

Some Chemistry of Metal Alkynyls: Formation of Odd and Even Bridging Carbon Chains

by

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B.Sc. (Hons)

A Thesis Submitted Towards the Degree of Doctor of Philosophy



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December 2006

Statement of Originality

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university and to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference is given.

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Abstract

This thesis continues the study into the synthesis and analysis of metal poly-yndiyl complexes. These molecules have shown promise as model molecular wires. Chapter one provides a general overview of the interest in carbon based molecules and introduces the need for molecular electronics. Some of the most promising classes of molecular wires are described before outlining the methods of evaluation.

Chapter two describes the synthesis of some extended chain complexes containing five or more alkynyl linkages. Several different methodologies that can be used to synthesise poly-yndiyl complexes are discussed with a gold coupling reaction providing a new and very useful route to complexes with extended carbon chains. Variations of this methodology allow for the formation of complexes containing either an even or an odd number of alkynyl linkages within the chain. The electrochemical effects of increasing chain length within the series, $\{\text{Cp}^*(\text{dppe})\text{Ru}\}_2(\text{C}\equiv\text{C})_n$ ($n = 1 - 10$), is examined.

Chapter three discusses the synthesis of some novel odd-membered carbon chains. Single-crystal X-ray structure determinations are reported for many of the complexes. The reactions described significantly add to the series of complexes containing the $\text{Tp}'\text{M}(\text{CO})_2$ group ($\text{Tp}' = \text{Tp}, \text{Tp}^*$; $\text{M} = \text{Mo}, \text{W}$) end-capping a carbon chain, with examples containing three, four, five and seven carbons within the chain having been obtained. Some interesting cluster-capped, even-numbered carbon chains are also described, formed by linking of the well-known carbon-tricobalt complex with the Group 6 precursors by means of the $\text{AuX}(\text{PR}_3)$ elimination reaction. The electrochemistry of each of these complexes is examined and comparisons made with similar measurements carried out on the individual end-caps.

Chapter four discusses the synthesis and electrochemistry of carbon chain complexes containing the 1,4-diethynylbenzene or 1,4-diethynyltetrafluorobenzene linkers. Comparisons on the electrochemical effects of these two linkers and polyynyl bridges of similar length are discussed. A convenient synthetic route to the organic

compounds 1,4-bis(butadiynyl)benzene and 4-(butadiynyl)phenylethyne compounds via the gold coupling reaction is also described.

Chapter five examines the synthesis of some cluster complexes. A number of new gold containing cluster complexes are prepared from the reaction of gold alkynyl complexes, $M-(C\equiv C)-AuPPh_3$, with the activated ruthenium carbonyl, $Ru_3(CO)_{10}(NCMe)_2$. The adducts which result from the treatment of $\{Tp(CO)_2Mo\}\equiv CC\equiv CSiMe_3$ with the cobalt carbonyl reagents $Co_2(CO)_8$ and $Co_2(CO)_6(dppm)$ are also described along with the formation of the mixed metal cluster complexes $MoRu_2(CCCH_3)(CO)_8Tp$ and $MoFe_2(CCCH_3)(CO)_8Tp$.

Abbreviations

General:

| | |
|-----------------|--|
| [M] | general metal-ligand fragment |
| ° | degrees |
| °C | degrees Celsius |
| Å | angstrom |
| Ac | acyl, -COCH ₃ |
| anal. | analysis |
| ap | 2-anilinopyridinate |
| Atm | atmosphere |
| av. | average |
| Bu ⁿ | normal butyl, -(CH ₂) ₃ CH ₃ |
| Bu ^t | tertiary butyl, -C(CH ₃) ₃ |
| calcd | calculated |
| cm | centimetres |
| Cp | cyclopentadienyl |
| Cp* | pentamethylcyclopentadienyl |
| dbu | 1,8-diazabicyclo[5.4.0]undec-7-ene |
| depe | 1,2-bis(diethylphosphino)ethane |
| DF | density-functional |
| dippe | 1,2-bis(diisopropylphosphino)ethane |
| DMF | <i>N, N</i> -dimethylformamide |
| dmpe | 1,2-bis(dimethylphosphino)ethane |
| dmpz | 3,5-dimethylpyrazolyl |
| dppe | 1,2-bis(diphenylphosphino)ethane |
| dppm | bis(diphenylphosphino)methane |
| e ⁻ | Electron |
| eq | equivalents |
| Et | ethyl, -CH ₂ CH ₃ |
| EtOH | Ethanol |
| eV | electron volts |
| h | hour(s) |
| HOMO | highest occupied molecular orbital |
| IR | Infrared |
| J | Joules |
| K | Kelvin |
| K _{eq} | equilibrium constant |
| LUMO | lowest unoccupied molecular orbital |
| M | Molarity |

| | |
|-----------------|--|
| Me | methyl, -CH ₃ |
| MeOH | Methanol |
| mg | milligrams |
| MHz | megahertz |
| min | Minutes |
| mL | Millilitres |
| mm | millimetres |
| mmol | millimoles |
| MO | Molecular orbital |
| MV | mixed-valence |
| NIR | near-infrared |
| nm | nanometres |
| NMR | nuclear magnetic resonance |
| Nu | nucleophile |
| OPE | oligophenylethyne |
| ORTEP | Oak Ridge Thermal Ellipsoid Plot program |
| PCC | pyridinium chlorochromate |
| Ph | phenyl, -C ₆ H ₅ |
| PP | bis-phosphine |
| Pr ⁱ | isopropyl, -CH(CH ₃) ₂ |
| pz | Pyrazol-1-yl |
| R | general organic group |
| r.t. | room temperature |
| Ref | Reference |
| R _f | retention factor |
| s | Seconds |
| SAM | self-assembled monolayer |
| STM | scanning tunnelling microscope |
| SWCNT | single-walled carbon nanotube |
| T | temperature (K) |
| TCNE | tetracyanoethylene |
| thf | tetrahydrofuran |
| t.l.c. | thin layer chromatography |
| tmeda | tetramethylethylenediamine |
| TMS | trimethylsilyl, Si(CH ₃) ₃ |
| tol | <i>para</i> -tolyl, -C ₆ H ₄ CH ₃ |
| Tp | hydrotris(pyrazolyl)borate |
| Tp* | hydrotris(3,5-dimethylpyrazolyl)borate, HB(dmpz) ₃ |
| UV | ultraviolet |
| Vis | visible |
| X | halide |

ΔG_{th} thermal activation barrier

NMR:

d doublet
 Hz hertz
 m multiplet
 ${}^n J_{IJ}$ n bond coupling constant between nuclei I and J
 ppm parts per million
 s singlet
 t triplet
 tt triplet of triplets
 δ chemical shift

IR:

br broad
 cm^{-1} wavenumbers (reciprocal centimetres)
 m medium
 s strong
 sh shoulder
 w weak

Mass Spectroscopy:

CID collision-induced dissociation
 ES electrospray
 FAB fast atom bombardment
 M molecular ion
 m/z mass per unit charge
 MS-MS mass spectrometry-mass spectrometry

UV/Vis/NIR:

$(\Delta v_{1/2})_{\text{theo}}$ calculated band-width at half-height
 Abs absorbance
 IL intraligand
 IVCT intervalence charge transfer
 LMCT ligand-to-metal charge transfer
 MLCT metal-to-ligand charge transfer
 V_{ab} electronic coupling parameter

| | |
|------------------|------------------------------------|
| $\Delta v_{1/2}$ | observed band-width at half-height |
| ε | extinction coefficient |
| λ | wavelength |

Electrochemistry:

| | |
|------------|--|
| A | amperes |
| CE | counter electrode |
| E | potential |
| E_n | potential of n^{th} redox process |
| $E_{1/2}$ | half-wave potential |
| E_a | anodic potential |
| E_c | cathodic potential |
| I | current |
| i_a | anodic peak current |
| i_c | cathodic peak current |
| irr. | irreversible |
| K_c | comproportionation constant |
| V | volts |
| ΔE | potential difference |

Acknowledgments

Firstly I would like to thank my supervisor Professor Michael Bruce for both the opportunity to work in his lab and all of his help throughout my PhD. He has provided me with not only an interesting and enjoyable project but also a very pleasant working environment for the past four years. I am also very grateful for the help of my co-supervisor Dr Marcus Cole. To Professor Allan White and Dr Brian Skelton a big thankyou for their crystallography works.

I would also like to thank Professor Brian Nicholson for running many of my mass spectra as well as enabling me to spend a month at The University of Waikato, Hamilton, New Zealand, learning to use the mass spectrometers. I thoroughly enjoyed the opportunity to work as a part of your group and learn new techniques.

To the many members of labs 9 and 10, who have come and gone over the years, I would like to say thankyou for the laughs in addition to all of the technical advice. I would especially like to acknowledge Dr Benjamin Ellis for his enthusiastic introduction to organometallic chemistry, Dr Natasha Zaitseva for teaching me all that I know about growing crystals and Dr Benjamin Hall for reading and editing this Thesis.

I would also like to thank my family and friends for their unwavering support over my years of study. To my parents, a special thankyou for their support and motivation throughout my PhD. Finally I must thank Brett for his patience and understanding without which I could never have made it this far.