

# Synthesis of metal complexes with thiophene ligands

by

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Submitted in partial fulfilment of the degree

PHILOSOPHIAE DOCTOR

in the Faculty of Science

UNIVERSITY OF PRETORIA  
PRETORIA

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January 2000

# Acknowledgments

I would hereby like to express my gratitude to the following people and institutions for their individual roles in the completion of this study:

My supervisor, Professor Simon Lotz, for his encouragement, assistance and support;

Mr Eric Palmer for recording of all the NMR spectra;

Dr Helmar Görls for structural elucidations of crystallographic data;

Mr Ian Vorster of RAU for MS data of all the novel organometallic complexes;

Mr Mauritz Wentzel of Protechnik Laboratories, for MS data of all the organic substances;

The NRF and University of Pretoria for financial support;

My friends and colleagues at the University of Pretoria and UNISA for their encouragement and camaraderie;

My family for their understanding, support and interest.

Thank you!

Marilé

# Summary

The syntheses of carbene complexes with thiophene ligands were performed. Conjugated ligands comprising one (thiophene), two (thienothiophene) and three (dithienothiophene) condensed thiophene units were utilized in the syntheses. The reactivity, stability and structural features of the novel complexes were prepared. Metal carbonyls used to prepare the novel carbene complexes, were  $\text{Cr}(\text{CO})_6$ ,  $\text{W}(\text{CO})_6$ ,  $\text{Mo}(\text{CO})_6$ ,  $\text{MnCp}(\text{CO})_3$  en  $\text{Mn}(\text{MeCp})(\text{CO})_3$ . The carbene complexes were prepared *via* the classical Fischer method, which constitutes the reaction of the dilithiated thiophene derivative with the respective metal carbonyl complex, followed by the subsequent quenching with triethyl oxonium tetrafluoroborate to afford the alkoxy carbene complexes. In most cases the reactions afforded monocarbene complexes, biscarbene complexes and decomposition products. These decomposition products were formed on reaction of the biscarbene complexes with oxygen, affording an ester functionality on one side of the thiophene ligand and a monocarbene moiety on the other side. In the case of molybdenum, unexpected C-C coupling reactions yielded complexes containing extended thiophene spacers. Spectroscopical data and crystal structure determinations were employed in characterizing the novel complexes. It was concluded that, by increasing the number of thiophene units in the condensed ligand, the stability of the carbene complexes is enhanced.

Iron complexes of thiophene and thienothiophene were synthesized, employing several synthetic routes, in order to try and obtain optimum yields. The stabilities of these complexes were mutually compared. Several compounds were isolated which represented products formed by intermolecular C-C coupling reactions. In this case, however, it was concluded that by increasing the number of thiophene units in the ligand, the stability of the complexes decreased. These studies are to be extended towards a material science program and the results of this project will aid in the design of complexes specifically tailored for electronic transfer within the molecule.

# Opsomming

Die sintese van karbeenkomplekse met tiofeen ligande is uitgevoer. Gekonjugeerde ligande wat uit een (tiofeen), twee (tiënotiofeen) en drie (ditiënotiofeen) gekondenseerde tiofeen eenhede bestaan, is in hierdie sinteses gebruik. Die reaktiwiteit, stabiliteit en struktuur eienskappe van die nuwe komplekse is vergelyk. Metaalkarboniele wat gebruik is in die bereiding van die nuwe karbeenkomplekse, is  $\text{Cr}(\text{CO})_6$ ,  $\text{W}(\text{CO})_6$ ,  $\text{Mo}(\text{CO})_6$ ,  $\text{MnCp}(\text{CO})_3$  en  $\text{Mn}(\text{MeCp})(\text{CO})_3$ . Die karbeenkomplekse is berei volgens die klassieke Fischer metode, wat die reaksie van die gediliteerde tiofeen derivaat met die onderskeie metaalkarboniel komplekse behels, gevolg deur alkilering met behulp van triëtiel oksonium tetrafluoroboraat om alkoksi-karbeen komplekse te lewer. In die meeste gevalle is die monokarbeenkompleks, die biskarbeenkompleks asook 'n ontbindingsproduk verkry. Hierdie ontbindingsproduk is gevorm in die reaksie van die biskarbeenkomplekse met suurstof, wat 'n ester funksionaliteit aan die een kant van die tiofeen eenheid en 'n monokarbeen fragment aan die ander kant van die ligand tot gevolg het. Onverwagte C-C koppelingsreaksies het in die geval van molibdeen plaasgevind en komplekse met uitgebreide eenhede is gevorm. Spektroskopiese data en kristalstruktuurbevestigings is gebruik om die nuwe komplekse te karakteriseer. Daar is tot die gevolgtrekking gekom dat, deur die aantal tiofeen eenhede in die gekondenseerde ringsisteem te vermeerder, die stabiliteit van die komplekse toeneem.

Yster komplekse van tiofeen en tiënotiofeen is gesintetiseer deur van verskeie sintese roetes gebruik te maak om die optimum opbrengs te probeer verkry. Die stabiliteite van die komplekse is onderling met mekaar vergelyk. Verskeie verbindings is geïsoleer wat produkte verteenwoordig wat gevorm is deur intermolekulêre C-C koppelingsreaksies. In hierdie geval is daar tot die slotsom gekom dat deur die aantal tiofeen eenhede in die ringsisteem te vermeerder, die stabiliteite van die komplekse afneem. Hierdie studie sal uitgebrei word tot 'n program in materiale en die resultate van hierdie projek sal aangewend word in die ontwerp van komplekse, spesiaal geformuleer vir elektroniese oordrag in die molekule.

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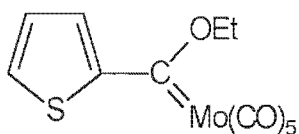


# List of abbreviations

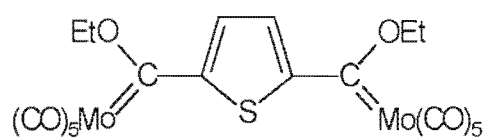
br	:	broad
Bu	:	butyl
Cp*	:	$\eta^5\text{-C}_5\text{Me}_5$
Cp	:	$\eta^5\text{-C}_5\text{H}_5$
d	:	doublet
dec	:	decomposition
DMF	:	dimethyl formamide
DMTT	:	3,6-dimethylthieno[3,2- <i>b</i> ]thiophene
DTT	:	dithieno[3,2- <i>b</i> :2',3'- <i>d</i> ]thiophene
Et	:	ethyl
HMPT	:	hexamethylphosphoric triamide
IR	:	infrared
m	:	multiplet
Me	:	methyl
MeCp	:	$\eta^5\text{-C}_5\text{H}_4\text{CH}_3$
NLO	:	non-linear optical
NMR	:	Nuclear magnetic resonance spectroscopy
n.o.	:	not observed
Ph	:	phenyl
q	:	quartet
s	:	singlet
t	:	triplet
T	:	thiophene/ thienyl/ thienylene
TT	:	thieno[3,2- <i>b</i> ]thiophene
THF	:	tetrahydrofuran
TMS-Cl	:	trimethylchlorosilane
TMEDA	:	tetramethyl ethylene diamine
Tol	:	toluene

# List of compounds

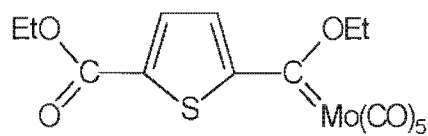
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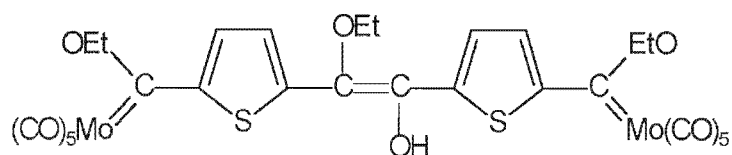
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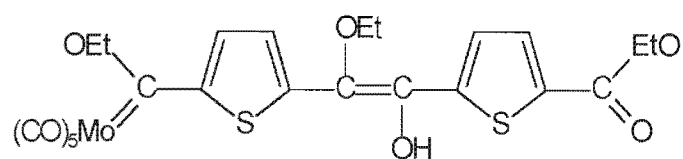
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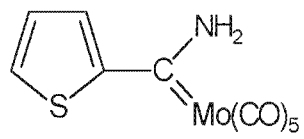
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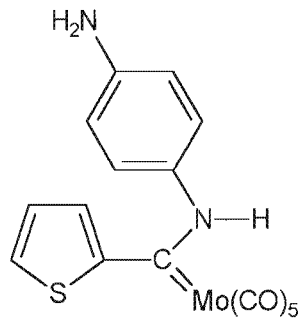
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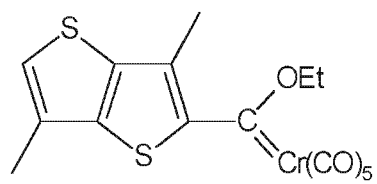
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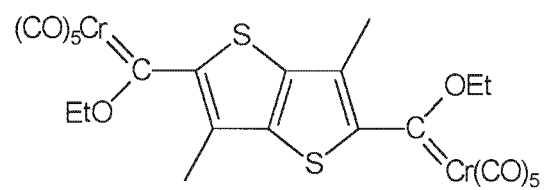
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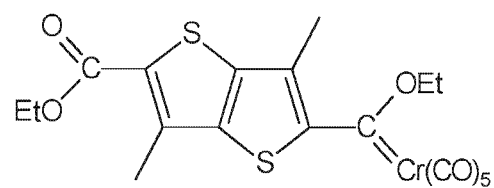
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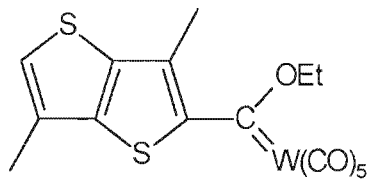
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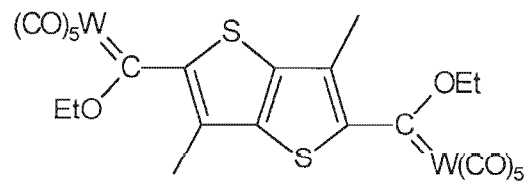
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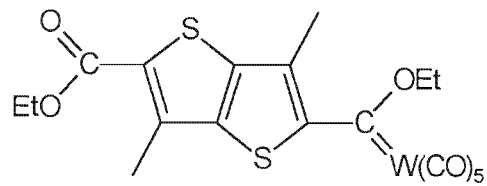
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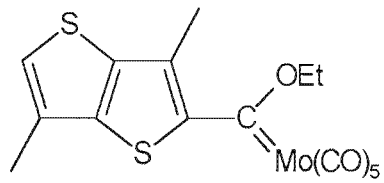
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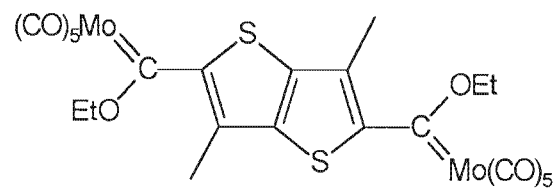
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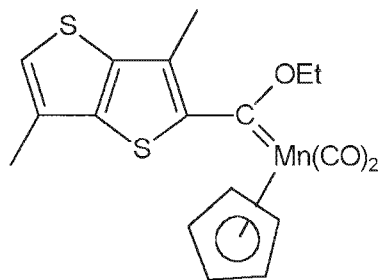
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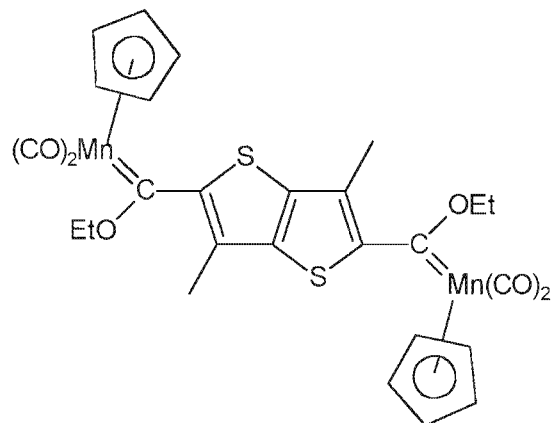
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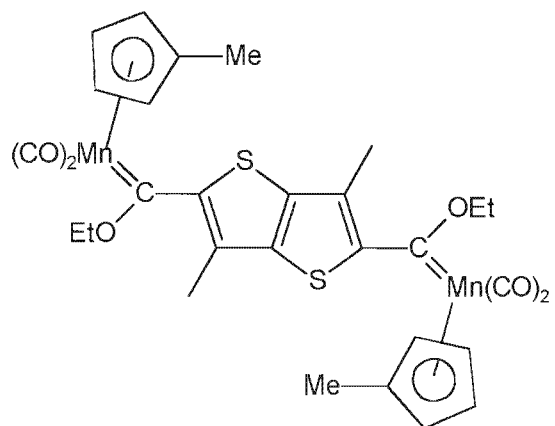
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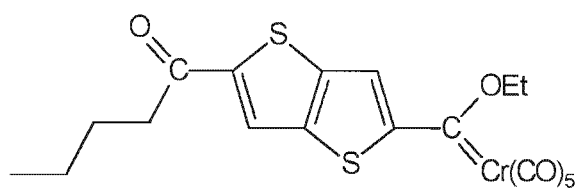
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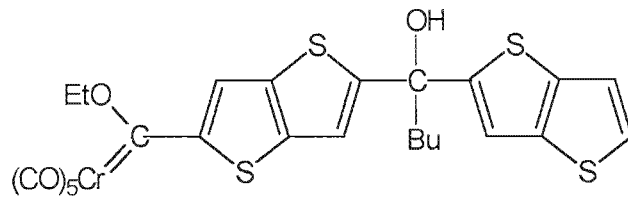
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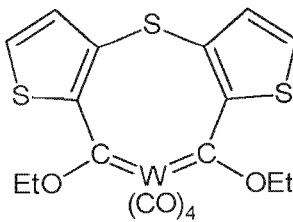
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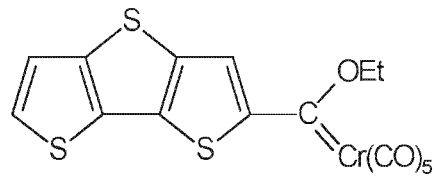
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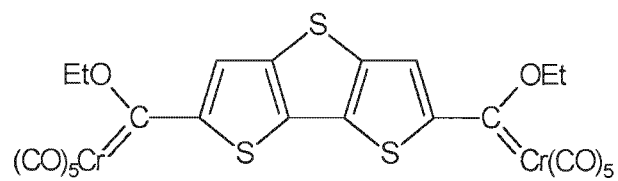
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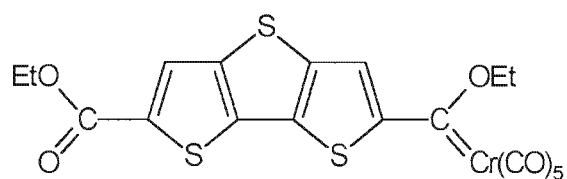
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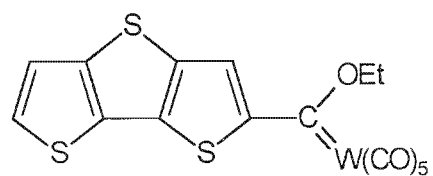


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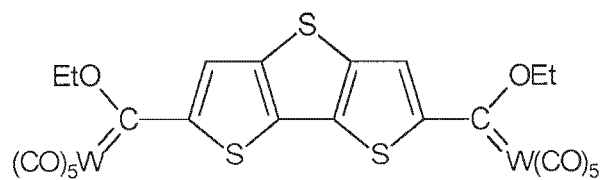




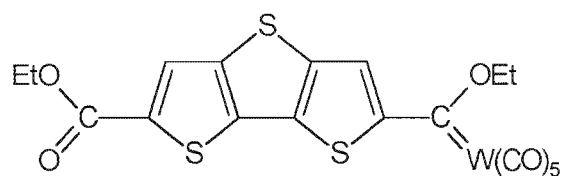
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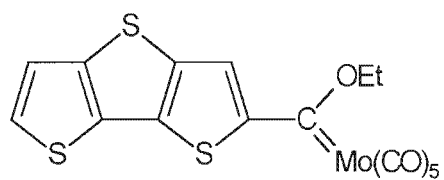
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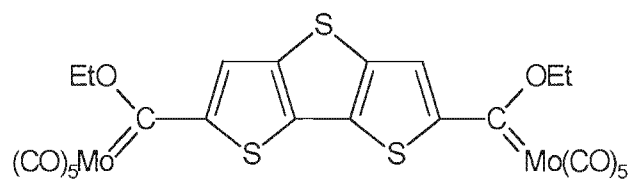
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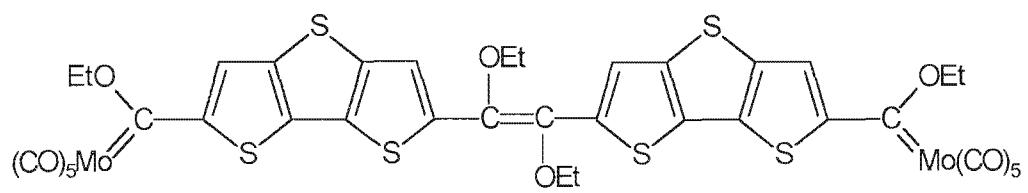
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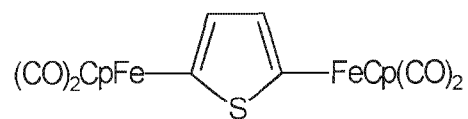
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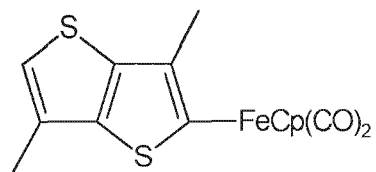
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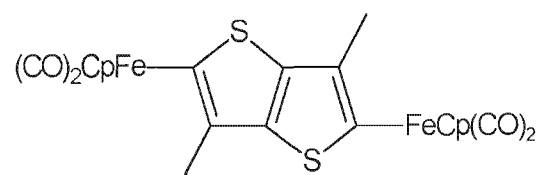
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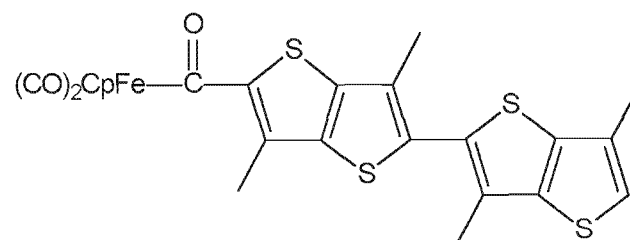
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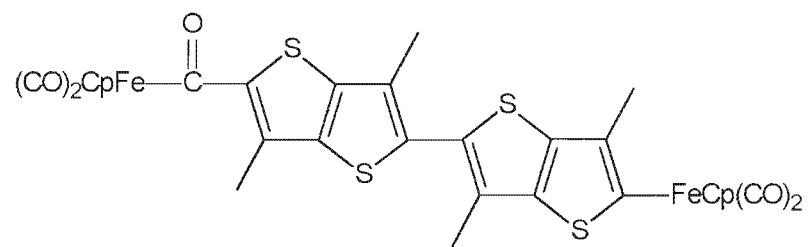
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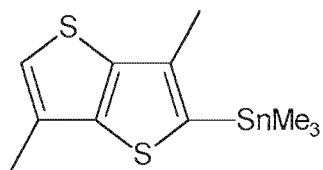
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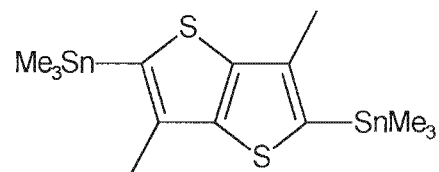
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