

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	... i
LIST OF FIGURES	... xi
LIST OF TABLES	... xv
ABSTRACT	... xviii
I INTRODUCTION	
1.1 A review on the syntheses and structures of transition-metal compounds containing arsenic atoms and units	... 1
1.1.1 Compounds containing a single arsenic atom	... 1
1.1.2 Compounds containing the diarsenic unit	... 3
1.1.3 Compounds containing the <i>cyclo</i> -As ₃ ligands	... 5
1.1.4 Compounds containing the As ₄ unit	... 7
1.1.5 Compounds containing the <i>cyclo</i> -As ₅ ligands	... 8
1.1.6 Compounds containing the <i>cyclo</i> -As ₆ ligands	... 10
1.1.7 Compounds containing the <i>cyclo</i> -As ₇ ligands	... 11
1.1.8 Compounds containing the <i>cyclo</i> -As ₈ ligands	... 12
1.1.9 Reactivity of coordinated phosphorus or arsenic atoms and units	... 13
1.2 Reactivity of mixed Pnicogen Chalcogenides, E ₄ X ₃ (E = P, As; X = S, Se), with transition metal complexes	
1.2.1 Nondisruptive process	... 16
1.2.2 Disruptive process	... 19

1.3	Reactions of As ₄ S ₄ with transition-metal complexes	... 26
1.4	Objectives	... 30
II RESULTS AND DISCUSSION		
2.1	The reaction of [CpCr(CO) ₃] ₂ with elemental Phosphorus	... 31
2.1.1	Isolation of [CpCr(CO) ₂] ₅ P ₁₀	... 31
2.1.2	Spectral characteristics	... 34
2.1.2.1	NMR spectra	... 34
2.1.2.2	Mass spectrum	... 36
2.1.2.3	EPR spectrum	... 39
2.1.3	Electrochemical studies	... 39
2.1.4	Molecular structure	... 39
2.2	Studies with elemental Arsenic	
2.2.1	The reaction of [CpCr(CO) ₃] ₂ with elemental Arsenic	... 47
2.2.2	The reaction of [CpCr(CO) ₂] ₂ with elemental Arsenic	... 47
2.2.3	Mechanistic pathways : Formation of [CpCr(CO) ₂] ₂ As ₂ and CpCr(CO) ₂ As ₃	... 48
2.2.4	Physical properties	... 50
2.2.5	Spectral characteristics	... 52
2.2.5.1	I.R. spectra	... 52
2.2.5.2	N.M.R. spectra	... 52
2.2.5.3	Mass spectra	... 55
2.2.6	Molecular structures	... 55

2.3	Studies with Tetraphosphorus Trisulfide	
2.3.1.	The reaction of $[\text{CpCr}(\text{CO})_3]_2$ with Tetraphosphorus Trisulfide	... 64
2.3.2	The reaction of $[\text{CpCr}(\text{CO})_2]_2$ with Tetraphosphorus Trisulfide	... 65
2.3.3	NMR spectral studies	... 66
2.3.4	Thermolysis of $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{S}_3)$... 70
2.3.5	Mechanistic pathways : Formation of $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{S}_3)$... 72
2.3.6	Physical properties	... 72
2.3.7	Spectral characteristics	... 76
2.3.7.1	I.R. spectra	... 76
2.3.7.2	N.M.R. spectra	... 76
2.3.7.3	Mass spectra	... 89
2.3.8	Molecular structures	... 89
2.4	Studies with Tetraphosphorus Triselenide	
2.4.1	The reaction of $[\text{CpCr}(\text{CO})_3]_2$ with Tetraphosphorus Triselenide	... 102
2.4.2	The reaction of $[\text{CpCr}(\text{CO})_2]_2$ with Tetraphosphorus Triselenide	... 104
2.4.3	The reaction of $[\text{CpCr}(\text{CO})_2]_2\text{Se}$ with Tetraphosphorus Triselenide	... 104
2.4.4	The reaction of $[\text{CpCr}(\text{CO})_2]_2\text{Se}$ with Tetraphosphorus Trisulfide	... 104
2.4.5	NMR spectral studies	... 105
2.4.6	Thermolysis of $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{Se}_3)$ and $\text{Cp}_4\text{Cr}_4(\text{CO})_8(\text{P}_2\text{Se}_2)$... 109
2.4.7	Mechanistic pathways : Formation of $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{Se}_3)$ and $\text{Cp}_4\text{Cr}_4(\text{CO})_8(\text{P}_2\text{Se}_2)$... 113
2.4.8	Physical properties	... 118

2.4.9 Spectral characteristics	... 118
2.4.9.1 I.R. spectra	... 118
2.4.9.2 N.M.R. spectra	... 118
2.4.9.3 Mass spectra	... 123
2.4.10 Molecular structures	... 123
2.5 Studies with Realgar, As_4S_4	
2.5.1 The reaction of $[\text{CpCr}(\text{CO})_3]_2$ with As_4S_4	... 138
2.5.2 The reaction of $[\text{CpCr}(\text{CO})_2]_2$ with As_4S_4	... 138
2.5.3 Mechanistic pathways : Formation of $[\text{CpCr}(\text{CO})_2]_2 \text{As}_2\text{S}_2$... 139
2.5.4 Physical properties	... 139
2.5.5 Spectral characteristics	... 140
2.5.5.1 I.R. spectrum	... 140
2.5.5.2 N.M.R. spectra	... 140
2.5.5.3 Mass spectrum	... 140
2.6 Conclusion	... 143
2.7 Coordination of the (μ - η^2 -As ₂) ligand to Group 6 transition-metal carbonyl fragments, M(CO) ₅ (THF) [M = Cr, W]	... 146
2.7.1 The reaction of $[\text{CpCr}(\text{CO})_2]_2\text{As}_2$ with M(CO) ₅ (THF) [M = Cr, W]	... 146
2.7.2 Physical properties	... 146
2.7.3 Spectral characteristics	... 148
2.7.3.1 I.R. spectra	... 148
2.7.3.2 N.M.R. spectra	... 148

2.7.3.3	Mass spectra	... 148
2.7.4	Molecular structures	... 148
2.8	Coordination of the (μ - η^2 -P ₂) ligand to Fe(CO) ₄ fragments from Fe ₂ (CO) ₉	... 159
2.8.1	The reaction of [CpCr(CO) ₂] ₂ P ₂ with Fe ₂ (CO) ₉	... 159
2.8.2	Physical properties	... 159
2.8.3	Spectral characteristics	... 161
2.8.3.1	I.R. spectra	... 161
2.8.3.2	N.M.R. spectra	... 161
2.8.3.3	Mass spectra	... 161
2.8.4	Molecular structures	... 165
III	EXPERIMENTAL	
3.1	General Procedures	... 171
3.1.1	Elemental analysis	... 171
3.1.2	Physical measurements	... 171
3.1.3	Solvents and reagents	... 172
3.2	Preparation of starting complexes	... 172
3.2.1	Preparation of Dicyclopentadienylhexacarbonyldichromium, CpCr(CO) ₃] ₂	... 172
3.2.2	Preparation of Dicyclopentadienyltetracarbonyldichromium, CpCr(CO) ₂] ₂	... 173
3.2.3	Synthesis of (η^5 -C ₅ H ₅)Cr(CO) ₃ H	... 173
3.2.4	Preparation of Metal Carbonyl fragments, M(CO) ₅ (THF)	... 174
3.2.5	Preparation of Tetraphosphorus Triselenide, P ₄ Se ₃	... 174

3.2.6 Preparation of Diiron Enneacarbonyl, $\text{Fe}_2(\text{CO})_9$... 175
3.2.7 Preparation of $[\text{CpCr}(\text{CO})_2]_2\text{Se}$... 175
3.3 Cothermolysis of $[\text{CpCr}(\text{CO})_3]_2$ with elemental Phosphorus - isolation and characterisation of $[\text{CpCr}(\text{CO})_2]_5\text{P}_{10}$... 176
3.4 Reactions with elemental Arsenic	
3.4.1 Reactions of $[\text{CpCr}(\text{CO})_3]_2$... 177
3.4.1.1 Isolation of products	
(a) Cothermolysis at 110°C for 1.5 h : isolation of $[\text{CpCr}(\text{CO})_2]_2\text{As}_2$, $\text{CpCr}(\text{CO})_2\text{As}_3$, and $\text{Cp}_2\text{Cr}_2\text{AsO}_5$... 177
(b) Cothermolysis at 110°C for 16 h : isolation of $\text{Cp}_2\text{Cr}_2\text{As}_5$... 179
(c) Cothermolysis at 140°C for 6 h : isolation of $\text{Cp}_5\text{Cr}_5\text{As}_4\text{O}_8$... 180
3.4.1.2 Thermolysis of products	
(a) Thermolysis of $[\text{CpCr}(\text{CO})_2]_2\text{As}_2$... 180
(b) Thermolysis of $\text{CpCr}(\text{CO})_2\text{As}_3$... 181
3.4.2 Reactions of $[\text{CpCr}(\text{CO})_2]_2$... 182
3.4.2.1 Isolation of products	
(a) Cothermolysis at 110°C for 1h : isolation of $[\text{CpCr}(\text{CO})_2]_2\text{As}_2$, $\text{CpCr}(\text{CO})_2\text{As}_3$ and $\text{Cp}_2\text{Cr}_2\text{AsO}_5$... 182
(b) Cothermolysis at 110°C for 5 h : isolation of $[\text{CpCr}(\text{CO})_2]_2\text{As}_2$ and $\text{Cp}_2\text{Cr}_2\text{AsO}_5$... 182
3.5 Reactions with Tetraphosphorus Trisulfide	
3.5.1 Reactions of $[\text{CpCr}(\text{CO})_3]_2$... 183

3.5.1.1 Isolation of products	
(a) At ambient temperature	... 182
(b) From cothermolysis at 60°C	... 184
3.5.1.2 Reaction of $[CpCr(CO)_3]_2$ with P_4S_3 in the presence of isoprene	... 185
3.5.2 Reaction of $[CpCr(CO)_2]_2$... 186
3.5.3 NMR Tube Reactions	... 187
3.5.4 Thermolysis of $Cp_4Cr_4(CO)_9(P_4S_3)$... 188
3.6 Reactions with Tetraphosphorus Triselenide	
3.6.1 Reactions of $[CpCr(CO)_3]_2$... 189
3.6.1.1 Isolation of products	
(a) At ambient temperature for 6 days : isolation of $Cp_4Cr_4(CO)_9(P_4Se_3)$... 189
(b) At ambient temperature for 12 days : isolation of $Cp_4Cr_4(CO)_8(P_2Se_2)$... 190
(c) From cothermolysis at 60°C	... 191
3.6.2 Reactions of $[CpCr(CO)_2]_2$... 192
3.6.3 Reactions of $[CpCr(CO)_2]_2Se$... 193
3.6.3.1 Isolation of products	
(a) From a reaction with P_4Se_3	... 193
(b) From a reaction with P_4S_3	... 193
3.6.3.2 NMR Tube Reactions	... 194
3.6.4 Thermolysis of products	... 195
(a) Thermolysis of $Cp_4Cr_4(CO)_9(P_4Se_3)$... 195
(b) Thermolysis of $Cp_4Cr_4(CO)_8(P_2Se_2)$... 196

3.7 Reactions with Realgar, As ₄ S ₄	197
3.7.1 Reactions of [CpCr(CO) ₃] ₂	197
3.7.1.1 Isolation of products	
(a) At ambient temperature	197
(b) From cothermolysis at 60°C	198
3.7.2 Reactions of [CpCr(CO) ₂] ₂	198
3.7.3 Thermolysis of [CpCr(CO) ₂] ₂ As ₂ S ₂	199
3.8 Formation of some metal carbonyl fragments adducts of [CpCr(CO) ₂] ₂ E ₂ (E = P, As)	
3.8.1 Reactions of [CpCr(CO) ₂] ₂ As ₂ with M(CO) ₅ THF (M= Cr, W)	200
3.8.1.1 Isolation of products	
(a) [CpCr(CO) ₂] ₂ As ₂ [Cr(CO) ₅] ₂	200
(b) [CpCr(CO) ₂] ₂ As ₂ [W(CO) ₅] ₂	200
3.8.2 Reaction of [CpCr(CO) ₂] ₂ P ₂ with Fe ₂ (CO) ₉	201
3.8.2.1 Isolation of [CpCr(CO) ₂] ₂ P ₂ [Fe(CO) ₄]and [CpCr(CO) ₂] ₂ P ₂ [Fe(CO) ₄] ₂	201
3.9 Crystal structure determinations	
3.9.1 Structure determinations of [CpCr(CO) ₂] ₂ As ₂ and CpCr(CO) ₂ As ₃	203
3.9.2 Structure determinations of Cp ₄ Cr ₄ (CO) ₉ (P ₄ S ₃), CpCr(CO) ₃ H and P ₄ S ₃	206
3.9.3 Structure determinations of Cp ₄ Cr ₄ (CO) ₉ (P ₄ Se ₃) and Cp ₄ Cr ₄ (CO) ₈ (P ₂ Se ₂)	209

3.9.4 Structure determinations of $[CpCr(CO)_2]_2As_2[M(CO)_5]_2$ [M = Cr, W]	... 212
3.9.5 Structure determinations of $[CpCr(CO)_2]_2P_2[Fe(CO)_4]_m$ [m = 1, 2]	... 212
IV REFERENCES	... 221
V APPENDIX	

LIST OF FIGURES

	Page
Figure 1. Structure of the [(triphos)Co(As) ₃ Co(triphos)] ²⁺ (36) dication.	6
Figure 2. Structure of [Co ₄ (μ ₃ -As) ₃ (μ ₃ , η ³ -As ₃)(PPh ₃) ₄] (38) (without phenyl groups).	6
Figure 3. Molecular structure of [(η ⁵ -MeC ₅ H ₄)Mo(CO)] ₂ (μ ₂ , η ² -As ₂) ₂ (39).	7
Figure 4. Structure of [η ⁵ -C ₅ Me ₅](CO) ₂ Nb(η ⁴ -As ₄) (40a).	8
Figure 5. Molecular structure of (CpMo) ₂ [μ-(η ⁴ -As ₅)] (41).	8
Figure 6. Cyclo-As ₅ ^θ ligand (42).	9
Figure 7. Crystal structure of [(η ⁵ -C ₅ Me ₄ Et)Mo(μ, η ⁶ -As ₆)Mo-(η ⁵ -C ₅ Me ₄ Et)] (44).	10
Figure 8. Ball-and-stick Chem-X representation of 45 .	11
Figure 9. Molecular structure of [(Cp ["] Nb) ₂ (μ, η ^{4:4} -As ₈)] (46).	12
Figure 10. Molecular structure of [(Cp ["] Nb) ₂ {As ₈ Cr(CO) ₅ }] (47).	13
Figure 11. The atomic arrangement in E ₄ X ₃ molecule.	16
Figure 12. Perspective view of the [(np ₃)Ni(P ₄ S ₃)] (55) molecule.	17
Figure 13. Structure of Mo(CO) ₅ (P ₄ S ₃) (56).	18
Figure 14. A view of the [{Pt(μ-P ₄ S ₃)(PPh ₃) ₃ }] (57) molecule.	19
Figure 15. Crystal structure of [Ir(μ-P ₄ S ₃)(PPh ₃)Cl(CO)] ₂ (58).	20
Figure 16. Perspective view of the [(triphos)Rh(P ₃ S ₃)] (59) molecule.	21
Figure 17. Perspective view of the [(triphos)CoP ₂ Se] ⁺ (60) cation.	23
Figure 18. Molecular structure of [(triphos)Ni(P ₃)] ⁺ (61) cation.	24
Figure 19. Molecular structure of (C ₅ Me ₅) ₂ Mo ₂ P ₂ S ₃ ·Cr(CO) ₅ (64).	25

Figure 20. Molecular structure of $(C_5Me_5)_2Mo_2P_4S \cdot Cr(CO)_5$ (65).	25
Figure 21. Molecular structure of $[(C_5Me_5)_2Co_2As_2S_3]$ (67).	27
Figure 22. Crystal structure of $[Cp^X_2Co_2(CO)As_2S_2]$ (68).	28
Figure 23. Crystal structure of $[Cp^X_3Co_3As_2S_4]$ (69).	29
Figure 24. Temperature-dependent spectra of a solution of $[CpCr(CO)_2]P_{10}$ (8) in d_8 -toluene.	35
Figure 25. $^{31}P\{^1H\}$ NMR spectrum of $[CpCr(CO)_2]_5P_{10}$ (8).	37
Figure 26. 35-Ghz EPR spectrum of an arbitrarily oriented crystal of $[CpCr(CO)_2]_5P_{10}$ (8) at 6.1 K.	40
Figure 27. Structure of $[CpCr(CO)_2]_5P_{10}$ (8).	41
Figure 28. Stereoview of the Cr_5P_{10} unit of $[CpCr(CO)_2]_5P_{10}$ (8). CO and Cp groups are removed for clarity.	41
Figure 29. CO stretching frequencies of $Cp_2Cr_2(CO)_4(\mu, \eta^2-As_2)$ (2) in toluene.	53
Figure 30. CO stretching frequencies of $CpCr(CO)_2(\eta^3-As_3)$ (3) in toluene	54
Figure 31. ORTEP drawing of the molecular structure of $Cp_2Cr_2(CO)_4(\mu, \eta^2-As_2)$ (2).	59
Figure 32. Molecular structure of $CpCr(CO)_2(\eta^3-As_3)$ (3).	62
Figure 33. Bond-breaking and Bond-making (.....) in the P_4S_3 cage.	74
Figure 34. CO stretching frequencies of $Cp_4Cr_4(CO)_9(P_4S_3)$ (9) in nujol.	77
Figure 35. Comparison of CO stretching frequencies of $CpCr(CO)_3H$ (11) with synthesized authentic sample of $CpCr(CO)_3H$ in THF.	78
Figure 36. 1H NMR spectrum of $Cp_4Cr_4(CO)_9(P_4S_3)$ in C_6D_6 .	79
Figure 37. Temperature-dependent 1H NMR spectra of a 2mM solution of $Cp_4Cr_4(CO)_9(P_4S_3)$ in d_8 -toluene.	80
Figure 38. ^{31}P NMR spectrum of $Cp_4Cr_4(CO)_9(P_4S_3)$ (9).	81
Figure 39a. ABCD Spin System I.	83

Figure 39b. ABCD Spin System II.	84
Figure 40. Calculated Sum of System I and System II.	85
Figure 41. Proposed isomers for 9a and 9b .	88
Figure 42. Molecular structure of Cp ₄ Cr ₄ (CO) ₉ (P ₄ S ₃) (9).	92
Figure 43. Molecular packing of Cp ₄ Cr ₄ (CO) ₉ (P ₄ S ₃) (9) in the unit cell.	93
Figure 44. Molecular structure of CpCr(CO) ₃ H (11).	98
Figure 45. Molecular packing of CpCr(CO) ₃ H (11) in the unit cell.	99
Figure 46. Time-dependent ¹ H NMR spectra for an NMR tube reaction of a 2 mM solution of Cp ₂ Cr ₂ (CO) ₄ Se (17) with one molar equivalent of in P ₄ Se ₃ at ambient temperature under argon.	107
Figure 47. Time-dependent ¹ H NMR spectra for an NMR tube reaction of a 2 mM solution of Cp ₂ Cr ₂ (CO) ₄ Se (17) with one molar equivalent of in P ₄ S ₃ at ambient temperature under argon.	110
Figure 48. The time-dependent ¹ H NMR spectral changes of a 2mM solution of Cp ₄ Cr ₄ (CO) ₈ (P ₂ Se ₂) C ₆ D ₆ at 50°C.	112
Figure 49. CO stretching frequencies of Cp ₄ Cr ₄ (CO) ₉ (P ₄ Se ₃) (12) in nujol	119
Figure 50. CO stretching frequencies of Cp ₄ Cr ₄ (CO) ₈ (P ₂ Se ₂) (13) in nujol	120
Figure 51. Temperature-dependent ¹ H NMR spectra of a 2mM solution of Cp ₄ Cr ₄ (CO) ₈ (P ₂ Se ₂) in d ₈ -toluene.	122
Figure 52. Molecular Structure of [Cp ₄ Cr ₄ (CO) ₉](P ₄ Se ₃) (12).	126
Figure 53. Molecular packing of [Cp ₄ Cr ₄ (CO) ₉](P ₄ Se ₃) (12) in the unit cell.	127
Figure 54. Molecular Structure of [Cp ₄ Cr ₄ (CO) ₈](P ₂ Se ₂) (13).	132
Figure 55. Molecular packing of [Cp ₄ Cr ₄ (CO) ₈](P ₂ Se ₂) (13) in the unit cell.	133
Figure 56. CO stretching frequencies of [CpCr(CO) ₂] ₂ As ₂ S ₂ (20) in nujol.	141
Figure 57. CO stretching frequencies of [CpCr(CO) ₂] ₂ As ₂ [Cr(CO) ₅] ₂ (21) in nujol.	149

Figure 58. CO stretching frequencies of $[\text{CpCr}(\text{CO})_2]_2\text{As}_2[\text{W}(\text{CO})_5]_2$ (22) in nujol.	150
Figure 59. Molecular Structure of $[\text{CpCr}(\text{CO})_2]_2\text{As}_2[\text{Cr}(\text{CO})_5]_2$ (21).	153
Figure 60. CO stretching frequencies of $[\text{CpCr}(\text{CO})_2]_2\text{P}_2[\text{Fe}(\text{CO})_4]$ (23) in nujol.	162
Figure 61. CO stretching frequencies of $[\text{CpCr}(\text{CO})_2]_2\text{P}_2[\text{Fe}(\text{CO})_4]_2$ (24) in nujol.	163
Figure 62. Molecular Structure of $[\text{CpCr}(\text{CO})_2]_2\text{P}_2[\text{Fe}(\text{CO})_4]$ (23).	166
Figure 63. Molecular Structure of $[\text{CpCr}(\text{CO})_2]_2\text{P}_2[\text{Fe}(\text{CO})_4]_2$ (24).	167

LIST OF TABLES

Page

Table 1. Product Composition from the reaction of $[CpCr(CO)_3]_2$ (1) with Various Mole Equivalents of P_4^a .	32
Table 2. $^{31}P\{^1H\}$ NMR Resonances of $[CpCr(CO)_2]_5P_{10}$ (8).	37
Table 3. Fast atom bombardment mass spectrum of $[CpCr(CO)_2]_5P_{10}$ (8).	38
Table 4. Positional parameters for $[CpCr(CO)_2]_5P_{10}$ (8).	43
Table 5. Selected bond lengths and angles for $[CpCr(CO)_2]_5P_{10}$ (8).	44
Table 6. Fast atom bombardment mass spectrum of $[CpCr(CO)_2]_2As_2$ (2)	56
Table 7. Fast atom bombardment mass spectrum of $CpCr(CO)_2As_3$ (3).	57
Table 8. Electron impact mass spectrum of $Cp_2Cr_2P_5$ (5).	58
Table 9. Bond Lengths (\AA) and Bond Angles (deg) for $[CpCr(CO)_2]_2As_2$ (2).	60
Table 10. Comparison of Selected Bond Distances (\AA) and Angle (deg) for $[CpM(CO)_2]_2As_2$ (2)	60
Table 11. A Comparison of As-As and M-As Bond Lengths (\AA) in (η^3 -As ₃) Complexes.	63
Table 12. Time-dependent variation of product composition [#] from the reaction of $[CpCr(CO)_3]_2$ (1) with 0.5 mole equivalent of P_4S_3 at 60°C.	67
Table 13. Time-dependent variation of product composition ^a from the reaction of $[CpCr(CO)_3]_2$ with an equivalent of P_4S_3 at 80°C.	68
Table 14. Time-dependent variation of product composition ^a from the reaction of $[CpCr(CO)_2]_2$ (4) with n equivalents of P_4S_3 at 60°C	69
Table 15. Time-dependent variation of product composition from (a) the thermolysis of $Cp_4Cr_4(CO)_9(P_4S_3)$ at 60°C* and (b) its cothermolysis with an equimolar equivalent of P_4S_3 at 60°C.	71
Table 16. Product composition ^a from the reactions of $[CpCr(CO)_3]_2$ with P_4S_3 at R.T. and 60°C, and thermolysis of $Cp_4Cr_4(CO)_9(P_4S_3)$ (9) at 80°C.	75

Table 17. $^{31}\text{P}\{^1\text{H}\}$ NMR Chemical Shifts [#] and Peak Frequencies of $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{S}_3)$ (9).	86
Table 18. Summary of NMR parameters of spin systems I and II.	87
Table 19. Fast atom bombardment mass spectrum of $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{S}_3)$ (9).	90
Table 20. Electron impact mass spectrum of $\text{CpCr}(\text{CO})_3\text{H}$ (11).	91
Table 21. Atomic Coordinates and their Equivalent Displacement Parameters for $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{S}_3)$ (9).	95
Table 22. Bond Lengths (\AA) and Bond Angles ($^\circ$) for $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{S}_3)$ (9).	97
Table 23. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{CpCr}(\text{CO})_3\text{H}$.	100
Table 24. Bond Lengths (\AA) and Bond Angles ($^\circ$) for $\text{CpCr}(\text{CO})_3\text{H}$ (11).	101
Table 25. Variation of product composition ^a from the reaction of $[\text{CpCr}(\text{CO})_3]_2$ with equimolar equivalent of P_4Se_3 under ultrasonication at ambient temperature.	106
Table 26. Product composition from the reactions of $[\text{CpCr}(\text{CO})_3]_2$ with P_4Se_3 at R.T. and 60°C and thermolysis of $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{Se}_3)$ (12) and $\text{Cp}_4\text{Cr}_4(\text{CO})_8(\text{P}_2\text{Se}_2)$ (13).	114
Table 27. Electron impact mass spectrum of $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{Se}_3)$ (12).	124
Table 28. Electron impact mass spectrum of $\text{Cp}_4\text{Cr}_4(\text{CO})_8(\text{P}_2\text{Se}_2)$ (13).	125
Table 29. Bond Lengths (\AA) for $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{Se}_3)$ (12).	128
Table 30. Bond Angles ($^\circ$) for $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{Se}_3)$ (12).	130
Table 31. Bond Lengths (\AA) and Bond Angles ($^\circ$) for $\text{Cp}_4\text{Cr}_4(\text{CO})_8(\text{P}_2\text{Se}_2)$ (13).	135
Table 32. Electron impact mass spectrum of $[\text{CpCr}(\text{CO})_2]_2\text{As}_2\text{S}_2$ (20).	142
Table 33. Electron impact mass spectrum of $[\text{CpCr}(\text{CO})_2]_2\text{As}_2[\text{Cr}(\text{CO})_5]_2$ (21).	151
Table 34. Electron impact mass spectrum of $[\text{CpCr}(\text{CO})_2]_2\text{As}_2[\text{W}(\text{CO})_5]_2$ (22).	152
Table 35. Bond Lengths (\AA) and angles ($^\circ$) for $[\text{CpCr}(\text{CO})_2]_2\text{As}_2[\text{Cr}(\text{CO})_5]_2$ (21).	154
Table 36. Bond Lengths (\AA) and angles ($^\circ$) for $[\text{CpCr}(\text{CO})_2]_2\text{As}_2[\text{W}(\text{CO})_5]_2$ (22).	155

Table 37. A Comparison of Selected Bond Parameters of the Cr ₂ As ₂ Core of [CpCr(CO) ₂] ₂ As ₂ [Cr(CO) ₅] ₂ (21) and [CpCr(CO) ₂] ₂ As ₂ [W(CO) ₅] ₂ (22) with those of [CpCr(CO) ₂] ₂ As ₂ (2).	156
Table 38. Some Selected Bond Parameters of [CpMCO) ₂] ₂ As ₂ [Cr(CO) ₅] ₂ (M = Cr (21), Mo (32a)) and [CpMCO) ₂] ₂ As ₂ (30a).	157
Table 39. Electron impact mass spectrum of [CpCr(CO) ₂] ₂ P ₂ [Fe(CO) ₄] (23).	164
Table 40. Bonding Parameters of [CpCr(CO) ₂] ₂ P ₂ [Fe(CO) ₄] (23) ^a .	168
Table 41. Bonding Parameters of [CpCr(CO) ₂] ₂ P ₂ [Fe(CO) ₄] ₂ (24) ^a .	169
Table 42. Some Selected Bond Lengths (Å) and Bond Angles (°) in [CpCr(CO) ₂] ₂ P ₂ [Fe(CO) ₄] (23) and [CpCr(CO) ₂] ₂ P ₂ -[Fe(CO) ₄] ₂ (24) and Its Parent Compound (15).	170
Table 43. R.F. values on silica gel 60F ₂₅₄ plate.	178
Table 44. Data Collection and Processing Parameters for [CpCr(CO) ₂] ₂ As ₂ .	204
Table 45. Data Collection and Processing Parameters for CpCr(CO) ₂ As ₃ .	205
Table 46. Data Collection and Processing Parameters for Cp ₄ Cr ₄ (CO) ₉ (P ₄ S ₃), CpCr(CO) ₃ H and P ₄ S ₃ .	207
Table 47. Data Collection and Structure Refinement for Cp ₄ Cr ₄ (CO) ₉ (P ₄ Se ₃).	210
Table 48. Data Collection and Structure Refinement for Cp ₄ Cr ₄ (CO) ₈ (P ₂ Se ₂).	211
Table 49. Data Collection and Processing Parameters for [CpCr(CO) ₂] ₂ As ₂ -[Cr(CO) ₅] ₂ (21) and [CpCr(CO) ₂] ₂ As ₂ [W(CO) ₅] ₂ (22)	213
Table 50. Atomic coordinates and equivalent isotropic temperature factors for [CpCr(CO) ₂] ₂ As ₂ [Cr(CO) ₅] ₂ .	215
Table 51. Atomic coordinates and equivalent isotropic temperature factors for [CpCr(CO) ₂] ₂ As ₂ [W(CO) ₅] ₂ .	216
Table 52. Data Collection and Processing Parameters for [CpCr(CO) ₂] ₂ P ₂ -[Fe(CO) ₄] (23) and [CpCr(CO) ₂] ₂ P ₂ [Fe(CO) ₄] ₂ (24).	217
Table 53. Positional and Equivalent Displacement Parameters for the Non-Hydrogen Atoms of [CpCr(CO) ₂] ₂ P ₂ [Fe(CO) ₄] (23)	219
Table 54. Positional and Equivalent Displacement Parameters for the Non-Hydrogen Atoms of [CpCr(CO) ₂] ₂ P ₂ [Fe(CO) ₄] ₂ (24)	220