



Department of Chemistry

# **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

**Nancy Scoleri**

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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(diyndiyl) ruthenium(II) complexes of general formula  $\{L_nM\}-C\equiv CC\equiv C-\{M''L''_p\}-C\equiv CC\equiv C-\{M'L'_m\}$ , 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 *trans*- $Ru(C_4H)_2(dppe)_2$  (**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  $Ru(C\equiv CC\equiv CH)(dppe)Cp^*$  and  $Ru(C\equiv CC\equiv CH)(PPh_3)_2Cp$  with *n*-BuLi yields the lithium complexes  $Ru(C\equiv CC\equiv CLi)(dppe)Cp^*$  and  $Ru(C\equiv CC\equiv CLi)(PPh_3)_2Cp$ . 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  $[Ru](C\equiv CC\equiv C)\{ML_n\}$  (where  $[Ru] = Ru(dppe)Cp^*, Ru(PPh_3)_2Cp$ ).

Chapter Four investigates the reactivity of the novel lithium complex  $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CLi})(\text{dppe})\text{Cp}^*$  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 diyne ruthenium(II) complexes  $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CR})(\text{dppe})\text{Cp}^*$  (where  $\text{R} = \text{H}, \text{TMS}, \text{Au}(\text{PPh}_3)$ ) with three azide reagents  $\text{TMSN}_3$ ,  $\text{TsN}_3$  and  $\text{AuN}_3(\text{PPh}_3)$ . 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  $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{PPh}_3)_2\text{Cp}$  and  $\text{Ru}(\text{C}\equiv\text{CH})(\text{dppe})\text{Cp}^*$  with azides to give the ruthenium azido complexes  $[\text{Ru}]\text{N}_3$  (where  $[\text{Ru}] = \text{Ru}(\text{PPh}_3)_2\text{Cp}$ ,  $\text{Ru}(\text{dppe})\text{Cp}^*$ ) 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.

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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 <sup>-</sup>	Electron
EH	Extended Hückel theory
eq	Equivalent
ESR	Electron spin resonance
Et	Ethyl, -CH <sub>2</sub> CH <sub>3</sub>
Et <sub>2</sub> O	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, LiNPr <sub>2</sub> <sup>i</sup>
LUMO	Lowest unoccupied molecular orbital
Me	Methyl, CH <sub>3</sub>

MeLi	Methyl lithium
MeOH	Methanol
mg	Milligrams
min	Minutes
ML <sub>n</sub>	General metal-ligand fragment
mL	Millilitres
mm	Millimetres
mmol	Millimoles
NMR	Nuclear magnetic resonance
Na[BPh <sub>4</sub> ]	Sodium tetraphenylborate
Na[PF <sub>6</sub> ]	Sodium hexafluorophosphate
NaOMe	Sodium methoxide
[NBu <sub>4</sub> ]F	Tetrabutylammonium fluoride
NHEt <sub>2</sub>	Diethylamine
NEt <sub>3</sub>	Triethylamine
OAc	Acetate
OTf	Triflate, trifluoromethanesulfonate, CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>
ORTEP	Oak Ridge Thermal Ellipsoid Plot program
Pd(PPh <sub>3</sub> ) <sub>4</sub>	Palladium(0)tetrakis(triphenylphosphine)
ppn	Bis(triphenylphosphine)iminium
Ph	Phenyl, -C <sub>6</sub> H <sub>5</sub>
PPh <sub>3</sub>	Triphenylphosphine
Pz	Pyrazole
Tol	Tolyl
R	General organic group
[Ref]	Reference
r.t.	Room temperature
Rc	Ruthenocenyl
s	Seconds
<sup>t</sup> Bu	Tertiary butyl, -C(CH <sub>3</sub> ) <sub>3</sub>
TCNE	Tetracyanoethylene
Temp.	Temperature
THF	Tetrahydrofuran
TLC	Thin layer chromatography
tmeda	Tetramethylethylenediamine
TMS	Trimethylsilyl, -Si(CH <sub>3</sub> ) <sub>3</sub> , SiMe <sub>3</sub>
Tp'	Hydridotris(3,5-dimethylpyrazolyl)borate
Ts	Tosyl
Δ	Reflux
μ	Micro
X	Halide

**NMR:**

br	Broad
d	Doublet
dt	Doublet of triplet
Hz	Hertz
m	Multiplet
${}^nJ_{IJ}$	n bond coupling constant between nuclei I and J
ppm	Parts per million
s	Singlet
sept	Septet
t	Triplet
$\delta$	Chemical shift
COSY	Correlation Spectroscopy

**IR:**

br	Broad
$\text{cm}^{-1}$	Wavenumbers
m	Medium
sh	Shoulder
w	Weak
s	Strong

**Mass Spectroscopy:**

ES-MS	Electrospray mass spectrum
M	Molecular ion
$m/z$	Mass per unit charge

**Electrochemistry:**

E	Potential
$E_n$	Potential of $n^{\text{th}}$ redox process
$E_{1/2}$	Half-wave potential
$\Delta E$	Potential difference
$i_a$	Anodic peak current
$i_c$	Cathodic peak current
mV	Millivolts
V	Volts
CV	Cyclic voltammogram