

ORGANOMETALLIC COMPLEXES FEATURING
OLIGO-PHENYLENE ETHYNYLENE LIGANDS

WAN MOHD KHAIROL WAN MOHAMED ZIN

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OLIGO-PHENYLENE ETHYNYLENE LIGANDS**

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To Mek and Wae,

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

DECLARATION

The work described in this thesis was carried out in the Department of Chemistry at the University of Oxford 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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• Paper presented entitled "New Organic Electrochromic Polymers: Synthesis, Characterisation and Application" during "Advanced in Organic Chemistry"

• XXV International Conference on Organometallic Chemistry,
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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, $[\text{Ru}(\text{C}\equiv\text{C}\text{Ar})(\text{L}_2)\text{Cp}'^+]^+$ (Ar = phenyl, p-tolyl, 1-naphthyl, 9-anthryl; $\text{L}_2 = (\text{PPh}_3)_2$, $\text{Cp}' = \text{Cp}$; $\text{L}_2 = \text{dppe}$; $\text{Cp}' = \text{Cp}^*$)**', *Journal of Organometallic Chemistry*, 2007, **692**, 3277.

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Abstract

Organometallic Complexes Featuring Oligo-Phenylene Ethynylene Ligands

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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 $\text{Me}_3\text{SiC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{R}$ (**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 $\text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{R}$ (**6-10**). Furthermore, the extended “three-ring” 1,4-bis(phenyl ethynyl)benzene derivatives $\text{Me}_3\text{SiC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C}_6\text{H}_4\text{C}\equiv\text{CSiMe}_3$, **11** and $\text{Me}_3\text{SiC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6(\text{OMe})_2(\text{H})_2\text{C}\equiv\text{C}_6\text{H}_4\text{C}\equiv\text{CSiMe}_3$, **13** and the terminal alkyne $\text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6(\text{OMe})_2(\text{H})_2\text{C}\equiv\text{C}_6\text{H}_4\text{C}\equiv\text{CH}$, (**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 $\text{AuCl}(\text{PL}_3)$ (L = Ph or Cy) in the presence of NaOMe to afford complexes $\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{R})\text{PPh}_3$ [R = Me (**15**), OMe (**16**), CO_2Me (**17**), NO_2 (**18**) and

CN (**19**) and $\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{R})\text{PCy}_3$ [$\text{R} = \text{Me}$ (**20**), OMe (**21**) and NO_2 (**22**)]. The “three-ring” complexes $\{\text{Au}(\text{PPh}_3)\}_2(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C}_6\text{H}_4\text{C}\equiv\text{C})$, **23** and $\{\text{Au}(\text{PPh}_3)\}_2(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6(\text{OMe})_2\text{H}_2\text{C}\equiv\text{C}_6\text{H}_4\text{C}\equiv\text{C})$, **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 $\text{Ru}(\text{L}_2)\text{Cp}'$ [$\text{L} = \text{PPh}_3$, $\text{Cp}' = \text{Cp}$; $\text{L}_2 = \text{dppe}$, $\text{Cp}' = \text{Cp}^*$] 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 $\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{R})(\text{PPh}_3)$ react readily with $\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})$ to afford phenylene ethynylene derivatives $\text{Ru}_3(\mu\text{-AuPPh}_3)(\mu\text{-C}_2\text{C}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{-R})(\mu\text{-dppm})(\text{CO})_7$ (**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 ($\text{R} = \text{Me}$, OMe , CO_2Me , NO_2 , CN). The clusters **38-42** are linked to the hydrido clusters $\text{Ru}_3(\mu\text{-H})(\mu\text{-C}_2\text{C}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{R})(\text{CO})_7$ (**36** and **37**) through the well-known isolobal relationship between H and $\text{Au}(\text{PR}_3)$. In addition, the bis-cluster $\{\text{Ru}_3(\mu\text{-dppm})(\text{CO})_7\}_2\{(\mu\text{-AuPPh}_3)\}_2(\mu\text{-C}_2\text{C}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{C}_2)$ (**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 $\text{Au}(\text{C}\equiv\text{CR})(\text{PPh}_3)$ ($\text{R} = \text{Ph}$ or $\text{C}_6\text{H}_4\text{Me}$) complexes. These gold(I) complexes have been treated with several inorganic and organometallic compounds MXL_n [$\text{M} = \text{metal}$, $\text{L}_n = \text{supporting ligands}$, $\text{X} = \text{halide}$], to afford the corresponding metal-acetylide complexes $\text{M}(\text{C}\equiv\text{CR})\text{L}_n$, 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-phenylene ethynylene 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.