

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

THE SYNTHESIS AND REACTIVITY  
OF PNICTOGEN LIGAND  
COMPLEXES OF TRANSITION  
METAL CARBONYLS

Simon Shu Tong, Wong

A thesis presented in partial  
fulfilment of the requirements  
for the degree of Master of Science

Chemistry/Biochemistry/Biophysics Department,  
Massey University.

December 1975.

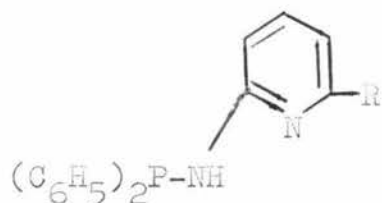
TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	iv
ACKNOWLEDGEMENTS	v
LIST OF FIGURES	vi
LIST OF TABLES	vii
CHAPTER 1. Introduction	8
CHAPTER 2. Monosubstituted Complexes	11
2.1 Introduction	11
2.2 Synthesis	12
2.3 Infra-red Spectra	13
2.4 $^{31}\text{P}$ nmr Spectra	16
2.5 UV Spectra	16
2.6 Experimental and Analytical Data	19
CHAPTER 3. Chelate Complexes	26
3.1 Introduction	26
3.2 Infra-red Spectra	27
3.3 $^1\text{H}$ nmr Spectra	34
3.4 Mass-Spectra	35
3.5 Experimental Analytical Data	37
CHAPTER 4. Reactivity Studies	43
4.1 Introduction	43
4.2 Reaction with a Limited Amount of HX to form Protonated Complexes	44
4.3 Infra-red Spectra of Protonated Complexes	45
4.4 Conductivity of Protonated Complexes	52
4.5 $^{13}\text{C}$ nmr Spectra of Protonated Complexes	55
4.6 $^{31}\text{P}$ nmr Spectra of Protonated Complexes	59
4.7 $^1\text{H}$ nmr Data	60
4.8 UV Spectral Data of Protonated Complexes	61
4.9 Reaction with Excess HX	63
4.10 Bridging $\text{W}(\text{CO})_5\text{PAPW}(\text{CO})_5$ Complex	65

	<u>Page</u>
4.11 $(W(CO)_5PAP)_2CoCl_2$ Complex	69
4.12 Methylation	70
4.13 Oxidation Reactions with Iodine	71
4.14 Experimental. Analytical data of the Protonated Complexes	74
CHAPTER 5. Mono and Bis Chelate Manganese Complexes	88
5.1 Mono Chelate Manganese Complexes	88
5.2 Infra-red Spectra of Mono Chelate Manganese Complexes	88
5.3 Bis Chelate Manganese Complexes	94
5.4 Infra-red Spectra of Bis Chelate Manganese Complexes	95
5.5 $Mn(CO)_3(6 PAP)S_2P(CH_3)_2$ Complex	99
5.6 Experimental and Analytical Data	100
CHAPTER 6. Instrumentation and Materials	104
6.1 Instrumentation	104
6.2 Materials	105
APPENDIX. Synthesis and Characterisation of 2-[dimethylphosphinothioylamino]-pyridine	107
REACTION SCHEME 1. Reactions of $W(CO)_5L$	111
REACTION SCHEME 2. Reactions of Free PAP Ligand	112
REACTION SCHEME 3. Reactions of PAP and 6 PAP Ligands with $Mn(CO)_5Br$	113
BIBLIOGRAPHY	114
ABBREVIATIONS	118

ABSTRACT

Metal carbonyl complexes of the type  $M(\text{CO})_5\text{L}$ ,  $M(\text{CO})_4\text{L}$  and  $(M(\text{CO})_5)_2\text{L}$  where M is Cr, Mo and W, and L is a pnictogen ligand ((I) or (II)).



have been synthesised by the addition of L to UV-irradiated tetrahydrofuran solutions of the appropriate metal carbonyl. Complexes of the type  $M(\text{CO})_3\text{LBr}$  (III) and  $M(\text{CO})_2\text{L}_2\text{Br}$  (IV) where M = Mn and L = (I) or (II) have also been synthesised by refluxing  $\text{Mn}(\text{CO})_5\text{Br}$  and L in a 1 : 1 molar ratio to form (III) and in a 1 : 2 molar ratio to form (IV). The  $\text{W}(\text{CO})_5\text{L}$  complexes react with acids HX (where  $\text{X}^- = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{BF}_4^-$  or  $\text{PF}_6^-$ ) to give the cationic ligand complexes,  $\text{W}(\text{CO})_5\text{LHX}$ . The conductivity of the complexes is anion dependent. The complexes were characterised by Infra-Red spectroscopy, Visible-UV spectroscopy,  $^{31}\text{P}$  nmr,  $^1\text{H}$  nmr,  $^{13}\text{C}$  nmr, and Mass-spectra. Excess acid (e.g. HBr) cleaves the P-N bond yielding primarily  $\text{W}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_2\text{Br}$  and the protonated amine. The complex  $\text{W}(\text{CO})_5\text{L}$  (where L = (I)) acts as a ligand towards  $\text{CoCl}_2$  in the complex  $(\text{W}(\text{CO})_5\text{L})_2\text{CoCl}_2$  as well as in the bridging complex  $(\text{W}(\text{CO})_5)_2\text{L}$ .

ACKNOWLEDGEMENTS

I am most grateful to:

My supervisors, Dr. E.W. Ainscough and Dr. A.M. Brodie for their invaluable guidance and keen interest in this project.

Dr. K. Mackay of the Chemistry Department, School of Science, Waikato University, for  $^{31}\text{P}$  nuclear magnetic resonance spectra.

Professor A.D. Campbell of Otago University for microanalyses.

Dr. P.T. Callaghan and Miss L. Hughes of the Chemistry, Biochemistry and Biophysics Department, Massey University for  $^{13}\text{C}$  nuclear magnetic resonance spectra.

Professor R. Hodges of the Chemistry, Biochemistry and Biophysics Department, Massey University for mass-spectra.

Mr. A.A. Trow of Massey University for  $^1\text{H}$  nuclear magnetic resonance spectra and other assistance.

And to Mrs. J.R. Parry for typing this thesis.

LIST OF FIGURES

	<u>Page</u>
1. UV apparatus	22
2(i) Carbonyl stretching spectrum of $W(CO)_5(6\text{ PAP})$	30
2(ii) Carbonyl stretching spectrum of $W(CO)_4(6\text{ PAP})$	30
3(i) Infra-red spectrum of $W(CO)_5(6\text{ PAP})$	48
3(ii) Infra-red spectrum of $\angle W(CO)_5(6\text{ PAPH})\angle Cl$	48
4(i) Infra-red spectrum of $\angle W(CO)_5(6\text{ PAPH})\angle PF_6$	49
4(ii) Infra-red spectrum of $\angle W(CO)_5(6\text{ PAPH})\angle BF_4$	49
5. UV spectra of protonated and unprotonated complexes	62
6. Carbonyl stretching spectrum of $W(CO)_5PAPW(CO)_5$	66
7(i) Carbonyl stretching spectrum of $Mn(CO)_3(6\text{ PAPBr})$	98
7(ii) Carbonyl stretching spectrum of $\angle Mn(CO)_2(6\text{ PAP})_2\angle Br$	98
REACTION SCHEME 1	111
REACTION SCHEME 2	112
REACTION SCHEME 3	113

LIST OF TABLES

	<u>Page</u>
1. Infra-red data of monosubstituted complexes	14
2. $^{31}\text{P}$ nmr data of monosubstituted complexes	17
3. UV spectral data of monosubstituted complexes	18
4. Infra-red data of chelate complexes	32-33
5. $^1\text{H}$ nmr data	35
6. Analytical data of chelate complexes	42
7. Infra-red data of ammine and pyridinium complexes	47
8. Carbonyl stretching data of protonated complexes	51
9. Molar conductivities of protonated complexes	53
10. $^{13}\text{C}$ nmr data of protonated and unprotonated complexes	57
11. $^{31}\text{P}$ nmr data of protonated and unprotonated complexes	60
12. $^1\text{H}$ nmr data of protonated complexes	60
13a. UV spectral data of protonated and unprotonated complexes	61
13b. UV data of $\text{Cr}(\text{CO})_5\text{L}$ complexes	63
14. Mass-spectral data	64
15. Carbonyl stretching absorptions of bridging complexes	68
16. Carbonyl stretching absorptions of iodo-complexes	73
17. Analytical data of protonated complexes	78
18. Carbonyl stretching absorptions of Manganese complexes	92
19. Carbonyl stretching absorptions of bis manganese complexes	96