

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)

© 2003

Alexandre Edouard Meier

All Rights Reserved

*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 H₂O/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)H₃. We synthesized a chromium(V)oxo compound by reaction between (tpfc)H₃ and Cr(CO)₆ in refluxing toluene. Characterization of the compound via EPR and MS revealed a d¹ metal species. Hyperfine splittings for the compound are A(⁵³Cr) 1.64 mT, A(¹⁴N) 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⁻¹s⁻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: $4.1 \cdot 10^{-5}$ - $62 \cdot 10^{-5} M^{-1} s^{-1}$). 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

Acknowledgements.....	iv
Abstract	viii
Table of Contents	x
List of Figures, Tables, and Schemes.....	xiv
List of Abbreviations.....	xviii
Chapter 1	1
References.....	5
Chapter 2	8
Introduction.....	9
Experimental Section	10
Synthesis	10
Structure.....	10
Spectroscopy	11
Electrochemistry.....	11
Results and Discussion	11
References.....	24
Chapter 3	27
Introduction.....	28
Experimental Section	29
$[(tpfc)CrO]$ (2).....	32
$[(tpfc)Cr(py)_2]$ (3)	32
$[Cp_2Co][(tpfc)CrO]$ (4).....	34
$[(tpfc)Cr(OPPh_3)_2]$ (5)	35

[(tpfc [•])CrO](6).....	35
Spectroscopy	36
Electrochemistry.....	36
Results and Discussion	37
Electrochemistry.....	37
Oxidation and Reduction Products of 2	43
Chromium(III) Corroles 3 and 5	54
Concluding Remarks	65
References and Notes	65
Chapter 4	71
Introduction.....	72
Experimental Section	76
Methods	76
Spectroscopy	76
Electrochemistry.....	76
Materials	77
Kinetic measurements.....	77
Oxidation of PPh ₃ by (tpfc)Cr(O) (2)	77
Aerobic oxidation of 5 to 2	77
Results	79
Kinetic analysis for oxygenation of 5 to 2	79
Kinetics of oxygen-atom transfer from 2 to PPh ₃	89
Discussion.....	89

Conclusion	95
References.....	96
Chapter 5.....	98
Introduction.....	99
Experimental	100
Materials	100
Electrochemistry.....	100
Spectroscopy	100
Synthesis of (tpfc)Ga(py).....	101
Synthesis of (Br-tpfc)Ga(py)	101
Synthesis of (Br ₂ -tpfc)Ga(py) and (Br ₃ -tpfc)Ga(py)	101
Synthesis of (Br ₇ -tpfc)Ga(py)	102
Results	103
Synthesis of partially brominated gallium corroles.....	103
Determination of the structure of partially brominated corroles.....	107
Electrochemistry of brominated corroles.....	123
Steric deformation in corroles.....	127
UV-Vis of partially brominated corroles.....	128
Conclusion	132
References.....	135
Chapter 6.....	136
Introduction.....	137
Experimental	138

Materials	138
Preparation of (Br ₈ tpfc)Cr(py) ₂ , (8)	138
Preparation of (Br ₈ tpfc)Cr(O) (7)	139
Preparation of (Br ₈ tpfc)Cr(OPPh ₃) ₂ (9)	139
Oxidation of PPh ₃ by (Br ₈ tpfc)Cr(O) (7)	139
Oxidation of 4-substituted styrenes by (Br ₈ tpfc)Cr(O) (7)	140
Aerobic oxidation of (Br ₈ tpfc)Cr(py) ₂ (8) to 7	140
Reaction between (Br ₈ tpfc)Cr(py) ₂ and TFA at low concentrations.....	141
Reaction between (Br ₈ tpfc)Cr(py) ₂ and TFA at high concentrations	141
Preparation of pyridine-free/acid-free (Br ₈ tpfc)Cr(O)	141
Reactivity of pyridine-free/acid-free 7	142
Results and discussion	143
Bromination of 2 (synthesis of 8, 9, and 7)	143
Oxygen atom transfer from 7 to styrenes	152
Reoxidation of (Br ₈ -tpfc)Cr(py) ₂ in the presence of TFA	159
Role of TFA during oxidation.....	160
Preparation of pyridine-free (Br ₈ tpfc)Cr(O)	165
Reactivity of (Br ₈ tpfc)Cr(O)	165
Conclusion	172
References.....	177

List of Figures, Tables, and Schemes

Scheme 2.1. Synthesis of 2	13
Table 2.1. EPR parameters and reduction potentials for oxochromium(V) complexes.....	15
Figure 2.1. EPR spectrum of 2 in CH ₂ Cl ₂ at room temperature.....	17
Figure 2.2. Structure of the twisted conformer of 2	20
Table 2.2. Selected bond lengths (Å) and angles (°).....	22
Scheme 3.1. Interconversion between the various oxidation states of chromium corroles.....	30
Figure 3.1. Cyclic voltammogram of 2 in 0.1 M TBAPF ₆ /CH ₂ Cl ₂ solution (22 °C). Scan rate: 25 mV/s.....	39
Figure 3.2a. Spectroelectrochemical oxidation of a solution of 2 in 0.1 M TBAPF ₆ /CH ₂ Cl ₂ at an applied potential of 1.64 V vs. Ag/AgCl (22 °C). Inset: Spectral changes upon treatment of a CH ₂ Cl ₂ solution of 2 with 11 . The band marked by (*) is due to the excess organic radical present.....	41
Figure 3.2b. Spectroelectrochemical reduction of a solution of 2 in 0.1 M TBAPF ₆ /CH ₂ Cl ₂ at an applied potential of 0.0 V vs. Ag/AgCl (22 °C). Inset: spectrum obtained after treatment of 2 with Cp ₂ Co.....	45
Figure 3.3. EPR spectrum of electrochemically generated 6 in 0.1 M TBAPF ₆ /CH ₂ Cl ₂ frozen solution (30 K). Inset: total signal intensity vs. temperature (the solid line was calculated for ΔE=9 cm ⁻¹).....	48
Figure 3.4. ¹⁹ F and ¹ H-NMR (inset) spectra of [(tpfc)Cr ^{IV} O] ⁻ (4) in acetone-d ₆ solution (22 °C).....	50
Scheme 3.2 Chemical oxidation and reduction of 2	52

Figure 3.5. Molecular structure of 3 : the Cr-corrole core is flat and the axial pyridines are nearly coplanar; Cr ^{III} -N distances are 1.926(4)-1.952(4) Å (pyrrole) and 2.109(4)-2.129(4) Å (pyridine).....	57
Figure 3.6. UV-Vis spectra of [(tpfc)Cr(py) ₂] (solid line) and [(tpfc)Cr(OPPh ₃) ₂] (dashed line) in toluene solution (22 °C).....	59
Table 3.1. Selected structural parameters for related [(tpfc)M ^{III} (py) ₂] complexes (diffraction measurements at 110 K).....	61
Figure 3.7. (a) Frozen solution EPR spectrum of [(tpfc)Cr(III)(py) ₂] (solvent 10:1 CD ₂ Cl ₂ /pyridine-d ₅ , 77 K). (b) Experimental vs. computer simulated EPR spectra of a polycrystalline sample of [(tpfc)Cr(III)(py) ₂] co-crystallized with [(tpfc)Co(III))(py) ₂] (expl, 3.9 K).	63
Scheme 4.1. Numbering scheme for the various chromium compounds.....	74
Figure 4.1. Spectral changes upon aerobic oxidation of a 12.8 μM solution of 5 in 1.69 mM OPPh ₃ /CH ₂ Cl ₂	81
Figure 4.2. Plot of k _{obs} as a function of the partial pressure of oxygen, for the transformation of 5 to 2	83
Figure 4.3. The rate constants for aerobic oxidation of 5 in CH ₂ Cl ₂ as a function of the concentration of OPPh ₃ . The solid line is based on a non-linear regression of Equation 7	87
Table 4.2. Kinetic parameters for aerobic oxidation of 5	91
Figure 4.4. Spectral changes for the reaction between 2 and PPh ₃	93

Figure 5.1. Typical ESI-MS patterns for some partially brominated corroles. The left column shows the full spectrum, while the right column shows the detailed isotopic pattern	105
Figure 5.2a. Labeling scheme for the corrole protons.....	109
Figure 5.2b. ^1H NMR spectrum of (tpfc)Ga(py) in CH_2Cl_2 at room temperature.....	111
Figure 5.3. ^{13}C NMR spectrum of (tpfc)Ga(py) in CH_2Cl_2 at room temperature.....	113
Figure 5.4. HMQC spectrum of (tpfc)Ga(py) in CH_2Cl_2 at room temperature.	115
Figure 5.5. HMBC spectrum of (tpfc)Ga(py) in CH_2Cl_2 at room temperature.....	117
Figure 5.6. ^1H NMR spectra of : a) (Br-tpfc)Ga(py), b) (Br ₂ -tpfc)Ga(py),.....	121
and c)(Br ₃ -tpfc)Ga(py) in CH_2Cl_2 at room temperature.....	121
Figure 5.7. a) Typical cyclic voltamogram of (tpfc)Ga(py) in 0.1M TBAPF ₆ / CH_2Cl_2 ;	
b) dependence of E^{ox} and E^{red} on the number of bromine substituents.	125
Figure 5.8. UV-Vis spectrum of brominated gallium corroles in CH_2Cl_2 . Soret and Q bands are shown in inserts.	129
Figure 5.9. Relative shift of the two HOMOs in (TPP)Zn (a) and (tpfc)Ga(py) (b)..	133
Figure 6.1. ESI-MS of (Br ₈ tpfc)Cr(py) ₂ in methanol. Main peak is (Br ₈ tpfc)Cr(OMe). Small peak is (Br ₈ tpfc)Cr(O).	144
Figure 6.2a. UV-Vis spectra of (Br ₈ tpfc)Cr(py) ₂ (solid line) and (Br ₈ tpfc)Cr(OPPh ₃) ₂ (dashed line) in toluene.....	146
Figure 6.2b. EPR spectrum of (Br ₈ tpfc)Cr(py) ₂ in pyridine/toluene 1:9. Inset: EPR of (Br ₈ tpfc)Cr(O) in CH_2Cl_2	148
Table 6.1. EPR parameters for 2 and 7	150

Figure 6.3. Linear free energy plot for the reactivity of <i>para</i> -substituted styrenes in toluene in terms of the Hammett σ parameter.	154
Table 6.2. Kinetic parameters for O-atom transfer to substrates in toluene.	156
Figure 6.4. Absorbance traces at 502, 472, and 481 nm, showing the disappearance of 8 , appearance of an intermediate, and formation of 7	161
Figure 6.5. Comparison of the spectra of : a) 8 and intermediate in pentane. b) 7 and intermediate in pentane. The intermediate is always shown as a broken line.	163
Figure 6.6. Dependence of the rate of oxidation of 8 in pentane upon the concentration of TFA.	167
Figure 6.7. Typical traces for the reaction of 7 with increasing amounts of 4-methoxystyrene in the absence (a) and the presence (b) of pyridine.	169
Table 6.3. Products in the aerobic oxidation of 4-methoxystyrene catalyzed by 7	173
Figure 6.8. a) UV-Vis traces of the reaction between 7 and 4-methoxystyrene over several hours. b) final product.	175

List of Abbreviations

(tpfc)H₃ (**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)]Cp₂Co (**4**): (Tris(perfluorophenyl)corrolato)chromium(IV)oxo,
cobaltocenium salt

(tpfc)Cr(OPPh₃)₂ (**5**): (Tris(perfluorophenyl)corrolato)
bis(triphenylphosphinochromium(III))

[(tpfc)Cr(O)]SbCl₆ (**6**): (Tris(perfluorophenyl)corrolato)chromium(V)oxo
ligand radical

(Br₈-tpfc)Cr(O) (**7**): (octabromo-Tris(perfluorophenyl)corrolato)chromium(V)oxo

(Br₈-tpfc)Cr(py)₂ (**8**): (octabromo-Tris(perfluorophenyl)corrolato)bispyridino
chromium(III)

(Br₈-tpfc)Cr(OPPh₃)₂ (**9**): (octabromo-Tris(perfluorophenyl)corrolato)
bis(triphenylphosphinochromium(III))

(tpfc)Cr(OPPh₃) (**10**): five-coordinate species of **5**