Chapter 1

IRIDIUM CORROLES

A few months after showing up in the lab, I had a meeting with Harry Gray and Zeev Gross (of the Technion, in Haifa, Israel) where I apparently suggested that we might be able to use iridium(III) corroles to achieve the type of oxygen atom transfer reactions that had been demonstrated by Seth Brown and co-workers for George Wilkinson's trimesityliridium(III)/oxotrimesityliridium(V) system. Synthetically, it took a lot of barking up a lot of trees before I located one that actually contained something interesting. In the beginning, I naively believed that iridium(III) or iridium(IV) chlorides could somehow be induced to give up their halide atoms and enter a deprotonated corrole coordination sphere as if waltzing into an octahedral chelate complex of bpy or edta. Not only that, but I thought that I would obtain a square-planar Ir(III) complex as well, one that could activate dioxygen bonds to form a square-planar oxoiridium(V) corrole. After all, it works for chromium, right?

As it turns out, both of these expectations were wildly inaccurate on a variety of counts. For one thing, octahedral Ir(III) complexes are notoriously kinetically inert, while Ir(IV) hexachloride and hexabromide compounds are highly oxidizing and liable to halogenate or otherwise degrade any electron-rich aromatics they stumble across in solution. In addition, the d^6 Ir(III) ion is just not stable in a square-planar coordination environment, much preferring to form octahedral or pseudo-octahedral complexes (like every other low-spin d^6 metal ion). In fact, even the three-coordinate Ir(III) complex that inspired my work is horrifically unstable; thus, it activates the strong O_2 double bond immediately upon exposure to air.

All of my initial attempts to incorporate iridium into a corrole having failed, I sought a new starting material that would be neither as inert as hexachloroiridium(III) nor as oxidizing (and therefore chlorinating) as hexachloroiridium(IV). I had some old $[Ir(cod)Cl]_2$ sitting around in a glove box from my prior attempts at producing iridium complexes of the Kläui ligand, and so, borrowing a J. Young NMR tube from Dave Weinberg in the Bercaw group, I resolved to attempt the synthesis of an Ir(III) corrole complex starting from an iridium(I) material which is neither inert nor capable of oxidizing much of anything. I was certain it would work, and I would have an oxoiridium(V) corrole complex by the next afternoon.

This time, unlike the last, I was 50% correct. The initial reaction run in d^8-thf (thanks, BP!) at 90^oC in a J. Young tube, produced a new set of sharply resolved proton NMR doublets in the corrole β-proton chemical shift region along with what appeared to be shifted cod peaks. These signals have been assigned to a four-coordinate iridium(I)(cod)(tpfc) in chemical analogy to products observed upon reaction of corroles with low-valent rhodium complexes, but this compound is very reactive and has not been isolated (full *in situ* characterization presents other difficulties, mostly owing to large quantities of $[Ir(cod)Cl]_2$ and K_2CO_3 in the reaction mixture making both proton NMR and ESI-MS unpalatable). When tma N-oxide was added in excess to the warm reaction mixture, the color of the solution changed from brown to red, and a new deep red compound could be observed by TLC. What was this new compound? That, dear reader, is the subject of the JACS Communication presented in this section, Iridium Corroles.

Iridium Corroles

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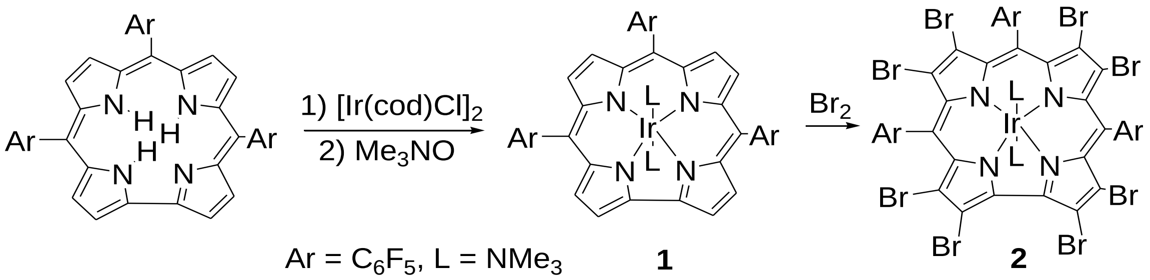
Interest in the chemistry of iridium has accelerated greatly in recent years,[1] owing in part to reports of high-valent oxo and nitrido species as well as other complexes possessing wide ranging catalytic activities.[2] Concurrent with this increased interest, much effort has been directed toward the goal of developing new metallocorrole systems for applications including, but not limited to, medical diagnostics and therapeutics, as well as catalysis.[3] This recent surge in corrole research is due in large part to the development of facile methods for the synthesis of the stable 5,10,15-*tris*-pentafluorophenylcorrole [H_3tpfc; tpfc (**1**) is the trianionic form] synthon and of other *tris*-aryl-substituted corroles.[4,5]

First-row transition metal corroles exhibit striking reactivity, including the activation of O_2 by trivalent chromium,[6] manganese,[7] and iron;[8] catalytic reduction of CO_2 by iron(I) and cobalt(I);[9] and iron(IV)-mediated aziridination of olefins.[10] Metals in high oxidation states enjoy the strong σ-donor environment of corroles; this property is typified by stable nitrido chromium(VI) and manganese(VI) species.[11] Several second-row transition metals also form stable corrole complexes: (oxo)molybdenum(V);[12] ruthenium(III), as triply bonded Ru-Ru dimers and nitric oxide bound monomers;[13] rhodium(III), which catalyzes carbene-transfer reactions;[14] and silver(III).[15] It is noteworthy that hitherto there has been only one report of a third-row metallocorrole, an (oxo)rhenium(V) species.[16]

Trianionic ligands should stabilize high oxidation states of iridium, so an Ir(III) corrole might be as reactive as porphyrinic Ir(II) toward substrates.[17] Herein we report the first fully characterized corrolato Ir(III) complex, (tpfc)Ir(III)(tma)$_2$ [**1-Ir(tma)$_2$**], and an octabromo-β-pyrrole derivative, (Br_8-tpfc)Ir(III)(tma)$_2$ [**1b-Ir(tma)$_2$**], where tma = trimethylamine (Scheme 1:1).



Scheme 1-1: Synthesis of iridium(III) corroles

Compound **1-Ir(tma)$_2$** was obtained in 27% yield *via* reaction of H_3tpfc with excess [Ir(cod)Cl]$_2$ (cod = cyclooctadiene) and K_2CO_3 in hot THF under Ar to form (tpfc)Ir(I)(cod), which was converted to an axially tma-ligated Ir(III) complex upon addition of tma *N*-oxide and exposure to the atmosphere.[18] Full bromination of **1-Ir(tma)$_2$** was achieved via reaction with excess Br_2 in methanol, providing green crystals of **1b-Ir(tma)$_2$** in about 65% yield.[19] Both complexes were fully characterized by spectroscopy, electrochemistry, and X-ray diffraction as six-coordinate Ir(III) corroles. The ^{19}F and ^{1}H NMR spectra (Figure 1-1, and Supporting Information) demonstrate that they are diamagnetic (sharp resonances), possess high symmetry (only one type of *ortho*-F for any C_6F_5 ring), and contain two axial tma groups (18 H atoms at –2.96 ppm for **1-Ir(tma)$_2$** and -2.59 ppm for **1b-Ir(tma)$_2$**).

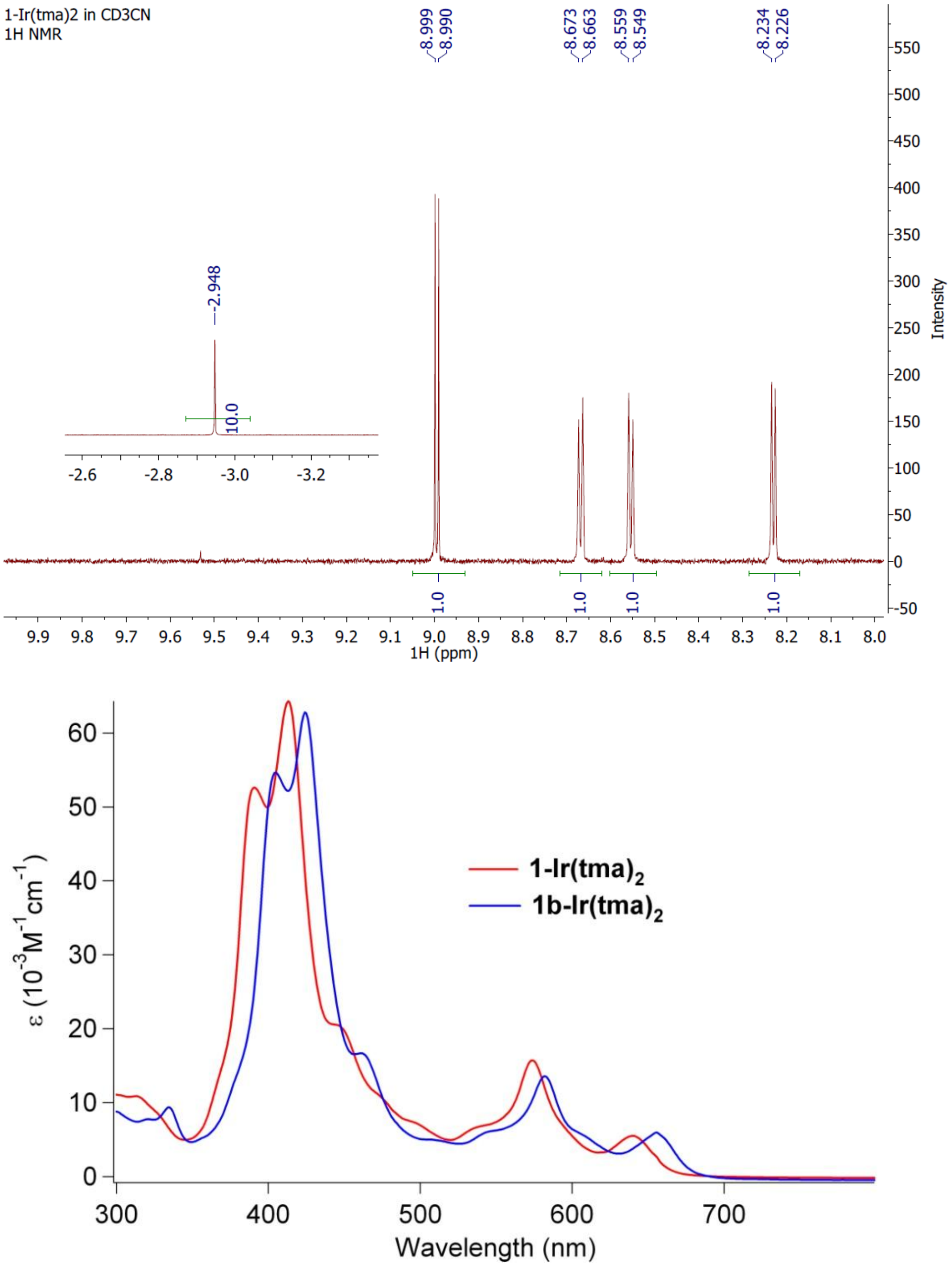


Figure 1-1: ^{1}H NMR spectrum of **1** in CD_3CN (top, inset is the tma methyl proton resonances) and UV-vis spectra of **1-Ir(tma)$_2$** (red, higher energy) and **1b-Ir(tma)$_2$** (blue, lower energy) in toluene (bottom)

The red shifts of the principal features in the electronic spectrum of **1b-Ir(tma)$_2$** relative to **1-Ir(tma)$_2$** (8–16 nm, Figure 1-1) are similar to those observed upon bromination of other metallocorroles,[6,20] but the intense Soret band system is uniquely split, as are the Q-bands (roughly 70 nm). We suggest that the shoulders at 448 and 458 nm for **1-Ir(tma)$_2$** and **1b-Ir(tma)$_2$**, respectively, are attributable to MLCT transitions, and that couplings to these excited states give rise to large splittings of the corrole-based π-π* states. Based on HOMO and LUMO energies extracted from the redox potentials of **1b-Ir(tma)$_2$**, the MLCT transitions should indeed fall in the 400–500 nm region of the visible spectrum.

Cyclic voltammetry (CV, Figure 1-2)[21] reveals that Ir(III) corroles are very electron-rich: Ir(II) is not electrochemically accessible and Ir(IV) is obtained at relatively low potentials. Only **1b-Ir(tma)$_2$** could be reduced within the electrochemical window of the solvent and the reversibility of that process ($E_{1/2}$ = -1.21 V vs. SCE) is consistent with the formation of a corrole radical anion rather than Ir(II), as the latter would rapidly release its axial ligand(s) and most likely also dimerize.[17] All other reversible electron transfer processes are also obtained at quite positive potentials. Guided by the electrochemistry of other metallocorroles,[8] the first and second redox processes of **1-Ir(tma)$_2$** ($E_{1/2}$ = +0.66 and +1.28 V vs. SCE, respectively) may tentatively be assigned as metal-centered (Ir^{III}/Ir^{IV}) and corrole-centered ($tpfc/tpfc^{+\cdot}$), respectively. As full bromination at the □-pyrrole positions is known to upshift the potentials of metallocorroles by a few hundred mV,[6,20] the feature at +1.19 V can be assigned to the Ir^{III}/Ir^{IV} couple in **1b-Ir(tma)$_2$**. Our data show clearly that Ir(III) is more electron-rich in corroles than in other coordination environments. The $E_{1/2}$ value for the $[(tpp)Ir]^{+}/[(tpp)Ir]^{2+}$ (tpp = tetraphenylporphyrinato) redox couple is about +1.4 V vs. SCE,[22] and Ir^{III}/Ir^{IV} processes in cyclometalated bpy complexes also occur at much more positive potentials than in **1-Ir(tma)$_2$**.[23]

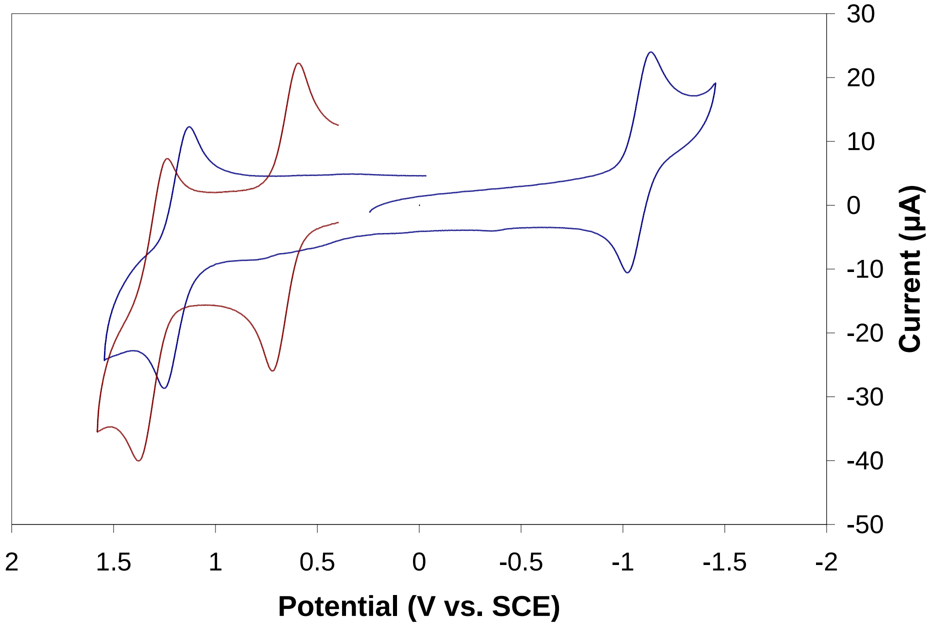


Figure 1-2: CV traces of **1-Ir(tma)$_2$** (red) and **1b-Ir(tma)$_2$** (blue) in CH_2Cl_2 solution at 23 °C

The molecular structures of **1-Ir(tma)$_2$** and **1b-Ir(tma)$_2$** (Figure 1-3) reveal that their macrocyclic frameworks are isostructural, with the iridium atom located in the plane of an essentially flat corrole.[24] The Ir-N axial bonds are about 0.2 Å longer than the in-plane Ir-N equatorial bonds, as might be expected. The one clear difference between **1-Ir(tma)$_2$** and **1b-Ir(tma)$_2$** is that the aryl rings are nearly perpendicular with respect to the corrole in the latter to avoid steric clash with the bromine atoms. The structure of **1b-Ir(tma)$_2$** is distinctly different from those of analogous tetraarylporphyrins, where β-pyrrole bromination induces large distortions of the macrocycle that produce dramatic red shifts in UV-vis absorptions and higher reduction potentials.[25] For iridium corroles, the 530 mV upshift in the potential of **1b-Ir(tma)$_2$** vs. **1-Ir(tma)$_2$** implies major Br-induced electronic effects.

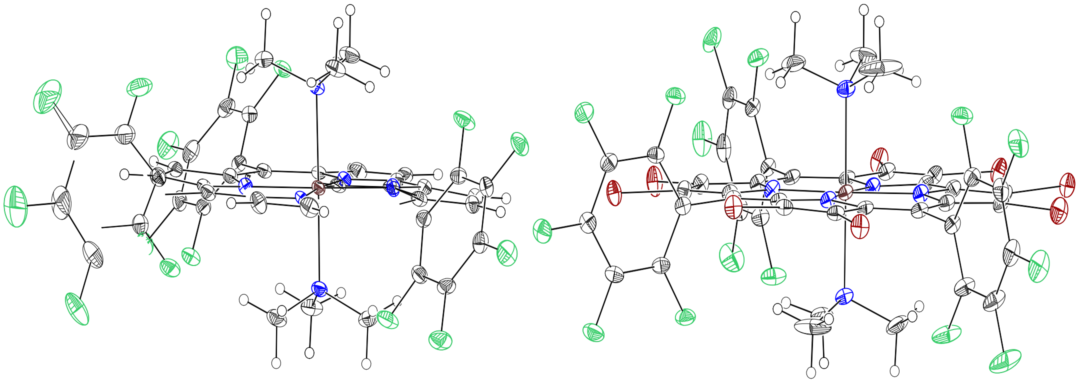


Figure 1-3: X-ray structures of **1-Ir(tma)$_2$** (left) and **1b-Ir(tma)$_2$** (right): 50% probability displacement ellipsoids. Average distances (Å), for **1-Ir(tma)$_2$, 1b-Ir(tma)$_2$**: Ir-N(equatorial), 1.965(9), 1.974(3); Ir-N(axial), 2.185(9), 2.189(3)

We have demonstrated that a corrole can readily accommodate a 5d transition metal in our work on the first nonorganometallic Ir(III) porphyrinoid. We also report an X-ray diffraction structure of a fully brominated derivative. The electron transfer processes demonstrated for **1-Ir(tma)$_2$** and **1b-Ir(tma)$_2$** suggest that they may prove useful as redox catalysts. Studies are in progress to develop methodologies for opening an axial coordination site on the metal, a requirement for testing the catalytic potential of these complexes.

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(17) Iridium(II) porphyrins react readily with olefins; they also form Ir–Ir bonded dimers (de Bruin, B.; Hetterscheid, D.G.H. *Eur. J. Inorg. Chem*. **2007**, 211–230. Song, X.; Chan. K.S. *Organomet.* **2007,** *26*, 965–970). Nearly all reported iridium(III) porphyrins are organometallic in nature (Zhai, H.; Bunn, A.; Wayland, B. *Chem. Commun.* **2001,** 1294–1295).

(18) H_3tpfc (80 mg), [Ir(cod)Cl]$_2$ (335 mg), and K_2CO_3 (140 mg) were dissolved/suspended in 150 mL of degassed THF, and the mixture was refluxed under argon for 90 min (until the corrole fluorescence was negligible to the eye upon long–wave irradiation with a hand–held lamp). Tma N–oxide (110 mg) was added, and the solution was allowed to slowly cool to room temperature while open to the laboratory atmosphere. Column chromatography of the black solution (silica, 4:1 hexanes:CH_2Cl_2) provided purple crystals of (tpfc)Ir(III)(tma)$_2$ (30 mg, 27% yield). ^{1}H NMR (CD_2Cl_2): δ 8.93 (d, 2H), 8.54 (d, 2H), 8.42 (d, 2H), 8.12 (d, 2H), –2.96 (s, 18H). ^{19}F NMR (CD_2Cl_2): δ –139.1 (m, 6H), –156.2 (m, 3H), –164.3 (m, 6H). MS (ESI): 1105.1 ([M$^+$]), 1046.0 ([M$^+$–tma]), 986.5 ([M$^+$–2tma]). UV–vis (nm): 390, 412, 448 (sh), 572, 638

(19) Complex **1** (15 mg) and Br_2 (70 μL) were dissolved in 20 mL MeOH and stirred overnight. Column chromatography (silica, 4:1 hexanes:CH_2Cl_2) of the red solution provided green crystals of (Br_8–tpfc)Ir(III)(tma)$_2$ (15 mg, 63% yield). ^{1}H NMR (CD_2Cl_2): δ –2.59 (s, 18H). ^{19}F NMR (CD_2Cl_2): δ –138.4 (q, 2H), –139.0 (q, 4H), –153.9 (t, 3H), –164.4 (m, 4H), –164.7 (m, 2H). UV–vis (nm): 406, 422, 458 (sh), 580, 646

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