REACTIVITY STUDIES OF CYCLOPENTADIENYL COMPLEXES OF GROUP 6 METALS WITH ARYLSULFIDES, ORGANO P-S AND P-Se HETEROCYCLES AND ARYLTHIOLATE PHOSPHINE LIGANDS

OOI MEI LEE

THESIS SUBMITTED IN FULFILMENT OF THE REQUIREMENT FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR

2011

ABSTRACT

The reactivity of $[CpM(CO)_3]_2$ (M = Cr (**1**), Mo (**3**)) together with their congeners, $[CpM(CO)_2]_2$ (M = Cr (**2**), Mo (**4**)) towards alkyl sulfides such as bibenzyl di- and trisulfide, organophosphorus chalcogen heterocycles such as 2,4-bis(p-tolylthio)1,3-dithia-2,4-diphosphetane-2,4-disulfide (Davy's reagent), 1,3,2,4-dithiadiphosphetane 2,4-diselenides (Woollins' Reagent) and thioarylphosphines have been investigated. Reactions that occurred under mild conditions for **1** was found to proceed *via* the highly reactive monomer radical, $CpCr(CO)_3$•. However, the reactions with **2** and **4** required more forcing conditions at elevated temperature.

Forty metal complexes were synthesized and characterized in this work. All the products were elucidated *via* IR, ^1H, ^{13}C and ^{31}P NMR, LCMS, elemental analyses and single crystal x-ray diffraction. Mechanistic pathways were proposed for most of the reactions investigated based on evidence obtained from thermolysis, NMR and mass spectra studies. The outcomes of this work are summarized below.

(i) The reaction of **1** with Bz_2S_2 at R.T. gave $[CpCr(CO)_2(SBz)]_2$ (**6**) followed by $[CpCr(CO)_2]_2S$ (**5**) and $[CpCr(SBz)]_2S$ (**7**) as secondary products which undergo complete decarbonylation to give the final thermolyzed product $Cp_4Cr_4S_4$ (**8**). It is postulated that the formation of **6** proceeds *via* the $17e^-$ radical pathway which involves S-S bond cleavage of the ligand.

At elevated temperature, reaction of **4** with Bz_2S_2 gave isomeric *trans-syn* and *trans-anti* $[CpMo(CO)(SBz)]_2$ (**12a**, **b**), $[CpMo(SBz)S]_2$ (**10**) and $[CpMo(CO)(SBz)]_2S$ (**11**) as main products.

(ii) The facile reaction of $[CpCr(CO)_3]_2$ (**1**) with Bz_2S_3 at ambient temperature has led to the isolation of $[CpCr(CO)_2(SBz)]_2$ (**6**) with $[CpCr(SBz)]_2S$ (**7**) as main products. Thermolytic studies showed that **6** underwent complete

decarbonylation to give $[CpCr(SBz)]_2S$ (**7**). Prolonged thermolysis of **6** and **7** led to decomposition which eventually yielded $Cp_4Cr_4S_4$ (**8**).

The reaction of $[CpMo(CO)_3]_2$ (**3**) with Bz_2S_3 at an elevated temperature afforded $[CpMo(CO)_2(SBz)]_2$ (**9**), $[CpMo(CO)(SBz)]_2S$ (**11**), $[CpMo(CO)(SBz)]_2$ (**12**) and $[CpMo(SBz)S]_2$ (**10**). Thermolytic studies showed that **9** underwent stepwise decarbonylation to give **11** and **10**. The totally decarbonylated **10** was isolated as two polymorphs.

(iii) The reaction of **4** with an equivalent of 2,4-bis(p-tolylthio) 1,3-dithia-2,4-diphosphetane-2,4-disulfide (Davy's reagent) led to the isolation of $CpMo(CO)_2(S_2P(SC_6H_4Me)_2)$ (**14**), $Cp_2Mo_2(CO)_5(S_2P(SC_6H_4Me))$ (**15**) and $Cp_2Mo_2(\mu\text{-}S)(\mu\text{-}S_2)(\mu\text{-}SC_6H_4Me)$ (**16**) with yields dependent on reaction conditions. However, reaction of **4** with half an equivalent of Davy's reagent gave $Cp_2Mo_2(CO)_5(S_2P(SC_6H_4Me))$ (**15**), *trans-syn/trans-anti*-isomer of $[CpMo(CO)(SC_6H_4Me)]_2$ (**17**), $Cp_2Mo_2(CO)_2(\mu\text{-}PS)(\mu\text{-}SC_6H_4Me)_2$ (**18**), $[CpMo(CO)_2S]_2$ (**19**) and $Cp_3Mo_3(\mu\text{-}S)_2(\mu\text{-}S_2)(\mu_3\text{-}S)$ (**20**). Thermolytic studies followed by ^{1}H NMR spectroscopy analyses indicated that **14** and **15** had degraded to **16**. The postulated mechanism involves P–S bond cleavage in Davy's reagent leading to a ring opening and desulfurization process.

(iv) The reaction of **1** with 1,3,2,4-dithiadiphosphetane 2,4-diselenides or Woollins' Reagent at ambient temperature gave mainly $[CpCr(CO)_2]_2Se$ (**21**) but with an excess of **1**, *trans*-$[CpCr(CO)_2(SePPh)]_2$ (**22**) was isolated. However thermolytic reaction with the triply bonded congener $Cp_2Cr_2(CO)_4$ (**2**) led to the isolation of *trans*-$[CpCr(CO)_2(SePPh)]_2$ (**22**), $CpCr(CO)_2(SeP(H)Ph)$ (**23**) and $[CpCr(Se_2P(O)Ph)]_2$ (**24**). The ring-opening reaction of Woollins' Reagent *via* an initial homolytic P-Se bond cleavage by $CpCr(CO)_n\cdot$ (n = 2 (**2A**) or 3 (**1A**)) depicts a new approach to coordination chemistry involving P-Se based ligands. The thermolytic reaction of **4** with Woollins' reagent led to the isolation of $[Cp_2Mo_2\{(\mu\text{-}Se)_2(PPh(Se))\}\{(\mu\text{-}Se)(PPh)_3\}]$ (**25**), $Cp_4Mo_4(CO)_3Se_4$ (**26**) and a pair of polymorphic products of $Cp_3Mo_3(CO)_4[Se_3(PPh)_2]$ (**27a**, **b**). A dual pathway *via* the 15 e^- radical, $CpMo(CO)_2\cdot$ and the triply-bonded complex **4**, was indicated.

(v) Reactivity studies of **1** and **3** towards $P(C_6H_4SMe\text{-}p)_3$, $PPh_2(C_6H_4SMe\text{-}o)$, $PPh(C_6H_4SMe\text{-}o)_2$ and $P(C_6H_4SMe\text{-}o)_3$ under varying reaction conditions have led to the isolation of sixteen products. The (P, S) donor ligands of $P(C_6H_4SMe\text{-}p)_3$, $PPh_2(C_6H_4SMe\text{-}o)$, $PPh(C_6H_4SMe\text{-}o)_2$ and $P(C_6H_4SMe\text{-}o)_3$ having one, two and three thiomethylphenyl groups, preferred mono-, bi- and tridentate coordination modes, respectively.

(vi) The facile adduct formation of $[CpCr(SBz)]_2S$ (**7**) and $[CpMo(SBz)(S)]_2$ (**10**) with 2 moles equivalents of $Fe_2(CO)_9$ was found to give both mono- and dimetallated complexes $[Cp_2Cr_2(SBz)]S_2[Fe(CO)_3]$ (**44**), $[CpMo]_2S_4[Fe(CO)_3]_2$ (**45**), $[CpMo]_2S_3[Fe(CO)_3]_2$ (**46**) and $[CpMo(SBz)]_2S_2[Fe(CO)_2]$ (**47**), respectively.

(vii) The thermolytic reaction of $[CpMo(CO)_2(S_2P(SC_6H_4Me)_2)]$ (**14**) with a mole equivalent of **1** gave $[CpMo(CO)_2(\mu\text{-}S)]_2$ (**19**), $[CpMo(CO)(SC_6H_4Me)]_2$ (**17**) $[CpCr(\mu\text{-}SC_6H_4Me)]_2S$ (**48**) and $Cp_4Cr_4S_4$ as products.

ABSTRAK

Kereaktifan $[CpM(CO)_3]_2$ (M = Cr (**1**), Mo (**3**)) bersama-sama dengan kongener mereka, $[CpM(CO)_2]_2$ (M = Cr (**2**), Mo (**4**)) terhadap alkil sulfida seperti bibenzyl di- dan trisulfida, heterosikal kalkogen organofosfat seperti 2,4-bis (p-tolylthio) 1,3-dithia-2,4-diphosphetane-2,4-disulfida (reagen Davy), 1,3,2,4-dithiadiphosphetana 2,4-diselenida (reagen Woollins') dan thioarylfosfine telah diselidik. Tindak balas yang terjadi pada suhu bilik untuk **1** didapati bermula melalui monomer radikal yang sangat reaktif, $CpCr(CO)_3$•. Namun, tindak balas dengan **2** dan **4**, telah dilakukan pada suhu yang lebih tinggi dari biasa.

Empat puluh kompleks logam telah disintesis dan dicirikan dalam penyelidikan ini. Semua produk tersebut telah dikenalpastikan melalui IR, ^{1}H, ^{13}C dan ^{31}P NMR, LCMS, analisis elemental dan kristal tunggal x-ray difraksi. Mekanisma tindak balas telah dicadangkan untuk sebahagian besar tindak balas yang diselidiki dengan bantuan bukti yang diperolehi dari termolisis, NMR dan kajian spektra jisim. Keputusan penyelidikan ini adalah seperti berikut.

(i) Tindak balas **1** dengan Bz_2S_2 pada suhu bilik menghasilkan $[CpCr(CO)_2(SBz)]_2$ (**6**) diikuti oleh $[CpCr(CO)_2]_2S$ (**5**) dan $[CpCr(SBz)]_2S$ (**7**) sebagai hasil sekunder yang mengalami kehilangan karbon dioksida yang lengkap untuk memberi $Cp_4Cr_4S_4$ (**8**) sebagai hasil terakhir daripada proses pemanasan. Dari keputusan ini dicadangkan bahawa pembentukan **6** dimulakan dengan 17e-radikal yang melibatkan pemutusan ikatan S-S dalam ligan.

Pada suhu yang tinggi, **4** bertindak dengan Bz_2S_2 dan memberikan hasil isomerik *trans-syn* serta *trans-anti* $[CpMo(CO)(SBz)]_2$ (**12a, b**), $[CpMo(SBz)S]_2$ (**10**) dan $[CpMo(CO)(SBz)]_2S$ (**11**) sebagai hasil utama.

(ii) Tindak balas yang mudah iaitu antara $[CpCr(CO)_3]_2$ (**1**) dengan Bz_2S_3 pada suhu bilik telah menghasilkan $[CpCr(CO)_2(SBz)]_2$ (**6**) dan $[CpCr(SBz)]_2S$ (**7**) sebagai hasil utama, kedua-duanya telah diasingkan. Kajian pemanasan menunjukkan bahawa **6** mengalami kehilangan karbon dioksida yang lengkap untuk memberikan $[CpCr(SBz)]_2S$ (**7**). Proses pemanasan yang panjang untuk **6** dan **7** menyebabkan penguraian yang akhirnya menghasilkan $Cp_4Cr_4S_4$ (**8**).

Suhu yang lebih tinggi diperlukan untuk tindak balas $[CpMo(CO)_3]_2$ (**3**) dengan Bz_2S_3 untuk menghasilkan $[CpMo(CO)_2(SBz)]_2$ (**9**), $[CpMo(CO)(SBz)]_2S$ (**11**), $[CpMo(CO)(SBz)]_2$ (**12**) and $[CpMo(SBz)S]_2$ (**10**). Kajian termolitik menunjukkan bahawa **9** mengalami kehilangan karbon dioksida secara berperingkat untuk memberikan **11** dan **10**. Kompleks **10** yang telah mengalami kehilangan semua karbon dioksida telah diasingkan sebagai dua polimorf.

(iii) Reaksi **4** dengan 2,4-bis(*p*-tolylthio) 1,3-dithia-2,4-diphosphetane-2,4-disulfida (reagen Davy) yang sama kemolaran telah menghasilkan $CpMo(CO)_2(S_2P(SC_6H_4Me)_2)$ (**14**), $Cp_2Mo_2(CO)_5(S_2P(SC_6H_4Me))$ (**15**) and $Cp_2Mo_2(\mu\text{-}S)(\mu\text{-}S_2)(\mu\text{-}SC_6H_4Me)$ (**16**) dengan peratusan hasil bergantung pada keadaan reaksi. Namun, reaksi **4** dengan 0.5 molar reagen Davy memberikan $Cp_2Mo_2(CO)_5(S_2P(SC_6H_4Me))$ (**15**), *trans-syn/trans-anti*-isomer $[CpMo(CO)(SC_6H_4Me)]_2$ (**17**), $Cp_2Mo_2(CO)_2(\mu\text{-}PS)(\mu\text{-}SC_6H_4Me)_2$ (**18**), $[CpMo(CO)_2S]_2$ (**19**) dan $Cp_3Mo_3(\mu\text{-}S)_2(\mu\text{-}S_2)(\mu_3\text{-}S)$ (**20**). Kajian termolitik yang diikuti dengan ^1H NMR menunjukkan bahawa **14** dan **15** telah bertukar ke **16**. Mekanisme yang dicadangkan melibatkan belahan ikatan P-S dalam reagen Davy diikuti dengan pembukaan gelang dan proses nyah sulfur.

(iv) Tindak balas **1** dengan 1,3,2,4-dithiadiphosphetana2,4-diselenida atau reagen Woollins' pada suhu bilik telah memberikan $[CpCr(CO)_2]_2Se$ (**21**) sebagai hasil utama, tetapi dengan **1** yang berlebihan, *trans*-$[CpCr(CO)_2(SePPh)]_2$ (**22**) telah dihasilkan. Namun, tindak balas pemanasan dengan kongener ikatan ganda tiga, $Cp_2Cr_2(CO)_4$ (**2**) menyebabkan pengasingan *trans*-$[CpCr(CO)_2(SePPh)]_2$ (**22**), $CpCr(CO)_2(SeP(H)Ph)$ (**23**) and $[CpCr(Se_2P(O)Ph)]_2$ (**24**). Tindak balas yang melibatkan pembukaan gelang pada reagen Woollins' dimula oleh $CpCr(CO)_n\cdot$ (n = 2 (**2A**) or 3 (**1A**)) melalui pembelahan ikatan P-Se secara homolitik menggambarkan pendekatan baru untuk kimia koordinatan yang melibatkan ligan jenis P-Se.

Tindak balas termolitik dari **4** dengan reagen Woollins' menyebabkan pengasingan $[Cp_2Mo_2\{(\mu\text{-Se})_2(PPh(Se))\}\{(\mu\text{-Se})(PPh)_3\}]$ (**25**), $Cp_4Mo_4(CO)_3Se_4$ (**26**) dan sepasang produk polimorfik dari $Cp_3Mo_3(CO)_4[Se_3(PPh)_2]$ (**27a**, **b**). Dua lalui melalui 15 e-radikal, $CpMo(CO)_2\cdot$ dan ikatan ganda tiga kompleks **4** telah dikenalpasti.

(v) Kajian kereaktifan **1** dan **3** terhadap $P(C_6H_4SMe\text{-}p)_3$, $PPh_2(C_6H_4SMe\text{-}o)$, $PPh(C_6H_4SMe\text{-}o)_2$ dan $P(C_6H_4SMe\text{-}o)_3$ dalam pelbagai keadaan tindak balas telah menyebabkan pengasingan enam belas produk. Ligan penderma (P, S) seperti $P(C_6H_4SMe\text{-}p)_3$, $PPh_2(C_6H_4SMe\text{-}o)$, $PPh(C_6H_4SMe\text{-}o)_2$ dan $P(C_6H_4SMe\text{-}o)_3$ masing-masing mempunyai satu, dua dan tiga kumpulan tiomethylphenyl, lebih cenderung kepada cara koordinasi dalam mono-, bi- dan tridentate.

(vi) Pembentukan aduk yang mudah dari $[CpCr(SBz)]_2S$ (**7**) dan $[CpMo(SBz)(S)]_2$ (**10**) dengan 2 molar $Fe_2(CO)_9$ yang setara telah dikenalpasti masing-masing untuk memberi mono dan kompleks dwilogam $[Cp_2Cr_2(SBz)]S_2[Fe(CO)_3]$ (**44**),

$[CpMo]_2S_4[Fe(CO)_3]_2$ (**45**), $[CpMo]_2S_3[Fe(CO)_3]_2$ (**46**) dan $[CpMo(SBz)]_2S_2[Fe(CO)_2]$ (**47**).

(vii) Reaksi termolytik dari $[CpMo(CO)_2(S_2P(SC_6H_4Me)_2)]$ (**14**) dengan molar setara **1** memberikan $[CpMo(CO)_2(\mu\text{-}S)]_2$ (**19**), $[CpMo(CO)(SC_6H_4Me)]_2$ (**17**) $[CpCr(\mu\text{-}SC_6H_4Me)]_2S$ (**48**) and $Cp_4Cr_4S_4$ sebagai hasil.

ACKNOWLEDGEMENTS

I wish to express my deepest gratitude and appreciation to Assoc. Prof. Dr. Richard Wong Chee Seng for his inspiring guidance, supervision, invaluable advice and keen interest throughout the course of this study. I would also like to thank my co-supervisor, Prof. Dr. Tan Guan Huat for his advice and guidance especially during the LCMS analysis and his kindness and patience during the final hectic months needed to complete the thesis. Assistance from Prof. Dr. Ng Seik Weng and Prof. Dr. Ward T. Robinson for the X-ray diffraction analyses of most of the complexes, Assoc. Prof. Dr. Noel F. Thomas (advice in proposing certain mechanism), Miss Norzalida Zakaria (NMR spectroscopy analysis) and Mr. Siew Yau Foo (LCMS analysis), respectively, are also gratefully acknowledged.

I would like to sincerely thank my colleague Miss Chan Chun Foong and my juniors Miss Elizabeth Fong Yew Mei, Miss Ngue Chin May, Mr. Ngan Ngui Khiong and Mr. Ang Chun Hui for their advice and support during my study.

I would also like to thank University Of Malaya for granting a tutorship and scholarship (Biasiswazah Tuanku Pro-Cancelor) throughout my study. Research grants from the Academy of Sciences, Malaysia (SAGA), MOSTI (Science Fund) and UMRG (Cluster Fund) are gratefully acknowledged.

Finally, I like to dedicate this work to my ever supportive parents and my siblings.

TABLE OF CONTENTS

CHAPTER III EXPERIMENTAL

LIST OF FIGURES

LIST OF TABLES

Page

LIST OF ABBREVIATIONS

e^-	Electron
σ	Sigma
π	Pi
λ	Lambda (wavelength)
δ	PPM
Ar	Aromatic ring
Bz	Benzyl
Bu^t	*tert*-Butyl
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
Cp'	Methylcyclopentadienyl
Cp''	Ethyltetramethylcyclopentadienyl
C_6D_6	Deuterated benzene-d_6
$C_6D_5CD_3$	Deuterated toluene-d_8
Cosy	Correlation spectroscopy
dppe	1,2-Bis(diphenylphosphino)ethane
Eqn	Equation
ESI	Electrospray ionization
Et	Ethyl
h	Hour
HMBC	Hetero-nuclear multiple-bond connectivity
HMQC	Hetero-nuclear multiple quantum coherence
IR	Infrared spectroscopy

J	Coupling constant
Me	Methyl
LCMS	Liquid chromatography mass spectrometry
Ph	Phenyl
PBu_3	Tributylphosphine
PEt_3	Triethylphosphine
PMe_2Ph	Dimethylphenylphosphine
PPh_2Me	Diphenylmethylphosphine
PPh_3	Triphenylphosphine
$P(OBu)_3$	Tributoxyphosphine
$P(OPh)_3$	Triphenoxyphosphine
^{i}Pr	Isopropyl
THF	Tetrahydrofuran
TLC	Thin layer chromatography
UV	Ultraviolet