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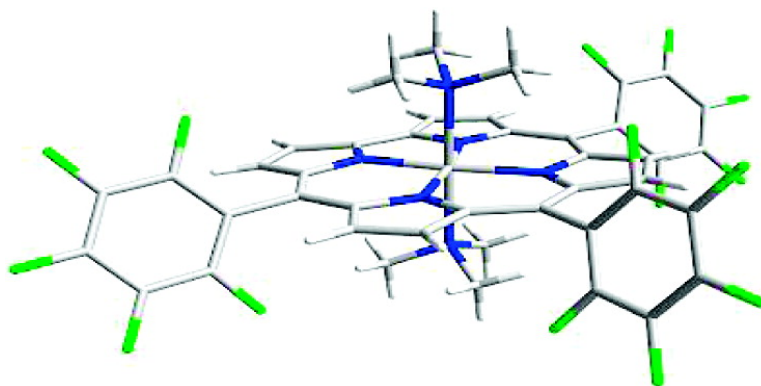
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## Iridium Corroles

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Interest in the chemistry of iridium has accelerated greatly in recent years,<sup>1</sup> owing in part to reports of high-valent oxo and nitrido species as well as other complexes possessing wide ranging catalytic activities.<sup>2</sup> 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.<sup>3</sup> 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<sub>3</sub>tpfc) synthon and of other *tris*-aryl-substituted corroles.<sup>4,5</sup>

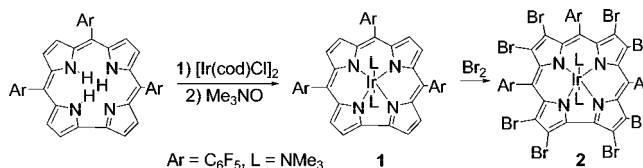
First-row transition metal corroles exhibit striking reactivity, including the activation of O<sub>2</sub> by trivalent chromium,<sup>6</sup> manganese,<sup>7</sup> and iron;<sup>8</sup> catalytic reduction of CO<sub>2</sub> by iron(I) and cobalt(I);<sup>9</sup> and iron(IV)-mediated aziridination of olefins.<sup>10</sup> Metals in high oxidation states enjoy the strong  $\sigma$ -donor environment of corroles; this property is typified by stable nitrido chromium(VI) and manganese(VI) species.<sup>11</sup> Several second-row transition metals also form stable corrole complexes: (oxo)molybdenum(V);<sup>12</sup> ruthenium(III), as triply bonded Ru–Ru dimers and nitric oxide bound monomers;<sup>13</sup> rhodium(III), which catalyzes carbene-transfer reactions;<sup>14</sup> and silver(III).<sup>15</sup> It is noteworthy that hitherto there has been only one report of a third-row metallocorrole, an (oxo)rhenium(V) species.<sup>16</sup>

Trianionic ligands should stabilize high oxidation states of iridium, so an Ir(III) corrole might be as reactive as porphyrinic Ir(II) toward substrates.<sup>17</sup> Herein we report the first fully characterized corrolato Ir(III) complex, (tpfc)Ir(III)(tma)<sub>2</sub> (**1**), and an octabromo- $\beta$ -pyrrole derivative, (Br<sub>8</sub>-tpfc)Ir(III)(tma)<sub>2</sub> (**2**), where tma = trimethylamine (Scheme 1).

Compound **1** was obtained in 27% yield via reaction of H<sub>3</sub>tpfc with excess [Ir(cod)Cl]<sub>2</sub> (cod = cyclooctadiene) and K<sub>2</sub>CO<sub>3</sub> 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.<sup>18</sup> Full bromination of **1** was achieved via reaction with excess Br<sub>2</sub> in methanol, providing green crystals of **2** in about 65% yield.<sup>19</sup> Both complexes were fully characterized by spectroscopy, electrochemistry, and X-ray diffraction as six-coordinate Ir(III) corroles. The <sup>19</sup>F and <sup>1</sup>H NMR spectra demonstrate that they are diamagnetic (sharp resonances, Figure 1), possess high symmetry (only one type of *ortho*-F for any C<sub>6</sub>F<sub>5</sub> ring), and contain two axial tma groups (18 H atoms at –2.96 ppm for **1** and –2.59 ppm for **2**).

The red shifts of the principal features in the electronic spectrum of **2** relative to **1** (8–16 nm, Figure 1) are similar to those observed upon bromination of other metallocorroles,<sup>6,20</sup> but the intense Soret band system is uniquely split, as are the Q-bands (roughly 70 nm).

## Scheme 1. Synthesis of Iridium(III) Corroles



We suggest that the shoulders at 448 and 458 nm for **1** and **2**, respectively, are attributable to MLCT transitions, and that couplings to these excited states give rise to large splittings of the corrole-based  $\pi$ - $\pi^*$  states. Based on HOMO and LUMO energies extracted from the redox potentials of **2**, the MLCT transitions should indeed fall in the 400–500 nm region of the visible spectrum.

Cyclic voltammetry (CV, Figure 2)<sup>21</sup> 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 **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.<sup>17</sup> All other reversible electron transfer processes are also obtained at quite positive potentials. Guided by the electrochemistry of other metallocorroles,<sup>8</sup> the first and second redox processes of **1** ( $E_{1/2} = +0.66$  and  $+1.28$  V vs SCE, respectively) may tentatively be assigned as metal-centered (Ir<sup>III</sup>/Ir<sup>IV</sup>) and corrole-centered (tpfc/tpfc<sup>•–</sup>), respectively. As full bromination at the  $\beta$ -pyrrole positions is known to upshift the potentials of metallocorroles by a few hundred mV,<sup>6,20</sup> the feature at  $+1.19$  V can be assigned to the Ir<sup>III</sup>/Ir<sup>IV</sup> couple in **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]<sup>+</sup>/[(tpp)Ir]<sup>2+</sup> (tpp =

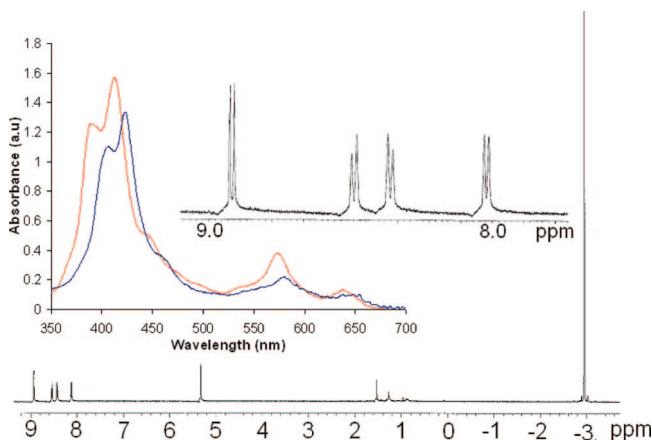
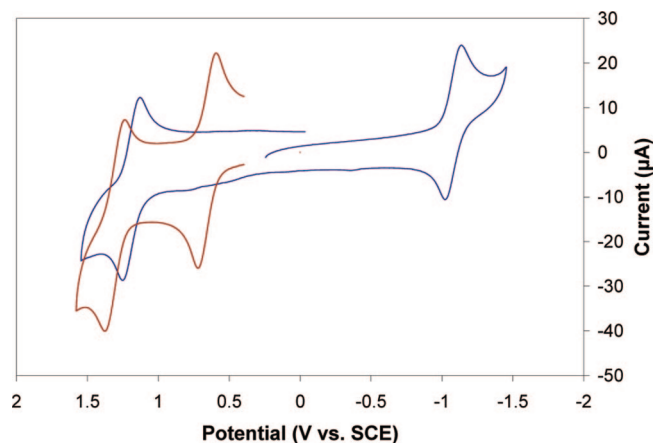
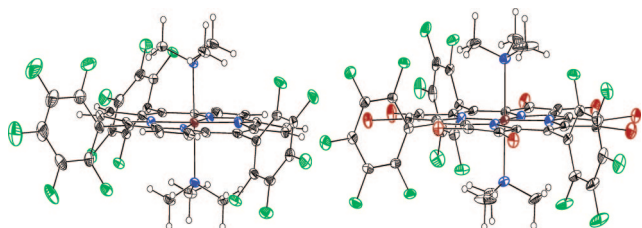


Figure 1. <sup>1</sup>H NMR spectrum of **1** in CD<sub>2</sub>Cl<sub>2</sub> and UV–vis spectra of **1** (red) and **2** (blue) in CH<sub>2</sub>Cl<sub>2</sub>. (Inset) The  $\beta$ -pyrrole proton resonances.

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**Figure 2.** CV traces of **1** (red) and **2** (blue) in  $\text{CH}_2\text{Cl}_2$  solution at 23 °C.



**Figure 3.** X-ray structures of **1** (left) and **2** (right): 50% probability displacement ellipsoids. Average distances (Å), for **1**, **2**: Ir–N(equatorial), 1.965(9), 1.974(3); Ir–N(axial), 2.185(9), 2.189(3).

tetraphenylporphyrinato) redox couple is about +1.4 V vs SCE,<sup>22</sup> and Ir<sup>III</sup>/Ir<sup>IV</sup> processes in cyclometalated bpy complexes also occur at much more positive potentials than in **1**.<sup>23</sup>

The molecular structures of **1** and **2** (Figure 3) reveal that their macrocyclic frameworks are isostructural, with the iridium atom located in the plane of an essentially flat corrole.<sup>24</sup> 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** and **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 **2** is distinctly different from those of analogous tetraarylporphyrins, where  $\beta$ -pyrrole bromination induces large distortions of the macrocycle that produce dramatic red shifts in UV–vis absorptions and higher reduction potentials.<sup>25</sup> For iridium corroles, the 530 mV upshift in the potential of **2** vs **1** implies major Br-induced electronic effects.

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** and **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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**Supporting Information Available:** CCDC 671270 (**1**) and CCDC 657602 (**2**) contain supplementary crystallographic data, and can be

obtained free of charge from the CCDC at [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). All other Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>.

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- (18) H<sub>3</sub>tpfc (80 mg), [Ir(cod)Cl]<sub>2</sub> (335 mg), and K<sub>2</sub>CO<sub>3</sub> (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<sub>2</sub>Cl<sub>2</sub>) provided purple crystals of (tpfc)Ir(III)(tma)<sub>2</sub> (30 mg, 27% yield). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.93 (d, 2H), 8.54 (d, 2H), 8.42 (d, 2H), 8.12 (d, 2H), –2.96 (s, 18H). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –139.1 (m, 6H), –156.2 (m, 3H), –164.3 (m, 6H). MS (ESI): 1105.1 ([M<sup>+</sup>]), 1046.0 ([M<sup>+</sup>–tma]), 986.5 ([M<sup>+</sup>–2tma]). UV–vis (nm): 390, 412, 448 (sh), 572, 638.
- (19) Complex **1** (15 mg) and Br<sub>2</sub> (70  $\mu$ L) were dissolved in 20 mL of MeOH and stirred overnight. Column chromatography (silica, 4:1 hexanes/CH<sub>2</sub>Cl<sub>2</sub>) of the red solution provided green crystals of (Br<sub>3</sub>–tpfc)Ir(III)(tma)<sub>2</sub> (15 mg, 63% yield). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –2.59 (s, 18H). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –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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