

Synthesis and structure of modified thiophene biscarbene complexes

by

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Declaration

The syntheses and characterizations outlined in this dissertation were carried out at the Department of Chemistry, University of Pretoria between the periods of January 2009 to January 2010 under the supervision of Prof. Simon Lotz. Crystal structure determinations (data collection and structure refinements) were performed by Mr. D.C. Liles at the same institute. I hereby declare that the dissertation was my own, independent work and has not been previously submitted for examination or a degree at another tertiary institute.

A handwritten signature in black ink, reading "Jaarsveld".

.....
Nina A. van Jaarsveld

1st day of February 2010



Acknowledgements

Jy is nooit te oud om iets nuuts te leer nie

Ma

Dis 'n loopbaan nie 'n renbaan nie

Pa

Relax, jy gaan dit maak

Liza

My sussie swot chemie, wil jy die lab sien?

Louise a.k.a (Peanut)

Maar baby!

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Moet ek vir jou koffie maak?

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Ek het 'n meeting, dans, reaksie, huis, kerk, draf, etc., maar waarmee kan ek help?

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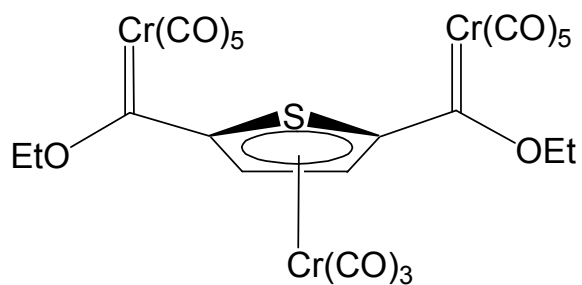
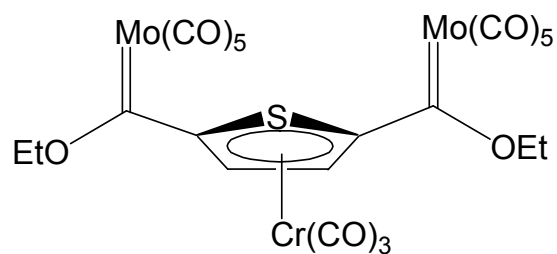
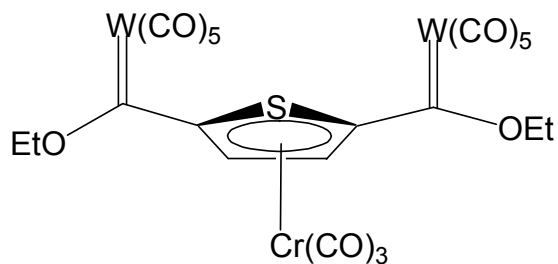
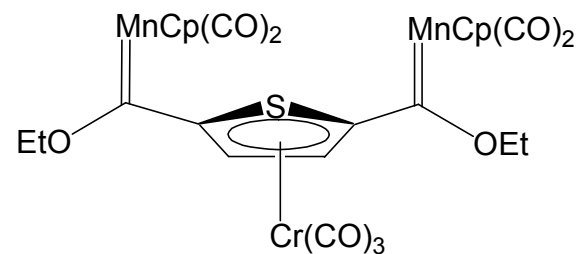
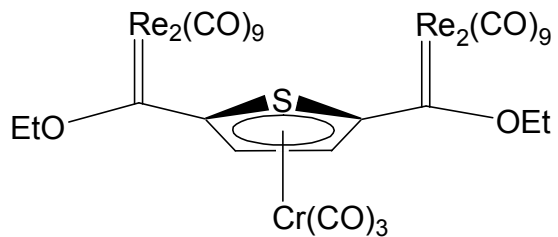
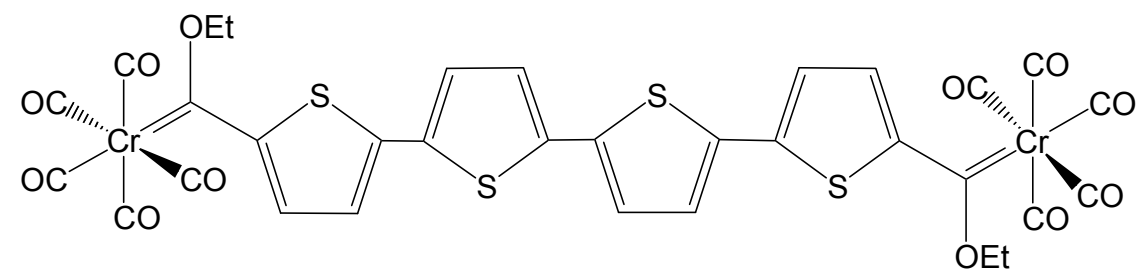


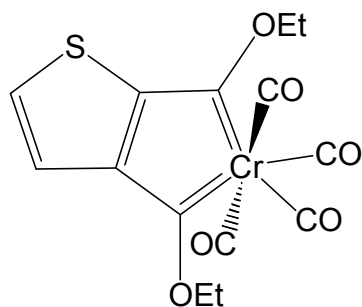
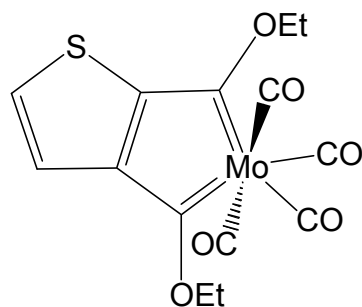
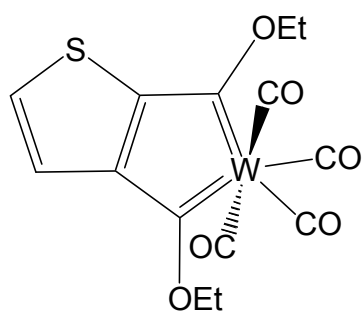
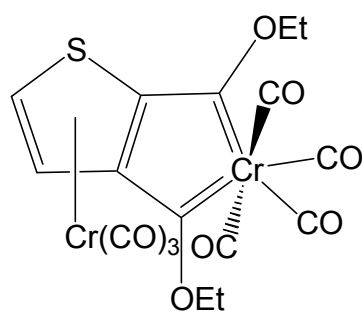
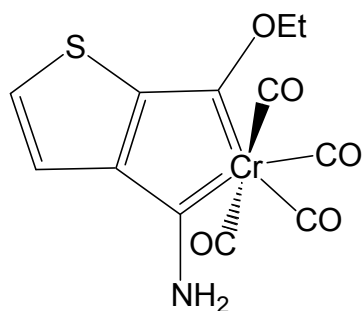
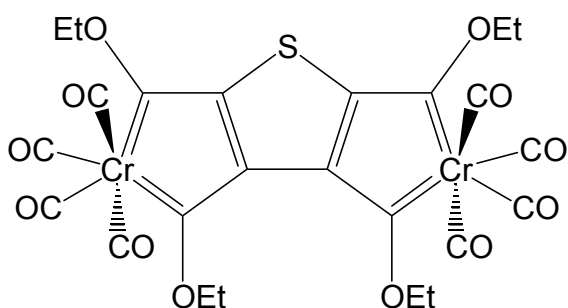
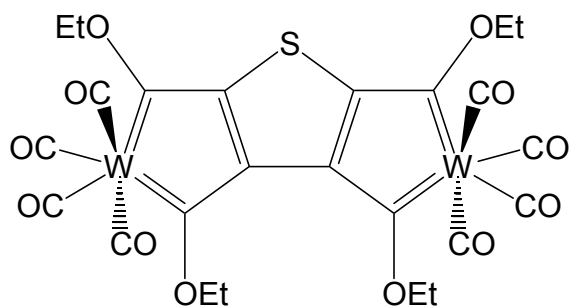
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Type B: MONONUCLEAR METAL BISCARBENE COMPLEXES**B1:****B2:****B3:****B4:****B5:****B6:****B7:**



LIST OF ABBREVIATIONS

Å	:	angstrom	m (IR)	:	medium
Ac	:	acetyl	m (NMR)	:	multiplet
ADC	:	acyclic diamino Carbene	Me	:	methyl
Bu	:	butyl	MLCT	:	metal ligand charge transfer
BuLi	:	<i>n</i> -butyllithium	nba	:	nitrobenzylalcohol
BTP	:	bithiophene	NHC	:	N-heterocyclic carbene
br	:	broad	n.o.	:	not observed
CBC	:	covalent bond classification	η^n	:	hapticity
Cp	:	η^5 -C ₅ H ₅	NMR	:	nuclear magnetic resonance
Cp*	:	η^5 -C ₅ H ₄ Me	Tf	:	triflate
δ	:	chemical shift	Ph	:	phenyl
d	:	doublet	PPh	:	triphenyl phosphine
DCM	:	dichloromethane	q	:	quartet
dd	:	doublet of doublets	QTP	:	quaterthiophene
DEE	:	diethyl ether	RT	:	room temperature
Et	:	ethyl	s (IR)	:	singlet
HETCOR	:	heteronuclear correlation	s (NMR)	:	strong
HOMO	:	highest occupied molecular orbital	t	:	triplet
IR	:	infrared spectroscopy	THP/thp	:	thiophene
I	:	intensity	THF/thf	:	tetrahydrofuran
<i>J</i>	:	coupling constant (Hz)	TMEDA:	:	N,N,N,N-tetramethyl ethylenediamine
λ	:	Wavelength	URO	:	urotropin
LCD	:	liquid crystal display	UV	:	ultraviolet
LDA	:	lithium diisopropylamine	VE	:	valence electron
LUMO	:	lowest unoccupied molecular orbital	vs	:	very strong
			w	:	weak



ABSTRACT

Investigation of thiophene as spacer ligand to afford mono and dinuclear biscarbene complexes was undertaken. Three different methods resulted in the selective activation of thiophene positions after deprotonation by BuLi.

Using the thienyl derivative, quaterthiophene (QTP), linked at the two and five position allowed for the successful lithiation of the two and five position of the outermost thienyls without the use TMEDA as with thiophene. The synthesis of $[\text{Cr}(\text{CO})_5\{\text{C}(\text{OEt})_2,5\text{-C}_{16}\text{H}_8\text{S}_4\text{C}(\text{OEt})\}\text{Cr}(\text{CO})_5]$ was afforded by addition of chromium hexacarbonyl and subsequent alkylation with $[\text{Et}_3\text{O}][\text{BF}_4]$. Localization of the conjugated π -electronic path on the thienyl spacer determined by X-ray diffraction studies was supplemented with computational studies and showed no communication between the metal fragments exist *via* the thiophene chain.

Similar activation to QTP was observed with the electron withdrawing influence of the metal fragment on $\text{Cr}(\eta^5\text{-C}_4\text{H}_4\text{S})(\text{CO})_3$ that permit for dilithiation on the 2 and 5 position to synthesize the carbene analogues $[\text{ML}_n\{\text{C}(\text{OEt})\eta^5\text{-2,5-C}_4\text{H}_2\text{SC}(\text{OEt})\}\text{ML}_n(\text{Cr}(\text{CO})_3)]$ where $\text{ML}_n = \text{Cr}(\text{CO})_5$, $\text{Mo}(\text{CO})_5$, $\text{W}(\text{CO})_5$, $\text{MnCp}(\text{CO})_2$ and $\text{Re}_2(\text{CO})_9$. NMR spectroscopic techniques were used for identification and showed that the carbene metal ligands have restricted movement resulting in signal duplication.

Selective replacement of thiophene hydrogens with bromine atoms and subsequent lithium-halogen exchange to utilize specific thiophene protons. Lithiation of 3-bromothiophene at cold temperatures and formation of the metal acylate allowed for the second lithiation at the 2 position of thiophene to form the carbene chelate, $[\text{Cr}\{\text{C}(\text{OEt})_2,3\text{-C}_4\text{H}_2\text{SC}(\text{OEt})\}(\text{CO})_4]$. Correspondingly the formation of $[\text{Cr}\{\text{C}(\text{OEt})\eta^5\text{-2,3-C}_4\text{H}_2\text{SC}(\text{OEt})\}(\text{CO})_4(\text{Cr}(\text{CO})_3)]$ was afforded by using the same procedure on chromium η^5 -(3-bromothiophene) tricarbonyl precursor.

The range of carbene chelates that could be synthesized warranted further investigation to advance the field in the study of these carbene complexes. For the first time it could be shown that it was possible to decorate all carbon atoms in a heteroarene with Fischer carbene ligands. Utilizing 2,3,4,5-tetrabromothiophene and lithium-halogen exchange methodology resulted in the synthesis of tetracarbene chelate complexes, $[2,3,4,5-C_4S\{C(OEt)\}_4\{Cr(CO)_4\}_2]$ and $[2,3,4,5-C_4S\{C(OEt)\}_4\{W(CO)_4\}_2]$. The reaction also afforded the respective monocarbene chelates, $[M\{C(OEt)2,3-C_4H_2SC(OEt)\}(CO)_4]$, $M = Cr$ and W . The syntheses were accomplished by sequential lithium-halogen exchange of the 2 and 5 positions followed by metal acylate formation and ring closure by a further lithium-halogen exchange of remaining bromine atoms. The stability of $[2,3,4,5-C_4S\{C(OEt)\}_4\{Mo(CO)_4\}_2]$ did not allow for isolation but the carbene monochelate analogue, $[Mo\{C(OEt)2,3-C_4H_2SC(OEt)\}(CO)_4]$, was fully characterised. Spectroscopic analysis indicated the difference in electronic environment of the respective carbene ligands and four distinct carbonyl vibrations and electron transitions were observed. Mass spectral data designated sequential carbonyl loss of molecular ions for representative compounds. The X-ray diffraction studies confirmed molecular structure and showed incomplete hydrolysis of lithium atoms present. The monochelate, $[Mo\{C(OEt)2,3-C_4H_2SC(OEt)\}(CO)_4]$ and $[W\{C(OEt)2,3-C_4H_2SC(OEt)\}(CO)_4]$ packed in a grid-like structure and the tetracarbene complex and aminolysis product showed more disorder. Partial aminolysis of $[Cr\{C(OEt)2,3-C_4H_2SC(OEt)\}(CO)_4]$ showed the relative stability of the ethoxy substituents. The resonance stabilised ethoxy group was retained in a stepwise aminolysis to form $[Cr\{C(OEt)2,3-C_4H_2SC(NH_2)\}(CO)_4]$. This behaviour was unique in carbene chemistry. Further reaction with ammonia resulted in decomposition due to the weakening of the metal carbon bonds in the chelate ring, resulting in the formation of $[Cr(CO)_4(NH_3)_2]$.