

Synthesis and Structural Investigations of Manganese Carbene Complexes

by

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Submitted in partial fulfilment of the degree

Magister Scientiae

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University of Pretoria
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Declaration

I declare that the dissertation, which I hereby submit for the degree Magister Scientiae at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution.

Results obtained from this study have also been published in:

S. Lotz, M. Landman, D.I. Bezuidenhout, A.J. Olivier, D.C. Liles, P.H. van Rooyen, *Journal of Organometallic Chemistry*, 690, **2005**, 5929-5937.

Signature:

Date:

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Daniela

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Summary

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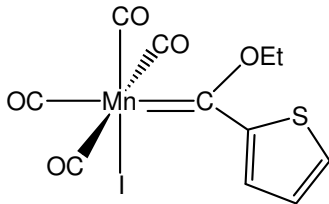
The study involves the synthesis and structural characterization of manganese carbene complexes. The synthesis of dimanganese monocarbene complexes $[\text{Mn}_2(\text{CO})_9\{\text{C}(\text{OEt})(\text{heteroaryl})\}]$ was done via the classical Fischer method, and a range of complexes containing heteroaromatic substituents, e.g. 2,2'-bithiophene, thiophene, furan and N-methyl pyrrole, was isolated. These complexes displayed a novel configuration with the carbene ligand in the axial position, in contrast to the equatorial position found for the analogous rhenium compound and other dimanganese complexes known from the literature.

The possibility of manipulating the position of the carbene ligand in the binuclear complexes was investigated by a nucleophilic substitution of the ethoxy substituent with an amine substituent. Only aminolysis with small, primary amines such as ammonia and propylamine, proved successful. The propylaminocarbene ligands retained their axial configuration, but a conversion to the more thermodynamically stable equatorially substituted carbene ligands was observed for the complexes $[\text{Mn}_2(\text{CO})_9\{\text{C}(\text{NH}_2)(\text{heteroaryl})\}]$, while mixtures of the equatorial and axial isomers were observed in solution. Structural X-ray analysis proved that although the equatorial position is more electronically favourable, steric hindrance by the second manganese pentacarbonyl moiety prevented ethoxy- and propylamino-substituted carbene ligands to adopt this configuration. A kinetic study of the

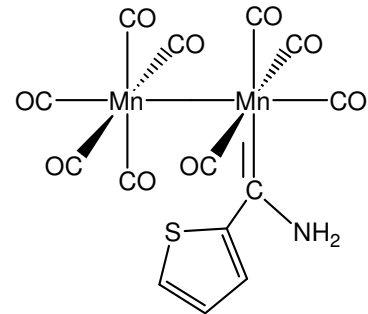
aminolysis reaction was done in an effort to elucidate the reaction mechanism and to explain the axial-equatorial conversion. Due to the competing decomposition reaction of the product and reagent complexes with that of the substitution reaction, no information about reaction intermediates could be obtained.

The target mononuclear complexes $[\text{Mn}(\text{CO})_4\{\text{C}(\text{OEt})(\text{heteroaryl})\}\text{X}]$ ($\text{X} = \text{Br}, \text{I}$) was obtained by cleavage of the metal-metal bond of the binuclear precursor complexes. Cleaving of the Mn-Mn bond was done oxidatively by halogens, without affecting the carbene ligand. The product complexes have an assembly resembling that of the Grubbs ruthenium metathesis catalyst. Interestingly, the cleaved complexes were found to have a *cis* configuration of the carbene and halide ligand.

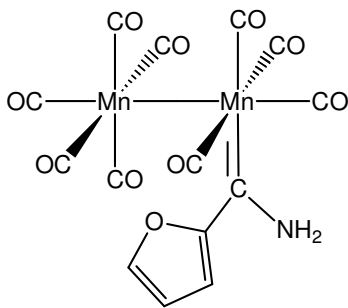
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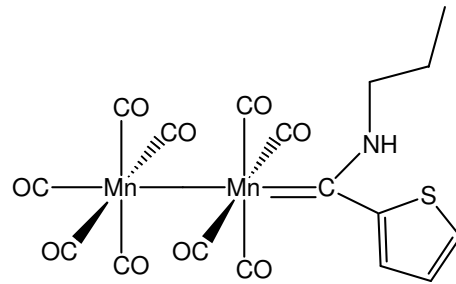
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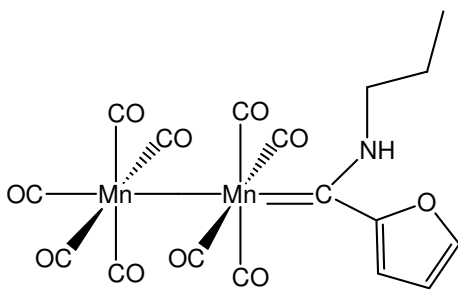
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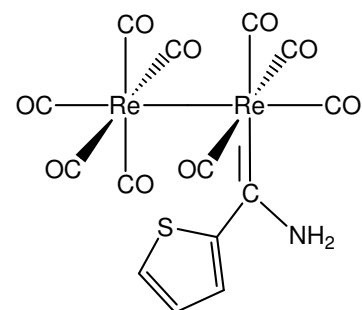
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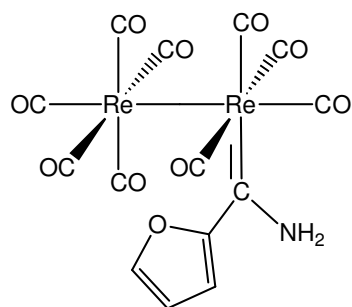
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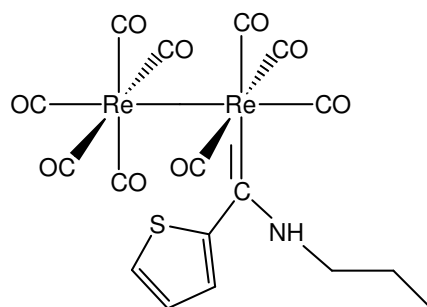
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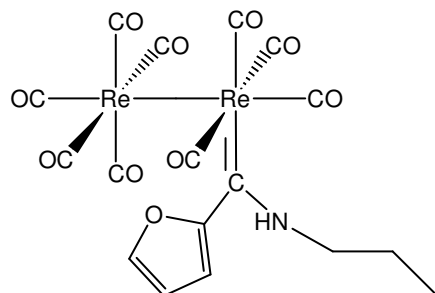
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List of Abbreviations

Bu	:	butyl
Cp	:	$\eta^5\text{-C}_5\text{H}_5$
d	:	doublet
DCM	:	dichloromethane
DEE	:	diethyl ether
dd	:	doublet of doublets
ddd	:	doublet of doublets of doublets
Et	:	ethyl
HETCOR	:	Heteronuclear Correlation Spectroscopy
IR	:	Infrared Spectroscopy
<i>J</i>	:	coupling constant
m	:	medium (IR)
Me	:	methyl
MLCT	:	metal-to-ligand charge transfer
NMR	:	Nuclear Magnetic Resonance Spectroscopy
n.o.	:	not observed
Ph	:	Phenyl
R	:	alkyl group
RT	:	room temperature
s	:	singlet (NMR)
s	:	strong (IR)
THF	:	tetrahydrofuran
UV	:	ultraviolet
vs	:	very strong (IR)
vis	:	visible
w	:	weak (IR)
Å	:	angstrom
δ	:	chemical shift
λ	:	wavelength

