Gallium and Chromium Corroles

Thesis by

Alexandre Edouard Meier

In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

2003

(Defended April 7th, 2003)

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

Acknowledgements

This is probably the most difficult part of a thesis to write, since you can't really do justice to all the people who were involved in this work in a page or two. But I'll give it my best.

First I want to thank my advisor, Harry Gray, for being the best advisor one could ever dream. It's been a great privilege for me to work in his research group. He has been steadily guiding me from A to B without me being really aware of it. There are two memorable moments which come to mind: the first time I met him (I was in the hallway between his office and the coffee pot and I literally ran into him and he looked down at my 5 ft 8 self and said " So you're looking for me?") and the starting point of the corrole project (phone call at 5 pm in the lab from Harry: " Hey, Alex, there's this guy you got to talk to. I told him you'd stop by tomorrow at ten"). I think Harry deserves the credit for putting me in touch with Zeev and all the beautiful science that resulted.

That leads me to the other important person: Zeev Gross. He is the one who introduced me to corrole chemistry in the first place and I am glad he did. I am always amazed by his incredible focus and ability to get things done. I also wanted to acknowledge his generosity as well as that of his research group at the Technion in their willingness to share any lab details and data I needed.

Then of course I have to thank all the wonderful people who make the Gray group such a great place. I'm sure I'm forgetting a few people, especially the new faces, whom I haven't had a chance to meet. Thanks go out to: Angelo, for some truly amazing EPR work, Chris, whom I inherited the project from, Kevin, for keeping stuff working and organized around here, Will and Julia, for many hours of discussions about a variety of topics, Mahdi and Phil, whom I shared an office with in my early days, Jeremy, who has taken the corrole project into new and fascinating directions, Randy, Corrina, and Jen, for organizing the parties, keeping us in the right solvent (dilute solution of maltose, humulinic acid and yeast extract in 95:5 H_2O/EtOH), and making it out of here ahead of me. Akif, Ivan, Liz, Cindy, for being the generation ahead of me and imparting some wisdom, Jason, Jeff, John, and all the other very talented postdocs I interacted with over the years, and to all of you I forgot or don't know about.

Then of course all the fantastic support staff here at Caltech, secretaries, purchasing, stockrooms, delivery peoples, janitors, administrative staff, librarians, all of whom form an indispensable part of any research project.

On a more personal note I am indebted to a great many family and friends who have supported me through this endeavor: my parents, who always supported me no matter what I did, my high school chemistry teacher who got me started into that crazy world of chemistry in the first place. A great many thanks go out to everyone at Vision Christian Fellowship: Keith, one of my pastors, and friend, for the many hours we spent together talking about God and other stuff, to Michael and Cindy, for being such great friends and challenging me both intellectually and spiritually, to everyone in the Torrance reading group, for their amazing contribution to bridging the gap between science and theology, and all the other 20 or so people who have always stood by me.

I need to acknowledge my fantastic neighbors, Mike and Rebecca, for being the greatest neighbors in the world, Jim and Liz for being a rock in times of trouble, Cleve and Betty for the many hours spent together, David for being the most awesome friend I have in LA, and my hairstylist Ray, for keeping me presentable. To anyone I might have forgotten, my apologies. Seven years is such a long time.

To my son Lúcás
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->Cr σ 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 β 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 $(Br_8\text{-tpfc})Cr(py)_2$. The oxidized compound $(Br_8\text{-tpfc})Cr(O)$ was indeed reactive enough to oxidize various styrenes, albeit slowly (rates in the range:$4.1 \bullet 10^{-5}$- $62 \bullet 10^{-5}$ M^{-1} 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 $(Br_8\text{-tpfc})Cr(py)_2$, 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.

Table of Contents

List of Figures, Tables, and Schemes

List of Abbreviations

$(tpfc)H_3$ (**1**): tris(perfluorophenyl)corrole

(tpfc)Cr(O) (**2**): (Tris(perfluorophenyl)corrolato)chromium(V)oxo

$(tpfc)Cr(py)_2$ (**3**): (Tris(perfluorophenyl)corrolato)bispyridinochromium(III)

$[(tpfc)Cr(O)]Cp_2Co$ (**4**): (Tris(perfluorophenyl)corrolato)chromium(IV)oxo, cobaltocenium salt

$(tpfc)Cr(OPPh_3)_2$ (**5**): (Tris(perfluorophenyl)corrolato) bis(triphenylphosphinochromium(III)

$[(tpfc)Cr(O)]SbCl_6$ (**6**): (Tris(perfluorophenyl)corrolato)chromium(V)oxo ligand radical

$(Br_8\text{-}tpfc)Cr(O)$ (**7**): (octabromo-Tris(perfluorophenyl)corrolato)chromium(V)oxo

$(Br_8\text{-}tpfc)Cr(py)_2$ (**8**): (octabromo-Tris(perfluorophenyl)corrolato)bispyridino chromium(III)

$(Br_8\text{-}tpfc)Cr(OPPh_3)_2$ (**9**): (octabromo-Tris(perfluorophenyl)corrolato) bis(triphenylphosphinochromium(III)

$(tpfc)Cr(OPPh_3)$ (**10**): five-coordinate species of **5**