Corrole Expansion

Nitrogen Insertion into a Corrole Ring: Iridium Monoazaporphyrins**

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Corroles are macrocycles that stabilize high-valent metal ions,[1] especially chromium and manganese,[2] which both form stable oxo complexes under aerobic conditions. The electronic structures of other proposed high-valent metal-locorroles, notably those of iron(IV)[3] and cobalt(IV),[4] have been subjects of lively discussion, as many experiments suggest that they contain corrole radicals complexed to lower-valent metal centers.[5] However, high oxidation states of corrole complexes with axial oxo and nitrido ligands, namely, those assigned as chromium(V),[6] manganese(V),[7] and even manganese(VI),[8] are well established.

We added Ir^{IV} to the list of high-valent metallocorroles[9] in a report that included UV/Vis absorption and EPR data[10] consistent with a 5d ($S = \frac{1}{2}$) metal in a rhombic ligand field. Computational results from our group[11] suggest that the high-valent ground state is highly delocalized, possessing both Ir^{IV} and corrole radical character. Here, we continue our pursuit of Ir^{V} or even higher-valent states by exploring routes to nitridoiridium(VI) corroles starting with the Ir^{III} complex **1-Ir(NH₃)₂** (Scheme 1), where **1** is the trianion of 5,10,15-(tris)pentafluorophenylcorrole.

1-Ir(NH₃)₂ was obtained by methods similar to published synthetic procedures (see the Supporting Information). The complex is green in solution, and displays UV/Vis absorption spectra similar to the known complex **1-Ir(py)₂** (py = pyri-

dine).[10] The crystallographically determined axial Ir—N bond lengths (Figure 1) are shorter for **1-Ir(NH₃)₂** than for **1-Ir(tma)₂** (tma = trimethylamine), while the equatorial bond lengths, in line with computationally derived geometries,[11] remain the same.
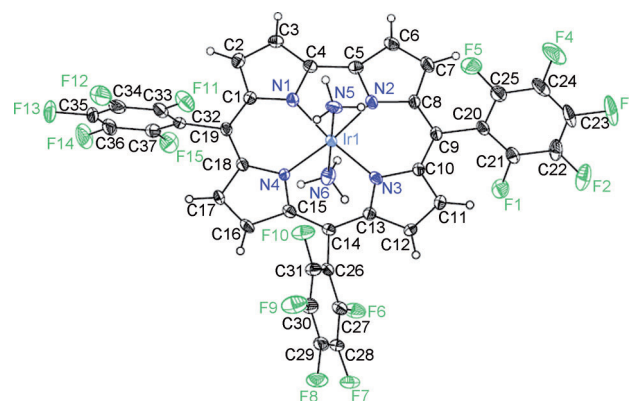

Figure 1. X-ray structure of **1-Ir(NH₃)₂**. Ir—N equatorial bond lengths average 1.964 Å and Ir—N axial bond lengths average 2.074 Å. In **1-Ir(tma)₂**, these bond lengths average 1.965 and 2.185 Å, respectively.[20]

Additionally, **1-Ir(NH₃)₂** is more easily oxidized ($E_{1/2}$ = 0.53 V vs. SCE, measured by cyclic voltammetry in CH_2Cl_2) 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 in the ammine complex. Like **1-Ir(tma)₂** and **1-Ir(py)₂**, **1-Ir(NH₃)₂** is luminescent in the near-IR region, with a slightly red-shifted emission maximum.

The cyclic voltammogram of **1-Ir(NH₃)₂** (Figure 2) shows two anodic waves in CH_2Cl_2 solution, one of which (at 0.53 V vs. SCE) is quasi-reversible, with the other (at 1.13 V vs. SCE) displaying scan-rate-dependent reversibility. The first oxida-
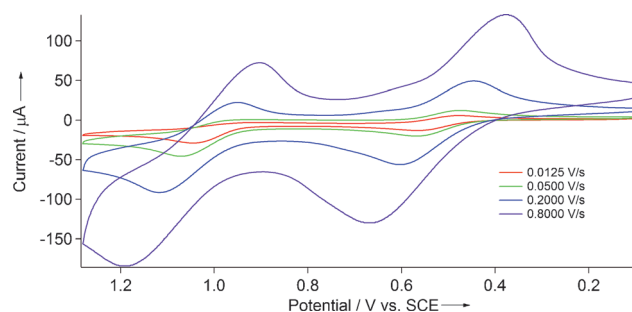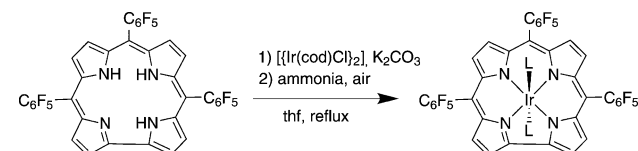

Scheme 1. Synthesis of **1-Ir(NH₃)₂** (L = NH₃). cod = 1,5-cyclooctadiene.

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Figure 2. Cyclic voltammetry traces of **1-Ir(NH₃)₂** in CH_2Cl_2, showing the dependence on the scan rate of the reversibility of the more anodic process.

tion produces a mixed Ir^{IV}–corrole radical, with similar EPR and spectroelectrochemical signatures (see the Supporting Information, Figures S-12 and S-13) to the one-electron oxidized form of **1-Ir(tma)₂**.[10] We reasoned that the second oxidation process might result in formation of an Ir^V complex, and we attempted chemically to oxidize the corrole. Treatment with *N*-bromosuccinimide (NBS) in the presence of ammonium hydroxide (which we hoped would remove protons from the ammine ligands) led to a rapid color change from green to red-purple and the appearance of new TLC (thin layer chromatography) spots.

Three different compounds, with an overall yield of about 50%, were isolated from the reaction mixture by gradient column chromatography (the Danish "dry column" technique[12] is recommended) in 1–5% CH_3OH/CH_2Cl_2. The most polar of these complexes, dubbed **[2-Ir(NH₃)₂]⁺**, has a mass corresponding to that of **1-Ir(NH₃)₂** plus one nitrogen atom; its ¹H NMR spectrum (Figure 3) demonstrates that the complex retains pseudo-C_{2v} symmetry, the ammine ligands remain attached to iridium, and all β-pyrrole protons are intact. The two other complexes exhibit similar NMR spectra and their mass spectra are consistent with replacement of one {**[2(Br)-Ir(NH₃)₂]⁺**} and two {**[2(Br₂)-Ir(NH₃)₂]⁺**} protons by bromines. The UV/Vis spectral signatures of these pink compounds (Figure 4), taken in combination with their NMR and mass spectra, point unambiguously to the formation of monoazaporphyrin complexes. We hypothesize that bromide

is the most likely counterion for these cationic species, but positive identification proved elusive.

Azaporphyrins, particularly those containing iron(III),[13] possess high-energy Soret bands and broad Q-band systems. Our iridium monoazaporphyrins (Scheme 2),[14] which exhibit similarly energetic Soret absorptions, are unique in that they have unsubstituted β-positions but are fully substituted at the *meso* positions, whereas most other azaporphyrins are heavily β-substituted but have no *meso* substituents.[15]
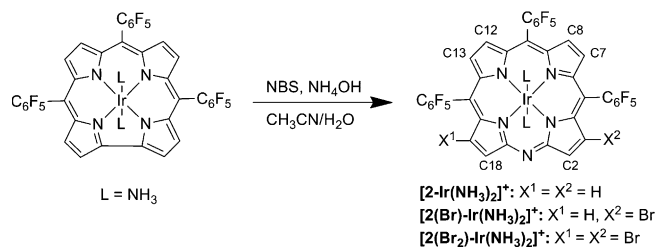
Scheme 2. Synthesis of **[2-Ir(NH₃)₂]⁺** and its brominated derivatives.

Figure 3. ¹H NMR spectrum of **[2-Ir(NH₃)₂]⁺** in [D₆]dmso.

Figure 4. UV/Vis absorption spectra of **[2-Ir(NH₃)₂]⁺**, **[2(Br)-Ir(NH₃)₂]⁺**, and **[2(Br₂)-Ir(NH₃)₂]⁺** in CH_3CN.

In order to gain insight into the mechanism of formation of **[2-Ir(NH₃)₂]⁺** and its brominated derivatives, we ran the NBS/NH₄OH reaction using ¹⁵N-labeled ammonium hydroxide; additionally, we attempted to drive the reaction to the hypothetical end product, octabromo(tris)pentafluorophenyl-monoazaporphyrinatoiridium(III) (bis)ammine, using both large excesses of NBS (in which case bromination is still halted at the **[2(Br₂)-Ir(NH₃)₂]⁺** stage) and elemental bromine (resulting in an inseparable mixture of variously brominated analogues). The ¹H NMR spectra of the monoazaporphyrins display a singlet resonance far upfield assigned to the ammine ligands; substitution by ¹⁵N would be expected to produce a doublet due to ¹⁵N-¹H coupling. In addition, the ¹⁵N-¹H HMBC NMR spectrum of **[¹⁵N-2(Br₂)-Ir(NH₃)₂]⁺** (see the Supporting Information) shows a strong signal corresponding to coupling between the N atom of the azaporphyrin and the protons on the C2 and C18 atoms of the ring. This HMBC signal also confirms the assignment of the bromine atoms to positions 3 and 17 on the corrole ring; if they were at positions 2 and 18, the other possibility, no 3-bond ¹⁵N-¹H coupling would be observed.

The implication of the labeling studies is that ammonium hydroxide acts as the source of nitrogen that is eventually inserted into the corrole framework during the reaction, so we thought it should be possible to convert other iridium corroles to azaporphyrins. However, attempted reactions for both **1-Ir(tma)₂** and **1-Ir(py)₂** were unsuccessful. Given that the ammine ligands play no active role in formation of **2**, we tentatively suggest that the ease with which **1-Ir(NH₃)₂** undergoes nitrogen insertion stems from its low redox potential; the ammine-ligated corrole is more than 100 mV easier to oxidize than either **1-Ir(tma)₂** or **1-Ir(py)₂**.

We propose that nitrogen insertion in the oxidatively generated metal/π-cation radical state involves nucleophilic attack by ammonia in solution. The initial intermediate is likely a ring-opened, brominated biladiene of the sort that has
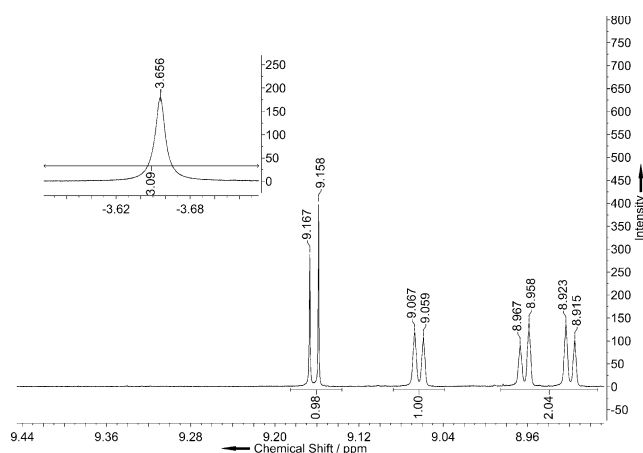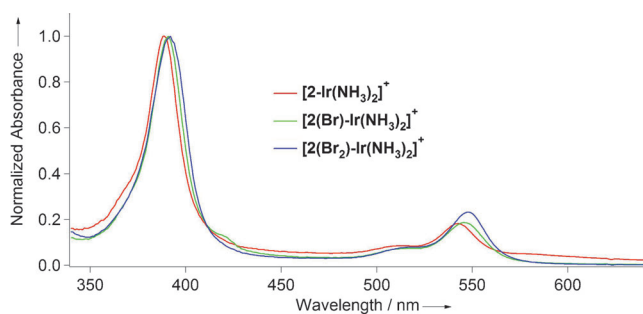
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been observed in stepwise syntheses of azaporphyrins.[16] In this process, the protons on the newly inserted nitrogen atom are removed by hydroxide, thereby rearomatizing the ring system. The azaporphyrins thus formed are resistant to bromination (the relative yield of **[2(Br₂)-Ir(NH₃)₂]⁺** does not increase even upon standing for long periods with excess NBS in solution), so halogenation must take place prior to insertion of nitrogen. We cannot be certain whether this occurs before oxidation or during intermediate steps, but we favor the latter pathway, as the solution turns purple immediately upon adding NBS to the corrole/NH₄OH mixture.

In addition to their interesting structures, **[2-Ir(NH₃)₂]⁺**, **[2(Br)-Ir(NH₃)₂]⁺**, and **[2(Br₂)-Ir(NH₃)₂]⁺**, like Ir^{III} corroles,[17] display long-lived emission at room temperature, with maxima at around 700 nm (Table 1 and Figure 5). Their luminescence lifetimes are on the order of microseconds, consistent with phosphorescence from a triplet state. The emission quantum yields of the complexes decrease with increasing bromination, possibly because of faster intersystem crossing (ISC). These quantum yields are slightly higher than those observed for Ir^{III} corroles (including **1-Ir(NH₃)₂**),[17] and are significantly lower than those recently reported for a series of Ir^{III} porphyrins.[18] As the standard was measured in benzene and the azaporphyrins in acetonitrile, a refractive index correction factor of 0.80 ($n_{CH_3CN}^2/n_{C_6H_6}^2$) was applied to those measurements.

Table 1: Photophysical parameters for Ir^{III} monoazaporphyrins.

Compound	λ_{max} [nm]	τ_0 [μs]	ϕ_{ph} [%]	k_r [s⁻¹], k_{nr} [s⁻¹]
1-Ir(NH₃)₂	801	2.16	0.12	5.55×10^2, 4.62×10^5
[2-Ir(NH₃)₂]⁺	697	3.41	1.34	3.93×10^3, 2.89×10^5
[2(Br)-Ir(NH₃)₂]⁺	700	1.69	0.89	5.26×10^3, 5.86×10^5
[2(Br₂)-Ir(NH₃)₂]⁺	701	1.02	0.71	6.96×10^3, 9.73×10^5
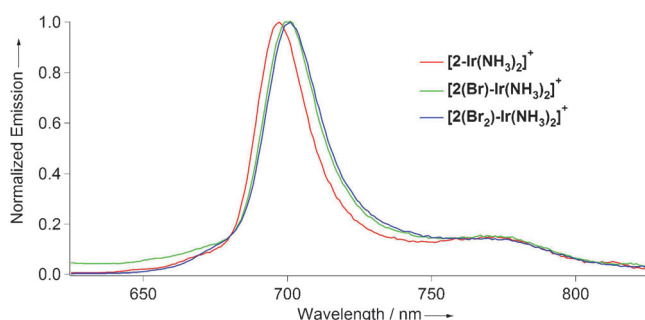
Figure 5. Emission spectra of **[2-Ir(NH₃)₂]⁺**, **[2(Br)-Ir(NH₃)₂]⁺**, and **[2-(Br₂)-Ir(NH₃)₂]⁺** at room temperature in CH₃CN.

We plan to develop more efficient syntheses for azaporphyrins starting from *meso*-substituted corroles, and we intend to expand this chemistry to include corrole complexes of metals other than iridium. In particular, we will attempt to prepare iron(III) monoazaporphyrins from parent corroles, as it is likely that these complexes could be converted to high-valent iron-oxos similar to reactive intermediates in heme oxidation reactions. Investigation of iron-oxo oxidations of substrates will then be vigorously pursued.

Experimental Section

Nearly all starting materials were used as received from Sigma-Aldrich. Pyrrole was distilled just before use, and ¹⁵NH₄OH was purchased from Cambridge Isotope Laboratories. H₃tpfc was prepared by a literature method.[19] The synthesis of **1-Ir(NH₃)₂**, which was performed according to a slight modification of literature procedures, is described in more detail along with the syntheses of **[2-Ir(NH₃)₂]⁺** and its brominated derivatives in the Supporting Information. Instrumental specifications and details of the spectroscopic experiments also are in the Supporting Information.

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[20] CCDC 769388 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.