Chapter 5

THE UNPRECEDENTED REACTIVITY OF AMMINE-LIGATED IRIDIUM CORROLES

In April of 2009, Theis Brock-Nannestad, a graduate student from Jesper Bendix' group at the University of Copenhagen, showed up in the Gray group to fulfill a Danish Ph.D. requirement mandating a six-month period of study in a foreign lab. During that time, we worked extensively on two main projects: one, the briefer, involved the development of an optimized synthesis of H_3tpfc, and mostly acted as a facilitator of our inorganic research by allowing us to produce unprecedentedly large amounts of corrole at once; the other project, which will be discussed here, began with an idea for the development of high-valent nitridoiridium corroles and ended with the synthesis of a novel porphyrinoid molecule. Throughout the course of this research project, I was introduced to a number of new techniques, including the safe use of corrosive gasses (ammonia in particular) and a battery of 2D NMR experiments. Atif Mahammed, a postdoctoral fellow in Zeev Gross' lab, was instrumental in developing some of the initial synthetic procedures which eventually led us to the formation of our new porphyrinoids. Additionally, David Vandervelde and Scott Virgil, two Caltech staff scientists, contributed important expertise to the project. David introduced me to a number of useful 2D NMR experiments, and Scott allowed Theis to use his HPLC for a very long and messy separation.

The Unprecedented Reactivity of Ammine-Ligated Iridium Corroles

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Corroles, macrocycles similar to porphyrins but possessed of lower symmetry and greater electron density, have often been posited as scaffolds for the synthesis and stabilization of high-valent metal complexes.[1] This goal has been achieved in numerous cases, especially with the first-row transition metals chromium and manganese,[2] which can both be induced to form stable oxometallocorrole complexes under fairly gentle treatment. Other claimed high-valent metallocorrole complexes, notably those of iron(IV)[3] and cobalt(IV),[4] have been subjects of controversy when detailed studies suggested they could more accurately be described as oxidized corrole radicals complexed to lower-valent metal centers.[5]

We have added a new entry to the list of high-valent metal-corrole complexes with our report of two Ir(III) corrole complexes[6] best characterized as possessing iridium(IV) central metal ions and unionized corrole ligands when they are oxidized.[7] In this report, we showed that UV-vis absorption and electron paramagnetic resonance spectroscopy are both consistent with a paramagnetic metal center possessing a rhombic ligand field. Recent computational results from our group have cast some doubt on the original experimental findings,[8] but the overall picture is of an oxidation event that produces a state with partial Ir(IV) and partial corrole radical character.[9]

Our published results suggest that corroles can provide a welcoming environment for iridium(IV) complexes, but they do not provide significant insight into the potential for developing possible catalysts with Ir(V) or even higher-valent central metals. Our original targets for such compounds comprised both oxoiridium(V) and (bis)oxoiridium(VII) corrole complexes, but these species have proven elusive. In an attempt to create alternative high-valent iridium compounds, namely nitridoiridium(VI) corroles, we have synthesized and fully characterized the ammine-ligated iridium 5,10,15-(*tris)*pentafluorophenylcorrole complex **1-Ir(NH$_3$)$_2$** (Figure 5-1) and its fully brominated analogue **1b-Ir(NH$_3$)$_2$**. Their surprising reactivity is discussed below.

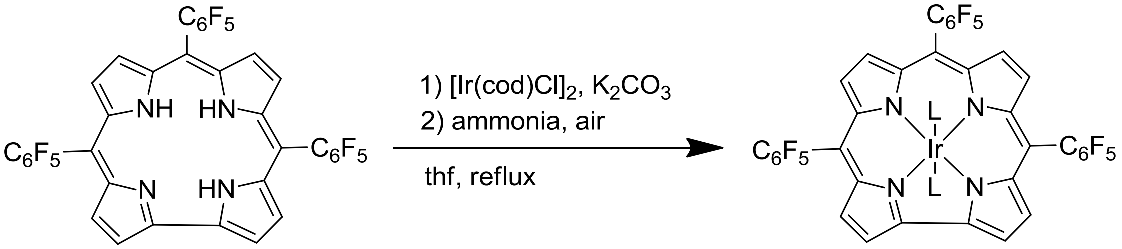


Figure 5-1: Synthesis of **1-Ir(NH$_3$)$_2$**. Conversion to **1b-Ir(NH$_3$)$_2$** could be achieved by stirring in C_6H_6 with Br_2 for a period of hours.

The synthesis of the ammine-ligated complexes was achieved in analogy to the published procedures for synthesis of our previous corrole complexes.[7] In the case of **1-Ir(NH$_3$)$_2$**, gaseous ammonia is run through the solution after the initial iridium insertion step. **1b-Ir(NH$_3$)$_2$** can then be synthesized in essentially quantitative yield by stirring **1-Ir(NH$_3$)$_2$** with an excess of elemental bromine in benzene for 2 hours. The complexes are green in solution, and display UV-vis absorption spectra similar to the known complex **1-Ir(py)$_2$** (py = pyridine).[7] The crystallographically determined axial Ir-N bond lengths (Figure 5-2) are quite a bit shorter for **1-Ir(NH$_3$)$_2$** as compared to **1-Ir(tma)$_2$** (tma = trimethylamine; the equatorial Ir-N bond lengths are equivalent within error), in line with the computed geometries published previously by our group. This is in spite of the stronger sigma-donating capability of the methylated ligand, so we assume the greater steric encumbrance of the methyl groups on tma leads to the longer bond length.

The ^{1}H NMR of **1-Ir(NH$_3$)$_2$** (Figure 5-3) shows a standard pattern of four doublets corresponding to the eight ring protons and a large upfield resonance (δ = -4.057 ppm) corresponding to the ammine protons. The ^{1}H NMR of **1b-Ir(NH$_3$)$_2$** also contains this peak, whose identity can be confirmed by comparison of its ^{15}N-^{1}H coupling magnitude to a ^{15}N-^{1}H HSQC NMR spectrum of **1-Ir(NH$_3$)$_2$** (Figure 5-4).

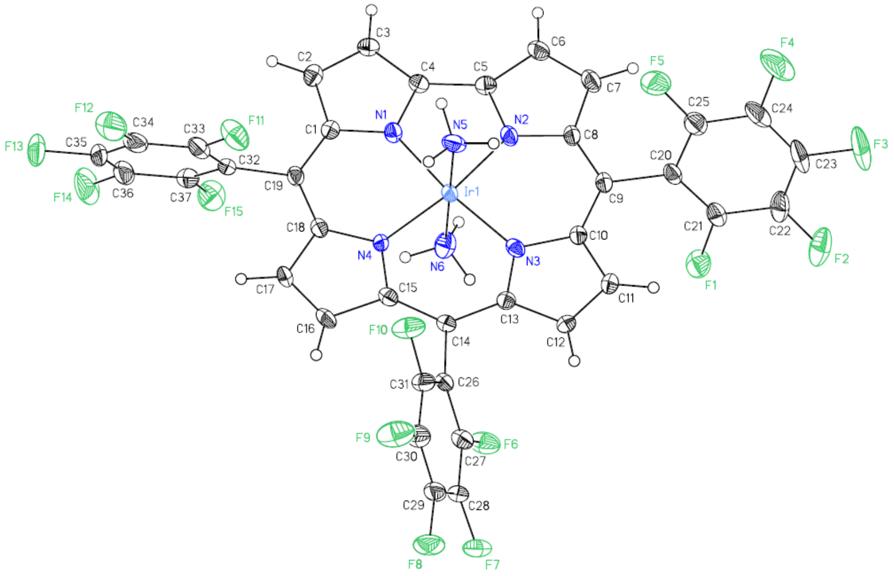


Figure 5-2: X-ray diffraction structure of **1-Ir(NH$_3$)$_2$**. Ir-N equatorial bond lengths average 1.964 Å and Ir-N axial bond lengths average 2.074 Å. In **1-Ir(tma)$_2$**, these bond lengths average 1.965 and 2.185 Å, respectively**.**

In line with the shorter axial Ir-N bonds in the ammine-ligated system, **1-Ir(NH$_3$)$_2$** is also more easily oxidized ($E_{1/2}$ = 0.53 V vs. SCE) than either **1-Ir(tma)$_2$** or **1-Ir(py)$_2$** ($E_{1/2}$ = 0.66 and 0.69 V vs. SCE, respectively), implying greater electron density on both the central metal and the ring. Like the published corroles **1-Ir(tma)$_2$**, **1b-Ir(tma)$_2$**, and **1-Ir(py)$_2$**, **1-Ir(NH$_3$)$_2$** and **1b-Ir(NH$_3$)$_2$** are luminescent in the near-IR, although their emission is slightly red-shifted compared to the previously reported complexes.

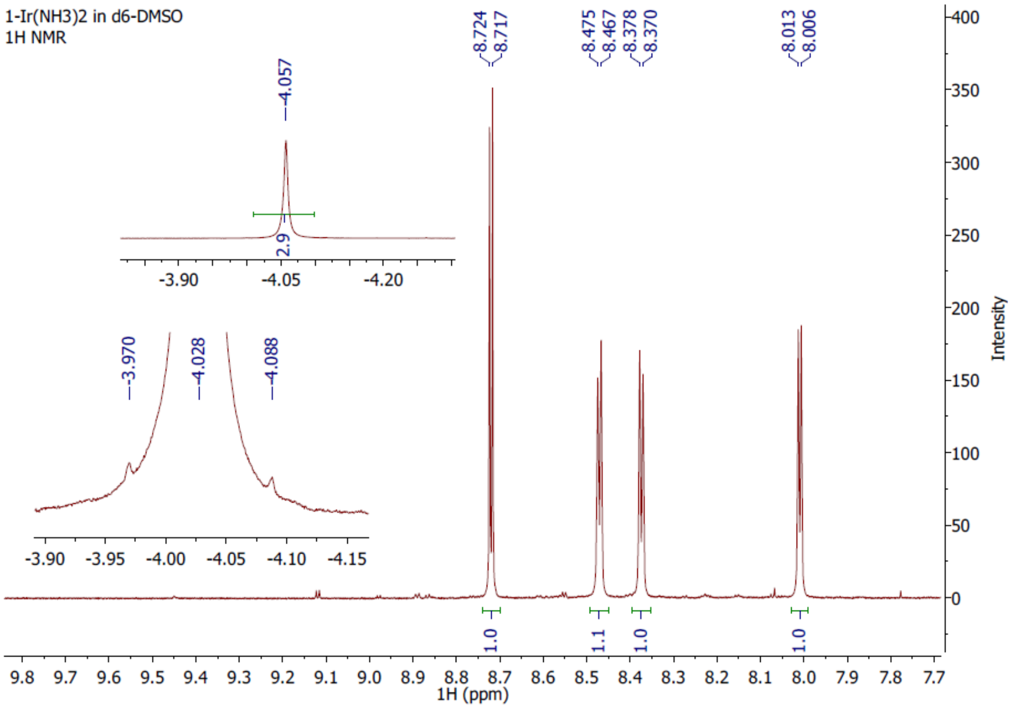


Figure 5-3: ^{1}H NMR of **1-Ir(NH$_3$)$_2$** in d^6-DMSO. The top inset shows the resonance peak corresponding to the ammine ligand protons, while the bottom inset shows the corresponding peak for **1b-Ir(NH$_3$)$_2$**, zoomed in so that the 71 Hz ^{15}N-^{1}H coupling to the ammine nitrogen is clearly visible.

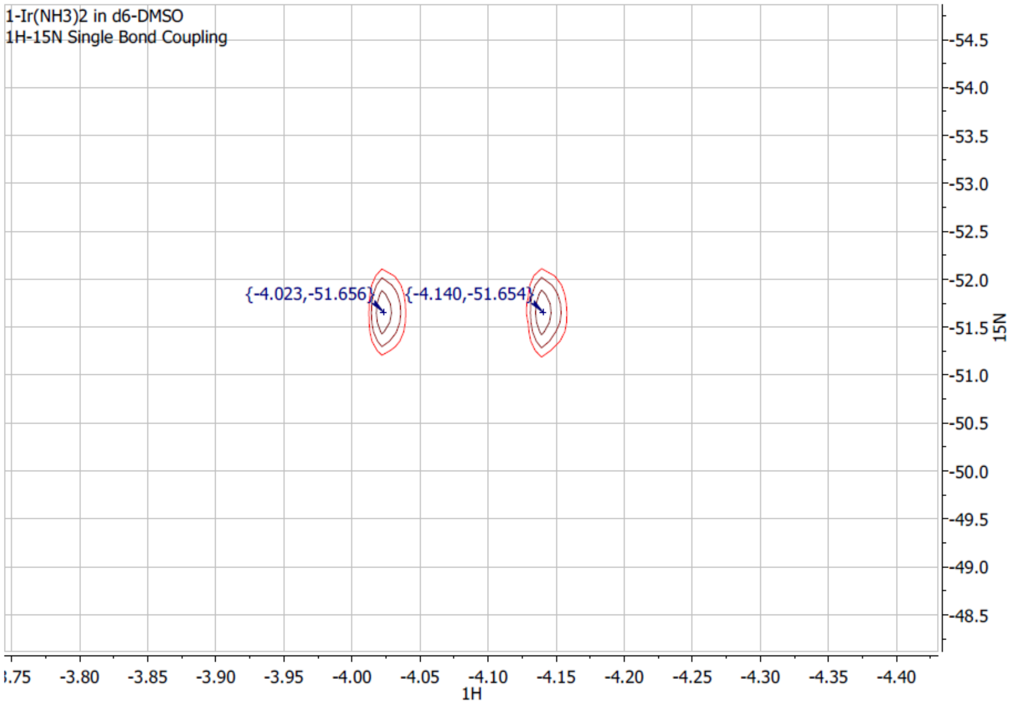


Figure 5-4: Natural abundance ^{15}N-^{1}H HSQC of **1-Ir(NH$_3$)$_2$** in d^6-DMSO, showing the 71 Hz coupling between the ammine nitrogen and protons

The CV of **1-Ir(NH_3)$_2$** (Figure 5-5) shows two anodic waves in methylene chloride solution, one of which (0.53 V vs. SCE) is essentially reversible (though this wave becomes irreversible in CH_3CN, presumably due to ligand substitution on the oxidized species) and the other of which (1.13 V vs. SCE) displays scan rate dependent reversibility. The first oxidation appears to produce a mixed Ir(IV)-corrole π-cation radical, with similar EPR and spectroelectrochemical signatures to the one-electron oxidized form of **1-Ir(tma)$_2$**. We reasoned that the more anodic wave might represent the formation of an Ir(V) compound, with the irreversibility being caused by loss of either ammonia protons or an ammine ligand, and we attempted to chemically oxidize the corrole and isolate the resulting product. Reaction with traditional harsh oxidants such as ammonium ceric nitrate led to the appearance of multiple unstable products by UV-vis, and appeared to promote decomposition, but oxidation with either sodium hypochlorite and ammonia or NBS and ammonium hydroxide (both in CH_3CN/H_2O) led to a color change to red and the appearance of new, highly polar pink spots on a TLC plate.

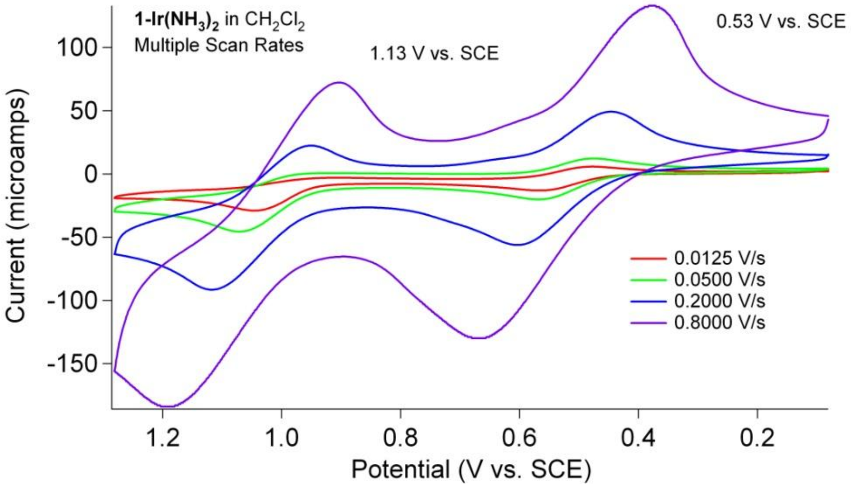


Figure 5-5: CV traces of **1-Ir(NH_3)$_2$** in dcm at a variety of scan rates, showing the dependence upon the scan rate of the reversibility of the more anodic process

The hypochlorite/ammonia reaction produced a mélange of reddish products; the only isolable product, eluted by HPLC in 1% yield in a 14 hour procedure, was a pink compound, insoluble in dcm or hexanes but quite soluble in acetonitrile or methanol, that showed four downfield-shifted doublets in its proton NMR spectrum, along with a three times as intense singlet at -3.6 ppm (in d^6-DMSO). Additionally, this compound, dubbed **2-Ir(NH$_3$)$_2$**, has an MS corresponding to **1-Ir(NH$_3$)$_2$** plus one additional nitrogen atom.

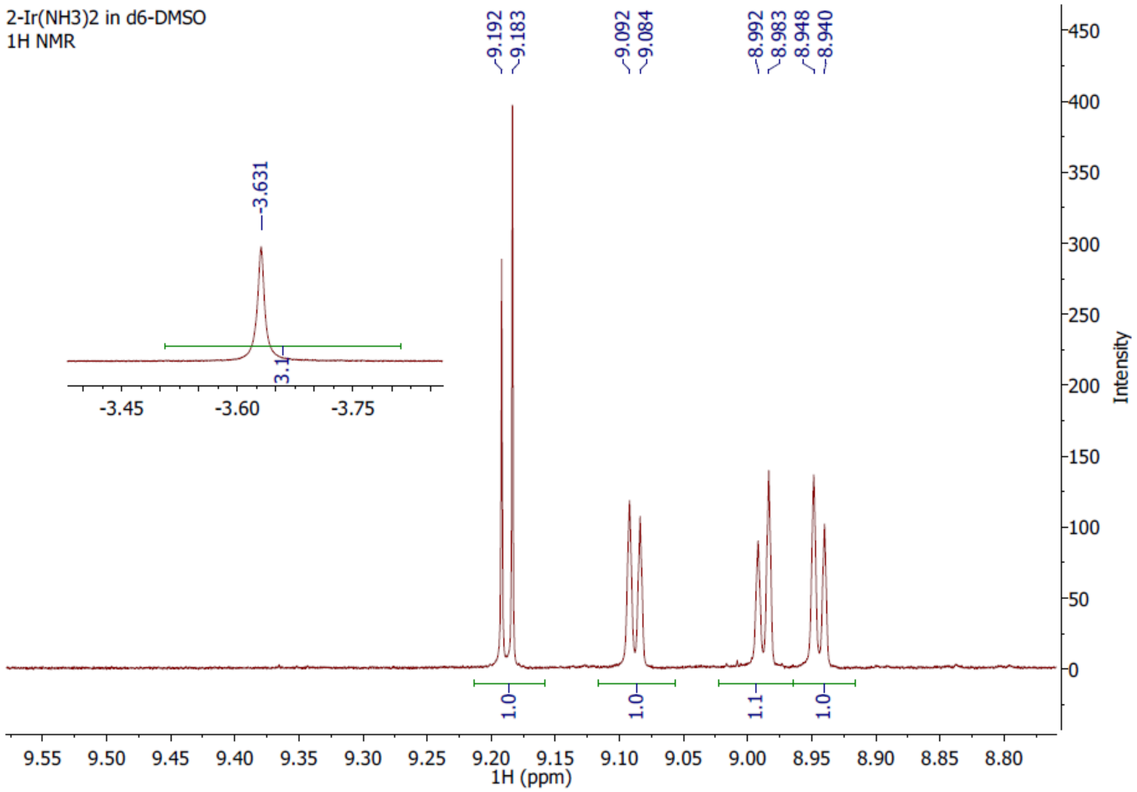


Figure 5-6: ^{1}H NMR of **2-Ir(NH$_3$)$_2$** in d^6-DMSO. Note the similarity to the parent corrole, as well as the downfield shifting of the β-proton resonances.

In order to more fully characterize the new complex, we had to first develop a more reliable and convenient synthesis of it. To that end, we tried a number of oxidants in the presence of NH$_4$OH (which we assumed to be critical to the success of the reaction owing to the insertion of an extra nitrogen atom somewhere along the way), and we found that addition of NBS to a mixture of **1-Ir(NH$_3$)$_2$** and NH$_4$OH in acetonitrile causes the immediate evolution of gas (presumably ammonia) from the reaction vessel and a concomitant color change from green to a deep red-purple. Three different compounds, with an overall yield of about 50%, could be isolated from the reaction mixture by gradient column chromatography (the Danish “dry column” technique is recommended) in 1–5% CH$_3$OH/CH$_2$Cl$_2$. The least polar of these complexes, and the major product, has two additional bromine atoms and two fewer protons than the original complex, and its UV-vis absorption spectrum displays significant bathochromic shifting. The second complex to elute from the column contains one additional bromine atom and is asymmetric by proton NMR, while the final complex to be removed from the column is the same compound produced by the hypochlorite reaction. All three compounds are fuchsia and display similar NMR and UV-vis spectral characteristics.

The UV-vis spectral signatures of the pink compounds, with their narrow, high-energy Soret bands and muted Q-band systems (Figure 5-7), look similar to those of the iron(III) azaporphyrin complexes explored as verdohemochrome analogues and spin-state curiosities by a number of groups in Japan and the United States.[10]

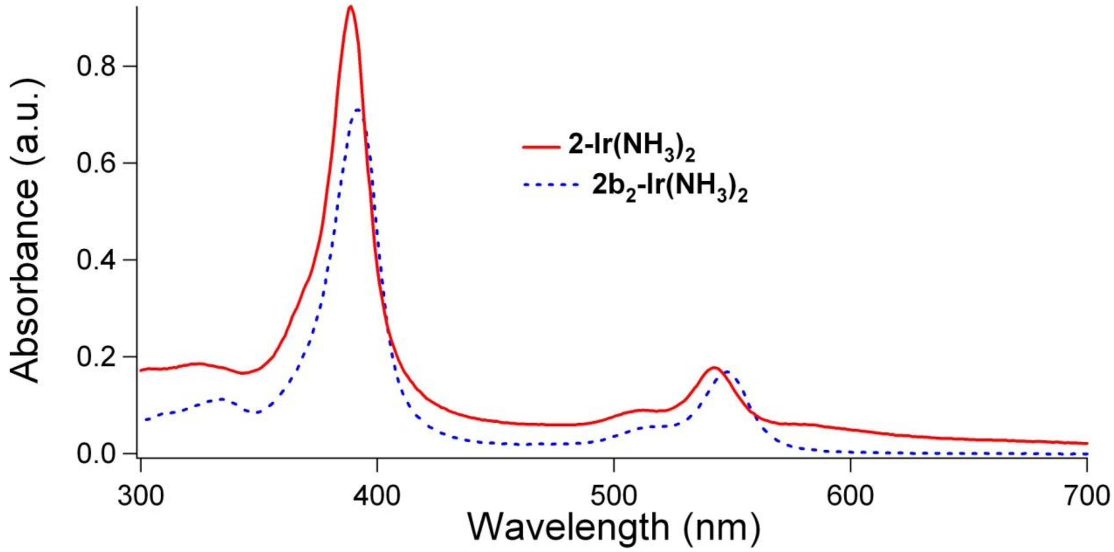
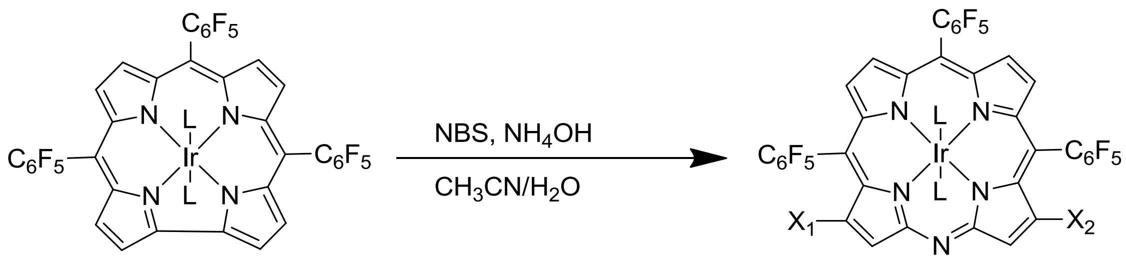


Figure 5-7: UV-vis absorption spectra of **2-Ir(NH$_3$)$_2$** (solid) and **2b$_2$-Ir(NH$_3$)$_2$** (dashed) in CH$_3$CN.

Based on this observation as well as our MS and NMR data, we have classified our new compounds as 3,17-dibromo-5,10,15-(tris)pentafluorophenylmonoazaporphyrinatoiridium(III) (bis)ammine [**2b$_2$-Ir(NH$_3$)$_2$**], 3-bromo-5,10,15-(tris)pentafluorophenylmonoazaporphyrinatoiridium(III) (bis)ammine [**2b-Ir(NH$_3$)$_2$**], and 5,10,15-(tris)pentafluorophenylmonoazaporphyrinatoiridium(III) (bis)ammine [**2-Ir(NH$_3$)$_2$**] (Figure 5-8). To the best of our knowledge, these compounds represent the first examples of true iridium azaporphyrins in the scientific literature, although there is a report, from 2002, of an iridium(III) tetraazaporphine compound.[11] Additionally, our complexes are unique in that they have unsubstituted beta positions but are fully substituted at the meso positions, whereas the vast majority of azaporphyrins and azaporphines in the literature are derived from porphyrins or verdohemochrome-type macrocycles with complete β-substitution and no meso-substituents.



2: $X_1 = X_2 = H$
2b: $X_1 = H, X_2 = Br$
2b$_2$: $X_1 = X_2 = Br$

Figure 5-8: Synthesis of **2-Ir(NH$_3$)$_2$** and its brominated derivatives

In order to gain insight into the mechanism of formation of **2-Ir(NH$_3$)$_2$** and its brominated derivatives, we ran the NBS/NH_4OH reaction using ^{15}N-substituted ammonium hydroxide; additionally, we attempted to drive the reaction to the hypothetical end product 2,3,7,8,12,13,17,18-octabromo-5,10,15-(tris)pentafluorophenylmonoazaporphyrinatoiridium(III) (bis)ammine using both massive excesses of NBS (in which case bromination is still halted at the **2b$_2$-Ir(NH$_3$)$_2$** stage) and elemental bromine (resulting in a deep red but inseparable mixture of variously brominated analogues). The ^{1}H NMR spectra of the monoazaporphyrin products formed in the NBS/$^{15}NH_4OH$ reaction (Figure 5-9) continues to display a singlet resonance far upfield corresponding to the ammine ligands; substitution by ^{15}N would be expected to produce a doublet due to ^{15}N-^{1}H coupling. In addition, the ^{15}N-^{1}H HMBC NMR spectrum of **^{15}N-2b$_2$-Ir(NH$_3$)$_2$**, which displays resonance between nitrogen and hydrogen atoms between two and three bonds distant (Figure 5-10), shows a strong signal corresponding to coupling between the new N atom on the azaporphyrin ring and the protons at the two and eighteen positions on the ring.

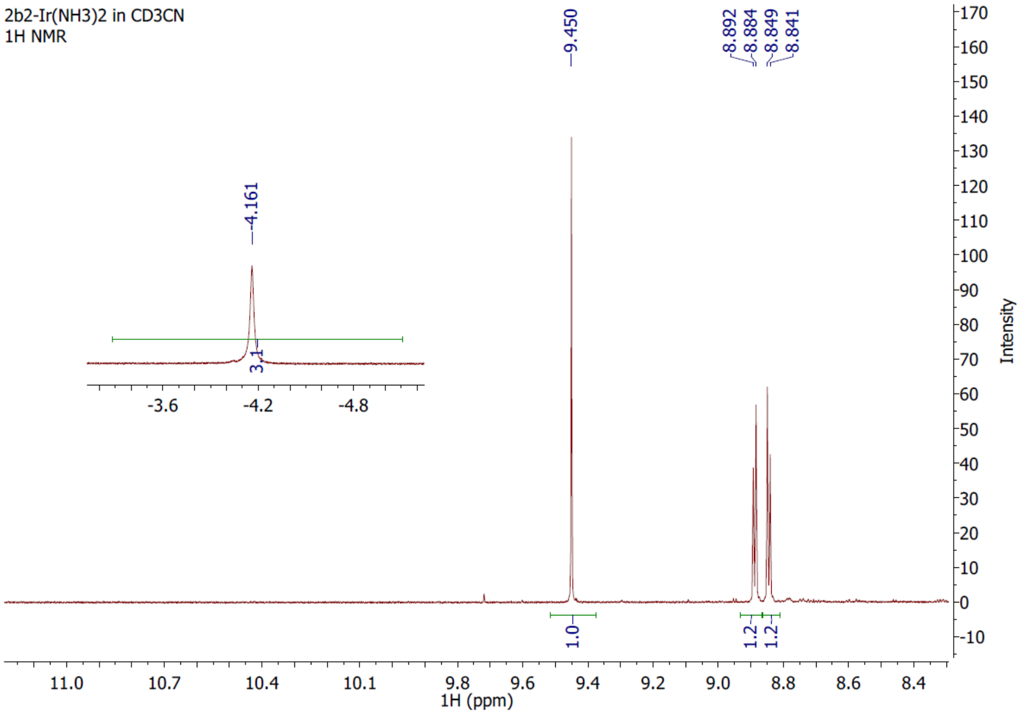


Figure 5-9: ^{1}H NMR of ^{15}N- labeled **2b$_2$-Ir(NH3)$_2$**. *Inset:* Upfield singlet resonance corresponding to the ammine ligand protons

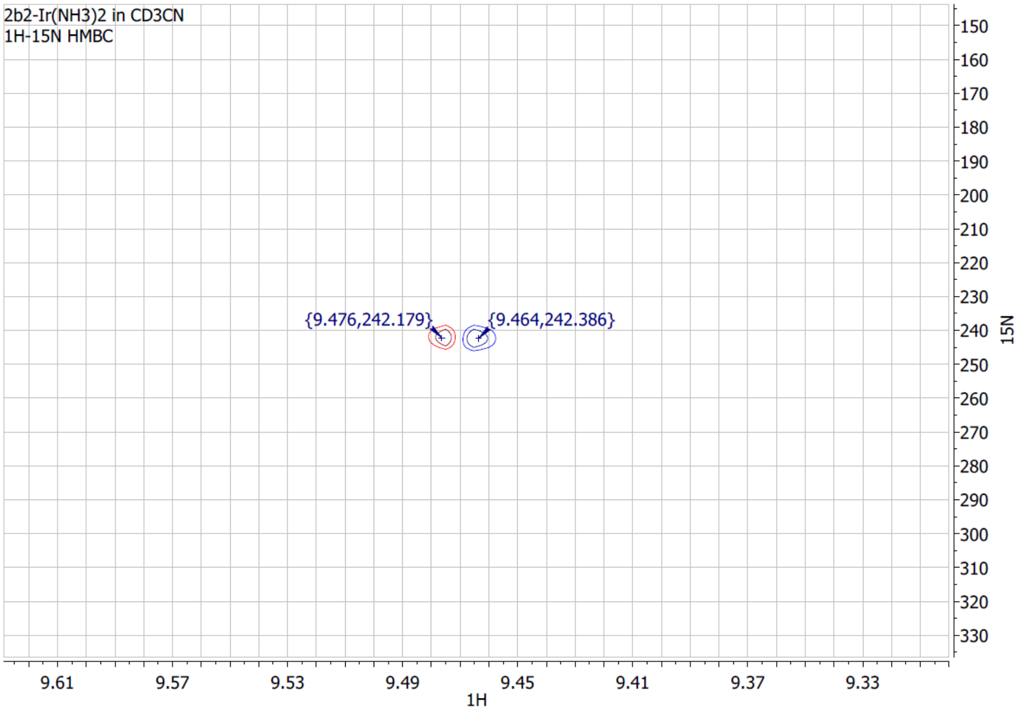


Figure 5-10: ^{15}N-^{1}H HMBC spectrum of **2b$_2$-Ir(NH$_3$)$_2$**, showing the correlation between the ring protons at positions two and eighteen and the inserted ^{15}N atom

The clear implication of the labeling studies is that the ammonium hydroxide is acting as the source of the nitrogen atom that becomes inserted into the corrole framework during the reaction, so it seems, at first glance, that this reaction should work on any of the iridium corroles in our possession. However, attempts at performing a similar reaction on either **1-Ir(tma)$_2$** or **1-Ir(py)$_2$** were completely unsuccessful. Given that our simple labeling studies imply strongly that the ammine ligands on the iridium play no active role in the formation of the monoazaporphyrin, we tentatively posit that the willingness of **1-Ir(NH$_3$)$_2$** to undergo nitrogen insertion stems from its low redox potential; the ammine-ligated corrole is more than 0.1 V easier to oxidize than either of the other corroles mentioned.

Based on the data we currently have, we can postulate a tentative mechanism of nitrogen insertion wherein the corrole is first oxidized by NBS to a mixed metal/π-cation radical state and then undergoes nucleophilic attack by the ammonia in solution. Then the protons on the newly inserted nitrogen atom must be removed by the hydroxide in solution resulting in rearomatization of the ring system. The resulting azaporphyrins are quite resistant to bromination (**2-Ir(NH$_3$)$_2$** and **2b-Ir(NH$_3$)$_2$** are not converted to **2b$_2$-Ir(NH$_3$)$_2$** even upon standing for long periods with excess NBS in solution), so the halogenation step must take place prior to insertion of the nitrogen atom. We cannot say for certain whether the bromination takes place on the corrole before oxidation or during the intermediate steps, but the distribution of the products and the speed of the reaction (the solution turns purple immediately upon adding NBS to the corrole/NH_4OH mixture) slightly favor the latter pathway.

In addition to their interesting molecular structures, **2-Ir(NH$_3$)$_2$** and **2b$_2$-Ir(NH$_3$)$_2$**, like their parent corroles, display long-lived phosphorescence at room temperature [**2b-Ir(NH$_3$)$_2$** was extremely difficult to purify, and therefore not subjected to photophysical studies]. Unlike the iridium(III) corrole compounds we have studied, the monoazaporphyrin complexes luminesce in the red end of the visible region (as opposed to the near-IR), with maxima at 695 and 691 nm for **2b$_2$-Ir(NH$_3$)$_2$** and **2-Ir(NH$_3$)$_2$**, respectively (Figure 5-11), and with an emission band shape that looks extremely similar to those of the iridium(III) corroles.[12] The luminescence lifetimes of the complexes are on the order of hundreds of nanoseconds, implying that the emission is phosphorescence from a triplet state.

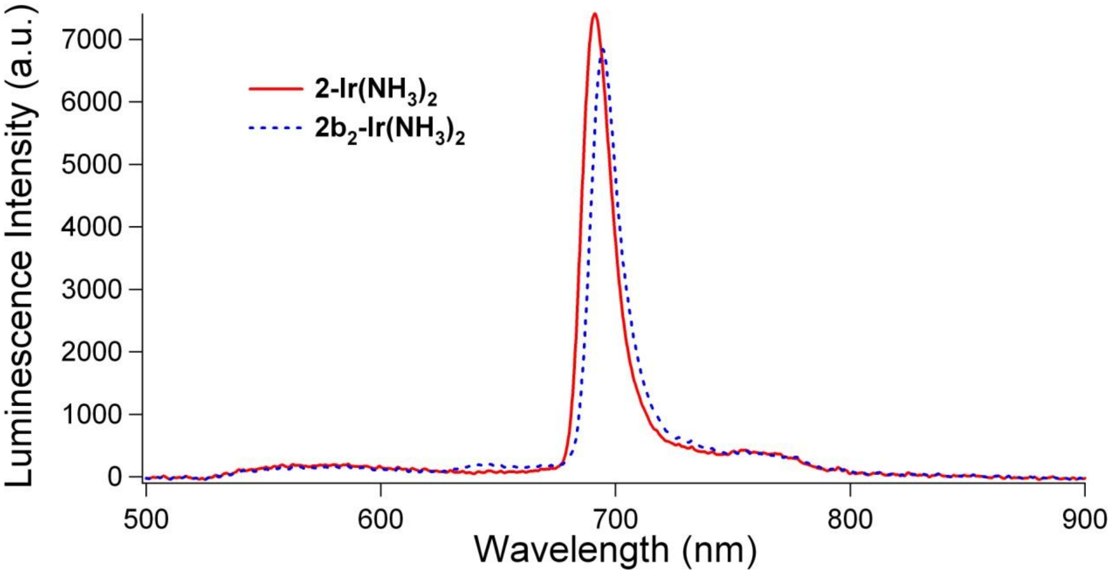


Figure 5-11: Emission spectra of **2-Ir(NH$_3$)$_2$** (solid) and **2b$_2$-Ir(NH$_3$)$_2$** (dashed) at 77K in frozen CH$_3$CN. Room temperature emission spectra can be viewed in Supporting Information.

Future work in our laboratories will focus on the development of more efficient syntheses for azaporphyrin complexes starting from a variety of meso-substituted corroles, as well as the expansion of the reaction to include corrole complexes of metals other than iridium. Monoazaporphyrin complexes of iron(III) have been studied to some extent as biomimetic heme complexes, but always with significant β-substitution and without meso-substituents; so the development of new iron(III) MAzP complexes from the parent corroles could produce an interesting new family of compounds. Additionally, we will further study the photophysics of the Ir(III) monoazaporphyrins, whose quantum yields of emission appear in preliminary experiments to be slightly higher than those of their parent corroles.

References

(1) Gross, Z.; Gray, H. B. *Comm. Inorg. Chem.* **2006**, *27*, 61–72.

(2) a) Golubkov, G.; Gross, Z. *Angew. Chem. Int. Ed.* **2003**, *42*, 4507–4510. b) Golubkov, G.; Gross, Z. *J. Am. Chem. Soc.* **2005**, *127*, 3258–3259. c) Mahammed, A.; Gray, H. B.; Meier–Callahan, A. E.; Gross, Z. *J. Am. Chem. Soc.* **2003**, *125*, 1162–1163. d) Gross, Z.; Golubkov, G.; Simkhovich, L. *Angew. Chem. Int. Ed. Eng.* **2000**, *39*, 4045–4047. e) Golubkov, G.; Bendix, J.; Gray, H. B.; Mahammed, A.; Goldberg, I.; DiBilio, A. J.; Gross, Z. *Angew. Chem. Int. Ed. Eng.* **2001**, *40*, 2132–2134. f) Mandimutsira, B. S.; Ramdhanie, B.; Todd, R. C.; Wang, H. L.; Zareba, A. A.; Czemuszewicz, R. S.; Goldberg, D. P. *J. Am. Chem. Soc.* **2002**, *124*, 15170–15171.

(3) Simkhovich, L.; Gross, Z. *Tet. Lett.* **2001**, *42*, 8089–8092.

(4) a) Adamian, V. A.; D'Souza, F.; Licoccia, S.; Di Vona, M. L.; Tassoni, E.; Paolesse, R.; Boschi, T.; Kadish, K. M. *Inorg. Chem.* **1995**, *34*, 532–540. b) Kadish, K. M.; Adamian, V. A.; Van Caemelbecke, E.; Gueletti, E.; Will, S.; Erben, C.; Vogel, E. *J. Am. Chem. Soc.* **1998**, *120*, 11986–11993.

(5) Zakharieva, O; Schunemann V.; Gerdan M.; Licoccia S.; Cai S.; Walker F. A.; Trautwein A. X. *J. Am. Chem. Soc.* **2002**, *124*, 6636–6648. b) Kadish, K. M.; Shen, J.; Fremond, L.; Chen, P.; El Ojaimi, M.; Chkounda, M.; Gros, C. P.; Barbe, J. M.; Ohkubo, K.; Fukuzumi, S.; Guilard, R. *Inorg. Chem.* **2008**, *47*, 6726–6737.

(6) Palmer, J. H.; Day, M. W.; Wilson, A. D.; Henling, L. M.; Gross, Z.; Gray, H. B. *J. Am. Chem. Soc.* **2008,** *130*, 7786–7787.

(7) Palmer, J. H.; Mahammed, A.; Lancaster, K. M.; Gross, Z.; Gray, H. B. *Inorg. Chem.* **2009,** *48,* 9308–9315.

(8) Dong, S. S.; Nielsen, R. J.; Palmer, J. H.; Gray, H. B.; Gross, Z.; Dasgupta, S.; Goddard, W. A. III. *Inorg. Chem.* **2011**, *ASAP.*

(9) Palmer, J. H.; Lancaster, K. M.; DeBeer, S.; Gray, H. B. *manuscript in preparation.*

(10) a) Nakamura, K.; Ikezaki, A.; Ohgo. Y.; Ikeue, T.; Neya, S.; Nakamura, M. *Inorg. Chem.* **2008,** *47,* 10299–10307. b) Balch, A. L.; Olmstead, M. M.; Safari, N. *Inorg. Chem.* **1993,** *32,* 219–296. c) Saito, S.; Tamura, N.; *Bull. Chem. Soc. Jpn.* **1987,** *60,* 4037–4049. d) Saito, S.; Sumita, S.; Iwai, K.; Sano, H. *Bull. Chem. Soc. Jpn.* **1988,** *61,* 3539–3547. e) For a somewhat dated but still relevant review, see: Kobayashi, N. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, **2000**, *2*, 301–360.

(11) Stuzhin, P. A.; Kabesheva, E. V.; Khelevina, O. G. *Russ. J. Coord. Chem.* **2003,** *29,* 377–381.

(12) Palmer, J. H.; Durrell, A. C.; Winkler, J. R.; Gross, Z.; Gray, H. B. *J. Am. Chem. Soc.* **2010,** *132,* 9230–9231.