New Methods for the Synthesis of Diynyl, Diyndiyl and Bis(diyndiyl) Ruthenium(II) Complexes

A Thesis Submitted Towards the Degree of Doctor of Philosophy

By

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B.Sc. (Hons)

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Abstract

Chapter One outlines the different methods described in the literature for the synthesis of diynyl, symmetric and asymmetric diyndiyl complexes. The extension to complexes containing a central bridging group within the carbon chain is also introduced with the description of two different linking groups, either an organic or organometallic moiety. A brief overview of molecular electronics and one method of evaluation of electronic communication, cyclic voltammetry, are also addressed.

Chapter Two describes the synthesis of novel symmetric and asymmetric bis(diynyl) ruthenium(II) complexes of general formula \{L_n M\}-C≡CC≡C-\{M"L"_p\}-C≡CC≡C-\{M'L'_{m}\}, featuring two transition metal fragments linked by either a Ru(dppe)_2 moiety or a trinuclear copper(I) or silver(I) cluster M_3(\mu-dppm)_3 (M = Cu, Ag). Through the use of cyclic voltammetry, it was shown that the inclusion of these three particular bridging groups allows electronic communication between the two terminal end-groups. The chemistry of the starting material \textit{trans}-Ru(C_8H_2)(dppe)_2 (1) is also described, forming novel complexes when reacted with AuCl(PPh_3) or TCNE.

Chapter Three describes a new convenient synthetic route to diynyl and diyndiyl ruthenium(II) complexes. Lithiation of the ruthenium(II) diynyl complexes Ru(C≡CC≡CH)(dppe)Cp* and Ru(C≡CC≡CH)(PPh_3)_2Cp with \textit{n}-BuLi yields the lithium complexes Ru(C≡CC≡CLi)(dppe)Cp* and Ru(C≡CC≡CLi)(PPh_3)_2Cp. The most favorable conditions for their formation are examined by using NMR spectroscopy and different assay reactions. These lithium species are further reacted with a range of metal halides to give new asymmetric diyndiyl complexes of general formula [Ru](C≡CC≡C){ML_n} (where [Ru] = Ru(dppe)Cp*, Ru(PPh_3)_2Cp).
Chapter Four investigates the reactivity of the novel lithium complex Ru(C≡C≡CLi)(dppe)Cp* synthesised in Chapter Three. The nucleophilic nature of this complex is assessed with a range of electrophiles such as organic substrates or polyfluoroaromatic compounds. A number of new complexes are prepared and single-crystal X-ray structure determinations are reported for many of the complexes. The electrochemistry of some of these complexes is also described.

Chapter Five summarises the reactions of diynyl ruthenium(II) complexes Ru(C≡C≡CR)(dppe)Cp* (where R = H, TMS, Au(PPh₃)) with three azide reagents TMSN₃, TsN₃ and AuN₃(PPh₃). The reactions are suggested to undergo a Huisgen 1,3-alkyne-azide cycloaddition to generate 1,2,3-triazoles which further react to give the various products. The complexes synthesised are characterised by spectroscopic methods and, where possible, by X-ray structure determination. Furthermore, the reactions of the complexes Ru(C≡CC≡CH)(PPh₃)₂Cp and Ru(C≡CH)(dppe)Cp* with azides to give the ruthenium azido complexes [Ru]N₃ (where [Ru] = Ru(PPh₃)₂Cp, Ru(dppe)Cp*) are described.
Declaration

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, contains no material previously published or written by another person except where due reference has been made.

I give consent for this thesis to be made available for photocopying and loan if applicable.

Nancy Scoleri

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Abbreviations

General:

° Degrees
°C Degrees Celsius
Å Ångstrom
anal. Analysis
Acac Acetylacetonate
av. Average
Bpy 2,2’-bipyridyl
Bu Butyl
ca Approximately
Calcd Calculated
cm Centimetres
Cp Cyclopentadienyl
Cp* Pentamethylcyclopentadienyl
Cy Cyclohexyl
dbu 1,8-diazabicyclo[5.4.0]undec-7-ene
DFT Density-functional theory
dippe 1,2-bis(diisopropylphosphino)ethane
dmpe 1,2-bis(dimethylphosphino)ethane
dppe 1,2-bis(diphenylphosphino)ethane
dppm Bis(diphenylphosphino)methane
e− Electron
EH Extended Hückel theory
eq Equivalent
ESR Electron spin resonance
Et Ethyl, -CH₂CH₃
Et₂O Diethyl ether
EtOH Ethanol
eV Electron volts
Fc Ferrocenyl
FMO Frontier molecular orbital
g Gram
h Hour(s)
HOMO Highest occupied molecular orbital
IR Infrared
LDA Lithium Diisopropylamide, LiNPr₂
LUMO Lowest unoccupied molecular orbital
Me Methyl, CH₃
MeLi          Methyl lithium
MeOH         Methanol
mg           Milligrams
min          Minutes
MLn          General metal-ligand fragment
mL           Millilitres
mm           Millimetres
mmol         Millimoles
NMR          Nuclear magnetic resonance
Na[BPh₄]     Sodium tetraphenylborate
Na[Pf₆]      Sodium hexafluorophosphate
NaOMe       Sodium methoxide
[NBu₄]F      Tetrabutylammonium fluoride
NHEt₂        Diethylamine
NEt₃         Triethylamine
OAc          Acetate
OTf          Triflate, trifluoromethanesulfonate, CF₃SO₃⁻
ORTEP       Oak Ridge Thermal Ellipsoid Plot program
Pd(PPh₃)₄    Palladium(0)tetrakis(triphenylphosphine)
ppn          Bis(triphenylphosphine)iminium
Ph           Phenyl, -C₆H₅
PPh₃         Triphenylphosphine
Pz            Pyrazole
Tol          Tolyl
R            General organic group
[Ref]        Reference
r.t.         Room temperature
Rc           Ruthenocenyl
s            Seconds
tBu          Tertiary butyl, -C(CH₃)₃
TCNE         Tetracyanoethylene
Temp.        Temperature
THF          Tetrahydrofuran
TLC          Thin layer chromatography
tmeda        Tetramethylethylenediamine
TMS          Trimethylsilyl, -Si(CH₃)₃, SiMe₃
Tp'          Hydridotris(3,5-dimethylpyrazolyl)borate
Ts           Tosyl
∆            Reflux
µ            Micro
X            Halide
**NMR:**

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<td>Broad</td>
</tr>
<tr>
<td>d</td>
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</tr>
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</tr>
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**IR:**

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**Electrochemistry:**

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<tr>
<td>( \Delta E )</td>
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