

Synthesis and structural studies of N- and P-donor ligands in Chromium(III) complexes

by

Nicholas Frederick Brennan

Submitted in partial fulfilment of the requirements for the degree

Philosophiae Doctor
in Chemistry

In the Faculty of Natural and Agricultural Sciences
University of Pretoria
Pretoria

June 2009

TABLE OF CONTENTS

Abstract	i
Acknowledgements	iii
Common abbreviations	iv
Complex abbreviations	v
Structural drawings	vi
List of Figures	viii
List of Tables	xvi

CHAPTER 1

INTRODUCTION.....	1
1.1 IMPORTANCE OF CATALYSIS	1
1.2 HOMOGENEOUS AND HETEROGENEOUS CATALYSIS.....	1
1.3 CATALYSIS AND TRANSITION METALS	2
1.4 CATALYTIC STEPS	2
1.5 OVERVIEW OF CATALYTIC DESIGN.....	3
1.6 ETHYLENE OLIGOMERISATIONS	4
1.6.1 1-Hexene	4
1.6.2 1-Octene.....	8
1.7 PROJECT OUTLINE	9
1.7.1 Monomeric and Dimeric States	10
1.7.2 Ligands.....	11
1.7.3 Characterisation and Analysis.....	13
1.7.3.1 X-ray Crystallography	13
1.7.3.2 Infrared and Raman Spectroscopy	14



1.7.3.3	NMR Spectroscopy	15
1.7.3.4	Computational Studies	17
1.7.3.5	Mass Spectrometry.....	18
1.8	EXPERIMENTAL.....	18
1.8.1	Safety Remarks	18
1.8.2	General Remarks.....	19
1.8.3	Standard Colour Changes	19
1.8.4	Synthesis of the Starting Material [CrCl ₃ (thf) ₃].....	20
1.8.5	General Procedure and Instrument Data: Infrared and Raman Spectroscopy	20
1.8.6	General Procedure and Instrument Data: X-ray Crystallography	21
1.8.7	General Procedure and Instrument Data: ¹ H NMR Scale Experiments	22
1.8.8	General Procedure and Instrument Data: Computational Studies	22
1.8.9	General Procedure and Instrument Data: Mass Spectrometry.....	23

CHAPTER 2

CHROMIUM(III) MONODENTATE NITROGEN LIGAND

CHEMISTRY

2.1	INTRODUCTION	24
2.2	CATEGORY ONE: SEQUENTIAL ADDITION OF PYRIDINE ...	25
2.2.1	Visual Analysis	27
2.2.2	Infrared and Raman Spectroscopy	27
2.2.3	Computational Study	33
2.2.4	NMR Spectroscopy	36
2.2.5	X-ray Crystallography	40
2.2.5.1	[CrCl ₃ (py) ₃].....	40

2.2.5.2	[Hpy][CrCl ₄ (py) ₂]	45
2.2.6	Mass Spectrometry.....	53
2.3	CATEGORY TWO: BULKY SUBSTITUENTS.....	54
2.3.1	Infrared Spectroscopy	56
2.3.1.1	Region 3114–2804 cm ⁻¹	56
2.3.1.2	Region 1660–1247 cm ⁻¹	57
2.3.1.3	Region 1219–448 cm ⁻¹	58
2.3.1.4	Region 415–214 cm ⁻¹	59
2.3.2	X-ray Crystallography	60
2.4	CATEGORY THREE: PARA-SUBSTITUTED PYRIDINES	64
2.4.1	Infrared and Raman Spectroscopy	65
2.4.1.1	Region 3321–2869 cm ⁻¹	66
2.4.1.2	Region 1638–1045 cm ⁻¹	68
2.4.1.3	Region 1030–499 cm ⁻¹	71
2.4.1.4	Ligand substituents	74
2.4.1.5	Bond Strength	74
2.4.1.6	Region 488–213 cm ⁻¹	78
2.4.1.7	Concluding remarks	79
2.4.2	Computational Studies	84
2.4.3	NMR of [CrCl ₃ (thf) ₃] and three equivalents of pyphenyl.....	90
2.4.4	Mass Spectrometry.....	90
2.4.5	X-ray Crystallography	92
2.4.5.1	[CrCl ₃ (pytb) ₃].....	92
2.5	EXPERIMENTAL.....	97
2.5.1	Synthesis of [CrCl ₃ (py)(thf) ₂] (1) and [CrCl ₃ (py) ₂ (thf)] (2)	97
2.5.2	Synthesis of [CrCl ₃ (py) ₃] (3)	98
2.5.3	Synthesis of [CrCl ₃ (2,6-dibromopy) ₃] and [CrCl ₃ (py) ₂ (DMF)] (5)... ..	98
2.5.4	Synthesis of [CrCl ₃ (pyNH ₂) ₃] (6)	99
2.5.5	Synthesis of [CrCl ₃ (pytb) ₃] (7)	99
2.5.6	Synthesis of [CrCl ₃ (pyphenyl) ₃] (8).....	100
2.5.7	Synthesis of [CrCl ₃ (pyOH) ₃]	100

CHAPTER 3

CHROMIUM(III) BIDENTATE NITROGEN LIGAND CHEMISTRY101

3.1	INTRODUCTION	101
3.2	SYNTHESIS	102
3.3	SYNTHETIC ROUTE TO PRODUCT FORMATION	102
3.4	INFRARED AND RAMAN SPECTROSCOPY	103
3.4.1	Region 3329–2291 cm ⁻¹	104
3.4.2	Region 1652–1104 cm ⁻¹	108
3.4.3	Region 1104–522 cm ⁻¹	111
3.4.3.1	Pyridine Specific	112
3.4.3.2	Bipyridine Specific	115
3.4.3.3	Thf Specific.....	115
3.4.3.4	Pyridinium Specific	117
3.4.4	Region 451–221 cm ⁻¹	118
3.5	COMPUTATIONAL STUDIES.....	132
3.5.1	[CrCl ₃ (bipy)(thf)]	132
3.5.2	[CrCl ₃ (bipy)(H ₂ O)]	135
3.5.3	[CrCl ₃ (bipy)(CH ₃ CN)]	137
3.5.4	[CrCl ₃ (bipy)(py)]	140
3.5.5	[CrCl ₃ (bipy)(pyphenyl)]	143
3.5.6	[HpyNH ₂][CrCl ₄ (bipy)]	146
3.5.7	HOMO and LUMO orbitals of the calculated complexes	149
3.6	NMR SPECTROSCOPY	152
3.7	MASS SPECTROMETRY	158
3.8	X-RAY CRYSTALLOGRAPHY	160
3.8.1	Solubility and Crystal Synthesis	160

3.8.2	[CrCl ₃ (bipy)(H ₂ O)].....	161
3.8.3	[HpyNH ₂][CrCl ₄ (bipy)]	167
3.8.4	[CrCl ₂ (bipy) ₂][Cl]·H ₂ O	171
3.9	SYNTHETIC ROUTE CONCLUSIONS	176
3.10	EXPERIMENTAL.....	177
3.10.1	Synthesis of [CrCl ₃ (bipy)(thf)] (9).....	177
3.10.2	Synthesis of [CrCl ₃ (bipy)(CH ₃ CN)] (10).....	178
3.10.3	Synthesis of [CrCl ₃ (bipy)(py)] (11).....	178
3.10.4	Synthesis of [CrCl ₃ (bipy)(pyNH ₂)] (12).....	178
3.10.5	Synthesis of [CrCl ₃ (bipy)(pytb)] (13).....	178
3.10.6	Synthesis of [CrCl ₃ (bipy)(pyphenyl)] (14)	179
3.10.7	Synthesis of [CrCl ₃ (bipy)(H ₂ O)] (16).....	179
3.10.8	Synthesis of [CrCl ₂ (bipy) ₂][Cl]·H ₂ O (17).....	179

CHAPTER 4

CHROMIUM(III) BIDENTATE PHOSPHORUS CHEMISTRY 180

4.1	INTRODUCTION	180
4.2	SYNTHESIS	181
4.3	SYNTHETIC ROUTE TO PRODUCT FORMATION	182
4.4	INFRARED AND RAMAN SPECTROSCOPY	183
4.4.1	Region 3313–2863 cm ⁻¹	184
4.4.2	Region 1651–1045 cm ⁻¹	188
4.4.3	Region 1026–519 cm ⁻¹	191
4.4.4	Region 495–215 cm ⁻¹	198
4.5	COMPUTATIONAL STUDY.....	210

4.6	NMR SPECTROSCOPY	214
4.7	MASS SPECTROMETRY	216
4.8	X-RAY CRYSTALLOGRAPHY	218
4.8.1	[Hpyphenyl][CrCl ₄ (dppe)]	218
4.9	EXPERIMENTAL	222
4.9.1	Synthesis of [CrCl ₃ (dppe)(thf)] / [Cr(dppe)Cl ₂ (μ-Cl)] ₂ (18)	222
4.9.2	Synthesis of [CrCl ₃ (dppe)(py)] (19)	223
4.9.3	Synthesis of [CrCl ₃ (dppe)(pyNH ₂)] (20)	223
4.9.4	Synthesis of [CrCl ₃ (dppe)(pytb)] (21)	223
4.9.5	Synthesis of [CrCl ₃ (dppe)(pyphenyl)] (22)	224

CHAPTER 5

CHROMIUM(III) BIDENTATE NITROGEN / PHOSPHORUS

MIXED LIGAND CHEMISTRY

5.1	INTRODUCTION	225
5.2	2-PYRIDYLDIPHENYLPHOSPHINE AND [CrCl ₃ (thf) ₃]	226
5.2.1	Synthesis	227
5.3	2-DIPHENYLPHOSPHINOETHYLAMINE AND [CrCl ₃ (thf) ₃].....	227
5.3.1	Synthesis	228
5.3.2	Infrared and Raman Spectroscopy	228
5.3.2.1	Region 3380–2867 cm ⁻¹	229
5.3.2.2	Region 1652–1117 cm ⁻¹	232
5.3.2.3	Region 1117–500 cm ⁻¹	237
5.3.2.4	Region 500–200 cm ⁻¹	243
5.3.3	Computational Study	250
5.3.4	Mass Spectrometry.....	253



5.4	EXPERIMENTAL.....	255
5.4.1	Synthesis of $[\text{CrCl}_3(\text{dppea})(\text{thf})] / [\text{Cr}(\text{dppea})\text{Cl}_2(\mu\text{-Cl})_2]$ (24).....	255
5.4.2	Synthesis of $[\text{CrCl}_3(\text{dppea})(\text{py})]$ (25).....	255
5.4.3	Synthesis of $[\text{CrCl}_3(\text{dppea})(\text{pyNH}_2)]$ (26)	255
5.4.4	Synthesis of $[\text{CrCl}_3(\text{dppea})(\text{pytb})]$ (27)	256
5.4.5	Synthesis of $[\text{CrCl}_3(\text{dppea})(\text{pyhenyl})]$ (28).....	256

CHAPTER 6

FUTURE WORK AND CONCLUSIONS.....	257
---	------------

6.1	FUTURE WORK.....	257
-----	------------------	-----

6.2	CONCLUSION.....	258
-----	-----------------	-----

REFERENCES.....	261
------------------------	------------

.....

APPENDIX.....	CD
----------------------	-----------

ABSTRACT

Synthesis and structural studies of N- and P-donor ligands in Chromium(III) complexes

by

Nicholas Frederick Brennan

Supervisor: Prof. P. H. van Rooyen

Co-supervisor: Prof. S. Lotz

Submitted in partial fulfilment of the requirements for the degree Philosophiae Doctor
Department of Chemistry, University of Pretoria

The fundamental knowledge of Cr(III) chemistry has been enhanced via detailed structural and spectroscopic studies of largely novel compounds that may potentially be active tri- and tetramerisation precursors.

The compounds are based on various monodentate and bidentate nitrogen and phosphorus ligands which have been coordinated to $[\text{CrCl}_3(\text{thf})_3]$. The few compounds that have been synthesised previously have in this study been made via novel synthetic routes and incorporate a combination of new and more detailed analysis than was carried out previously.

The eight structures determined, in addition to offering novel crystallographic data, also provided insights into the synthetic pathways leading to compound formation. The isolation of monomeric structures suggests direct ligand substitution, while the cationic-anionic structures suggest the presence of dimeric intermediates which have been cleaved asymmetrically.

Infrared and Raman spectra of these structures were able to add weight to these pathway proposals and, by means of vibrational comparisons, assisted in the general band assignments of the compounds' spectra where structures were not available.

Vibrational shifts relative to the free ligands, as well as metal–ligand vibrations in the far infrared region, were also of significant value in terms of ligand coordination and geometry.

Closely associated with the infrared and Raman spectra analysis was the generation of theoretical spectra using Density Functional Theory calculations. The excellent agreement between the calculated and experimental spectra confirmed the vibrational assignments.

Also generated by computational means were the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of the compounds which indicated the sites of potential nucleophilic and electrophilic attack.

^1H NMR spectroscopy is a technique normally avoided when studying paramagnetic materials. However, by employing a largely novel approach, information pertaining to both ligand coordination and reaction times was obtained.

FAB-MS assisted in the confirmation that the single crystal determinations did indeed reflect the composition of the bulk precipitated samples. It also provided additional structural information through the identification of fragmentation patterns which could not be gained by techniques such as elemental analysis.

ACKNOWLEDGEMENTS

I would very much like to thank my supervisors, Prof. P. H. van Rooyen and Prof. S. Lotz for all their help and guidance throughout the course of this project.

To Mike Green and SASOL – a sincere thank you for all the valued input as well as financial support.

Thank you to Eric Palmer, Dave Liles and Marilé Landman – your assistance was very much appreciated.

To my parents, Anne and John – thank you for your continuous love and support. I hope I've made you proud.

To my beautiful wife Cassandra who has been with me every step of the way and never once doubted me: I love you.

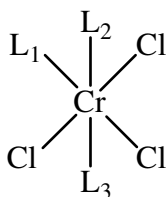
COMMON ABBREVIATIONS

• Acetyl acetate	acac
• 4-amino pyridine	pyNH ₂
• 2, 2'-bipyridine	bipy
• Bis-diphenylphosphinoethane	dppe
• 4-Bu ^t pyridine	pytb
• Density Functional Theory	DFT
• Dichloromethane	DCM
• Dimethylformamide	DMF
• Dimethylsulphoxide	DMSO
• 2-(diphenylphosphino)ethylamine	dppea
• 2-pyridyldiphenylphosphine	dpp
• Far-infrared	FIR
• Fast Atom Bombardment Mass Spectrometry	FAB-MS
• Highest Occupied Molecular Orbital	HOMO
• Infrared	IR
• Linear Alpha Olefins	LAOs
• Lowest Unoccupied Molecular Orbital	LUMO
• Mid-infrared	MIR
• Nuclear Magnetic Resonance	NMR
• Nuclear Overhauser Effect	NOE
• 4-phenyl pyridine	pyphenyl
• Pyridine	py
• Pyridinium ion	pyH
• Tetrahydrofuran	thf

COMPLEX ABBREVIATIONS

[CrCl ₃ (py)(thf) ₂]	1
[CrCl ₃ (py) ₂ (thf)]	2
[CrCl ₃ (py) ₃]	3
[Hpy][CrCl ₄ (py) ₂]	4
[CrCl ₃ (py) ₂ (DMF)]	5
[CrCl ₃ (pyNH ₂) ₃]	6
[CrCl ₃ (pytb) ₃]	7
[CrCl ₃ (pyphenyl) ₃]	8
[CrCl ₃ (bipy)(thf)]	9
[CrCl ₃ (bipy)(CH ₃ CN)]	10
[CrCl ₃ (bipy)(py)]	11
[CrCl ₃ (bipy)(pyNH ₂)]	12
[CrCl ₃ (bipy)(pytb)]	13
[CrCl ₃ (bipy)(pyphenyl)]	14
[HpyNH ₂][CrCl ₄ (bipy)]	15
[CrCl ₃ (bipy)(H ₂ O)]	16
[CrCl ₂ (bipy) ₂][Cl]·H ₂ O	17
[CrCl ₃ (dppe)(thf)]/ [Cr(dppe)Cl ₂ (μ-Cl)] ₂	18
[CrCl ₃ (dppe)(py)]	19
[CrCl ₃ (dppe)(pyNH ₂)]	20
[CrCl ₃ (dppe)(pytb)]	21
[CrCl ₃ (dppe)(pyphenyl)]	22
[Hpyphenyl][CrCl ₄ (dppe)]	23
[CrCl ₃ (dppea)(thf)]/ [Cr(dppea)Cl ₂ (μ-Cl)] ₂	24
[CrCl ₃ (dppea)(py)]	25
[CrCl ₃ (dppea)(pyNH ₂)]	26
[CrCl ₃ (dppea)(pytb)]	27
[CrCl ₃ (dppea)(pyphenyl)]	28

STRUCTURAL DRAWINGS



1 $L^1 = \text{py}, L^2, L^3 = \text{thf}$

3 $L^1, L^2, L^3 = \text{py}$

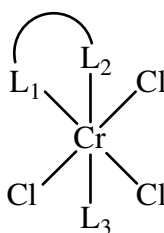
6 $L^1, L^2, L^3 = \text{pyNH}_2$

8 $L^1, L^2, L^3 = \text{pyphenyl}$

2 $L^1, L^2 = \text{py}, L^3 = \text{thf}$

5 $L^1, L^2 = \text{py}, L^3 = \text{DMF}$

7 $L^1, L^2, L^3 = \text{pytb}$



9 $L^1 L^2 = \text{bipy}, L^3 = \text{thf}$

CH_3CN

11 $L^1 L^2 = \text{bipy}, L^3 = \text{py}$

13 $L^1 L^2 = \text{bipy}, L^3 = \text{pytb}$

pyphenyl

16 $L^1 L^2 = \text{bipy}, L^3 = \text{H}_2\text{O}$

19 $L^1 L^2 = \text{dppe}, L^3 = \text{py}$

21 $L^1 L^2 = \text{dppe}, L^3 = \text{pytb}$

pyphenyl

24 $L^1 L^2 = \text{dppea}, L^3 = \text{thf} *$

26 $L^1 L^2 = \text{dppea}, L^3 = \text{pyNH}_2$

28 $L^1 L^2 = \text{dppea}, L^3 = \text{pyphenyl}$

10 $L^1 L^2 = \text{bipy}, L^3 =$

12 $L^1 L^2 = \text{bipy}, L^3 = \text{pyNH}_2$

14 $L^1 L^2 = \text{bipy}, L^3 =$

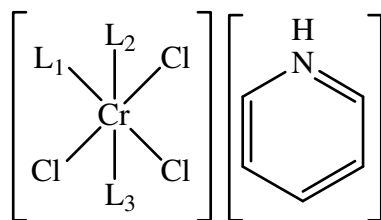
18 $L^1 L^2 = \text{dppe}, L^3 = \text{thf} *$

20 $L^1 L^2 = \text{dppe}, L^3 = \text{pyNH}_2$

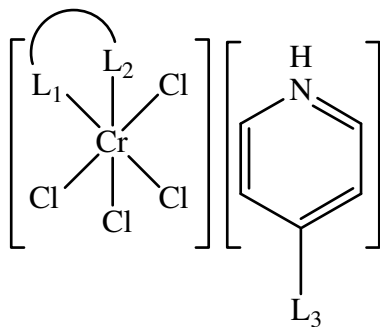
22 $L^1 L^2 = \text{dppe}, L^3 =$

25 $L^1 L^2 = \text{dppea}, L^3 = \text{py}$

27 $L^1 L^2 = \text{dppea}, L^3 = \text{pytb}$

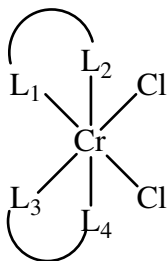


4 $L^1, L^2 = \text{py}$

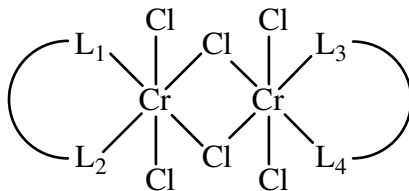


15 $L^1L^2 = \text{bipy}$, $L^3 = \text{NH}_2$

23 $L^1L^2 = \text{dppe}$, $L^3 = \text{phenyl}$



17 $L^1L^2, L^3L^4 = \text{bipy}$



18 $L^1L^2, L^3L^4 = \text{dppe} *$

24 $L^1L^2, L^3L^4 = \text{dppea} *$

LIST OF FIGURES

Figure 1.1	Typical key steps in the study of many catalytic systems [3]	3
Figure 1.2	Formation of 1-hexene via a metallacycle.....	4
Figure 1.3	The Kohn catalyst.....	6
Figure 1.4	The Wass catalyst	6
Figure 1.5	Variations of the Wass catalyst by McGuinness [31].....	7
Figure 1.6	Formation of the SNS complex	7
Figure 1.7	Variation in spacer length of tridentate ligands.....	8
Figure 1.8	The first tetramerisation catalyst	8
Figure 1.9	Pathways to 1-octene formation	9
Figure 1.10	Symmetrically (A) and asymmetrically (B) cleaved chloro dimers [100]	11
Figure 1.11	Direct ligand substitution and symmetrical dimeric cleavage pathways [100]	11
Figure 1.12	Ligands incorporated in this study.....	12
Figure 2.1	Sequential addition of pyridine to the chromium precursor	26
Figure 2.2	Olive green precipitate.....	27
Figure 2.3	Comparisons of the IR spectra of free pyridine (blue) and [CrCl ₃ (py) ₃] (red).....	28
Figure 2.4	Raman spectrum of [CrCl ₃ (py) ₃]	28
Figure 2.5	Shifting of the free pyridine band (blue) in the IR spectrum at 992 cm ⁻¹ upon coordination (red)	29
Figure 2.6	Comparison between [CrCl ₃ (thf) ₃] (blue) and [CrCl ₃ (py) ₃] (red) IR spectra.....	30
Figure 2.7	FIR comparison between [CrCl ₃ (thf) ₃] (blue) and [CrCl ₃ (py) ₃] (red) spectra.....	31
Figure 2.8	Experimental (red) and calculated (blue) MIR spectra of [CrCl ₃ (py) ₃]	33
Figure 2.9	Experimental (red) and calculated (blue) Raman spectra of [CrCl ₃ (py) ₃]	34
Figure 2.10	Experimental (red) and calculated (blue) FIR spectra of [CrCl ₃ (py) ₃]..	34
Figure 2.11	HOMO and LUMO orbitals of [CrCl ₃ (py) ₃]	36

Figure 2.12	^1H NMR spectrum of free thf in acetone- d_6	37
Figure 2.13	^1H NMR spectrum of $[\text{CrCl}_3(\text{thf})_3]$ in acetone- d_6	38
Figure 2.14	Stacked ^1H NMR spectra for the reaction of pyridne with $[\text{CrCl}_3(\text{thf})_3]$ over time. 1 = py, 2 = thf, 3 = water peak in acetone, 4 = acetone- d_6 , 5 = thf	38
Figure 2.15	^1H NMR spectrum of $[\text{CrCl}_3(\text{py})_3]$ in acetone- d_6 after a further hour...	39
Figure 2.16	^{13}C NMR spectrum of $[\text{CrCl}_3(\text{py})_3]$ precipitate formed after removal of above reaction from NMR instrument	40
Figure 2.17	A = Perspective drawing of $[\text{CrCl}_3(\text{py})_3]$ structure determined in this study, B = Perspective drawing of $[\text{CrCl}_3(\text{py})_3]$ structure determined by Howard [83].....	41
Figure 2.18	The ring twists observed for $[\text{CrCl}_3(\text{py})_3]$ of this study (grey) and that of Howard [83] (red).....	43
Figure 2.19	Short contacts observed in the packing arrangement of $[\text{CrCl}_3(\text{py})_3]$ of this study	44
Figure 2.20	Packing arrangement of $[\text{CrCl}_3(\text{py})_3]$ of this study which includes space fill arrangement.....	44
Figure 2.21	Possible pathways to product formation.....	47
Figure 2.22	The planarity of the pyridine rings as well as the tilting of the pyridinium ion	48
Figure 2.23	Hydrogen bonding observed in $[\text{Hpy}][\text{CrCl}_4(\text{py})_2]$	50
Figure 2.24	Packing arrangement of $[\text{Hpy}][\text{CrCl}_4(\text{py})_2]$	50
Figure 2.25	Alternative view of the packing arrangement of $[\text{Hpy}][\text{CrCl}_4(\text{py})_2]$	51
Figure 2.26	Packing and space fill of $[\text{Hpy}][\text{CrCl}_4(\text{py})_2]$	51
Figure 2.27	Alternative view of the packing and space fill of $[\text{Hpy}][\text{CrCl}_4(\text{py})_2]$	51
Figure 2.28	FAB-MS spectrum of $[\text{CrCl}_3(\text{py})_3]$	53
Figure 2.29	Bulky substituent reactions that were carried out.....	55
Figure 2.30	IR spectrum of the region $3114 - 2804 \text{ cm}^{-1}$	57
Figure 2.31	IR spectrum of the region $1660 - 1247 \text{ cm}^{-1}$	58
Figure 2.32	IR spectrum of the region $1219 - 448 \text{ cm}^{-1}$	59
Figure 2.33	IR spectrum of the region $415 - 214 \text{ cm}^{-1}$	60
Figure 2.34	A = Perspective drawing of $[\text{CrCl}_3(\text{py})_2(\text{DMF})]$ structure determined in this study, B = Perspective drawing of $[\text{CrCl}_3(\text{py})_2(\text{DMF})]$ structure determined by Broomhead [88]	61

Figure 2.35	Non-planarity of the <i>trans</i> pyridine ligands in $[\text{CrCl}_3(\text{py})_2(\text{DMF})]$ 61
Figure 2.36	Packing and space fill arrangement of $[\text{CrCl}_3(\text{py})_2(\text{DMF})]$ 63
Figure 2.37	Para-substituted pyridine ligands 65
Figure 2.38	IR and Raman spectra of $[\text{CrCl}_3(\text{pyNH}_2)_3]$ (red), $[\text{CrCl}_3(\text{pytb})_3]$ (blue) $[\text{CrCl}_3(\text{pyphenyl})_3]$ (green) in the region $3321 - 2869 \text{ cm}^{-1}$ 67
Figure 2.39	IR and Raman spectra of $[\text{CrCl}_3(\text{pyNH}_2)_3]$ in the region $1638 - 1045 \text{ cm}^{-1}$ 69
Figure 2.40	IR and Raman spectra of $[\text{CrCl}_3(\text{pytb})_3]$ in the region $1638 - 1045 \text{ cm}^{-1}$ 70
Figure 2.41	IR and Raman spectra of $[\text{CrCl}_3(\text{pyphenyl})_3]$ in the region $1638 - 1045 \text{ cm}^{-1}$ 71
Figure 2.42	IR and Raman spectra of $[\text{CrCl}_3(\text{pyNH}_2)_3]$ in the region $1030 - 499 \text{ cm}^{-1}$ 72
Figure 2.43	IR and Raman spectra of $[\text{CrCl}_3(\text{pytb})_3]$ in the region $1030 - 499 \text{ cm}^{-1}$ 73
Figure 2.44	IR and Raman spectra of $[\text{CrCl}_3(\text{pyphenyl})_3]$ in the region $1030 - 499 \text{ cm}^{-1}$ 74
Figure 2.45	Shifting of the characteristic ring breathing vibration in the IR spectra of $[\text{CrCl}_3(\text{pyNH}_2)_3]$, $[\text{CrCl}_3(\text{pytb})_3]$ and $[\text{CrCl}_3(\text{pyphenyl})_3]$, relative to free ligand positions (blue). Raman spectra of $[\text{CrCl}_3(\text{pyNH}_2)_3]$, $[\text{CrCl}_3(\text{pytb})_3]$ and $[\text{CrCl}_3(\text{pyphenyl})_3]$ 77
Figure 2.46	Experimental (red) and calculated (blue) MIR spectra of $[\text{CrCl}_3(\text{pyNH}_2)_3]$ 84
Figure 2.47	Experimental (red) and calculated (blue) Raman spectra of $[\text{CrCl}_3(\text{pyNH}_2)_3]$ 85
Figure 2.48	HOMO and LUMO orbitals of $[\text{CrCl}_3(\text{pyNH}_2)_3]$ 87
Figure 2.49	Experimental (red) and calculated (blue) MIR spectra of $[\text{CrCl}_3(\text{pytb})_3]$ 87
Figure 2.50	Experimental (red) and calculated (blue) Raman spectra of $[\text{CrCl}_3(\text{pytb})_3]$ 88
Figure 2.51	HOMO and LUMO orbitals of $[\text{CrCl}_3(\text{pytb})_3]$ 89
Figure 2.52	Stacked ^1H NMR spectrum for the reaction of pyphenyl with $[\text{CrCl}_3(\text{thf})_3]$ over time. 1 = pyphenyl, 2 = thf, 3 = acetone- d_6 , 4 = thf 90

Figure 2.53FAB-MS spectrum of [CrCl ₃ (pyphenyl) ₃].	91
Figure 2.54	FAB-MS spectrum of [CrCl ₃ (pyphenyl) ₃].	91
Figure 2.55	Perspective drawing of [CrCl ₃ (pytb) ₃] structure determined	92
Figure 2.56	Twisting of the aromatic systems relative to the axial chlorine atoms in [CrCl ₃ (pytb) ₃]	93
Figure 2.57	Packing arrangement of [CrCl ₃ (pytb) ₃]	96
Figure 2.58	Space fill representation of the packing arrangements	96
Figure 3.1	IR spectra of [CrCl ₃ (bipy)(pyNH ₂)] (blue), [HpyNH ₂][CrCl ₄ (bipy)] (red) and [CrCl ₃ (bipy)(H ₂ O)] (green) in the region 3329 – 2291 cm ⁻¹	105
Figure 3.2	IR spectra showing the presence of thf C–Hs in [CrCl ₃ (bipy)(thf)] (blue) and their absence in [CrCl ₃ (bipy)(H ₂ O)] (red).	106
Figure 3.3	Comparison of the IR spectra of [CrCl ₃ (thf) ₃] (blue) and [CrCl ₃ (bipy)(pyphenyl)] (red)	106
Figure 3.4	Characteristic IR and Raman vibrations in [CrCl ₃ (bipy)(CH ₃ CN)] (red) and [CrCl ₃ (bipy)(pytb)] (blue).	107
Figure 3.5	IR and Raman vibrations in [CrCl ₃ (bipy)(thf)] (blue), [CrCl ₃ (bipy)(py)] (red) and [HpyNH ₂][CrCl ₄ (bipy)] (purple)	109
Figure 3.6	Bipyridine specific IR vibrations present in all complexes represented by the comparison between [CrCl ₃ (bipy)(thf)] (red) and [CrCl ₃ (py) ₃] (blue).	110
Figure 3.7	IR and Raman vibrations of tertiary butyl-specific vibrations in the region 1652 – 1104 cm ⁻¹	111
Figure 3.8	Spectra showing the shifting of the characteristic ring breathing vibration in the IR of [CrCl ₃ (bipy)(py)], [CrCl ₃ (bipy)(pyNH ₂)], [CrCl ₃ (bipy)(pytb)] and [CrCl ₃ (bipy)(pyphenyl)] from free ligand positions. Raman spectra of [CrCl ₃ (bipy)(py)], [CrCl ₃ (bipy)(pytb)] and [CrCl ₃ (bipy)(pyphenyl)]	113
Figure 3.9	Evidence of coordinated pyridine in the IR spectra of [CrCl ₃ (bipy)(py)] (red), [CrCl ₃ (bipy)(pyNH ₂)] (blue), [CrCl ₃ (bipy)(pytb)] (purple) and [CrCl ₃ (bipy)(pyphenyl)] (green).	114

Figure 3.10	thf / unassigned / pyridinium vibration in IR and Raman spectra of [CrCl ₃ (bipy)(thf)] (red), [CrCl ₃ (bipy)(pytb)] (blue) and [HpyNH ₂][CrCl ₄ (bipy)] (green).....	116
Figure 3.11	IR spectrum of [CrCl ₃ (bipy)(thf)] (red), [CrCl ₃ (bipy)(pyNH ₂)] (blue), [CrCl ₃ (bipy)(pyphenyl)] (green) and [HpyNH ₂][CrCl ₄ (bipy)] (purple). Raman spectrum of [HpyNH ₂][CrCl ₄ (bipy)].....	117
Figure 3.12	IR and Raman bands associated with [HpyNH ₂][CrCl ₄ (bipy)]	118
Figure 3.13	FIR vibrations represented by spectra of [CrCl ₃ (bipy)(H ₂ O)] (red), [CrCl ₃ (bipy)(py)] (blue) and [HpyNH ₂][CrCl ₄ (bipy)] (green).....	120
Figure 3.14	Experimental (red) and calculated (blue) MIR spectra of [CrCl ₃ (bipy)(thf)]	133
Figure 3.15	Experimental (red) and calculated (blue) Raman spectra of [CrCl ₃ (bipy)(thf)]	133
Figure 3.16	Experimental (red) and calculated (blue) MIR spectra of [CrCl ₃ (bipy)(H ₂ O)].....	135
Figure 3.17	Experimental (red) and calculated (blue) MIR spectra of [CrCl ₃ (bipy)(CH ₃ CN)]	137
Figure 3.18	Experimental (red) and calculated (blue) Raman spectra of [CrCl ₃ (bipy)(CH ₃ CN)]	138
Figure 3.19	Experimental (red) and calculated (blue) MIR spectra of [CrCl ₃ (bipy)(py)].....	140
Figure 3.20	Experimental (red) and calculated (blue) Raman spectra of [CrCl ₃ (bipy)(py)].....	141
Figure 3.21	Experimental (red) and calculated (blue) MIR spectra of [CrCl ₃ (bipy)(pyphenyl)]	143
Figure 3.22	Experimental (red) and calculated (blue) Raman spectra of [CrCl ₃ (bipy)(pyphenyl)]	144
Figure 3.23	Experimental (red) and calculated (blue) Raman spectra of [HpyNH ₂][CrCl ₄ (bipy)].....	147
Figure 3.24	Experimental (red) and calculated (blue) Raman spectra of [HpyNH ₂][CrCl ₄ (bipy)].....	147
Figure 3.25	HOMO and LUMO orbitals of [CrCl ₃ (bipy)(thf)]	149
Figure 3.26	HOMO (left) and LUMO (right) orbitals of [CrCl ₃ (bipy)(H ₂ O)].....	150
Figure 3.27	HOMO and LUMO orbitals of [CrCl ₃ (bipy)(MeCN)].....	150

Figure 3.28	HOMO and LUMO orbitals of $[\text{CrCl}_3(\text{bipy})(\text{py})]$	151
Figure 3.29	HOMO and LUMO orbitals of $[\text{CrCl}_3(\text{bipy})(\text{pyphenyl})]$	151
Figure 3.30	HOMO and LUMO orbitals of $[\text{HpyNH}_2][\text{CrCl}_4(\text{bipy})]$	152
Figure 3.31	Stacked ^1H NMR spectra for the reaction of bipy with $[\text{CrCl}_3(\text{thf})_3]$ over time. 1 = bipy, 2 = thf, 3 = water peak in acetone, 4 = acetone d_6 , 5 = thf.....	153
Figure 3.32	Plot of integration of bipy:thf resonances over time.....	153
Figure 3.33	^1H NMR spectrum of $[\text{CrCl}_3(\text{bipy})(\text{thf})]$ final product in acetone- d_6 ..	154
Figure 3.34	^{13}C NMR spectrum of $[\text{CrCl}_3(\text{bipy})(\text{thf})]$ final product in DMSO- d_6 .	155
Figure 3.35	^1H NMR spectrum of $[\text{CrCl}_3(\text{bipy})(\text{CH}_3\text{CN})]$ in acetone- d_6	156
Figure 3.36	^1H NMR spectrum of $[\text{CrCl}_3(\text{bipy})(\text{py})]$ in acetone- d_6	157
Figure 3.37	^1H NMR spectrum of $[\text{CrCl}_3(\text{bipy})(\text{H}_2\text{O})]$ in DMSO- d_6	157
Figure 3.38	FAB-MS spectrum of $[\text{CrCl}_3(\text{bipy})(\text{thf})]$	158
Figure 3.39	FAB-MS spectrum of $[\text{CrCl}_3(\text{bipy})(\text{H}_2\text{O})]$	159
Figure 3.40	FAB-MS spectrum of $[\text{CrCl}_3(\text{bipy})(\text{CH}_3\text{CN})]$	159
Figure 3.41	FAB-MS spectrum of $[\text{CrCl}_3(\text{bipy})(\text{pyphenyl})]$	160
Figure 3.42	A = Perspective drawing of $[\text{CrCl}_3(\text{bipy})(\text{H}_2\text{O})]$ structure determined in this study, B = Perspective drawing of the structure determined by Namba [108].....	162
Figure 3.43	Hydrogen bond interactions.....	164
Figure 3.44	Short contacts between aromatic ring layers.....	165
Figure 3.45	Comparison of the experimental and theoretically obtained X-ray diffraction powder patterns of $[\text{CrCl}_3(\text{bipy})(\text{H}_2\text{O})]$	165
Figure 3.46	Hydrogen bond interactions.....	169
Figure 3.47	Staggered π - π interactions in the packing arrangement of $[\text{HpyNH}_2][\text{CrCl}_4(\text{bipy})]$	169
Figure 3.48	Packing and space fill of $[\text{HpyNH}_2][\text{CrCl}_4(\text{bipy})]$	170
Figure 3.49	Perspective drawing showing the two formula units of $[\text{CrCl}_2(\text{bipy})_2][\text{Cl}]\cdot\text{H}_2\text{O}$ in the asymmetric unit.....	172
Figure 3.50	Packing arrangements for $[\text{CrCl}_2(\text{bipy})_2][\text{Cl}]\cdot\text{H}_2\text{O}$	173

Figure 3.51	Packing and space fill arrangements for $[\text{CrCl}_2(\text{bipy})_2][\text{Cl}]\cdot\text{H}_2\text{O}$	174
Figure 3.52	Summary of routes to complex formation.....	177
Figure 4.1	Proposed routes to complex formation.....	183
Figure 4.2	IR spectra showing band shifts in $[\text{CrCl}_3(\text{dppe})(\text{thf})]$ (red) relative to free dppe (blue).....	185
Figure 4.3	IR spectra of $[\text{CrCl}_3(\text{dppe})(\text{pytb})]$ (red) and free dppe (blue)	186
Figure 4.4	N–H vibrations observed in the IR spectrum of $[\text{CrCl}_3(\text{dppe})(\text{pyNH}_2)]$ (blue).....	187
Figure 4.5	Comparisons between IR spectra of $[\text{CrCl}_3(\text{dppe})(\text{thf})]$ (red), $[\text{Hpyphenyl}][\text{CrCl}_4(\text{dppe})]$ (blue) and free dppe (green). Raman spectrum of $[\text{CrCl}_3(\text{dppe})(\text{thf})]$	188
Figure 4.6	Band intensity comparison between the IR spectra of $[\text{CrCl}_3(\text{dppe})(\text{py})]$ (red) and $[\text{Hpyphenyl}][\text{CrCl}_4(\text{dppe})]$ (blue).....	189
Figure 4.7	IR spectrum of $[\text{CrCl}_3(\text{dppe})(\text{pytb})]$ -specific vibrations	191
Figure 4.8	IR and Raman spectra of $[\text{CrCl}_3(\text{dppe})(\text{thf})]$ (red) with the IR highlighting the lack of shifting relative to free dppe (blue).....	192
Figure 4.9	Ring breathing shift in IR bands of $[\text{CrCl}_3(\text{dppe})(\text{py})]$ (red).....	193
Figure 4.10	IR and Raman spectra of $[\text{CrCl}_3(\text{dppe})(\text{pyNH}_2)]$ (green) and $[\text{CrCl}_3(\text{dppe})(\text{pytb})]$ (red)	194
Figure 4.11	Comparisons between IR spectra of $[\text{CrCl}_3(\text{dppe})(\text{pyphenyl})]$ (red), $[\text{Hpyphenyl}][\text{CrCl}_4(\text{dppe})]$ (blue) and free dppe (green).....	195
Figure 4.12	IR spectra showing pyH-specific vibration in $[\text{Hpyphenyl}][\text{CrCl}_4(\text{dppe})]$ (blue) which is absent in $[\text{CrCl}_3(\text{dppe})(\text{pyphenyl})]$ (red).....	196
Figure 4.13	IR spectra of $[\text{CrCl}_3(\text{dppe})(\text{py})]$ (red), $[\text{CrCl}_3(\text{dppe})(\text{pytb})]$ (blue), $[\text{CrCl}_3(\text{dppe})(\text{thf})]$ (purple) and free dppe (green).....	197
Figure 4.14	FIR spectra of $[\text{CrCl}_3(\text{dppe})(\text{thf})]$ (red), $[\text{CrCl}_3(\text{dppe})(\text{py})]$ (blue) and $[\text{CrCl}_3(\text{dppe})(\text{pytb})]$ (green).....	200
Figure 4.15	FIR spectra of $[\text{CrCl}_3(\text{dppe})(\text{pyphenyl})]$ (red) and $[\text{Hpyphenyl}][\text{CrCl}_4(\text{dppe})]$ (blue)	201
Figure 4.16	Experimental (red) and calculated (blue) MIR spectra of $[\text{CrCl}_3(\text{dppe})(\text{pytb})]$	211
Figure 4.17	Experimental (red) and calculated (blue) Raman spectra of $[\text{CrCl}_3(\text{dppe})(\text{pytb})]$	211

Figure 4.18	Experimental (red) and calculated (blue) FIR spectra of [CrCl ₃ (dppe)(pytb)]	212
Figure 4.19	HOMO and LUMO orbitals of [CrCl ₃ (dppe)(pytb)]	214
Figure 4.20	¹ H NMR spectrum of [CrCl ₃ (dppe)(thf)] final product in DMSO-d ₆ ..	215
Figure 4.21	³¹ P NMR spectrum free dppe in DMSO-d ₆	215
Figure 4.22	³¹ P NMR spectrum of [CrCl ₃ (dppe)(thf)] in DMSO-d ₆	216
Figure 4.23	FAB-MS spectrum showing peaks present in [CrCl ₃ (dppe)(thf)], [CrCl ₃ (dppe)(pyNH ₂)] and [CrCl ₃ (dppe)(pyphenyl)].....	217
Figure 4.24	FAB-MS spectrum of [CrCl ₃ (dppe)(pyphenyl)].....	217
Figure 4.25	Perspective drawing showing the asymmetric unit of [Hpyphenyl][CrCl ₄ (dppe)] showing hydrogen bond interactions	218
Figure 4.26	P–C–P torsion angle comparison between [Hpyphenyl][CrCl ₄ (dppe)]and the Gray structure.....	219
Figure 4.27	Packing arrangement with space-filled component of [Hpyphenyl][CrCl ₄ (dppe)]	221
Figure 5.1	Results of structural framework searches using Cambridge Database [117]	226
Figure 5.2	IR spectra of N–H bands in [CrCl ₃ dppea(pyNH ₂)] (red) and [CrCl ₃ (pyNH ₂) ₃] (blue).....	230
Figure 5.3	IR and Raman spectra of [CrCl ₃ (dppea)(pytb)].....	231
Figure 5.4	IR and Raman spectra of [CrCl ₃ (dppea)(py)].....	233
Figure 5.5	Pyridine-specific vibration absent in [CrCl ₃ (dppea)(thf)] (green) and free dppea (blue)	234
Figure 5.6	IR spectrum of pyNH ₂ vibrations observed in [CrCl ₃ (dppea)(pyNH ₂)]	236
Figure 5.7	IR spectra of free pyridine (blue), free dppe (green) and free dppea (red)	238
Figure 5.8	IR spectra comparison between [CrCl ₃ (dppea)(py)] (red) and free pyridine (blue)	239
Figure 5.9	IR spectra comparison between [CrCl ₃ (dppea)(pytb)] (red) and free pytb (blue)	240

Figure 5.10	IR spectra comparison between [CrCl ₃ (dppea)(pyphenyl)] (red) and free pyphenyl (green).....	241
Figure 5.11	IR and Raman spectra of [CrCl ₃ (dppeay)(py)] (red), [CrCl ₃ (dppea)(pyNH ₂)] (blue), [CrCl ₃ (dppea)(pytb)] (green) and [CrCl ₃ (dppea)(pyphenyl)] (purple) showing shifting of the characteristic ring breathing vibration.....	242
Figure 5.12	FIR and Raman spectra of [CrCl ₃ (dppea)(py)].....	245
Figure 5.13	Experimental (red) and calculated (blue) MIR spectra of [CrCl ₃ (dppea)(pytb)]	251
Figure 5.14	Experimental (red) and calculated (blue) Raman spectra of [CrCl ₃ (dppea)(pytb)]	251
Figure 5.15	HOMO and LUMO orbitals of [CrCl ₃ (dppea)(pytb)]]	253
Figure 5.16	FAB-MS spectrum of [CrCl ₃ (dppea)(pytb)].....	254
Figure 5.17	FAB-MS spectrum of [CrCl ₃ (dppea)(pyphenyl)].....	254
Figure 6.1	((RP)-1-[(1S)-1-aminoethyl]-2-(diphenylphosphino)ferrocene).....	258

LIST OF TABLES

Table 2.1	Characteristic pyridine shifts in the IR spectrum	Error! Bookmark not defined.
Table 2.2	Vibrational assignments of [CrCl ₃ (py)(thf) ₂] (1), [CrCl ₃ (py) ₂ (thf)] (2), [CrCl ₃ (py) ₃] (3)	32
Table 2.3	Selected experimental and calculated IR and Raman band assignments for [CrCl ₃ (py) ₃]	Error! Bookmark not defined.
Table 2.4	Scaling factors determined for [CrCl ₃ (py) ₃]	Error! Bookmark not defined.
Table 2.5	Selected bond lengths [Å] and angles [°] for [CrCl ₃ (py) ₃]	Error! Bookmark not defined.
Table 2.6	Selected torsion angles [°] for [CrCl ₃ (py) ₃]	Error! Bookmark not defined.
Table 2.7	Differences in crystal data between [CrCl ₃ (py) ₃] of this study and that of Howard [83]	Error! Bookmark not defined.
Table 2.8	Crystal data and structure refinement for [CrCl ₃ (py) ₃] of this study	Error! Bookmark not defined.
Table 2.9	Selected bond lengths [Å], bond angles [°] and torsion angles [°] for [Hpy][CrCl ₄ (py) ₂].....	Error! Bookmark not defined.

Table 2.10	Hydrogen bonds for [Hpy][CrCl ₄ (py) ₂] [Å and °].....	50
Table 2.11	Crystal data and structure refinement for [Hpy][CrCl ₄ (py) ₂].....	52
Table 2.12	Selected bond lengths [Å], bond angles [°] and torsion angles [°] for [CrCl ₃ (py) ₂ (DMF)]	62
Table 2.13	Crystal data and structure refinement for [CrCl ₃ (py) ₂ (DMF)]	63
Table 2.14	Infrared and Raman band shifts in the region 1 638 – 1 045 cm ⁻¹ [CrCl ₃ (pyNH ₂) ₃]	68
Table 2.15	IR and Raman band shifts in the region 1638 to 1045 cm ⁻¹ ¹ [CrCl ₃ (pytb) ₃]	69
Table 2.16	IR and Raman band shifts in the region 1030 – 499 cm ⁻¹ [CrCl ₃ (pyNH ₂) ₃]	71
Table 2.17	IR and Raman band shifts in the region 1030 – 499 cm ⁻¹ [CrCl ₃ (pytb) ₃]	72
Table 2.18	IR and Raman band shifts in the region 1030 – 499 cm ⁻¹ [CrCl ₃ (pyphenyl) ₃]	73
Table 2.19	Shifting of the characteristic ring breathing vibration in [CrCl ₃ py ₃], [CrCl ₃ (pyNH ₂) ₃], [CrCl ₃ (pytb) ₃] and [CrCl ₃ (pyphenyl) ₃].....	75
Table 2.20	Vibrational assignments of [CrCl ₃ (py) ₂ DMF] (5), [CrCl ₃ (pyNH ₂) ₃] (6), [CrCl ₃ (pytb) ₃] (7) and [CrCl ₃ (pyphenyl) ₃] (8).....	80
Table 2.21	Selected experimental and calculated IR and Raman band assignments for [CrCl ₃ (pyNH ₂) ₃]	86
Table 2.22	Scaling factors determined for [CrCl ₃ (pyNH ₂) ₃].....	86
Table 2.23	Selected experimental and calculated IR and Raman band assignments for [CrCl ₃ (pytb) ₃]	88
Table 2.24	Scaling factors determined for [CrCl ₃ (pytb) ₃].....	89
Table 2.25	Selected bond lengths [Å], bond angles [°] and torsion angles [°] for [CrCl ₃ (pytb) ₃]	94
Table 2.26	Crystal data and structure refinement for [CrCl ₃ (pytb) ₃]	94
Table 3.1	Bipyridine-specific vibrations present in the spectra of all complexes	109
Table 3.2	Pyridine specific vibrations	110
Table 3.3	Shifting of the characteristic ring breathing vibration in [CrCl ₃ (bipy)(py)], [CrCl ₃ (bipy)(pyNH ₂)], [CrCl ₃ (bipy)(pytb)] and [CrCl ₃ (bipy)(pyphenyl)]	112

Table 3.4	Vibrational assignments of [CrCl ₃ (bipy)(thf)] (9), [CrCl ₃ (bipy)(CH ₃ CN)] (10), [CrCl ₃ (bipy)(py)] (11), [CrCl ₃ (bipy)(pyNH ₂)] (12), [CrCl ₃ (bipy)(pytb)] (13), [CrCl ₃ (bipy)(pyphenyl)] (14), [HpyNH ₂][CrCl ₄ (bipy)] (15), [CrCl ₃ (bipy)(H ₂ O)] (16) and [CrCl ₂ (bipy) ₂][Cl]·H ₂ O (17) 121
Table 3.5	Selected experimental and calculated IR and Raman band assignments for [CrCl ₃ (bipy)(thf)] 134
Table 3.6	Scaling factors determined for [CrCl ₃ (bipy)(thf)] 134
Table 3.7	Selected experimental and calculated IR band assignments for [CrCl ₃ (bipy)(H ₂ O)] 136
Table 3.8	Scaling factors determined for [CrCl ₃ (bipy)(H ₂ O)] 136
Table 3.9	Selected experimental and calculated IR and Raman band assignments for [CrCl ₃ (bipy)(CH ₃ CN)] 139
Table 3.10	Scaling factors determined for [CrCl ₃ (bipy)(CH ₃ CN)] 140
Table 3.11	Selected experimental and calculated IR and Raman band assignments for [CrCl ₃ (bipy)(py)] 142
Table 3.12	Scaling factors determined for [CrCl ₃ (bipy)(py)] 143
Table 3.13	Selected experimental and calculated IR and Raman band assignments for [CrCl ₃ (bipy)(pyphenyl)] 145
Table 3.14	Scaling factors determined for [CrCl ₃ (bipy)(pyphenyl)] 146
Table 3.15	Selected experimental and calculated IR and Raman band assignments for [HpyNH ₂][CrCl ₄ (bipy)] 148
Table 3.16	Scaling factors determined for [HpyNH ₂][CrCl ₄ (bipy)] 149
Table 3.17	Selected bond lengths [Å], bond angles [°] and torsion angles [°] for [CrCl ₃ (bipy)(H ₂ O)] 163
Table 3.18	Crystallographic differences between the two structures 163
Table 3.19	Hydrogen bonds for [CrCl ₃ (bipy)(H ₂ O)] [Å and °] 164
Table 3.20	Crystal data and structure refinement for [CrCl ₃ (bipy)(H ₂ O)] 166
Table 3.21	Selected bond lengths [Å] and angles [°] for [HpyNH ₂][CrCl ₄ (bipy)] 167
Table 3.22	Hydrogen bonds for [HpyNH ₂][CrCl ₄ (bipy)] [Å and °] 168
Table 3.23	Crystal data and structure refinement for [HpyNH ₂][CrCl ₄ (bipy)] 170
Table 3.24	Crystallographic differences between the two structures 173
Table 3.25	Bond lengths [Å] and angles [°] for [CrCl ₂ (bipy) ₂][Cl]·H ₂ O 174
Table 3.26	Crystal data and structure refinement for [CrCl ₂ (bipy) ₂][Cl]·H ₂ O 175

Table 4.1	pytb-specific vibrations	190
Table 4.2	Shifting of the characteristic ring breathing vibration in [CrCl ₃ (dppe)(py)], [CrCl ₃ (dppe)(pyNH ₂)], [CrCl ₃ (dppe)(pytb)] and [CrCl ₃ (dppe)(pyphenyl)]	195
Table 4.3	pytb specific vibrations.....	198
Table 4.4	Vibrational assignments of [CrCl ₃ (dppe)(thf)] (19), [CrCl ₃ (dppe)(py)] (20), [CrCl ₃ (dppe)(pyNH ₂)] (21), [CrCl ₃ (dppe)(pytb)] (22), [CrCl ₃ (dppe)(pyphenyl)] (23) and [Hpyphenyl][CrCl ₄ (dppe)] (24).....	202
Table 4.5	Selected experimental and calculated IR and Raman band assignments for [CrCl ₃ (dppe)(pytb)]	212
Table 4.6	Scaling factors determined for [CrCl ₃ (dppe)(pytb)].....	213
Table 4.7	Bond lengths [Å] and angles [°] for [Hpyphenyl][CrCl ₄ (dppe)].....	219
Table 4.8	Hydrogen bonds for [Hpyphenyl][CrCl ₄ (dppe)] [Å and °]	220
Table 4.9	Crystal data and structure refinement for [Hpyphenyl][CrCl ₄ (dppe)].	221
Table 5.1	IR vibrations associated with coordinated pyridine	233
Table 5.2	IR vibrations associated with coordinated pyNH ₂	235
Table 5.3	IR vibrations associated with coordinated pyridine	239
Table 5.4	IR vibrations associated with coordinated pytb.....	240
Table 5.5	IR vibrations associated with coordinated pyphenyl.....	241
Table 5.6	Shifting of the characteristic ring breathing vibration in [CrCl ₃ (dppea)(py)], [CrCl ₃ (dppea)(pyNH ₂)], [CrCl ₃ (dppea)(pytb)] and [CrCl ₃ (dppea)(pyphenyl)]	242
Table 5.7	Vibrational assignments of [CrCl ₃ (dppea)(thf)] (26), [CrCl ₃ (dppea)(py)] (27), [CrCl ₃ (dppea)(pyNH ₂)] (28), [CrCl ₃ (dppea)(pytb)] (29) and [CrCl ₃ (dppea)(pyphenyl)] (30).....	246
Table 5.8	Selected experimental and calculated IR and Raman band assignments for [CrCl ₃ (dppea)(pytb)]	252
Table 5.9	Scaling factors determined for [CrCl ₃ (dppea)(pytb)].....	253