Department of Chemistry

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Polarised Alkynyl Ruthenium Complexes

A Thesis Submitted Towards the Degree of Doctor of Philosophy.

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In memory of my three greatest scientific influences while I was growing up:
Grandpa George Parker,
A. Bruce Gray (my chemistry teacher),
Des Baldock (my physics teacher).

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Abstract

Chapter 1 outlines the potential application of metal alkynyl complexes and then describes the different methods in the literature for the synthesis of alkynyl, poly-ynyl and homo- and hetero-metal complexes. Their chemistry will then be discussed. This Chapter concludes with an outline of the work to be described in the remainder of the thesis.

Chapter 2 describes a series of complexes containing a new tricyanovinylethynyl (3,4,4-tricyanobut-3-en-1-ynyl) ligand obtained by direct substitution of a CN group in tetracyanoethene by ethynyl complexes $M(C\equiv CH)(PP)Cp'$ [M = Ru, Os, (PP)Cp' = $(PPh_3)_2Cp$; M = Ru, PP = dppe, Cp' = Cp, Cp*]. The reactions proceed in higher yield as the metal environment becomes sterically larger and more donating; the normal [2 + 2]-cycloaddition / ring-opened product $M\{C[=C(CN)_2]CH=C(CN)_2\}(PP)Cp'$ is also formed in some cases. The diynyl $Ru(C\equiv CC\equiv CH)(dppe)Cp^*$ reacts with tcne to give only the ring-opened adduct $Ru\{C\equiv CC[=C(CN)_2]CH=C(CN)_2\}(dppe)Cp^*$. Protonation of $Ru\{C\equiv CC(CN)=C(CN)_2\}(dppe)Cp^*$ (**10**) afforded the vinylidene. A second transition metal fragment $\{ML_n\}$ [$\{ML_n\}$ = $Ru(PPh_3)_2Cp$, M'(dppe)Cp* (M' = Ru, Os), $RuCl(dppe)_2$] can be added to the CN group *trans* to the first. Compound **10** ready undergoes substitution of the 3-cyano group by nucleophiles. Some unexpected rearrangements and formation of *O*- and *N*-heterocyclic compounds were also found.

Chapter 3 describes reactions between 1,2-dichlorohexafluorocyclopentene and $Ru(C\equiv CH)(dppe)Cp^*$ (**1**) or $Ru(C\equiv CC\equiv CLi)(dppe)Cp^*$ which give $Ru(C\equiv C\text{-}c\text{-}C_5F_6Cl\text{-}2)(dppe)Cp^*$ (**36**) and $Ru(C\equiv CC\equiv C\text{-}c\text{-}C_5F_6Cl\text{-}2)(dppe)Cp^*$, respectively. Ready hydrolysis of **36** to $Ru\{C\equiv C[c\text{-}C_5F_4Cl(O)]\}(dppe)Cp^*$ occurs, which can be converted to $Ru\{C\equiv C(c\text{-}C_5F_4Cl[=C(CN)_2])\}(dppe)Cp^*$ by treatment with $CH_2(CN)_2$ / basic alumina. The cyano-fluorocarbon ligand in the latter is one of the most powerfully electron-withdrawing groups known.

Chapter 4 describes the three methods of synthesising heterometallic carbon-chain complex $\{Cp*(dppe)Ru\}C{\equiv}CC{\equiv}CC{\equiv}CC\{Co_3(\mu\text{-}dppm)(CO)_7\}$ (**40**), in two examples showing the first examples of $Ru\{(C{\equiv}C)_xI\}(dppe)Cp*$ ($x = 1, 2$) being used in a cross coupling reaction with $Ph_3PAu(C{\equiv}C)_{(3\text{-}X)}C\{Co_3(\mu\text{-}dppm)(CO)_7\}$. The reactivity of **40** with PPh_3, MeOTf, tcne, tcnq, $Fe_2(CO)_9$, $NiCp_2$ and $Co_2(CO)_8$ took place on either the C_7 bridge or on either metal centre.

Chapter 5 discusses the reaction of **1** with oxalyl chloride which gave $\{Cp*(dppe)RuC{\equiv}C\}_2CO$ (**52**). This complex can be methylated to give $[\{Cp*(dppe)RuC{\equiv}C\}_2C(OMe)]OTf$, which in turn can be protonated to the dication. Knövenagel condensation of **52** with $CH_2(CN)_2$ gave $\{Cp*(dppe)RuC{\equiv}C\}_2C\{{=}C(CN)_2\}$. The reaction of **1** and bis(2,4-dinitrophenyl) oxalate afforded $\{Cp*(dppe)Ru\}\{c\text{-}C{=}C[C_6H_3(NO_2)_2]C(O)C(O)O\}$. The transmetallation reaction of $\{(Ph_3P)AuC{\equiv}C\}_2CO$ and RuCl(dppe)Cp unexpectedly gave the cyclic complex $[1,4\text{-}\{Cp(dppe)Ru\}_2\{c\text{-}COC(OMe){=}CHCCH\}]PF_6$.

Chapter 6 gives an account of the electrochemistry of many of these redox-active compounds and examines the UV-Vis absorption of the more polarised compounds. Some discussion of the various observed trends is presented.

There is also a future direction of this chemistry given at the end of this work.

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.

Christian Parker **19th March 2010**

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Abbreviations

General:

$\{Co_3\}$	$Co_3(dppm)(CO)_7$
$\{ML_n\}$	general metal-ligand fragment
$\{M'L'_m\}$	general metal-ligand fragment
[Ru*] or {Ru*}	Ru(dppe)Cp*
{Ru}	Ru(dppe)Cp
°	degrees
°C	degrees Celsius
Å	angstroms
Ac	acyl, $-COCH_3$
anal.	analysis
av.	average
Bu	normal butyl, $-(CH_2)_3CH_3$
Bu^t	tertiary butyl, $-C(CH_3)_3$
Calcd	calculated
ca	approximately
cm	centimetres
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cp’	cyclopentadienyl ring, Cp or Cp*
C(TCNE)C	$\{C=C(CN)_2\}_2$
C(TCNQ)C	$C\{=CC_6H_4=C(CN)_2\}C=C(CN)_2$
d	Day (s)
dbu	1,8-diazabicyclo[5.4.0]undec-7-ene
DF	density-functional
DiMeOap	2-(3,5-dimethoxyanilino)pyridinate
dippe	1,2-bis(diisopropylphosphino)ethane
DMF	*N, N*-dimethylformamide
dmpe	1,2-bis(dimethylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
DTE	dithienylethene
Eq	equivalents
Et	ethyl, $-CH_2CH_3$
EtOH	ethanol
F_4-tcnq	2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane

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 or metal
Me	methyl, $-CH_3$
MeOH	methanol
mes	mesityl, $CH_2C_6H_3Me_2$-3,5
mg	milligrams
MHz	megahertz
min	minutes
mL	millilitres
mm	millimetres
mmol	millimoles
NLO	non-linear optic
MO	molecular orbital
MV	mixed-valence
NIR	near-infrared
nm	nanometres
NMR	nuclear magnetic resonance
Nu	nucleophile
ORTEP	Oak Ridge Thermal Ellipsoid Plot program
OTTLE	optically transparent thin-layer electrode
Ph	phenyl, $-C_6H_5$
PP	bis-phosphine, dppe or $(PPh_3)_2$
Pr^i	isopropyl, $-CH(CH_3)_2$
py	pyridine
R	general organic group
r.t.	room temperature
ref	reference
R_f	retention factor
S	second (s)
T	temperature (K)
TCNE	tetracyanoethylene
TCNQ	7,7,8,8-tetracyanoquinodimethane
thf	tetrahydrofuran

TLC	thin layer chromatography
tmeda	tetramethylethylenediamine
tol	*para*-tolyl, -$C_6H_4CH_3$
Tp*	hydrotris(3,5-dimethylpyrazolyl)borate, dmpz
UV	ultraviolet
vis	visible
X	halide or various group

NMR:

AB q	AB quartet
br	broad
d	doublet
dd	doublet of doublets
Hz	hertz
m	multiplet
J(IJ)	coupling constant between nuclei I and J
ppm	parts per million
s	singlet
quin	quintet
sept	septet
t	triplet
TMS	tetramethylsilane
t quin	triplet of quintets
tt	triplet of triplets
δ	chemical shift

IR:

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

Mass Spectroscopy:

ES	electrospray
HR	high resolution
M	molecular ion
m/z	mass per unit charge
MS	mass spectrometry

UV/Vis/NIR:

Abs	absorbance
CT	charge transfer
IL	intraligand
IVCT	intervalence charge transfer
LMCT	ligand-to-metal charge transfer
MLCT	metal-to-ligand charge transfer
ε	extinction coefficient
λ	wavelength
λ_{max}	maximum absorbance of peak

Electrochemistry:

A	amperes
CV	cyclic voltammogram
E	potential
E_n	potential of nth 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
^{i}	irreversible
K_c	comproportionation constant
Ox	oxidation
^{p}	partially reversible
Red	reduction
SCE	saturated calomel electrode
V	volts
ΔE	potential difference