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

by
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AUSTRALIA

Department of Chemistry
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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.

I give consent to this thesis being made available for photocopy or loan.

Maryka Gaudio
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Abstract

This thesis continues the study into the synthesis and analysis of metal poly-yndiyli 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-yndiyli 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, \{Cp*(dppe)Ru\}_2(C≡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 Tp’M(CO)\_2 group (Tp’ = Tp, Tp*; M = Mo, 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 AuX(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≡C)-AuPPh3, with the activated ruthenium carbonyl, Ru3(CO)10(NCMe)2. The adducts which result from the treatment of \{Tp(CO)2Mo\}≡CC≡CSiMe3 with the cobalt carbonyl reagents Co2(CO)8 and Co2(CO)6(dppm) are also described along with the formation of the mixed metal cluster complexes MoRu2(CCCH3)(CO)8Tp and MoFe2(CCCH3)(CO)8Tp.
### Abbreviations

**General:**

- **[M]** general metal-ligand fragment
- ° degrees
- °C degrees Celsius
- Å angstrom
- Ac acyl, -COCH₃
- anal. analysis
- ap 2-anilinopyridinate
- Atm atmosphere
- av. average
- Buⁿ normal butyl, -(CH₂)₃CH₃
- Buᵀ tertiary butyl, -C(CH₃)₃
- calcd calculated
- cm centimetres
- Cp cyclopentadienyl
- Cp* pentamethycyclopentadienyl
- 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 N,N-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, -CH₂CH₃
- 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
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>Me</td>
<td>methyl, -CH₃</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>mg</td>
<td>milligrams</td>
</tr>
<tr>
<td>MHz</td>
<td>megahertz</td>
</tr>
<tr>
<td>min</td>
<td>Minutes</td>
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<td>mL</td>
<td>Millilitres</td>
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<td>mm</td>
<td>millimetres</td>
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<tr>
<td>mmol</td>
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<tr>
<td>MO</td>
<td>Molecular orbital</td>
</tr>
<tr>
<td>MV</td>
<td>mixed-valence</td>
</tr>
<tr>
<td>NIR</td>
<td>near-infrared</td>
</tr>
<tr>
<td>nm</td>
<td>nanometres</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>Nu</td>
<td>nucleophile</td>
</tr>
<tr>
<td>OPE</td>
<td>oligophenylethyne</td>
</tr>
<tr>
<td>ORTEP</td>
<td>Oak Ridge Thermal Ellipsoid Plot program</td>
</tr>
<tr>
<td>PCC</td>
<td>pyridinium chlorochromate</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl, -C₆H₅</td>
</tr>
<tr>
<td>PP</td>
<td>bis-phosphine</td>
</tr>
<tr>
<td>Pr</td>
<td>isopropyl, -CH(CH₃)₂</td>
</tr>
<tr>
<td>pz</td>
<td>Pyrazol-1-yl</td>
</tr>
<tr>
<td>R</td>
<td>general organic group</td>
</tr>
<tr>
<td>r.t.</td>
<td>room temperature</td>
</tr>
<tr>
<td>Ref</td>
<td>Reference</td>
</tr>
<tr>
<td>Rᶠ</td>
<td>retention factor</td>
</tr>
<tr>
<td>s</td>
<td>Seconds</td>
</tr>
<tr>
<td>SAM</td>
<td>self-assembled monolayer</td>
</tr>
<tr>
<td>STM</td>
<td>scanning tunnelling microscope</td>
</tr>
<tr>
<td>SWCNT</td>
<td>single-walled carbon nanotube</td>
</tr>
<tr>
<td>T</td>
<td>temperature (K)</td>
</tr>
<tr>
<td>TCNE</td>
<td>tetracyanoethylene</td>
</tr>
<tr>
<td>thf</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>t.l.c.</td>
<td>thin layer chromatography</td>
</tr>
<tr>
<td>tmeda</td>
<td>tetramethylethylenediamine</td>
</tr>
<tr>
<td>TMS</td>
<td>trimethylsilyl, Si(CH₃)₃</td>
</tr>
<tr>
<td>tol</td>
<td>para-tolyl, -C₆H₄CH₃</td>
</tr>
<tr>
<td>Tp</td>
<td>hydrotris(pyrazolyl)borate</td>
</tr>
<tr>
<td>Tp*</td>
<td>hydrotris(3,5-dimethylpyrazolyl)borate, HB(dmpz)₃</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>Vis</td>
<td>visible</td>
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<tr>
<td>X</td>
<td>halide</td>
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\[ \Delta G_{th} \] thermal activation barrier

**NMR:**

d doublet
Hz hertz
m multiplet
\[ nJ_{IJ} \] n bound coupling constant between nuclei I and J
ppm parts per million
s singlet
t triplet
tt triplet of triplets
\( \delta \) chemical shift

**IR:**

br broad
\( \text{cm}^{-1} \) 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:**

\( (\Delta \nu_{1/2})_{\text{theo}} \) 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
\[ \Delta \nu_{1/2} \quad \text{observed band-width at half-height} \]
\[
\varepsilon \quad \text{extinction coefficient} \\
\lambda \quad \text{wavelength} \\

\textbf{Electrochemistry:}

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

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