



Oxidative Activation of Iron- and Ruthenium- Alkynyl Complexes: Toward Square-Shaped Molecules with Four Redox-Active Metal Centres

A Thesis Submitted Towards the Degree of Doctor of Philosophy

By

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Abstract

The synthesis of square molecules containing four redox-active metal centres and two positive charges which would be interesting as potential candidates for molecular Quantum-dot Cellular Automata (QCA) models constitutes the aim of this thesis. In this new paradigm, the binary information is encoded in the charge configuration of the QCA cell, and in the case of a molecular QCA, in the charge configuration of a single molecule.

In order to synthesise such molecules with metal centres of general formula $M(PP)Cp'$ [$M = Fe, Ru$; $PP = dppe, (PPh_3)_2$; $Cp' = Cp, Cp^*$], new synthetic methods have been developed. By chemically oxidising mono- or bi-metallic alkynyl complexes, radical coupling can occur, mainly depending on the nature of the metal (Fe or Ru) and the length of the carbon chain (C_2, C_4 or C_6), to give dimers with original geometry. Therefore, this thesis describes the oxidation studies of iron- and ruthenium-alkynyl complexes containing short (C_2) to long carbon chains (C_6), and the characterisations of the oxidised products.

The reactivity of the mononuclear 17-electron species $[Ru(C\equiv CR)(PPh_3)_2Cp]^{++}$ (**16**, $R = Ph$; **19**, $R = Tol$) and $[Fe(C\equiv CC\equiv CR)(dppe)Cp^*]^{++}$ (**2a**, $R = Ph$; **2b**, $R = Tol$) was investigated, dimerisation occurring in both cases. Intermolecular radical coupling of **16**⁺⁺ afforded a linear dimer by coupling at the C_β and C_{para} positions, whereas dimerisation of **2**⁺⁺ gives a single dicationic complex **[27]**[PF₆]₂ containing a squared C_4 ring centre and two $Fe(dppe)Cp^*$ units.

The reactivity of the bimetallic 35-electron species $[\{Cp'(dppe)M\}(C\equiv CC\equiv CC\equiv C)\{M(dppe)Cp'\}]^{++}$ ($M = Fe, Ru$; $Cp' = Cp, Cp^*$) was also investigated. The mixed-valence systems containing the $M(dppe)Cp^*$ ($M = Fe, Ru$) fragments were revealed to be stable and isolable: the first crystal structures of mixed-valence complexes with a carbon chain longer than C_4 were resolved for $[\{Cp^*(dppe)Fe\}_2(\mu-C\equiv CC\equiv CC\equiv C)]PF_6$ **[30]**PF₆ and $[\{Cp^*(dppe)Fe\}(C\equiv CC\equiv CC\equiv C)\{Ru(dppe)Cp^*\}]PF_6$ **[34]**PF₆. Electronic delocalisation in these stable mixed-valence complexes, between the two metal centres and through the C_6 bridge, was revealed to be strong which was unexpected for the unsymmetrical system **[34]**PF₆. In contrast, the mixed-valence systems containing the $Ru(dppe)Cp$ fragment were

not stable at room temperature and dimerised to afford dicationic square-shaped tetrametallic complexes with a C_4 ring centre. Two unsymmetrical dimers were characterised: one containing four Ru(dppe)Cp centres [**43**][PF₆]₂ and the other containing two Ru(dppe)Cp and two Fe(dppe)Cp* fragments [**44**][PF₆]₂. Compound [**43**][PF₆]₂ has been fully characterised and the positive charge revealed to be fully delocalised over the whole molecule. Even if unsymmetrical, these molecules are interesting for being potential molecular QCA models.

It has been shown that TCNQ acts as an oxidising agent for iron- and ruthenium-alkynyl complexes. The organometallic 17-e species generated further react by coupling between the cationic and anionic radical [TCNQ]⁻ to give specifically TCNQ adducts. These new complexes which contain two electrophores possess unique properties. The σ -linked electron donor organometallic centre and the organic electron withdrawing group via an alkyndiyl bridge allow intramolecular charge transfer. The X-ray crystal structure analyses, electrochemistry and UV-Vis spectroscopy have been investigated and reveal the interesting properties of these molecules.

Thesis declaration

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint-award of this degree.

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Abbreviations

°	degrees	eq.	equivalent
°C	degrees celsius	ES-MS	Electrospray Mass Spectrum
δ	chemical shift	eV	electron volts
A	amperes	ε	molar extinction coefficient
Å	angstrom	Fc	ferrocene
Anal.	analysis	Δg	anisotropy
Ant	anthracene	h	hour(s)
Ar	aryl	HOMO	Highest Occupied
Av.	average	Molecular Orbital	
br	broad	Hz	hertz
ⁿ Bu	<i>n</i> -butyl	I	current
ca	approximately	<i>i</i> _a	anodic peak current
Calcd	Calculated	<i>i</i> _c	cathodic peak current
cent	centroid	IR	infrared
cm ⁻¹	wavenumbers	irr	irreversible
Cp	cyclopentadienyl	IVCT	Intervalence Charge
Cp*	pentamethylcyclo-	Transfer	
pentadienyl		<i>J</i>	coupling constant
CV	Cyclic Voltammetry	K	kelvin
d	doublet	<i>K</i> _c	comproportionation
dbu	1,8-diazabicyclo[5.4.0]	constant	
undec-7-ene		L	litre
DFT	Density Functional Theory	LMCT	Ligand-to-Metal Charge
dppe	1,2-bis(diphenylphosphine)-	Transfer	
ethane		LUMO	Lowest Unoccupied
E	potential	Molecular Orbital	
ΔE	potential difference	λ	wavelength
e	electron	m	medium or multiplet
EPR	Electron Paramagnetic	M	metal or molarity or
Resonance		molecular ion	

Me	Methyl	TCNQ	7,7,8,8-
MeOH	Methanol		tetracyanoquinodimethane
mg	milligrams	THF	tetrahydrofuran
min	minutes	t.l.c.	thin layer chromatography
mL	millilitres	TMS	trimethylsilyl
MLCT	Metal-to-Ligand Charge	tol	<i>para</i> -tolyl
Transfer		UV-Vis	Ultraviolet-Visible
mmol	millimoles	V	volts
MO	Molecular Orbital	vs	versus
m/z	mass per unit charge	V_{ab}	electronic coupling
Near-IR	Near-Infrared	parameter	
nm	nanometres	w	weak
NMR	Nuclear Magnetic		
Resonance			
ORTEP	Oak Ridge Thermal		
Ellipsoid Plot			
OTTLE	Optically Transparent Thin-		
Layer Electrochemical			
Ph	phenyl		
PPh ₃	triphenylphosphine		
ppm	parts per million		
^{<i>i</i>} Pr	isopropyl		
R	general organic group		
R _f	retention factor		
s	strong or singlet or seconds		
SAM	self-assembled monolayer		
SCE	Saturated Calomel Electrode		
SOMO	Singly Occupied Molecular		
Orbital			
STM	Scanning Tunnelling		
Microscope			
t	triplet		
TCNE	tetracyanoethylene		