ORGANOMETALLIC COMPLEXES FEATURING OLIGO-PHENYLENE ETHYNYLENE LIGANDS

WAN MOHD KHAIRUL WAN MOHAMED ZIN

Ph.D. THESIS 2007

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A Thesis submitted for the degree of Doctor of Philosophy at the Durham University

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To Mek and Wae,

For simply being the most amazing and wonderful people I have ever met in my life….

STATEMENT OF COPYRIGHT

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DECLARATION

The work described in this thesis was carried out in the Department of Chemistry at the University of Durham between October 2004 and August 2007. All the work was carried out by the author unless otherwise stated and has not previously been submitted for a degree at this or any other university.

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Accompanying Compact Disc

Associated .cif files for the molecular structures, extra experimental data, the bond lengths (Å) and angles (°) not discussed in the thesis.

Memorandum

The following conferences and symposia were attended during the period of study

♦ **Materials Chemistry Forum; MC7: Functional Materials for the 21st Century**

University of Edinburgh, UK 5-8th July 2005

♦ **Departmental 2nd Year PG Symposium**

Durham University, Durham, UK 4th May 2006

Talk given entitled. *'Homo and Heterometallic Clusters Complexes Featuring Oligo-Phenylenene Ethynylene As Ligands'*

♦ **Chianti Meeting on Inorganic Electrochemistry**

Certosa di Pontignano, Siena, Italy 15-20th July 2006

Poster Presented entitled. *'Novel Organometallic Complexes Featuring Conjugated Oligo-ethynylbenzene Derivatives As Ligands'.*

♦ **XXII International Conference on Organometallic Chemistry,**

Zaragoza, Spain 23-28th July 2006.

Poster Presented entitled. *'Novel Homo- And Heterometallic Cluster Complexes Featuring Conjugated Oligo-Ethynylbenzene Derivatives As Ligands'.*

♦ **Royal Society Discussion Meeting: Mixed Valency in Chemistry, Physics and Biology.**

Royal Society of Chemistry, Burlington House, London, UK 19-20th March 2007

♦ **Departmental 3rd Year PG Symposium**

Durham University, Durham, UK 5th and 14th May 2007

Poster presented and Talk Given entitled. *'Transition Metal Acetylide Complexes Featuring Oligo-Ethynyl Benzene Derivatives As Ligands'.*

The Following Publications are based on work described on this thesis:

W. M. Khairul, L. Porrès, D. Albesa-Jové, M. S. Senn, M. Jones, D. P. Lydon, J. A. K. Howard, A. Beeby, T. B. Marder, P. J. Low, **'Metal-Terminated Molecular Wires'**, *Journal of Cluster Chemistry*, 2006, **17**, 65.

M. A. Fox, R. L. Roberts, W. M. Khairul, F. Hartl, P. J. Low, **'Spectroscopic properties and electronic structure of 17-electron half-sandwich monoruthenium acetylide complexes, $[Ru(C{\equiv}CAr)(L_2)Cp']^+$ (Ar = phenyl, p-tolyl, 1-naphthyl, 9-anthryl; $L_2 = (PPh_3)_2$, Cp' = Cp; L_2 = dppe; Cp' = Cp*)'**, *Journal of Organometallic Chemistry*, 2007, **692**, 3277.

W. M. Khairul, D. Albesa-Jové, D. S. Yufit, M. R. Al-Haddad, J. C. Collings, F. Hartl, J. A. K. Howard, T. B. Marder, P. J. Low, **'The syntheses, structures and redox properties of phosphine-gold(I) and triruthenium carbonyl cluster derivatives of tolans'**, *Inorganica Chimica Acta*, 2007, article in press.

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TABLE of CONTENTS

CHAPTER 3

'Synthesis and Structural Characterisation of Gold(I) Oligo-phenylene ethynylene Complexes'

CHAPTER 4

'Synthesis, Structural and Electronic Properties of Half-Sandwich Ruthenium Oligo-Phenylene Ethynylene Complexes'

CHAPTER 6

Novel Transmetallations From Simple Gold(I) Acetylide Moieties'

CHAPTER 7

Conclusions and Future Work

Abstract

Organometallic Complexes Featuring Oligo-Phenylene Ethynylene Ligands

Wan Mohd Khairul Wan Mohamed Zin

Durham University, 2007

This thesis describes the synthesis and analysis of organometallic complexes that feature oligo-phenylene ethynylene based ligands. **Chapter 1** introduces the general topic of molecular electronics and provides a general overview of the interest in phenylene ethynylene systems as foundation architectures for molecular wires. The role of metal complexes in molecular electronics and the application of the cluster - surface analogy to the study of model systems is also described.

Chapter 2 describes the synthesis of oligo-phenylene ethynylene pro-ligands of the general form $Me_3SiC{\equiv}CC_6H_4C{\equiv}CC_6H_4R$ (**1-5**), in which R is either an electron donor (Me, OMe) or acceptor (CO_2Me, NO_2, CN). The compounds were synthesised either *via* Sonogashira Pd/Cu cross-coupling reactions or *via* the nucleophilic attack of benzoquinones by lithiated acetylide anions and subsequent reduction. The desilylation of these compounds afforded the terminal alkynes $HC{\equiv}CC_6H_4C{\equiv}CC_6H_4R$ (**6-10**). Furthermore, the extended "three-ring" 1,4-bis(phenyl ethynylbenzene) derivatives $Me_3SiC{\equiv}CC_6H_4C{\equiv}CC_6H_4C{\equiv}C_6H_4C{\equiv}CSiMe_3$, **11** and $Me_3SiC{\equiv}CC_6H_4C{\equiv}CC_6(OMe)_2(H)_2C{\equiv}C_6H_4C{\equiv}CSiMe_3$, **13** and the terminal alkyne $HC{\equiv}CC_6H_4C{\equiv}CC_6(OMe)_2(H)_2C{\equiv}C_6H_4C{\equiv}CH$, (**14**) have also been prepared. These compounds were fully spectroscopically characterised and in the case of **14** the molecular structure analysis is discussed.

Chapter 3 discusses the synthesis of the gold(I) oligo-phenylene ethynylene complexes The complexes were prepared by treating the ligands precursors **1-5** with $AuCl(PL_3)$ (L = Ph or Cy) in the presence of NaOMe to afford complexes $Au(C{\equiv}CC_6H_4C{\equiv}CC_6H_4R)PPh_3$ [R = Me (**15**), **OMe** (**16**), CO_2Me (**17**), NO_2 (**18**) and

CN (**19**) and $Au(C{\equiv}CC_6H_4C{\equiv}CC_6H_4R)PCy_3$ [R = Me (**20**), OMe (**21**) and NO_2 (**22**)]. The "three-ring" complexes $\{Au(PPh_3)\}_2(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}CC_6H_4C{\equiv}C_6H_4C{\equiv}C)$, **23** and $\{Au(PPh_3)\}_2(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}CC_6(OMe)_2H_2C{\equiv}C_6H_4C{\equiv}C)$, **24** were also prepared. These complexes were spectroscopically characterised and molecular structural analyses reveal intermolecular interactions between the phenylene ethynylene portion of the molecules in the solid state, but not aurophilic interactions.

Chapter 4 examines the synthesis of half-sandwich $Ru(L_2)Cp'$ [$L = PPh_3$, Cp' = Cp ; L_2 = dppe, Cp' = Cp*) acetylide complexes derived from simple phenyl, tolan and oligo(phenylene ethynylene) based acetylenes. The electrochemical properties of these complexes have been explored, as have some of the molecular structural details.

Chapter 5 describes the synthesis of some cluster complexes. The gold acetylide complexes $Au(C{\equiv}CC_6H_4C{\equiv}CC_6H_4R)(PPh_3)$ react readily with $Ru_3(CO)_{10}(\mu\text{-dppm})$ to afford phenylene ethynylene derivatives $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}C_2C_6H_4C{\equiv}CC_6H_4\text{-}R)(\mu\text{-dppm})(CO)_7$ (**38-42**) in which the conjugated organic moiety is "end-capped" by the cluster and an R group that is either electron donating or withdrawing (R = Me, OMe, CO_2Me, NO_2, CN). The clusters **38-42** are linked to the hydrido clusters $Ru_3(\mu\text{-}H)(\mu\text{-}C_2C_6H_4C{\equiv}CC_6H_4R)(CO)_7$ (**36** and **37**) through the well-known isolobal relationship between H and $Au(PR_3)$. In addition, the bis-cluster $\{Ru_3(\mu\text{-dppm})(CO)_7\}_2\{(\mu\text{-}AuPPh_3)\}_2(\mu\text{-}C_2C_6H_4C{\equiv}CC_6H_4C{\equiv}CC_6H_4C_2)$ (**43**) has also been prepared. All the clusters reported in this chapter were crystallographically determined. Structural, spectroscopic, photophysical and electrochemical studies were conducted and have revealed little electronic interaction between the remote substituent and the organometallic end-caps.

Chapter 6 explores the novel, preparative scale stoichiometric transmetallation reactions involving the simple $Au(C{\equiv}CR)(PPh_3)$ (R = Ph or C_6H_4Me) complexes. These gold(I) complexes have been treated with several inorganic and organometallic compounds MXL_n [M = metal, L_n = supporting ligands, X = halide], to afforded the corresponding metal-acetylide complexes $M(C{\equiv}CR)L_n$, with

representative examples featuring metals from Groups *8-11*. The acetylide products were fully characterised by usual spectroscopic methods including the molecular structural analysis.

Chapter 7 concludes the general summary of the thesis and discusses briefly the findings achieved in each chapter and the vital role of oligo-phenyelene ethynylenes ligands in the construction of numerous organometallic complexes which show interesting and promising properties for the molecular wires development. In addition, further future work is also proposed on other systems that feature this ligands.