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Department of Chemistry



**THE UNIVERSITY
OF ADELAIDE**
AUSTRALIA

FROM TWO AND BEYOND!

**Synthesis and Chemistry of
Group 8 Alkynyl Complexes**

A Thesis Submitted Towards the Degree of Doctor of Philosophy.

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Abstract.

Chapter One gives an introduction to the history of molecular electronics and its importance in future electronic devices. A brief overview of the four classes of transition metal complexes as possible models for molecular wires, and the three most common methods of evaluating these complexes is given. This thesis furthers the work in Group 8 transition metal yndiyl and poly-yndiyl complexes with particular interest in their potential as models for molecular wires.

Chapter Two describes the synthesis of three diyndiyl complexes $\text{Cp}^*(\text{dppe})\text{OsC}\equiv\text{CC}\equiv\text{CM}(\text{dppe})\text{Cp}^*$ (where $M = \text{Fe}, \text{Ru}, \text{Os}$) along with the mono- and di-cations of $\{\text{Cp}^*(\text{dppe})\text{Os}\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})$. Detailed examination of the electrochemistry of these complexes revealed the expected three or four one-electron oxidation steps. These redox events for osmium occur at intermediate values compared to other symmetrical Group 8 complexes, while those mixed complexes appear at intermediate values to the two corresponding symmetrical complexes.

Chapter Three summarises the syntheses of several yndiyl complexes of the general formula $\text{Cp}(\text{dppe})\text{RuC}_2\text{M}(\text{dppe})\text{Cp}'$, prepared from $[\text{Cp}'(\text{dppe})\text{M}=\text{C}=\text{CH}_2][\text{PF}_6]$ (where $M = \text{Fe}, \text{Ru}, \text{Os}$ and $\text{Cp}' = \text{Cp}, \text{Cp}^*$), and $\text{RuCl}(\text{dppe})\text{Cp}$. Double deprotonation of $[\text{Cp}'(\text{dppe})\text{M}=\text{C}=\text{CH}_2][\text{PF}_6]$ with $n\text{BuLi}$ yields the lithium salt $\text{Cp}'(\text{dppe})\text{MC}\equiv\text{CLi}$, which can be further reacted with the ruthenium tetrahydrofuran cation to give the desired yndiyl complex. The electrochemistry of these complexes demonstrates the subtle variations in the three group 8 metals. Detailed examination of the metal-metal interactions also allows comparisons to be drawn about the effect of chain length on these interactions.

Chapter Four details the synthesis of several compounds containing the anthracene moiety. Starting from either $\text{TMSC}\equiv\text{CC}_{14}\text{H}_8\text{C}\equiv\text{CTMS}$ or $\text{Cp}^*(\text{dppe})\text{FeC}\equiv\text{CC}_{14}\text{H}_8\text{C}\equiv\text{CTIPS}$, treatment with $\text{RuCl}(\text{dppe})\text{Cp}^*$ in the presence of a desilylating reagent gives the symmetrical or asymmetric complexes $\text{Cp}^*(\text{dppe})\text{RuC}\equiv\text{CC}_{14}\text{H}_8\text{C}\equiv\text{CM}(\text{dppe})\text{Cp}^*$

(where M = Ru, Fe). An NMR study of the derived di-cations revealed that there is no singlet-triplet state interconversion as demonstrated by the diamagnetic nature of the ^1H NMR. Also reported are the syntheses of several anthracene compounds en-route to the synthesis of an organo-iron complex with a possible trapped singlet state.

Chapter Five summarises some reactions of two yndiyl complexes, $\text{OsC}\equiv\text{Cfc}(\text{dppe})\text{Cp}$ and $1,1'\text{-}\{\text{Cp}[m\text{-tol}_3\text{P}]_2\text{RuC}\equiv\text{C}\}_2\text{Rc}'$. A detailed electrochemical study of the parent complexes revealed that the ferroceneayl and ruthenoceneayl moieties act as insulators to the metal-metal interactions observed in the straight chain diyndiyl complexes. Treatment of $\text{OsC}\equiv\text{Cfc}(\text{dppe})\text{Cp}$ with TCNE resulted in addition of the electron-poor alkene across the electron-rich triple bond. The same reaction with $1,1'\text{-}(\text{Cp}[m\text{-tol}_3\text{P}]_2\text{RuC}\equiv\text{C})_2\text{Rc}'$ resulted in a similar addition across the electron-rich triple bond together with displacement of one *m*-tol₃P ligand.

Chapter Six describes the synthesis of several osmium organometallic starting materials. Previously these starting materials have been synthesised from the extremely toxic osmium tetroxide. Starting from the stable potassium osmate, treatment with concentrated hydrochloric acid gives $\text{K}_2[\text{OsCl}_6]$. This material can be easily reduced in the presence of triphenylphosphine and then further reacted with LiCp to give $\text{OsCl}(\text{PPh}_3)_2\text{Cp}$. This starting material undergoes a ready ligand exchange with bis(diphenylphosphino)ethane to yield the desired starting material $\text{OsCl}(\text{dppe})\text{Cp}$. Treatment of $\text{K}_2[\text{OsCl}_6]$ with pentamethylcyclopentadiene and then further with 1,5-cyclooctadiene yields $\text{OsCl}(\text{COD})\text{Cp}^*$. This complex also undergoes ready ligand exchange with bis(diphenylphosphino)ethane to give the desired $\text{OsCl}(\text{dppe})\text{Cp}^*$. The electrochemistry of these two complexes reveals lower first oxidation potentials when compared to both ruthenium analogues. X-ray crystal structure determinations are also reported for both of these novel starting materials. This chapter also summarises the advantages of using alcohol solvents in the synthesis of several known and novel organometallic vinylidene complexes.