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

by

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Submitted in partial fulfilment of the requirements for the degree

Philosophiae Doctor

in Chemistry

In the Faculty of Natural and Agricultural Sciences

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CHAPTER 3

CHROMIUM(III) BIDENTATE NITROGEN LIGAND CHEMISTRY 101

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 $[CrCl_3(thf)_3]$. 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.

^{1}H 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.

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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.

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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.

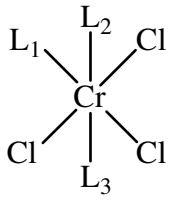
COMMON ABBREVIATIONS

• Acetyl acetonate	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

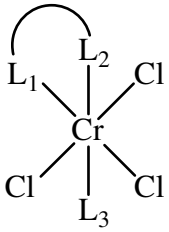
$[CrCl_3(py)(thf)_2]$	**1**
$[CrCl_3(py)_2(thf)]$	**2**
$[CrCl_3(py)_3]$	**3**
$[Hpy][CrCl_4(py)_2]$	**4**
$[CrCl_3(py)_2(DMF)]$	**5**
$[CrCl_3(pyNH_2)_3]$	**6**
$[CrCl_3(pytb)_3]$	**7**
$[CrCl_3(pyphenyl)_3]$	**8**
$[CrCl_3(bipy)(thf)]$	**9**
$[CrCl_3(bipy)(CH_3CN)]$	**10**
$[CrCl_3(bipy)(py)]$	**11**
$[CrCl_3(bipy)(pyNH_2)]$	**12**
$[CrCl_3(bipy)(pytb)]$	**13**
$[CrCl_3(bipy)(pyphenyl)]$	**14**
$[HpyNH_2][CrCl_4(bipy)]$	**15**
$[CrCl_3(bipy)(H_2O)]$	**16**
$[CrCl_2(bipy)_2][Cl]\cdot H_2O$	**17**
$[CrCl_3(dppe)(thf)]/ [Cr(dppe)Cl_2(\mu\text{-}Cl)]_2$	**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**
$[CrCl_3(dppea)(thf)]/ [Cr(dppea)Cl_2(\mu\text{-}Cl)]_2$	**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 = py, L^2,L^3 = thf
2 L^1,L^2 = py, L^3 = thf
3 L^1,L^2,L^3 = py
5 L^1,L^2 = py, L^3 = DMF

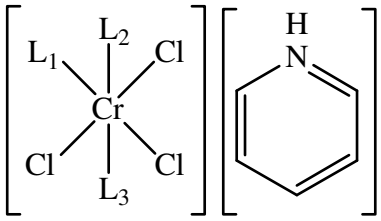
6 L^1,L^2,L^3 = $pyNH_2$
7 L^1,L^2,L^3 = pytb
8 L^1,L^2,L^3 = pyphenyl



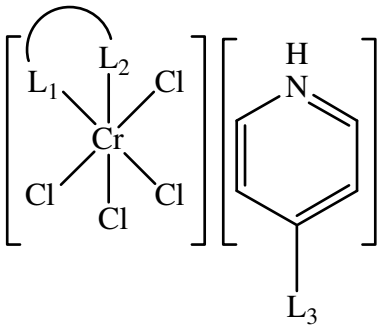
9 L^1L^2 = bipy, L^3 = thf
10 L^1L^2 = bipy, L^3 = CH_3CN
11 L^1L^2 = bipy, L^3 = py
12 L^1L^2 = bipy, L^3 = $pyNH_2$

13 L^1L^2 = bipy, L^3 = pytb
14 L^1L^2 = bipy, L^3 = pyphenyl
16 L^1L^2 = bipy, L^3 = H_2O
18 L^1L^2 = dppe, L^3 = thf *
19 L^1L^2 = dppe, L^3 = py
20 L^1L^2 = dppe, L^3 = $pyNH_2$
21 L^1L^2 = dppe, L^3 = pytb
22 L^1L^2 = dppe, L^3 = pyphenyl
24 L^1L^2 = dppea, L^3 = thf *
25 L^1L^2 = dppea, L^3 = py
26 L^1L^2 = dppea, L^3 = $pyNH_2$
27 L^1L^2 = dppea, L^3 = pytb

28 L^1L^2 = dppea, L^3 = pyphenyl

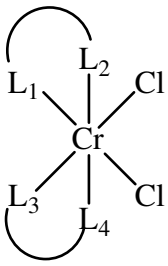


4 L^1,L^2 = py

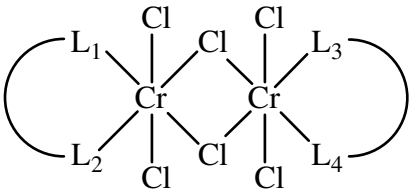


15 L^1L^2 = bipy, $L^3 = NH_2$

23 L^1L^2 = dppe, L^3 = phenyl



17 L^1L^2, L^3L^4 = bipy



18 L^1L^2, L^3L^4 = dppe *

24 L^1L^2, L^3L^4 = dppea *

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