

# **Cobalt organometallic compounds by electrochemistry**

**By**

**Winnie Kgabo Maboya**

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## DECLARATION

I declare that this dissertation is my own work. It is being submitted for the Degree of Master of Science in the University of Pretoria, Pretoria. It has not been submitted before for any degree or examination in any other University.

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W K Maboya

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## ABSTRACT

The electrochemical oxidation of  $\text{CoCl}_2(\text{PPh}_3)_2$  was investigated in a mixture of acetonitrile and pentanol (1:1) at a platinum disk working electrode using Cyclic Voltammetry (CV) and Chronoamperometry.

Elemental Analysis and Infrared Spectroscopy were used to characterise the synthesized compounds i.e.  $\text{CoCl}_2(\text{PPh}_3)_2$  and  $\text{CoCl}(\text{PPh}_3)_3$ .

Cyclic Voltammetry was utilised for the examination of different working electrode materials that could be used for the anodic voltammetric studies of  $\text{CoCl}_2(\text{PPh}_3)_2$ , to characterise the reactants and products of each electrode reaction, to investigate the chloride binding ability to a  $\text{CoCl}(\text{PPh}_3)_3$  complex, and to evaluate the electrocatalytic substitution of chloride by  $\text{PPh}_3$  from the complex  $\text{CoCl}_2(\text{PPh}_3)_2$ . Use of ferrocene as an internal standard during the anodic studies of  $\text{CoCl}_2(\text{PPh}_3)_2$  was also evaluated.

The number of electron involved in the electrode process,  $\text{Co}^{\text{II}}$  to  $\text{Co}^{\text{III}}$  from  $\text{CoCl}_2(\text{PPh}_3)_2$  and diffusion coefficient of ferrocene in a mixture of acetonitrile and pentanol (1:1) were determined using Chronoamperometry.

Ultraviolet-Visible (UV-Vis) and  $^{31}\text{P}$  Nuclear Magnetic Resonance ( $^{31}\text{P}$  NMR) spectra were used to assist with the characterisation of the electrode reactions involved during oxidation of  $\text{CoCl}_2(\text{PPh}_3)_2$ .

## DEDICATION

*In memory of my father in law*

*Albert Kgabo Maboya*

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## LIST OF SYMBOLS

$\mu$	Micro
$J_i(x)$	Flux of species $i$ ( $\text{mol s}^{-1}\text{cm}^{-2}$ ) at distance $x$ from the surface
$D$	Diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ )
$\delta C_i(x)/\delta x$	Concentration gradient at distance $x$
$\delta\phi(x)/\delta x$	Potential gradient
$z$	Charge (dimensionless)
$C$	Concentration ( $\text{mol}\cdot\text{cm}^{-3}$ )
$v(x)$	Velocity ( $\text{cm s}^{-1}$ )
$A$	Area of electrode ( $\text{cm}^2$ )
$i_j$	Current component at any value of $x$ arising from a flow of species $j$ (A)
$i_{m,j}$	Migration current of species $j$ (A)
$F$	Faraday's constant (96485 A s)
$R$	Gas constant ( $8.316 \text{ J K}^{-1} \text{ mol}^{-1}$ ) or solution resistance
$T$	Temperature (K)
$E_\lambda$	Switching potential (V)
$E_{1/2}$ or $E^\circ$	Half-wave potential (V)



$E_{pa}$	Anodic peak potential (V)
$E_{pc}$	Cathodic peak potential (V)
$I_{pa}$	Anodic peak current (A)
$I_{pc}$	Cathodic peak current (A)
$\beta$	Beta
$\gamma$	Gamma
$\delta$	Sigma
$E_p$	Peak potential (V)
$M$	Molar concentration ( $\text{mol dm}^{-3}$ )
$p$	Para
$m$	Meta
$o$	Ortho
$j_{p,ox}$	Peak current density
$d$	Distance (mm)
$t$	Time (s)
$k^\circ$	Standard heterogeneous rate constant (cm/s)
$\alpha$	Cathodic transfer coefficient
$1 - \alpha$	Anodic transfer coefficient

$n$	Number of electrons
$\nu$	Scan rate ( $\text{V s}^{-1}$ )
$\pi$	Pi bonding
$D^*$	Dispersion coefficient
ID	Internal diameter
$\Omega$	Ohm

## LIST OF ABBREVIATIONS

AE	Auxiliary electrode
Ag   AgCl	Silver-silver chloride
Ag   AgNO <sub>3</sub>	Silver-silver nitrate
A.R.	Analytical reagent
t-BuNC	Tert-butyl isocyanide
CDCl <sub>3</sub>	Deuterated chloroform
CINCH <sub>3</sub> TPP	Chloro-N-methyl- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphirins
CIMNCH <sub>3</sub> TPP	Chloro-N-methyl- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatometal (II) (M = Co, Zn)
CoTETPc	Cobalt-tetra-{2-(2-thienyl)ethoxy}phthalocyanine
CoTPP	Cobalt-tetraphenylporphirin
C.P.	Chemically pure
Cp	Cyclopentadienyl
CV	Cyclic Voltammetry
dbbip	2,6-(1'-butylbenzimidazol-2'-yl)pyridine
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide

ESR	Electron Spin Resonance
EPR	Electron Paramagnetic Resonance
ETC	Electron transfer chain
FeCp <sub>2</sub>	Ferrocene
FIA	Flow Injection Analysis
GC	Glassy carbon
IR	Infrared Spectroscopy
KF	Karl Fischer
NMR	Nuclear Magnetic Resonance Spectroscopy
OMC	Octamethyl corrole
(OMC)Co(PPh <sub>3</sub> )	(octamethylcorrolato) cobalt (III) triphenylphosphine
OMTX-PC	tri-X-phenyl octamethylcorrole
OTE	Optically transparent working electrode
PEEK	Polyetheretherketones
PET	Poly(ethyleneterephthalate)
PhCN	Benzonitrile
<sup>31</sup> P NMR	Phosphorus NMR
PPh <sub>3</sub>	Triphenylphosphine

RE	Reference electrode
Redox	Electron transfer reaction involving either oxidation or reduction
RX	Aryl- or alkyl-halides (R = CH <sub>3</sub> etc X = Cl, Br etc.)
SCE	Saturated calomel electrode
TBAP	Tetrabutyl ammonium perchlorate
TBAPF <sub>6</sub>	Tetrabutyl ammonium hexafluorophosphate
TEAP	Tetraethyl ammonium perchlorate
THF	Tetrahydrofuran
TPP	Tetraphenylporphirin
UHP	Ultra High Purity
UV-Vis	Ultraviolet-Visible Spectroscopy
WE	Working electrode