtained in 23.6% yield. Crystals of Complex B suitable for X-ray crystallography were grown via vapor diffusion with the solvent as ethanol and the antisolvent as cyclohexane.

Synthesis of [3-aminopyrazole-fac-tricarbonyl(1-(3-pyrazolylimino)-3-oxoisoindoline)rhenium(I)] chloride (Complex P) (**Scheme 7**): Rhenium(I) pentacarbonyl chloride (0.0503 g, 1.39×10^{-4} mol) was refluxed in ethanol (5.0 mL). After 30 minutes, 1,3-bis(3-pyrazolylimino)isoindoline (0.0400 g, 1.44×10^{-4} mol) was added into the reflux flask and the refluxing setup was left to run for 24 hours. The desired product was in solution, so the flask was

left out to evaporate. A red crystalline product (0.0420 g) was collected in 55.3% yield. Crystals of Complex P suitable for X-ray crystallography were formed from the slow, evaporation of ethanol.

Results and Discussion

With regard to the synthesis of the bis(arylimino)isoindoline (BAI) ligands, the most success was found with the Linstead method with 1-butanol as the solvent.[4] Melt reactions were also found to be useful, especially when the melting points of the two solids were relatively similar. The anhydrous Siegl method was the chosen reaction route for the synthesis of BPI, although success was found with the Linstead method, as well.[4] Schemes depicting each synthetic process for each BAI are gathered below (**Schemes 1-4**). For all of these reactions, ammonia is released. Temperatures for the refluxing reactions are dictated by the boiling solvent. With 1-butanol as the solvent, the temperature remained near 120°C. It should be noted that the synthesis of 1,3-bis(3-pyrazolylimino)isoindoline is quite important. This compound has not been previously reported in the literature. All work done with this tridentate BAI is new, while the rest of the BAIs synthesized have previously been characterized.
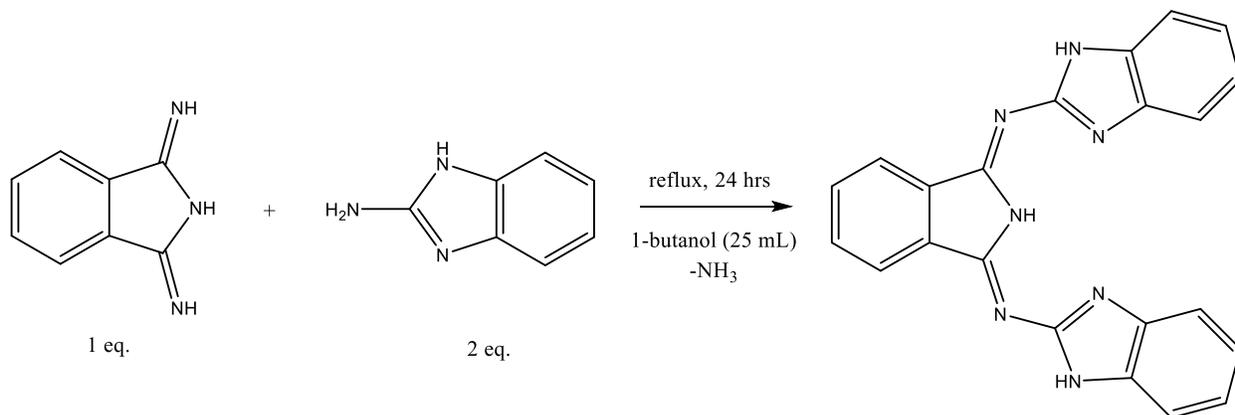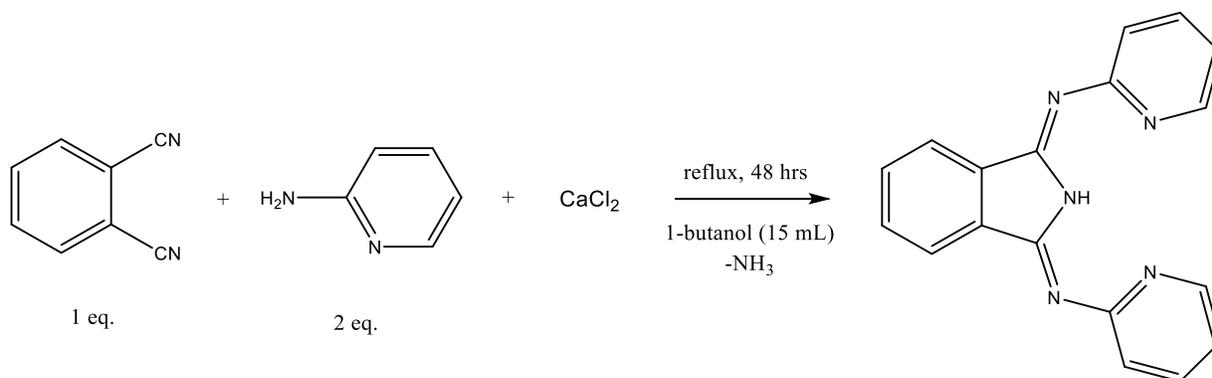

Scheme 1: The reaction layout for the synthesis of 1,3-bis(2-benzimidazolylimino)isoindoline. This layout follows the previously reported Linstead method.[4]
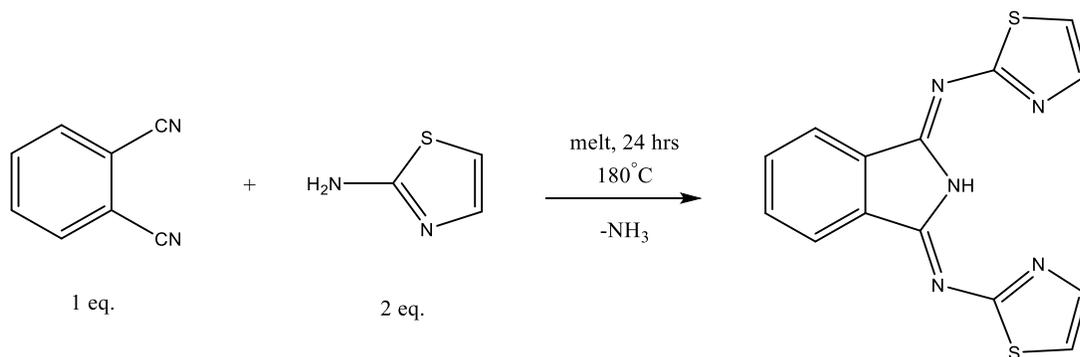
Scheme 2: The reaction layout for the synthesis of 1,3-bis(2-thiazolylimino)isoindoline.
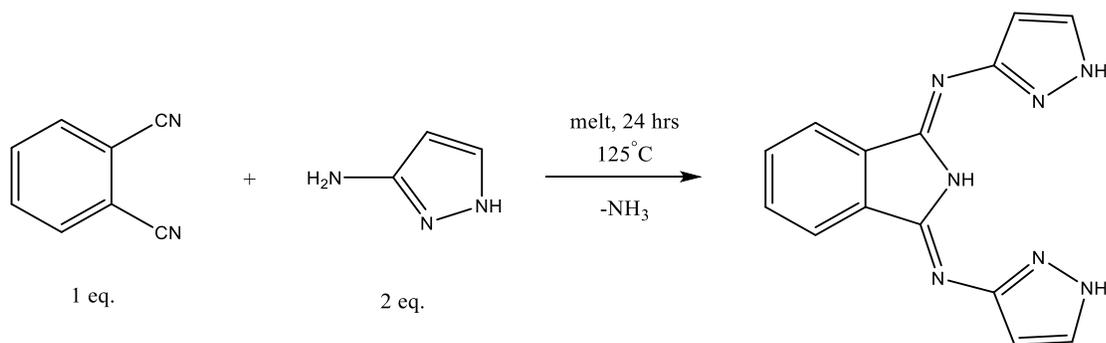
Scheme 3: The reaction layout for the synthesis of 1,3-bis(3-pyrazolylimino)isoindoline via melt reaction at 125°C for 24 hours. The crystal structure of this product is depicted in **Figure 3**.

Scheme 4: The reaction layout for the synthesis of 1,3-bis(2-pyridylimino)isoindoline (BPI). This synthetic procedure follows the previously reported Siegl method.[6]

The complexation reactions with the BAIs and rhenium(I) pentacarbonyl chloride are outlined in **Schemes 5-7**. These pathways show both the theoretical facial complex as well as the complex that was collected. For the case of BPI and Re(CO)$_3$(BPI) in **Scheme 5**, the actual complex matched the theoretical complex. **Scheme 7** employs a slightly modified reaction, utilizing a 30 minute preflux of rhenium(I) pentacarbonyl chloride in EtOH to allow for the release of the halide and two carbonyl groups. Solvent molecules (s) then fill the binding sites until 1,3-bis(3-pyrazolylimino)isoindoline is added to the reflux.
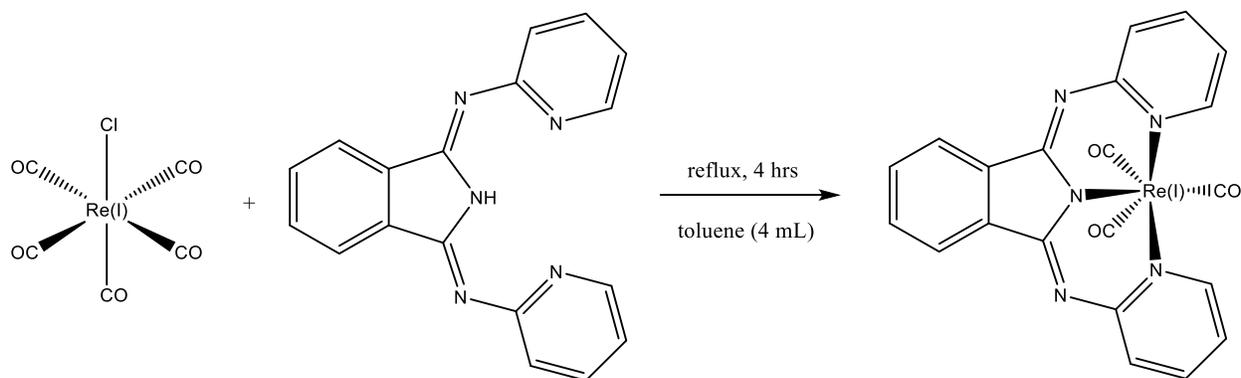
Scheme 5: The formation of the facial Re(CO)$_3$(BPI) complex from a reflux of BPI and rhenium(I) pentacarbonyl chloride. The crystal structure of this product is depicted in **Figure 4**.
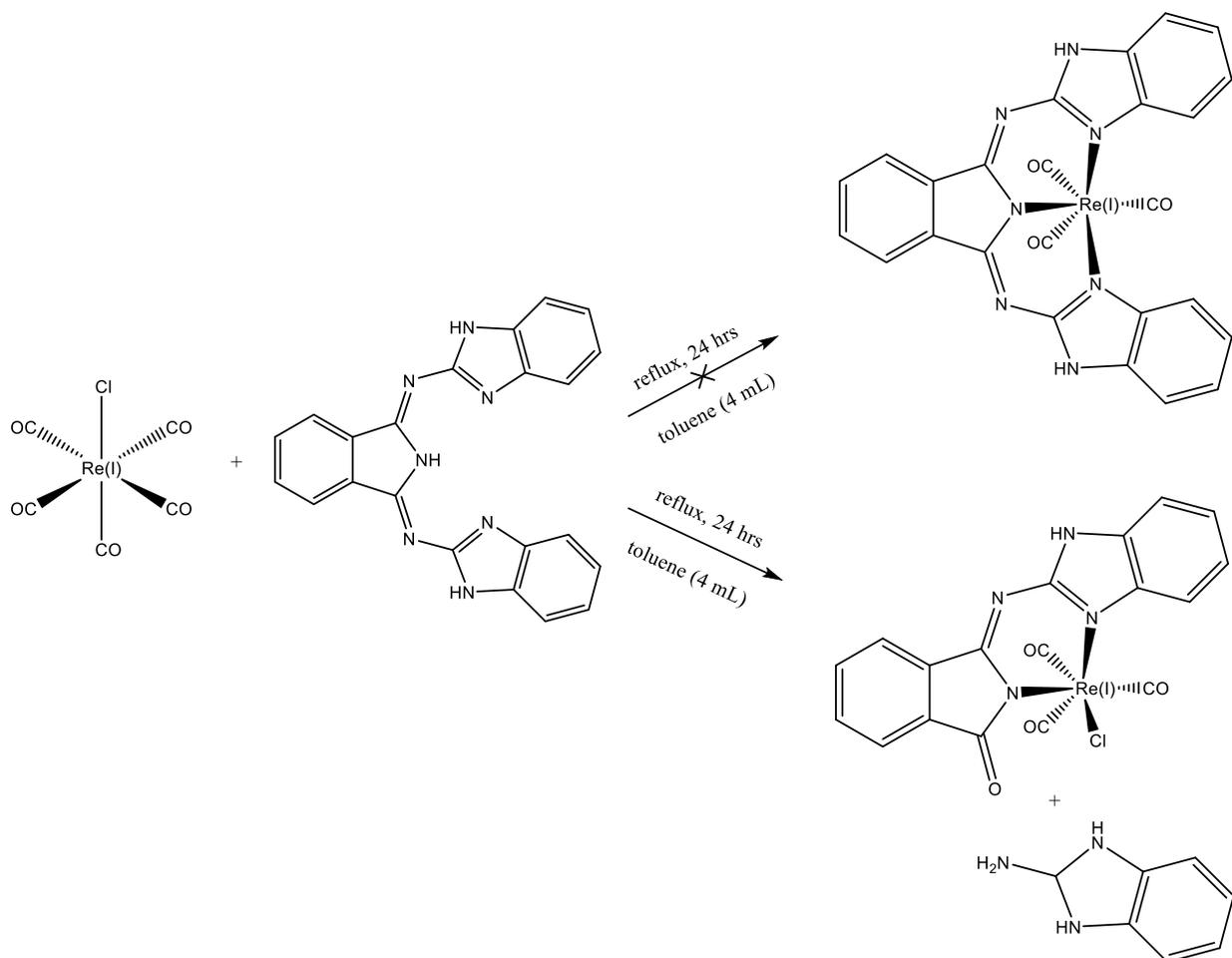
Scheme 6: The proposed complexation of 1,3-bis(2-benzimidazolylimino)isoindoline with rhenium(I) pentacarbonyl chloride. The product depicted above is the ideal product, not the actual product, Complex B, which is depicted below in the scheme.
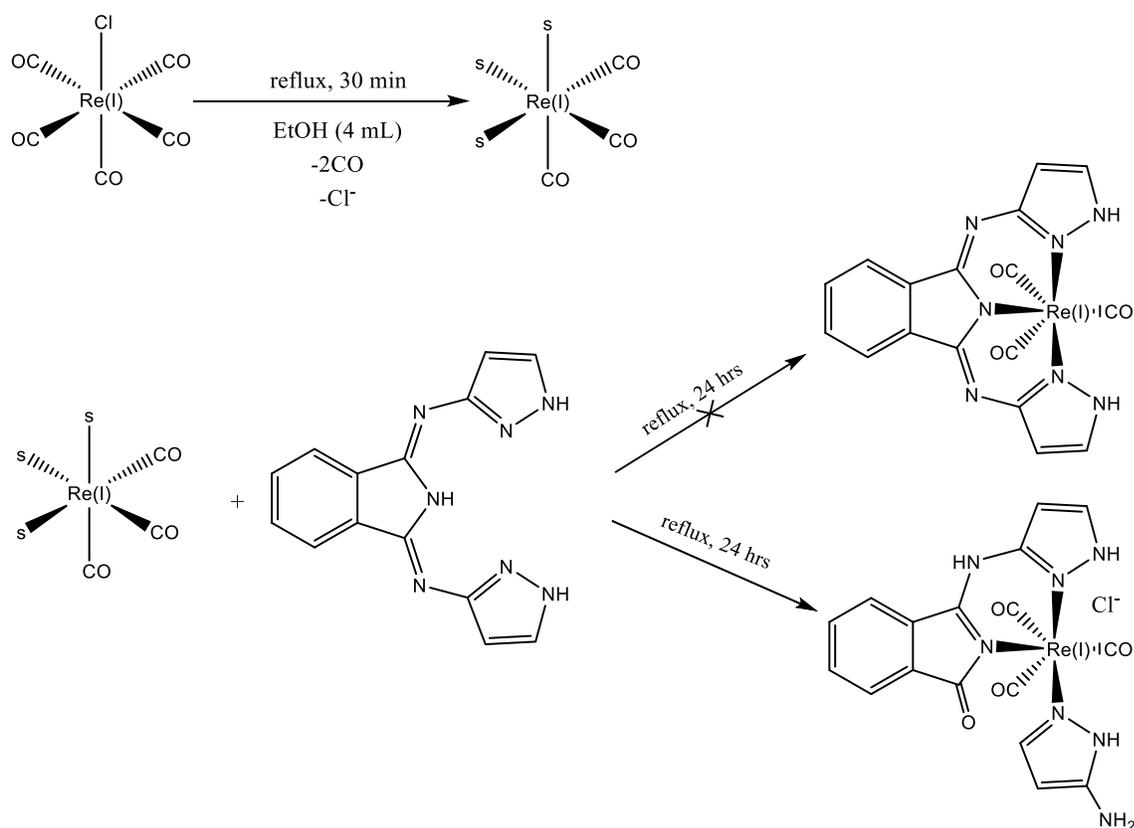
Scheme 7: The proposed multistep process of complexation of 1,3-bis(3-pyrazolylimino)isoindoline with rhenium(I) pentacarbonyl chloride. The first step involves the prereflux of rhenium(I)pentacarbonyl chloride, while the second step is the addition of the BAI. The product depicted above in the second step is the ideal product, which was not the resulting product. Complex P, which is depicted below in the scheme, was the actual product.

Attempts were made to synthesize two other novel BAIs using the aryl amines, 2-aminoimidazole and 2-aminooxazole. The 2-aminoimidazole was to be used to synthesize 1,3-bis(2-imidazolylimino)isoindoline, but the starting material was provided as the sulfate salt. Once the initial trials of the Linstead method failed, the subproject was set aside, with intentions of returning to it.[4] Time restrictions led to complete abandonment of the synthesis of this BAI. The 2-aminooxazole was used in synthetic trials following either the Linstead method or basic melt reaction protocol in order to synthesize 1,3-bis(2-oxazolylimino)isoindoline.[4] Although an extensive list of solvents and reaction lengths were tested, no stable products were formed.

When verifying the success of the synthesis of a desired BAI, ^{1}H NMR spectroscopy plays a key role. First, consider the isoindoline group. First, there is the characteristic deshielded head group N-H resonance far downfield on the spectrum, at 11 to 14 ppm. Then, there is the easily recognizable A,A',B,B' system for the aromatic hydrogen atoms. The six membered ring that is the "body" of the isoindoline contains four hydrogens, two pairs of two different hydrogens. Considering both that the two different hydrogens cause there to be two different resonances, and

the fact that there are 3 other hydrogens splitting each shift, the spectrum for this part of the molecule would show two quadruplet resonances that mirror each other. This characteristic feature can be shown within the ^{1}H NMR spectrum of each BAI synthesized. From that point, the remaining resonances are easily correlated with hydrogens on the two nitrogen-containing aryl rings of the molecule.

Figure S1a and **Figure S1b** depict the ^{1}H NMR spectrum of 1,3-bis(2-benzimidazolylimino)isoindoline. Far downfield around 12.8 ppm lies the single resonance of the N-H head group. Next, there is the signature A,A',B,B' mirrored quadruplets of the isoindoline hydrogens around 7.85 ppm and 8.1 ppm. Then, the benzimidazole arms of the ligand almost create another A,A',B,B' system around 7.3 ppm and 7.6 ppm, except the tautomerization of the hydrogen between the two nitrogens causes the uneven broadening of the two resonances, affecting the resonance representing the two hydrogens that are closer in proximity to the nitrogens more so than the further hydrogens.

Figure S2a and **Figure S2b** highlight the ^{1}H NMR spectrum of 1,3-bis(2-thiazolylimino)isoindoline. The N-H head group resonance is show around 13.5 ppm. The A,A',B,B' system quadruplets are shown near 7.7 ppm and 8.0 ppm, while the thiazole C-H bond that is adjacent to the sulfur atom is represented by the doublet shift at 7.8 ppm, and the thiazole C-H bond that is adjacent to the nitrogen atom is represented by the doublet at 7.2 ppm.

Figure S3a shows the ^{1}H NMR spectrum of 1,3-bis(3-pyrazolylimino)isoindoline. There are two resonances far downfield, the isoindoline N-H at 11.9 ppm and the pyrazole N-H bonds at 12.8 ppm. Around where the A,A',B,B' system is located, there is also evidence of phthalonitrile leftover in our product at this stage, suggesting that purification was needed. The remaining shift at 6.3 ppm pertains to the C-H in the pyrazole rings.

Figure S4a and **Figure S4b** both contain the ^{1}H NMR spectrum of BPI. The two quadruplets, one at 7.8 ppm and the other just downfield of 8.0 ppm, refer to the A,A',B,B' system of the isoindoline C-H bonds. Then we have four remaining multiplets, and four corresponding pyridine C-H bonds. The triplets of doublets at 7.29 ppm and 7.92 ppm refer to the two C-H bonds that are adjacent to two more C-H bonds. The other two shifts then are the C-H bonds that are adjacent to one C-H bond as well as either a nitrogen atom or a C-N bond. Lastly, the resonance at 14.00 ppm represents the N-H.

The crystallographic analysis of 1,3-bis(3-pyrazolylimino)isoindoline was the next step in the characterization of the BAI. The crystallographic structure (**Figure 3**) resembles the rest of the BAIs used in this project, with a planar geometry and the nitrogen atoms of the heterocyclic aryl rings facing inward. All crystallographic and structural refinement data for this compound can be found in **Table 1**.
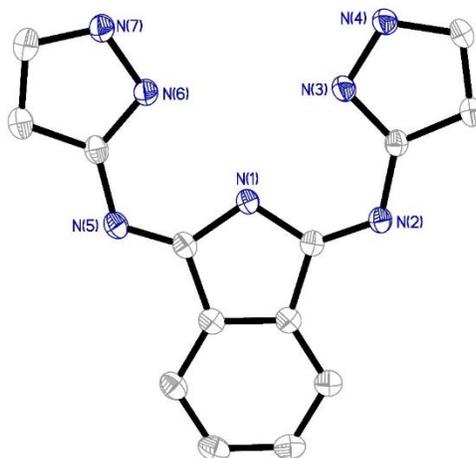
Figure 3: The structure of 1,3-bis(3-pyrazolylimino)isoindoline with 35% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Looking to the crystallographic structure of first the complex $Re(CO)_3(BPI)$ in **Figure 4**, the successful binding of the tridentate ligand in the facial conformation is shown. The monoanionic nature of the deprotonated isoindoline nitrogen stabilizes the monocationic metal center, allowing the complex to be neutral in charge.
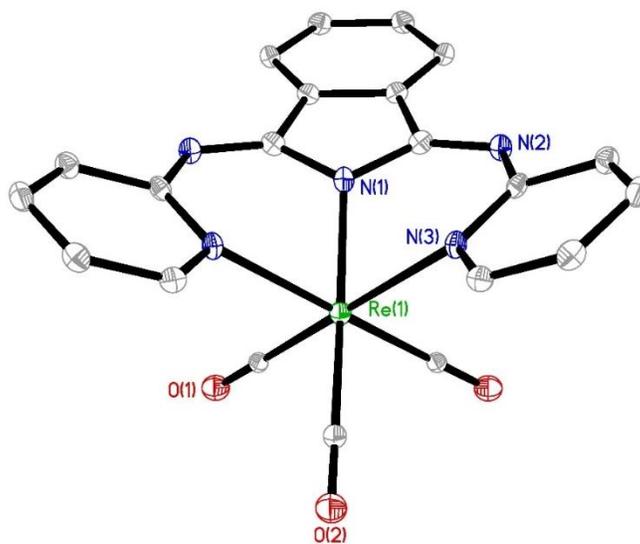
Figure 4: The structure of $Re(CO)_3(BPI)$ with 35% thermal ellipsoids. Hydrogen atoms are omitted from this structure for clarity.

The crystallographic structure of the attempt to complex 1,3-bis(2-benzimidazolylimino)isoindoline with the rhenium(I) pentacarbonyl chloride can be found in **Figure 5**. The structure suggests that the use of a nonpolar solvent did not allow the halide to leave the complex, therefore only two binding sites to the metal center were open. This in turn caused

the benzimidazole BAI to undergo hydrolysis and cleave one of the benzimidazole arms. Interestingly, the structure shows that the detached aminobenzimidazole, being protonated and therefore positive in charge, remains in the asymmetric unit to balance the charges. This result motivated the use of prereflux in polar solvents for all future reactions to allow for the removal of the halide and two carbonyls from rhenium(I) pentacarbonyl chloride. All crystallographic and structural refinement for this complex data can be found in **Table 1** in the SI.
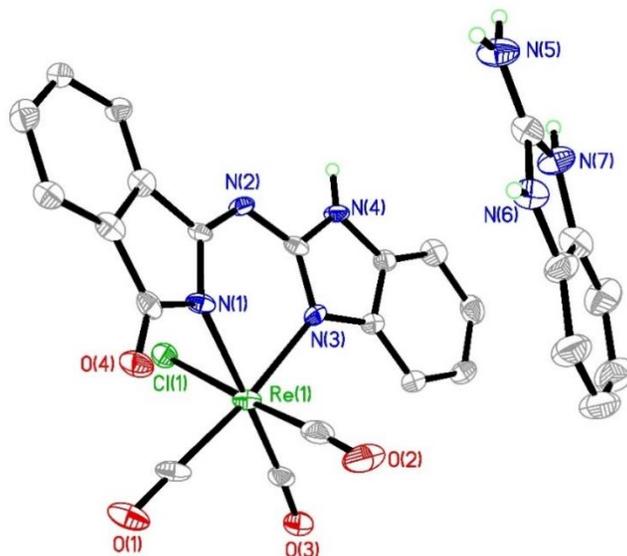
Figure 5: The structure of Complex B, the product from the reaction of $Re(CO)_5Cl$ and 1,3-bis(2-benzimidazolylimino)isoindoline in nonpolar toluene with 35% thermal ellipsoids. Hydrogen atoms on carbon positions have been omitted for clarity.

Finally, **Figure 6** shows the crystallographic structure of the product of the complexation reaction of 1,3-bis(3-pyrazolylimino)isoindoline with rhenium(I) pentacarbonyl chloride. The use of a polar solvent helped to induce the release of the halide from the complex, but the strain of the facial binding conformation induced hydrolysis, cleaving the bond connecting one of the pyrazole units to the isoindoline. Note that the remaining bridging nitrogen is protonated, neutralizing the charge of the bidentate ligand. Because of this, the complex remains monocationic, allowing the chloride ion to remain in the structure to balance the charge. All crystallographic and structural refinement data for this complex can be found in **Table 1** in the SI.

Figure 6: The structure of Complex P, the product from the reaction of Re(CO)$_5$Cl and 1,3-bis(2-pyrazolylimino)isoindoline with 35% thermal ellipsoids. Note that because of the hydrolysis and cleavage of the bridging bond, the solo 3-aminopyrazole is bound by N1 (N5 in the figure) and not N2 (N6 in the figure). Hydrogen atoms on carbon positions have been omitted for clarity.

Conclusion

Over the course of the semester, different bis(arylimino)isoindolines have been synthesized using techniques from the literature with the goal of facially binding these tridentate chelates to the rhenium(I) tricarbonyl subunit. This was done with the hope that the contorted binding would cause the destabilization of the bonding orbitals, opening the door for applications as dyes or photosensitizers.

Results indicate that the azole subclass of ligands is too prone to hydrolysis. The cleavage of the bond between the isoindoline and the bridging nitrogen is more favorable than the bent state of a facial tridentate ligand. The BPI ligand, however, was indeed able to bend and fit into the facial state. When comparing the two, it could be possible that the angle between the three binding nitrogens of a tridentate BAI with five-membered heterocyclic aryl rings, such as the ones synthesized with the azoles, is slightly too tight as opposed to a tridentate BAI with six-membered heterocyclic rings, such as BPI. Although no theory investigations have been carried out yet, it can be hypothesized that the bending of the BPI ligand has red-shifted the absorption spectrum by destabilizing the orbitals.

With the success of the BPI ligand, future work will continue in the same direction. BAIs containing substituted pyridine rings will be in the focus, as well as similar six-membered heterocyclic rings. It is also possible that more work will be put into the synthesis and characterization of new BAIs, as well as the continuation of characterization of semi-characterized ligands such as 1,3-bis(3-pyrazolylimino)isoindoline. As progress is made, both DFT and TD-DFT will be employed to quantify the orbital energies and other properties of the facially bent tridentate BAI ligands.

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