STEREOELECTRONIC MODIFICATION OF ORGANOCHROMIUM COMPLEXES

by

Benjamin E. Olafsen

B.Sc., The University of British Columbia Okanagan, 2017

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in

THE COLLEGE OF GRADUATE STUDIES

(Chemistry)

THE UNIVERSITY OF BRITISH COLUMBIA

(Okanagan)

September 2020

© Benjamin E. Olafsen, 2020
The following individuals certify that they have read, and recommend to the College of Graduate Studies for acceptance, a thesis/dissertation entitled:

Stereoelectronic modification of organochromium complexes

submitted by Benjamin E. Olafsen in partial fulfillment of the requirements of

the degree of Master of Science

Dr. Kevin M. Smith, Science/Chemistry

Supervisor

Dr. Frederic Menard, Science/Chemistry

Supervisory Committee Member

Dr. Stephen McNeil, Science/Chemistry

Supervisory Committee Member

Dr. Lukas Bichler, Engineering/Mechanical

University Examiner
Abstract

This thesis explores the intimate relationship between structure and reactivity between two classes of organochromium complexes. The stereoelectronic environment of a metal center can have profound impacts on the observed reactivity of the complex. By manipulating the coordination environment and observing how the reactivity and properties of the complex change, patterns can be teased out that guide future design of complexes tailored for specific reactivity.

In Chapter 2, cyclopentadienyl complexes of chromium featuring guanidinate complexes are synthesized and compared to cyclopentadienyl β-diketiminate organochromium complexes which have been previously investigated in the Smith research group. It was found that the reduced steric pressure of the guanidinate ligands compared to the β-diketiminate ligands results in increased reductive power of the complex as demonstrated by the ability to activate tertiary alkyl halides as well as subsequent trapping of the tertiary alkyl radical. Furthermore, increased rates of oxidative addition of primary alkyl halides were concluded by comparing activation of iodomethane using the β-diketiminate complexes and phenethyl chloride using the guanidinate complexes.

The reduced steric pressure of the guanidinate complexes results in stronger CrIII-X (X = alkyl, halide) bonds which leads to difficulties in reduction of the complex to regenerate the active chromium(II) complex. In the second part of Chapter 2 it was found that the use of a hypervalent silane is an effective homogeneous reductant for the reduction of both the chromium(III) β-diketiminate and guanidinate complexes. The chapter concludes with the implementation of this reductant in a simple radical homocoupling reaction using a series of CpCr(LX) catalysts.
Chapter 3 of this thesis explores unexpected photoactivity observed when exposing cationic [Cr(bpy)_2(Ar)_2]^+ complexes. It was found that exposure to light induces reductive elimination of the aryl groups forming biaryl compounds. Experiments previously conducted by Jesse Crescenzo as well as subsequent trapping and mass spectrometry experiments elucidate the mechanism of this reductive elimination event. It was found that replacement of one of the bipyridine ligands with LX ligands affords neutral compounds that exhibit similar photoactivity observed by ^1H NMR. Future experiments are outlined at the conclusion of this chapter to exploit this unique reactivity mode.
Lay Summary

This thesis explores the unique relationship between the structure of a chemical compound and its overall function. In general, it will explore the interactions between a metal (chromium) and the molecules bonded to that metal, and how the structure or shape of those molecules affect the overall function of the resulting complex as a whole. The goal of this thesis is to understand what structural factors affect the function in a broad sense in order to guide future design for specialized function. It will be shown that even minor modifications on a molecular scale lead to profound impacts to the reactivity of the complex. Systematic evaluation of these allow for extrapolation to broad patterns that can guide the future researcher.
Preface

The majority of the work outlined in Chapter 3 has been published and some figures reproduced with permission from: Olafsen, B.E.; Crescenzo, G.V.; Moisey, L.P.; Patrick, B.O.; Smith, K.M. Inorg. Chem. 2018, 57, 9611-9621. Initial synthetic and photochemical experiments for compounds 3.1 and their derivatives were carried out by Jesse Crescenzo. UV-vis analysis of these compounds as well as cyclic voltammetry experiments were also carried out by Jesse Crescenzo. The trapping experiments involving bipyridine were carried out by Jesse Crescenzo. The trapping experiments involving ZnCl$_2$ and benzoyl peroxide were carried out by Benjamin Olafsen. Synthetic experiments involving the neutral organochromium(III) bipyridine complexes outlined in subchapter 3.2 were carried out by Benjamin Olafsen. The complex, Cr(bpy)(quin)$_2$ was synthesized by Luke Moisey and characterized crystallographically by Dr. Brian O. Patrick.
Table of Contents

Abstract ............................................................................................................................... iii
Lay Summary ................................................................................................................... v
Preface ............................................................................................................................... vi
Table of Contents ............................................................................................................ vii
List of Tables .................................................................................................................. vii
List of Figures ................................................................................................................ x
List of Schemes ............................................................................................................ xiii
List of Symbols and Abbreviations .............................................................................. xv
Acknowledgements ....................................................................................................... xvii
Dedication ....................................................................................................................... xviii

1 Introduction ................................................................................................................. 1
  1.1 Catalysis with Noble Metals .................................................................................. 1
  1.2 History of Chromium Mediated Radical Reactivity .............................................. 2
  1.2.1 \([\text{Cr(OH}_2\text{)}_6]^2+\) ....................................................................................... 2
  1.2.2 Persistent Radical Effect .................................................................................. 3
  1.2.3 Nozaki-Hiyama-Kishi Reaction ...................................................................... 4
  1.3 Cyclopentadienyl \(\beta\)-Diketiminate Complex of Chromium ............................... 5
  1.4 Chemistry of Chromium Polypyridyl Complexes ................................................ 11
  1.5 Thesis Objectives .................................................................................................. 13

2 Reduction and Radical Reactions of Cyclopentadienyl Chromium Amidinate Complexes ...................................................................................................................... 15
  2.1 CpCr(guanidinate) Complexes .............................................................................. 15
    2.1.1 Alkyl Halide Activation ................................................................................. 22
    2.1.2 Attempted Alkylations .................................................................................. 26
    2.1.3 Homolysis of CpCr[(CyN)_2CN(SiMe_3)_2]Bn .................................................. 31
  2.2 Reduction of CpCr(LX)X Complexes .................................................................. 38
    2.2.1 Reduction Using Stoichiometric Manganese .................................................. 38
    2.2.2 Reduced Pyrazine Reagent for Catalyst Activation ...................................... 39
    2.2.3 Reduction using Pyridinium Salts .................................................................. 40
    2.2.4 Hypervalent Silanes as Reducing Agents ...................................................... 42
    2.2.5 Reactions Using Hypervalent Silane Reductant ............................................ 45
2.2.6 Attempted Synthesis of CpCr[(CyN)₂CMe]F..................................................... 50
2.3 Experimental Section ..................................................................................... 51
2.3.1 General Considerations .............................................................................. 51
2.3.2 Synthetic Procedures.................................................................................. 52

3 Photochemistry of Chromium(III) Bipyridine Complexes ............................... 68
3.1 Cationic Chromium(III) bis(Bipyridine) bis(Aryl) Complexes .................... 68
  3.1.1 Unexpected Photoreactivity ...................................................................... 68
  3.1.2 Substituent Effect on Reduction Potential and UV-vis absorption ............ 69
  3.1.3 Inhibition Experiments ............................................................................ 70
  3.1.4 Proposed Mechanism for Photochemical Formation of Biphenyl ............. 73
  3.1.5 Cross-Over Experiments ........................................................................... 74
  3.1.6 Trapping Experiments .............................................................................. 76
3.2 Neutral Chromium(III) Bipyridine bis(Aryl) Complexes .............................. 77
  3.2.1 Neutral Dithiocarbamate Complex ............................................................ 77
  3.2.2 Neutral Quinolinate Complex .................................................................. 78
3.3 Experimental Section ..................................................................................... 82
  3.3.1 General Considerations ............................................................................ 82
  3.3.2 Synthetic Procedures................................................................................ 83

4 Conclusion ........................................................................................................ 90

References ............................................................................................................ 92

Appendices ............................................................................................................ 95
  Appendix A: UV-vis Spectra of Select Compounds ........................................ 95
  Appendix B: Supplemental X-Ray Data............................................................ 98
  Appendix C: List of all numbered compounds............................................... 99
List of Tables

Table 2.1: Bibenzyl yields for various chromium catalysts and controls following timed reaction test ................................................................. 49

Table 2.2: Attempted reductions using reduced pyrazine reagents ........................................ 60

Table 2.3: Reagent amounts for catalytic bibenzyl formation (route B) .................................. 64

Table 2.4: Reagents and yields for timed test of bibenzyl formation (route B) ....................... 66

Table 3.1: UV-vis absorbance and electrochemical data for [Cr(R-bpy)(C₆H₄-R)₂][BPh₄]. a in acetonitrile. b Potentials reported vs. [Cp₂Fe]⁺/0. In THF at room temperature with 0.1 M [NBu₄][PF₆] .................................................................................................................. 70
List of Figures

Figure 1.1: Alkyl halide activation with [Cr(en)$_2$(OH)$_2$]$^{2+}$ ......................................................... 3
Figure 1.2: Catalytic NHK reaction ........................................................................................................ 5
Figure 1.3: Single-electron oxidative addition of alkyl halides with CpCr(LX) complexes .............. 6
Figure 1.4: Steric interference caused by N-arylantho substituents .................................................. 8
Figure 1.5: Oxidation states of 2,2'-bipyridine and interpyridyl bond lengths ............................ 13
Figure 2.1: Commonly employed carbodiimides and nucleophiles used in the synthesis of amidinate ligand salts .................................................................................................................... 16
Figure 2.2: Proposed orbital energy diagrams for compound 2.1 (right) and compound 2.2 (left) ............................................................................................................. 19
Figure 2.3: Complex 2.2 front and side view. Thermal ellipsoids shown at 50 % probability. Selected bond lengths in Å. Cr(1)-C(1) 2.302(2), Cr(1)-C(2) 2.329(2), Cr(1)-C(3) 2.350(2), Cr(1)-C(4) 2.314(2), Cr(1)-C(5) 2.330(2), Cr(1)-N(1) 2.0292(17), Cr(1)-N(2) 2.0358(16). Cr-Cp centroid length 1.991 Å. .......................................................... 20
Figure 2.4: Complex 2.1 thermal ellipsoid diagram (50 % probability). Selected bond lengths in Å. Cr1-C1 2.265(2), Cr1-C2 2.2474(19), Cr1-C3 2.2354(18), Cr1-C4 2.2457(18), Cr1-C5 2.2606(19), Cr1-N1 2.0116(13), Cr1-N2 2.00532(13), Cr1-C11 2.2995(6). Cr-Cp centroid length 1.904 Å........................................................... 21
Figure 2.5: Complex 2.1a thermal ellipsoid diagram (50 % probability). Select Bond Lengths in Å. Cr1-C1 2.238(2), Cr1-C2 2.236(2), Cr1-C3 2.246(2), Cr1-C4 2.256(2), Cr1-C5 2.248(2), Cr1-N1 1.9975(18), Cr1-N2 2.0026(16), Cr1-C11 2.2960(6). Cr-Cp centroid length 1.900 Å. ......... 22
Figure 2.6: Rate law derivation for single electron oxidative addition reaction............................... 23
Figure 2.7: Plot of observed rate constant versus concentration of tert-butyl chloride for CpCr[(CyN)$_2$CN(SiMe$_3$)$_2$] .......................................................................................................................... 24
Figure 2.8: Plot of observed rate constant versus concentration of (2-chloro)ethyl benzene for CpCr[(CyN)$_2$CN(SiMe$_3$)$_2$] .......................................................................................................................... 25
Figure 2.9: 2.4 Thermal ellipsoid diagram (50 % probability). Selected bond lengths in Å. Cr1-C1 2.2582(16), Cr1-C2 2.2768(16), Cr1-C3 2.3018(16), Cr1-C4 2.3013(16), Cr1-C5 2.297(3), Cr1-N1 2.0235(12), Cr1-N2 2.0237(12), Cr1-C25 2.1184(16). Cr-Cp centroid distance 1.943 Å. .................................................................................................................. 28
Figure 2.10: Complex 2.5 Thermal ellipsoid diagram (50 % probability). Selected Bond lengths in Å. Cr1-C1 2.260(3), Cr1-C2 2.254(3), Cr1-C3 2.265(3), Cr1-C4 2.299(3), 2.297(3), Cr1-N1 2.0159(19), Cr1-N2)2.032(2), Cr1-C62.064(4). Cr-Cp centroid length 1.934 Å. ................. 30
Figure 2.11: UV-vis spectra of 2.4 in presence of PhSSPh for 17 hour in dark (blue) followed by 30 min exposure to light (orange)................................................................................................. 32

Figure 2.12: UV-vis absorption trace of reacting CpCr(CyN)_2CN(SiMe)_3]Bn with 207 equiv. PhSSPh. [Cr] = 2.70x10^-4 M, [PhSSPh] = 5.59x10^-2 M in hexanes. UV-vis spectra taken every 5 min. ....................................................................................................................................... 34

Figure 2.13: Plot of decaying absorbance at 540 nm showing decreasing concentration of CpCr[(CyN)_2CN(SiMe)_3]Bn during photolysis reaction with PhSSPh. k_obs calculated at 9.93x10^-2 min^-1 .................................................................................................................................. 35

Figure 2.14: UV-vis absorption trace of reacting CpCr[(CyN)_2CN(SiMe)_3]Bn with 207 equiv. PhSSPh. [Cr] = 2.70x10^-4 M, [PhSSPh] = 5.59x10^-2 M in hexanes. UV-vis spectra taken every 5 min using 395 nm cut-on filter........................................................................................................ 36

Figure 2.15: Plot of decaying absorbance at 540 nm showing decreasing concentration of CpCr[(CyN)_2CN(SiMe)_3]Bn during homolysis reaction with PhSSPh with 395 nm (lower) and 435 nm (upper) cut-on filters. k_obs calculated at 4.21x10^-2 min^-1 and 1.91x10^-2 min^-1 respectively. .................................................................................................................................. 36

Figure 2.16: UV-vis absorption trace of reacting CpCr[(CyN)_2CN(SiMe)_3]Bn with 9.9 equiv. PhSSPh. [Cr] = 5.48x10^-4 M, [PhSSPh] = 5.40x10^-3 M in hexanes. UV-vis spectra taken every 5 min using 515 nm cut-on filter .................................................................................................................................. 37

Figure 2.17: UV-vis spectrum of CpCr[(CyN)_2CN(SiMe)]Bn, 1.69x10^-4 M in hexanes indicating possible area responsible for homolysis. ................................................................................................................................. 38

Figure 2.18: UV-vis spectrum of CpCr^II(nacnac) before and after air exposure ................. 44

Figure 2.19: Crystal structure obtained following reduction of CpCr^III(xyl-nacnac)Cl with pentavalent silane................................................................................................................................. 44

Figure 2.20: Thermal ellipsoid diagram (50% probability) of CpCr[(CyN)_2C(Me)](η^1-Cp) (compound 2.10). Select bond lengths in Å Cr1-C1 2.2559(16), Cr1-C2 2.2718(15), Cr1-C3 2.2680(15), Cr1-C4 2.2572(15), Cr1-C5 2.2473(15), Cr1-N1 2.0202(13), Cr1-N2 2.0165(12), Cr1-C6 2.1916(15). Cr-Cp centroid length 1.913 Å. .................................................................................................................................. 51

Figure 3.1: Unexpected photoactivity of [Cr(bpy)_2(Ar)]^+ and observed colour change upon photolysis ........................................................................................................................................ 68

Figure 3.2: UV-vis spectra of [Cr(bpy)_2(Ph)]_2[BPh_4] (3.3x10^-4 M in THF) before photolysis (green), after photolysis with 395 nm cut-on filter (red), 435 nm cut-on filter (yellow), 475 nm cut-on filter (blue). .................................................................................................................................. 71

Figure 3.3: Absorbance at 578 nm [Cr(bpy)_2(Ph)]_2[BPh_4] (3.48x10^-4 M in THF) upon photolysis with excess bipyridine (upper), and without (lower). .................................................................................................................................. 72

Figure 3.4: Absorbance at 545 nm [Cr(bpy)_2(Ph)]_2[PF_6] (7.84x10^-4 M in MeCN) upon photolysis with excess ZnCl_2 (lower), and without (upper) ... 73
Figure 3.5: GC/MS traces of crossover experiment......................................................... 75
Figure A.1: UV-vis spectra of compound 2.1 (1.00x10^-3 M in THF)............................... 95
Figure A.2: UV-vis spectra of compound 2.3 (5.76x10^-3 M in hexanes) ......................... 95
Figure A.3: UV-vis spectra of compound 2.4 (9.7x10^-4 M in THF)............................... 96
Figure A.4: UV-vis spectra of compound 2.5 (2.00x10^-4 M in hexanes) ....................... 96
Figure A.5: UV-vis spectrum of CpCr[(CyN)_2CN(SiMe_3)_2](Bu) (1.15x10^-3 M in THF)..... 97
Figure A.6: UV-vis spectrum of CpCr[(CyN)_2CN(SiMe_3)_2(CH_2CH_2Ph) (qualitative in THF) ... 97
List of Schemes

Scheme 1.1: Sneeden and Zeiss synthesis of cationic \([\text{Cr(bpy)}_2(o-\text{OMePh})_2]^+\) ........................................... 11

Scheme 2.1: Chromium(II) amidinate complexes formed observed by Gambarotta with varying R,R’ amidinate substituents ................................................................. 17

Scheme 2.2: Synthetic route to complex 2.1................................................................. 18

Scheme 2.3: Synthetic route to complex 2.2................................................................. 18

Scheme 2.4: Synthetic route to complex 2.3................................................................. 27

Scheme 2.5: Synthetic route to complex 2.4................................................................. 27

Scheme 2.6: Observed formation of 2.2 when reacting 3.1 with 2-phenyl-2-methylpropylmagnesiumchloride .......................................................................................... 28

Scheme 2.7: Isolated magnesium complex from reacting 3.1 with cyclohexylmagnesiumbromide .............................................................................................................. 29

Scheme 2.8: Isolated chromium(II) dimer from reacting 2.1 with methylmagnesium iodide..... 30

Scheme 2.9: Synthetic route to complex 2.5................................................................... 30

Scheme 2.10: Light-induced homolysis of Cr-Bn bond followed by trapping with PhSSPh to form complex 2.6.................................................................................. 33

Scheme 2.11: Synthesis of reduced pyrazine reagent for catalyst activation .................. 39

Scheme 2.12: Attempted reduction of CpCr(LX)X complexes with Mashima’s reagent ....... 39

Scheme 2.13: Turner’s synthesis of pyridinium salts for reduction of organohalides............. 40

Scheme 2.14: Activation of pyridinium salts by reduction with sodium hydride ................. 41

Scheme 2.15: Activation of pyridinium salts by reduction with potassium bis(trimethylsilyl)amide............................................................................................................. 41

Scheme 2.16: Attempted reduction of CpCr(nacnac)Cl complex with activated pyridinium salt 42

Scheme 2.17: Synthesis of hypervalent silane................................................................... 42

Scheme 2.18: Successful reduction of CpCr(xyl-nacnac)Cl with hypervalent silane .......... 43

Scheme 2.19: Oxidized product of CpCrII(xyl-nacnac) upon air exposure characterized by Cory MacLeod ................................................................. 43

Scheme 2.20: Bibenzyl formation via radical coupling using phenylsilane and sodium tert-butoxide as reducing agent................................................................. 46
Scheme 2.21: Mechanism of bibenzyl formation ................................................................. 46
Scheme 2.22: Organic products collected from bibenzyl reaction .............................................. 47
Scheme 2.23: Proposed mechanism for reduction of CpCr\textsuperscript{III}(nacnac)Cl............................... 48
Scheme 2.24: Benzyl chloride and benzylmagnesiumchloride coupling using various chromium catalysts ......................................................................................................................... 48
Scheme 2.25: Timed reaction test coupling benzyl chloride and benzylmagnesiumchloride ..... 49
Scheme 2.26: Attempted synthesis of CpCr[(CyN)\textsubscript{2}CMe]F.................................................. 50
Scheme 3.1: Proposed mechanism for photochemical formation of biphenyl from [Cr(bpy)\textsubscript{2}(Ar)\textsubscript{2}]\textsuperscript{+} .......................................................................................................................... 73
Scheme 3.2: Crossover photolysis experiment between 3.2I and 3.3I ........................................... 74
Scheme 3.3: Formation of compound 3.4PF\textsubscript{6} ....................................................................... 76
Scheme 3.4: Independent synthesis of [Cr(bpy)\textsubscript{2}(O\textsubscript{2}CPh)\textsubscript{2}][PF\textsubscript{6}] ........................................................... 77
Scheme 3.5: Marchese and West synthesis of neutral dithiocarbamate bis(aryl) complex 3.5 .... 77
Scheme 3.6: Photochemically induced reductive elimination of neutral dithiocarbamate complex .................................................................................................................................... 78
Scheme 3.7: Trapping and attempted synthesis of neutral Cr(bpy)(Me\textsubscript{2}NCS)\textsubscript{2}(O\textsubscript{2}CPh)\textsubscript{2} ....... 78
Scheme 3.8: Synthesis of neutral 3.6 by protonolysis route using Müller’s Cr(bpy)(Ph)\textsubscript{3}(THF) complex ....................................................................................................................... 79
Scheme 3.9: Photochemical reaction pathway of (quin) complex and synthetic route ............. 80
Scheme 3.10: Closing the cycle for photochemical biaryl formation ........................................ 81
Scheme 3.11: Potential future application for photochemical C-H functionalization .......... 82
List of Symbols and Abbreviations

The following is a list of abbreviations and symbols employed in this Thesis, most of which are in common use in the chemical literature.

Å Ångstrom, $10^{-10}$ m
Ar aryl group, $C_6H_4R$ (R = H, alkyl)
bpy $2,2'$-bipyridine
¹Bu tert-butyl, $Me_3C$-
C degree Celsius
$cm^{-1}$ wavenumber, $1.877 \cdot 10^{-23}$ J
Cp cyclopentadienyl, $\square^5C_5H_5$
CV cyclic voltammogram, or cyclic voltammetry
d days, or doublet (in a spectrum)
DCC dicyclohexylcarbodiimide
dep 2,6-diethylphenyl
DIC diisopropylcarbodiimide
dpp 2,6-diisopropylphenyl
EDC $N$-ethyl-$N'$-dimethylaminopropylcarbodiimide
eq equation
equiv equivalents
Et ethyl, $CH_2CH_2$-
g grams
¹H proton
h hours
HOMO highest occupied molecular orbital
iPr isopropyl, $(CH_3)_2CH$-
IR infrared
K Kelvin
k rate constant
$\lambda_m$ lambda max, local UV-vis absorbance maxima
L neutral, 2-electron-donor ligand; or litre, $10^{-3}$ m$^{-3}$
LUMO lowest unoccupied molecular orbital
LX monoanionic, bidentate, 3-electron donor ligand
$\mu_B$ Bohr magneton, $9.274 \cdot 10^{-24}$ JT$^{-1}$
M metal; or molar, $molL^{-1}$
$m/z$ mass-to-charge ratio (in mass spectrometry)
Me methyl, $CH_3$-
min minutes
mmol millimole, $10^{-3}$ mole
MO molecular orbital
mol mole, $6.022 \cdot 10^{23}$ particles
mL  millilitre, 10^{-3} \text{ L}
MS  mass spectrum, mass spectrometry
Nacnac  \( \beta \)-diketiminate ligand \{ArNCMe\}_2CH
NMR  nuclear magnetic resonance
no.  number
Ph  phenyl, C_6H_5-
ppm  parts per million
py  pyridine, C_5H_5N
R  alkyl
\textsuperscript{t}Bu  \textit{tert}-butyl group, -CMe_3
THF  tetrahydrofuran, C_4H_8O
X  halide or other anionic 1-electron-donor ligand
xyl  xylyl group, 2,6-dimethylphenyl
Acknowledgements

I would like to first acknowledge my sincerest gratitude to Dr. Kevin M. Smith and his incredible support throughout both my Honour’s as well as Master’s of Science program. He has been an exceptional supervisor and I could not do this without his continued guidance. I would also like to acknowledge my committee members, Dr. Frederic Menard and Dr. Stephen McNeil for their wisdom over the course of my academic career. To my lab-mates, specifically Chelsey Brien, Danika Cheater, Simon Edelmann, and Tanner Thiessen, thank you for making the lab a fun and inspiring place to research. Finally, I would like to acknowledge my partner, Jeff Denney for keeping me going all these years and supporting this passion of mine. Thank you all.
Dedication

I dedicate this body of work to you mom. Thank you for pushing me further than I thought I could go. I hope you are watching to see me prove you right.
1 Introduction

1.1 Catalysis with Noble Metals

Catalysis offers chemists unique ways to achieve targeted transformations by manipulating substrates and creating reactive intermediates that cascade toward the desired molecule. In this regard, well defined examples of second and third row metals like ruthenium, iridium, and especially palladium have dominated and provided synthetic organic chemists with a myriad of methodology to achieve a desired transformation. Palladium catalyzed cross-coupling reactions such as Heck, Negishi, and Suzuki-Miyaura have become commonplace in the organic synthesis of natural products and academia.\(^1\) The classic two-electron oxidation of alkyl- and aryl halides by a palladium(0) compound generates a Pd(II) intermediate. Reacting this intermediate with a transmetalating reagent installs the second alkyl or aryl group on the palladium ion, and the cycle is completed by reductive elimination of the two organic substrates to afford the new carbon-carbon bond.\(^1\) Iridium has been employed as an effective hydrogenation catalyst with excellent stereoselectivity with the correct choice of ligand.\(^2\) And recently, both iridium and ruthenium polypyridyl complexes have been shown to be good photocatalysts employed in visible light induced transformations in organic synthesis.\(^3\) The robustness of these catalysts and their applicability in a variety of different reaction manifolds makes them indispensable tools in the synthetic chemist’s toolbox.

While these noble metals demonstrate broad applicability, strong tolerance and selectivity, their relative scarcity and toxicity represents problems for their industrial implementation. In contrast, Earth-abundant first-row metal catalysts tend to be significantly more environmentally benign, and their abundance makes them more economically efficient for industrial applications. Lastly, they tend to have reactivity patterns that are complementary to their isoelectronic second
and third row counterparts. Specifically, their ability to effect radical transformations on organic substrates represents a growing area of interest in the literature. To this effect, organometallic complexes of chromium offer a unique opportunity to study this radical reactivity based on a significant breadth of literature that can inform and guide the rational design of novel organochromium complexes for metal mediated radical reactivity.

This thesis addresses a gap in the literature of paramagnetic organometallic compounds with a specific focus on reactivity consequences of stereoelectronic modification of a set of organochromium compounds. Classical characterization techniques such as NMR spectroscopy tend to be ineffective for paramagnetic compounds due to broadening of resonances in the NMR spectrum. It is only due to the improvement of techniques such as X-ray diffraction and electron paramagnetic spectroscopy that researchers are now able to probe the structural and electronic consequences of ligand modification. This allows for broad trends to be extracted from the data that can guide future compound design.

1.2 History of Chromium Mediated Radical Reactivity

1.2.1 \([\text{Cr(OH}_2\text{)}_6]^{2+}\)

An early reported example of an aqueous organochromium compound was initially prepared by Anet and Leblanc by reacting benzyl chloride with aqueous \([\text{Cr(OH}_2\text{)}_6]^{2+}\) to afford \([\text{Cr(OH}_2\text{)}_5(\text{CH}_2\text{Ph})]^{2+}\) and \([\text{Cr(OH}_2\text{)}_5(\text{Cl})]^{2+}\). Mechanistic investigation into the reaction profile by Kochi found that this reaction proceeded through two subsequent single-electron oxidation events; the first reaction was the oxidation of one equivalent of \([\text{Cr(OH}_2\text{)}_6]^{2+}\) which afforded the chloropentaaquochromium(II) ion as well as a benzyl radical, this radical was then quickly scavenged by a second equivalent of \([\text{Cr(OH}_2\text{)}_6]^{2+}\) to generate the observed \([\text{Cr(OH}_2\text{)}_5(\text{CH}_2\text{Ph})]^{2+}\) complex. The authors also noted a rate increase upon the addition of ethylenediamine ligands.
to the reaction mixture. Addition of ethylenediamine results in increased electron donation to the metal center allowing for faster halogen atom abstraction leading to the observed rate increase (Figure 1.1).

![Chemical structure](image)

**Figure 1.1: Alkyl halide activation with [Cr(en)2(OH)2]2+**

### 1.2.2 Persistent Radical Effect

Generation of organic radicals can lead to undesired homocoupling controlled at the diffusion rate limit (10^9 M^-1s^-1). In order to discourage this reaction and favour cross-coupling the kinetic phenomenon of the persistent radical effect can be exploited. A persistent radical is defined as a radical species with a lifetime of longer than 10^-3 s. These molecules can be stabilized electronically or sterically shield the unpaired electron to satisfy their long lifetime. If a radical has a lifetime of less than 10^-3 s, it is defined as a transient radical. In the case of the reaction between aqueous chromium(II) and benzyl chloride, oxidative addition of the benzyl chloride first generates a transient benzyl radical. A second equivalent of aqueous chromium(II), a persistent radical, captures it, resulting in cross-coupling to afford an organometallic species. The concentration of chromium(II) is significantly higher than the concentration of benzyl radicals over the course of this reaction. Furthermore, two hexaaquo chromium(II) complexes do not couple with each other. Because of this, the homocoupling of the benzyl radicals becomes suppressed and the formation of the organometallic complex [Cr(OH)5(CH2Ph)]2+ becomes favoured leading to its observed formation. By employing this observed phenomenon with
chromium(II) complexes, organic radicals can be used for selective carbon-carbon bond forming reactions following their sequestration via the metal complex.

1.2.3 Nozaki-Hiyama-Kishi Reaction

Another important example of chromium mediated radical reactivity is the coupling of alkyl halides and aldehydes. Synthetic chemists employed the reaction of alkyl halides with chromium(II) in organic solvents using chromium(II) chloride to first make organic radicals that can be trapped. They then observed that these organometallic species exhibited selective carbon-carbon bond formation with electrophilic aldehydes which ultimately affords a functionalized alcohol. Reacting activated alkyl halides, such as allyl chloride, with stoichiometric chromium(II) chloride generates chromium(III) chloride, and an allyl radical that can be captured by a second equivalent of chromium(II) chloride. Introduction of an aldehyde results in insertion into the chromium-alkyl bond forming a functionalized alkoxide that can be protonated off to give the desired alcohol. This transformation demonstrates exquisite selectivity for the insertion reaction with aldehydes and is robust to chromium-alkyl protonolysis with high functional group tolerance. In order to make the reaction catalytic in chromium, transmetalation of the alkoxide with trimethylsilyl chloride generates chromium(III) chloride which can be reduced to the active chromium(II) chloride through the addition of a sacrificial stoichiometric reductant such as manganese (Figure 1.2). The reaction could be extended to less activated vinyl and aryl halides (or triflates) through the addition of a nickel cocatalyst to assist in the activation of the carbon-halogen bond.
1.3 Cyclopentadienyl β-Diketiminate Complex of Chromium

The Smith group has previously synthesized and characterized a series of organochromium complexes bearing cyclopentadienyl and β-diketiminate (nacnac) ligands. These chromium(II) complexes were observed to undergo single-electron oxidative addition reactions with alkyl halides (Figure 1.3, step 1), analogous to the hexaaquochromium(II) and chromium(II) chloride salts discussed earlier. Oxidative addition of the alkyl halide generates an equivalent of a carbon-based radical that can be reversibly trapped by a second equivalent of the chromium(II) starting material (Figure 1.3, step 2). Under ambient conditions (under N₂, room temperature, in the dark), the chromium-alkyl bond formed was found to undergo homolysis with certain alkyl radicals (Figure 1.3, step 3). The rate of homolysis was observed to be controlled by the stability of the radical, as well as the steric interference of the alkyl group with the ancillary ligands. The CpCr(nacnac)X (X = halide) complexes generated as a result of the oxidation can then be
recycled back to the chromium(II) complex by reduction with stoichiometric manganese metal (Figure 1.3, step 4).

Figure 1.3: Single-electron oxidative addition of alkyl halides with CpCr(LX) complexes
In order to modify step 1 of Figure 1.3, the chromium(III)-halide complex needs to be stereolectronically favoured. The energy difference between the chromium(II) and the alkyl halide starting materials and the chromium(III) halide complex and the resulting organic radical is primarily controlled by the difference in bond strength between the alkyl halide bond and the weaker chromium halide bond.\(^{12}\) In order to sterically favour oxidation, the ancillary ligand set must be small enough to allow for easier access to the coordination sphere. However, if the ancillary ligands are too small, this can lead to formation of bimetallic complexes and lead to deactivation of the compound. Cory MacLeod and Wen Zhou previously investigated the steric effects of the activation of iodomethane with complexes of the type CpCr(nacnac) (Figure 1.3, step 1). It was found that varying the ortho substituents of the \(N\)-aryl groups had little effect on the rate constants (xyl-nacnac \(k = 2.4 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}\); dep-nacnac \(k = 1.9 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}\); dpp-nacnac \(k = 2.8 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}\)).\(^{13}\) This surprising result could perhaps be rationalized by a long Cr-I interaction in the transition state during the halogen atom abstraction that renders the steric interaction between the ortho substituents ineffective at modifying the rate significantly. However, the synthesis of asymmetric \(\beta\)-diketiminate ligands significantly impacted the rate constant. The use of asymmetric [DppNC(Me)CHC(Me)NC\(_6\)H\(_4\)(OMe)] resulted in a rate constant of \(k = 9.8 \times 10^{-1} \text{ M}^{-1}\text{s}^{-1}\), an almost 35 fold increase from the symmetric dpp-nacnac complex.\(^{14}\) This is hypothesized to be due to the relaxation of steric interference in the chromium(III) complexes by allowing the alkyl or halo ligand to bend away from the ortho-disubstituted \(N\)-aryl group towards the para-substituted aryl, stabilizing the chromium(III) complexes resulting in the observed rate increases (Figure 1.4). This subtle change led to an order of magnitude increase in the observed rate constants highlighting the sensitivity of this system to ancillary modifications.
Figure 1.4: Steric interference caused by \(\text{N-aryl ortho substituents}\)

However, too much steric reduction can also lead to irreversible formation of the chromium-alkyl species in step 2 of Figure 1.3. While formation of the chromium(III)-alkyl species is desired in order to control the concentration of free radicals \textit{in situ}, the reduction in steric presence can lead to a deactivation of chromium-alkyl bond homolysis in step 3. This would result in a build-up of both the chromium(III) halide and the chromium(III)-alkyl and ultimately lead to a shutdown of the system by saturation. Installation of ortho substituents on the \(\text{N-aryl groups}\) was found to induce homolysis of the chromium(III)-benzyl and -neopentyl complexes (\(R = \text{CH}_2\text{Ph, CH}_2\text{CMe}_3\) respectively) under \(\text{N}_2\), at room temperature, in the absence of light at appreciable rates as measured previously by Cory MacLeod. In order to monitor the rate of homolysis, MacLeod employed a radical trap that scavenged both excess radical and chromium(II) that built up over the course of the reaction. The choice of radical trap required the complex formed to be distinguishable from the complex being decomposed so kinetic data could...
be extracted from UV-vis spectra collected. Based on the analysis, diphenyl disulfide was used which readily acted as a single electron oxidant for the chromium(II) complexes forming CpCr(nacnac)(SPh) which exhibited $\lambda_m$ distinct from that of the alkyl complexes. The rate constants extracted showed that the rates of homolysis were similar between the dep-nacanc and dpp-nacnac ($k = 1.1 \times 10^{-2}$ s$^{-1}$ and $9 \times 10^{-3}$ s$^{-1}$ respectively for $R = \text{CH}_2\text{Ph}$) as well as for the xyl-nacnac and mes-nacnac ($k = 3.2 \times 10^{-3}$ s$^{-1}$ and $3.2 \times 10^{-3}$ s$^{-1}$ respectively for $R = \text{CH}_2\text{Ph}$). Unpublished results found by Jesse Crescenzo further demonstrated that if the $N$-aryl ortho substituents were removed (Ph-nacnac), the homolysis rate constant for $R = \text{CH}_2\text{Ph}$ drops orders of magnitude to $k = 4.62 \times 10^{-5}$ s$^{-1}$. This result is in good agreement with the previously discussed observations that increased steric demand the $\beta$-diketiminate ligand result in increased steric interference with the alkyl ligand leading to its destabilization.

This delicate balancing act demonstrates the interwoven nature of this reaction manifold: pronounced reduction in steric influence can lead to bimetallic complex formation and deactivation of the single electron oxidative addition reaction, while design of a complex that does not exhibit bimetallic formation while maximizing access to the chromium(II) metal ion leads to a significant increase in the reductive power of the complex. Conversely, this leads to a fundamental increase in the chromium(III)-X bond strength ($X = \text{alkyl}, \text{halide}$). In the case of the alkyls this can then lead to a shutdown of the ambient homolysis requiring the use of an initiator such as broad spectrum light as previously demonstrated in the Smith research group. In the case of the halide, this leads to the necessity of a stronger, more empowered reductant that can then lead to chemical incompatibility under catalytic conditions. This thesis investigates this fine balance. The implementation of well-defined amidinate ligands explored in the literature by Gambarotta that preclude formation of bimetallic compounds while maximizing steric access to the active Cr(II) metal center as well as the investigation of novel reductants described in the
literature and their amenability to our system. We will conclude the effective use of a hypervalent silane as a chemically compatible reductant for radical coupling reactions. It will also be presented that the use of amidinate ligands featuring distal trimethyl(silyl) groups provide unique remote steric benefits that do indeed enhance the rate of single electron oxidative addition of organo-chlorides. Furthermore, this sterically accessible complex will be shown to be able to trap tertiary organic radical species, a behavior not previously observed with cyclopentadienyl beta-diketiminate complexes of chromium(II). The ability to discretely characterize species of this type demonstrates the significance of the stereoelectronic environment around the active chromium(II). The prescribed chromium(III)-tert-butyl complex will be examined in detail and, while unstable with respect to chromium-carbon bond homolysis under ambient conditions (under N₂, at room temperature) can be isolated and characterized by single crystal X-ray diffraction as well as UV-vis spectroscopy. The distinct absorption bands of this unique complex allow for examination of reaction kinetics of the single electron oxidative addition reaction of 2-methyl-2-chloro propane (tert-butyl chloride) under pseudo-first order kinetics. The results of this study will show that the second order rate constant primarily governed by the initial halogen atom abstraction (HAA) are comparable (albeit not directly comparable) with the iodomethane activation using CpCr(nacnac) complexes previously investigated by Cory MacLeod, Wen Zhou, and others in the Smith research group.

As an alternative to the coordinatively limited piano stool complexes described previously, the use of redox non-innocent ligands of chromium(III) provides an alternative reaction manifold to accomplish the desired carbon-carbon bond forming reaction. Exploiting the ability for specific ligands to harbor electron density over the course of the cycle would allow for facile access to both the chromium(III) ion capable of facilitating the reductive elimination of the organic substrates while simultaneously allowing for activation of the substrate. This represents
elegant reactivity obviating the addition of co-catalysts such as nickel or magnesium that are
commonly employed in NHK type reactions. The use of redox non-innocent ligands allows facile
shuttling of electron density between the metal ion when it is or is not required to effect the
desired transformation. Specifically, addition of 2,2'-bipyridine provides access to its low lying
$\pi^*$-antibonding orbital as a means of access to the chromium(III) ion via metal to ligand charge
transfer (MLCT).

1.4 Chemistry of Chromium Polypyridyl Complexes

Cationic complexes of the type [Cr(bpy)$_2$(Ar)$_2$]$^+$ were prepared and characterized
previously by Sneeden and Zeiss (Scheme 1.1).$^{16}$ Reaction of dibromobis(tetrahydrofuran)
chromium(II) with two equivalents of 2-methoxyphenylmagnesium bromide and two equivalents
of 2,2'-bipyridine afforded the neutral octahedral chromium(III) complex. Air oxidation in the
presence of potassium iodide or treatment with allylic halides of this complex then afforded the
cationic species. The observed magnetic moments of the neutral species, Cr(bpy)$_2$(o-OMePh)$_2$
($\mu_{\text{eff}} = 2.58$ BM) corresponds to two unpaired electrons ($S = 1$) suggesting a low-spin $d^4$
electron configuration at the metal center. Magnetic susceptibility of the oxidized cations ($\mu_{\text{eff}} = 3.80$
BM) corresponds to three unpaired electrons consistent with a $d^3$ electron configuration.

![Scheme 1.1: Sneeden and Zeiss synthesis of cationic [Cr(bpy)$_2$(o-OMePh)$_2$]$^+$](image)

These cations were found to be anomalously stable with respect to air and water induced
decomposition. While the complexes feature incomplete, 15 electron valence shells, coordination
of a seventh donor is disfavoured due to a resultant spin-pairing energy penalty that takes the quartet ground state to a high energy $d^3$ doublet electron configuration.\textsuperscript{17} It is also known from investigation into Hein’s aryl coupling reaction that reductive elimination from chromium(III) complexes is preceded first by initial neutral ligand loss.\textsuperscript{18} By installing strongly chelating ligands, such as bipyridine diimines, this ligand loss can be avoided preventing decomposition by ligand labilization. Reversible chromium-alkyl bond homolysis, explored previously in the Smith research group, would therefore be the final mode of decomposition. It was observed that rather than the strength of the chromium-alkyl bond, the stability of the radical generated by homolysis is a key factor that dictates rates of homolysis.\textsuperscript{15} Homolysis of the chromium-aryl bond would result in formation of a highly unstable phenyl radical which disfavours this final mode of decomposition.

Bipyridine ligands have been found to exhibit redox-noninnocence due to a relatively low lying $\pi^*$-antibonding orbital. Redox non-innocence is the ability for a ligand to exist in multiple oxidation states. This can create difficulty in assigning formal oxidation states to a metal center when one of these ligands is employed. Wieghardt and Scarborough scrutinized the oxidation state of $[\text{Cr}(\text{bpy})_3]^{2+}$ cations, which were initially believed to be low-spin chromium(II) $d^7$ complexes.\textsuperscript{19} It was found by paramagnetic spin resonance spectroscopy and confirmed by analysis of the bond lengths in the crystal structure that the central chromium ion exists formally in the +3 oxidation state, with a ligand centered bipyridine radical anion that engages in antiferromagnetic coupling with the three unpaired electrons on chromium, giving rise to the observed triplet ground state.\textsuperscript{13} The interpyridyl ring bond length is a useful tool in assigning the oxidation state of the bipyridine ligand. The nature of this orbital is such that single or double electron occupation shortens the distance between the rings allowing for facile determination of the oxidation state of the ligand and therefore the metal (Figure 1.5). Using this key bond length,
three separate oxidation states can be assigned to bipyridine ligands: L\textsubscript{2} neutral, LX\textsuperscript{·} monoanionic and, X\textsubscript{2} dianionic.

![Diagram of bipyridine oxidation states and bond lengths](image)

**Figure 1.5: Oxidation states of 2,2’-bipyridine and interpyridyl bond lengths**

Based on this analysis of [Cr(bpy)\textsubscript{3}]\textsuperscript{2+} cations, it is concluded that the neutral complexes synthesized by Sneeden and Zeiss are much better considered as formal chromium(III) complexes with bipyridine localized radical anions prior to air oxidation to afford the corresponding cation.

### 1.5 Thesis Objectives

The goal of this thesis is the examination of a series of organochromium(III) complexes with specific interest in the factors that govern their ability to affect carbon-carbon bond forming reactions. The synthesis and characterization of these complexes by UV-vis spectroscopy, X-ray crystallography, electrochemistry, and mass spectrometry will provide structural information which can then be related to their reactivity profiles in order to rationalize the observed patterns. This will allow future designs and experiments to be tailored to these patterns for optimized success.

Chapter 2 of this thesis investigates cyclopentadienyl complexes of chromium(III). Specifically, the design and synthesis of these complexes that also feature a monoanionic, bidentate, guanidinate (or amidinate) LX type ligand. Initial experiments take inspiration from previous work in the Smith research group, focusing on the activation of alkyl halide substrates
and the reversible homolysis of chromium(III)-alkyl species. The second part of chapter 2 focuses on attempts to reduce chromium(III)-halide complex with a variety of novel reductants. This section culminates in the successful implementation of a hypervalent silane as a homogeneous reductant for cyclopentadienyl chromium(III) complexes featuring beta-diketiminate ligands and subsequent reactions using this reductant.

Chapter 3 of this thesis will explore chromium(III) polypyridyl bis(aryl) complexes and their uniquely observed photoactivity to induce reductive elimination of the aryl moieties to afford biaryl products. Special attention is paid to experimental design in order to understand the mechanism of this reductive elimination event. This includes inhibition experiments to understand what happens immediately following the reductive elimination event, as well as cross-over experiments to understand whether the event is monometallic or bimetallic in nature. Furthermore, trapping experiments are conducted using peroxides (weak X₂ species) to determine a possible reactivity manifold following the reductive elimination event. From the results determined in the analysis of the cationic complexes initially investigated, neutral complexes are designed, synthesized, and investigated for similar photoactivity. It was found that both a neutral dithiocarbamate complex as well as a neutral quinolinate complex undergo similar photoinduced reductive elimination of aryl groups to afford the biaryl. Further work is proposed in order to exploit the general reactivity profile observed with chromium(III) bipyridine bis(aryl) complexes.
2 Reduction and Radical Reactions of Cyclopentadienyl Chromium Amidinate Complexes

2.1 CpCr(guanidinate) Complexes

It was hypothesized that changing the beta-diketiminate ligand for a smaller guanidinate ligand would allow for increased reductive power of the CpCr\textsuperscript{II}(LX) complex; by squeezing the bite angle inward and exposing more of the metal center, the complex could be sterically favoured towards the CpCr\textsuperscript{III}(LX)R species. This could allow for isolation of species with less persistent radicals such as the neopentyl and neophyl radical. The smaller guanidinate ligands could, however, lead to bimolecular decomposition pathways due to increased exposure of the metal center. To counter this, large hydrocarbyl groups installed on the coordinating guanidinate nitrogens could shield the metal center and prevent this decomposition pathway. With these thoughts in mind, generation one of complex 2.1 was designed featuring a guanidinate core, two cyclohexyl moieties off the coordinating nitrogens and bulky trimethylsilyl groups off the distal nitrogen to increase both solubility in organic solvent and aid in crystallinity (Scheme 2.2). Additionally, the bulky trimethylsilyl groups function similarly to the methyl groups in \(\beta\)-diketiminate ligands by pushing the cyclohexyl groups forward thereby increasing their steric influence via remote steric effects.\textsuperscript{20}

The NCN amidinate coordination environment is attractive from a preparatory standpoint due to the commercial availability of carbodiimide precursors. The prevalence of available carbodiimides is owed to their expansive use in peptide coupling.\textsuperscript{21} While dicyclohexylcarbodiimide (DCC) remains one of the most widely employed and thus, one of the most economically efficient, there are others available including diisopropylcarbodiimide (DIC), and asymmetrical \(N\)-ethyl-\(N'\)-dimethylaminopropylcarbodiimide (EDC) (Figure 2.1). This allows for an array of steric and coordinative properties to be obtained for the amidinate ancillary
based on choice of starting material. Furthermore, the choice of nucleophile used to attack can impart additional steric and/or electronic properties to the amidinate ligand. The use of bulky hexamethyldisilazide, for example, can create steric interactions between the remote trimethylsilyl groups and the amidinate N-substituents. When coordinated to the metal center, this remote steric bulk could potentially shield a metal center and eliminate proclivitous bimetallic decomposition pathways.

![Common Carbodiimides and Nucleophiles](image)

**Figure 2.1: Commonly employed carbodiimides and nucleophiles used in the synthesis of amidinate ligand salts**

Indeed, in the literature, it has been demonstrated that the choice of substituents on the amidinate framework is important to prevent formation of bimetallic species. Winter has demonstrated even changing one of the two amidinate N-substituents from a tert-butyl group to an ethyl group forms a bimetallic chromium(II)/chromium(II) complex with a quadruple bond between the metal centers. The analogous ligand with two N-tert-butyl substituents forms a monometallic complex coordinated by two amidinates. Gambarotta further investigated the effect of the backbone substituent on the formation of these bimetallic species (Scheme 2.1). It was observed that treatment of DCC with MeLi, PhLi, and (o-CH₂NMe₂)PhLi followed by
reaction with one half equivalent of CrCl₂ led to formation of a monometallic chromium(II) complex coordinated by two equivalents of the amidinate ligand, however, treatment of DCC with LiH followed by reaction with CrCl₂ led to formation of a bimetallic paddlewheel Cr(II)/Cr(II) complex. This result indicated the importance of the steric influence of the backbone moiety in preventing formation of bimetallic species. Careful choice of carbodiimide and nucleophile would requisite the necessary properties to achieve a monometallic chromium complex with the desired properties.

\[
\begin{align*}
\text{Scheme 2.1: Chromium(II) amidinate complexes formed observed by Gambarotta with varying R,R' amidinate substituents}
\end{align*}
\]

Reacting dicyclohexylcarbodiimide with lithium bis(trimethylsilyl)amide afforded the ligand as a lithium salt. Treatment of chromium(III) chloride with this ligand salt in THF followed subsequently by sodium cyclopentadienylide afforded the desired complex (2.1). Crystals suitable for X-ray diffraction were grown from hexanes and confirmed the structure of the product. The chromium(II) analog (2.2) could be prepared by reacting chromium(II) chloride with sodium cyclopentadienylide followed subsequently by the lithium salt of the ligand (Scheme 2.3).
In the solid state the Cr-C bonds to the cyclopentadienyl ligand were found on average to be 0.074 Å longer in the chromium(II) complex compared to the chromium(III)-chloride complex (average Cr-C length of 2.325 Å in 2.2 versus 2.251 Å in 2.1). This indicates that even with a smaller coordination number, the bond to the cyclopentadienyl ligand may be weaker due to some antibonding influence in the Cr-Cp interactions. The high-spin $d^4$ chromium(II) complex would singly populate either the $d_{xz}$ orbital which is $\pi^*$ antibonding with respect to the metal-Cp interaction.
bonds therefore resulting in observed lengthening. Complex 2.1 singly occupies three lower energy orbitals with characteristics of the $d_{x^2-y^2}$, $d_{xy}$, and $d_{z^2}$ orbitals. The two former localize electron density in the xy plane, removed from directly interacting in a $\pi^*$-antibonding fashion with any of the coordinated ligands (Figure 2.2). Because of this, the ligands are bound tighter to the metal center resulting in shorter bond lengths in 2.1. (Cr-Cp = 1.991 for Cr$^{II}$, 1.904 for Cr$^{III}$; Figure 2.3 and 2.4 respectively).

![Proposed orbital energy diagrams for compound 2.1 (right) and compound 2.2 (left)](image)

**Figure 2.2: Proposed orbital energy diagrams for compound 2.1 (right) and compound 2.2 (left)**

By decreasing the bite angle of the ancillary ligand from a $\beta$-diketiminate ligand to a guanidinate ligand, it can also be observed that the $d_{xz}$ orbital localizes electron density closer towards the LX ligand, resulting in unfavourable stereoelectronic effects. This would consequentially favour the chromium(III) compound over the chromium(II) complex.
It is also interesting to note that the guanidinate ligand of 2.2 bends slightly out of the plane as shown in Figure 2.3. This bending could be due to crystal packing interactions within the lattice or electronic repulsion with the ligand in the plane.

Figure 2.3: Complex 2.2 front and side view. Thermal ellipsoids shown at 50 % probability. Selected bond lengths in Å Cr(1)-C(1) 2.302(2), Cr(1)-C(2) 2.329(2), Cr(1)-C(3) 2.350(2), Cr(1)-C(4) 2.314(2), Cr(1)-C(5) 2.330(2), Cr(1)-N(1) 2.0292(17), Cr(1)-N(2) 2.0358(16). Cr-Cp centroid length 1.991 Å.
Figure 2.4: Complex 2.1 thermal ellipsoid diagram (50 % probability). Selected bond lengths in Å: Cr1-C1 2.265(2), Cr1-C2 2.2474(19), Cr1-C3 2.2354(18), Cr1-C4 2.2457(18), Cr1-C5 2.2606(19), Cr1-N1 2.0116(13), Cr1-N2 2.00532(13), Cr1-Cl1 2.2995(6). Cr-Cp centroid length 1.904 Å.

Alternative derivatives can be synthesized by modifying the base or carbodiimide used to form the amidinate LX ligand. Exchanging LiHMDS for MeLi creates a smaller amidinate ligand with a methyl backbone, whereas use of diisopropylcarbodiimide changes the nitrogen substituents from bulky cyclohexyl groups to smaller isopropyl substituents. Preparation of complex 2.1a exploited both of these changes and was characterized by x-ray diffraction (Figure 2.5).
Figure 2.5: Complex 2.1a thermal ellipsoid diagram (50% probability). Select Bond Lengths in Å: Cr1-C1 2.238(2), Cr1-C2 2.236(2), Cr1-C3 2.246(2), Cr1-C4 2.256(2), Cr1-C5 2.248(2), Cr-N1 1.9975(18), Cr1-N2 2.0026(16), Cr1-Cl1 2.2960(6). Cr-Cp centroid length 1.900 Å.

The chromium-cyclopentadienyl centroid length in 2.1a is in good agreement with 2.1, as are the chromium-nitrogen amidinate bond lengths. It is observed that the chromium-chloride bond length is unperturbed by the smaller amidinate nitrogen substituents. This indicates that modification of the amidinate substituents has little observed effect on the coordination of the halides, as well as the cyclopentadienyl ligand.

2.1.1 Alkyl Halide Activation

In order to establish a measure of the reductive power of the CpCr(guanidinate) complexes, they were treated with a series of alkyl halides under varying concentrations. The chromium(II) complexes undergo single electron oxidative addition reactions with the alkyl halides generating an equivalent of an organic radical (Figure 1.3, step 1). The organic radical is then trapped by a second equivalent of the chromium(II) complex. By performing the experiment...
under *pseudo* first-order kinetics (with at least a 10-fold excess of alkyl halide), the second order rate constant for alkyl halide could be extracted. The chromium(III)-alkyl complexes exhibited unique UV-vis absorption bands that were far enough removed from absorption bands in the chromium(III)-halide and chromium(II) complex spectrums which allowed for facile monitoring of the kinetics. By varying the concentration of alkyl halide and plotting the observed rate constants against the concentrations, the rate constant was extracted from the slope of the line fitted (Figure 2.6).

\[
\begin{align*}
\text{slow} & \\
R-X + [\text{Cr}] & \xrightarrow{k_1} [\text{Cr}]-X + R^* \\
\text{fast} & \\
[\text{Cr}] + R^* & \xrightarrow{k_2} [\text{Cr}]-R
\end{align*}
\]

\[k_2 \gg k_1 \text{ therefore assume rate is governed by } k_1\]

Rate = \(k_1[R-X][\text{Cr}]\) (2 [Cr] consumed per formation of [Cr]-R)

Keep \(R-X\) high; *pseudo first-order kinetics*

Rate = \(k'[\text{Cr}]\) where \(k' = 2k_1[R-X]\)

*Plot of \(k'\) versus \(R-X\) gives slope of \(2k_1\)*

**Figure 2.6: Rate law derivation for single electron oxidative addition reaction**

*Tert*-butyl chloride was tested for alkyl halide activation. Independent synthesis of the Cr-^t^Bu complex indicated a unique UV-vis absorption band localized around 524 nm. Both the chloro complex and the chromium(II) complex exhibited significantly reduced absorption in this area of the spectrum, allowing for facile monitoring of the kinetics by UV-vis trace at this wavelength. Reaction of the chromium(II) complex with five separate concentrations of *tert*-butyl chloride allowed for a plot of the observed rate constants versus concentration of substrate
to be generated. The slope of this curve was then extracted to obtain the second-order rate constant for this reaction \((\text{slope} = 2k_i)\). It was found that the second order rate constant was observed to be \(4.58 \times 10^{-1} \text{ M}^{-1} \text{s}^{-1}\) (Figure 2.7).

\[
[\text{Cr}^{\text{II}}] + \text{'Bu-Cl} \xrightarrow{k_1} [\text{Cr}^{\text{III}}]\text{-Cl} + \text{'Bu•}
\]

\[
[\text{Cr}^{\text{II}}] + \text{'Bu•} \xrightarrow{k_2} [\text{Cr}^{\text{III}}]\text{-'Bu}
\]

\(\lambda_m = 524 \text{ nm}\)

**Figure 2.7:** Plot of observed rate constant versus concentration of tert-butyl chloride for CpCr[(CyN)2CN(SiMe3)2] and reaction equation for activation of tert-butyl chloride

(2-chloro)ethyl benzene was also tested for alkyl halide activation in a similar manner to tert-butyl chloride. Independent synthesis of the CpCr[(CyN)2CN(SiMe3)2](CH2CH2Ph) showed a unique absorption band at 534 nm that was used for the kinetics trace. Four separate
concentrations of (2-chloro)ethyl benzene were used to generate a plot of $k_{obs}$ versus concentration of substrate and extract the second order rate constant from the slope ($slope = 2k_1$; $k_1 = 1.53 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}$, Figure 2.8).

![Graph showing observed rate constant versus concentration of (2-chloro)ethyl benzene](image)

$$[\text{Cr}^{III}] + \text{PhCH}_2\text{CH}_2\text{Cl} \xrightleftharpoons[k_f]{k_i} [\text{Cr}^{III}]-\text{Cl} + \text{PhCH}_2\text{CH}_2\bullet$$

$$[\text{Cr}^{III}] + \text{PhCH}_2\text{CH}_2\bullet \xrightarrow[k_2]{k_f} [\text{Cr}^{III}]-\text{CH}_2\text{CH}_2\text{Ph}$$

$\lambda_m = 534 \text{ nm}$

**Figure 2.8: Plot of observed rate constant versus concentration of (2-chloro)ethyl benzene for CpCr[(CyN)$_2$CN(SiMe$_3$)$_2$]**

Comparison of this rate constant to Cory MacLeod’s rate constant for the activation of iodomethane with CpCr(xyl-nacnac) ($k_f = 2.4 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}$) allows for an indirect comparison of the reductive power of the two complexes. While the substrates differ, we can approximate them
both as unactivated alkyl halides that generate primary alkyl radicals. Kochi examined the kinetics of alkyl halide activation by \([\text{Cr(en)}_2(\text{OH})_2]^{2+}\) and found the relative rates of alkyl halide reduction between \(n\)-butyl chloride and \(n\)-butyl iodide to be 1:10000. This highlights that alkyl iodides should be activated significantly faster than alkyl chlorides however the second-order rate constants are relatively similar. This does seem to suggest that the decreased bite angle of the guanidinate ligand versus the beta-diketiminate ligand does lead to increased reductive power. This is further supported by work outlined by Labinger in that rate constants for the activation of alkyl iodides should be several orders of magnitude larger than alkyl chlorides which is also consistent with halogen atom abstraction as the rate determining step.\(^{24}\) It is also interesting to compare the rate constants of the \textit{tert}-butyl chloride activation to the (2-chloro)ethyl benzene activation. It is observed that the \textit{tert}-butyl chloride rate constant is an order of magnitude larger than that of (2-chloro)ethyl benzene. Examination of the nature of the radicals generated, however, shows that this result is in good agreement with the argument that the stability of the radical generated is a significant factor that also influences the single-electron oxidative addition of alkyl halides.\(^{8,27,12}\)

\subsection*{2.1.2 Attempted Alkylation\(s\)}

The \(\text{CpCr[(CyN)CN(SiMe}_3]_2]}\) complex 2.3 was synthesized cleanly by reacting \(\text{CpCr[(CyN)CN(SiMe}_3]_2]}\) with one half equivalent of \(\text{I}_2\) (Scheme 2.4). Crystals suitable for X-ray analysis were grown from hexanes. The iodide complex was observed as a green solid, very similar to the chloride complex synthesized from chromium(III) chloride. It exhibited absorption bands at 357 nm and 607 nm, consistent with the absorption bands of the similar chloro-complex (349 nm, and 600 nm).
Scheme 2.4: Synthetic route to complex 2.3

Treatment of CpCr[(CyN)2CN(SiMe3)2]Cl 2.1 with an array of organomagnesium reagents led to several interesting results, characterized by X-ray diffraction. Reacting 2.1 with benzylmagnesiumchloride did afford the desired benzyl complex 2.4 in 35.3 % yield as purple crystals (Scheme 2.5, Figure 2.9).

Scheme 2.5: Synthetic route to complex 2.4
Figure 2.9: 2.4 Thermal ellipsoid diagram (50 % probability). Selected bond lengths in Å. Cr1-C1 2.2582(16), Cr1-C2 2.2768(16), Cr1-C3 2.3018(16), Cr1-C4 2.3013(16), Cr1-C5 2.2624(16), Cr1-N1 2.0235(12), Cr1-N2 2.0237(12), Cr1-C25 2.1184(16). Cr-Cp centroid distance 1.943 Å.

Reacting 2.1 with neophylmagnesiumchloride afforded the chromium(II) complex 2.2 (Scheme 2.6). This indicated likely formation of the [CrIII]-neophyl complex followed by homolysis of the chromium-alkyl bond leading to formation of 2-methyl-2-phenylpropane which was likely removed upon work-up in vacuo.

Scheme 2.6: Observed formation of 2.2 when reacting 3.1 with 2-phenyl-2-methylpropylmagnesiumchloride
It was believed that a secondary alkyl species may be more amenable and thus 2.1 was treated with cyclohexylmagnesiumbromide. Only a few crystals were isolated from this reaction mixture, and analysis of them by X-ray diffraction revealed a magnesium ion coordinated by the cyclohexyl group, a diethyl ether molecule, and the guanidinate ligand, suggesting decomposition of 2.2 over the course of the reaction (Scheme 2.7).

![Chemical structures](image)

**Scheme 2.7: Isolated magnesium complex from reacting 3.1 with cyclohexylmagnesiumbromide**

Treatment of 2.1 with MeMgI initially formed a dimer, bridging through iodide anions with the loss of the cyclopentadienyl ligand (Scheme 2.8). A subsequent methylation experiment did result in formation of the desired complex 2.5 which co-crystallized with the starting material 2.1 from hexanes in 22 % yield (Scheme 2.9, Figure 2.10). This could suggest problems during the alkylation experiments that lead to various side products during the experiment. It is believed based on the structures observed in the X-ray experiments that a mixture of products is likely formed under experimental conditions, and further optimization is required to select for the desired product.
Scheme 2.8: Isolated chromium(II) dimer from reacting 2.1 with methylmagnesium iodide

Scheme 2.9: Synthetic route to complex 2.5

Figure 2.10: Complex 2.5 Thermal ellipsoid diagram (50 % probability). Selected Bond lengths in Å: Cr1-C1 2.260(3), Cr1-C2 2.254(3), Cr1-C3 2.265(3), Cr1-C4 2.299(3), 2.297(3), Cr1-N1 2.0159(19), Cr1-N2)2.032(2), Cr1-C62.064(4). Cr-Cp centroid length 1.934 Å.
The series of attempted alkylations highlight decomposition routes during the transmetalation process. It is proposed here that the decomposition observed during transmetalation with organomagnesium reagents could be due initial reduction of 2.1 to 2.2. This then leads to the weakening of the metal-ligand bonding interactions based on the increased Cr-Cp bond lengths in the solid state of 2.2 which subsequently results in ligand abstraction by the organomagnesium reagents observed in the methylation reaction. In the cyclohexyl reaction, reduction to 2.2 could be followed by κ²-κ¹ isomerization of the guanidinate ligand, facilitating easier abstraction by the Grignard, leading to formation of the observed Mg[(CyN)₂CN(SiMe₃)₂](Cy)(Et₂O) complex in the crystal structure. Addition of nucleophiles to these amidinate type complexes has also been investigated previously by Gambarotta; reacting the dimer {[(CyN)₂CN(SiMe₃)₂]Cr}₂ with trimethylaluminum or methyl lithium results in abstraction of two of the amidinate ligands and installation of two methyl groups featuring agostic Cr-H interactions that tighten the chromium-chromium interaction at the core of the dimer.²⁵ This example demonstrates literature precedent for ligand abstraction from chromium amidinate type complexes using nucleophilic reagents similarly employed in the aforementioned transmetalation experiments.

2.1.3 Homolysis of CpCr[(CyN)₂CN(SiMe₃)₂]Bn

The benzyl complex, 2.4, could be reliably prepared using the aforementioned method and allowed for exploration into the homolytic properties of the chromium-alkyl bond. It was observed that in the absence of stimuli, the benzyl complex 2.4, did not homolyze the chromium-alkyl bond at room temperature in the dark.
This result was consistent with the hypothesis proposed in section 2.1. Homolysis could, however, be induced by exposing solutions of the complex to bright white light sources (Figure 2.11). Photolyzing 2.4 in the presence of diphenyl disulfide allowed for formation of CpCr[(CyN)₂CN(SiMe₃)₂](SPh) 2.6, whose formation could be monitored by UV-vis spectroscopy similarly to the experiments conducted by Cory MacLeod (Scheme 2.10).
Scheme 2.10: Light-induced homolysis of Cr-Bn bond followed by trapping with PhSSPh to form complex 2.6

Indeed, following the reaction by spectrophotometry showed a decrease in the absorption band at 540 nm (characteristic of the benzyl complex) and an increase in the absorption band at 609 nm, characteristic of the phenylsulfide complex (Figure 2.12).
Figure 2.12: UV-vis absorption trace of reacting CpCr(CyN)2CN(SiMe3)2Bn with 207 equiv. PhSSPh. [Cr] = 2.70x10^{-4} M, [PhSSPh] = 5.59x10^{-2} M in hexanes. UV-vis spectra taken every 5 min.
Absorption bands around 540 – 550 nm were typically found to be diagnostic for CpCr(LX)R type complexes in both the nacnac and amidinate case and therefore it was hypothesized that perhaps this absorption band could correspond to the transition required to homolyze the chromium-alkyl bond. Cut-on filter experiments were carried out using a 395 nm, 435 nm, and 515 nm cut-on filter. Cut-on filters remove all wavelengths of light lower (higher energy) than the set cut-on wavelength. It was found that both the 395 nm and 435 nm slowed photolysis by a factor of approximately two and four respectively (Figure 2.14, 2.15).
Figure 2.14: UV-vis absorption trace of reacting CpCr(CyN)$_2$CN(SiMe$_3$)$_2$Bn with 207 equiv. PhSSPh. [Cr] = 2.70x$10^{-4}$ M, [PhSSPh] = 5.59x$10^{-2}$ M in hexanes. UV-vis spectra taken every 5 min using 395 nm cut-on filter.

Figure 2.15: Plot of decaying absorbance at 540 nm showing decreasing concentration of CpCr[(CyN)$_2$CN(SiMe$_3$)$_2$]Bn during homolysis reaction with PhSSPh with 395 nm (lower) and 435 nm (upper) cut-on filters. $k_{obs}$ calculated at 4.21x$10^{-2}$ min$^{-1}$ and 1.91x$10^{-2}$ min$^{-1}$ respectively.
The 515 nm cut-on filter arrested homolysis of the chromium-benzyl bond (Figure 2.16). This result is inconsistent with the $\lambda = 540$ nm absorption band as the homolysis-inducing electronic transition. Based on the results it is proposed that the absorption band around 375 nm is responsible for inducing homolysis of the chromium-alkyl bond (Figure 2.17). Computational modelling may allow for elucidation of the nature of this transition.

Figure 2.16: UV-vis absorption trace of reacting CpCr[CyN]$_2$CN(SiMe$_3$)$_2$Bn with 9.9 equiv. PhSSPh. [Cr] = 5.48x10$^{-4}$ M, [PhSSPh] = 5.40x10$^{-3}$ M in hexanes. UV-vis spectra taken every 5 min using 515 nm cut-on filter.
2.2 Reduction of CpCr(LX)X Complexes

2.2.1 Reduction Using Stoichiometric Manganese

Previously in the Smith lab, Cory MacLeod had employed stoichiometric manganese as a reductant in his radical reactions of CpCr$^{II}$(nacnac) complexes. An interesting application of this is the radical cyclization of bromo and chloro acetals, or the Ueno-Stork reaction. Single electron oxidative addition of the halo-acetal affords CpCr$^{III}$(nacnac)X which needs to be reduced down to the active chromium(II) complex to complete the cycle. However, due to the heterogeneity of the manganese metal, these cyclizations required long reaction times (upwards of 38.5 h). Additionally, the manganese halide salts that are the byproduct of reduction are Lewis acidic and could affect reactivity of the complexes when built up over time. It was thus desired to find an
alternative reductant that was preferably homogeneous in solution and resulted in relatively inert byproducts.

2.2.2 Reduced Pyrazine Reagent for Catalyst Activation

Early work in my Chemistry Honour’s program investigated the amenability of Mashima’s organosilicon reducing agents to our chromium system.\(^{26,27}\) Reacting pyrazine or 2,3,5,6-tetramethylpyrazine with trimethylsilylchloride and potassium metal afforded a reduced pyrazine reagent capable of acting as two equivalents of a one-electron reductant (Scheme 2.11).

\[
\begin{align*}
\text{R} = \text{H, Me} \\
\text{R} \\
\text{R} \\
\text{R} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\end{align*}
\]

\[
\begin{align*}
\text{SiMe}_3 \\
\text{SiMe}_3 \\
\text{SiMe}_3 \\
\text{SiMe}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{R} = \text{H, Me} \\
\text{R} \\
\text{R} \\
\text{R} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\end{align*}
\]

\[
\begin{align*}
\text{SiMe}_3 \\
\text{SiMe}_3 \\
\text{SiMe}_3 \\
\text{SiMe}_3 \\
\end{align*}
\]

Scheme 2.11: Synthesis of reduced pyrazine reagent for catalyst activation

Unfortunately, all attempts to reduce CpCr\(^{\text{III}}\)(nacnac)X complexes using this reagent did not result in formation of the desired chromium(II) complex, or conversion of the chromium(III)-halide in any capacity (Scheme 2.12).

\[
\begin{align*}
\text{R}_1 \\
\text{R}_1 \\
\text{R}_2 \\
\text{R}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\end{align*}
\]

\[
\begin{align*}
\text{SiMe}_3 \\
\text{SiMe}_3 \\
\text{SiMe}_3 \\
\text{SiMe}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{Cr} \\
\text{L} \\
\text{X} \\
\text{X} \\
\end{align*}
\]

\[
\begin{align*}
\text{Cr} \\
\text{L} \\
\text{X} \\
\text{X} \\
\end{align*}
\]

Scheme 2.12: Attempted reduction of CpCr(LX)X complexes with Mashima’s reagent
Due to silicon’s oxophilicity, a future experiment should attempt transmetalation of a chromium(III)-alkoxide using Mashima’s reagent.

### 2.2.3 Reduction using Pyridinium Salts

Turner et al synthesized pyridinium salts by reacting dimethylaminopyridine (DMAP) with 1,3-diiodopropane in refluxing acetonitrile under dinitrogen to afford 2.7 (Scheme 2.13).

![Scheme 2.13: Turner’s synthesis of pyridinium salts for reduction of organohalides](image)

2.7

Then, reducing the pyridinium salt using sodium hydride to afford 2.8 as a dark red/purple product. 2.8 was shown to be an excellent “super-electron donor” and was employed by Turner in dehalogenation reactions of organic substrates (Scheme 2.14). It was envisaged that this reductant could potentially reduce the chromium(III) halide complexes down to the active chromium(II) complexes via a similar reaction, albeit with organometallic substrates.
Scheme 2.14: Activation of pyridinium salts by reduction with sodium hydride

Treatment of 2.7 with potassium bis(trimethylsilyl)amide also yielded the dark red 2.8 in situ (Scheme 2.15) which was reacted with CpCr$^{\text{III}}$(xyl-nacnac)Cl and CpCr$^{\text{III}}$(dep-nacnac)Cl (xyl = 2,6-dimethylphenyl; dep = 2,6-diethylphenyl). Both reactions afforded an intractable brown mixture, inconsistent with formation to the well-defined chromium(II) complexes (Scheme 2.16). Analysis by UV-vis showed emergence of a new band around 385 nm in both spectra however further structural analysis was not carried out.

Scheme 2.15: Activation of pyridinium salts by reduction with potassium bis(trimethylsilyl)amide
Scheme 2.16: Attempted reduction of CpCr(nacnac)Cl complex with activated pyridinium salt

2.2.4 Hypervalent Silanes as Reducing Agents

The Thomas research group had found that a mixture of phenyl silane and sodium tert-butoxide generated a pentavalent silane that was capable of generating low-valent base metal catalysts for hydrosilylation reactions (Scheme 2.17).29 Pre-treatment of the silane with base forms the hypervalent anion which can then reduce metal halide complexes down to the necessary oxidation state to achieve the desired hydrofunctionalization.

Scheme 2.17: Synthesis of hypervalent silane

Based on the observation that this reducing agent was successful for a variety of base metal catalysts (manganese, iron, cobalt, and nickel), it was hypothesized it could be amenable to our reaction manifold.

The chromium(II)/(III) redox couple for CpCr(nacnac)/CpCr(nacnac)X complexes feature distinctive UV-vis spectroscopic properties that were previously well-defined in the
Smith research group. Because of this, the beta-diketiminate system was chosen as a model for testing against the hypervalent silanes.

It was found that CpCr(xyl-nacnac)Cl was able to be reduced using a mixture of sodium tert-butoxide and phenyl silane (Scheme 2.18). This was first characterized by a shift in the absorption band in the UV-vis spectrum from 418 nm to 425 nm. Furthermore, the air exposed product of the reduced chromium(II) complex was previously characterized by Cory MacLeod, and exposure of the reaction mixture to atmospheric dioxygen resulted in the characteristic change in the UV-vis spectrum associated with formation of a bridging μ-oxo dimer 2.9 (Scheme 2.18, Figure 2.17).

Scheme 2.18: Successful reduction of CpCr(xyl-nacnac)Cl with hypervalent silane

green/green

burnt autumnal orange

Scheme 2.19: Oxidized product of CpCrII(xyl-nacnac) upon air exposure characterized by Cory MacLeod
Figure 2.18: UV-vis spectrum of CpCr\textsuperscript{II}(nacnac) before and after air exposure

Figure 2.19: Crystal structure obtained following reduction of CpCr\textsuperscript{III}(xyl-nacnac)Cl with pentavalent silane
Additional evidence for successful reduction of the chromium(III) chloride complex was obtained by growing single crystals of the product in the reaction mixture which confirmed the presence of the reduced chromium(II) complex (Figure 2.19).

It is important to note that premixing the silane and base is required to achieve successful reduction of the chromium(III) halide. Separate addition of base then silane or silane then base did not reduce the chromium(III) halide complex in any case tested. This can, however, lead to difficulties with stoichiometry as the hypervalent silane readily decomposes to a variety of silane gasses and unwanted side products. It is also therefore required to use super-stoichiometric equivalents of the activated silane in order to achieve successful and complete reduction.

Furthermore, reaction of the alkyl halide directly with sodium tert-butoxide results in etherification via salt metathesis, affording benzyl tert-butyl ether. This again highlights the importance of pre-mixing the base and silane prior to addition to the reaction mixture.

### 2.2.5 Reactions Using Hypervalent Silane Reductant

To test the efficacy of the silane reductant, a simple model reaction was tested. CpCr(2,6-xyl-nacnac)Cl was treated with solutions of the hypervalent silane in the presence of benzyl chloride. Benzyl chloride would undergo single electron oxidative addition with the reduced metal species generating the chromium(III) halide complex as well as benzyl radicals. Coupling of two benzyl radicals would afford bibenzyl. A maximum yield of 48.3 % of bibenzyl was achieved using this reductant system, indicating room for improvement but successful implementation of a novel homogeneous reductant for the organochromium radical reactions investigated by Cory MacLeod previously (Scheme 2.20, Scheme 2.21).
Scheme 2.20: Bibenzyl formation via radical coupling using phenylsilane and sodium tert-butoxide as reducing agent

Scheme 2.21: Mechanism of bibenzyl formation
In an effort to expand the generality of reduction and to determine the byproducts of the reduction, an alternative pentavalent silane was prepared by reacting triethoxysilane with potassium ethoxide. Analysis of the organics by $^1$H NMR following reduction in the presence of benzyl chloride showed the presence of tetraethylorthosilicate, toluene, unreacted benzyl chloride as well as bibenzyl (Scheme 2.22).

![Scheme 2.22: Organic products collected from bibenzyl reaction](image)

Based on this observation, it was proposed that the reduction proceeds via a chromium(III)-hydride intermediate, which then disproportionates hydrogen gas to afford the active chromium(II) complex (Scheme 2.23). This result is consistent with similar reactivity observed by Cory MacLeod when reacting CpCr(nacnac)F complexes with phenylsilane which leads to the formation of the reduced chromium(II) complex, presumably via a chromium(III)-hydride intermediate.$^{30}$
Scheme 2.23: Proposed mechanism for reduction of CpCr\textsuperscript{III}(nacnac)Cl

A final suite of reactions was tested by reacting benzyl chloride and benzylmagnesium chloride in the presence of either CpCr(dep-nacnac)Cl, CpCr(Ph-nacnac)Cl, or CpCr[(CyN)\textsubscript{2}CN(SiMe\textsubscript{3})\textsubscript{2}]Cl. Using 2.0 mol\% of the catalyst yields of 94.5 \%, 99.9\%, and 93.8 \% were achieved respectively under N\textsubscript{2}, at room temperature (Scheme 2.24).

Scheme 2.24: Benzyl chloride and benzylmagnesiumchloride coupling using various chromium catalysts

A timed test was also carried out to compare the rates of bibenzyl formation of the different catalysts in the presence of a light source to accelerate homolysis of the Cr-Bn bond. It was found that after 1 h reaction time, the highest yielding catalyst was CpCr(dep-nacnac)Cl at 10.6 \%, while the lowest was CpCr[(CyN)\textsubscript{2}CN(SiMe\textsubscript{3})\textsubscript{2}]Cl at 1.9 \%. This result was in good agreement with previous experiments showing that the benzyl complex of the amidinate ligand
shows no homolysis in the absence of light indicating a stronger Cr-Bn bond than the ambiently homolyzing beta-diketiminate complexes (under N\textsubscript{2}, at room temperature, in the dark). A dark and light control were also run in the absence of any chromium complex which both yielded 2.3 % bibenzyl after 1 h. This result is not entirely unexpected based on the ability of the Grignard to transmetalate the benzyl anion to the benzyl chloride with the formation of magnesium(II) chloride salt. It was interesting to note however that both controls yielded marginally greater bibenzyl than the amidinate complex. All yields for this experiment were determined by \textsuperscript{1}H NMR using an internal standard (Scheme 2.25, Table 2.1).

Scheme 2.25: Timed reaction test coupling benzyl chloride and benzylmagnesiumchloride

**Table 2.1: Bibenzyl yields for various chromium catalysts and controls following timed reaction test**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Chromium Catalyst</th>
<th>% Yield Bibenzyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>CpCr(dep-nacnac)Cl</td>
<td>10.6</td>
</tr>
<tr>
<td>B</td>
<td>CpCr(ph-nacnac)Cl</td>
<td>4.6</td>
</tr>
</tbody>
</table>
### 2.2.6 Attempted Synthesis of CpCr[(CyN)₂CMe]F

Based on Cory MacLeod’s observation that the CpCr(nacnac)F complexes were readily reduced by phenylsilane to the chromium(II) complex, it was envisaged that similar reactivity would be observed with the amidinate system. Reaction of CpCr[(CyN)₂CMe] with an equivalent of silver fluoride however yielded predominantly CpCr[(CyN)₂CMe](η¹⁻C₅), with a small amount of the fluoride complex detected in the X-ray diffraction experiment (roughly 93:7 CpCr[(CyN)₂CMe](η¹⁻C₅) : CpCr[(CyN)₂CMe]F) (Scheme 2.26, Figure 2.20).

\[
\text{CpCr[(CyN)₂CMe]} + \text{AgF} \rightarrow \text{CpCr[(CyN)₂CMe](η¹⁻C₅)} + \text{CF}_2
\]

**Scheme 2.26: Attempted synthesis of CpCr[(CyN)₂CMe]F**
Figure 2.20: Thermal ellipsoid diagram (50% probability) of CpCr[(CyN)2C(Me)](η1-Cp) (compound 2.10). Select bond lengths in Å: Cr1-C1 2.2559(16), Cr1-C2 2.2718(15), Cr1-C3 2.2680(15), Cr1-C4 2.2572(15), Cr1-C5 2.2473(15), Cr1-N1 2.0202(13), Cr1-N2 2.0165(12), Cr1-C6 2.1916(15). Cr-Cp centroid length 1.913 Å.

2.3 Experimental Section

2.3.1 General Considerations

Unless otherwise stated, all reactions were carried out under dinitrogen using standard Schlenk and glove box techniques. Hexanes, diethyl ether, dichloromethane, and tetrahydrofuran were purified by passage through activated alumina and deoxygenizer columns from Glass Contour Co. (Laguna Beach, CA, USA). Celite (Aldrich) was dried overnight at 130 °C before being evacuated and then stored under nitrogen. DCC, DIP, lithium-, potassium, and sodium bis(trimethylsilyl)amide, MeLi (1.6 M, Et₂O), sodium cyclopentadienylide (2.0M, THF), iodine, benzylmagnesium chloride (1.0 M, THF), 2-phenyl-2-methyl-propylmagnesium chloride (0.5 M, Et₂O), cyclohexylmagnesium bromide (2.0 M, Et₂O), methylmagnesium iodide (3.0 M, Et₂O), diphenyldisulfide, 2,3,5,6-tetramethylpyrazine, trimethylsilylchloride, potassium metal (in mineral oil), dimethylaminopyridine, 1,4-diodopropane, sodium tert-butoxide, and
chromium(III) chloride were purchased from Aldrich and used as received. Chromium(II) chloride was purchased from Strem and stored under nitrogen prior to use.

UV-vis spectroscopic data were collected on a Shimadzu UV 2550 UV-vis spectrophotometer in a specially constructed cell for air-sensitive samples: a Kontes Hi-Vac Valve with PTFE plug was attached to a Hellma 10 mm path length quartz absorption cell with a quartz-to-glass graded seal. $^1$H NMR spectra were recorded on a Varian Mercury Plus 400 spectrometer with chemical shifts referenced to the solvent signal.

X-ray diffraction data collection was performed by Dr. Brian O. Patrick at the University of British Columbia Vancouver. Crystals are mounted on a mylar loop in oil on a Bruker APEX II area detector diffractometer and analyzed at 90 K. Using Olex2 the structure was solved with the XT structure solution program, using the intrinsic phasing method. The model was refined with version 2017/1 of XL using least squares minimization.$^{31}$

2.3.2 Synthetic Procedures

Synthesis of CrCl$_3$(THF)$_3$

This complex was prepared using a modified version of the original procedure.$^{32}$ A 500 mL pear-shaped Schlenk flask was cooled on the Schlenk line. To this was added 2.66 g (10.00 mmol, 1 equiv) of forest green CrCl$_3 \cdot 6$H$_2$O. The flask was evacuated and backfilled with nitrogen three times to remove oxygen. In a separate 200 mL Schlenk, 78.2 mL of TMSCl (616 mmol, 61.6 equiv) was injected under nitrogen, followed by approximately 40 mL of anhydrous THF. The TMSCl solution was then cannulated under nitrogen over the CrCl$_3 \cdot 6$H$_2$O. The flask was sealed and the contents left stirring at room temperature overnight. The next day the forest green suspension had changed to a rich magenta colour with a visible
precipitate. The precipitated product was collected over a frit and dried *in vacuo* before being brought into the glove box to prevent decomposition. A total of 3.05 g (81%) of the dried magenta product was collected and stored in the glove box

**Synthesis of [(CyN)$_2$CN(SiMe$_3$)$_2$]Li**

880. mg of *N,N*-dicyclohexylcarbodiimide (5.26 mmol, 1 equiv) was dissolved in approximately 5 mL of anhydrous diethyl ether in a 100 mL Schlenk flask in the glove box. To this was added a 5 mL etheric solution of 1.08 g of lithium bis(trimethylsilyl)amide (5.24 mmol, 0.996 equiv) affording a pale-yellow solution. The mixture was allowed to react overnight for 24 h. before the solvent was removed *in vacuo*. The product was collected as a crude solid and used for subsequent experiments (1.66 g, 85%).

**Synthesis of CpCr[(CyN)$_2$CN(SiMe$_3$)$_2$]Cl complex 2.1**

957 mg of CrCl$_3$(THF)$_3$ (2.56 mmol, 1 equiv) was suspended in approximately 10 mL of anhydrous THF in a 100 mL Schlenk flask in the glove box. To this was added 969 mg of [(CyN)$_2$CN(SiMe$_3$)$_2$]Li as a 10 mL THF solution (2.59 mmol, 1.01 equiv) resulting in a colour change to a dark purple solution. This mixture was allowed to react overnight before adding 1.4 mL of sodium cyclopentadienylide (2.8 mmol, 1.1 equiv) causing an immediate colour change to a deep blue-green. The mixture was again allowed to react overnight. The solvent was then removed *in vacuo* and the green residue was extracted into hexanes before being filtered over Celite to remove ionic salts. The green filtrate was concentrated to approximately 40 mL then filter pipetted into two 20 mL scintillation vials and the product was allowed to crystallize. A total of 469 mg of green crystals were collected over three separate crops (36 % yield).
Synthesis of CpCr[(CyN)\textsubscript{2}CN(SiMe\textsubscript{3})\textsubscript{2}] complex 2.2

64 mg of grey CrCl\textsubscript{2} (0.52 mmol, 1 equiv) was suspended in 5 mL THF in a 20 mL scintillation vial. To this was added 0.29 mL of NaCp (0.58 mmol, 1.1 equiv) causing a colour change to an orange mixture. After reacting overnight, 190 mg of [(CyN)\textsubscript{2}CN(SiMe\textsubscript{3})\textsubscript{2}]Li (0.50 mmol, 0.96 equiv) was added as a 3 mL THF solution causing a gradual colour change to deep purple. The mixture was again allowed to react overnight before the solvent was removed \textit{in vacuo}. The residue was taken up in hexanes and filtered over Celite to remove ionic salts. The cherry red filtrate was concentrated, and crystals were allowed to grow. A total of 32 mg of dark purple crystals were isolated from the supernatant (13 % yield).

Synthesis of CpCr[(\textit{i}PrN)\textsubscript{2}CMe]\textsubscript{2}Cl complex 2.1a

A 100 mL bomb flask was cooled on the Schlenk line. 388 mg of diisopropylcarbodiimide (3.07 mmol, 1.03 equiv) was injected under nitrogen followed by 15 mL of THF from the SPS, then 2.0 mL of MeLi (3.2 mmol, 1.1 equiv). The bomb was sealed under nitrogen and the mixture allowed to react overnight. The following day, the bomb was brought into the glovebox and the solution was added to a suspension of 475 mg of CrCl\textsubscript{3} (2.90 mmol, 1 equiv) in 5 mL THF in a 100 mL Schlenk flask. Next, 1.65 mL of NaCp (3.30 mmol, 1.11 equiv) was added causing a rapid colour change to dark blue green. The mixture was allowed to react overnight before the solvent was removed \textit{in vacuo}. The green reside was taken up in hexanes before being filtered over Celite to remove ionic salts. The solvent from the filtrate was removed \textit{in vacuo} and the residue was taken up in a minimum of fresh hexanes. This supernatant was then passed through a Celite filter pipette, placed in the
freeze and allowed to crystallize. A total of 159 mg of green crystals were isolated over two crops (18 %).

**Synthesis of CpCr[(CyN)$_2$CN(SiMe$_3$)$_2$]Bn complex 2.4**

In a 20 mL scintillation vial, 53 mg of 2.1 was dissolved in approximately 5 mL of Et$_2$O. To this was added 0.12 mL of benzylmagnesium chloride (0.12 mmol, 1.2 equiv), causing a gradual colour change to a deep violet colour over 24 h. The solvent was then removed in vacuo. The residue was then extracted into hexanes before filtering over Celite. The violet filtrate was then concentrated before being passed through a Celite filter pipette then placed in the freezer to crystallize. A total of 21 mg of violet crystals were isolated over 3 crops (35 % yield).

**Attempted synthesis of CpCr[(CyN)$_2$CN(SiMe$_3$)$_2$](CH$_2$CMe$_2$Ph)**

In a 100 mL Schlenk flask, 52 mg of 2.1 (0.10 mmol, 1 equiv) was dissolved in 5 mL Et$_2$O. 0.22 mL of ClMg(CH$_2$CMe$_2$Ph) (0.11 mmol, 1.1 equiv) was then added. The mixture was allowed to react for approximately 3 h. during which time the colour had changed from green to red. The solvent was removed in vacuo and the residue extracted into hexanes before being filtered over Celite. The filtrate was concentrated then passed through a Celite filter pipette before being placed in the freezer and allowed to crystallize. A total of 34 mg of purple powder was isolated (55 % yield). Crystals suitable for X-ray analysis were grown from hexanes and indicated that the complex isolated was 2.2.

**Attempted synthesis of CpCr[(CyN)$_2$CN(SiMe$_3$)$_2$]Cy**
In a 100 mL Schlenk flask, 104 mg of \textbf{2.1} (0.204 mmol, 1 equiv) was dissolved in 6 mL of diethyl ether to afford dark green solution. To this was added 0.08 mL of methylmagnesium iodide (0.24 mmol, 1.2 equiv) causing a colour change from green to red over fifteen minutes. The reaction was allowed to proceed for approximately two hours before the solvent was removed \textit{in vacuo}. The residue was extracted into hexanes and filtered over a frit with Celite. The solvent was then removed \textit{in vacuo} and the residue was taken up in a minimum of fresh hexanes (~2 ml). The solution was passed through a Celite pipette and stored in the freezer to crystallize. 22 mg (22 \% yield) of purple crystals were isolated and a sample was sent for X-ray analysis revealing formation of dimer \{[(CyN)_2CN(SiMe_3)_2](OEt_2)Cr(µ-I)}_2 .

**Synthesis of CpCr[(CyN)_2CN(SiMe_3)_2]Me 2.5**

In a 100 mL Schlenk flask, 106 mg of \textbf{2.1} (0.204 mmol, 1 equiv) was dissolved in 6 mL of diethyl ether. To this was added 0.08 mL of methylmagnesium iodide (0.24 mmol, 1.2 equiv) causing a colour change from green to red over fifteen minutes. The reaction was allowed to proceed for approximately two hours before the solvent was removed \textit{in vacuo}. The residue was extracted into hexanes and filtered over a frit with Celite. The solvent was then removed \textit{in vacuo} from the filtrate and the residue was taken up in a minimum of fresh hexanes (2 mL). It was then filtered thru a Celite pipette and stored in the freezer to crystallize. Crystals were harvested and sent for X-ray analysis revealing a decomposition product collected from the supernatant.
In a 20 mL scintillation vial, 135 mg of 2.1 (0.259 mmol, 1 equiv) was dissolved in 3 mL of diethyl ether affording a green solution. To this was added 0.11 mL of methylmagnesium iodide (0.33 mmol, 1.3 equiv) causing a colour change to purple over forty-five minutes. The reaction was allowed to proceed overnight. The following day, 0.3 mL of 1,4-dioxane causing immediate precipitation of a grey solid (presumably MgX₂ salts). The mixture was transferred to a 100 mL Schlenk flask and the solvent was removed in vacuo. The purple residue was extracted into hexanes and filtered over a frit with Celite. The solvent was again removed in vacuo and the residue was extracted into a minimum of fresh hexanes (2 mL). It was passed through a filter pipette then stored in the freezer to crystallize. A total of 30. mg of purple crystals were isolated (23 % yield) and a sample was prepared for X-ray analysis revealing successful formation of 2.5.

**Homolysis of CpCr[(CyN)₂CN(SiMe₃)₂]Bn 2.4 in dark vs. light**

A stock solution of 2.4 was prepared by dissolving 2.8 mg (0.0049 mmol) in 10.0 mL of hexanes (4.9x10⁻⁴ M) in a volumetric flask. A stock solution of diphenyl disulfide was prepared by dissolving 239 mg (1.12 mmol) in 10.0 mL of hexanes (1.12x10⁻¹ M) in a volumetric flask. In a screw top UV-vis cuvette, 1.00 mL of each stock was added ([Cr] = 2.4x10⁻⁴ M ; [PhSSPh] = 5.6x10⁻³ M, 233 equiv). The cuvette was wrapped in tinfoil and allowed to stand for 17 h. in the glovebox. The following day, the tinfoil was removed, and spectrum collected, indicating no homolysis of 2.4. The cuvette was then exposed to a 100 W incandescent light bulb placed approximately 15 cm away for approximately half an hour over which time the colour of the solution changed from purple to green. The spectrum was again collected and indicated formation of a new complex proposed to be CpCr[(CyN)₂CN(SiMe₃)₂](SPh).
Homolysis of 2.4 using cut-on filters

A stock solution of 2.4 was prepared by dissolving 3.1 mg of 2.4 in hexanes in a 10.0 mL volumetric flask (5.39x10^{-4} M). A stock solution of diphenyl disulfide was prepared by dissolving 244.3 mg in hexanes in a 10.0 mL volumetric flask (1.12 mmol, 1.12x10^{-1} M, 208 equiv). In a screw top cuvette in the glovebox, 1.00 mL of each solution was added. The cuvette was quickly sealed, brought out of the glovebox, and placed in a cardboard box with a small opening fitted with a cut-on filter (395 nm, and 435 nm). A 100 W incandescent bulb light source was used to irradiate the sample behind the filter, with UV-vis spectra taken periodically to monitor the progress of homolysis. The experiment was done using separate stocks for the 515 nm filter: 6.3 mg of 2.4 (0.011 mmol) in hexanes in a 10.0 mL volumetric flask (1.10x10^{-3} M), 23.6 mg of diphenyl disulfide in hexanes in a 10.0 mL volumetric flask (0.108 mmol, 1.08x10^{-2} M, 9.9 equiv). These stocks were not used for the 395 nm and 435 nm filter due to degradation overnight.

Synthesis of 2,3,5,6-tetramethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (A)

This compound was prepared according to a literature procedure. In a 100 mL Schlenk flask in the glovebox, 809 mg of 2,3,5,6-tetramethylpyrazine (5.92 mmol, 1 equiv) was added and dissolved in approximately 30 mL of THF. To this was added 2.4 mL of trimethylsilyl chloride (19 mmol, 3.2 equiv). 1.07g of potassium metal (in mineral oil) (27.5 mmol, 4.60 equiv) was washed with hexanes and chopped using a sturdy spatula into small pieces. The pieces were added to the yellow mixture slowly. Following addition of the potassium metal the solution changed to a dark purple blue colour and was allowed to react for approximately seven days. The reaction mixture was then filtered over Celite, removing a blue solid and isolating a green filtrate. The solvent was removed in vacuo leaving a
greenish solid and a white powder. The white powder was sublimed using a cold finger to
isolate it from the green inorganic salts and stored in the glovebox freezer to prevent
decomposition. A total of 1.1404g of white crystals were isolated (68 % yield).

Synthesis of 1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (B)

This compound was prepared according to a literature procedure. In a 100 mL Schlenk
flask in the glovebox, 536 mg of pyrazine (6.69 mmol) was dissolved in approximately 40
mL of THF. To this was added 3.00 mL of trimethylsilyl chloride (23.6 mmol, 3.50 equiv).
1.01g of potassium metal was washed with hexanes then weighed before being chopped into
small pieces and added slowly to the reaction mixture. The mixture was allowed to react for
four days upon which time it changed from yellow to a muddy blue grey colour. The
mixture was filtered over Celite to remove the blue impurity and isolate a yellow liquid. The
solvent was removed in vacuo leaving a yellow goo-like residue in the bottom of the
Schlenk flask. The product was sublimed from this residue and isolated as yellow rock
candy-like crystals (0.945 g, 62 % yield).

Attempted reductions using reduced pyrazine reagents

A typical experiment involved reaction of CpCr(LX)X type complexes with one or one-half
equivalent of the reduced pyrazine reagent overnight in THF. Spectra of the reaction
mixtures were compared with spectra of the authentic starting chromium(III) halide
complexes and indicated no reduction in any case. Specific details of one attempted
reduction are listed here for completeness, followed by a table showing all attempted
reductions.
16 mg of CpCr(xyl-nacnac)F (0.036 mmol, 1 equiv) was added to 20 mL sintered glass vial. A 0.05 M solution of A was prepared by dissolving 142 mg in 10.0 mL of THF in a volumetric flask. 0.72 mL of this solution was added to the solid chromium complex (0.036 mmol, 1.0 equiv) to afford a green solution. The mixture was allowed to react overnight with no changes observed visually or spectroscopically the following day.

Table 2.2: Attempted reductions using reduced pyrazine reagents

<table>
<thead>
<tr>
<th>Chromium Complex</th>
<th>Reductant</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpCr(xyl-nacnac)F</td>
<td>A</td>
<td>THF</td>
</tr>
<tr>
<td>CpCr(Ph-nacnac)Cl</td>
<td>A</td>
<td>THF</td>
</tr>
<tr>
<td>CpCr(xyl-nacnac)F</td>
<td>A</td>
<td>Toluene</td>
</tr>
<tr>
<td>CpCr(dpm)Cl</td>
<td>A</td>
<td>THF</td>
</tr>
<tr>
<td>CpCr(xyl-nacnac)Cl</td>
<td>B</td>
<td>THF</td>
</tr>
</tbody>
</table>

Synthesis of 1,3-bis(N,N-dimethyl-4-aminopyridinium)propane diiodide (C)

This compound was prepared according to a literature procedure. A 100 mL bomb flask was cooled on the Schlenk line. To this was added 2.46 g of 4-dimethylaminopyridine (DMAP, 20.1 mmol, 2.51 equiv). The bomb was evacuated and backfilled with nitrogen three times to remove oxygen. 50 mL of acetonitrile from the glovebox was cannulated into the bomb flask to afford a clear, colourless solution. 2.37 g of 1,3-diiodopropane was injected into the reaction mixture and the bomb was sealed under nitrogen. The mixture was refluxed in an oil bath set at
approximately 90° Celsius overnight. The following day the mixture was cooled to 0° Celsius using an ice bath inducing precipitation of the product salt. Diethyl ether was added to loosen the mixture and the product was isolated by filtration over a Buchner funnel. The product was washed with 3x30 mL of diethyl ether and dried in vacuo. A total of 5.14 g of white powder was isolated (119 % yield). An NMR of the crude material in CDCl₃ indicated the presence of water and acetonitrile so the product was brought into the glovebox, washed again with 3x20 mL diethyl ether and dried under vacuum for several hours. A total of 4.30 g of white powder was isolated (99 % yield).

**Attempted reduction of CpCr(dep-nacnac)Cl using C**

In a 20 mL sintered glass vial, 13 mg of C was added (0.024 mmol, 1 equiv) and suspended in approximately 2 mL of THF. To this was added 17 mg of potassium bis(trimethylsilyl)amide (0.086 mmol, 3.5 equiv), affording a deep purple red solution over 45 m. Next was added 25 mg of CpCr(dep-nacnac)Cl as a 2 mL THF solution causing an immediate colour change to dark brown. UV-vis analysis of the solution did not suggest formation of the reduced chromium(II) complex. Analysis of the organics by proton NMR following work-up indicated the presence of free dep-nacnac. Subsequent reiterations of the experiment resulted in similar outcomes. Based on these results the reductant was abandoned.

**Reduction of CpCr(xyl-nacnac)Cl with Na[SiH₃Ph(OtBu)]**

230. mg of CpCr(xyl-nacnac)Cl (0.502 mmol, 1 equiv) was weighed and brought into the glove box. 50 mg of sodium tert-butoxide (0.53 mmol, 1.1 equiv) and 54 mg of phenyl silane (0.50 mmol, 1.0 equiv) were weighed into separate 4 mL vials and diluted with 1 mL of THF each. The solutions were transferred to a 100 mL Schlenk flask and mixed causing the evolution of gas
(various silanes). The chromium complex was then added as a 5 mL THF solution (dark green) and reacted with the hypervalent silane. Visual confirmation of reduction was confirmed by shining a light through the reaction solution: the chromium(III) halide complexes exhibit a transmitted colour of dark green (similar to the colour of the solution) whereas the chromium(II) reduced complexes transmit a magenta colour. Magenta was observed. A UV-vis spectrum was collected and compared to the authentic chromium(II) complex and exhibited the same $\lambda_m = 425$ nm. The following day, the solvent from the reaction was removed in vacuo and the green residue was extracted with hexanes and filtered over Celite. The solvent was removed from the filtrate in vacuo and the residue was extracted again with a minimum of fresh hexanes (~2 mL). The solution was filter pipetted into a 4 mL vial and stored in the freezer to crystallize. 68.0 mg of black crystals were isolated from the supernatant (32 % yield). A quantitative UV-vis spectrum was collected by dissolving 3.9 mg of the compound in hexanes in a 10.0 mL volumetric flask ($9.25 \times 10^{-4}$ M), however it showed mostly the oxidized chromium(III) $\mu$-oxo complex, presumably due to the glove box atmosphere. A sample for XRD was prepared and structure elucidation confirmed the presence of the reduced chromium(II) complex.

**Catalytic bibenzyl formation (route A)**

In a 100 mL Schlenk flask in the glove box, 135 mg of benzyl chloride (1.06 mmol, 1 equiv), 9 mg of CpCr(xyl-nacnac)Cl (0.02 mmol, 0.02 equiv) and 171 mg of 1,3,5-trimethoxybenzene (internal standard, 1.02 mmol, 0.961 equiv) were dissolved in approximately 5 mL of THF affording a very dark green mixture. In a 20 mL sintered glass vial, 149 mg of sodium tert-butoxide (1.55 mmol, 1.47 equiv) was mixed with 168 mg of phenyl silane (1.55 mmol, 1.46 equiv) in approximately 20 mL THF affording a bubbling mixture. The hypervalent silane solution was reacted for approximately 5 minutes before being added to a pressure equalizing
dropping funnel. An additional 40 mL of THF was added to the solution in the dropping funnel. The funnel was fitted to the Schlenk flask and the hypervalent silane solution was very slowly added to the stirring benzyl chloride solution. The apparatus was sealed and allowed to react overnight. The following day, all the reductant had been deposited into the reaction Schlenk and the mixture was observed as a muddy orange colour. The Schlenk flask was removed from the glove box and the solution was transferred to a round bottomed flask. The THF was removed \textit{in vacuo} and the residue was taken up in diethyl ether resulting in precipitation of a white solid (presumably sodium chloride). The mixture was transferred to a separatory funnel and washed with 3x30 mL of water. The organic phase was collected and dried with magnesium sulfate then filtered into a round bottomed flask. The solvent was removed \textit{in vacuo}. The brown residue was taken up in CDCl$_3$ for $^1$H NMR. A total of 48 % yield of bibenzyl was observed based on the internal standard.

\textbf{Byproducts of reduction reaction}

In a 50 mL Schlenk flask, 72 mg of benzyl chloride (0.57 mmol, 1 equiv), 42 mg of 1,3,5-trimethoxybenzene (internal standard, 0.25 mmol, 0.44 equiv), and 7 mg of CpCr(dep-nacnac)Cl (0.014 mmol, 0.024 equiv) were dissolved in approximately 5 mL of diethyl ether to afford a green solution. In a separate flask was weighed 145 mg of K[HSi(OEt)$_4$] (0.583 mmol, 1.03 equiv). Both Schlenk flasks were sealed under nitrogen and brought out of the glovebox and hooked up to the Schlenk line. The chromium solution was cannulated over the solid reductant and left to react overnight. The following day the reaction mixture was transferred to a separatory funnel and diluted with an additional 20 mL of diethyl ether. The organic layer was washed with 2x20 mL of water then 20 mL of a saturated solution of sodium chloride, followed by a final 20 mL of water. The organic phase was collected and dried over magnesium sulfate.
then gravity filtered into a round bottomed flask. The solvent was removed in vacuo and the residue was taken up in CDCl₃ and analyzed by ¹H NMR spectroscopy. Analysis of organic benzyl containing products indicated 14 % yield bibenzyl, 13 % recovery of benzyl chloride, and 17 % yield of toluene.

**Catalytic bibenzyl formation (route B)**

The following procedure is outlined for one of the three complexes used in this experiment. Reagent amounts of the catalyst and internal standard are listed for the remaining two following this procedure as well as % yield of bibenzyl. In a 20 mL sintered glass vial in the glovebox was measured 115 µL of benzyl chloride (0.999 mmol, 1 equiv), 10 mg of CpCr(dep-nacnac)Cl (0.021 mmol, 0.021 equiv). These reagents were dissolved in approximately 5 mL of diethyl ether. Next was added 86 mg of 1,3,5-trimethoxybenzene (0.51 mmol, 0.51 equiv). Finally, was added 1.40 mL of 1.0 M in diethyl ether benzylmagnesium chloride (1.40 mmol, 1.40 equiv). The vial was sealed, and the mixture allowed to react over four days. The vial was then removed from the glovebox and the solution was transferred to a separatory funnel. The organic phase was diluted with an additional 25 mL of diethyl ether then washed with 3x30 mL of water. The organic phase was collected and dried over magnesium sulfate, then gravity filtered into a round bottomed flask. The solvent was removed in vacuo and the residue was taken up in CDCl₃ and analyzed by ¹H NMR spectroscopy (95 % yield bibenzyl based on internal standard).

**Table 2.3 : Reagent amounts for catalytic bibenzyl formation (route B)**

<table>
<thead>
<tr>
<th>Chromium Complex (mg, mmol)</th>
<th>Amount I.S. used (mg, mmol)</th>
<th>Bibenzyl % yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>Yield (%)</td>
<td>ee (%)</td>
</tr>
<tr>
<td>----------</td>
<td>-----------</td>
<td>--------</td>
</tr>
<tr>
<td>CpCr(Ph-nacnac)Cl</td>
<td>83.6, 0.497</td>
<td>99.9</td>
</tr>
<tr>
<td>(8.4, 0.021)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpCr[(CyN)₂CN(SiMe₃)₂]Cl</td>
<td>85.0, 0.505</td>
<td>93.8</td>
</tr>
<tr>
<td>(11.2, 0.0216)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Catalytic bibenzyl formation timed test (route B)**

In the glovebox, in separate 20 mL sintered glass vials, five trials were set up according to the different catalysts used listed in the table below. To each of the vials was added benzyl chloride and the internal standard, 1,3,5-trimethoxybenzene and the corresponding catalyst (or none in case of the dark and light control). Next was added approximately 3 mL of diethyl ether. Finally, 1.40 mL of 1.0 M in diethyl ether benzylmagnesium chloride (1.40 mmol, approximately 1.4 equiv) was added to each. A 100 W incandescent bulb was placed outside the glovebox window facing the reaction vials (the dark control reaction was wrapped in tinfoil to prevent exposure). The vials were sealed, and the reactions were allowed to proceed for exactly 63 minutes. All five reactions were then brought out of the glovebox and quenched simultaneously by the addition of 5 mL of water. The solutions were then transferred to separatory funnels and diluted with approximately 20 mL of diethyl ether. The organic phases were washed with 3x30 mL of water. The organic phases were then collected and dried over magnesium sulfate and gravity filtered into round bottomed flasks. The solvent was removed *in vacuo* and the residues were taken up in CDCl₃ and analyzed by ¹H NMR spectroscopy. Yields of bibenzyl are listed in table 5 below.
Table 2.4: Reagents and yields for timed test of bibenzyl formation (route B)

<table>
<thead>
<tr>
<th>Chromium Complex (mg, mmol)</th>
<th>Benzyl Chloride (mg, mmol)</th>
<th>Internal Standard (mg, mmol)</th>
<th>Bibenzyl % yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpCr(dep-nacnac)Cl (10.9, 0.0212)</td>
<td>128, 1.01</td>
<td>86, 0.51</td>
<td>11</td>
</tr>
<tr>
<td>CpCr(Ph-nacnac)Cl (8.2, 0.020)</td>
<td>123, 1.03</td>
<td>84, 0.50</td>
<td>5</td>
</tr>
<tr>
<td>CpCr[(CyN)₂CN(SiMe₃)₂]Cl (10.2, 0.0199)</td>
<td>123, 0.974</td>
<td>87, 0.52</td>
<td>2</td>
</tr>
<tr>
<td>Dark Control</td>
<td>123, 0.973</td>
<td>83, 0.49</td>
<td>2</td>
</tr>
<tr>
<td>Light Control</td>
<td>126, 0.993</td>
<td>86, 0.51</td>
<td>2</td>
</tr>
</tbody>
</table>

Attempted synthesis of CpCr[(CyN)₂CMe]F

In a 100 mL Schlenk flask on the line, 420 mg of dicyclohexylcarbodiimide (2.04 mmol, 1.03 equiv) was added. The flask was evacuated and backfilled with nitrogen three times to remove
oxygen. Next was added 8 mL of THF followed by 1.4 mL of 1.6 M in diethyl ether methyl lithium (2.24 mmol, 1.13 equiv). The reaction was sealed under dinitrogen and allowed to react for approximately 20 m. In a 100 mL Schlenk flask in the glovebox was weighed 244 mg of chromium(II) chloride (1.98 mmol, 1 equiv). This was suspended in 6 mL of THF to afford a turbid grey mixture. To this was added 1.10 mL of 2.0 M in THF sodium cyclopentadienylide (2.20 mmol, 1.11 equiv), causing an immediate colour change to a brownish mixture. The Schlenk flask was sealed under dinitrogen, brought out of the glovebox and hooked up to the line. After approximately 20 m., the carbodiimide solution was cannulated over the brownish chromium mixture causing a colour change to a deep cherry red solution. This solution was allowed to react overnight. The following day the solution was cannulated into a bomb flask and brought back into the glovebox. The solvent was removed \textit{in vacuo} and taken up in hexanes before being filtered over a glass frit with Celite to remove ionic salts. The hexanes were then removed from the red filtrate \textit{in vacuo} and the residue was taken up in approximately 5 mL of THF. It was then treated with 273 mg of silver fluoride (2.15 mmol, 1.08 equiv) causing a rapid colour change to an emerald green. This mixture was allowed to react over 10 d. The solvent was then removed \textit{in vacuo} and the residue taken up in hexanes before being filtered over a frit with Celite. The green filtrate was concentrated down to approximately 4 mL then filter pipetted into a 5 mL sintered glass vial. The supernatant was placed in the freezer and allowed to crystallize. 13 mg (2 % yield) of dark green crystals were collected and analyzed by X-ray diffraction and indicated the presence of CpCr[(CyN)2CMe]([η]1-Cp).
3 Photochemistry of Chromium(III) Bipyridine Complexes

3.1 Cationic Chromium(III) bis(Bipyridine) bis(Aryl) Complexes

3.1.1 Unexpected Photoreactivity

It was observed that cationic [Cr(bpy)$_2$(Ph)$_2$]$^+$ (3.1) complexes exhibited interesting reactivity towards bright white light sources: exposure of a solution of the cationic complex under dinitrogen resulted in a dramatic colour change from pale orange to dark purple, along with the formation of biphenyl, detected by $^1$H NMR spectroscopy (Figure 3.1). Monitoring the photochemical reaction by UV-vis spectroscopy showed the emergence of a new absorption band between 525-650 nm, characteristic of bipyridine radical anions observed by Weighardt and Scarbourough in their scrutinization of [Cr(bpy)$_3$]$^{3+}$. This unexpected photoreactivity demonstrated a novel method for biaryl formation initiated under mild conditions with air and water stable cationic complexes. Understanding both the factors that affect this transformation as well as the mechanism of the reductive elimination event spurred the investigation that is described in this chapter.

Figure 3.1: Unexpected photoactivity of [Cr(bpy)$_2$(Ar)$_2$]$^+$ and observed colour change upon photolysis
3.1.2 Substituent Effect on Reduction Potential and UV-vis absorption

Previous work done by Jesse Crescenzo in the Smith research group evaluated the effects of substituent on both the reduction potentials and the UV-vis absorption spectra of the cationic complexes. It was observed that reversible single electron reduction waves for all \([\text{Cr(bpy)}_2(\text{Ar})_2]^+\) cations were found at more negative potentials than \([\text{Cr(bpy)}_3]^{3+}\). This result is consistent with the reduction in formal charge of the monometallic cation and the presence of strongly σ-donating aryl ligands. Addition of more electron donating tert-butyl substituents on either the bipyridine ligands or the aryl ligands lead to a decrease in the reduction potential of the complex, with the bipyridine having a larger effect overall (Table 3.1).

Adding tert-butyl groups on the aryl ligands shifted the absorption band in the UV-vis spectrum to a higher, more low-energy wavelength (375 nm to 392 nm), whereas addition of tert-butyl groups on the bipyridine ligands shifted the absorption band to a lower, more high-energy wavelength (375 nm to 369 nm). Adding tert-butyl groups to both ligand types led a combination of both effects with a net increase in the wavelength of the absorption band (Table 3.1).

It is proposed here that the shift to more negative reduction potentials in the cyclic voltammetry experiments is caused by the presence of more electron rich tert-butyl substituents providing the complex with an increase in electron density, disfavouring reduction compared to the unmodified complex. This results in a more negative observed potential required to induce reduction of the metal complex.
The shift in absorbance bands requires more nuanced explanation. This absorption band is also typically characteristic of chromium(III)-phenyl compounds. It is hypothesized that this electronic transition promotes an electron from the chromium(III)-phenyl bond to the low lying \( \pi^* \)-antibonding orbital of the bipyridine ligand resulting in the formation of the bipyridine radical anion. The presence of more strongly electron donating substituents on the bipyridine ligand would destabilize the LUMO, raising its energy therefore requiring more energy (and a lower \( \lambda_m \)) to induce this electronic transition. Conversely, the strongly electron donating tert-butyl substituents on the aryl ligand may stabilize this transition by providing extra electron density localized in the metal-aryl bonding interaction allowing for lower energy absorptions (with higher \( \lambda_m \)) to induce to electronic transition.

**Table 3.1: UV-vis absorbance and electrochemical data for \([Cr(R-bpy)_{2}(C_6H_5-R)_2][BPh_4]_a\) in acetonitrile.**

<table>
<thead>
<tr>
<th>Complex</th>
<th>R-bpy</th>
<th>C_6H_5-R</th>
<th>( \lambda_{max}^{a}/\text{nm} )</th>
<th>( \varepsilon^{a}/M^{-1}cm^{-1} )</th>
<th>( E_{1/2}^{+/0 b} /V )</th>
<th>( E_{1/2}^{0/-b} /V )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1(BPh_4)</td>
<td>bpy</td>
<td>C_6H_5</td>
<td>373</td>
<td>2750</td>
<td>-1.56</td>
<td>-2.07</td>
</tr>
<tr>
<td>3.1a(BPh_4)</td>
<td>'Bu-bpy</td>
<td>C_6H_5</td>
<td>369</td>
<td>2970</td>
<td>-1.69</td>
<td>-2.24</td>
</tr>
<tr>
<td>3.2(BPh_4)</td>
<td>bpy</td>
<td>C_6H_4-Bu</td>
<td>385</td>
<td>3060</td>
<td>-1.60</td>
<td>-2.14</td>
</tr>
<tr>
<td>3.2a(BPh_4)</td>
<td>'Bu-bpy</td>
<td>C_6H_4-Bu</td>
<td>382</td>
<td>3570</td>
<td>-1.71</td>
<td>-2.30</td>
</tr>
</tbody>
</table>

### 3.1.3 Inhibition Experiments

Jesse Crescenzo additionally performed cut-on filter experiments to elucidate possible absorption bands inducing the reductive elimination from the cationic complexes. It was found
that 395 nm cut-on filter did not inhibit reductive elimination at all over 60 min, while a 435 nm cut-on filter slightly inhibited reductive elimination over 60 min, and a 475 nm cut-on filter completely shut down photochemical reductive elimination over the course of an entire weekend (Figure 3.2).

**Figure 3.2:** UV-vis spectra of [Cr(bpy)$_2$(Ph)$_2$][BPh$_4$] (3.3x10$^{-4}$ M in THF) before photolysis (green), after photolysis with 395 nm cut-on filter (red), 435 nm cut-on filter (yellow), 475 nm cut-on filter (blue).

The photolysis of complex 3.1BPh$_4$ was also carried out in the presence of excess bipyridine. This was shown to result in an increased rate of increasing absorption at 578 nm, the area characteristic of bipyridine radical anions (Figure 3.3).
Figure 3.3: Absorbance at 578 nm \([\text{Cr(bpy)}_2(\text{Ph})_2][\text{BPh}_4]\) (3.48x10^{-4} M in THF) upon photolysis with excess bipyridine (upper), and without (lower).

Photolysis of complex \(3.1\text{PF}_6\) in the presence of a known bipyridine scavenger, ZnCl$_2$, however resulted in arrestation of this increase in absorption (Figure 3.4). Based on these and previous experiments a mechanism was proposed.
3.1.4 Proposed Mechanism for Photochemical Formation of Biphenyl

Photolysis of complex 3.1 promotes an electron from the chromium-phenyl bond to the bipyridine $\pi^*$-antibonding orbital. This then induces reductive elimination of the two aryl groups forming the observed biphenyl. The four coordinate chromium intermediate can then decompose to release free bipyridine, or trap bipyridine to form the observed $[\text{Cr(bpy)}_3]^+$ species. This explains how the presence of excess bipyridine increases the rate of increasing absorption at 578 nm, and why the presence of excess ZnCl$_2$ arrests the increase in absorption (Scheme 3.1).

![Scheme 3.1: Proposed mechanism for photochemical formation of biphenyl from $[\text{Cr(bpy)}_2(\text{Ar})_2]^+$](image)

Figure 3.4: Absorbance at 545 nm $[\text{Cr(bpy)}_2(\text{Ph})_2][\text{PF}_6]$ (7.84x10^{-4} M in MeCN) upon photolysis with excess ZnCl$_2$ (lower), and without (upper).
3.1.5 Cross-Over Experiments

To further explore the nature of the biphenyl formation, cross-over experiments were conducted using two differently substituted derivatives of complex 3.1. A mixture of 3.2I and 3.3I under dinitrogen was subjected to bright white light and allowed to react. Analysis of the product mixture by GC/MS showed formation of two discrete compounds. Authentic samples of the proposed biaryls were prepared by homocoupling the corresponding aryl Grignard using catalytic FeCl₃ in the presence of excess 1,2-dichlorobutane. By spiking the product mixture of the cross-over experiment with these authentic biaryls, it was observed that the only product of photolysis is the homocoupled biaryl, consistent with a monometallic reductive elimination event. This result is inconsistent with formation of aryl radicals, as the heterocoupled and substituted benzene products would be observed in the product mixture as well. Additionally, with use of an internal standard, it was observed that formation of the biaryl proceeded with >95% yield for both complexes (Scheme 3.2, Figure 3.5).

Scheme 3.2: Crossover photolysis experiment between 3.2I and 3.3I
Figure 3.5: GC/MS traces of crossover experiment
3.1.6 Trapping Experiments

It was hypothesized that the initial intermediate of photolysis could be trapped using a suitable reagent to generate a new complex. This was supported by UV-vis analysis suggesting the formation of [Cr(bpy)₃]⁺ in the presence of excess bipyridine concluded by Jesse Crescenzo.

Photolysis of a mixture of 3.1PF₆ and benzoyl peroxide led to formation of a dark red mixture, distinctly different from the typically purple solutions observed when photolyzing only complex 3.1 (Scheme 3.3). Authentic [Cr(bpy)₂(O₂CPh)₂][PF₆] was independently synthesized by first reacting chromocene with two equivalents of bipyridine and two equivalents of benzoic acid. Addition of one bipyridine molecule to chromocene changes coordination of one Cp moiety from η⁵ to η¹ allowing for more facile anionic ligand protonolysis by the benzoic acid. This sequential addition of bipyridine and benzoate ligands affords a neutral Cr(bpy)₂(O₂CPh)₂ with a bipyridine radical anion that can be quenched to form the cationic metal complex by the addition of ferrecinium hexafluorophosphate as an oxidant (Scheme 3.4). Theopold and Wieghardt synthesized the analogous [Cr(bpy)₂(OAc)₂][PF₆] by addition of two equivalents of bipyridine to the dimer {Cr(OAc)₂}₂ followed by oxidation with [Cp₂Fe][PF₆].

Analysis by UV-vis showed formation of a new complex consistent with independently synthesized [Cr(bpy)₂(O₂CPh)₂]⁺PF₆⁻.

Scheme 3.3: Formation of compound 3.4PF₆
3.2 Neutral Chromium(III) Bipyridine bis(Aryl) Complexes

3.2.1 Neutral Dithiocarbamate Complex

A neutral dithiocarbamate complex prepared by Marchese and West was synthesized by reacting chromium(II) chloride with bipyridine and one half equivalent of tetramethylthiuram disulfide. This dichloride complex was then arylated by reacting it with two equivalents of an aryl Grignard (Scheme 3.5). This compound was also found to be anomalously stable with respect to air and water degradation, unlike the related bis(pyridyl) species, most likely for similar reasons as the cationic complexes, including the prevention of neutral ligand labilization due to the chelate effect. This stability allowed the dithiocarbamate complex to be a useful comparison to the previously discussed cationic complexes.

Scheme 3.5: Marchese and West synthesis of neutral dithiocarbamate bis(aryl) complex 3.5
Exposure of the dithiocarbamate complex to bright light under dinitrogen did yield biphenyl, however at significantly reduced yield (Scheme 3.6).

Scheme 3.6: Photochemically induced reductive elimination of neutral dithiocarbamate complex

Photolysis of 3.5 under dinitrogen in the presence of benzoyl peroxide did form a new complex as detected by UV-vis, however attempts to independently synthesize the bis(benzoate) complex using silver benzoate were unsuccessful. It is believed that this is due to interaction between the soft silver reagent and the soft sulfur atoms of the dithiocarbamate ligand which could result in abstraction of the dithiocarbamate ligand leading to decomposition of the complex (Scheme 3.7).

Scheme 3.7: Trapping and attempted synthesis of neutral Cr(bpy)(Me₂NCS₂)(O₂CPh)₂

3.2.2 Neutral Quinolinate Complex

Preparation of other neutral chromium(III) bipyridine bis(aryl) complexes was initially attempted by reacting similar dichloro precursors with Grignard reagents. However, the products isolated from the reaction mixtures indicated decomposition by various routes. Development of an alternative reaction pathway was required. Inspiration from the literature was taken and a
chromium(III) bipyridine tris(aryl) complex synthesized by Müller was prepared.\textsuperscript{37} The presence of the third aryl ligand allowed for anionic ligand protonolysis using HLX ligands, releasing volatile arenes which could be easily removed \textit{in vacuo} as well as concurrent installation of the desired LX ligand. Reaction of 8-hydroxyquinoline (quinH) with red Cr(bpy)(Ph)_3 released benzene and afforded 3.6 as an orange solid (Scheme 3.8).

\textbf{Scheme 3.8: Synthesis of neutral 3.6 by protonolysis route using Müller’s Cr(bpy)(Ph)_3(THF) complex}

Exposure of the quin complex under dinitrogen to bright white light sources caused a rapid colour change to dark green. Analysis of the product solution by $^1$H NMR against an internal standard showed an 82.3 \% yield of the biaryl product, significantly higher than the dithiocarbamate, and comparable to the cationic complexes.

The initial product of photolysis of 3.6 could also be captured using benzoyl peroxide. This was supported by UV-vis analysis of 3.7 that was independently synthesized by first preparing a dichloro precursor. The dichloro precursor was synthesized by reacting CrCl\textsubscript{3}(THF)\textsubscript{3} with one equivalent of bipyridine followed by one equivalent of 8-hydroxyquinoline. Reacting the bright green Cr(bpy)(quin)Cl\textsubscript{2} with two equivalents of silver benzoate afforded an orange mixture with a UV-vis spectrum consistent with the product of photolysis in the presence of benzoyl peroxide (Scheme 3.9).
Scheme 3.9: Photochemical reaction pathway of (quin) complex and synthetic route

The work outlined in chapter 3 highlights beautiful examples of carbon-carbon bond formation initiated photochemically from chromium(III) bipyridine complexes. Additionally the ability to oxidatively add peroxide species from the reduced product of reductive elimination allows for a potentially new reaction manifold based on work outlined by Ribas et al; the presence of carboxylate groups may allow for directed C-H functionalization reactions using properly designed substrates in the future. They also provide a potential synthetic handle for more classical transmetalation reactions that could close the cycle on these C<sub>sp2</sub>-C<sub>sp2</sub> bond forming reactions. Reaction of the carboxylate species with an aryl Grignard reagent could theoretically lead back to the bis(aryl) complex thereby completing the cycle of photochemical biaryl formation (Scheme 3.10).
Scheme 3.10: Closing the cycle for photochemical biaryl formation

A potentially viable substrate for a C-H activation type reaction is presented here below. The success of the photochemical reductive elimination reaction using 8-hydroxyquinoline as an ancillary presents the opportunity to also explore 8-aminoquinoline as a viable ancillary. Furthermore, functionalization of the amino moiety with a benzoyl group could lead to directed C-H functionalization via anionic ligand protonolysis, which has been previously explored in the literature.\textsuperscript{39} Reaction of A with the substrate would first eliminate HX (X = Ph, HO\textsubscript{2}CPh, halide) to afford B. Direction by the carbonyl group then leads to metalation of the phenyl group via concerted metalation deprotonation to afford organometallic intermediate C. Transmetalation of the remaining X ligand using a Grignard installs the aryl group D and photochemically induced reductive elimination functionalizes the benzoyl group E (Scheme 3.11).
Scheme 3.11: Potential future application for photochemical C-H functionalization

Future work in this project should focus on testing the amenability of these reaction pathways in order to ultimately complete the cycle and test catalytic potentiality.

3.3 Experimental Section

3.3.1 General Considerations

Unless otherwise stated, all reactions were carried out under dinitrogen using standard Schlenk and glove box techniques. Hexanes, diethyl ether, dichloromethane, and tetrahydrofuran were purified by passage through activated alumina and deoxygenizer columns from Glass Contour Co. (Laguna Beach, CA, USA). Celite (Aldrich) was dried overnight at 130 °C before being evacuated and then stored under nitrogen. 2,2’-bipyridine, 8-hydroxyquinoline, tetramethylthiuram disulfide, benzoyl peroxide, ammonium hexafluorophosphate, phenylmagnesium chloride (2.0 M in THF), 4-methoxyphenylmagnesium bromide (0.5 M in THF), 4-tert-butylmagnesium chloride (0.5 M in THF), 4-tolylmagnesium bromide (1.0 M in THF), zinc(II) chloride (0.5 M in THF), 1,2-dichlorobutane, iron(III) chloride, benzoic acid,
silver benzoate, 1,3,5-trimethoxybenzene, and chromium(III) chloride were purchased from Aldrich and used as received. Chromium(II) chloride was purchased from Strem and stored under nitrogen prior to use.

UV-vis spectroscopic data were collected on a Shimadzu UV 2550 UV-vis spectrophotometer in a specially constructed cell for air-sensitive samples: a Kontes Hi-Vac Valve wit PTFE plug was attached to a Hellma 10 mm path length quartz absorption cell with a quartz-to-glass graded seal. $^1$H NMR spectra were recorded on a Varian Mercury Plus 400 spectrometer with chemical shifts referenced to the solvent signal.

3.3.2 Synthetic Procedures

**Synthesis of [Cr(bpy)$_2$Ph$_2$][PF$_6$] 3.1PF$_6$**

In a 100 mL Schlenk flask in the glovebox, 252 mg of chromium(II) chloride (2.05 mmol, 1 equiv) was suspended in 10 mL of THF. To this was added 639 mg of 2,2’-bipyridine (4.09 mmol, 2.00 equiv) as a 5 mL THF solution causing a colour change from grey to dark blue. Next was added 2.20 mL of phenylmagnesium chloride (2.0 M in THF, 4.40 mmol, 2.15 equiv) causing another colour change to dark purple. The mixture was allowed to react overnight. The next day the solvent was removed in vacuo and the flask was brought out of the glovebox. 1.04 g of ammonium hexafluorophosphate (6.40 mmol, 3.12 equiv) was added as a 30 mL solution in 2:1 methanol: water. Air was passed through the solution for approximately 90 min. causing a gradual colour change from dark purple to bright orange. The suspension was filtered over a Buchner funnel to isolate the product as an orange solid. The solid was washed with 10 mL of water then an additional 2x5 mL of water and suction dried overnight. A total of 1.12g of canary yellow powder was isolated the following day (83 % yield).
**Photolysis of [Cr(bpy)$_2$Ph$_2$][PF$_6$] $3.1$PF$_6$ with excess ZnCl$_2$**

In a 100 mL thick-walled glass vessel, 55 mL of anhydrous acetonitrile was degassed by bubbling N$_2$ through the solution. The vessel was sealed under nitrogen and brought into the glovebox. A 25.0 mL stock solution was prepared by dissolving 13.0 mg of $3.1$PF$_6$ in the degassed acetonitrile in a volumetric flask (0.0196 mmol, 7.84x10$^{-4}$ M). A 5.00 mL pipette was then used to transfer two aliquots to separate 10.0 mL volumetric flasks (A and B respectively). Solution A was used as a control and made up to the mark with degassed acetonitrile ([Cr]$_A$ = 3.92x10$^{-4}$ M). Into solution B was added 0.10 mL of 0.5 M ZnCl$_2$ in THF (0.0500 mmol, 12.8 equiv). The remaining volume was made up with degassed acetonitrile. Two separate sealable cuvettes were filled with either solution A or solution B and labelled. The cuvettes were sealed and brought out of the glovebox and irradiated with 100 W incandescent bulbs placed approximately 10 cm away from the samples. UV-vis spectra of the two solutions were collected every 5 min. for one hour. Solution A was observed to change color after a short induction period while solution B remained yellow.

**GC/MS analysis of photolysis 3.2I and 3.3I (crossover experiment)**

A solution of 10.9 mg of Cr(bpy)$_2$(C$_6$H$_4$COMe)$_2$I (0.0143 mmol) and 10. mg of [Cr(bpy)$_2$(C$_6$H$_4$COMe)$_2$I (0.0146 mmol) in 20 mL THF in a 50 mL straight Schlenk flask under N$_2$ was photolyzed with a 100 W incandescent light bulb placed 20 cm away. After 20 h of photolysis, the solvent was removed from the purple solution in vacuo, the residue was extracted with dichloromethane in air and filtered through silica to remove the chromium-containing byproduct. The diluted CH$_2$Cl$_2$ extracts were analyzed by GC/MS. The only two peaks observed were at 9.329 min (m/z 215.0) and 9.926 min (m/z 266.1). These products were confirmed as 4,4’-dimethoxybiphenyl and 4,4’-di-tert-butylnphenyl respectively by re-running the GC/MS
with aliquots spiked with authentic samples of each of the two biaryl species. Peaks were not observed for the mixed biaryl species or the corresponding C₆H₃R (R = CMe₃ or OMe) arenes.

**Photolysis of [Cr(bpy)₂Ph₂][PF₆] 3.1PF₆ with excess benzoyl peroxide**

To a 50 mL Schlenk flask was added 3 mg of 3.1PF₆ (0.005 mmol) along with 13 mg of benzoyl peroxide (0.052 mmol, 11 equiv). The flask was evacuated and backfilled with nitrogen three times to expel oxygen from the system. Under N₂, 10.0 mL of THF was added to afford a yellow solution ([Cr] = 4.67x10⁻⁵ M). The flask was sealed under N₂ and the solution was irradiated with a 100 W incandescent bulb placed approximately 10 cm away overnight. The next day, the reaction mixture was observed as a yellow-pink solution. A UV-vis spectrum was collected and compared to independently synthesized [Cr(bpy)₂(O₂CPh)][PF₆].

**Synthesis of neutral Cr(bpy)(S₂CNMe₂)Ph₂ compound 3.6**

The neutral dithiocarbamate bis(phenyl) complex was synthesized according to a literature procedure.⁴⁰ A solution of 164 mg of bipyridine (1.05 mmol) in 3 mL of THF was added to a stirring grey suspension of CrCl₂ (127 mg, 1.03 mmol) in 6 mL THF in a 20 mL scintillation vial. To the resulting dark mixture was added a pale yellow-green solution of 126 mg of tetramethylthiuram disulfide (0.520 mmol) in 3 mL THF. Within approximately 2 min, a flocculent olive-green precipitate had formed. After stirring for 2 h, 1.0 mL of PhMgCl (2.0 M in THF, 2.0 mmol) was added dropwise, initially resulting in a red solution that then formed a red-brown suspension. After 20 min, the solution was taken from the glovebox, poured into a beaker in air, and washed with 30 mL of 2:1 methanol: water. The red-orange solid was isolated on a sintered glass crucible and washed with 10 mL methanol. After drying, 407 mg of crude Cr(bpy)(S₂CNMe₂)Ph₂ (82 % yield) was isolated as an orange powder. Recrystallization of a 293
mg sample of this crude powder under N₂ in a mixture of 20 mL CH₂Cl₂ and 5 mL hexanes at -20 °C overnight gave 146 mg of Cr(bpy)(S₂CNMe₂)Ph₂ (50 % recovery) as a fine orange powder.

**Photolysis of 3.6**

In a 50 mL straight Schlenk flask, 15 mg of Cr(bpy)(S₂CNMe₂)Ph₂ (0.030 mmol) was weighed. The flask was then evacuated and backfilled with nitrogen three times to expel oxygen from the system. With N₂ blowing, 20.0 mL of THF was added through a septum. The resulting orange solution was sealed under inert atmosphere and irradiated with a 100 W incandescent bulb placed approximately 10 cm away from the Schlenk flask for 4 h. Over the course of photolysis, a colour change from orange to dark grey-green was observed. After photolysis, the solution was transferred in air to a 100 mL RBF resulting in a colour change to orange. Next, 5 mg of 1,3,5-trimethoxybenzene (0.03 mmol, 1 equiv) was added as an internal standard. The solvent was removed *in vacuo*, and the concentrate was then taken up in diethyl ether and filtered through Celite to remove the insoluble chromium product. The solvent was again removed from the clear, colorless filtrate and the residue taken up in deuterated chloroform for ¹H NMR. Analysis of the NMR spectrum showed biphenyl in 31% yield based on comparison to the internal standard signals.

**Synthesis of Cr(bpy)Ph₃(THF)**

In a 100 mL Schlenk flask in the glovebox, 158 mg of CrCl₃ was suspended in approximately 5 mL of THF (0.999 mmol, 1 equiv). To this was added 157 mg of 2,2’-bipyridine (1.01 mmol, 1.01 equiv). Next was added 1.5 mL of PhMgCl dropwise (2.0 M in THF, 3.0 mmol, 3.0 equiv) causing a colour change to yellow then to deep red with an observable precipitate. The reaction
was allowed to proceed overnight. The following day, the mixture was filtered over a glass frit to isolate the red solid from the solution. The product was washed with approximately 3 mL of THF and the powder was dried under reduced pressure. A total of 450 mg of bright red powder was isolated (88 % yield) and stored under nitrogen).

**Synthesis of 3.7**

In a 100 mL Schlenk flask in the glovebox, 247 mg of Cr(bpy)Ph$_3$(THF) was suspended in approximately 2 mL of THF (0.482 mmol, 1 equiv). 71 mg of 8-hydroxyquinoline (quinH, 0.49 mmol, 1.0 equiv) was dissolved in 2 mL THF and added to the red suspension. The mixture was allowed to react overnight. The following day the reaction was observed as an orangey-brown suspension with a visible precipitate. The mixture was filtered over a frit to isolate the crude product and washed with 2x2 mL of THF. After drying under reduced pressure, a total of 152 mg of cumin coloured crude product was isolated (62 % yield). A 118 mg sample of the product was recrystallized in a 1:1 mixture of DCM:MeCN with a total of 12 mg of red-orange powder recovered from the supernatant (10 % recovery).

**Synthesis of Cr(bpy)(C$_6$H$_4$Me)$_3$(THF)**

In a 20 mL scintillation vial, 168 mg of CrCl$_3$ was suspended in 10 mL THF (1.06 mmol, 1 equiv). To this was added first 163 mg of 2,2’-bipyridine (1.04 mmol, 0.985 equiv) followed by 3.30 mL of 4-tolylmagnesium bromide (1.0 M in THF, 3.30 mmol, 3.11 equiv) dropwise affording a deep red mixture which was allowed to react overnight. The following day the red product had precipitated from solution and was isolated on a glass frit and washed with 2x5 mL THF. After drying under reduced pressure, it was collected and stored under nitrogen (476 mg, 83 % yield).
Synthesis of Cr(bpy)(quin)(C₆H₄Me)$_2$

476 mg of Cr(bpy)(C₆H₄Me)$_3$(THF) was suspended in 10 mL diethyl ether in a 20 mL scintillation vial in the glovebox (0.859 mmol, 1 equiv). 110. mg of 8-hydroxyquinoline (quinH, 0.755 mmol, 1.11 equiv) was added as a 3 mL diethyl ether solution. The vial was sealed and allowed to react overnight after which time it had changed from a red suspension to an orange suspension. The orange product was collected on a glass frit and washed with 2x5 mL of diethyl ether and dried under reduced pressure. The orange product was collected and stored under nitrogen (388 mg, 95 % yield)

Photolysis of Cr(bpy)(quin)(C₆H₄Me)$_2$

16 mg of Cr(bpy)(quin)(C₆H₄Me)$_2$ was dissolved in approximately 9 mL THF in a 10 mL Schlenk flask in the glovebox affording an orange solution (0.030 mmol, 1 equiv). The flask was sealed under nitrogen and brought out of the box and irradiated with a 100 W incandescent bulb placed approximately 10 cm away for 24 h. The following day the reaction was observed as a very dark green solution. It was transferred to a round bottomed flask in air and 6 mg of 1,3,5-trimethoxybenzene was added (0.03 mmol, 1 equiv). The solvent was removed in vacuo and the organics were extracted using diethyl ether from the residue in the flask. The organic phase was passed through a filter pipette to remove insoluble chromium-containing byproducts. The solvent of the yellow filtrate was then removed in vacuo and the oil residue was taken up in deuterated acetone for $^1$H NMR analysis. Based on the internal standard signal a total of 82 % yield of the homocoupled biaryl product was detected.

Photolysis of 3.7 in presence of benzoyl peroxide
In the glovebox in two separate 10.0 mL volumetric flasks (A and B), two 3 mg samples of Cr(bpy)(quin)Ph$_2$ were dissolved in THF to afford orange solutions $[\text{Cr}]_A = [\text{Cr}]_B = 6 \times 10^{-4}$ M. In solution B, 15 mg of benzoyl peroxide (0.065 mmol, 11 equiv) was added. Two air-tight quartz cuvettes were filled with either solution A or solution B. Both cuvettes were sealed and taken out of the glovebox. An initial UV-vis spectrum was taken of each sample and then the two were subsequently irradiated by a 100 W incandescent bulb placed approximately 10 cm away. Solution A served as a control. After four hours of photolysis, solution A was observed as a dark green solution and solution B was observed as an orange solution. UV-vis spectra were taken of each sample and the spectrum of solution B was compared to independently synthesized 3.7

**Photolysis of 3.7 in presence of excess bipyridine**

In a 50 mL straight Schlenk was weighed 9.6 mg of Cr(bpy)(quin)Ph$_2$ (0.0190 mmol, 1 equiv) and 36 mg of 2,2′-bipyridine (0.23 mmol, 12 equiv) in the glovebox. To this was added 30.0 mL of THF to afford a translucent orange solution ($[\text{Cr}] = 6.3 \times 10^{-4}$ M). A UV-vis spectrum of the solution was collected under dinitrogen. The flask was sealed, and the solution was irradiated through the glove box window by a 100 W incandescent bulb placed approximately 10 cm away. After two hours of photolysis, a second UV-vis spectrum was taken (under inert atmosphere) of the now green solution. Air exposure of the solution results in a colour change from green to orange.
4 Conclusion

It was found that the use of sterically reduced guanidinate ligands provided enhanced reductive power based on the observed increased rates of alkyl halide activation outlined in Chapter 2. Furthermore, the increased access to the metal center allowed for the capture of tertiary alkyl radical species, something not observed with the previously studied β-diketiminate complexes.

This does however lead to increased Cr\textsuperscript{III}-X (X = halide, alkyl) bond strength. The benzyl complex, 2.4, was not found to homolyze at room temperature, under N\textsubscript{2}, in the dark highlighting this observation. The introduction of light could induce homolysis of the chromium-benzyl bond and the observed rate constants were extracted using trapping experiments involving diphenyl disulfide. Future experiments could involve studying the photochemical rate constants associated with this homolysis event.

Due to the increased Cr\textsuperscript{III}-X bond strength, novel reductants were investigated for amenability in regenerating the active chromium(II) compound. It was found that reacting phenyl silane with sodium tert-butoxide generated a pentavalent silane that was capable of reducing the CpCr(LX)Cl complexes to CpCr(LX), presumably via a chromium-hydride species followed by disproportionation. This reductant system was employed in the simple radical homocoupling of two benzyl radicals to afford bibenzyl. A maximum of 48 % yield bibenzyl was achieved indicating room for optimization of the system. Future experiments should explore this more thoroughly and apply the system to novel metal mediated radical reactions.

In Chapter 3, the photochemical formation of biaryl species was explored using cationic [Cr(bpy)\textsubscript{2}(Ar)\textsubscript{2}]\textsuperscript{+} complexes. It was found through a combination of work previously conducted
by Jesse Crescenzo and subsequent experiments that the mechanism proceeds via electron transfer to the redox non-innocent bipyridine ligand which induces reductive elimination of the aryl groups affording the biaryl product. Cross-over experiments showed that the reaction is a monometallic reduction event from the lack of hetero-coupled biaryls or arenes observed in the GC/MS experiment.

Replacement of one of the bipyridine ligands with a monoanionic, bidentate, LX ligand were found to afford neutral compounds the were competent for similar photoactivity, however, with overall reduced yield of the biaryl product. The initial products of photolysis could also be trapped using benzoyl peroxide to afford a bis(carboxylate species). This species provides a synthetic handle that could potentially be used in transmetalation experiments to regenerate the bis(aryl) species and close the cycle on biaryl formation. Alternatively, the carboxylate groups can be used as directing groups in specific substrates for C-H activation reactions as outlined in Chapter 3.

Modification of the stereoelectronic environment of a metal center, even on subtle levels, has been shown in this thesis to effect dramatic reactivity consequences. In Chapter 2, the use of a guanidinate LX ligand resulted in increased reductive power of the complex at the cost of stronger Cr-X bonds which necessitated the use of a stronger reductant system. In Chapter 3, octahedral chromium(III) bipyridine (neutral and cationic) were found to exhibit unique photoactivity due to the presence of a low-lying π*-antibonding orbital on the redox non-innocent ligand.
References


24 Labinger, J.L. Organometallics, 2015, 34, 4784-4795.


Appendices

Appendix A: UV-vis Spectra of Select Compounds

Figure A.1: UV-vis spectra of compound 2.1 (1.00x10^{-3} M in THF).

Figure A.2: UV-vis spectra of compound 2.3 (5.76x10^{-3} M in hexanes)
Figure A.3: UV-vis spectra of compound 2.4 (9.7x10^{-4} M in THF)

Figure A.4: UV-vis spectra of compound 2.5 (2.00x10^{-4} M in hexanes)
Figure A.5: UV-vis spectrum of CpCr[(CyN)\textsubscript{2}CN(SiMe\textsubscript{3})\textsubscript{2}]('Bu) (1.15x10\textsuperscript{-3} M in THF)

Figure A.6: UV-vis spectrum of CpCr[(CyN)\textsubscript{2}CN(SiMe\textsubscript{3})\textsubscript{2}(CH\textsubscript{2}CH\textsubscript{2}Ph) (qualitative in THF)
### Appendix B: Supplemental X-Ray Data

<table>
<thead>
<tr>
<th></th>
<th>2.1</th>
<th>2.1a</th>
<th>2.2</th>
<th>2.4</th>
<th>2.5</th>
<th>2.10</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>$\text{C}_2\text{H}_6\text{N}_3\text{Cr}_2\text{Cl}$</td>
<td>$\text{C}_2\text{H}_6\text{N}_3\text{Cr}_2\text{Cl}$</td>
<td>$\text{C}_2\text{H}_6\text{N}_3\text{Si}_2\text{Cr}$</td>
<td>$\text{C}_2\text{H}_6\text{N}_3\text{Si}_2\text{Cr}$</td>
<td>$\text{C}_2\text{H}_6\text{N}_3\text{Si}_2\text{Cr}$</td>
<td>$\text{C}_2\text{H}_6\text{N}_3\text{Si}_2\text{Cr}$</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>519.27 g/mol</td>
<td>293.78 g/mol</td>
<td>483.81 g/mol</td>
<td>574.95 g/mol</td>
<td>498.85 g/mol</td>
<td>403.54 g/mol</td>
</tr>
<tr>
<td><strong>Crystal colour, habit</strong></td>
<td>Green, prism</td>
<td>Green, rod</td>
<td>Purple, plate</td>
<td>Black, tablet</td>
<td>Purple, irreg.</td>
<td>Green, tablet</td>
</tr>
<tr>
<td><strong>Dimension, mm</strong></td>
<td>0.16x0.28x0.33</td>
<td>0.23x0.11x0.07</td>
<td>0.15x0.13x0.03</td>
<td>0.24x0.16x0.06</td>
<td>0.30x0.29x0.27</td>
<td>0.28x0.20x0.15</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P2/$\text{i}$</td>
<td>P2/$\text{c}$</td>
<td>P2/$\text{c}$</td>
<td>C2/$\text{c}$</td>
<td>P2/$\text{i}$</td>
<td>P-1</td>
</tr>
<tr>
<td><strong>a, Å</strong></td>
<td>15.396(3)</td>
<td>13.4148(5)</td>
<td>10.0554(14)</td>
<td>31.6049(12)</td>
<td>18.869(2)</td>
<td>8.9783(8)</td>
</tr>
<tr>
<td><strong>b, Å</strong></td>
<td>10.920(2)</td>
<td>13.894(5)</td>
<td>21.294(3)</td>
<td>10.8766(4)</td>
<td>16.4909(19)</td>
<td>10.8195(10)</td>
</tr>
<tr>
<td><strong>c, Å</strong></td>
<td>17.243(3)</td>
<td>16.1612(6)</td>
<td>13.1183(19)</td>
<td>19.2210(8)</td>
<td>27.900(3)</td>
<td>11.9662(10)</td>
</tr>
<tr>
<td><strong>$\alpha, ^\circ$</strong></td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>99.324(2)</td>
</tr>
<tr>
<td><strong>$\beta, ^\circ$</strong></td>
<td>107.154(5)</td>
<td>101.3020(10)</td>
<td>110.793(3)</td>
<td>102.439(2)</td>
<td>100.134(2)</td>
<td>111.448(2)</td>
</tr>
<tr>
<td><strong>$\gamma, ^\circ$</strong></td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>96.043(2)</td>
</tr>
<tr>
<td><strong>V, Å$^3$</strong></td>
<td>2770.1(9)</td>
<td>2953.86(19)</td>
<td>2625.9(7)</td>
<td>6452.2(4)</td>
<td>8546.0(17)</td>
<td>1050.35(16)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
<td>8</td>
<td>4</td>
<td>8</td>
<td>14</td>
<td>2</td>
</tr>
<tr>
<td><strong>Dcalc, g/cm$^3$</strong></td>
<td>1.245</td>
<td>1.321</td>
<td>1.224</td>
<td>1.184</td>
<td>1.364</td>
<td>1.276</td>
</tr>
<tr>
<td><strong>$\mu$(MoKα), mm$^{-1}$</strong></td>
<td>1116</td>
<td>1240</td>
<td>1048</td>
<td>2488</td>
<td>3881</td>
<td>434</td>
</tr>
<tr>
<td><strong>2$\theta$ max</strong></td>
<td>60.2$^\circ$</td>
<td>55.796$^\circ$</td>
<td>56.604$^\circ$</td>
<td>59.98$^\circ$</td>
<td>61.326$^\circ$</td>
<td>61.246</td>
</tr>
<tr>
<td><strong>Reflections msrd</strong></td>
<td>34607</td>
<td>29071</td>
<td>27921</td>
<td>39669</td>
<td>110550</td>
<td>24602</td>
</tr>
<tr>
<td><strong>Unique reflcn, R$_{int}$</strong></td>
<td>8110, 0.040</td>
<td>7062, 0.0360</td>
<td>6538, 0.0668</td>
<td>9392, 0.0439</td>
<td>26319, 0.0529</td>
<td>6428, 0.0426</td>
</tr>
<tr>
<td><strong>Absorption, T$<em>{min}$, T$</em>{max}$</strong></td>
<td>0.860, 0.907</td>
<td>0.7009, 0.7456</td>
<td>0.930, 0.983</td>
<td>0.901, 0.973</td>
<td>0.6394, 0.7461</td>
<td>0.8390, 0.9201</td>
</tr>
<tr>
<td><strong>Obsrved data (I&gt;2.00σ(I))</strong></td>
<td>6867</td>
<td>5409</td>
<td>4823</td>
<td>7508</td>
<td>18131</td>
<td>5430</td>
</tr>
<tr>
<td><strong>No. parameters</strong></td>
<td>326</td>
<td>317</td>
<td>277</td>
<td>340</td>
<td>889</td>
<td>245</td>
</tr>
<tr>
<td><strong>R1, wR2 (F$^2$, all data)</strong></td>
<td>0.049, 0.104</td>
<td>0.440, 0.1101</td>
<td>0.0683, 0.0957</td>
<td>0.0553, 0.1150</td>
<td>0.1074, 0.2119</td>
<td>0.0512, 0.1047</td>
</tr>
<tr>
<td><strong>R1, wR2 (F, I&gt;2.00σ(I))</strong></td>
<td>0.040, 0.098</td>
<td>0.0609, 0.1196</td>
<td>0.0411, 0.0858</td>
<td>0.0419, 0.1067</td>
<td>0.0762, 0.1869</td>
<td>0.0401, 0.0990</td>
</tr>
<tr>
<td><strong>Goodness of Fit</strong></td>
<td>1.05</td>
<td>1.062</td>
<td>1.016</td>
<td>1.050</td>
<td>1.047</td>
<td>1.030</td>
</tr>
<tr>
<td><strong>Max, Min peak, e/Å$^3$</strong></td>
<td>1.10, -0.68</td>
<td>1.26, -0.29</td>
<td>0.643, -0.442</td>
<td>0.830, -0.284</td>
<td>2.74, -0.62</td>
<td>1.60, -0.76</td>
</tr>
</tbody>
</table>
Appendix C: List of all numbered compounds

<table>
<thead>
<tr>
<th>Chapter 2 Compounds</th>
<th>Chapter 3 Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Compound 2.1" /></td>
<td><img src="image2" alt="Compound 3.1X" /></td>
</tr>
<tr>
<td>2.1</td>
<td>3.1X (X refers to counter anion)</td>
</tr>
<tr>
<td><img src="image3" alt="Compound 2.2" /></td>
<td><img src="image4" alt="Compound 3.21" /></td>
</tr>
<tr>
<td>2.2</td>
<td>3.21</td>
</tr>
<tr>
<td><img src="image5" alt="Compound 2.1a" /></td>
<td><img src="image6" alt="Compound 3.31" /></td>
</tr>
<tr>
<td>2.1a</td>
<td>3.31</td>
</tr>
<tr>
<td>2.3</td>
<td>3.4PF₆</td>
</tr>
<tr>
<td>-----</td>
<td>--------</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>2.4</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>