

**Gallium and Chromium Corroles**

Thesis by

Alexandre Edouard Meier

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*I know that my Redeemer lives,  
And that in the end He will stand  
Upon the earth  
And after my skin has been  
Destroyed  
Yet in my flesh I will see God  
I myself will see Him  
With my own eyes- I, and not  
Another.*

*Job 19:25-27*

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*To my son Lúcas  
That you may know to always chase your dreams  
No matter what*

**Abstract**

We report on the synthesis and characterization of various chromium and gallium complexes of the corrole 1,5,15-trispentafluorophenylcorrole (tpfc) $H_3$ . We synthesized a chromium(V)oxo compound by reaction between (tpfc) $H_3$  and  $Cr(CO)_6$  in refluxing toluene. Characterization of the compound via EPR and MS revealed a  $d^1$  metal species. Hyperfine splittings for the compound are  $A(^{53}Cr)$  1.64 mT,  $A(^{14}N)$  0.30 mT. Combined with the X-ray bond lengths (Cr-O, 1.545(2) Å; Cr-N, 1.969/1.991 Å) those data suggest that the stability of the Cr-O bond is mainly due to the strong N $\rightarrow$ Cr  $\sigma$  donation. The compound (tpfc)Cr(O) provided the starting point for all other oxidation states we made and isolated.

By treatment with dioxinium hexachloroantimonate we were able to form the ligand radical chromium(V) oxo species, which was shown by EPR to be in its triplet ground state. By treatment with cobaltocene, we were able to isolate the chromium(IV) oxo species, which was proven diamagnetic via NMR. Reaction with phosphines, gave rise to the chromium(III) species, which is hexa-coordinated. The two axial ligands could be either pyridine, or triphenylphosphine oxide, and were readily exchanged with one another.

The reactivity of (tpfc)Cr(O) was found to be quite low, exhibiting a rate constant of  $9.7 M^{-1}s^{-1}$  for reaction with triphenylphosphine. The chromium(III) counterpart was readily reoxidized in air, with a mechanism involving a five coordinate intermediate as the reactive species.

In a bid to increase reactivity, we examined the effect of bromination at the  $\beta$  position on reactivity. To ascertain the electronic effects, we prepared a series of gallium corroles with various degrees of bromination. After characterization via MS and 2D NMR, electrochemical as well as UV-Vis measurements demonstrated that there is little steric deformation of the ligand framework upon increased bromination, which leads to a maximum of activity at maximum bromination.

We then successfully prepared the octabromo chromium corrole ( $\text{Br}_8\text{-tpfc}$ )Cr(py)<sub>2</sub>. The oxidized compound ( $\text{Br}_8\text{-tpfc}$ )Cr(O) was indeed reactive enough to oxidize various styrenes, albeit slowly (rates in the range:  $4.1 \cdot 10^{-5}$  -  $62 \cdot 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ ). More surprisingly, the chromium(III) counterpart was found to oxidize in air, back to the oxo. The reoxidation is painfully slow, due in part to the difficulty in dissociating an axial ligand, and part to the low reactivity of the five-coordinate species. To speed up the reoxidation, we switched to adding TFA to ( $\text{Br}_8\text{-tpfc}$ )Cr(py)<sub>2</sub>, in a bid to drive the ligand dissociation via trapping of the free pyridine.

The presence of an acid indeed leads to dramatically improved rates of air reoxidation of the compound, but at the same time, TFA was shown to play a non-innocent role in the process. We then proceeded to get rid of all the axial ligands altogether by treating the compound with HCl. The compound obtained displayed catalytic activity in the oxygenation of styrenes (~10 turnovers). The low turnover is due to product inhibition of the catalyst.

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**List of Abbreviations**

- (tpfc)H<sub>3</sub> (**1**): tris(perfluorophenyl)corrole
- (tpfc)Cr(O) (**2**): (Tris(perfluorophenyl)corrolato)chromium(V)oxo
- (tpfc)Cr(py)<sub>2</sub> (**3**): (Tris(perfluorophenyl)corrolato)bispyridinochromium(III)
- [(tpfc)Cr(O)]Cp<sub>2</sub>Co (**4**): (Tris(perfluorophenyl)corrolato)chromium(IV)oxo,  
cobaltocenium salt
- (tpfc)Cr(OPPh<sub>3</sub>)<sub>2</sub> (**5**): (Tris(perfluorophenyl)corrolato)  
bis(triphenylphosphinochromium(III))
- [(tpfc)Cr(O)]SbCl<sub>6</sub> (**6**): (Tris(perfluorophenyl)corrolato)chromium(V)oxo  
ligand radical
- (Br<sub>8</sub>-tpfc)Cr(O) (**7**): (octabromo-Tris(perfluorophenyl)corrolato)chromium(V)oxo
- (Br<sub>8</sub>-tpfc)Cr(py)<sub>2</sub> (**8**): (octabromo-Tris(perfluorophenyl)corrolato)bispyridino  
chromium(III)
- (Br<sub>8</sub>-tpfc)Cr(OPPh<sub>3</sub>)<sub>2</sub> (**9**): (octabromo-Tris(perfluorophenyl)corrolato)  
bis(triphenylphosphinochromium(III))
- (tpfc)Cr(OPPh<sub>3</sub>) (**10**): five-coordinate species of **5**