

# **Modification of Rhenium carbonyls with thienyl nucleophiles**

By

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## Declaration

I hereby state that the work described in this thesis was performed by me at the Department of Chemistry, University of Pretoria, South Africa from August 2001 to August 2008 under the supervision of Prof. Simon Lotz and Dr. Marilé Landman. I declare that this thesis is my own, unaided work submitted for the degree of Philosophiae Doctor and has not before been submitted for a degree or examination at this university or any other institution.

The X-ray structure determinations of complexes **1**, **3**, **5**, **6**, **7**, **8**, **13** and **15** were performed by David Liles at the University of Pretoria.

.....  
(Andrew John Olivier)

.....day of ....., 2009.

## **Thank you...**

I express my sincere gratitude to the following people who have helped me complete my Ph.D. in chemistry.

Of course, the people who have helped me the most are my promoter, Prof. Dr. Simon Lotz and my parents (Bernard and Juriena Olivier). There is much I can say of them. They have all played the role of teacher, mentor, parent, critic, promoter and inspirer at some time or another. For this I am deeply grateful. I also cannot omit mention of my co-promoter, Dr. Marilé Landman, in this paragraph. She was an inspiration to me and a true friend. Her guidance was invaluable.

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.....  
Andrew John Olivier.

## Summary

In the reaction between  $[\text{Re}(\text{CO})_5\text{Br}]$  and 2-lithiumthienyl, X-ligand substitution was expected.  $\text{Li}^+\{\text{C}_4\text{H}_3\text{S}\}^-$  did not substitute  $\text{Br}^-$ , but an intermediate negatively charged complex was obtained (non-mobile on silica gel) and it was found that the thienyl had bonded to a carbonyl ligand, producing a dirhenium acylate complex. Such complexes are the precursors to neutral Fischer carbene complexes. After alkylation with  $\text{Et}_3\text{OBF}_4$ ,  $[\text{Re}_2(\text{CO})_9\text{C}(\text{OEt})\text{C}_4\text{H}_3\text{S}]$  (**1**) was obtained, instead of a monorhenium monocarbene complex.

Greater yields of **1** could be obtained, from reactions with  $[\text{Re}_2(\text{CO})_{10}]$  instead of  $[\text{Re}(\text{CO})_5\text{Br}]$ .  $[\text{Re}_2(\text{CO})_{10}]$  reacted with 5-lithium-2,2'-bithienyl and 2-lithium-3,6-dimethylthieno[3,2-*b*]thienyl and was then alkylated with  $\text{Et}_3\text{OBF}_4$ . The reactions proceeded smoothly and  $[\text{Re}_2(\text{CO})_9\text{C}(\text{OEt})\text{C}_8\text{H}_5\text{S}_2]$  (**2**) and  $[\text{Re}_2(\text{CO})_9\text{C}(\text{OEt})\text{C}_8\text{H}_7\text{S}_2]$  (**3**) were obtained.

The substrates thiophene, 2,2'-bithiophene and 3,6-dimethylthieno[3,2-*b*]thiophene, can all be doubly lithiated under appropriate reaction conditions. These lithiated species were reacted with two equivalents of  $[\text{Re}_2(\text{CO})_{10}]$ . In the case of bithiophene this produced, in good yield, the tetrametal biscarbene complex  $[\text{Re}_2(\text{CO})_9\text{C}(\text{OEt})\text{C}_8\text{H}_4\text{S}_2\text{C}(\text{OEt})\text{Re}_2(\text{CO})_9]$  (**8**). In the thiophene and dimethylthieno[3,2-*b*]thiophene cases  $[\text{Re}_2(\text{CO})_9\text{C}(\text{OEt})\text{C}_4\text{H}_2\text{SC}(\text{OEt})\text{Re}_2(\text{CO})_9]$  (**7**) and  $[\text{Re}_2(\text{CO})_9\text{C}(\text{OEt})\text{C}_8\text{H}_6\text{S}_2\text{C}(\text{OEt})\text{Re}_2(\text{CO})_9]$  (**9**) could be isolated in meagre quantities. This was ascribed to poor double lithiation (also steric hindrance in the case of **7**).

The carbene ligands reacted with water on the silica gel during column chromatography or in a control experiment with degassed water to produce aldehydes by reductive elimination from the metal. Protonation of the acylrhenate afforded rhenium hydrides which is also a potential precursor to aldehyde formation. This is believed to be a facile process for especially complex **9**, isolated in very small quantity.

Complexes **7–9** produced monocarbene aldehyde complexes  $[\text{Re}_2(\text{CO})_9\text{C}(\text{OEt})\text{C}_4\text{H}_2\text{SC}(\text{O})\text{H}]$  (**12**),  $[\text{Re}_2(\text{CO})_9\text{C}(\text{OEt})\text{C}_8\text{H}_4\text{S}_2\text{C}(\text{O})\text{H}]$  (**13**) and  $[\text{Re}_2(\text{CO})_9\text{C}(\text{OEt})\text{C}_8\text{H}_6\text{S}_2\text{C}(\text{O})\text{H}]$  (**14**), as well as dialdehyde compounds. Complexes **2** and **3** also produced aldehyde compounds. The formation of aldehydes from ethoxycarbene complexes is believed to involve hydroxycarbene intermediate species. Experiments were performed on  $[\text{Re}_2(\text{CO})_{10}]$  and  $[\text{Re}(\text{CO})_5\text{Br}]$ . They were reacted with 2–lithiumthienyl and then protonated. In the case of  $[\text{Re}_2(\text{CO})_{10}]$ , hydride signals were observed on the  $^1\text{H}$  NMR spectrum, as well as aldehyde signals. In the case of  $[\text{Re}(\text{CO})_5\text{Br}]$  there was strong NMR evidence indicating the formation of a hydroxycarbene complex.

Complexes **1**, **2**, and **3** were reacted with  $\text{Br}_2(\text{l})$ . The metal–metal bonds were cleaved by the bromine to produce monorhenium carbene complexes  $[\text{Re}(\text{CO})_4\{\text{C}(\text{OEt})\text{C}_4\text{H}_3\text{S}\}\text{Br}]$  (**4**),  $[\text{Re}(\text{CO})_4\{\text{C}(\text{OEt})\text{C}_8\text{H}_5\text{S}_2\}\text{Br}]$  (**5**), and  $[\text{Re}(\text{CO})_4\{\text{C}(\text{OEt})\text{C}_8\text{H}_7\text{S}_2\}\text{Br}]$  (**6**) and  $[\text{Re}(\text{CO})_5\text{Br}]$ . Complex **8** reacted with bromine to produce a monocleaved complex  $[\text{Re}_2(\text{CO})_9\text{C}(\text{OEt})\text{C}_8\text{H}_4\text{S}_2\text{C}(\text{OEt})\text{Re}(\text{CO})_4\text{Br}]$  (**11**) and a biscleaved complex  $[\text{Re}(\text{CO})_4\text{Br}\{\text{C}(\text{OEt})\text{C}_8\text{H}_4\text{S}_2\text{C}(\text{OEt})\}\text{Re}_2(\text{CO})_4\text{Br}]$  (**10**).

Unique complexes  $[\text{Re}(\text{CO})_4\{\text{C}(\text{OH})\text{C}_4\text{H}_3\text{S}\}\{\mu\text{-H}\}\text{Re}(\text{CO})_4\{\text{C}(\text{O})\text{C}_4\text{H}_3\text{S}\}]$  (**15**) and  $[\text{Re}(\text{CO})_4\{\text{C}(\text{OH})\text{C}_8\text{H}_5\text{S}_2\}\{\mu\text{-H}\}\text{Re}(\text{CO})_4\{\text{C}(\text{O})\text{C}_8\text{H}_5\text{S}_2\}]$  (**16**) were obtained by starting with  $[\text{Re}(\text{CO})_5\text{Br}]$  or  $[\text{Re}_2(\text{CO})_{10}]$  and reacting them with 2–lithiumthienyl and 5–lithium–2,2′–bithienyl. These complexes were isolated from the column as very polar compounds after elution of the aldehyde complexes. The dirhenium complex was obtained with a carbonyl–modified ligand (hydroxycarbene/acyl) on each of the metals. The complexes consist of two fragments held together by a hydrogen atom that bridges the two rhenium atoms (hydrido) and one that bridges the oxygen atoms of the carbene/acyl ligands (protonic).



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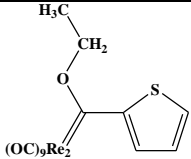
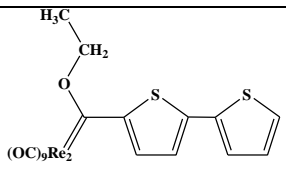
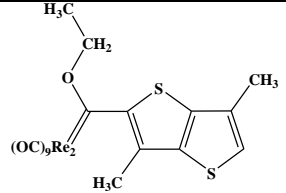
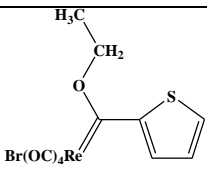
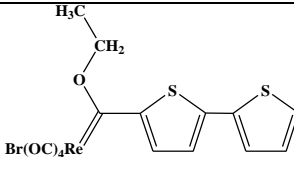
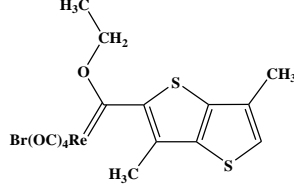
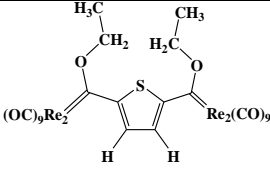
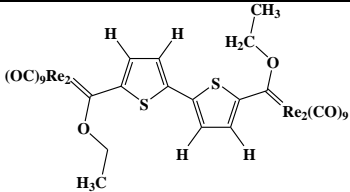
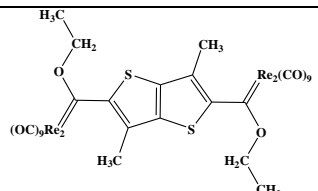


## List of acronyms

acac	– acetylacetone
br	– broad
Cp	– cyclopentadienyl
Cp*	– pentamethylcyclopentadienyl
d	– doublet
DCM	– dichloromethane
dd	– doublet of doublet
dppe	– 1,2-bis(diphenylphosphino)ethane
Hex	– hexane
IR	– Infrared
m	– multiplet
<i>m/z</i>	– mass charge ratio
Me	– methyl
MS	– Mass Spectrometry
NHC	– N-heterocyclic carbene
NMR	– Nuclear Magnetic Resonance
Ph	– phenyl
s	– singlet
solv	– solvent molecule or solvent
T	– thiophene or thienyl derivative
THF	– tetrahydrofuran
TLC / tlc	– thin layer chromatography
TT	– 3,6-dimethylthieno[3,2- <i>b</i> ]thiophene
T-T	– bithiophene
$\nu$	– wavenumber



## List of Complexes

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<b>Figure 3.9:</b> $^1\text{H}$ NMR data ( $\delta$ , ppm) for 5-formyl-2,2'-bithiophene (acetone- $d_6$ ) and 5,5'-diformyl-2,2'-bithiophene (chloroform- $d$ )
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<b>Figure 3.11:</b> $^{13}\text{C}$ NMR spectrum of <b>2</b> in $\text{CDCl}_3$
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<b>Scheme 3.1:</b> Double bond delocalization in thienyl substituents
<b>Scheme 3.2:</b> Resonance forms for complex <b>8</b>
<b>Scheme 3.3:</b> Competing resonance forms for <b>11</b>
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<b>Figure 4.1:</b> Molecular structure of <b>1</b>
<b>Figure 4.2:</b> A five-membered intermediate complex ring
<b>Figure 4.3:</b> Bond distances in (Å) of rhenium carbene complexes
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<b>Figure 4.18:</b> Hydrogen bonding between H3 and bromo ligand
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