

# **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.

The following people are also at the University of Pretoria and have helped me in many ways. Eric Palmer is the NMR wizard and Dave Liles the crystallographer. My Ph.D. would not have been possible, were it not for what these people did for me. My closest colleague is Daniela Bezuidenhout, who will also soon be Dr. Bezuidenhout. I hope I have meant as much to her as she has meant to me and I wish for her much success in the future in whatever she pursues. Other friends at the department of chemistry, decent people all, include the following: Nick Brennan, Werner Barnard, Amos Mbele, Annatjie Kok, Naomi Steenkamp, Melanie Rademeyer, Profs. Vlegaar and Rohwer, Dan Molefe, Jacorien Coetzee, Nina van Jaarsveld, Belinda van der Westhuizen, Leon Engelbrecht and the list goes on.

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I learned much about chemistry, about life and about being a better person during my years at the University of Pretoria. It is still, I believe, one of the best academic institutions in the world. I leave it a better man and with faith in myself for accomplishing great things in the future.

.....  
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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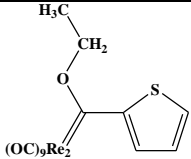
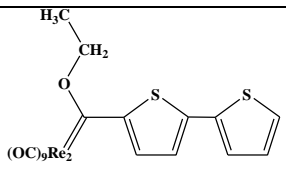
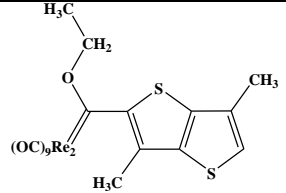
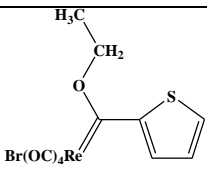
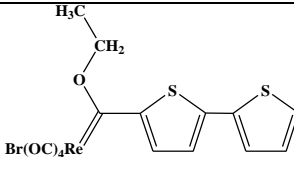
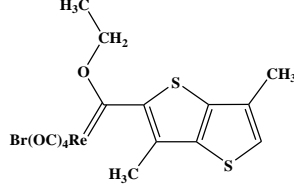
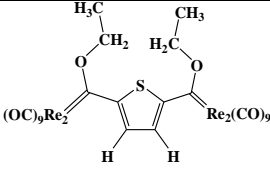
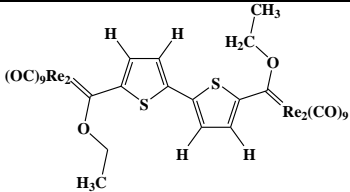
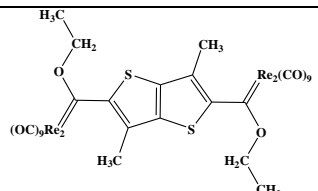


## List of acronyms

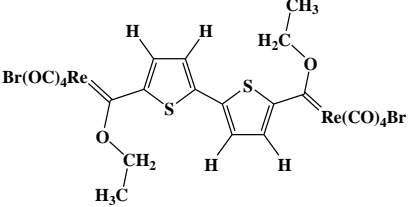
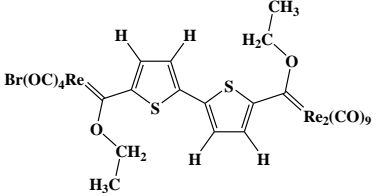
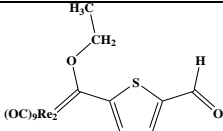
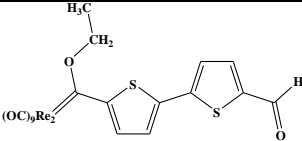
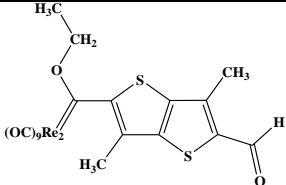
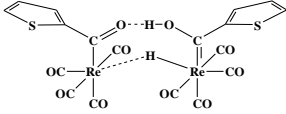
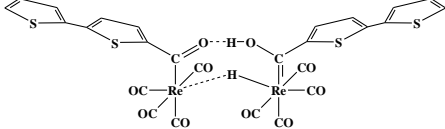
acac	– acetylacetone
br	– broad
Cp	– cyclopentadienyl
Cp*	– pentamethylcyclopentadienyl
d	– doublet
DCM	– dichloromethane
dd	– doublet of doublet
dppe	– 1,2-bis(diphenylphosphino)ethane
Hex	– hexane
IR	– Infrared
m	– multiplet
<i>m/z</i>	– mass charge ratio
Me	– methyl
MS	– Mass Spectrometry
NHC	– N-heterocyclic 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

	1
	2
	3
	4
	5
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	7
	8
	9



	<b>10</b>
	<b>11</b>
	<b>12</b>
	<b>13</b>
	<b>14</b>
	<b>15</b>
	<b>16</b>

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**Scheme 1.27:** Reaction of a nucleophile with  $[\text{Mn}(\text{CO})_5\text{Br}]$

**Scheme 1.28:** Reaction of a  $\pi$ -coordinated thiophene with  $[\text{Re}(\text{CO})_5\text{Br}]$

**Figure 2.1:** Axial and equatorial substituted carbene ligands

**Figure 2.2:** Radical cleaving of Re–Re bond by Br<sub>2</sub>

**Scheme 2.1:** Possible reactions of [Re(CO)<sub>5</sub>Br] with 2–lithiumthienyl

**Scheme 2.2:** Preparation of a rhenium Fischer carbene complex

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## Chapter 1: General Introduction

### 1.1. Carbene ligand

The chemistry of metal carbene complexes and of related complexes was introduced by Nobel Laureate Ernst Otto Fischer in 1964<sup>1</sup>. Today, carbene complexes similar to those original Group 6 carbene complexes are referred to as Fischer carbene complexes. In this study, the somewhat neglected low-valent Fischer carbene complexes of rhenium were synthesized and studied and aspects of their chemistry were investigated.

#### 1.1.1 Free carbene species

A free carbene molecule is comprised of a carbon with two substituents. One of the four carbon valence electrons is involved in  $\sigma$ -bonding to each of the substituents. The remaining two valence electrons are available for bonding. The carbene carbon atom therefore represents a six-electron species and is very reactive (unfilled octet). The two electrons not involved in bonding may be paired in one of the remaining orbitals and such a carbene is defined as a singlet carbene. In a triplet carbene, on the other hand, the two electrons each occupy its own orbital. Reactive carbene moieties can be stabilized by coordination to transition metals and Arduengo<sup>2</sup> and Bertrand<sup>3</sup> pioneered research in the isolation of free carbenes (Figure 1.1).

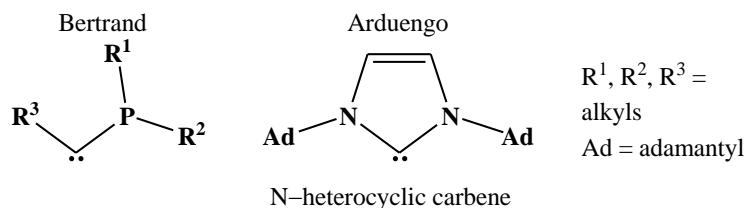
The bent structure of the carbene ligand comes from the carbene carbon atom being  $sp^2$  hybridized.

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<sup>1</sup> E.O. Fischer, A. Maasböl; *Angew. Chem., Int. Ed. Engl.*, **1964**, 3, 580–581

<sup>2</sup> A. J. Arduengo, R. L. Harlow, M. Kline; *J. Am. Chem. Soc.*, **1991**, 113, 361–363

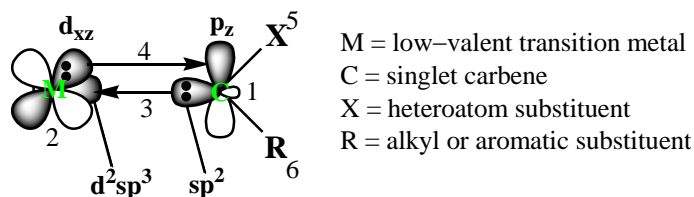
<sup>3</sup> (a) A. Igau, H. Grutzmacher, A. Baceiredo, G. Bertrand; *J. Am. Chem. Soc.*, **1988**, 110, 6463–6466; (b) A. Igau, A. Baceiredo, C. Trinquier, G. Bertrand; *Angew. Chem. Int. Ed. Engl.*, **1989**, 28, 621–622; (c) Y. Canac, M. Soleilhavoup, S. Conejero, G. Bertrand; *J. Organomet. Chem.*; **2004**, 689, 3857–3865



**Figure 1.1:** The Bertrand and Arduengo carbenes

### 1.1.2 Low-valent metal carbene complexes

The carbene function of a Fischer carbene complex can be generated from the stepwise reaction of a metal carbonyl precursor with organolithium agents (which nucleophilically attack a carbonyl ligand), followed by alkylation. After alkylation the carbene displays an alkoxy substituent. A Fischer carbene complex in this context can be seen as an organometallic analogue of an organic ester. The nature of bonding, however, is different than that of an ester. The bonding of the carbene ligand is shown in Figure 1.2<sup>4</sup>.



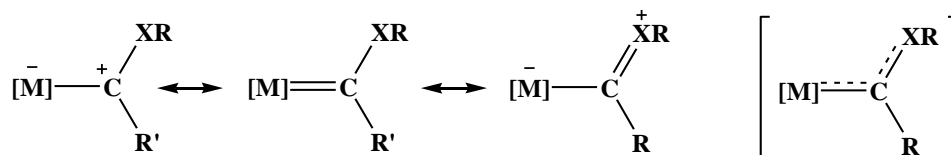
**Figure 1.2:** Typical Fischer carbene complex showing the bonding between the carbene carbon and its substituents

In a typical Fischer carbene complex, the  $sp^2$  singlet carbene ligand (1) is an L-type ligand (Green classification<sup>5</sup>), bonding to the transition metal (2), which is formally in a low oxidation state, by dative  $\sigma$ -donation of an electron-pair in a  $sp^2$ -hybrid orbital (3).

<sup>4</sup> In an ester, electrons are shared in normal covalent bonds, but in the Fischer carbene complex the electron-pairs are donated by the two partners in a synergic fashion, i.e. the metal atom and the carbon atom.

<sup>5</sup> M. L. H. Green; *J. Organomet. Chem.*, **1995**, 500, 127–148

A second dative back-donation from the metal ( $t_{2g}$ -orbitals) into the empty p-orbital on the carbene carbon makes a  $\pi$ -bond (4). Commonly, oxygen or nitrogen (with their own substituents) is the heteroatom (5). These heteroatoms contain electron lone-pairs (Lewis bases) that can be donated into the carbene carbon's empty p-orbital. The competition for  $\pi$ -stabilization between the metal and the heteroatom might be depicted by the following resonance forms (Scheme 1.1).



**Scheme 1.1:**  $\pi$ -Bonding interactions in Fischer carbene complexes

Because nitrogen has a lower electronegativity than oxygen, nitrogen will more effectively participate in backbonding to the carbene carbon atom. If the substituents of the carbene carbon can dominate the stabilization of the carbene carbon through  $\pi$ -donation, the metal back-donation into the carbene carbon p-orbital is of only minor relevance. Under these circumstances the bond between the metal atom and carbon atom is longer, and one would not necessarily draw the bond as containing double bond character. This is the case with N-heterocyclic carbene ligands (NHCs), which are quite stable as free uncomplexed molecules<sup>6</sup> – they are usually stabilized by bulky nitrogen substituents. As another example, consider a high-valent metal species that has no  $t_{2g}$  electrons<sup>7</sup> available in a low-lying orbital to  $\pi$ -donate into the carbene carbon p-orbital.

### 1.1.3 Applications of Fischer carbene complexes

Fischer carbene complexes have current impact in chemistry in template reactions in

<sup>6</sup> M. F. Lappert; *J. Organomet. Chem.*, **2005**, 690, 5467–5473

<sup>7</sup> W. A. Herrmann, K. Öfele, M. Elison, F. E. Kuhn, P. W. Roesky; *J. Organomet. Chem.*, **1994**, 480, C7–C9

organic chemistry<sup>8</sup>, in catalysis<sup>9</sup> and in materials science<sup>10</sup>. NHCs, that are superior to phosphines in many respects, are found as ancillary ligands for coupling–reaction catalysts<sup>11</sup> and metathesis (Grubbs) catalysts<sup>12</sup>.

A metal–carbene connection can be made by attachment of the free carbene species at a vacant coordination site on a metal, which is an application of free carbenes<sup>13</sup>. This is not the most common method of carbene complex synthesis, because free carbenes are difficult to work with as they tend to dimerize<sup>14</sup>.

## **1.2. Group 7 metal carbene complexes**

### **1.2.1 Background/Introduction**

Group 7 transition metals have an uneven number of valence electrons and thus require at least one X–type ligand (see Green classification of ligands<sup>5</sup>). Synthesis of Group 7 carbene complexes, in this study, involved low–valent dirhenium decacarbonyl or rheniumpentacarbonyl bromide. The X–type ligand of each rhenium in the dimer complex  $(\text{CO})_5\text{Re–Re}(\text{CO})_5$  is “ $\text{Re}(\text{CO})_5$ ” and in  $[\text{Re}(\text{CO})_5\text{Br}]$ , it is the bromo ligand. For

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<sup>8</sup> J. W. Herndon; *Coord. Chem. Rev.*, **2000**, 206–207, 237–262

<sup>9</sup> C. W. Bielawska, R. H. Grubbs; *Progress in Polymer Science*, **2007**, 32, 1–29

<sup>10</sup> J. Barluenga, D. de S a, A. G omez, A. Ballesteros, J. Santamar a, A. de Prado, M. Tom as, A. L. Su arez–Sobrino; *Angew. Chem. Int. Ed.*, **2008**, 47, 6225–6228

<sup>11</sup> R. Chinchilla, C. N ajera; *Chem. Rev.* **2007**, 107, 874–922

<sup>12</sup> a) S. T. Nguyen, R. H. Grubbs, J. W. Ziller; *J. Am. Chem. Soc.*, **1993**, 115, 9858–9859; b) G. C. Fu, S. T. Nguyen, R. H. Grubbs; *J. Am. Chem. Soc.*, **1993**, 115, 9856–9857; c) T. M. Trnka, R. H. Grubbs; *Acc. Chem. Res.*, **2001**, 34, 18–29; (d) P. Schwab, M. B. France, J. W. Zille, R. H. Grubbs; *Angew. Chem., Int. Ed. Engl.*, **1995**, 34, 2039–2041; (e) E. L. Dias, S. T. Nguyen, R. H. Grubbs; *J. Am. Chem. Soc.*, **1997**, 119, 3887–3897; (f) T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich, W. A. Herrmann; *Angew. Chem., Int. Ed. Engl.*, **1999**, 38, 2416–2419; (g) S. F. Vyboishchikov, M. B uhl, W. Thiel; *Chem. Eur. J.*, **2002**, 8, 3962–3975

<sup>13</sup> A. M. Voutchkova, M. Feliz, E. Clot, O. Eisenstein, R. H. Crabtree; *J. Am. Chem. Soc.*, **2007**, 129, 12834–12846

<sup>14</sup> W. Kirmse; *Angew. Chem. Int. Ed. Engl.*, **2005**, 44, 2476–2479

different complexes  $[M(CO)_4LX]$  ( $L = CO, C(OR)R'$ ;  $X = \text{halide, H, } M(CO)_5$ ), we have isolobal relationships for the X-type ligands, as indicated below<sup>15</sup>:



### 1.2.2 X-ligands in Group 7 metal carbene chemistry

Halogen substitution is a common tool in chemical transformation. As an example: a charged organic nucleophile can replace a halogen ligand of a Group 7 metal complex<sup>16</sup>. Then there are examples of an organic group bearing a halogen that couples with an anionic metal complex<sup>17</sup>. Shown in Scheme 1.2 is a reaction that was reported by King<sup>18</sup>; the reaction of the metal carbonyl anionic complex,  $[\text{Mn}(\text{CO})_5]^-$ , with 1,3-dibromopropane. The structure of the product was assigned incorrectly by King, as indicated in Scheme 1.2, because three signals in the proton NMR spectrum were misinterpreted. Proton NMR spectroscopy was later employed by Casey to assign the correct structure<sup>19</sup>.

The true structure of the complex that was obtained by King raises the interesting question of how it might have formed. A mechanism for the formation of the dimanganese monocarbene complex is provided in Scheme 1.3. It shows a replacement of one of the 1,3-dibromopropane bromines by  $[\text{Mn}(\text{CO})_5]^-$ . The new alkyl ligand on the manganese migrates to a carbonyl ligand and a vacant coordination site is created. An attack by  $[\text{Mn}(\text{CO})_5]^-$  on this intermediate complex induced electron movement and bond-formation between the acyl oxygen atom and the farthest carbon atom (with bromide expulsion), produced the final Fischer carbene complex. King was correct in

<sup>15</sup> R. Hoffmann; *Angew Chem. Int. Ed. Engl.*, **1982**, 21, 711–724

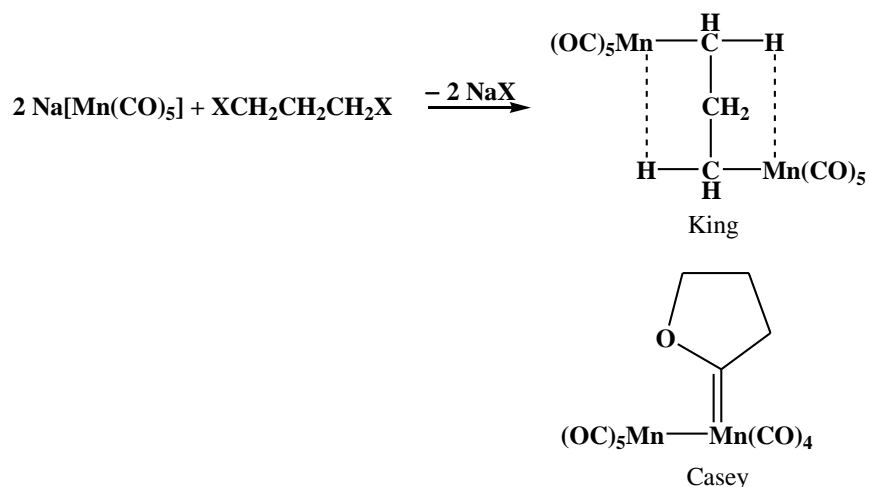
<sup>16</sup> (a) S. Lotz, M. Schindehutte, P. H. Van Rooyen; *Organometallics*, **1992**, 11, 629–639; (b) T. A. Waldbach, P. H. van Rooyen, S. Lotz; *Organometallics*, **1993**, 12, 4250–4253; (c) T. A. Waldbach, P. H. van Rooyen, S. Lotz; *Angew. Chem. Int. Ed. Engl.*, **1993**, 32, 710–712

<sup>17</sup> Y. Matsuo, Y. Kuninobu, A. Muramatsu, M. Sawamura, E. Nakamura; *Organometallics*, **2008**, 27, 3403–3409

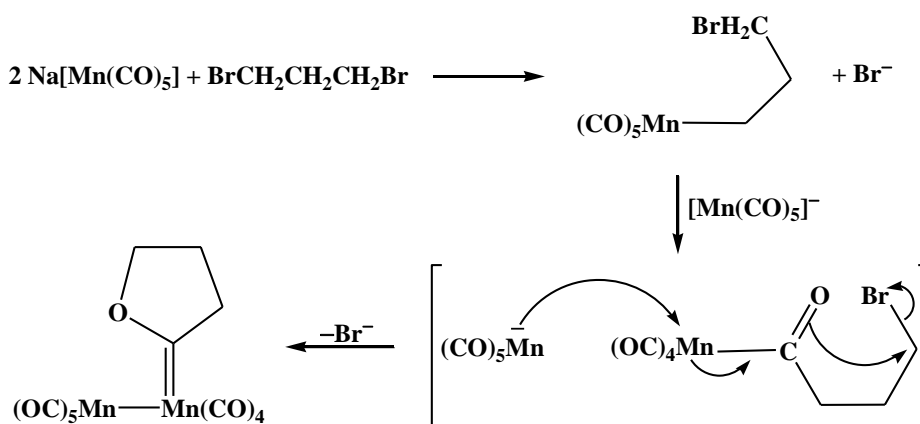
<sup>18</sup> R. B. King; *J. Am. Chem. Soc.*, **1963**, 85, 1922–1926

<sup>19</sup> C. P. Casey; *J. C. S. Chem. Comm.*, **1970**, 1220–1221

assuming a path where both the halogen atoms were lost from the reagent, as the final carbene complex is indeed without any halogens.



**Scheme 1.2:** King and Casey structures for the dimanganese carbene complex

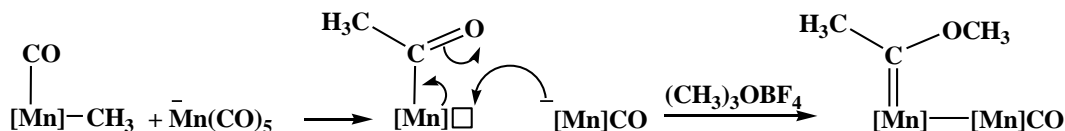


**Scheme 1.3:** A mechanism for the formation of the ‘King’ complex

Casey also showed that the anionic complex  $[\text{Mn}(\text{CO})_5]^-$  attacks on the manganese complex  $[\text{Mn}(\text{CO})_5(\text{CH}_3)]$ , induces the alkyl ligand to migrate to a carbonyl ligand, and then binds to the manganese. Alkylating agent was added and the carbene complex

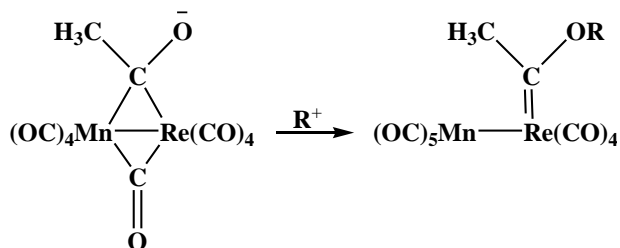
formed<sup>20</sup>, as illustrated in Scheme 1.4.

[Mn] = Mn(CO)<sub>4</sub> □ = vacated coordination site



**Scheme 1.4:** Nucleophilic attack induces methyl migration

Interestingly, in the reaction of Na[Re(CO)<sub>5</sub>] and [Mn(CO)<sub>5</sub>CH<sub>3</sub>], the carbene ligand of the resulting mixed Mn–Re complex is found on the rhenium fragment. An intermediate (Scheme 1.5) with a bridging acylate ligand was postulated.



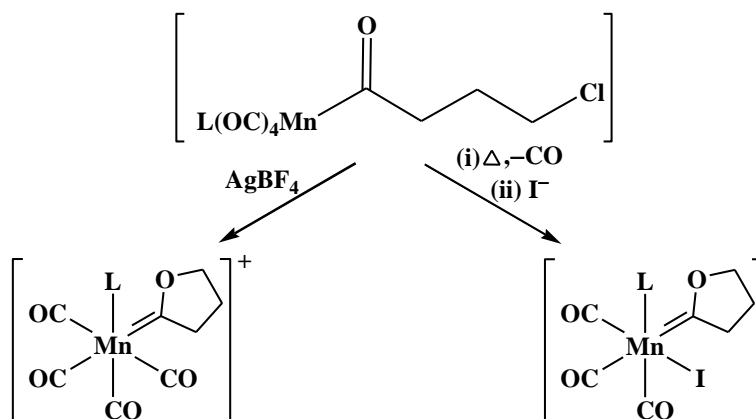
**Scheme 1.5:** Mn–Re carbene complex

Monomanganese carbene complexes were synthesized by reacting Na[Mn(CO)<sub>4</sub>L] with 4-chlorobutyryl chloride (has carbonyl functionality built into the organic substrate), to give an intermediate chloro acyl compound. Abstraction of the terminal chlorine of the acyl ligand by AgBF<sub>4</sub> gave a cationic carbene complex, whilst heating and reacting with iodide gave a neutral carbene complex<sup>21</sup> (Scheme 1.6).

<sup>20</sup> (a) C. P. Casey, R. L. Anderson; *J. Am. Chem. Soc.*, **1971**, 93, 3554–3555; (b) C. P. Casey, C. R. Cyr, R. L. Anderson, D. F. Marten; *J. Am. Chem. Soc.*; **1975**; 97; 3053–3059

<sup>21</sup> C. H. Game, M. Green, J. R. Moss, F. G. A. Stone; *J.C.S. Dalton Trans.*, **1974**, 351–357





**Scheme 1.6:** Carbene ligand formation through cyclization

In another interesting reaction, the replacement of two of the carbonyl ligands of the manganese acyl complex  $[\text{Mn}(\text{CO})_5\{\text{C}(\text{O})\text{Me}\}]$  by 1,2-bis(diphenylphosphino)ethane (dppe) facilitates the alkylation of the acyl ligand. The resultant complex,  $[\text{Mn}(\text{CO})_3(\text{dppe})\{\text{C}(\text{O})\text{Me}\}]$ , reacts with  $\text{CF}_3\text{SO}_3\text{CH}_3$  and the monomanganese cationic carbene complex  $[\text{Mn}(\text{CO})_3(\text{dppe})\{\text{C}(\text{OMe})\text{Me}\}]^+\text{OSO}_2\text{CF}_3$  forms<sup>22</sup>.

### 1.3 Reactions of Group 7 metal complexes with nucleophiles

#### 1.3.1 Fischer carbene complexes

Nucleophiles (even halides<sup>23</sup>) can transform carbonyl and isocyanide ligands into Fischer carbene ligands, by nucleophilic attack on the carbon atom of these ligands. The carbon of CO and  $\text{CNR}^{24}$  ligands donates an electron-pair to the metal and has a hetero-atom already bonded to it, similar to the Fischer carbene carbon atom.

E. O. Fischer synthesized dirhenium carbene complexes by his established method of reaction with a nucleophile ( $\text{Nu}^-$ ), which attacks on a carbonyl ligand, and then

<sup>22</sup> P. M. Treichel, K. P. Wagner; *J. Organomet. Chem.*, **1975**, 88, 199–206

<sup>23</sup> E. O. Fischer, J. Chen, K. Scherzer; *J. Organomet. Chem.*, **1983**, 253, 231–241

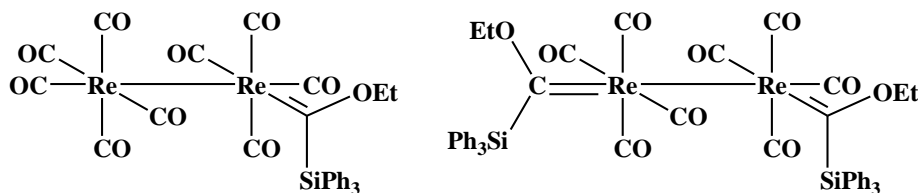
<sup>24</sup> F. E. Hahn, V. Langenhahn, T. Pape, *Chem. Commun.*, **2005**, 5390–5392

alkylation (electrophile:  $R^+$ ) of the intermediate<sup>25</sup>:



In the same way Fischer prepared dimanganese monocarbene complexes, starting with  $Mn_2(CO)_{10}$ <sup>26</sup>, as well as equatorial technetium monocarbene complexes, starting with  $Tc_2(CO)_{10}$ <sup>27</sup>.

Schubert reported some very interesting dirhenium biscarbene complexes with silyl nucleophiles<sup>28</sup> (Figure 1.3). One of the complexes is the only example that we are aware of where two carbene ligands are coordinated to a dirhenium system, with one carbene ligand coordinated in an axial position and the other in an equatorial position.



**Figure 1.3:** Rustemeyer dirhenium carbene complexes

### 1.3.2 Possible reaction intermediates

By contrast to Group 6 transition metal carbonyl complexes, more reactive intermediates are possible when Group 7 transition metal complexes react with the nucleophiles, because both L-type and X-type ligands are present in the precursors: “[ $Re(CO)_5X$ ]”. With X being “[ $Re(CO)_5$ ]”, the outcome of the Fischer carbene synthesis reaction is

<sup>25</sup> E. O. Fischer, E. Offhaus, J. Muller, D. Nöthe; *Chem. Ber.*, **1972**, *105*, 3027–3035

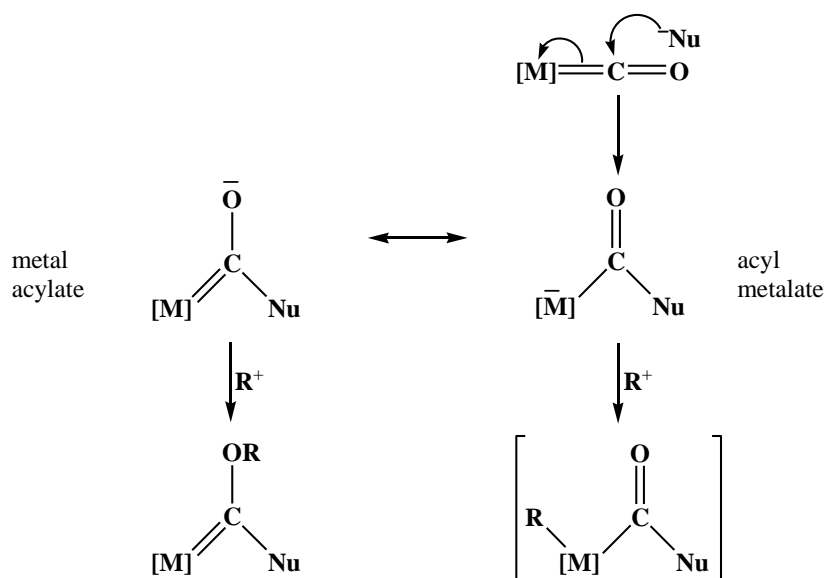
<sup>26</sup> E. O. Fischer, E. Offhaus; *Chem. Ber.*, **1969**, *102*, 2449–2455

<sup>27</sup> E. O. Fischer, E. Offhaus, J. Müller, D. Nöthe; *Chem. Ber.*, **1972**, *105*, 3027–3035

<sup>28</sup> E. O. Fischer, P. Rustemeyer; *J. Organomet. Chem.*, **1982**, *225*, 265–277; (b) U. Schubert, K. Ackermann, P. Rustemeyer; *J. Organomet. Chem.*, **1982**, *231*, 323–334; (c) E. O. Fischer, P. Rustemeyer, O. Orama, D. Neugebauer, U. Schubert; *J. Organomet. Chem.*, **1983**, *247*, 7–19

however the same as for Group 6 transition metal carbonyl complexes.

When the nucleophile attacks on the carbonyl carbon atom, the bond order of the bond between the carbon and the metal or of the bond between the carbon and the oxygen is affected (Scheme 1.7). The carbon is rehybridized from  $sp$  to  $sp^2$ . The electrophile that is added, for instance an alkylating agent (oxonium salts like  $[R_3O]BF_4$  are commonly used), will react with the atom of higher negative charge. A metalate normally forms if the anionic nucleophile attacks on the carbon atom of a carbonyl ligand. A metal acylate is a resonance form of the former. Both cases are illustrated in Scheme 1.7. The double bond location between the carbon atom and one of its three substituents is of consequence as it impacts on the nature of the  $\sigma$ -bonding around the carbon atom.

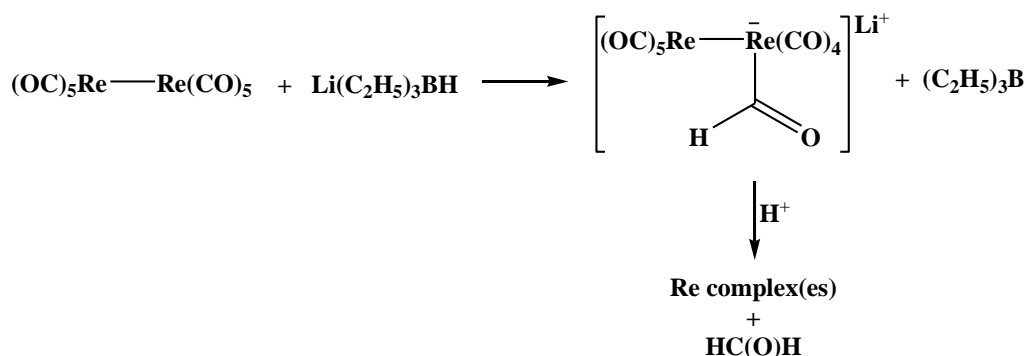


**Scheme 1.7:** Possible intermediates and products after attack of a nucleophile and subsequent alkylation

The alkylation on the metal of the acyl metalate species generally affords unstable complexes with two X-type ligands, whose reductive elimination gives an organic product (for instance ketones). Semmelhack showed that such iron tetracarbonyl phenyl carbene intermediates react with alkylating agents ( $R-X$ ) to be alkylated at the metal –

PhCOR and PhCO<sub>2</sub>R were obtained (FeCl<sub>3</sub> was added).<sup>29</sup>

Gladysz and co-workers made X-type formyl ligands by reacting [Re<sub>2</sub>(CO)<sub>10</sub>] and [Mn<sub>2</sub>(CO)<sub>10</sub>] with a hydride source<sup>30</sup>. Nucleophilic attack on a carbonyl ligand by the hydride resulted in the shift of an electron to the metal and not the oxygen atom. The complexes could then dissociate formaldehyde by reaction with acid (Scheme 1.8). The proton presumably bonds to the rhenium and is then reductively eliminated with the acyl ligand.



**Scheme 1.8:** Anionic formyl complex formation

The metal acylate form is found in most cases to be alkylated to give neutral Fischer carbene complexes. Fischer alkoxy-carbene carbon atoms generally display the following order of  $\pi$ -stabilization: M > O >> C(R).

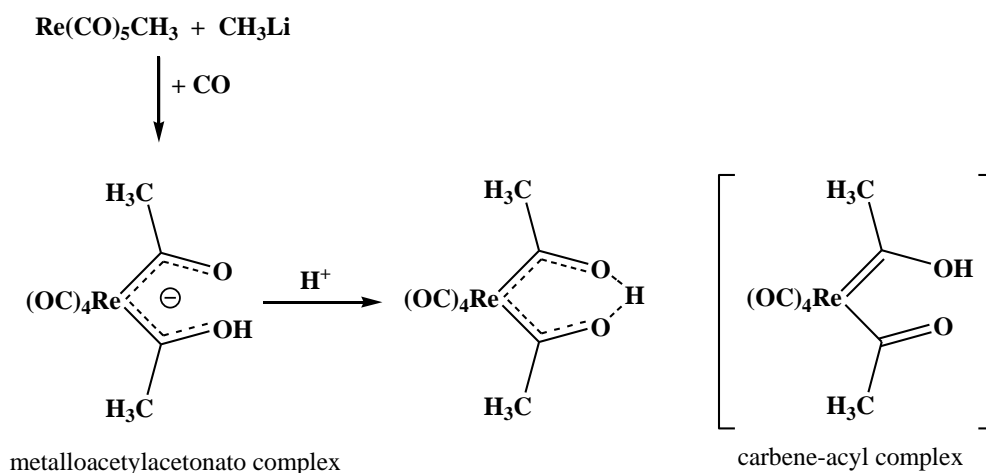
An alternative to alkylating the oxygen of the metal acylate is to protonate it with an acid, a process that produces hydroxycarbene complexes. In the 1960s E. O. Fischer prepared hydroxycarbene complexes and the carbene ligands were found to be transformed into

<sup>29</sup> (a) H. Alper, J-L. Fabre; *Organometallics* **1982**, *1*, 1037–1040; (b) W. Petz; *Organometallics*, **1983**, *2*, 1044–1046; (c) K. H. Dötz, U. Wenicker, G. Muller, H. G. Alt, D. Seyferth; *Organometallics* **1986**, *5*, 2570–2572; (d) M. F. Semmelhack, R. Tamura; *J. Am. Chem. Soc.*, **1983**, *105*, 4099–4100

<sup>30</sup> W. Tam, M. Marsi, J. A. Gladysz; *Inorg. Chem.*, **1983**, *22*, 1413–1421

aldehydes (a product one might expect if the protonation was on the metal)<sup>31</sup>.

Lukehart prepared a fascinating monorhenium compound displaying both acyl and hydroxycarbene ligands<sup>32</sup> – the synthesis is shown in Scheme 1.9. The intermediate was referred to as a metalloacetylacetonato complex because it is the organometallic analogue of acac and may itself be a ligand to other metals. What is most interesting is that, where one might define one of the ligands in the final complex as being a hydroxycarbene ligand and the other as being an acyl ligand, both of the ligands actually have carbene and acyl character. It was illustrated in Scheme 1.7 that the intermediate forms of Fischer carbene complex synthesis may be a metal acylate or an acyl metalate species, depending on the location of the charge and of the double bond. In the Lukehart complex, the delocalization of negative charge and double bond is also evident.



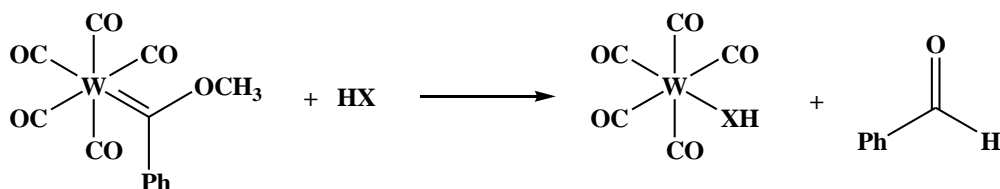
**Scheme 1.9:** Lukehart's rhenium acetylacetonato complex

The reaction between a tungsten Fischer carbene complex and a strong acid also leads to aldehydes and strong acid complexes being formed by cleavage of the metal–carbene

<sup>31</sup> (a) E. O. Fischer, G. Kreis, F. R. Kreissl; *J. Organomet. Chem.*, **1973**, 56, C37–C40; (b) M. Ryang, I. Rhee, S. Tsutsumi; *Bull. Chem. Soc. Jpn.*, **1964**, 37, 341–343

<sup>32</sup> (a) C. M. Lukehart, G. Paull Torrence, J. V. Zeile; *J. Am. Chem. Soc.*; **1975**; 97, 6903–6904; (b) C. M. Lukehart, J. V. Zeile; *J. Am. Chem. Soc.*; **1976**, 98, 2365–2367

bond<sup>33</sup>:



**Scheme 1.10:** Aldehyde formation from Fischer carbene complexes

The carbene carbon is bonded to three atoms that may or may not stabilize it by  $\pi$ -donation into the empty carbene p-orbital. It has been shown how there may be double bonding between the metal and the oxygen atom. The former attacking nucleophile is usually a carbon substituent ( $sp$ ,  $sp^2$ ,  $sp^3$ -C) and less stabilization, through  $\pi$ -interaction, is expected to come from a carbon substituent than from the metal or oxygen substituent. If it is an aromatic ring, for instance,  $\pi$ -interaction between it and the carbene carbon would correspond to a loss of aromaticity, which would be energetically unfavourable. The third substituent may however also be a heteroatom that has available electron-pairs. Examples of these are the N-heterocyclic carbene complexes where the  $\pi$ -stabilization from the ring nitrogen atoms is greater than that from the metal.

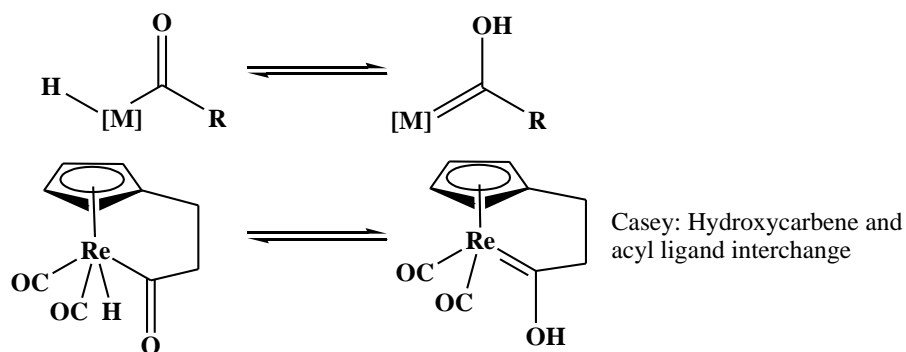
In the carbonyl transition metal complexes of transition metals that have an even number of valence electrons (complexes that may only have L-type ligands), the carbene synthesis could produce an acyl intermediate with a negative charge on the metal. Alkylation on the metal will then give a complex with two X-type ligands, which may both reductively eliminate. Group 7 metals differ in that they already have to have an X-type ligand or a ligand with X-functionality built in (for instance the  $L_2X$  Cp ligand) for an eighteen electron configuration. If  $[Re(CO)_5Br]$  is reacted with a nucleophile, an interesting anionic intermediate may be obtained, which is the eighteen electron acyl intermediate  $[Re(CO)_4\{C(O)Nu\}Br]^-$ . If the bromo ligand is lost from the intermediate rhenium complex as bromide, one X-type ligand is lost, not two, as with reductive

<sup>33</sup> E. O. Fischer, S. Walz, G. Kreis, F. R. Kreissl; *Chem. Ber.*, **1977**, *110*, 1651–1658

elimination. An unsaturated neutral acyl complex is left. This occurrence represents an added dimension of reactivity that does not exist with Group 6 or 8 metal carbene intermediates and it forms an integral part of this study.

#### 1.4 Dual nature of ligands (L, X) in Group 7 metal complexes

The hydroxycarbene ligand of a Fischer carbene complex is an L-type ligand, formed by oxygen protonation of the metal acylate intermediate. If the hydrogen atom that is bonded to the oxygen substituent migrates to the metal, the carbene ligand is transformed into two X-type ligands, i.e. the acyl and hydride (Scheme 1.11). These interchangeable species are organometallic analogues of keto–enol tautomerization in organic chemistry (Scheme 1.11). Casey showed that a hydroxycarbene complex and a metal acyl–hydride complex are in equilibrium (the favoured form depends on the solvent)<sup>34</sup>. The carbene could be converted to a non–heteroatom stabilized amphiphilic carbene complex (can behave like a Fischer or a Schrock carbene)<sup>35</sup>.



**Scheme 1.11:** “Metallo–keto” and “metallo–enol” tautomers

It has been discussed that a rhenium ligand can show properties intermediate between

<sup>34</sup> C. P. Casey, C. J. Czerwinski, R. K. Hayashi; *J. Am. Chem. Soc.*; **1995**, *117*, 4189–4190

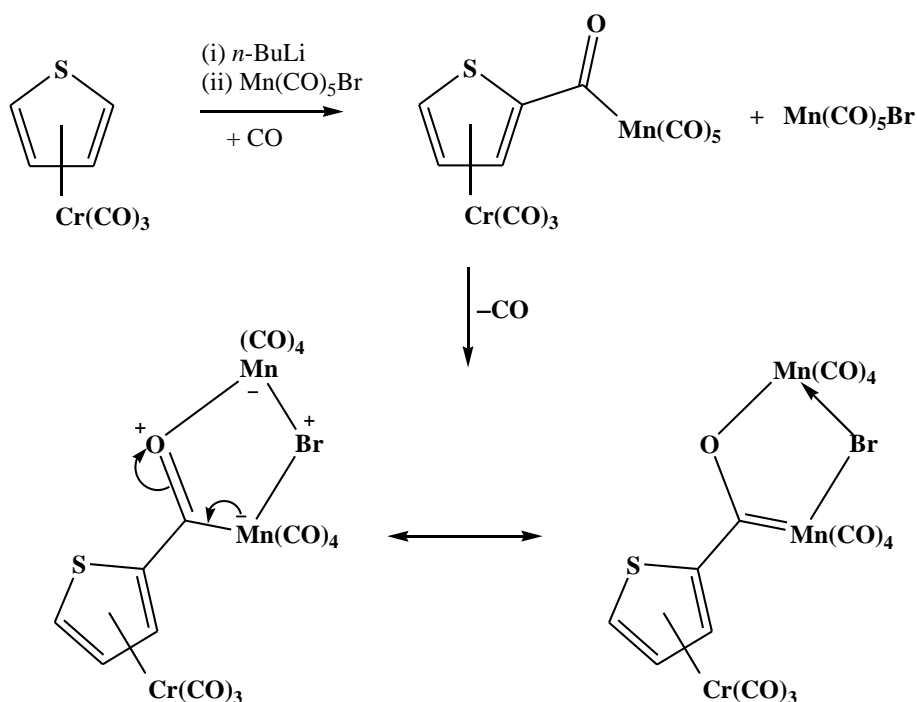
<sup>35</sup> (a) C. P. Casey, C. J. Czerwinski, K. A. Fusie, R. K. Hayashi; *J. Am. Chem. Soc.*, **1997**, *119*, 3971–3978;

(b) C. P. Casey, C. J. Czerwinski, D. R. Powell, R. K. Hayashi; *J. Am. Chem. Soc.*, **1997**, *119*, 5750–5751;

(c) C. P. Casey, H. Nagashima; *J. Am. Chem. Soc.*, **1989**, *111*, 2352–2353; (d) C P. Casey, P. C. Vosejпка,

F. R. Askham; *J. Am. Chem. Soc.*, **1990**, *112*, 3713–3715

those of a carbene and an acyl ligand<sup>32</sup>. Manganese also has seven valence electrons, like rhenium. The reaction of lithiated  $[\text{Cr}\{\eta^5\text{-C}_4\text{H}_4\text{S}\}(\text{CO})_3]$  with  $[\text{Mn}(\text{CO})_5\text{Br}]$  was studied in our laboratories and a major product was a bimetallic manganese acyl complex (Scheme 1.12)<sup>36</sup>. Reaction with additional manganesepentacarbonyl bromide led to the formation of a novel trimetallic complex, which displays two  $\text{Mn}(\text{CO})_4$  fragments bridged by an acyl and a bromo ligand. The manganese–carbon and carbon–oxygen bond lengths of the complex are intermediate and describe two contributing structures for the dimetallacycle: those of a bridging acyl and a bridging carbene–oxy ligand, as shown in Scheme 1.12.



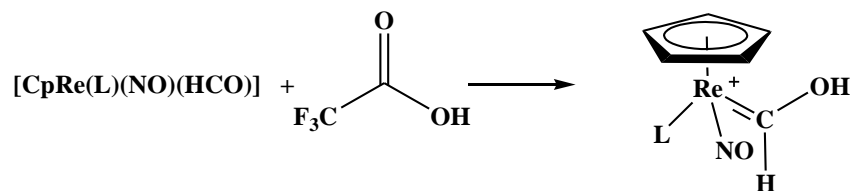
**Scheme 1.12:** Carbene and acyl ligands in a dimanganese complex

Gladysz and co-workers also showed that formyl ligands of Re could be transformed into hydroxycarbene ligands by reactions with strong organic acids<sup>37</sup>.

<sup>36</sup> T. A. Waldbach, R. van Eldik, P. H. van Rooyen, S. Lotz; *Organometallics*, **1997**, *16*, 4056–4070

<sup>37</sup> W–K. Wong, W. Tam, J. A. Gladysz; *J. Am. Chem. Soc.*; **1979**, *101*, 5440–5442

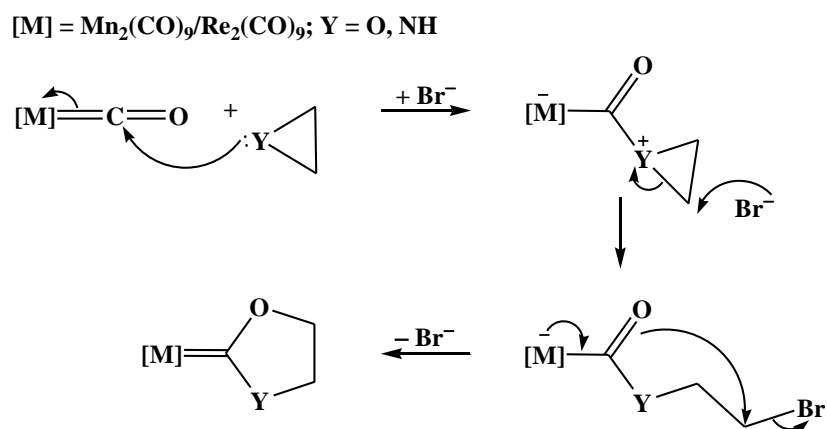




**Scheme 1.13:** Formyl ligand transformed into carbene ligand

### 1.5 Carbene formation through halide catalysis

Angelici reported dirhenium and dimanganese carbene complexes, synthesized by using bromide to catalyze the ring-opening of oxirane and aziridine<sup>38</sup> (Scheme 1.14). Cyclic oxy-carbene complexes can also be prepared from Group 7 pentacarbonyl cationic species<sup>39</sup>.



**Scheme 1.14:** Synthesis of carbene complexes using halide ( $\text{X}^-$ ) as catalyst

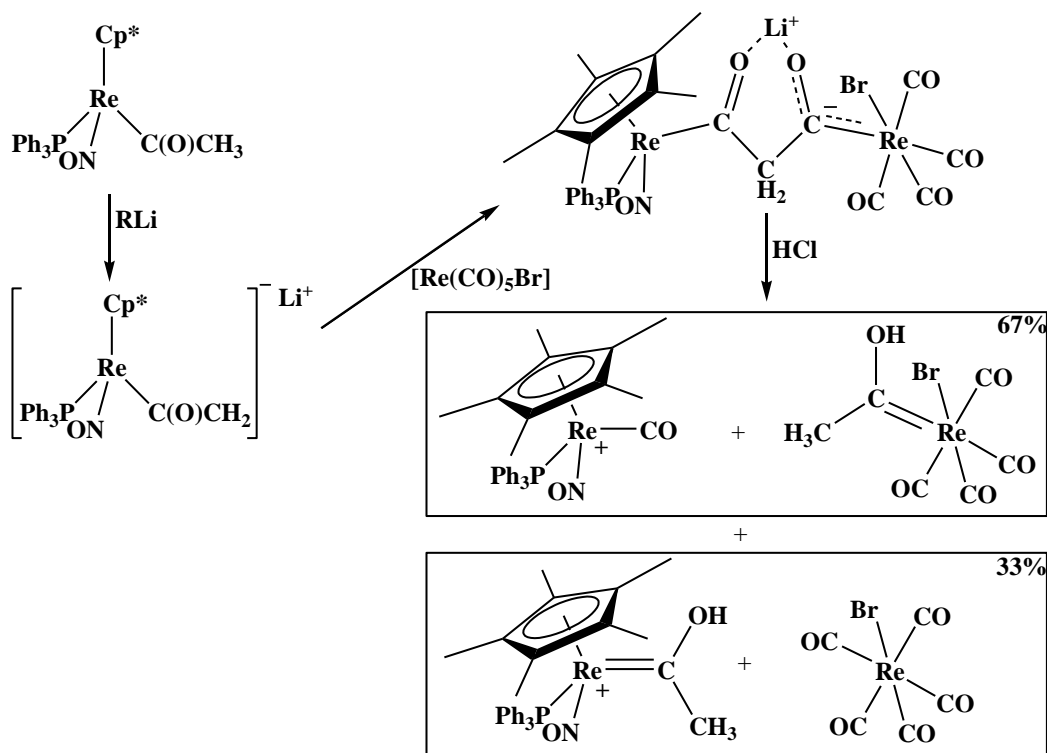
### 1.6 Hydroxycarbene complexes

An important goal of this study was to learn more about the fascinating relationship

<sup>38</sup> (a) M. M. Singh, R. I. Angelici; *Inorg. Chim. Acta*, **1985**, *100*, 57–63; (b) M. M. Singh, R. J. Angelici; *Inorg. Chem.*, **1984**, *23*, 2699–2705

<sup>39</sup> E. Fritsch, T. Kerscher, K. Polborn, W. Beck; *J. Organomet. Chem.*, **1993**, *460*, C25–C27

between acyl and carbene ligands. For an acyl ligand to be transformed into a hydroxycarbene ligand, a hydrogen atom is required. In a hydride–acyl metal complex the hydrogen atom is available as a metal ligand and its migration to the acyl oxygen atom leads to the formation of the hydroxycarbene complex. A complex was reported that consist of a  $\text{ReCp}(\text{NO})(\text{PPh}_3)$  and a  $\text{Re}(\text{CO})_4\text{Br}$  unit, spanned by a malonyl ligand. Neither metal fragment has a hydride ligand. The introduction of a proton led to the formation of a hydroxycarbene complex<sup>40</sup> (Scheme 1.15). The stability of the fragments generated in the cleavage reactions is reported by the authors to be a driving force for the reaction.

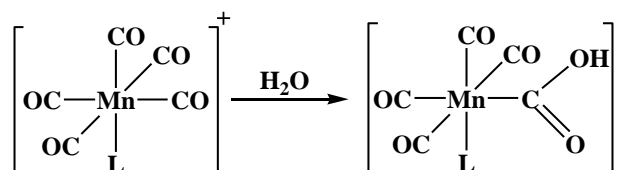


**Scheme 1.15:** Formation of hydroxycarbene complex from acyl complex

The carbonyl oxygen atom of a cationic manganese complex may be exchanged for the

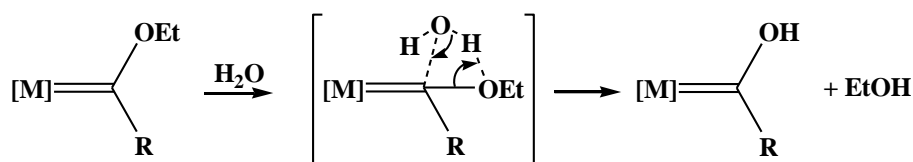
<sup>40</sup> J. M. O'Connor, R. Uhrhammer, R. K. Chadha, B. Tsu, A. L. Rheingold; *J. Organomet. Chem.*, **1993**, 455, 143–156 and references therein.

oxygen atom of water (Scheme 1.16)<sup>41</sup>. The intermediate acyl species that forms is interesting for its relationship to a hydroxycarbene complex. Elimination of CO<sub>2</sub> could afford the metal hydride through β-hydrogen transfer.



**Scheme 1.16:** Reaction of a manganese carbonyl cationic derivative with water

The formation of hydroxycarbene intermediates was observed in a kinetic study of the reaction of alkoxy carbene complexes with nucleophiles such as OH<sup>-</sup> and H<sub>2</sub>O (Schemes 1.17 and 1.18)<sup>42</sup>. Ylide formation, from reactions of nucleophiles with carbene complexes, has been documented for Group 6 metal carbene complexes<sup>43</sup>. Attack of a hydroxide on an alkoxy carbene complex could lead to the formation of an anionic ylide intermediate, which could regenerate a hydroxycarbene ligand by elimination of ethanol, shown below:

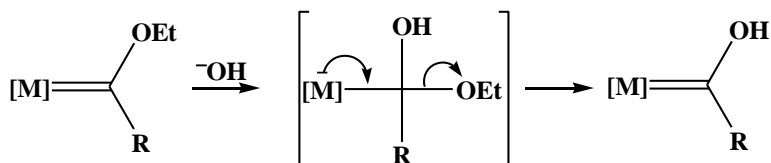


**Scheme 1.17:** Hydroxycarbene complexes via water-ethanol exchange

<sup>41</sup> D. J. Darensbourg, J. A. Froelich; *J. Am. Chem. Soc.*; **1977**, *99*, 5940–5946

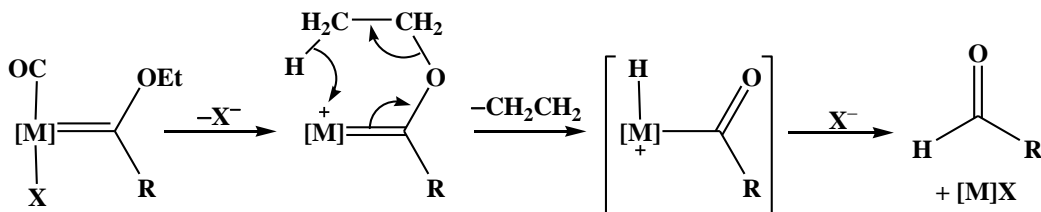
<sup>42</sup> (a) C. F. Bernasconi; *Chem. Soc. Rev.*, **1997**, *26*, 299–307; (b) Aminolysis: M. Ali, S. Gangopadhyay, M. Mijanuddin; *J. Organomet. Chem.*, **2005**, *690*, 4878–4885

<sup>43</sup> (a) F. R. Kreissl, E. O. Fischer; *Chem. Ber.*, **1973**, *107*, 183–188; (b) E. O. Fischer, G. Kreis, F. R. Kreissl, C. G. Kreiter, J. Müller; *Chem. Ber.*, **1973**, *106*, 3910–3919



**Scheme 1.18:** Hydroxycarbene complexes via ylide intermediates

A different scenario can be proposed for going from an ethoxycarbene complex to a metal complex containing an acyl and hydride ligand. Scheme 1.19 shows a potential reaction based on C–H activation of a terminal methyl group. This is a less likely, but interesting alternative process which is, as far as we are aware, without a precedent in literature. It also represents a modification of  $ZL \rightarrow X_2$  ligands according to the Green classification method and could be initiated by carbonyl loss and a remote agostic H–interaction.



**Scheme 1.19:** Metal hydrides from ethoxycarbene complexes

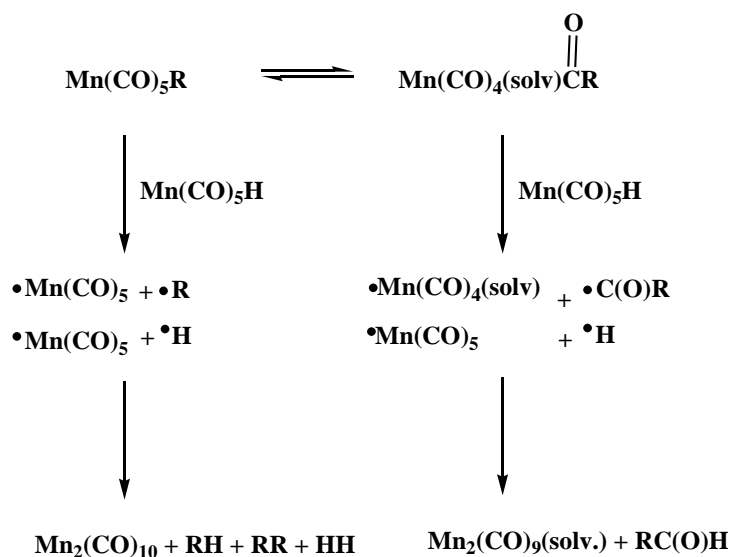
### 1.7 Mechanism for decomplexation of X–type ligands of Group 7 metals

Decomplexation reactions of alkyl and acyl ligands have been studied by Halpern (manganese complexes)<sup>44</sup>, and Norton (rhenium complexes)<sup>45</sup>. By examining the reaction kinetics, they ascribed specific mechanisms to the reactions.

<sup>44</sup> (a) M. J. Nappa, R. Santi, J. Halpern; *Organometallics*, **1985**, *4*, 34–41; (b) R. L. Sweany, J. Halpern; *J. Am. Chem. Soc.*, **1977**, *99*, 8335–8337

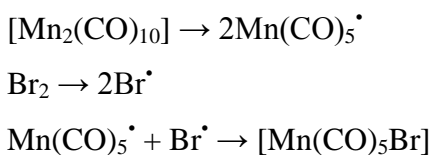
<sup>45</sup> B. D. Martin, K. E. Warner, J. R. Norton; *J. Am. Chem. Soc.*, **1986**, *108*, 33–39

Halpern found that the decomplexation reactions of manganese complexes proceeded via a radical mechanism, as is illustrated in Scheme 1.20. Upon addition of  $[\text{Mn}(\text{CO})_5\text{H}]$ , dimanganese complexes were obtained and in addition, organic products. The bond between the metal and the X-type ligand was cleaved homolytically and the formed radicals recombined to yield the new products.

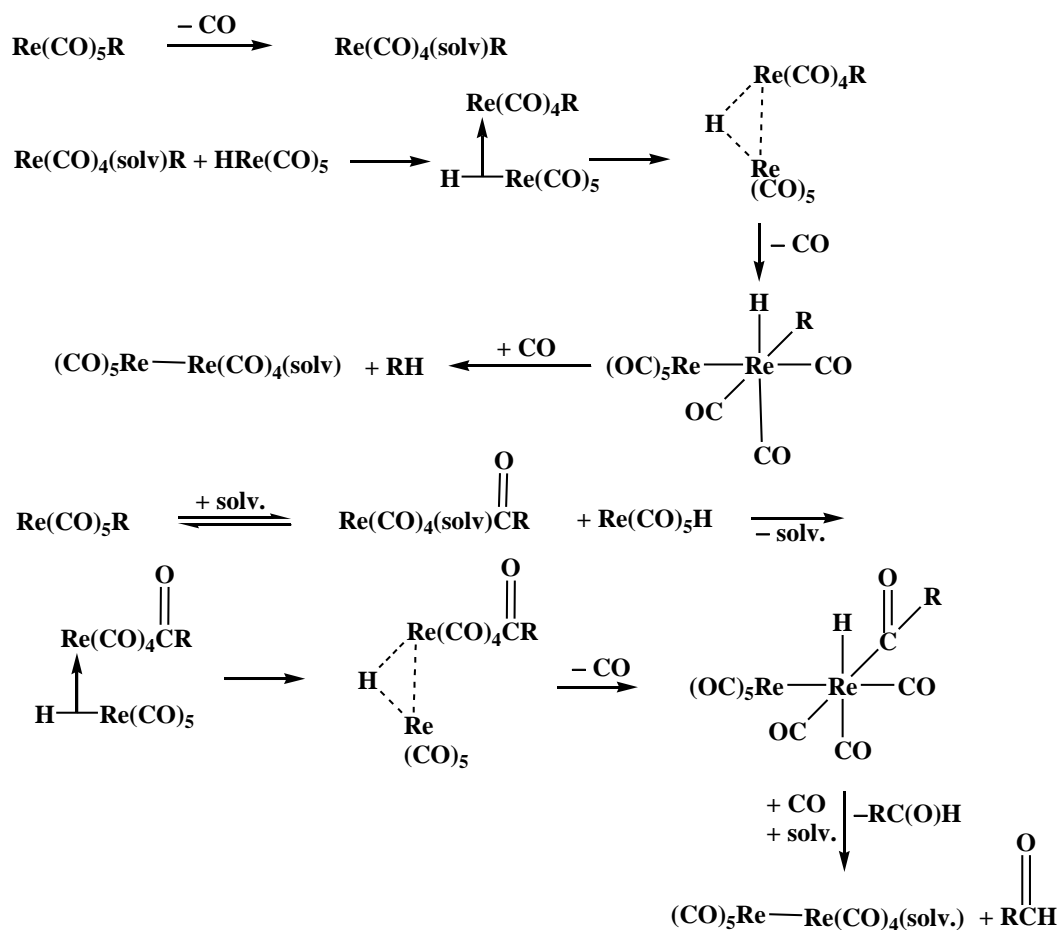


**Scheme 1.20:** Halpern's mechanism of Mn–ligand decomplexation

A similar radical mechanism was also proposed for the cleaving of  $[\text{Mn}_2(\text{CO})_{10}]$  by halogens:



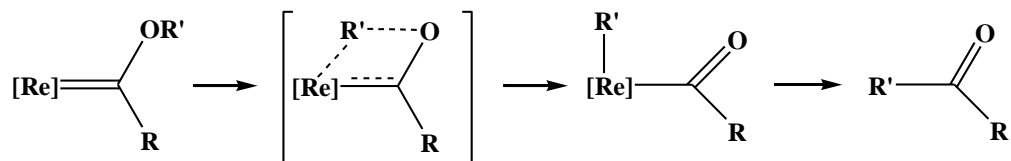
Norton and co-workers found that the analogous reaction with  $[\text{Re}(\text{CO})_5\text{R}]^{37}$  and  $[\text{Re}(\text{CO})_5\text{H}]$  proceeded differently and that a radical mechanism was not operative. They postulated a dinuclear intermediate (Scheme 1.21). In this case bond-formation occurred between Re–H (through the electrons in the Re–H bond of  $[\text{Re}(\text{CO})_5\text{H}]$ ) and the rhenium atom of  $[\text{Re}(\text{CO})_5\text{R}]$ , as is shown below:



**Scheme 1.21:** Elimination of RH or RC(O)H from a rhenium complex

In the mechanism a 3-centered, 2-electron bond is formed between the two Re atoms and the H atom. The elimination of RH or RC(O)H can be described as a reductive elimination reaction. In this study the bridging hydrogen plays an important role in the transfer of a hydrogen atom from one Re to the other.

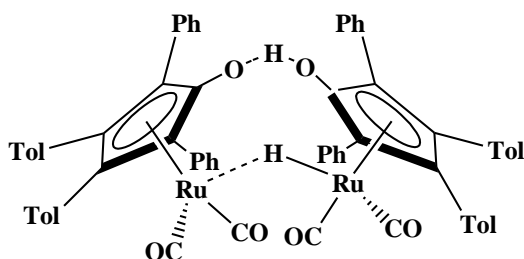
A third possible reaction to consider, not investigated in the Norton mechanism, is shown in Scheme 1.22. It represents an alkyl or hydrogen transfer from a carbene precursor to the rhenium centre. Elimination of a ketone (R = alkyl) or aldehyde (R = H) proceeds by reductive elimination.



**Scheme 1.22:** Reductive elimination can produce aldehydes or ketones ( $R' = R, H$ )

### 1.8 Shvo catalyst

The useful and versatile Shvo diruthenium catalyst<sup>46</sup> contains a protonic hydrogen atom between two oxygen atoms and a hydridic hydrogen atom, situated between the ruthenium atoms. The Shvo catalyst is a keto–enol/hydride complex.



**Figure 1.4:** The Shvo catalyst

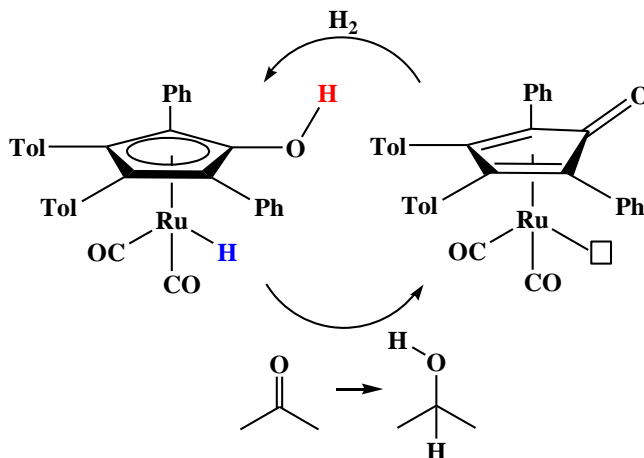
Two features of the Shvo complex are specifically of interest and relevant to this study – they are the bridging hydride atom and the pendant oxygen atoms with a protonic hydrogen between them. The formation of hydride species was expected to occur during the reactions planned for this study.

Karvembu *et al*<sup>47</sup> explains that the dissociation of a ligand of the catalyst is an important reason for catalytic activity. The Shvo catalyst dissociates into a 16–electron (Ru(0)) and

<sup>46</sup> (a) Y. Shvo, D. Czarkie, Y. Rahamim; *J. Am. Chem. Soc.*, **1986**, *108*, 7400–7402; (b) C. P. Casey, S. W. Singer, D. R. Powell, R. K. Hayashi, M. Kavana; *J. Am. Chem. Soc.*, **2001**, *123*, 1090–1100; (c) R. M. Bullock; *Chem. Eur. J.*, **2004**, *10*, 2366–2374

<sup>47</sup> R. Karvembu, R. Prabhakaran, K. Natarajan; *Coord. Chem. Rev.*, **2005**, *249*, 911–918

an 18–electron (Ru(II)) species and has found application in redox reactions, hydrogenation reactions and racemization reactions. Its hydrogenation activity of a polar double bond is shown below. Hydrogen transfer to ketones, following a hydridic route, has been suggested to go through an “inner–sphere” or “outer–sphere” pathway. In both, the hydride migrates to the carbon atom of the ketone, but in the former the substrate coordinates to the catalyst and in the latter not<sup>48</sup>.



**Scheme 1.23:** Shvo catalyst: ketone hydrogenation

The Shvo catalyst was the first ligand–metal bifunctional (metal has a hydridic hydrogen, ligand has a protonic hydrogen) hydrogenation catalyst to be developed and was found to make inefficient use of Ru, because much of it is present as the diruthenium species (not active in reduction)<sup>49</sup>. Only the hydride mononuclear species can be obtained if the Shvo catalyst is reacted with H<sub>2</sub> or formic acid<sup>50</sup>.

A cycle has been developed whereby the catalytic species are regenerated and it acts as

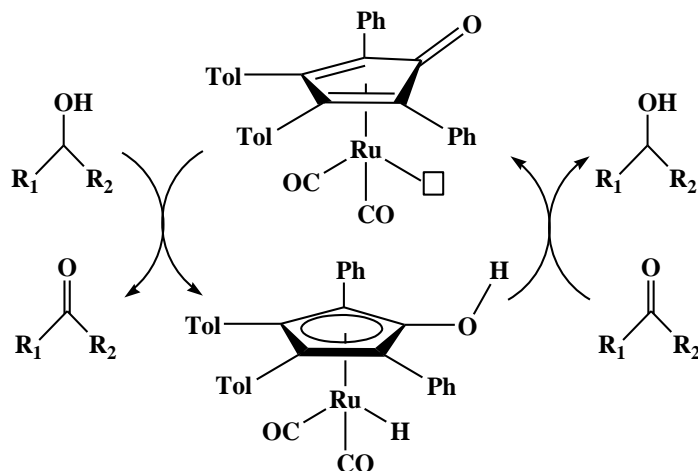
<sup>48</sup> A. Comas–Vives, G. Ujaque, A. Lledos; *Organometallics*, **2007**, 26, 4135–4144

<sup>49</sup> (a) C. P. Casey, S. E. Beetner, J. B. Johnson; *J. Am. Chem. Soc.*, **2008**, 130, 2285–2295; (b) A more efficient phosphine–substituted Ru catalyst has been developed by Casey’s group for the hydrogenation of aldehydes: C. P. Casey, N. A. Strotman, S. E. Beetner, J. B. Johnson, D. C. Priebe, T. E. Vos, B. Khodavandi, I. A. Guzei; *Organometallics*, **2006**, 25, 1230–1235

<sup>50</sup> C. P. Casey, S. W. Singer, D. R. Powell; *Can. J. Chem.*, **2001**, 79, 1002–1011



an oxidation catalyst. Here the 16-electron species is the active species. Alcohols are dehydrogenated by the Shvo catalyst<sup>51</sup>. Hydrogen atoms that are abstracted may be transferred to quinone. The hydroquinone that formed is reoxidized by air with a Co-salen complex's aid. A part of the cycle is given below.



**Scheme 1.24:** Part of catalytic cycle of the Shvo catalyst

## 1.9. Aims of project

Carbene to acyl and acyl to carbene ligand conversions featured prominently as a central theme and this capability was taken into consideration in setting goals for this study.

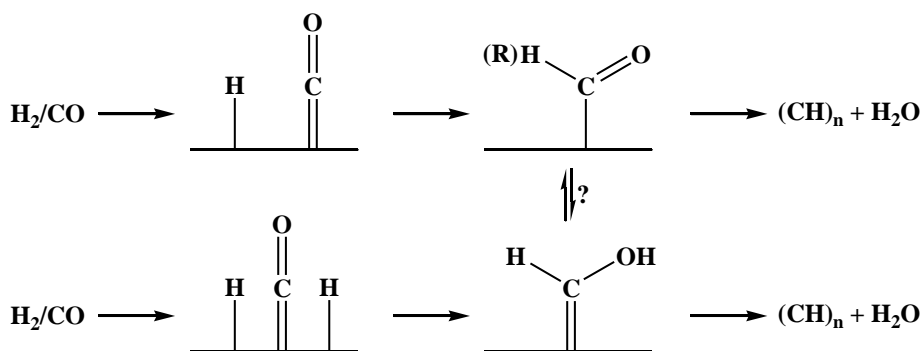
### 1.9.1 Introduction

A basic aim of this study was to investigate aspects of the synthesis and chemistry of rhenium carbene complexes with thienyl substituents. With rhenium having an uneven number of valence electrons there are interesting possibilities for synthesizing complexes with unique characteristics. The factors affecting carbene or acyl formation is not clearly understood in literature and rhenium carbene chemistry has not attracted nearly the same amount of attention than Group 6 Fischer carbene complexes. The possibility of

<sup>51</sup> J. B. Johnson, J.-E. Bäckvall; *J. Org. Chem.*, **2003**, 68, 7681–7684

preparing stable hydroxycarbene complexes from protonation instead of alkylation of acylmetalates or from hydride transfer processes was an interesting possibility.

In the important Fischer–Tropsch synthesis<sup>52</sup>, mechanisms for the heterogeneous catalysis of the reaction of syngas ( $H_2/CO$ ) to give hydrocarbons and water have been proposed<sup>53</sup>. The carbide mechanism was the first suggested mechanism and it was proposed by Fischer and Tropsch<sup>54</sup>. The hydroxycarbene mechanism was suggested by Anderson and Emmett and the acyl–mechanism by Pichler and Shultz. The possible interchange between hydroxycarbene and acyl–hydride complexes could be of interest with respect to the mechanisms shown below (Scheme 1.25). These proposed mechanisms are shown below.



**Scheme 1.25:** Acyl mechanism (top) and hydroxycarbene mechanism (bottom)

## 1.9.2 Thiophene derivatives

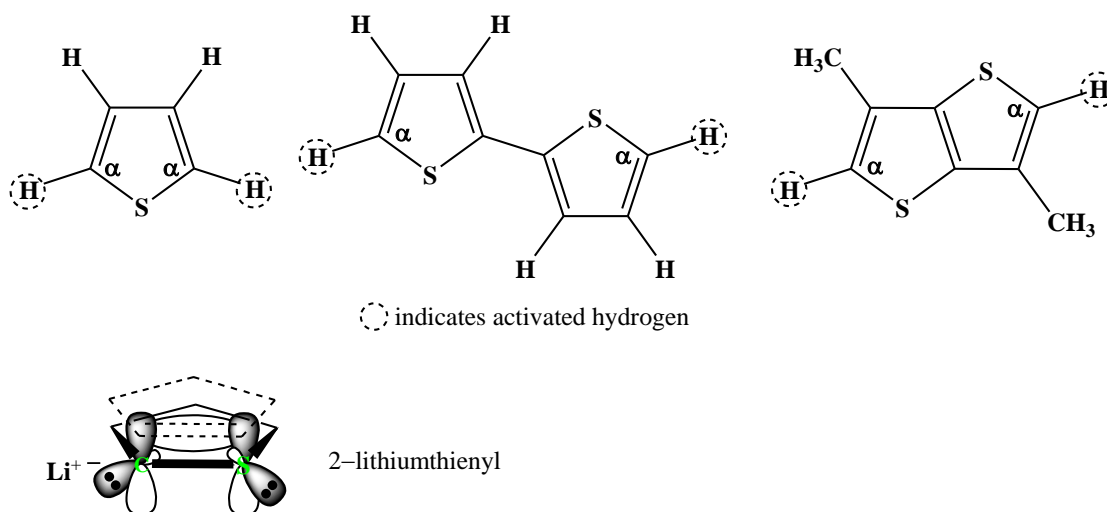
Thiophene derivatives are aromatic, flat, electron excessive, and display double bond delocalization. This makes them versatile reagents and substituents in carbene chemistry.

<sup>52</sup> (a) P. M. Maitlis; *J. Organomet. Chem.*, **2004**, 689, 4366–4374; (b) W. A. Herrmann, *Applied Homogenous Catalysis With Organometallic Compounds*, Vol. 2; Editors: B Cornils, W.A. Herrmann; VCH Weinheim, **1996**, 747

<sup>53</sup> R. C. Brady III, R. Pettit; *J. Am. Chem. Soc.*, **1981**, 103, 1287–1289

<sup>54</sup> F. Fischer, H. Tropsch; *Chem. Ber.*, **1926**, 59, 830–831

The heteroaromatic rings are activated at the carbon atom  $\alpha$  to the sulfur atom<sup>55</sup> by proton abstraction with a strong base like *n*-BuLi.



**Figure 1.5:** Thiophene, thiophene derivatives and 2-lithiumthienyl

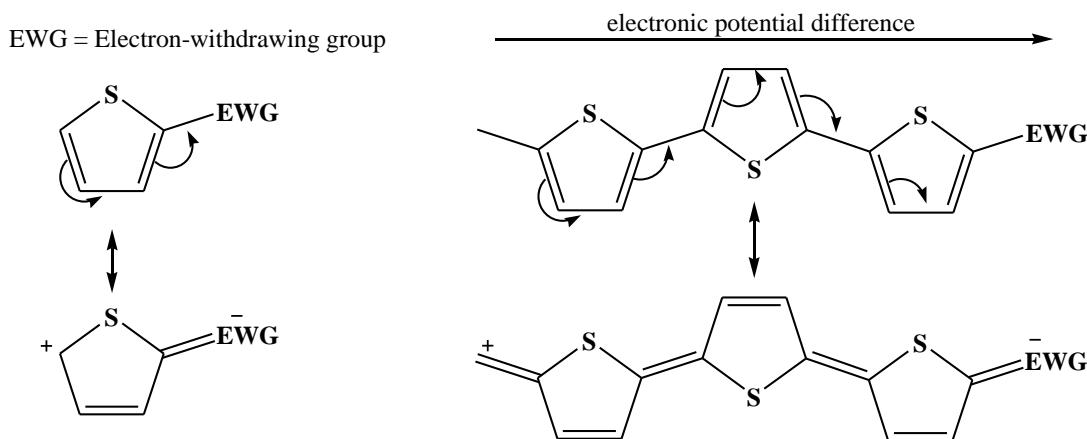
If rings have hetero-atoms that can coordinate to the metal (like pyridine or pyrrole substrates) there may also be bonding through the hetero-atom. The sulfur atom also has two electron pairs in two non-bonding orbitals, but because of the ring aromaticity does not strongly feature as a Lewis base to transition metals. In fact, coordination to transition metals is mostly through the  $\pi$ -system and  $\eta^5$ - and  $\eta^2$ -coordination are common. However, the carbon atom with the negative charge is the more reactive nucleophile. 2-Lithiumthienyl can be directly attached to rhenium, if there is a vacant coordination site on the metal<sup>56</sup>.

Thiophene is readily polymerized or oligomerized and its electrons can be transported, due to extended conjugation, as shown in Figure 1.6. Metals can be bound to these

<sup>55</sup> C. H. DePuy, S. R. Kass, G. P. Bean; *J. Org. Chem.*, **1988**, 53, 4427–4433

<sup>56</sup> T. B. Gunnoe, M. Sabat, W. D. Harman; *J. Am. Chem. Soc.*, **1998**, 120, 8747–8754

oligomers or polymers to furnish complexes with special characteristics. Examples include inorganic–organic hybrid materials<sup>57</sup> and chromophores<sup>58</sup>.



**Figure 1.6:** Electron conjugation over the thienyl ring system

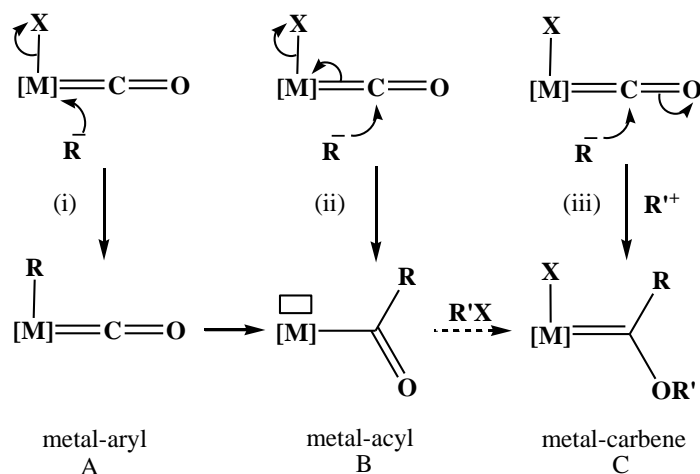
### 1.9.3 Reaction of organolithium agents with Group 7 metal carbonyls

Anionic reagents can react with group 7 metal carbonyls in many different ways, depending on electronic and steric properties, the nature of the transition metal and the properties of the lithiated substrate. Scheme 1.26 summarizes different possible reaction routes already observed, affording, if the substrate is an aryl, a metal–aryl, metal–acyl or metal–carbene complex. Earlier reference was made to all of these types of products. In Scheme 1.25 the following occurs: (i) attack of the aryl on the metal with the elimination of the halogen ligand (ii), attack of the aryl on a carbonyl carbon with the elimination of the halogen ligand and (iii) transformation of a carbonyl ligand into a carbene ligand with retention of the halogen ligand.

<sup>57</sup> M. H. Chisholm, A. J. Epstein, J. C. Gallucci, F. Feil, W. Pirkle; *Angew. Chem. Int. Ed.*, **2005**, *44*, 6537–6540

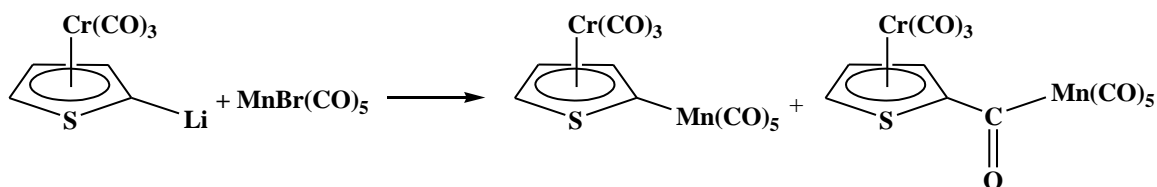
<sup>58</sup> S. Goeb, A. De Nicola, R. Ziessel, C. Sabatini, A. Barbieri, F. Barigelletti; *Inorg. Chem.*, **2006**, *45*, 1173–1183

R = aryl, X = halogen, R' = alkylating agent



**Scheme 1.26:** Aryl, acyl and alkoxy-carbene complexes

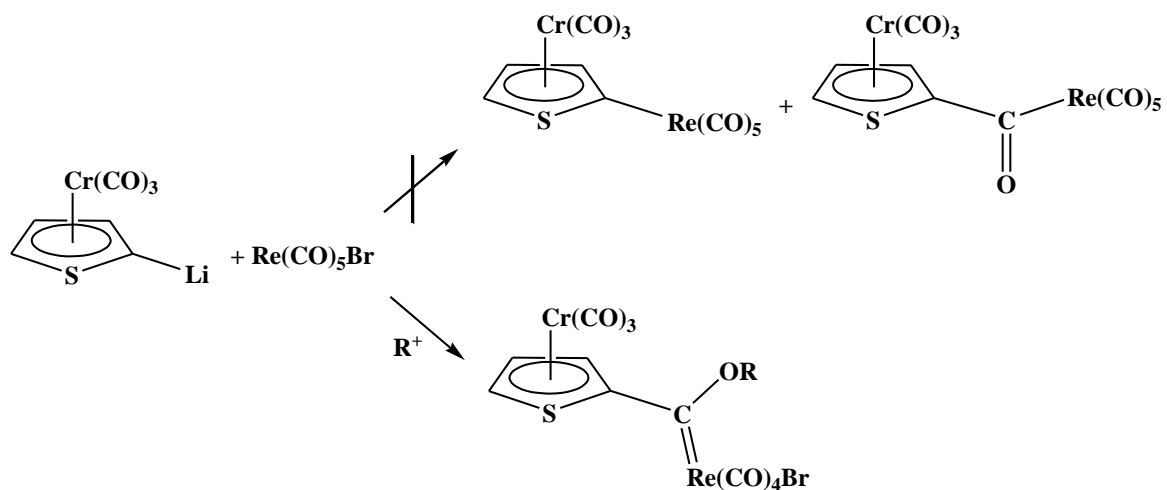
Previous studies with 2-lithiumthienyl  $\pi$ -bonded to chromium tricarbonyl in our laboratories revealed complexes of types A and B (Scheme 1.26). When reacted with  $[\text{Mn}(\text{CO})_5\text{Br}]$  both products reveal reactions that proceed by  $\text{Br}^-$  elimination (Scheme 1.27)<sup>59</sup>. By contrast, the reaction of 2-lithiumthienyl with  $[\text{Mn}(\text{CO})_5\text{Br}]$  gave a deep red unstable compound.



**Scheme 1.27:** Reaction of a nucleophile with  $[\text{Mn}(\text{CO})_5\text{Br}]$

$[\text{Re}(\text{CO})_5\text{Br}]$  reacted differently as shown in Scheme 1.28. The bromo-carbene complex was afforded after alkylation of the intermediate (type C).

<sup>59</sup> T. A. Waldbach, P. H. van Rooyen, S. Lotz; *Organometallics*, **1993**, *12*, 4250–4253



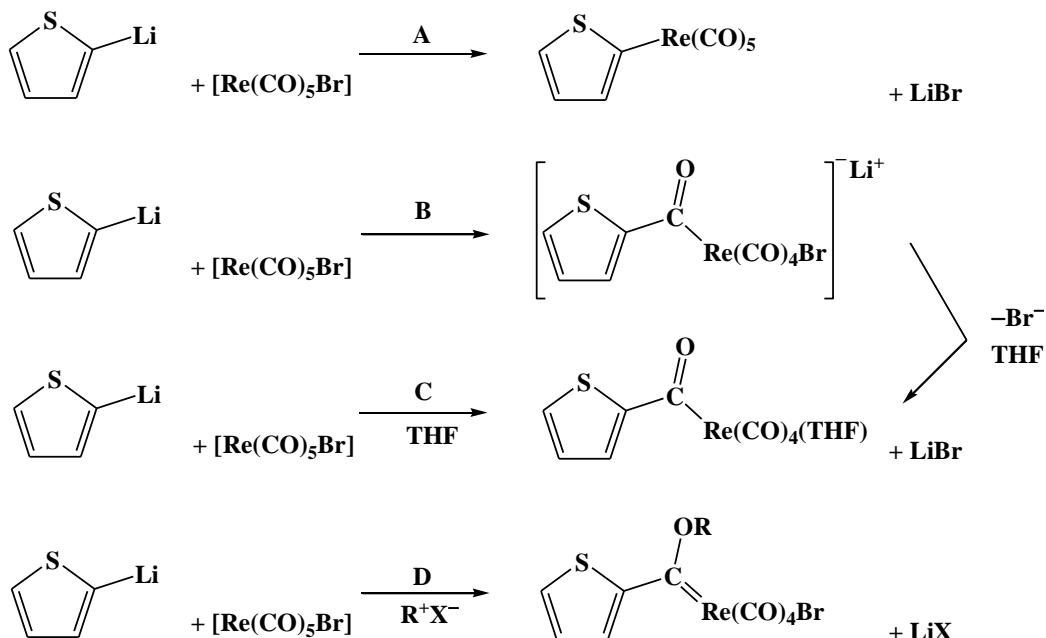
**Scheme 1.28:** Reaction of a  $\pi$ -coordinated thiophene with  $[\text{Re}(\text{CO})_5\text{Br}]$

In this study the reactions of lithiated thiophene derivatives with  $[\text{Re}(\text{CO})_5\text{X}]$  ( $\text{X} = \text{Br}, \text{Re}(\text{CO})_5$ ) were going to be investigated. This study extends the above results by focusing on Re-carbene chemistry and anticipates the formation of hydroxycarbene intermediates.

## Chapter 2: Synthesis of carbene complexes

### 2.1 Introduction

In preliminary studies in our laboratories, the reactivity of manganese carbonyls towards lithiated thiophene derivatives was investigated. 2-Lithiumthienyl was reacted with manganesepentacarbonyl bromide and afforded a solution that initially turned dark red, but then the colour changed to brown as the product rapidly decomposed. An added phosphine ligand did not stabilize the unstable intermediate, nor did the addition of alkylating agent afford an isolable complex. If the corresponding reaction with rheniumpentacarbonyl bromide was to be performed, the reaction pathways shown in Scheme 2.1 can be envisaged.



**Scheme 2.1:** Possible reactions of  $[\text{Re}(\text{CO})_5\text{Br}]$  with 2-lithiumthienyl

Path A describes an exchange of ligands on the metal, where attack of the thienyl anion on the rhenium is accompanied by the release of the bromo ligand, affording a rhenium-

thienyl bond. This type of complex has been prepared before, but by reaction with a chlorothienylzinc(II) precursor<sup>1</sup>.

The other three paths – B, C and D – originate from attacks by the nucleophile occurring on the carbon atom of a carbonyl ligand. In B an anionic bromo–acyl complex is produced. This type of complex, as far as we are aware, has not yet been isolated. The negative charge is located on the metal, and from the previous chapter, it is known that such complexes are unstable<sup>2</sup>. However, if the bromo–ligand were to be eliminated as Br<sup>−</sup>, as indicated in path C, a neutral acyl complex is obtained. Rhenium acyl complexes are well–known<sup>3</sup> and the vacant coordination site can be filled with another ligand. This product can also be formed from a rhenium complex with a coordinated thienyl migrating to a carbonyl ligand, in the presence of an auxiliary ligand.

In pathway D the bromo ligand is retained and the negative charge neutralized by alkylation to produce a carbene ligand and complex. As an example of this fourth case we observed that in a reaction to make  $\sigma$ ,  $\pi$ –complexes with bridging thienyl ligands, the attack by the thienyl nucleophile was on a carbonyl ligand. The bromo ligand was retained to afford an anionic intermediate which, after alkylation, gave a Fischer carbene complex (see Scheme 2.2)<sup>4</sup>.

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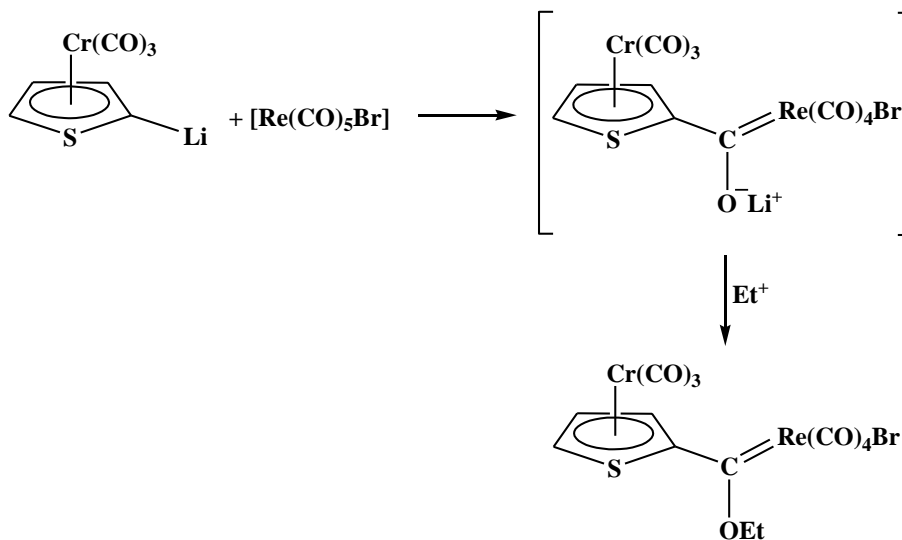
<sup>1</sup> (a) P. R. Stafford, T. B. Rauchfuss, S. R. Wilson; *Inorg. Chem.*, **1995**, *34*, 5220–5225; (b) The bromide ligand can be replaced by other ligands, for instance in an orthometallation reaction where HBr is removed from the molecule: K.–L. Lu, C.–M. Wang, H.–H. Lee, L.–C. Chen, Y.–S. Wen; *J. Chem. Soc., Chem. Commun.*, **1993**, 706–707

<sup>2</sup> (a) H. Alper, J.–L. Fabre; *Organometallics* **1982**, *1*, 1037–1040; (b) W. Petz; *Organometallics*, **1983**, *2*, 1044–1046; (c) K. H. Dötz, U. Wenicker, G. Muller; *Organometallics*, **1986**, *5*, 2570–2572; (d) M. F. Semmelhack, R. Tamura; *J. Am. Chem. Soc.*, **1983**, *105*, 4099–4100

<sup>3</sup> P.K. Sazonov, G.A. Artamkina, V.N. Khrustalev, M.Y. Antipin, I.P. Beletskaya; *J. Organomet. Chem.*, **2003**, *681*, 59–69; (b) M. Bergamo, T. Beringhelli, G. D’Alfonso, D. Maggioni, P. Mercandelli, A. Sironi; *Inorg. Chim. Acta*, **2003**, *350*, 475–485; (c) C. Bianchini, N. Mantovani, L. Marvelli, M. Peruzzini, R. Rossi, A. Romerosa; *J. Organomet. Chem.*, **2001**, *617–618*, 233–241

<sup>4</sup> T. A. Waldbach, R. van Eldik, P. H. van Rooyen, S. Lotz; *Organometallics*, **1997**, *16*, 4056–4070





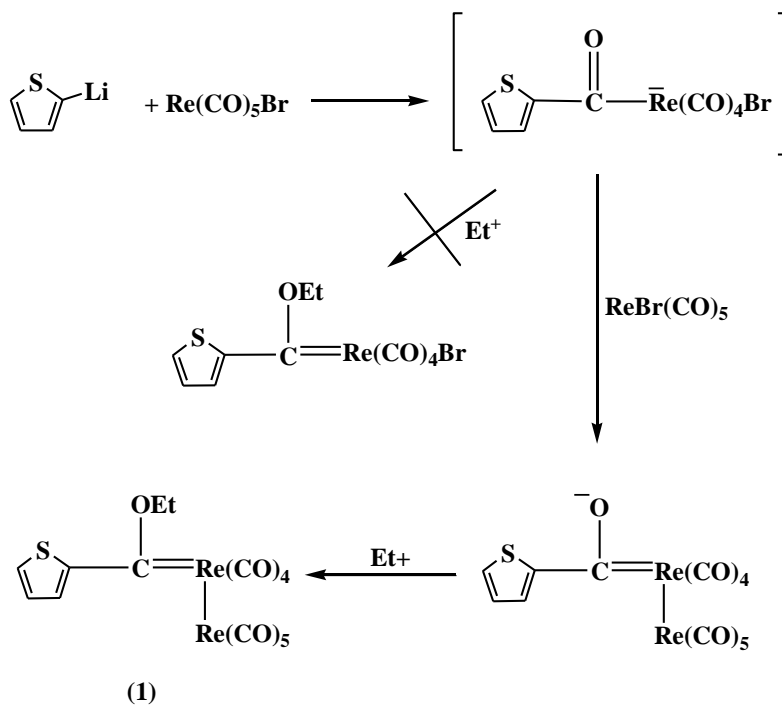
**Scheme 2.2:** Preparation of a rhenium Fischer carbene complex

With these possible reaction routes in mind the reaction of 2-lithiumthienyl with rheniumpentacarbonyl bromide was investigated.

## 2.2 Reaction of 2-lithiumthienyl with rheniumpentacarbonyl bromide

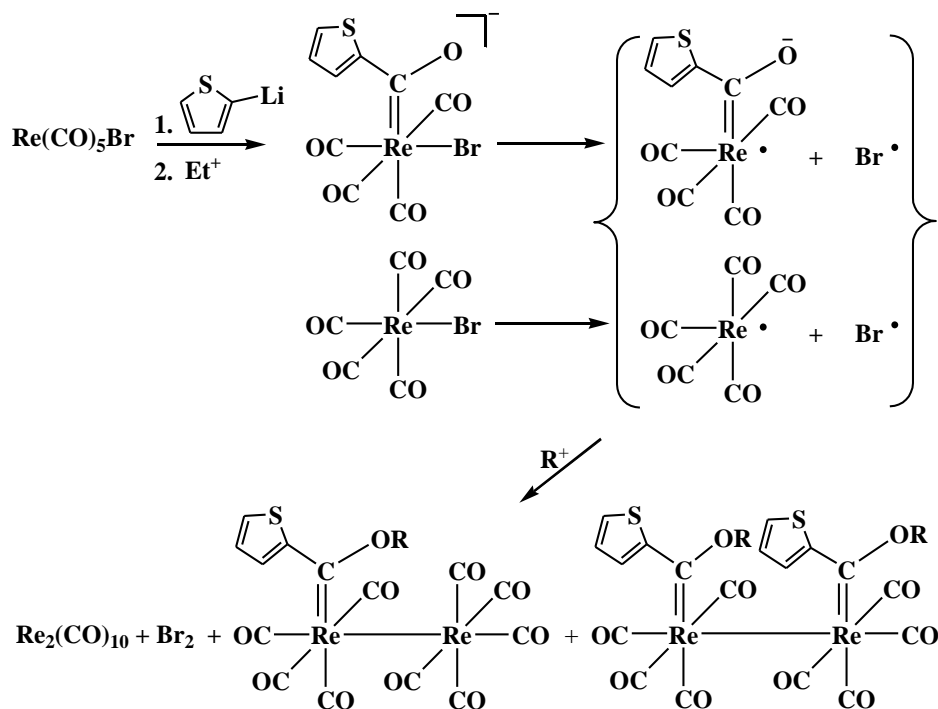
2-Lithiumthienyl was reacted with rheniumpentacarbonyl bromide. The lithiation reaction was performed at low temperature in THF and the mixture turned light yellow, indication that 2-lithiumthienyl had formed. [Re(CO)<sub>5</sub>Br] was added at very low temperature and the solution stirred – first in the cold and afterwards at room temperature. The solution turned red-brown. Investigation of the reaction mixture by thin layer chromatography showed the formation of a red salt that was immobile on silica. The mixture was alkylated with triethyloxonium tetrafluoroborate (Et<sub>3</sub>OBF<sub>4</sub>) and produced as major product (isolated from the reaction mixture in low yield) the dirhenium monocarbene complex **1** as is illustrated in Scheme 2.3. This result indicated that in the final complex, another X-type ligand – “Re(CO)<sub>5</sub>” – has taken the place of the bromo ligand.

When the reaction was repeated with rheniumpentacarbonyl triflate, products of ligand exchange were also not observed.



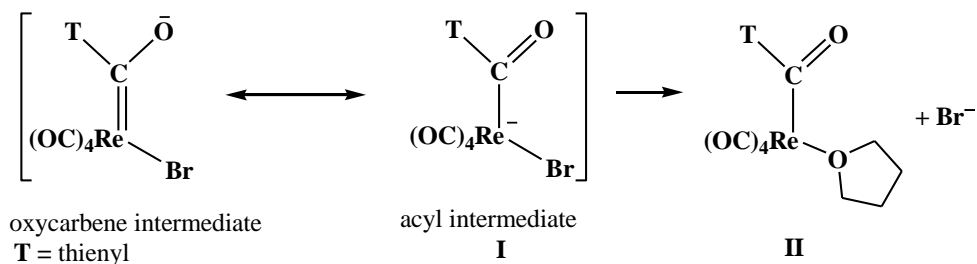
**Scheme 2.3:** 2-Lithiumthienyl reaction with  $[\text{Re}(\text{CO})_5\text{Br}]$

Based on a radical mechanism for the formation of complex **1**, Scheme 2.4 shows the formation of radical precursors of complex **1** and other possible products, including  $[\text{Re}_2(\text{CO})_{10}]$  and  $\text{Br}_2$ , as well as complex **1** and a dirhenium biscarbene complex (carbene complexes which could have been obtained after alkylation). However, as neither a dirhenium biscarbene complex, nor dirhenium decacarbonyl could be detected in the reaction mixture, a heterolytic mechanism may instead be operative.



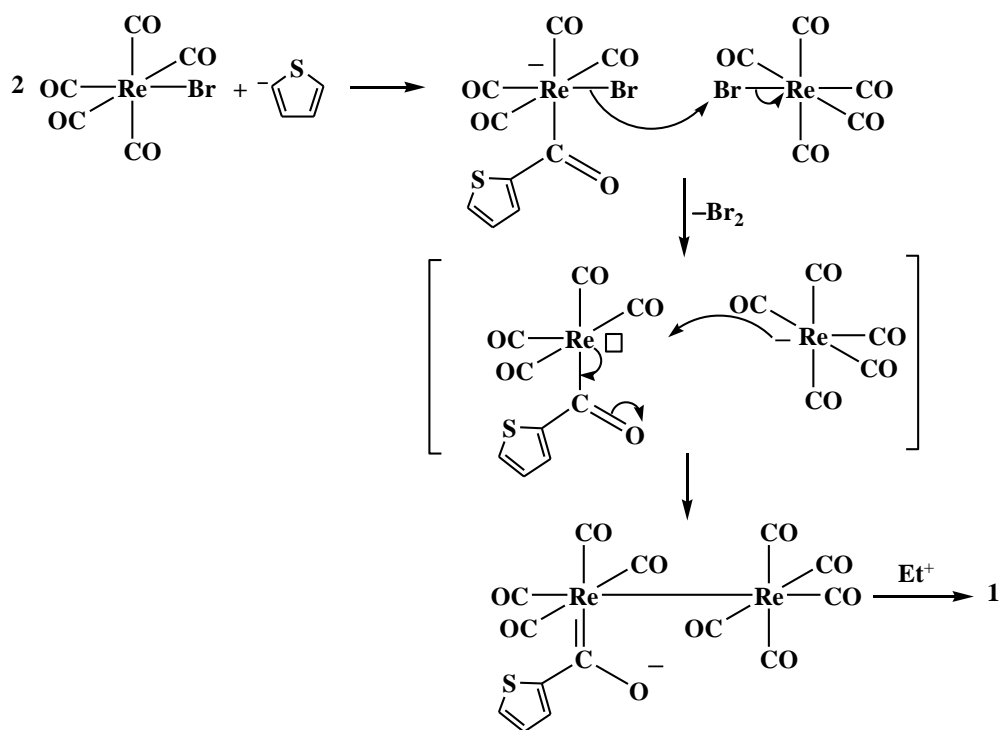
**Scheme 2.4:** Homolytic cleavage of Br ligand as  $\text{Br}^\bullet$  and expected products

To investigate the reaction pathway that produced complex **1**, intermediate species I and II were considered. ‘I’ is a bromo intermediate and ‘II’ a neutral acyl intermediate with a solvent molecule filling the vacated coordination site. Note the release of the bromo ligand during the formation of II. The bromide ( $\text{Br}^-$ ) may have been eliminated to alleviate the problem of having two X-type ligands bound to the metal in an acyl anionic intermediate.



**Scheme 2.5:** Acylate and rhenate structures

A mechanism for the formation of **1** is proposed, based on these intermediates (Scheme 2.5), and is given in Scheme 2.6. The mechanism incorporates the formation of an acyl ligand, bromide loss and metal–metal bond formation. The expelled bromide ion could be an important facilitator to promote the formation of a dirhenium bond, as is shown below.



**Scheme 2.6:** Postulated mechanism for the formation of complex **1**

The sequence of events are not clear, especially at what stage the bromo ligands are eliminated. Whether the nucleophile replaces the bromo ligand and then migrates to a carbonyl ligand, or whether it attacks directly on a carbonyl ligand and bromide dissociates, the same intermediate complex is eventually obtained. According to the above scheme, under these reaction conditions, the bromo ligand is readily removed from the metal to give  $[\text{Re(CO)}_5]^-$ . The latter promotes acylate formation and then the subsequent formation of dirhenium monocarbene complexes after alkylation. An analogy

is found in the early reaction of King/Casey<sup>5</sup>. The formation of  $[\text{Re}(\text{CO})_4\{\text{C}(\text{OEt})\text{thienyl}\}\text{Br}]$  from  $[\text{Re}(\text{CO})_5\text{Br}]$  and 2-lithiumthienyl was not found.

### **2.3 Reaction of 2-lithiumthienyl derivatives with $[\text{Re}_2(\text{CO})_{10}]$**

This work was also extended to include 2,2'-bithiophene and 3,6-dimethylthieno[3,2-*b*]thiophene substrates. Because of the complexity of the  $[\text{Re}(\text{CO})_5\text{Br}]$  system and the low yield of the above reaction to make **1**, it was decided to rather use  $[\text{Re}_2(\text{CO})_{10}]$  as precursor complex. It is well-known from Fischer carbene synthesis of Group 7 transition metals that the carbene complexes can be obtained in high yields from the dimetal decacarbonyl precursors<sup>6</sup>. With these syntheses, the carbonyl ligands of the metal complexes are transformed with little effect on the metals, beside the transformation of an L-type (carbonyl) ligand into another L-type ligand (carbene). The second  $\{\text{Re}(\text{CO})_5\}$  fragment remains unaffected.

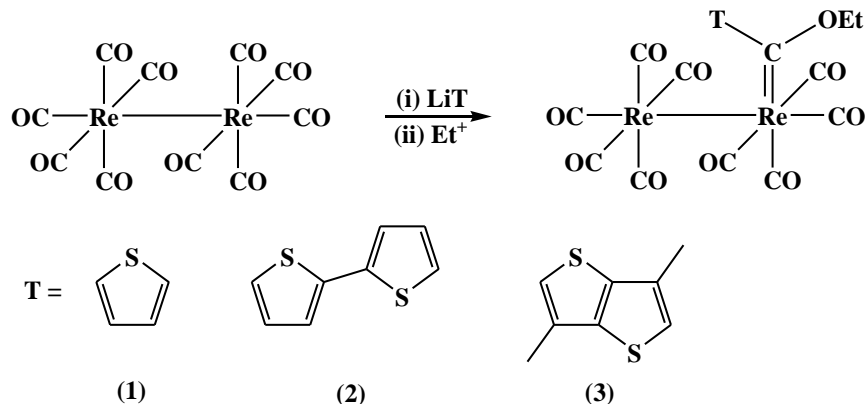
Reaction of the monolithiated thiophene derivatives with dirhenium decacarbonyl was performed in THF at low temperatures. Lithiation of thiophene derivatives afforded yellow solutions and red acylates after reactions with  $[\text{Re}_2(\text{CO})_{10}]$ . Alkylation of these intermediates produced the carbene complexes **1**, **2** and **3** (Scheme 2.7).

The reaction of two or more equivalents of lithiated thiophene derivatives with  $[\text{Re}_2(\text{CO})_{10}]$ , followed by alkylation (monitored by tlc), did not yield dirhenium biscarbene complexes (see Scheme 2.4). We ascribed this observation to steric crowding between two equatorial carbene ligands and carbonyl ligands. An electronic reason which could account for the unsuccessful synthesis of a dirhenium biscarbene complex is the cleaving of the weak metal-metal bond in the dianionic dirhenate intermediate. Why a dirhenium biscarbene complex with one or more of the carbene ligands in the axial position, did not form, is difficult to explain. In dirhenium monocarbene complexes two possible structural isomers, as determined by the position of the carbene ligand with

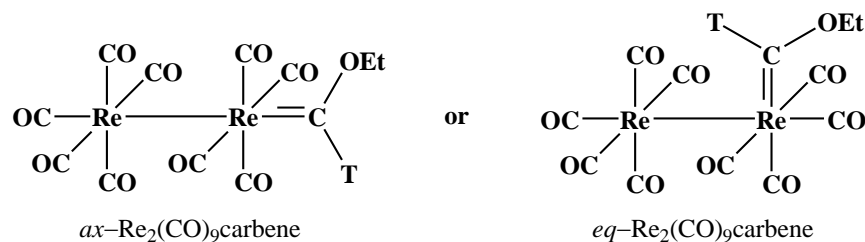
<sup>5</sup> (a) R. B. King; *J. Am. Chem. Soc.*, **1963**, 85, 1922–1926; (b) C. P. Casey; *J. C. S. Chem. Comm.*, **1970**, 1220–1221

<sup>6</sup> E. O. Fischer, E. Offhaus, J. Muller, D. Nöthe; *Chem. Ber.*, **1972**, 105, 3027–3035

respect to the rhenium–rhenium bond, are possible (Figure 2.1). The carbene can be *trans* to the metal–metal bond in an axial position, in which case it is sterically favoured, but electronically at a disadvantage, or it can be *cis* to the rhenium–rhenium bond in the equatorial position, which is the electronically favoured and sterically less favoured position. The *cis*-Re(CO)<sub>5</sub> substituent is a very bulky ligand compared to a CO ligand. Work done by Bezuidenhout<sup>7</sup>, in our laboratories has shown the electronic preference for the equatorial position in manganese carbonyl complexes. The aminolysis of *ax*-[Mn<sub>2</sub>(CO)<sub>9</sub>{C(OEt)C<sub>4</sub>H<sub>3</sub>S}] with NH<sub>3</sub> afforded an *eq*-[Mn<sub>2</sub>(CO)<sub>9</sub>{C(NH<sub>2</sub>)C<sub>4</sub>H<sub>3</sub>S}] whereas the more bulky amine, HN<sup>i</sup>Pr<sub>2</sub>, afforded an *ax*-[Mn<sub>2</sub>(CO)<sub>9</sub>{C(N<sup>i</sup>Pr<sub>2</sub>)C<sub>4</sub>H<sub>3</sub>S}], emphasizing the steric influence of the modified ligands.



**Scheme 2.7:** Preparation of dirhenium monocarbene complexes



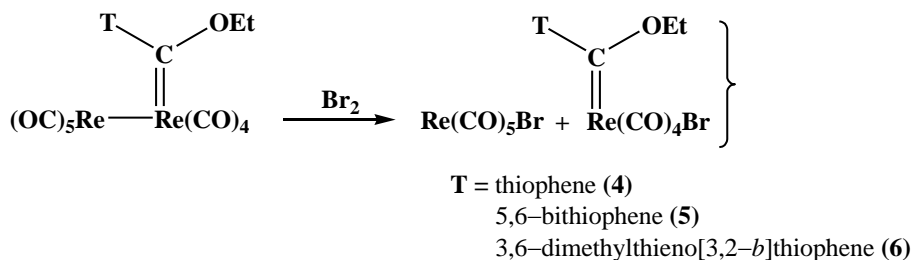
**Figure 2.1:** Axial and equatorial substituted carbene ligands

<sup>7</sup> D. I. Bezuidenhout, D. C. Liles, P.H. van Rooyen, S. Lotz; *J. Organomet. Chem.*, **2007**, 692, 774–783

The target monorhenium bromo carbene complexes were not accessible via the  $[\text{Re}(\text{CO})_5\text{Br}]$  route, but the successful synthesis of the dirhenium monocarbene complexes opened the possibility to cleave the Re–Re bond with  $\text{Br}_2$  to generate  $[\text{Re}(\text{CO})_5\text{Br}]$  and the desired complex  $[\text{Re}(\text{CO})_4(\text{carbene})\text{Br}]$ . If successful, the original targeted monorhenium bromo carbene complexes could be obtained along this route.

## 2.4 Reaction of rhenium carbene complexes with bromine

The cleaving of the M–M bond of  $[\text{M}_2(\text{CO})_{10}]$  (M = Mn/Re) by bromine, affording  $[\text{M}(\text{CO})_5\text{Br}]$ , is well–documented<sup>8</sup>. The prepared dirhenium carbene complexes **1–3** were reacted with  $\text{Br}_2$  in hexane. The reaction mixtures were stirred for two hours and the products precipitated from solution. The bromine had cleaved the rhenium–rhenium bonds of the dimetal carbene complexes, yielding brominated metal complexes (Scheme 2.8). The brightly–coloured solution of carbene complexes was observed to become more dull and gray in colour during the formation of **4–6**.



**Scheme 2.8:** Bromine–cleaving of Re–Re bonds in monocarbene complexes

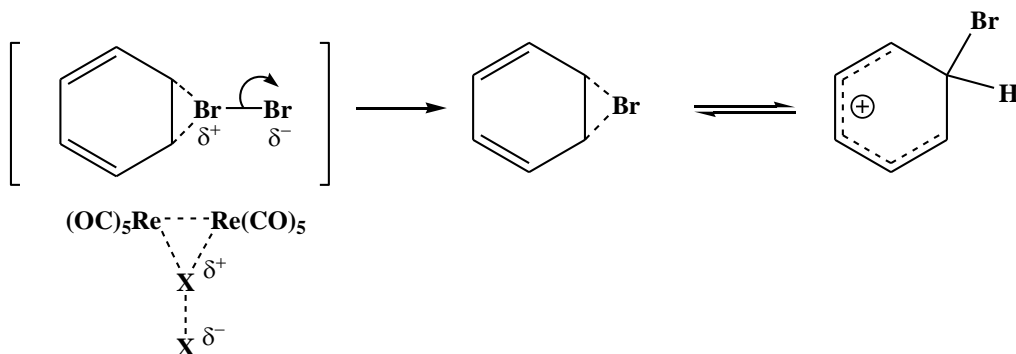
No products of Re–carbene double bond bromination were isolated. The Br–Br bond of bromine can be polarized in a reaction with *electron–rich* olefins<sup>9</sup> and bromine adds to the double bond by first association of  $\text{Br}^+$ . For instance, nucleophilic attack of an aromatic ring is by one of the aromatic ring’s double bonds on  $\text{Br}_2$ <sup>10</sup> (into an empty d–

<sup>8</sup> S. P. Schmidt, W. C. Trogler, F. Basolo; *Inorg. Synth.*, **1990**, 28, 162

<sup>9</sup> (a) S. R. Merrigan, D. A. Singleton; *Org. Lett.*, **1999**, 1, 327–329; (b) R. S. Brown; *Acc. Chem. Res.*, **1997**, 30, 131–137

<sup>10</sup> A.V. Vasilyev, S.V. Lindeman, J.K. Kochi; *New J. Chem.*, **2002**, 26, 582–592

orbital of Br), see Scheme 2.9. Schmidt, Trogler and Basolo<sup>11</sup> have shown that a similar halonium intermediate may be involved in the halogenation of  $[\text{Mn}_2(\text{CO})_{10}]$  and  $[\text{Re}_2(\text{CO})_{10}]$ . A free halide ion is generated in the reaction and is suggested to nucleophilically attack on and open the bridged intermediate.



**Scheme 2.9:** Bromine addition to metal–metal bond

The same reactions with electron–poorer alkenes<sup>12</sup> require strongly electrophilic  $\text{Br}^+$  or polarized  $\text{Br}-\text{X}$  bonds and they are more likely to undergo radical reactions<sup>13</sup>. Metal–carbene bonds have been used in reactions to bond to transition metals with vacant coordination sites<sup>14</sup>. These bonds are not as electron–rich as olefinic bonds and reaction with  $\text{Br}_2$  in this way (charge transfer) is less likely. In contrast, Schrock carbenes have an electron–rich metal–carbene bond, and display a different reactivity pattern<sup>15</sup>.

The Fischer group<sup>16</sup> reported that in the reaction between a chromium Fischer carbene complex and  $\text{HBr}$ , the electrophilic chromium carbene carbon was attacked by  $\text{Br}^-$  and the proton believed to be bonded to the chromium metal in an unstable intermediate. As shown in Scheme 2.10, in the final product the hydrogen atom is bound to the carbene

<sup>11</sup> S. P. Schmidt, W. C. Trogler, F. Basolo; *J. Am. Chem. Soc.*, **1984**, *106*, 1308–1313

<sup>12</sup> V.A. Petrov, C.G. Krespan; *J. Org. Chem.*, **1996**, *61*, 9605–9607

<sup>13</sup> O. Bortolini, S. Campestrini, V. Conte, G. Fantin, M. Fogagnolo, S. Maietti; *Eur. J. Org. Chem.*, **2003**, 4804–4809

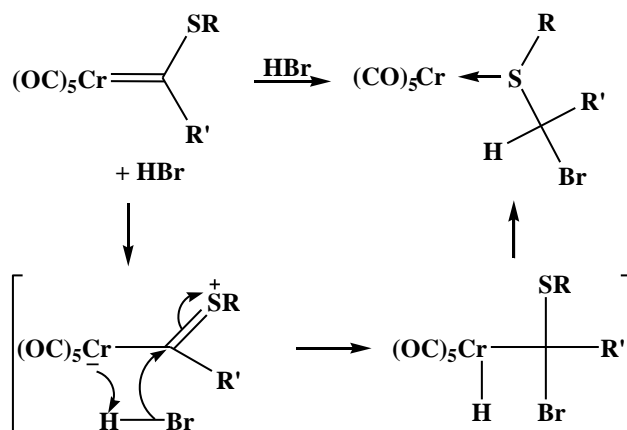
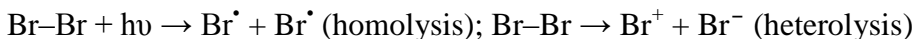
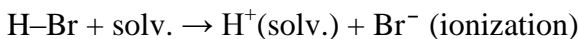
<sup>14</sup> (a) J–P. Djukic, A. Maisse–Francois, M. Pfeffer, K. H. Dötz, A. De Cian, J. Fischer; *Organometallics*, **2000**, *19*, 5484–5499; (b) Y. Tang, J. Sun, J. Chen; *Organometallics*, **2000**, *19*, 72–80

<sup>15</sup> J. Ushio, H. Nakatsuji, T. Yonezawa; *J. Am. Chem. Soc.*, **1984**, *106*, 5892–5901

<sup>16</sup> (a) E.O. Fischer, G. Kreis; *Chem. Ber.*, **1973**, *106*, 2310–2314; (b) E.O. Fischer, K.R. Schmid, W. Kalbfus, C.G. Kreiter; *Chem. Ber.*, **1973**, *106*, 3893–3909

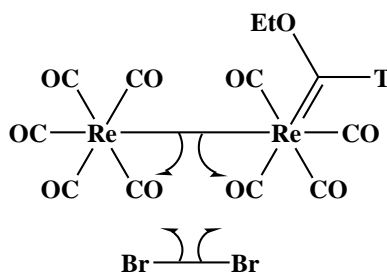


carbon atom and the carbene ligand had been modified to a thio-ether ligand (Scheme 2.11). HBr and Br<sub>2</sub> differ though, the former is a polar substrate and the latter a non-polar substrate:



**Scheme 2.10:** Reaction of a chromium carbene complex with HBr

The M–M bond energy (Mn(CO)<sub>5</sub>–Mn(CO)<sub>5</sub> ≈ 170 kJ/mol<sup>17</sup>; Re(CO)<sub>5</sub>–Re(CO)<sub>5</sub> ≈ 213 kJ/mol<sup>18</sup>) is approximately half as strong as a similar carbon–carbon (C–C ≈ 350 kJ/mol)<sup>19</sup> bond in organic chemistry. Homolysis of the weaker Re–Re and the Br<sub>2</sub> bonds produces isolobal fragments which can exchange and afford the final cleaved products.



**Figure 2.2:** Radical cleaving of Re–Re bond by Br<sub>2</sub>

<sup>17</sup> E. Folga, T. Ziegler; *J. Am. Chem. Soc.*, **1993**, *115*, 5169–5176

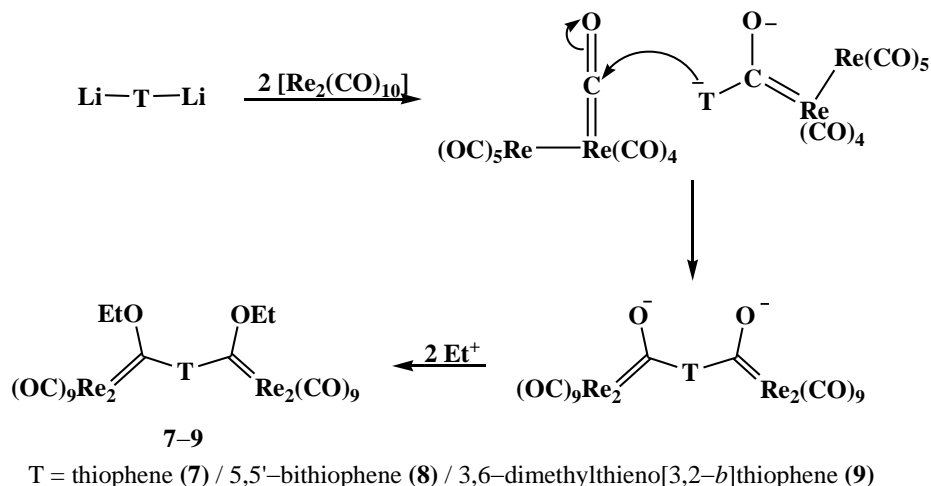
<sup>18</sup> B. C. Gilbert, A. F. Parsons; *J. Chem. Soc., Perkin Trans.*, **2002**, 367–387

<sup>19</sup> *Advanced Organic Chemistry, 4<sup>th</sup> Ed.*, John Wiley & Sons, Editor: J. March; 24 (Table 1.7)

Although it is possible to synthesize  $[\text{Re}(\text{CO})_4\{\text{C}(\text{OEt})\text{R}\}\text{Br}]$  complexes along this route, one half of the starting complex is lost as  $[\text{Re}(\text{CO})_5\text{Br}]$ . One would ideally have liked to start with  $[\{\text{Re}(\text{CO})_4\{\text{C}(\text{OEt})\text{R}\}\}_2]$  (R = thienyl derivative), but this precursor could not be obtained.

## 2.5 The synthesis of tetrarhenium biscarbene complexes

It was found that reactions of dilithiated thiophene with group 6 metal carbonyls afforded dimetal biscarbene complexes<sup>20</sup>. The dilithiation of the thiophene derivatives was achieved in dry THF at low temperatures with two equivalents of *n*-BuLi. The reaction was executed by adding two equivalents of  $[\text{Re}_2(\text{CO})_{10}]$ , and thereafter adding two equivalents  $\text{Et}_3\text{OBF}_4$  in dichloromethane. The red complex **7** and deep red complex **8** were purified by column chromatography and recrystallized. A similar reaction yielded complex **9**, again in very low yields (Scheme 2.11).



**Scheme 2.11:** Preparation of complexes **7-9**

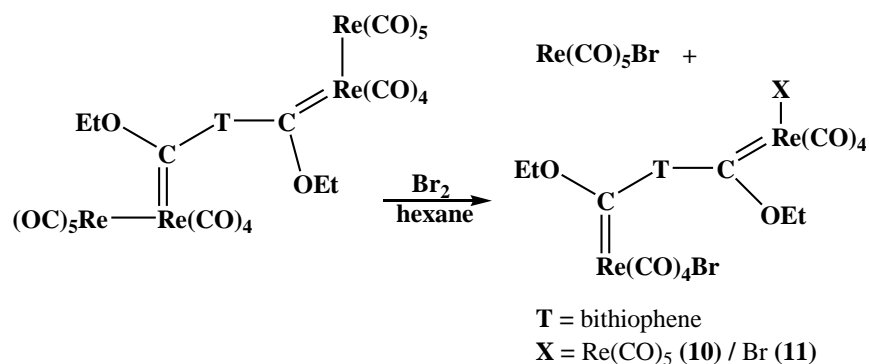
<sup>20</sup> (a) Y. M. Terblans, H. M. Roos, S. Lotz; *J. Organomet. Chem.*, **1998**, 566, 133–142; (b) M. Landman, H. Görls, S. Lotz; *Z. Anorg. Allgem. Chem.*, **2002**, 628, 2037–2043; (c) S. Lotz, C. Crause, A. J. Olivier, D. C. Liles, H. Görls, M. Landman, D. I. Bezuidenhout; *Dalton Trans.*, **2009**, 4, 697–710

The dilithiation of thiophene was not very successful and even with three equivalents of butyl lithium less than 20% of the dilithiated precursor could be obtained. Dilithiation of thiophene is typically achieved in hexane in the presence of tetramethylethylenediamine at higher temperatures. These conditions do not work well with  $[\text{Re}_2(\text{CO})_{10}]$  because of the coordination of the tetramethylethylenediamine to rhenium. Higher yields of dilithiated thiophene can be achieved starting with 2,5-dibromothiophene (~50%), but this avenue was not pursued.

The biscarbene complexes are more reactive than the corresponding monocarbene complexes and the carbene ligand is more readily accessible for attack by nucleophiles in solution.

## 2.6 Bromination of complex 8

To test whether bromination would again only cleave the metal–metal bond, and not react with the carbene ligand, biscarbene complex **8** was dissolved in hexane and reacted with one equivalent of bromine, at room temperature. The colour of the solution was observed to change from deep red to a lighter red, more grayish colour. Interestingly, complex **10** was a minor product and complex **11** the major product (Scheme 2.12), as was indicated by  $^1\text{H}$  NMR spectroscopy.

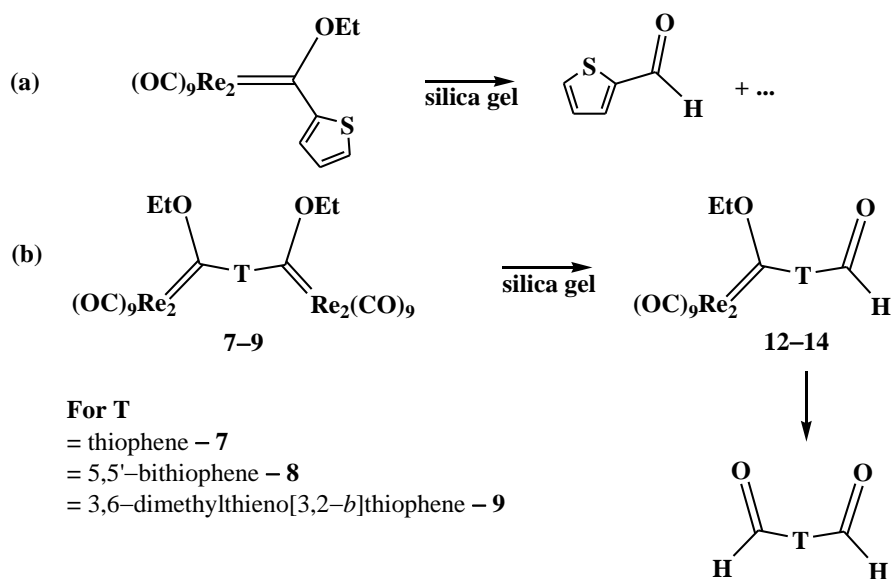


**Scheme 2.12:** Bromine–cleaving of Re–Re bonds in tetrametal biscarbene complexes

Thus the biscarbene complexes' Re–Re bonds could be cleaved in reaction with bromine, as with monocarbene complexes **1**, **2** and **3**.

## 2.7 Aldehyde compounds

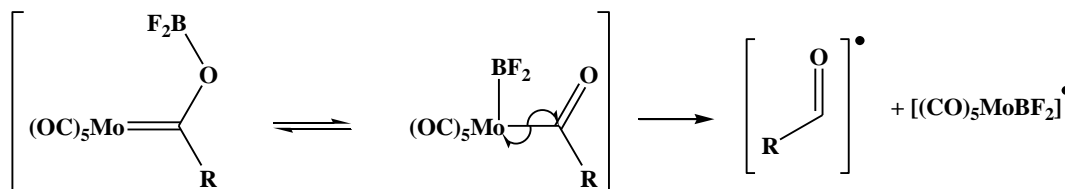
The formation of aldehyde compounds is illustrated in Scheme 2.13. During the purification of monocarbene complex **2** on a silica gel column, 5-formyl-2-thienyl was isolated. Interestingly, during column chromatography of complexes **1** and **3** the formation of the corresponding monoaldehyde compounds was not detected. Purification of the biscarbene complexes on silica gel afforded aldehydes in far greater yields for **7–9**. The monocarbene aldehyde complexes **12–14** could be further converted into dialdehyde compounds. What was clear from these studies was that the aldehyde formed over prolonged periods of time and was only observed after being in contact with the silica gel columns during purification. The reactivity at the carbene site was notably higher for the biscarbene complexes, compared to monocarbene complexes. It is significant that the yield increases with the time spent on the column.



**Scheme 2.13:** Formation of aldehyde species

Complex **9** was more reactive towards aldehyde formation than complex **8**. Although no aldehyde formation was observed during workup for the monocarbene complex, replacement of H by C(O)H at ring position 7 rendered the monocarbene active enough to enable a second aldehyde formation.

A molybdenum carbene complex with a BF<sub>2</sub>-group attached to oxygen could generate an acyl radical that reacts to give, amongst others, aldehydes<sup>21</sup> (Scheme 2.14).



**Scheme 2.14:** Ligand decomplexation to give acyl synthons

The formation of aldehydes via a radical mechanism for manganese precursors and via an ionic mechanism for rhenium precursors was discussed in Chapter 1. What is clear from this information is that a metal acyl and a metal hydride are key components in the reaction to generate aldehydes along these routes (see Scheme 1.21).

### 2.7.1 Hydroxycarbene modification

Fischer and co-workers prepared hydroxycarbene complexes by acidifying the metalacylates. They reported that a hydroxycarbene species could dissociate to an aldehyde<sup>22</sup>. Hydroxycarbene complexes are usually stabilized in the solid state through hydrogen-bonding<sup>23</sup>.

<sup>21</sup> J. Barluenga, F. Rodríguez, F. J. Fañanás; *Chem. Eur. J.*, **2000**, *6*, 1930–1937

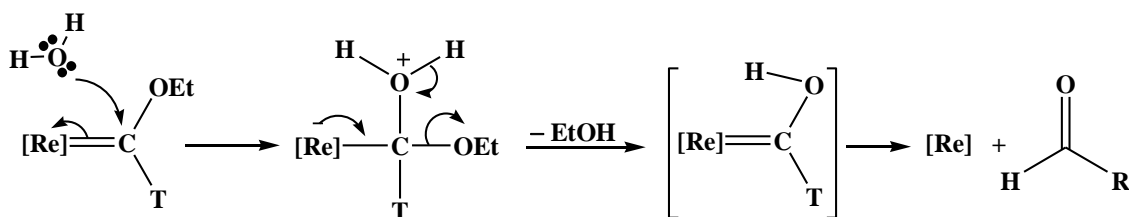
<sup>22</sup> (a) E. O. Fischer; *Angew. Chem.*, **1974**, *86*, 651–663; (b) E. O. Fischer, G. Kreis, F. R. Kreissl; *J. Organomet. Chem.*, **1973**, *56*, C37–C40; (c) M. Ryang, I. Rhee, S. Tsutsumi; *Bull. Chem. Soc. Jpn.*, **1964**, *37*, 341–343

<sup>23</sup> (a) P. L. Motz, D. M. Ho, M. Orchin; *J. Organomet. Chem.*, **1991**, *407*, 259–269; (b) M. W. Esterhuysen, H. G. Raubenheimer; *Eur. J. Inorg. Chem.*, **2003**, 3861–3869

The aldehydes observed in this study were likely formed from a reactive hydroxycarbene intermediate which is in equilibrium with a hydrido–acyl intermediate. This conclusion was supported by a control experiment whereby the reaction mixture containing the acylate of a thiophene derivative was protonated with HBF<sub>4</sub>. When this procedure was followed the thiophene and 3,6–dimethylthieno[3,2–*b*]thiophene aldehyde compounds were also obtained.

In a further control experiment **8** was dissolved in THF and degassed water added (1 ml in 20 ml THF). The reaction mixture changed colour from red to orange and stirring was continued overnight. All of the biscarbene complex either decomposed or was transformed into orange **13** and the yellow 5,5'–diformyl–2,2'–bithiophene. Water attacks the carbene carbon nucleophilically to form an ylide and ultimately produces a hydroxycarbene complex (Scheme 2.15) in a reaction that resembles the well–known aminolysis reaction of Fischer carbene complexes<sup>24</sup>.

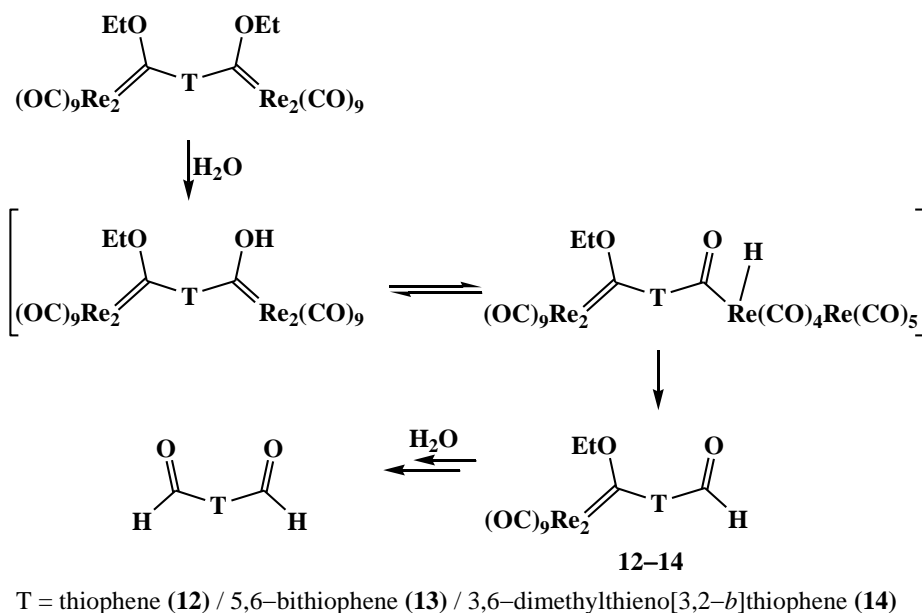
The hydroxycarbene complex is convertible into a very reactive hydrido–acyl complex<sup>25</sup>. As Schemes 2.15 and 2.16 shows, the aldehyde is obtained by reductive elimination of the hydride and acyl ligand.



**Scheme 2.15:** Hydroxycarbene intermediates

<sup>24</sup> (a) C. F. Bernasconi, M. Pérez–Lorenzo, S. J. Coddling; *J. Org. Chem.*, **2007**, *72*, 9456–9463; (b) M. E. Z. Michoff, R. H. de Rossi, A. M. Granados; *J. Org. Chem.*, **2006**, *71*, 2395–2401; (c) C. F. Bernasconi, F. X. Flores, K. W. Kittredge; *J. Am. Chem. Soc.*, **1997**, *119*, 2103–2110

<sup>25</sup> C. P. Casey, C. J. Czerwinski, R. K. Hayashi; *J. Am. Chem. Soc.*, **1995**, *117*, 4189–4190



**Scheme 2.16:** Formation of aldehyde monocarbene and dialdehyde compounds

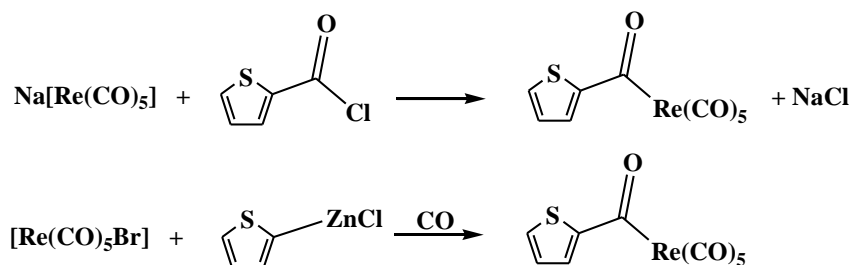
## 2.8 Synthesis of hydroxycarbene complexes

Because it appeared that hydroxycarbene complexes play an important role as intermediates in the formation of aldehydes from the carbene ligands, direct synthesis of the hydroxycarbene complexes was attempted.  $[\text{Re}_2(\text{CO})_{10}]$  and  $[\text{Re}(\text{CO})_5\text{Br}]$  were reacted with 2-lithiumthienyl in THF. The reaction solutions were separated into two parts after the lithiation reaction – one part was stripped of its solvent under reduced pressure and the residue dissolved in deoxygenated distilled water. Both parts were then acidified with the  $\text{HBF}_4$  and the solvents removed for  $^1\text{H}$  NMR studies of the mixtures.

For the reaction of  $[\text{Re}(\text{CO})_5\text{Br}]$  with protonation in THF, a single major product was indicated by  $^1\text{H}$  NMR spectroscopy. The NMR data of this compound was consistent with a hydroxycarbene complex,  $[\text{Re}(\text{CO})_4\{\text{C}(\text{OH})\text{C}_4\text{H}_3\text{S}\}\text{Br}]$ . Signals are observed at 13.57 (s), 8.41 (d), 8.20 (d) and 7.38 (t) ppm. No aldehyde or hydride signals were observed at this early stage in this mixture and it is believed that interaction between the bromide ligand and the hydroxy proton prevents it from migrating to the metal. According to the bands in the infrared spectrum the 2-lithiumthienyl attacked a carbonyl

in a position *cis* to the bromide ligand. Efforts to obtain crystals for X-ray diffraction studies failed and the compound decomposed over time. It was not possible to obtain analytically pure samples of the complex.

There is an indication of three products by  $^1\text{H}$  NMR spectroscopy for the water fraction.  $[\text{Re}(\text{CO})_5\{\text{C}(\text{O})\text{C}_4\text{H}_3\text{S}\}]$  was one of the three complexes that had formed and according to signal strength it was the major complex. In a separate reaction, the thienyl acyl complex  $[\text{Re}(\text{CO})_5\{\text{C}(\text{O})\text{C}_4\text{H}_3\text{S}\}]$  was prepared by reacting the rhenium carbonyl anion  $[\text{Re}(\text{CO})_5]^-$  with 2-thienyl acetylchloride (it was previously prepared by Rauchfuss *et al*<sup>1a</sup> by a different method).  $[\text{Re}(\text{CO})_5\{\text{C}(\text{O})\text{C}_4\text{H}_3\text{S}\}]$  shows thienyl signals in the  $^1\text{H}$  NMR spectrum at 7.97 (dd), 7.72 (dd) and 7.18 ppm (dd). Both preparative methods are shown below:

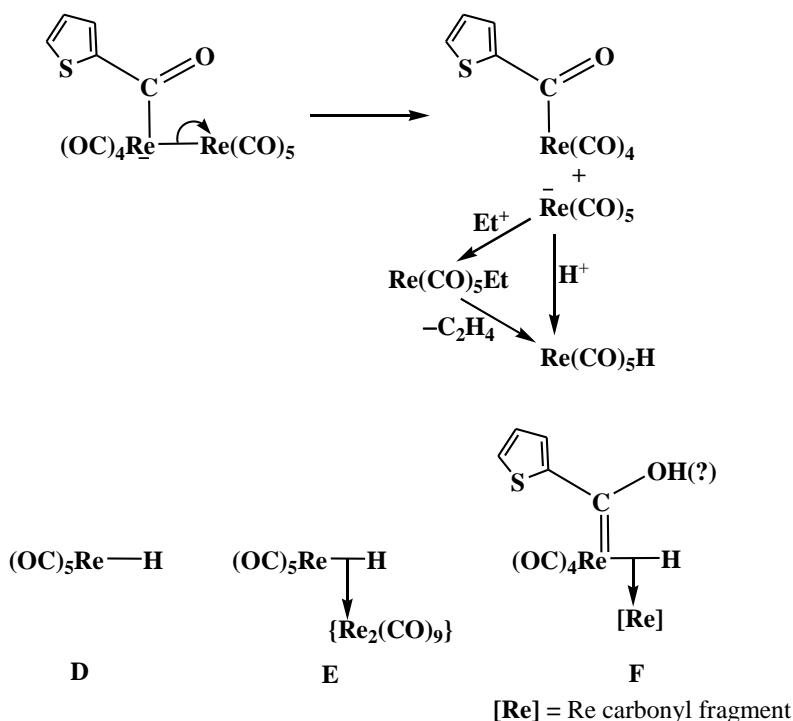


**Scheme 2.17:**  $[\text{Re}(\text{CO})_5\{\text{C}(\text{O})\text{C}_4\text{H}_3\text{S}\}]$  synthesis

The reaction with  $[\text{Re}_2(\text{CO})_{10}]$  afforded various products and not all could be identified. Importantly, NMR bands belonging to  $[\text{Re}_2(\text{CO})_9\{\text{C}(\text{OH})\text{C}_4\text{H}_3\text{S}\}]$ , the hydroxycarbene complex of the dirhenium unit, could not be assigned unambiguously, but signals belonging to 2-formyl-thienyl were clearly visible and were assigned. It was assumed that the aldehyde formed via the decomposition of a dirhenium hydroxycarbene complex. Also, another feature of the reaction of lithiated thiophene with  $[\text{Re}_2(\text{CO})_{10}]$  is the formation of Re-hydrides with bands at -6 ppm and between -13 and -16 ppm. These probably formed from anionic monorhenium fragments being protonated after Re-Re bond cleavage.  $[\text{Re}(\text{CO})_5]^-$  can be alkylated ( $\text{Et}^+$ ) and after  $\beta$ -H elimination again give



[Re(CO)<sub>5</sub>H], with a Re–H <sup>1</sup>H NMR chemical shift value recorded at –5.7 ppm<sup>26</sup>. [Re(CO)<sub>5</sub>H] coordinates through the Re–H bond to a coordinatively unsaturated Re–intermediate to give E (–15.2 ppm)<sup>27</sup>. The formation of [Re(CO)<sub>5</sub>H] and hydride complexes are shown below in Scheme 2.18:



**Scheme 2.18:** Formation of [Re(CO)<sub>5</sub>H] and other hydride complexes

The band at –15.7 ppm could not be assigned unambiguously, but it clearly represents a compound with a bridging hydride and a carbene ligand with a thienyl substituent was evident from the resonances in the thiophene region. No signals indicating a hydroxycarbene proton around 14 ppm was observed.

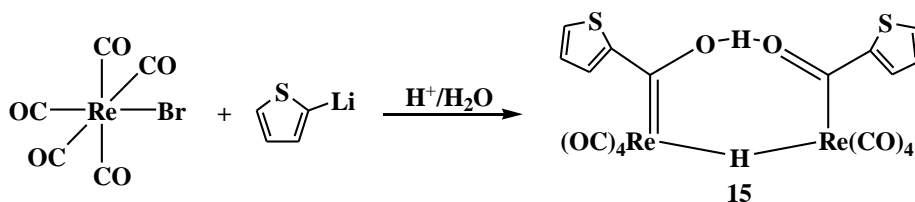
We presume the chemical shifts of the bands may be mixture sensitive as they represented mixtures of complexes.

<sup>26</sup> I. del Rosal, L. Maron, R. Poteau, F. Jolibois; *Dalton Trans.*, **2008**, 3959–3970

<sup>27</sup> D. I. Bezuidenhout, unpublished results

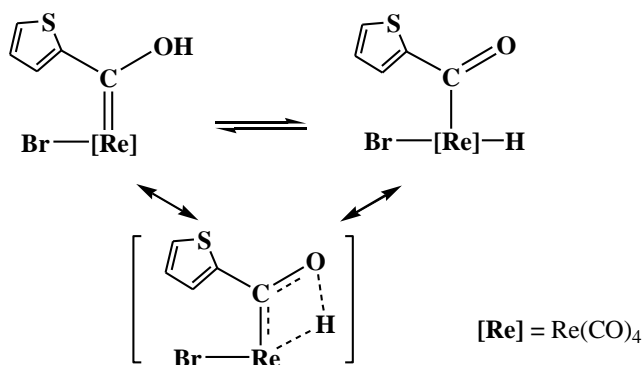
## 2.9 Hydroxycarbene–acyl complex

One of the products (Scheme 2.19) initially observed during column chromatography was a very polar yellow compound that could only be eluted with dichloromethane or THF. In a reaction of  $[\text{Re}(\text{CO})_5\text{Br}]$  and 2–lithiumthienyl, and subsequent alkylation with  $\text{Et}_3\text{OBF}_4$  or protonation with  $\text{HBF}_4$ , the novel complex **15** was isolated (Scheme 2.19). The structure of **15** was confirmed by a single crystal X–ray diffraction study.



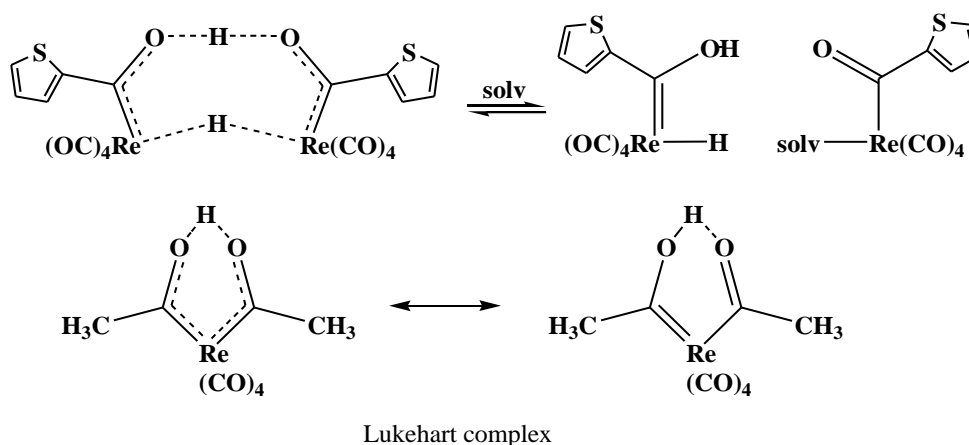
**Scheme 2.19:** Complex **15** formation

Complex **15** consists of two key functionalities, i.e. the hydroxycarbene and acyl ligands, which form an integral part of this project. The hydride ligand that bridges the two rhenium atoms represents a 3–centre, 2–electron bond. In Scheme 2.20, protonation of the intermediates to give the two tautomeric forms, is shown and it is conjectured that a proton might migrate between the metal and oxygen atoms *via* a four–membered intermediate.



**Scheme 2.20:** Proposed metal–to–oxygen migration of a hydrogen atom

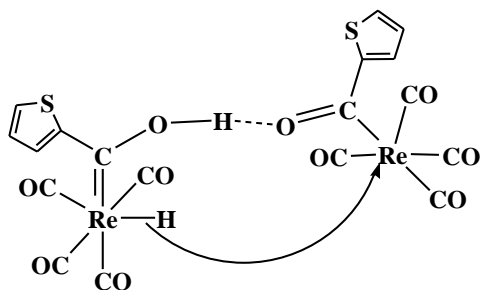
In complex **15** a hydroxycarbene complex is trapped by an oxygen atom of an acyl ligand (H-bonding; electronic stabilization) and through a bridging hydride (M-H coordination) in a dinuclear complex. This novel complex can be seen as consisting of two fragment complexes held together by a proton and a hydride (Scheme 2.21). Where the Lukehart complex<sup>28</sup>, also shown in the scheme, display these two functionalities on one rhenium atom, in **15** they are found on two separate rhenium atoms.



**Scheme 2.21:** Fragments of complex **15**

Shifting the two hydrogen atoms from one fragment to the other in **15**, and retaining bonding integrity, generates the other fragment. Scheme 2.22 shows how the two complex fragments may have initially become associated by ‘sharing’ of a proton between the oxy atoms of the carbene and acyl ligands and a coordinative bond of the rhenium hydride bond to the coordinatively unsaturated acyl complex. Hydroxycarbene complexes are generally not stable unless stabilized through hydrogen-bonding, at least in the solid state. Therefore the hydrogen bonding proposed in Scheme 2.22 also shows a way for the hydroxycarbene species to be stabilized.

<sup>28</sup> (a) C. M. Lukehart, G. Paull Torrence, J. V. Zeile; *J. Am. Chem. Soc.*; **1975**; 97, 6903–6904; (b) C. M. Lukehart, J. V. Zeile; *J. Am. Chem. Soc.*, **1976**, 98, 2365–2367



**Scheme 2.22:** Attachment of two rhenium species through hydrogen bonding

The source of the hydrogen atoms for the ethoxycarbene complexes are believed to be either protons from water on the column material (silica gel column) or from  $[\text{Re}(\text{CO})_5\text{H}]$  formed *in situ* (Scheme 2.18). When the preparation was repeated, adding either  $\text{HBF}_4$  or magic methyl, instead of  $\text{Et}_3\text{OBF}_4$ , the same complex was obtained.

2-Lithiumthienyl attacks on a carbonyl ligand of  $[\text{Re}(\text{CO})_5\text{Br}]$  and imparts a negative charge to the complex. The formation of this anionic intermediate facilitates the loss of a bromo ligand as bromide and ultimately the formation of complex **1** (Scheme 2.3). An alternative is that the bromo ligand is not lost as bromide, but is retained and then protonation of the metal acylate intermediate complex yields a bromo hydroxycarbene complex. A precedent for such a complex is found in literature whereby the hydroxycarbene ligand is stabilized intramolecularly by a bromo-hydrogen interaction<sup>29</sup>. Complex **15** is suggested to have formed from such a species, as is shown in Scheme 2.23.

The  $\text{Re}(\text{CO})_5\text{-H}$  bond strength is  $310 \text{ kJ/mol}$ <sup>30</sup>. Unfortunately no bond energy of  $\text{Re}(\text{CO})_5\text{-Br}$  data could be found in literature, but the ordering of  $\text{Mn-X}$  bond dissociation energies follows the following pattern<sup>31</sup>:

$$(\text{CO})_5\text{Mn-X} (\Delta(\text{Mn-X}), \text{kJ/mol})$$

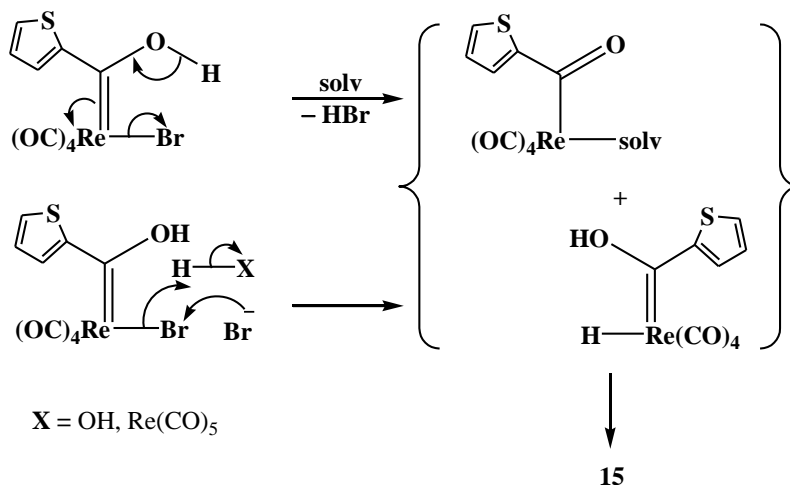
<sup>29</sup> K. P. Darst, C. M. Lukehart; *J. Organomet. Chem.*, **1979**, *17*, 65–71

<sup>30</sup> M. Tilset, V. D. Parker; *J. Am. Chem. Soc.*, **1989**, *111*, 6711–6717 (corrections: *J. Am. Chem. Soc.*, **1990**, *112*, 2843)

<sup>31</sup> (a) J. A. Connor; *Topics Curr. Chem.*, **1977**, *71*, 71–110; (b) J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke; University Science Books; *Principles and Applications of Organotransition Metal Chemistry*, and references therein, **1987**

X = Br (280) > H (250) > Ph ( $sp^2$ -C) (205) > CH<sub>3</sub> ( $sp^3$ -C) (185) > C(O)CH<sub>3</sub> (165) > Mn(CO)<sub>5</sub> (160).

Re–X bonds are approximately 20% stronger and according to the above approximate values, Re–H and Re–Br would be very similar and much stronger than a Re–Re bond.



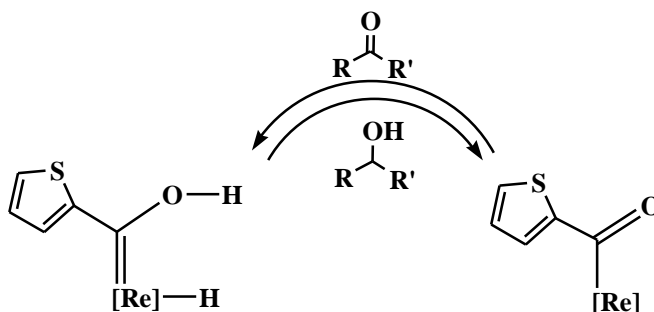
**Scheme 2.23:** Possible reaction route to **15**

The reaction of 2–lithiumthienyl or 5–lithium–2,2′–bithienyl with [Re<sub>2</sub>(CO)<sub>10</sub>] and protonation instead of alkylation again affords **15** and equivalent bithiophene complex **16**. These complexes were isolated in low yields as highly polar fractions from the chromatographic separation of the reaction products.

Several important features of complexes **15** and **16** need to be recognized. It is similar to the Shvo catalyst<sup>32</sup>, which also contains a protonic hydrogen atom between two oxygen atoms and a hydridic hydrogen atom between two transition metals. The Shvo catalyst is a keto–enol/hydride complex and the prepared complex an acyl–carbene/hydride complex. An important question regarding the possible application of complexes **15** and **16** is whether they could also behave like the Shvo catalyst? One can assume that it will also fragment into an 18 electron and a 16–electron species. The former (hydroxycarbene

<sup>32</sup> (a) Y. Shvo, D. Czarkie, Y. Rahamim; *J. Am. Chem. Soc.*, **1986**, *108*, 7400–7402; (b) C. P. Casey, S. W. Singer, D. R. Powell, R. K. Hayashi, M. Kavana; *J. Am. Chem. Soc.*, **2001**, *123*, 1090–1100; (c) R. M. Bullock; *Chem. Eur. J.*, **2004**, *10*, 2366–2374

hydride complex) could donate hydrogen atoms to a ketone function, for instance, or the latter (acyl complex) could take hydrogen atoms from an alcohol (Scheme 2.24). The potential catalytic properties of **15** and **16**, was not part of this study and forms part of further investigations in our laboratories with phosphine–modified analogues.



**Scheme 2.24:** Proposed activity of complex **15**

Importantly, it was noted that complex **15** dissociated after a few days and that the products that formed (two fractions were isolated when separation was done with column chromatography) did not have a hydride – there were no signals at higher field strength than  $-2$  ppm on the  $^1\text{H}$  NMR spectrum. The recognition of the signal of the hydroxycarbene proton is elusive on the  $^1\text{H}$  NMR spectrum. No signal was observed that may belong to this hydrogen. Evidence of acyl and aldehyde formation was found in the  $^1\text{H}$  NMR spectrum of a decomposition mixture of **15**. Although this is not conclusive, it may show that the complex has lost  $\text{H}_2$ , a sign that the complex might be active as a catalyst, similar to the Shvo catalyst, but may not necessarily be effective in similar systems.

## Chapter 3: Characterization of carbene complexes

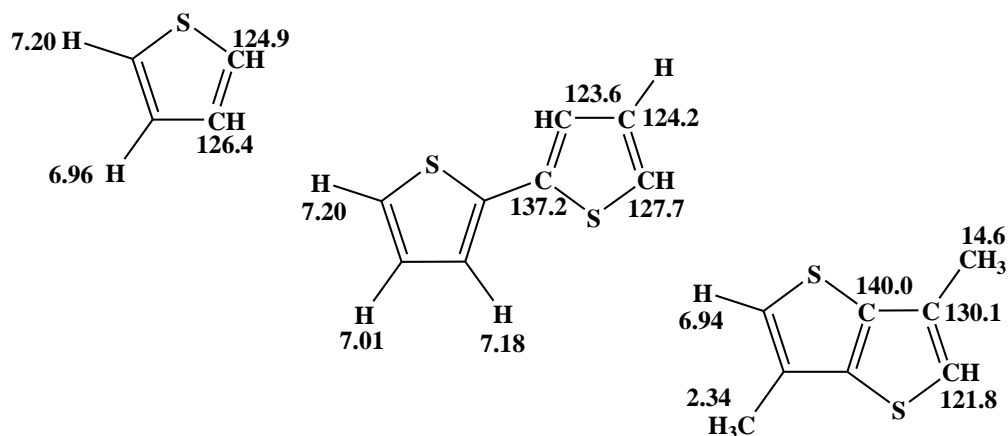
The new complexes were characterized and studied by infrared and NMR spectroscopy, as well as by mass spectrometry. In dealing with metal carbonyl carbene complexes, valuable information can be obtained from the spectral features and band positions. NMR spectroscopy is invaluable in assigning structures to the complexes that were synthesized and the technique of IR spectroscopy confirms the presence and symmetry of metal carbonyls. Observing an  $M^+$  ion in the mass spectrum is strong evidence that the complex was identified correctly.

### 3.1 Proton NMR spectroscopy data

#### 3.1.1 Monocarbene dirhenium nonacarbonyl complexes

##### 3.1.1.1 Thiophene precursors

The NMR chemical shifts ( $^1\text{H}$ ,  $^{13}\text{C}$ ) for thiophene, bithiophene and 3,6-dimethylthieno[3,2-*b*]thiophene (carbene R-substituents) are shown in Figure 3.1.



**Figure 3.1:** Chemical shifts ( $^1\text{H}$ ;  $^{13}\text{C}$ ) NMR spectroscopy data (ppm) for thiophene and the thienyl substituents

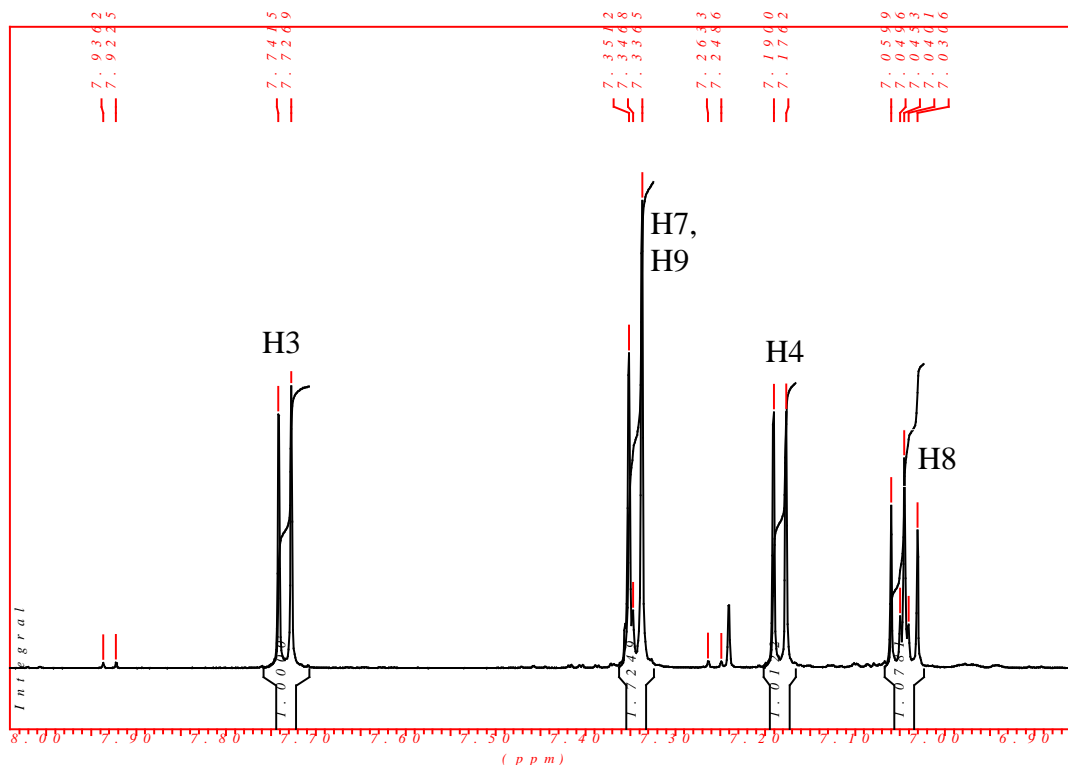
### 3.1.1.2 Dirhenium complexes

The dirhenium monocarbene complexes **1** to **3** were prepared from the 2–lithiumthienyl precursors, as discussed in Chapter 2. The aromatic region of the  $^1\text{H}$  NMR spectrum of complex **2** is shown in Figure 3.2. The spectrum was recorded in deuterated chloroform and the chloroform peak in the spectrum used for calibration (7.24 ppm).

There are two doublets – at 7.73 and 7.18 ppm – that belong to the hydrogen atoms on the thiophene ring to which the carbene is attached. The two hydrogen atoms couple and their signals are split into doublets. The signal at 7.73 ppm is identified as belonging to ring hydrogen H3, because it is shifted furthest downfield by the adjacent electrophilic carbene carbon atom (0.72 ppm, Table 3.1), whilst the signal of H4 is not shifted at all from its position in the  $^1\text{H}$  NMR spectrum of bithiophene. The highest field signal belongs to H8 and it lies at 7.05 ppm. This signal is shifted slightly downfield from its position in the spectrum of bithiophene. It is split because H8 couples to the two neighbouring hydrogen atoms, H7 and H9. The signal does not appear as a doublet of doublets, but as a triplet with satellite signals each side of the middle peak of the signal. Interestingly, the signal of the ring proton (H9) that is the farthest from the electron–drawing carbene carbon is shifted more downfield than that of H8. The sum of the integration values of the peaks give a value of 4.82, close enough to 5 to be indicative of five protons.

There are two unidentified small doublet signals at 7.93 and 7.25 ppm. These signals are presumed to go together and belong to a symmetrical complex or molecule. The species could not be identified, but it is not 5,5'–diformyl–2,2'–bithiophene.





**Figure 3.2:** Aromatic region of the  $^1\text{H}$  NMR spectrum of **2** in  $\text{CDCl}_3$

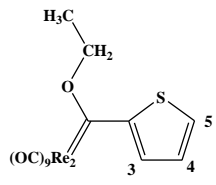
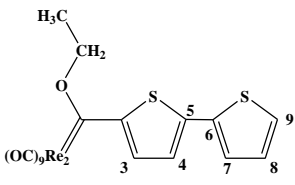
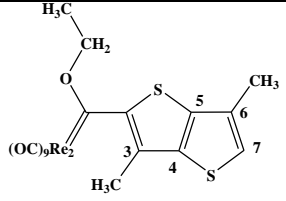
The  $^1\text{H}$  NMR data for the three monocarbene complexes are given in Table 3.1.

The electron-withdrawing carbene carbon is directly attached to a thienyl ring. The molecular configuration can be compared to other aromatic ring systems that have electron-withdrawing groups. For thiophene, there are a multitude of examples that have been synthesized, from thiophene rings with carboxylic groups at the  $\alpha$ -position to halides, metals and other thienyl rings<sup>1</sup>. There are not as many examples for bithiophene and 3,6-dimethylthieno[3,2-*b*]thiophene. 2-Thiophenecarboxylate<sup>2</sup> is an organic analogue of the thiophene monocarbene complex **1**. Its ring protons have signals at 7.80 (H3), 7.10 (H4) and 7.55 ppm (H5) in  $\text{CD}_2\text{Cl}_2$ . The same signal pattern is observed in the aromatic region of the thiophene complex **1**.

<sup>1</sup> (a) S. P. Ivonin, A. A. Tolmachev, A. M. Pinchuk; *Curr. Org. Chem.*, **2008**, *12*, 25–38; (b) W–Y. Wong, K–H. Choi, G–L. Lu; *Organometallics*, **2002**, *21*, 4475–4481

<sup>2</sup> H. Satonaka; *Bull. Chem. Soc. Jpn.*, **1983**, *56*, 2463–2468

**Table 3.1:**  $^1\text{H}$  NMR spectral data ( $\delta$ , J (Hz),  $\text{CDCl}_3$ ) of **1–3**

$\Delta\delta_{\text{R}}$ = difference from free substituent; value in ppm			
Complexes:			
<b>H3</b>	7.65 (d, 4.4) <sup>a</sup> $\Delta\delta_{\text{R}}^{\text{b}} = 0.69$	7.73 (d, 4.6) $\Delta\delta_{\text{R}} = 0.72$	–
<b>Me3</b>	–	–	2.16 (s) $\Delta\delta_{\text{R}} = -0.18$
<b>H4</b>	7.11 (t, 4.4; 4.7) $\Delta\delta_{\text{R}} = 0.15$	7.18 (d, 4.6) $\Delta\delta_{\text{R}} = 0.00$	–
<b>H5</b>	7.65 (d, 4.7) $\Delta\delta_{\text{R}} = 0.45$	–	–
<b>H7</b>	–	7.35 (d, 4.6) $\Delta\delta_{\text{R}} = 0.17$	7.04 (q, 1.0) $\Delta\delta_{\text{R}} = 0.10$
<b>H8</b>	–	7.05 (dd, 1.3, 4.6) $\Delta\delta_{\text{R}} = 0.04$	–
<b>Me6</b>	–	–	2.39 (d, 1.0) $\Delta\delta_{\text{R}} = 0.05$
<b>H9</b>	–	7.35 (d, 4.4) $\Delta\delta_{\text{R}} = 0.15$	–
<b>OCH<sub>2</sub>CH<sub>3</sub></b>	4.51 (q, 7.0)	4.54 (q, 7.0)	4.40 (q, 7.0)
<b>OCH<sub>2</sub>CH<sub>3</sub></b>	1.58 (t, 7.0)	1.60 (t, 7.0)	1.50 (t, 7.0)

<sup>a</sup> (J in Hz)

<sup>b</sup>  $\Delta\delta_{\text{R}}$  = difference between the chemical shifts of the corresponding protons of the thiophene substrates and the thienyl substituent of the complexes

The protons of the aromatic substituent in complexes **1** and **2** that are closest to the carbene carbon atom are the H3 protons. Their signals are shifted downfield, which indicates that the carbene carbon atom has a deshielding effect on the thienyl ring. Overall the perception is that the ester carbon (2–thiophenecarboxylate) and the carbene carbon have a very similar electron–withdrawing effect on the thiophene ring.

The change in chemical shift of H3's signal in complex **2** (versus the same hydrogen in bithiophene) is about the same as the signal–shift of proton H3 of complex **1**. In complex **1** H3's signal is shifted 0.69 ppm downfield (6.96→7.65 ppm) and in the bithiophene monocarbene complex **2**, it is shifted downfield by 0.72 ppm (7.01→7.73 ppm). On the other hand, the signal of H4 of complex **1** is shifted downfield ( $\Delta\delta_R = 0.15$  ppm) whereas H4 of complex **2** is not shifted downfield at all ( $\Delta\delta_R = 0.00$  ppm).

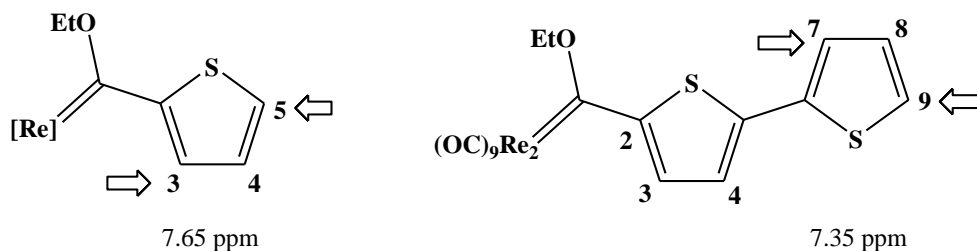
The second ring of bithiophene complex **2** has three hydrogen atoms. Their signals are also shifted downfield by the attachment of the electrophilic carbene carbon in the 2 position. The signals of H7 and H9 are shifted the most and H8's signal is shifted downfield the least (respectively  $\Delta\delta_R = 0.17$ , 0.15 and 0.04 ppm).

In the spectrum of complex **3**, it was unexpected to observe that the signal of the closest methyl, Me3, is shifted upfield instead of downfield. There are two probable signals for the thienyl methyls and the assignment was made by looking at the coupling. Me6 couples to H7 and its signal is split into a doublet whereas the signal of Me3 is a singlet.

The three monocarbene complexes have the following ring protons that are farthest from the carbene carbon atom: in **1** it is H5, in **2** it is H9 and in **3** H7. H5 of complex **1** is shifted downfield the most of these three complexes, as is expected. However, the H9 signal of complex **2** is shifted downfield more than the H7 signal of complex **3**.

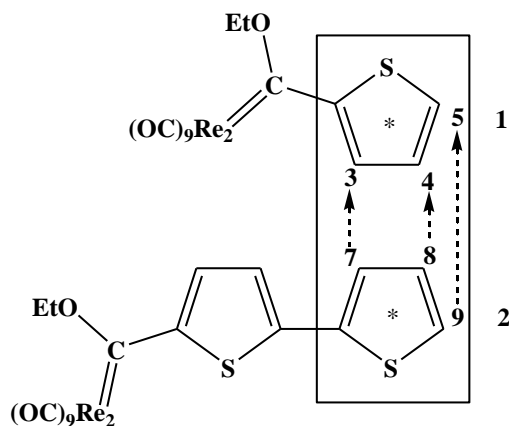
It is interesting that in complex **1** the signals of the closest thiophene proton, H3, and of the farthest thiophene proton, H5, are at the same chemical shift value. The same is also

seen for the second ring of the bithiophene monocarbene complex (H7 and H9 signals fall at the same shift value), as is indicated below.



**Figure 3.3:** Ring hydrogen atoms that have coinciding signals in the  $^1\text{H}$  NMR spectra

It can be shown with a calculation, that the electron-withdrawing property of the carbene carbon atom is transmitted to the second ring of **2** through the first. Consider the similarities of the two rings marked with asterisks in Figure 3.4.



**Figure 3.4:** Correlation between ring hydrogen atoms of two different complexes

The electron-withdrawing power, exercised by the group at pseudo-position '2' on ring two in bithiophene complex **2**, is about  $\frac{1}{4}$  to a  $\frac{1}{3}$  of what is exercised on a thiophene ring that is directly attached to the carbene carbon atom, as given here:

$$(0.17 \text{ ppm}/0.69 \text{ ppm} = 0.25) (\Delta\delta(\text{H7}) \text{ of } \mathbf{2} / \Delta\delta(\text{H3}) \text{ of } \mathbf{1})$$

$$(0.04 \text{ ppm}/0.15 \text{ ppm} = 0.27) (\Delta\delta(\text{H8}) \text{ of } \mathbf{2} / \Delta\delta(\text{H4}) \text{ of } \mathbf{1})$$

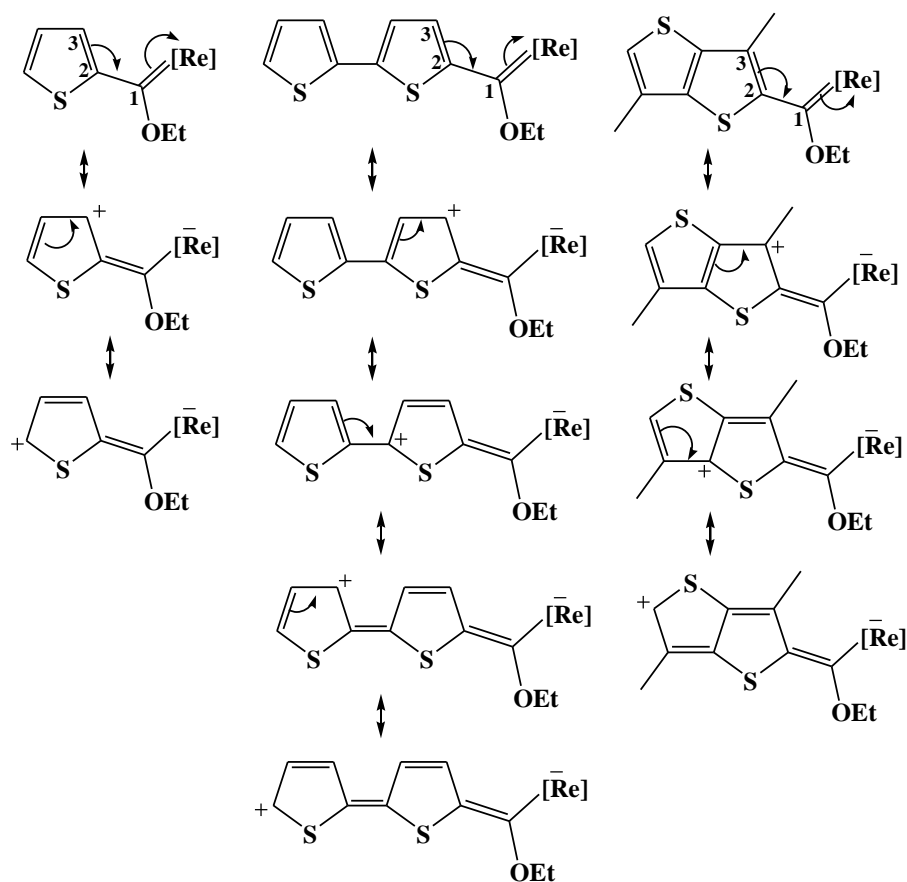
$$(0.15 \text{ ppm}/0.45 \text{ ppm} = 0.33) (\Delta\delta(\text{H9}) \text{ of } \mathbf{2} / \Delta\delta(\text{H5}) \text{ of } \mathbf{1})$$

Thiophene and the thienyl substituents have double bonds in conjugation. Resonance delocalization of these double bonds directly affects the distribution of electron density in the molecules. Thus it plays an important role in the NMR shifts that one observes for these complexes. In Scheme 3.1 the resonance delocalization of the three monocarbene complexes is illustrated. Even the farthest double bond can be involved in the stabilization of the carbene carbon. The resonance structures of Scheme 3.1 show how double bond delocalization produces partial positive charges on certain carbon atoms. The C1 carbon is the carbene carbon. The delocalization of bond C2–C3 to C1–C2 would for instance place a partial positive charge on ring carbon atom 3.

The greatest signal shifts observed are those of H3 (in complexes **1** and **2**) and so the delocalization is taken to be greatest for the C2–C3 (first) double bond. The bithiophene complex has more double bonds available that can be brought into conjugation than the thiophene or 3,6-dimethylthieno[3,2-*b*]thiophene complexes. The transfer of electron density from the distant thiophene ring in bithiophene is not so great, but still relevant. The same is true for H7 of the 3,6-dimethylthieno[3,2-*b*]thiophene substituent in complex **3**. Therefore the chemical shifts confirm that the farther away, the less involvement there is in carbene stabilization by ring electron delocalization, even though the ligands are flat and  $\pi$ -conjugation is possible.

Besides local  $\pi$ -effects there is a general loss of electron density from the electron-excessive thienyl rings towards the carbene carbon atom.

At room temperature the two CH<sub>2</sub> hydrogen atoms of the ethoxy substituent are equivalent and so are the three CH<sub>3</sub> hydrogen atoms. Their signals are observed as, respectively, a quartet and a triplet in the <sup>1</sup>H NMR spectra of the three complexes because the CH<sub>2</sub> and CH<sub>3</sub> protons couple.



**Scheme 3.1:** Double bond delocalization in thienyl substituents

The above conclusions can also be illustrated by a simple calculation that can be done for each individual ring hydrogen atom of a complex to determine the percentage of shift of the ring protons relative to the shift of the proton that has the largest shift (100%). The outcome supports the conjugation explanation for deshielding of ring hydrogen atoms:

**1:** H3 (100%), H5 (65%) and H4 (22%)

**2:** H3 (100%), H7 (24%), H9 (21%), H8 (6%), H4 (0%)

The data of the biscarbene complexes **7–9** are discussed next, as they have similar shifts on the  $^1\text{H}$  NMR spectrum than the monocarbene complexes **1–3**. The bromine-cleaved complexes (**4–6**) will be discussed in section 3.1.3.

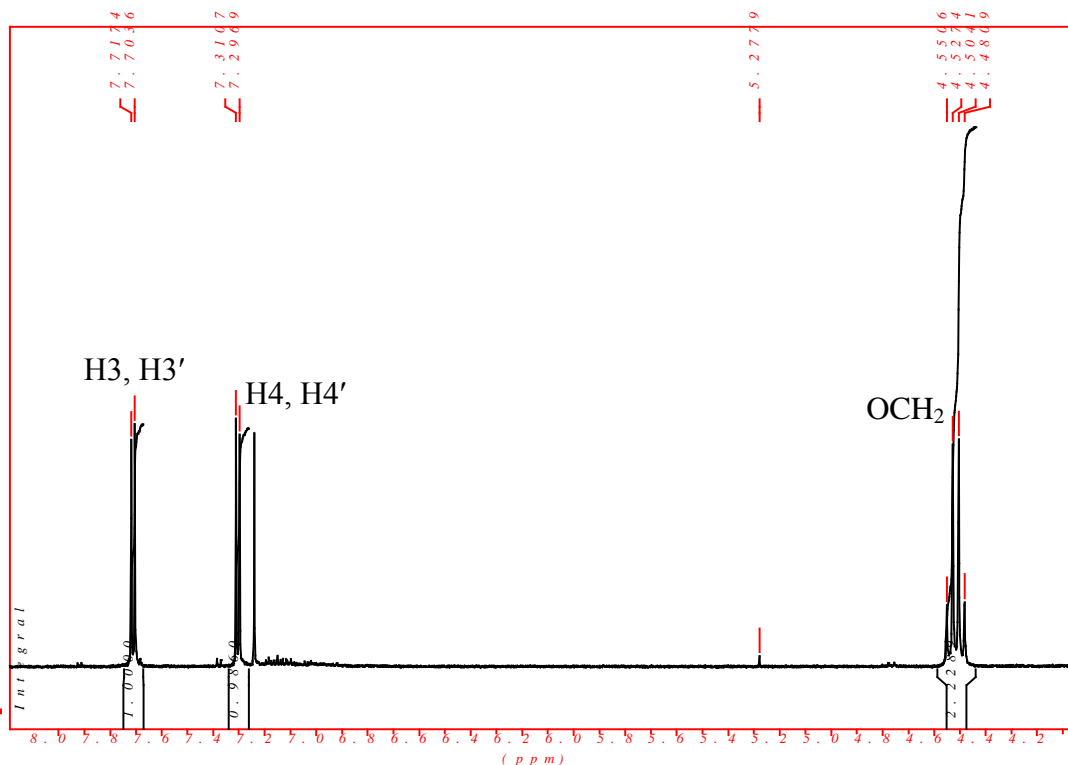
### 3.1.2 Biscarbene tetrarhenium complexes

The biscarbene complexes (**7–9**) were prepared by reacting  $[\text{Re}_2(\text{CO})_{10}]$  with dilithiated thiophene substrates. The biscarbene complexes **7** and **9** proved elusive, forming in low yield and reacting on the column with trace amounts of water. The bithiophene biscarbene complex **8** formed in higher yield and reacted slower on the silica gel column. Proton NMR spectra were measured for these complexes (Table 3.2).

The aromatic to  $\text{CH}_2$  (of the ethoxy substituent) region of the  $^1\text{H}$  NMR spectrum of complex **8** is shown in Figure 3.5. The spectrum was recorded in deuterated chloroform and the chloroform peak was used for calibration. A singlet at 5.28 ppm belongs to residual dichloromethane. Integration values show that the two aromatic signals in the spectrum belong to the same number of hydrogen atoms – it is known that each signal corresponds to two hydrogen atoms. The integration value (2.23) for the four equivalent  $\text{CH}_2$  (of  $\text{OCH}_2\text{CH}_3$ ) protons is slightly high, but still acceptable and indicates a 1:2 ratio between outer, or inner, ring hydrogen atoms and  $\text{CH}_2$  hydrogen atoms.

The two outer hydrogen atoms and the two inner hydrogen atoms of the bridging bithiophene are equivalent, because the molecule has a symmetry centre. Thus there are only two signals for the four ring protons. The protons on each ring couple with each other and their signals are split into doublets. At 7.30 ppm, the  $\text{H}_4$  and  $\text{H}_4'$  signals appear close to where the signals of  $\text{H}_7$  and  $\text{H}_9$  of complex **2** were found. The  $\text{H}_4$  signal of complex **2** appears at higher field strength, though.

The signal of the  $\text{CH}_2$  protons of the ethoxy carbene substituent is split into the expected quartet by the  $\text{CH}_3$  protons of the ethoxy substituent. The quartet location at 4.51 ppm shows again how the electronegative oxygen atom, under the influence of the carbene carbon atom, deshields the attached  $\text{CH}_2$  protons.



**Figure 3.5:** A part of the  $^1\text{H}$  NMR spectrum of complex **8** in  $\text{CDCl}_3$

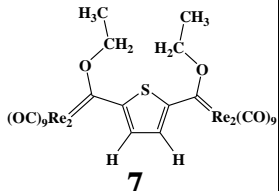
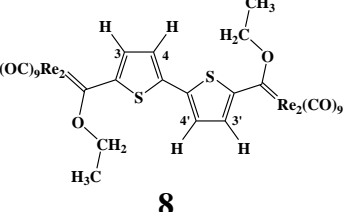
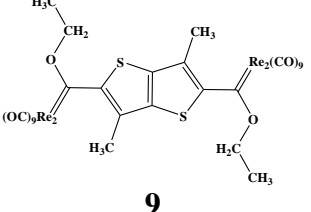
The  $^1\text{H}$  NMR data of thiophene biscarbene complex **7** displays a signal for the two ring proton that appear upfield from the H3 position in the spectrum of monocarbene complex **1**. It may be that resonance delocalization is reduced in this complex, possibly due to a larger twist between the thiophene plane and the carbene planes. The  $\text{CH}_2$  signal of the ethoxy substituents is also found upfield from its position in complex **1**, so there is less electron–density donation from this carbene substituent to the carbene carbon atom.

The H3/H3' signals of biscarbene complex **8** are very close to those of H3 of monocarbene complex **2**. According to the data, H4 of complex **8** is more deshielded than H7 of complex **2**. The carbene attached to the other thiophene ring can produce a partial positive charge on C4 through resonance delocalization. With respect to this carbene H4 is in the same location as H7 is with respect to the carbene in the monocarbene complex. There is, in this complex, the combined effect of two electron withdrawing carbene

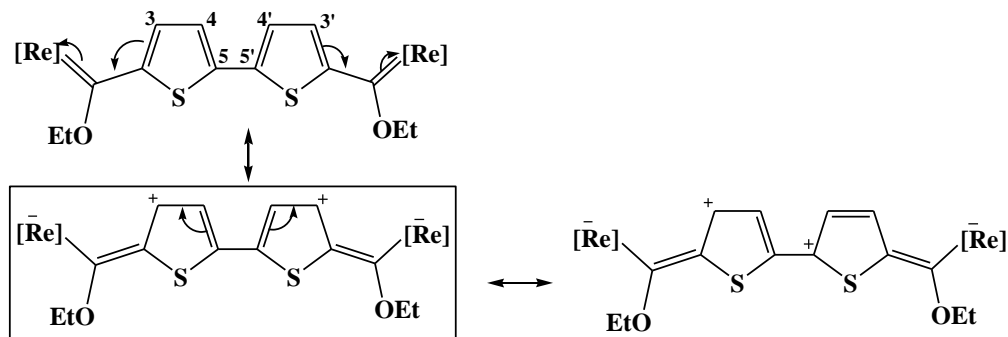


carbon atoms, compared to one in **2**, and there should generally be less electron density on the thiophene rings.

**Table 3.2:**  $^1\text{H}$  NMR spectral data ( $\delta$ , J (Hz),  $\text{CDCl}_3$ ) of **7–9**

Complexes:			
<b>H3</b>	7.47 (s) $\Delta\delta_R = 0.67$	7.71 (d, 4.1) $\Delta\delta_R = 0.70$	—
<b>H4</b>	—	7.30 (d, 4.1) $\Delta\delta_R = 0.12$	—
<b>Me3</b>	—	—	2.21 (s) $\Delta\delta_R = -0.13$
<b>OCH<sub>2</sub>CH<sub>3</sub></b>	4.42 (q, 7.0)	4.51 (q, 7.0)	4.41 (q, 7.0)
<b>OCH<sub>2</sub>CH<sub>3</sub></b>	1.57 (t, 7.0)	1.61 (t, 7.0)	1.54 (t, 7.0)

In complex **8** the most important resonance form is the one that depicts a deshielding of hydrogen atoms H3 and H3'. A resonance form that places partial positive charges on C5 and C5' is not considered feasible (Scheme 3.2).



**Scheme 3.2:** Resonance forms for complex **8**

For complex **9** there are no signals in the aromatic region as the four ring carbon atoms have either a methyl or a carbene fragment as external group. Because the complex is symmetrical, only one signal is observed for the two methyls. Recalling that the  $^1\text{H}$  NMR values for the pendant methyl groups of monocarbene complex **3** are 2.16 (Me3) and 2.39 ppm (Me6), it is interesting to find a value for complex **6** (2.21 ppm) that lies between these two values. With the  $^1\text{H}$  NMR shift of the methyl groups of the free substituent being 2.34 ppm, one also again observes an odd upfield shift of the signal.

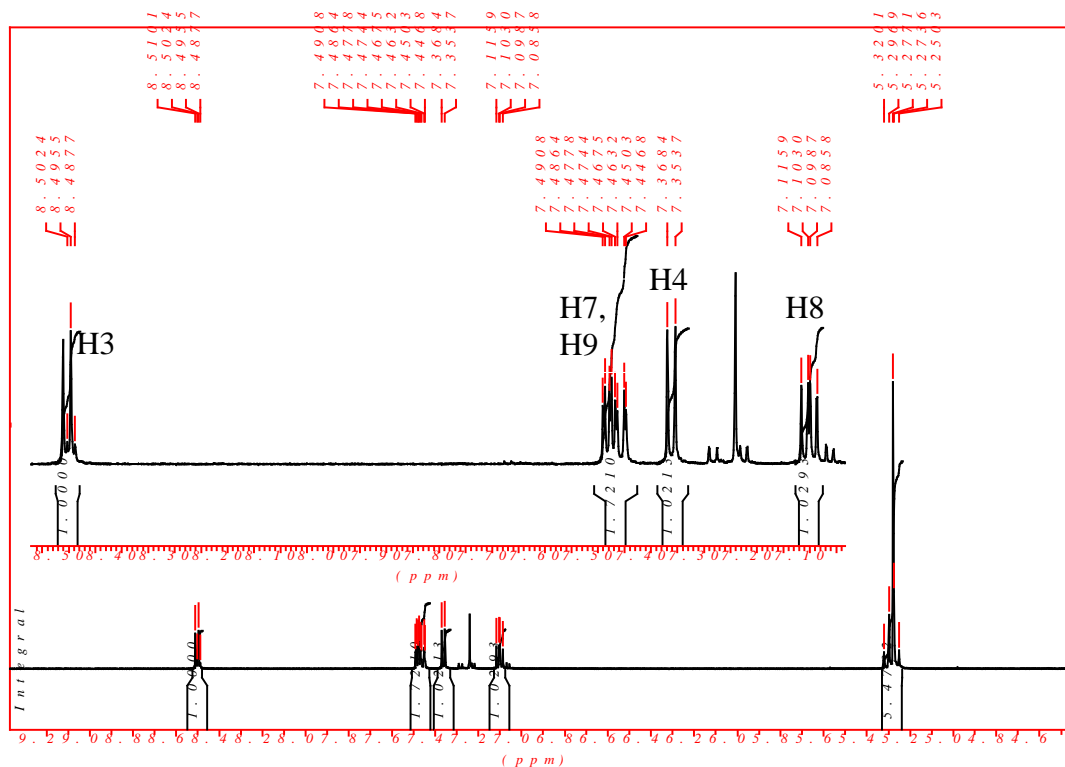
### 3.1.3 Bromo monocarbene complexes of rhenium

The bromo monocarbene complexes (**4–6**) of rhenium were prepared by reacting dirhenium carbene complexes **1–3** with bromine. The structural difference between the cleaved and uncleaved complexes is X in  $[\text{Re}(\text{CO})_4\{\text{C}(\text{OEt})\text{thienyl}\}\text{X}]$ , with X either being “ $\text{Re}(\text{CO})_5$ ” or “Br”.

In Figure 3.6, a section of the proton NMR spectrum of complex **5** is shown. The  $^1\text{H}$  NMR spectrum was recorded in deuterated chloroform and the chloroform signal at 7.24 ppm used for calibration. This complex is a bithiophene monocarbene complex similar to complex **2** and the same signal pattern is observed as that seen for complex **2**. It is evident that the signals of the aromatic ring protons of these complexes are shifted downfield if the rheniumpentacarbonyl fragment is replaced by a bromo ligand. H3's signal, specifically, is shifted downfield drastically. The signal of this proton is split into a doublet by coupling to the other hydrogen atom of the thiophene ring and there is also a small doublet that may indicate another isomer.

The H7 and H9 signals almost overlap, as for complex **2**. Their signals are not much shifted downfield from their position in the uncleaved complex. The signal of H8 is split into a doublet of doublets, as it couples with H7 and H9. The signals of these protons are split into doublets of doublets, indicating that they also couple with each other.

The quartet signal of the CH<sub>2</sub> protons is also shifted downfield. The signal overlaps with that of dichloromethane.

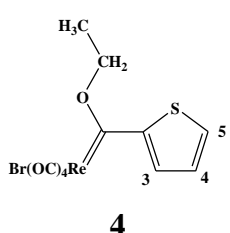
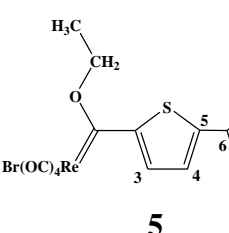
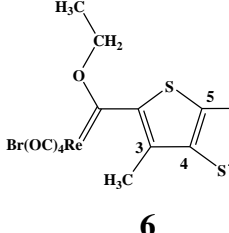


**Figure 3.6:** <sup>1</sup>H NMR spectrum of complex 5 in CDCl<sub>3</sub>

The data for the three cleaved monocarbene complexes are given in Table 3.3.

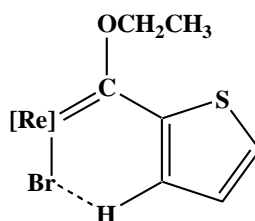
As with the uncleaved complexes, the ring hydrogen atoms are affected by the electrophilic carbene carbon atom. Their shifts are even more downfield, compared to the free substituents. For a bromo ligand, less electron density is placed on the metal, which is back bonded to the π-acceptor ligands. Thus, a greater demand for electron density is transferred to the thienyl substituent by the electrophilic carbene carbon atom.

**Table 3.3:**  $^1\text{H}$  NMR spectral data ( $\delta$ , J (Hz),  $\text{CDCl}_3$ ) for **4–6**

Complexes:			
<b>H3</b>	7.98 (dd, 4.9; 1.0) $\Delta\delta_{\text{R}} = 1.02$ ; $\Delta\delta_{\text{U}}^{\text{a}} = 0.33$	8.50 (d, 4.4) $\Delta\delta_{\text{R}} = 1.49$ ; $\Delta\delta_{\text{U}} = 0.77$	–
<b>Me3</b>	–	–	2.56 (s) $\Delta\delta_{\text{R}} = 0.22$ ; $\Delta\delta_{\text{U}} = 0.17$
<b>H4</b>	7.19 (dd, 4.5; 4.2) $\Delta\delta_{\text{R}} = 0.23$ ; $\Delta\delta_{\text{U}} = 0.08$	7.36 (d, 4.4) $\Delta\delta_{\text{R}} = 0.18$ ; $\Delta\delta_{\text{U}} = 0.18$	–
<b>H5</b>	7.79 (dd, 4.5; 1.0) $\Delta\delta_{\text{R}} = 0.59$ ; $\Delta\delta_{\text{U}} = 0.14$	–	–
<b>H7</b>	–	7.48 (dd, 3.6; 1.0) $\Delta\delta_{\text{R}} = 0.30$ ; $\Delta\delta_{\text{U}} = 0.08$	7.50 (s) $\Delta\delta_{\text{R}} = 0.56$ ; $\Delta\delta_{\text{U}} = 0.46$
<b>H8</b>	–	7.09 (dd, 3.6; 5.2) $\Delta\delta_{\text{R}} = 0.08$ ; $\Delta\delta_{\text{U}} = 0.04$	–
<b>Me6</b>	–	–	2.42 (d, 1.3) $\Delta\delta_{\text{R}} = 0.07$ ; $\Delta\delta_{\text{U}} = 0.26$
<b>H9</b>	–	7.45 (dd, 5.2; 1.0) $\Delta\delta_{\text{R}} = 0.25$ ; $\Delta\delta_{\text{U}} = 0.11$	–
<b>OCH<sub>2</sub>CH<sub>3</sub></b>	4.78 (q, 7.0) $\Delta\delta_{\text{U}} = 0.27$	5.28 (q, 7.0) $\Delta\delta_{\text{U}} = 0.74$	5.57 (q, 7.0) $\Delta\delta_{\text{U}} = 1.17$
<b>OCH<sub>2</sub>CH<sub>3</sub></b>	1.68 (t, 7.0) $\Delta\delta_{\text{U}} = 0.10$	1.66 (t, 7.0) $\Delta\delta_{\text{U}} = 0.06$	1.69 (t, 7.0) $\Delta\delta_{\text{U}} = 0.19$

<sup>a</sup>  $\Delta\delta_{\text{U}}$  = difference between the chemical shifts of the corresponding protons of the thienyl substituent of the Br-cleaved and the uncleaved complexes

If one were to specifically consider ring proton H3 of complex **4**, it can be seen (as depicted in Figure 3.7), that a rigid six-membered ring will place H3 close to the more electronegative bromide ligand. Electronic interaction of Br with H3 will deshield the nucleus of H3 (see solid state structure of complex **5** in Chapter 4), leading to its signal being significantly shifted downfield in the  $^1\text{H}$  NMR spectrum.



**Figure 3.7:** Intramolecular hydrogen bonding between Br and H in **4**

Comparison shows that all the ring hydrogen atoms are not affected to the same extent by the carbene carbon. A calculation was done for **4** and **5** to determine which resonance forms carry the highest weight. Again the values relative to the proton farthest downfield is expressed as a percentage:

**4:** H3 (100%), H5 (58%) and H4 (23%)

**5:** H3 (100%), H7 (20%), H9 (17%), H4 (12%), H8 (5%)

These values act as verification of the influence of double bond delocalization to produce partial positive charges on certain ring carbon atoms. In the thiophene monocarbene complex **4**, the ring proton with the largest shift, due to bromide replacement of “ $\text{Re}(\text{CO})_5$ ”, is H3. In complex **1** there seems to be a slightly greater contribution to stabilization from H5 (which indicates C4–C5 delocalization), than in the cleaved thiophene complex **4** (it was 65% in the case of **1**).

The same trend is observed when one compares bithiophene uncleaved and cleaved complexes **2** and **5**. In fact, the signal of H3 is dramatically shifted downfield, possibly pointing to a significant interaction between the bromo ligand and this hydrogen atom.

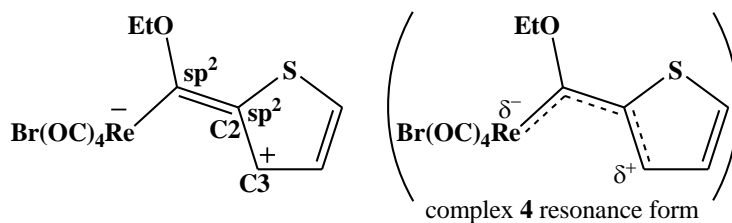
The second ring of the bithiophene complex is little affected by the ligand change on the metal. One notes that H9's NMR signal is more downfield-shifted than that of H7, although it lies farthest away from the carbene.

In complex **6**, the resonance form that places a partial positive charge at position 3 of the ring may be the dominating resonance form (as is the case for the thiophene and bithiophene complexes). The Me6 signal is shifted downfield even more than that of Me3 (as compared to the free substituent), whereas its signal was seen to be shifted upfield in **3**. A downfield shift is a more intuitive adjustment. The signal of Me6 is a doublet because it couples with H7. The signal of H7 was observed to be a quartet, as expected.

The relocation of electron density from the aromatic substituents to the carbene carbon has the effect of the ring hydrogen NMR signals being shifted downfield (because they are partially deshielded). The difference between the corresponding ring hydrogen NMR values of the uncleaved and the cleaved complexes, allows for certain structure predictions.

A complex is proposed and shown in Figure 3.8. In the complex the ring has lost its aromatic character. A full positive charge is located on C3, and it would be expected that in this complex, the  $^1\text{H}$  NMR signal of H3 would be shifted downfield substantially.

The carbene and aromatic substituent planes in **4** are not coplanar (see Chapter 4 for crystal structure and discussion) and therefore it is not expected that the proposed complex would be obtained by complete delocalization of the electron density in the C2–C3 double bond of **4**, to C1–C2. However, a more downfield-shifted H3 signal might point to a smaller angle between the carbene plane and the substituent plane. Crystal data have shown that indeed, for the cleaved complexes the possibilities of conjugation are greater because the angles between the planes are in fact smaller.



**Figure 3.8:** Double bond delocalization of **4**

There are significant changes in the value of the “CH<sub>2</sub>” protons of the ethoxy substituent upon reaction with Br<sub>2</sub>, but as expected, not in the values of the distant “CH<sub>3</sub>” protons.

It is expected that, of the three complexes, the carbene  $\pi$ -stabilization from the rhenium in **4** should be the largest, since both the thiophene substituent and the ethoxy group hydrogen atom signals are not shifted downfield as dramatically. In **5**, the <sup>1</sup>H NMR data provides one with a sense that more contribution comes from the thienyl substituent to alleviate the electron shortage on the carbene carbon atom than that which is provided by the thienyl substituent in **6**. The ethoxy group in turn contributes more in **6** (the “CH<sub>2</sub>” signal is shifted downfield the furthest).

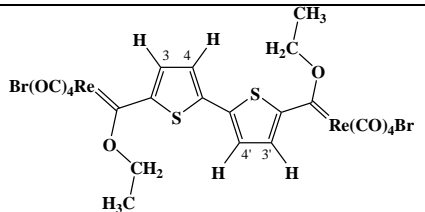
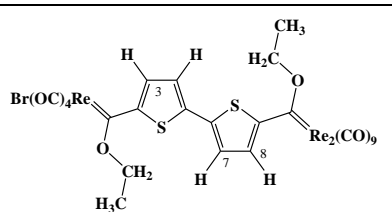
### 3.1.4 Biscarbene bromo-carbene complexes

The cleavage of the rhenium–rhenium bonds of the biscarbene tetrarhenium bithiophene complex **8** was studied and products associated with a stepwise rhenium–rhenium cleavage could be isolated. Biscarbene complex **8** was reacted with one equivalent of Br<sub>2</sub>(l) to produce **10** (major product) and **11** (minor product). It is interesting that one equivalent of Br<sub>2</sub>(l) already produced mostly the bis-cleaved complex. Proton NMR data is given in Table 3.4.

Complex **10** displays a similar shift in the H3 signal (versus the uncleaved biscarbene complex and free bithiophene) as was seen in the case of monocarbene bromo complex **5**. The ethoxy group “CH<sub>2</sub>” protons are slightly more deshielded in **10** than in the precursor **8**, relative to what was seen on going from **2** to **5** (monocarbene complexes). It also

shows a greater involvement of the ethoxy groups in the carbene stabilization of the bromo-carbene complexes than in the  $\text{Re}(\text{CO})_5$ -carbene complexes.

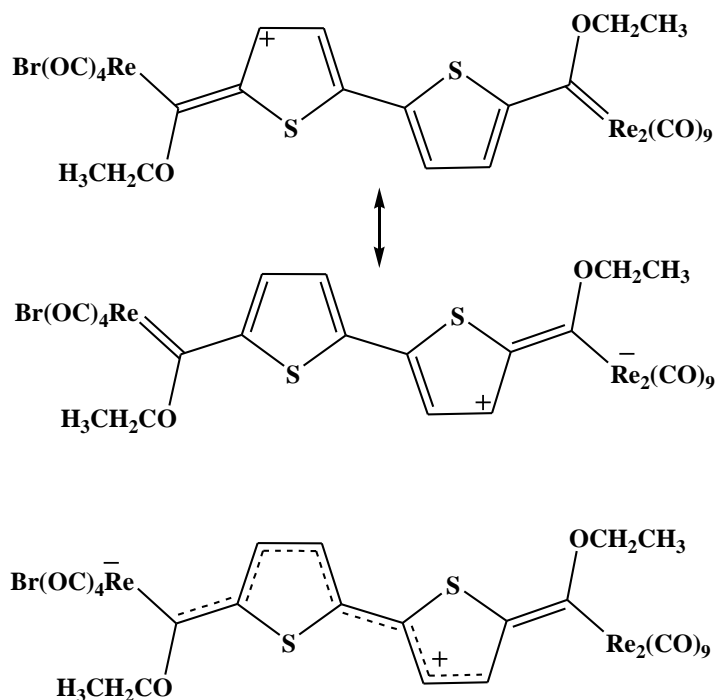
**Table 3.4:**  $^1\text{H}$  NMR data ( $\delta$ , J (Hz),  $\text{CDCl}_3$ ) of bithiophene complexes **10** and **11**

Complexes:	 <p style="text-align: center;"><b>10</b></p>	 <p style="text-align: center;"><b>11</b></p>
<b>H3</b>	8.56 (d, 4.4) $\Delta\delta_{\text{R}} = 1.55$ ; $\Delta\delta_{\text{U}} = 0.85$	8.52 (dd, 4.5) $\Delta\delta_{\text{R}} = 1.51$ ; $\Delta\delta_{\text{U}} = 0.81$
<b>H4</b>	7.58 (d, 4.7) $\Delta\delta_{\text{R}} = 0.40$ ; $\Delta\delta_{\text{U}} = 0.28$	7.43 (d, 4.6) $\Delta\delta_{\text{R}} = 0.25$ ; $\Delta\delta_{\text{U}} = 0.13$
<b>H7</b>	–	7.41 (d, 4.2) $\Delta\delta_{\text{R}} = 0.23$ ; $\Delta\delta_{\text{U}} = 0.11$
<b>H8</b>	–	7.73 (d, 4.2) $\Delta\delta_{\text{R}} = 0.72$ ; $\Delta\delta_{\text{U}} = 0.02$
$\text{ReBr}(\text{CO})_5$ : $\text{OCH}_2\text{CH}_3$	5.35 (q, 7.0) $\Delta\delta_{\text{U}} = 0.94$	5.35 (q, 7.0) $\Delta\delta_{\text{U}} = 0.94$
$\text{ReBr}(\text{CO})_5$ : $\text{OCH}_2\text{CH}_3$	1.66 (t, 7.0) $\Delta\delta_{\text{U}} = 0.05$	1.70 (t, 7.0) $\Delta\delta_{\text{U}} = 0.00$
$\text{Re}_2(\text{CO})_9$ : $\text{OCH}_2\text{CH}_3$	–	4.41 (q, 7.0)
$\text{Re}_2(\text{CO})_9$ : $\text{OCH}_2\text{CH}_3$	–	1.61 (t, 7.0) $\Delta\delta_{\text{U}} = 0.00$

Mixed-carbene complex **11** is perhaps a more interesting complex than complex **10** as **11** has two different metal fragments attached to the bithiophene. Two separate resonance sets can be described for the bithiophene biscarbene complex, because the carbene



carbons have independent and competitive electron withdrawing effects on the adjacent thiophene ring protons. It is possible to compare the two attached metal fragments' electron-drawing ability. Because the ring hydrogen atom located closest to the  $\{\text{Re}(\text{CO})_4\text{Br}\}$  fragment has a resonance at 8.52 ppm, versus 7.73 ppm for the ring hydrogen atom closest to the  $\{\text{Re}_2(\text{CO})_9\}$  fragment, in Scheme 3.3 below, the upper resonance form is assumed to be more contributing. The bromo-carbene fragment has a stronger electron-withdrawing effect, compared to a  $\text{Re}(\text{CO})_5$ -carbene fragment.



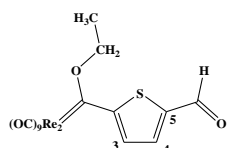
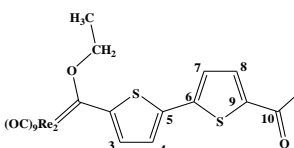
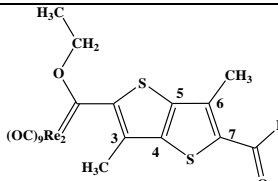
**Scheme 3.3:** Competing resonance forms for **11**

The differences between the outer ring hydrogen atoms of **11** ( $\text{H}_3\text{--H}_9 = 8.52 \text{ ppm--}7.73 \text{ ppm} = 0.79 \text{ ppm}$ ), are similar to the difference between the  $\text{H}_3/\text{H}_3'$  hydrogen atoms of cleaved biscarbene complex **10** (8.56 ppm) and the uncleaved biscarbene complex **8** (7.71 ppm).

### 3.1.5 Carbene–aldehyde complexes

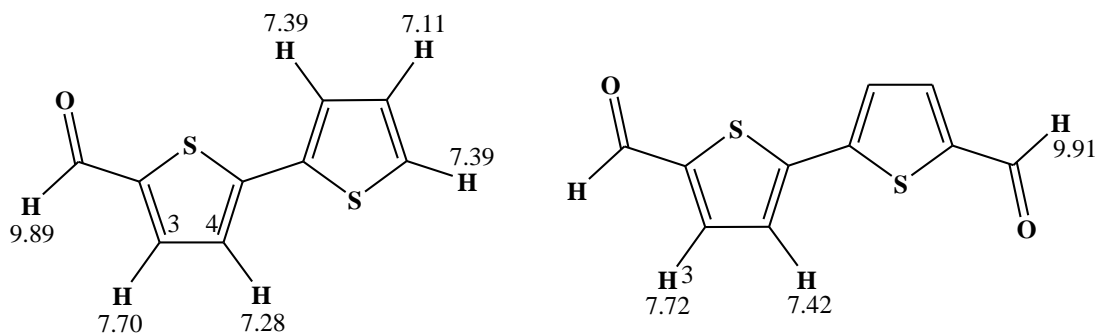
The reactive biscarbene tetrarhenium complexes were modified to carbene–aldehyde complexes. Based on spectroscopic data the conversion of metal–carbene units to aldehydes is postulated to commence via an intermediate that contains a hydroxycarbene ligand. The  $^1\text{H}$  NMR data of the aldehyde complexes is given in Table 3.5.

**Table 3.5:**  $^1\text{H}$  NMR data ( $\delta$ , J (Hz),  $\text{CDCl}_3$ ) for **12–14**

Complexes:	 <p style="text-align: center;"><b>12</b></p>	 <p style="text-align: center;"><b>13</b></p>	 <p style="text-align: center;"><b>14</b></p>
<b>H3</b>	7.82 (d, 4.1) $\Delta\delta_R = 0.86$	–	
<b>H4</b>	7.72 (d, 4.1) $\Delta\delta_R = 0.76$	7.34 (d, 4.4) $\Delta\delta_R = 0.33$	
<b>H5</b>		–	–
<b>H7</b>	–	7.23 (d, 4.1) $\Delta\delta_R = 0.05$	
<b>H8</b>	–	7.70 (d, 4.1) $\Delta\delta_R = 0.69$	
<b>C(O)H</b>	9.95 (s)	9.95 (s)	10.09 (s)
<b>OCH<sub>2</sub>CH<sub>3</sub></b>	4.39 (q, 7.0)	4.42 (q, 7.0)	4.36 (q, 6.98)
<b>OCH<sub>2</sub>CH<sub>3</sub></b>	1.72 (t, 7.0)	1.61 (t, 7.0)	1.51 (d, 6.99)
<b>Me3</b>	–	–	2.34 (s)
<b>Me6</b>	–	–	2.15 (s)

The aldehyde hydrogen of the carbene complexes shows a characteristic proton NMR signal at around 10 ppm. The  $^1\text{H}$  NMR values of organic aldehydes are given below. It is

believed that differences between the signal locations of 5-formyl-2,2'-bithiophene, isolated and characterized in this study, and reported 5-formyl-2,2'-bithiophene <sup>1</sup>H NMR spectroscopy values are due to different solvents having been used to determine the <sup>1</sup>H NMR spectra.



**Figure 3.9:** <sup>1</sup>H NMR data (ppm) for 5-formyl-2,2'-bithiophene<sup>3</sup> (acetone-*d*<sub>6</sub>) and 5,5'-diformyl-2,2'-bithiophene<sup>4</sup> (chloroform-*d*)

Complex **12** presents an interesting case as one can compare the effect that the carbene and the aldehyde have on the ring proton that is closest to it. The signal of H3 is shifted downfield more than H3 of **1**. The aldehyde functionality also draws electron density out of the ring and competes with the carbene functionality.

Complex **14**, having no ring hydrogen atoms, displays the characteristic aldehyde signal around 10 ppm and also the ethoxy substituent's signals at 4.36 and 1.51 ppm. These signals fall almost at the same locations as the equivalent signals of **3**. It means that the aldehyde does not greatly affect the ethoxy substituent in terms of proton shielding/deshielding.

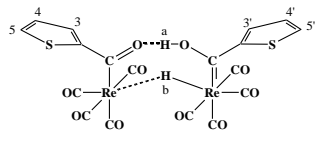
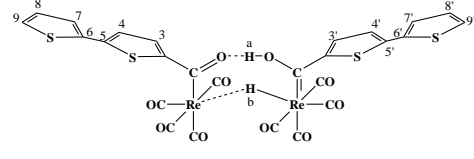
<sup>3</sup> Patent – see website: <http://www.wipo.int/pctdb/en/wo.jsp?IA=CA2005000131&DISPLAY=DESC>

<sup>4</sup> G.-M Xia, P. Lu, G.-B. Xu; *J. Serb. Chem. Soc.*, **2004**, *69*, 335–341



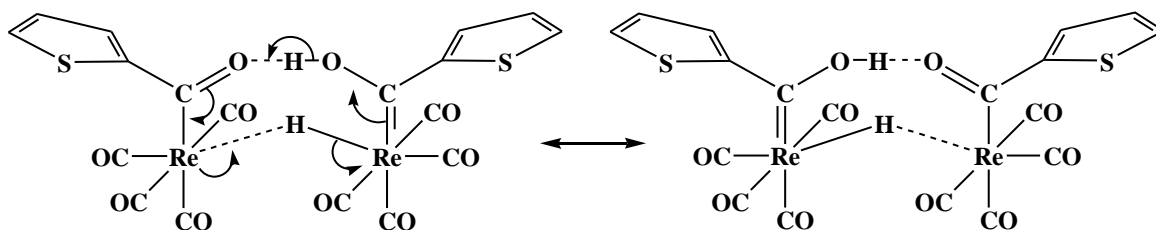
A small hydride signal at  $-13.95$  ppm has not been assigned. It is possible that the complex dissociates in solution to another hydride complex<sup>5</sup>. Proton NMR data is given in Table 3.6.

**Table 3.6:**  $^1\text{H}$  NMR data ( $\delta$ , J (Hz),  $\text{CDCl}_3$ ) for **15–16**

Complexes:	 <b>15</b>	 <b>16</b>
<b>H3</b>	8.09 (d, 3.0)	8.01 (d, 3.8)
<b>H4</b>	7.28 (dd, 3.0; 1.5)	7.49 (d, 3.8)
<b>H5</b>	7.86 (d, 1.5)	–
<b>H7</b>	–	7.18 (d, 4.5)
<b>H8</b>	–	7.05 (t, 4.5)
<b>H9</b>	–	7.72 (d, 4.4)
<b>Ha</b>	21.5 (br)	21.3 (br)
<b>Hb</b>	$-15.7$ (s)	$-15.7$ (s)

It is interesting that corresponding hydrogen atoms on the two thiophene rings (**15**) and the bithiophene rings (**16**) are equivalent (their signals coincide). This shows that at room temperature in solution the complexes are symmetrical, and the two constituent parts lose their individual identity. Since peaks are not broadened one could also assume that the complexes are rigid. The inflexibility is believed to come from the framework created by the O–H–O and Re–H–Re bonds. Also, the extended double bond character, between the rhenium atoms and the carbene carbon atoms and the carbene carbon atoms and the oxygen atoms, may contribute to rigidity. For complex **15** the following two resonance structures can be drawn which changes the one fragment into the other (Scheme 3.4). The same is held to be true and applicable for **16**.

<sup>5</sup> C. S. Yang, C. P. Cheng, L. W. Guo, Y. Wang; *J. Chin. Chem. Soc.*, **1985**, 22, 17–22



**Scheme 3.4:** Resonance forms of **15**

A high-field hydride signal is a positive indication of these complexes. For most monorhenium complexes the hydride signal is seen in the range  $-4$  to  $-10$  ppm and for the dirhenium complexes with a bridging hydride, its signal is commonly seen in the range of about  $-14$  to  $-20$  ppm<sup>6</sup>. The protonic hydrogen NMR signals can appear over a large range. In the Shvo catalyst<sup>7</sup>, the signal of the bridging protonic hydrogen atom is at 8 ppm, versus signals around 21 ppm for **15** and **16**. The signal of the bridging hydride in the Shvo complex appears at  $-17.91$  ppm, which is closer to the observed proton NMR spectroscopy values of the two complexes' hydride atoms.

A comparison of  $^1\text{H}$  NMR signals of the thiophene substituents of **15**, with the equivalent thiophene signals of the thiophene monocarbene complexes **1** and **7**, would indicate that the double bond delocalization towards the carbene (acyl) carbon is most effective for **15**. The H3 signal at 8.09 ppm is at lowest field strength and the same goes for the other two ring protons, H4 and H5. The same can however not be said for **16**. For instance, the H3 signal of the monorhenium bithiophene complex **5** is at lowest field strength, lower than the H3 signal of **16**.

<sup>6</sup> Re(Cp) complexes: (a) C. P. Casey, C. J. Czerwinski, R. K. Hayashi; *J. Am. Chem. Soc.*, **1995**, *117*, 4189–4190; (b) J. R. Krumper, R. L. Martin, P. J. Hay, C. M. Yung, J. Veltheer, R. G. Bergman; *J. Am. Chem. Soc.*, **2004**, *126*, 14804–14815

Dirhenium complexes with bridging hydrogen atom: (c) R. D. Adams, B. Captain, C. B. Hollandsworth, M. Johansson, J. L. Smith, Jr.; *Organometallics*, **2006**, *25*, 3848–3855

Clusters: (d) R. D. Adams, O.-S. Kwon, J. L. Perrin; *J. Organomet. Chem.*, **2000**, *596*, 102–108

<sup>7</sup> Y. Shvo, D. Czarkie, Y. Rahamim; *J. Am. Chem. Soc.*, **1986**, *108*, 7400–7402

### 3.2. Carbon NMR spectroscopy data

The carbene carbon NMR resonance of rhenium Fischer carbene complexes can appear over a large range of chemical shift values and they reflect the electrophilic nature of the carbene carbon. In Table 3.7, some carbene carbon NMR data from literature is given, values that appear in the same range as those of the carbene carbon atoms of the prepared complexes.

**Table 3.7:**  $^{13}\text{C}$  NMR chemical shifts for monocarbene complexes of rhenium,  $[\text{ReL}_5(\text{carbene})]^{n+}$  ( $n = 0, 1$ )

Re Ligands	Carbene substituents	Carbene carbon resonance (ppm)	Ref.
Triphos 2xCO	-OCH <sub>3</sub> ; -1-CH <sub>2</sub> -(1,2-hexene)	307.8 (CDCl <sub>3</sub> )	8
Cp 2xCO	-OCH <sub>3</sub> -CH <sub>3</sub>	289.5 (C <sub>6</sub> D <sub>6</sub> )	9
Triphos 2xCO	-OH; -C(H)=C(H)(C <sub>6</sub> H <sub>5</sub> )	282.7 (CD <sub>2</sub> Cl <sub>2</sub> )	5
Cp 2xCO	-OCH <sub>3</sub> -Cp(Re(CO) <sub>3</sub> );	271.2 (CD <sub>2</sub> Cl <sub>2</sub> )	10

#### 3.2.1 Monocarbene dirhenium nonacarbonyl complexes

In the  $^{13}\text{C}$  NMR spectrum of complex **1** the carbene carbon signal is observed at 294.8 ppm. Of all the carbon atoms of the complex, its signal falls at lowest field strength, showing significant deshielding of the carbene carbon atom (a Fischer carbene carbon atom is electron-poor). Three signals between 120 and 140 ppm are assigned to thiophene ring carbon atoms C3, C4 and C5. The signal of the *ipso* carbon C2 is at lower

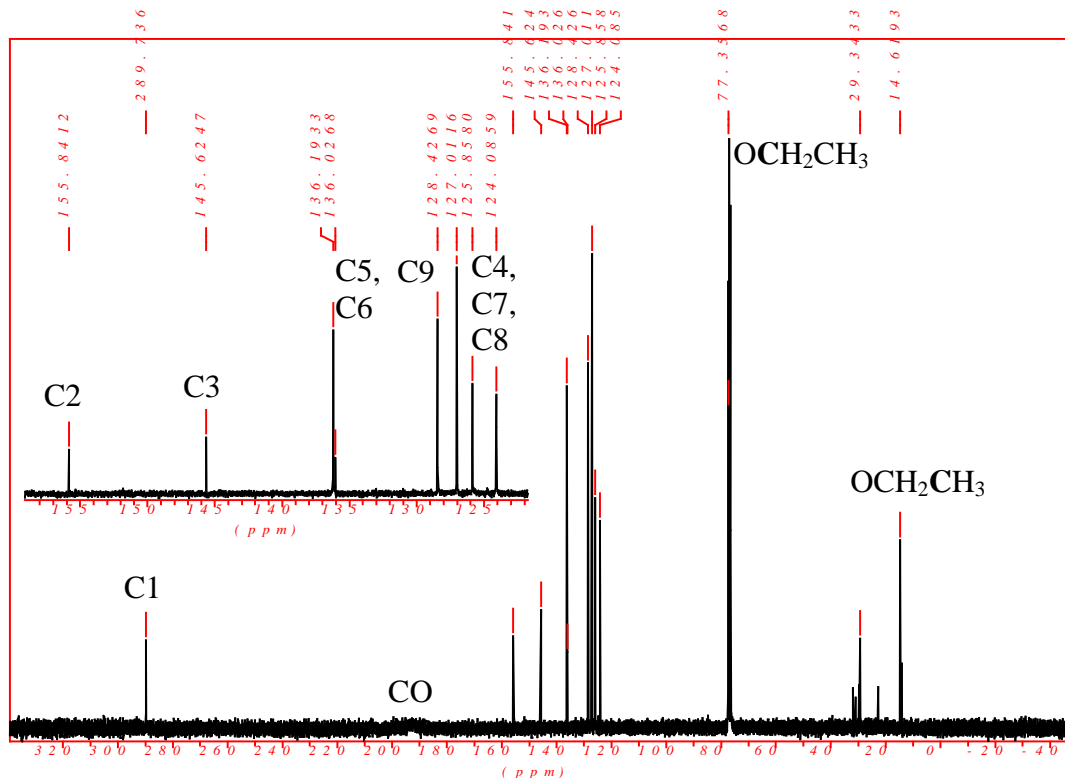
<sup>8</sup> C. Bianchini, N. Mantovani, L. Marvelli, M. Peruzzini, R. Rossi, A. Romerosa; *J. Organomet. Chem.*, **2001**, 617–618, 233–241

<sup>9</sup> K. I. Goldberg, R. G. Bergman; *J. Am. Chem. Soc.*, **1989**, 111, 1285–1299

<sup>10</sup> C. P. Casey, C. J. Czerwinski, R.K. Hayashi; *Organometallics*, **1996**, 15, 4362–4365

field strength and of weaker intensity. The carbon NMR shift of the carbonyl ligands of the dirhenium fragment appear as a broad signal around 192.5 ppm. Signals are broadened due to scrambling of carbonyl signals. None of the spectra were recorded at low temperature.

The  $^{13}\text{C}$  NMR spectrum of **2** is shown in Figure 3.11. The carbene signal is at higher field strength than that of **1**. There are a greater number of signals in the region of the aromatic rings, corresponding to the substituent in this monocarbene complex being bithiophene and not thiophene and they appear over a larger range: 120 to 160 ppm. Signals between 20 and 32 ppm belong to impurities in the deuterated solvent.

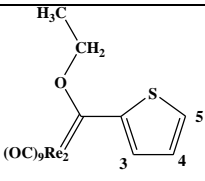
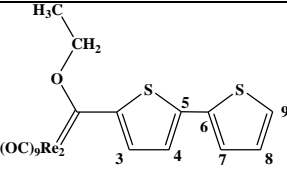
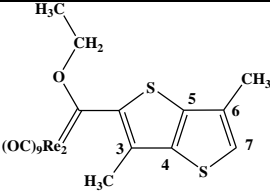


**Figure 3.11:**  $^{13}\text{C}$  NMR spectrum of **2** in  $\text{CDCl}_3$

The  $^{13}\text{C}$  NMR spectral data for the complexes are given in Table 3.8. Again the carbonyl signals are broad because of CO scrambling. These signals are poorly visible for **1** and **3**, but well-defined for **2**.



**Table 3.8:**  $^{13}\text{C}$  NMR spectral data for monocarbene complexes ( $\delta$ ,  $\text{CDCl}_3$ )

Complex	$^{13}\text{C}$ NMR bands (ppm)
 <p><b>1</b></p>	294.8 (carbene); 192.8 (CO); 157.9 (C2) 132.8 (C3); 132.5 (C5); 127.6 (C4); 77.3 ( $\text{OCH}_2\text{CH}_3$ ); 14.6 ( $\text{OCH}_2\text{CH}_3$ )
 <p><b>2</b></p>	289.8 (carbene); 198–186 (CO); 158.0 (C2); 145.6 (C3); 136.2 (C5); 136.0 (C6), 128.4 (C9), 127.0, 125.9, 124.1 (C4, C7, C8); 77.4 ( $\text{OCH}_2\text{CH}_3$ ); 14.6 ( $\text{OCH}_2\text{CH}_3$ )
 <p><b>3</b></p>	301.7 (carbene); C2 not observed; CO not assigned; 130.6, 125.0 (ring carbon atoms); 67.0 ( $\text{OCH}_2\text{CH}_3$ ); 31.0, 32.3 (Me3, Me6)

Complex **2**'s carbene carbon signal is at highest field strength. Based on this data, the ethoxy groups of **1** and **2** provide equivalent carbene stabilization ( $\pi$ -donation), but the ethoxy group of **3** provides significantly less stabilization to the carbene carbon of the complex.  $^1\text{H}$  NMR spectroscopy data (Table 3.1) also shows the ethoxy signals of **3** at slightly higher field, versus the same signals of **1** and **2**.

The signals of the C2 carbon atoms are expected to be shifted downfield significantly (compared to the free thienyl substrates) and that of the other thiophene ring carbon atoms to a lesser extent. This shift for complex **1** is 33.0 ppm downfield and for **2** is 16.6 ppm downfield. The C2 signal of **3** was not observed.

### 3.2.2 Biscarbene tetrarhenium complexes

Uncleaved biscarbene complexes **7** and **8** could be studied by  $^{13}\text{C}$  NMR spectroscopy. Excessive decomposition left  $^{13}\text{C}$  NMR spectra of complex **9** useless.

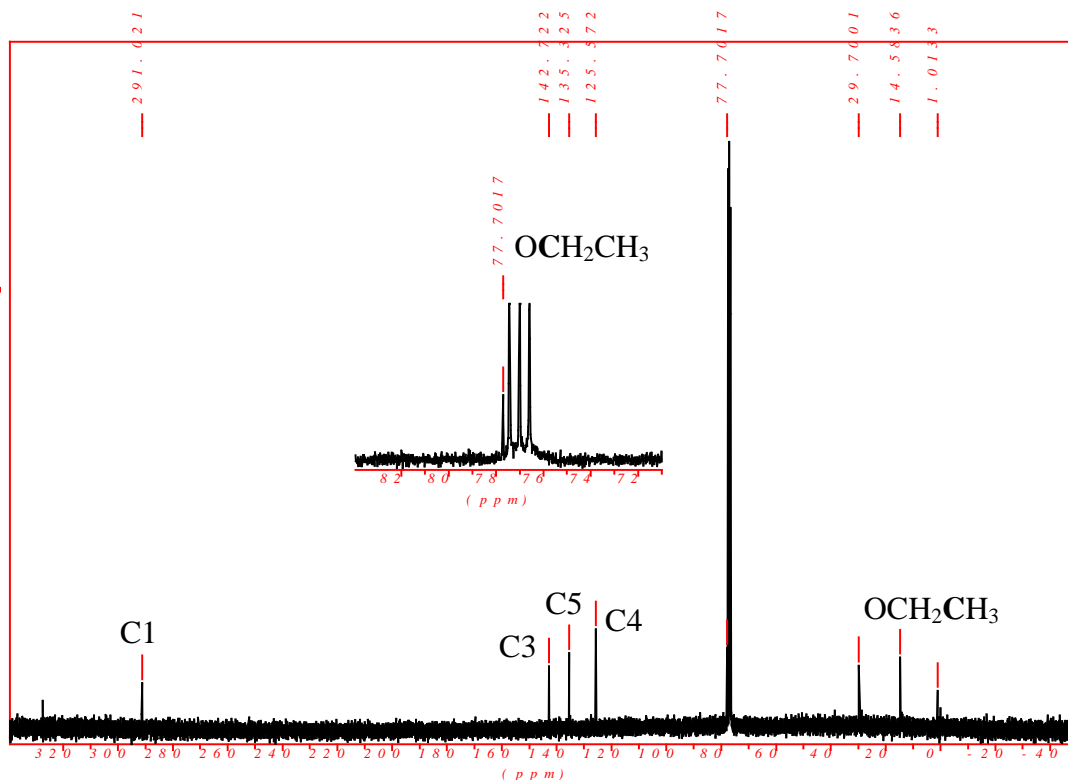
Compared to the  $^{13}\text{C}$  NMR spectrum of **2**, the spectrum of **8** (Figure 3.12) is much simpler due to the fact that the complex is symmetrical and equivalent carbon atoms on the two sides are in the same chemical environments. One expects four signals for the ring carbon atoms. As was the case with complex **2**, the signals for the ring carbon atoms of **8** appear over a range from 120 to 160 ppm.

Note that the signal of C2 is not observed in the spectrum given in Figure 3.12, but it was indeed observed on another  $^{13}\text{C}$  NMR spectrum measured at a different pulse width. The signals for the other three ring carbon atoms are seen at 143, 135 and 126 ppm.

Unfortunately no signal is seen for the carbonyl ligands of the rhenium metals.

The signals of the ethoxy group carbon atoms are located at 77.7 ( $\text{OCH}_2\text{CH}_3$ ) and 14.6 ppm ( $\text{OCH}_2\text{CH}_3$ ). The value of the “ $\text{CH}_2$ ” carbon atom is close to the location of the equivalent carbon atom of monocarbene bithiophene complex **2** and the “ $\text{CH}_3$ ” is at the same location as its equivalent in **2**.

Peaks at 29.7 and 1.01 ppm are impurities in the  $\text{CDCl}_3$ .

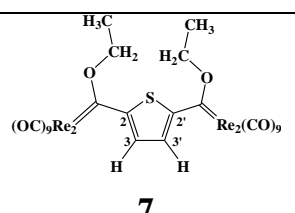
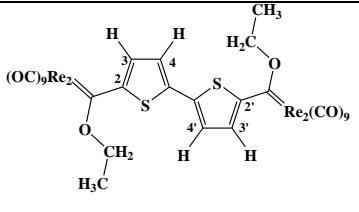


**Figure 3.12:**  $^{13}\text{C}$  NMR spectrum of **8** in  $\text{CDCl}_3$

The carbene carbon atom signals of the complexes are close to that seen for the carbene carbon atoms of the monocarbene complexes and the same is true for the signals of the ethoxy carbon atoms.

It can be seen that the  $\text{C}2/\text{C}2'$  signals of the thiophene biscarbene complex are shifted downfield slightly compared to the location of the  $\text{C}2$  signal of complex **1**. The  $\text{C}3/\text{C}3'$  signals are shifted upfield, slightly. Compared to **2**, the signals of  $\text{C}2$  and  $\text{C}5$  of **8** are about at the same locations. Based on the principle that there is some independence between the two sides of **8**, one side can be approximated to the thiophene monocarbene complex. The values do not have a direct correspondence. The signals at  $\text{C}2$  and  $\text{C}4$  are found upfield and the signals at  $\text{C}3$  and  $\text{C}5$  are found downfield compared to the equivalent protons of thiophene monocarbene complex **1**.

**Table 3.9:**  $^{13}\text{C}$  NMR spectral data for biscarbene complexes ( $\delta$ ,  $\text{CDCl}_3$ )

Complex	$^{13}\text{C}$ NMR bands (ppm)
 <p style="text-align: center;"><b>7</b></p>	<p>295.6 (carbene); 193.2 (br, CO); 161.0 (C2, C2'); 130.3 (C3, C3'); 77.5 (<math>\text{OCH}_2\text{CH}_3</math>); 14.6 (<math>\text{OCH}_2\text{CH}_3</math>)</p>
 <p style="text-align: center;"><b>8</b></p>	<p>291.0 (carbene); 155.8 (C2, C2'); 142.7 (C3, C3'); 125.6 (C4, C4'); 135.3 (C5, C5'); 77.7 (<math>\text{OCH}_2\text{CH}_3</math>); 14.6 (<math>\text{OCH}_2\text{CH}_3</math>)</p>

### 3.2.3 Cleaved monocarbene complexes

The  $^{13}\text{C}$  NMR spectroscopy data of the three complexes are given in Table 3.10.

Compared to their locations in the uncleaved complexes **1–3**, the signals of the carbene carbon atoms are shifted upfield and not downfield. The following values reflect it:

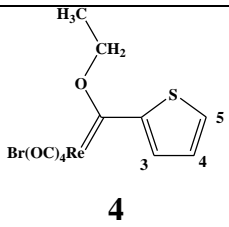
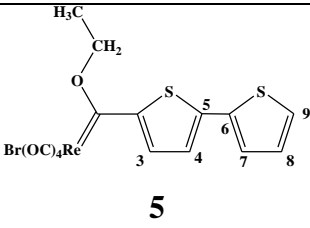
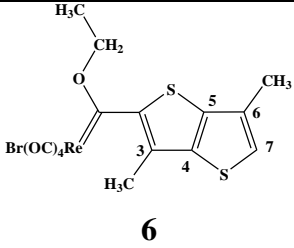
Complex **4**: 294.8 to 260.4 ppm (–34.4 ppm)

Complex **5**: 289.8 to 268.0 ppm (–21.8 ppm)

Complex **6**: 301.7 to 272.1 ppm (–29.6 ppm)

The carbene carbon  $^{13}\text{C}$  NMR signals of the three complexes appear within a range of about 12 ppm, with the thiophene complex's carbene carbon being most shielded and the 3,6-dimethylthieno[3,2-*b*]thiophene complex's carbene carbon being least shielded. It is possible that the pendant methyl group at location 3 of complex **9**'s thienyl substituent may prevent coplanarity between the aromatic substituent and the ring and thus reduce electron delocalization from the R-group into the empty carbene p-orbital.

**Table 3.10:**  $^{13}\text{C}$  NMR data for monocarbene complexes ( $\delta$ ,  $\text{CDCl}_3$ )

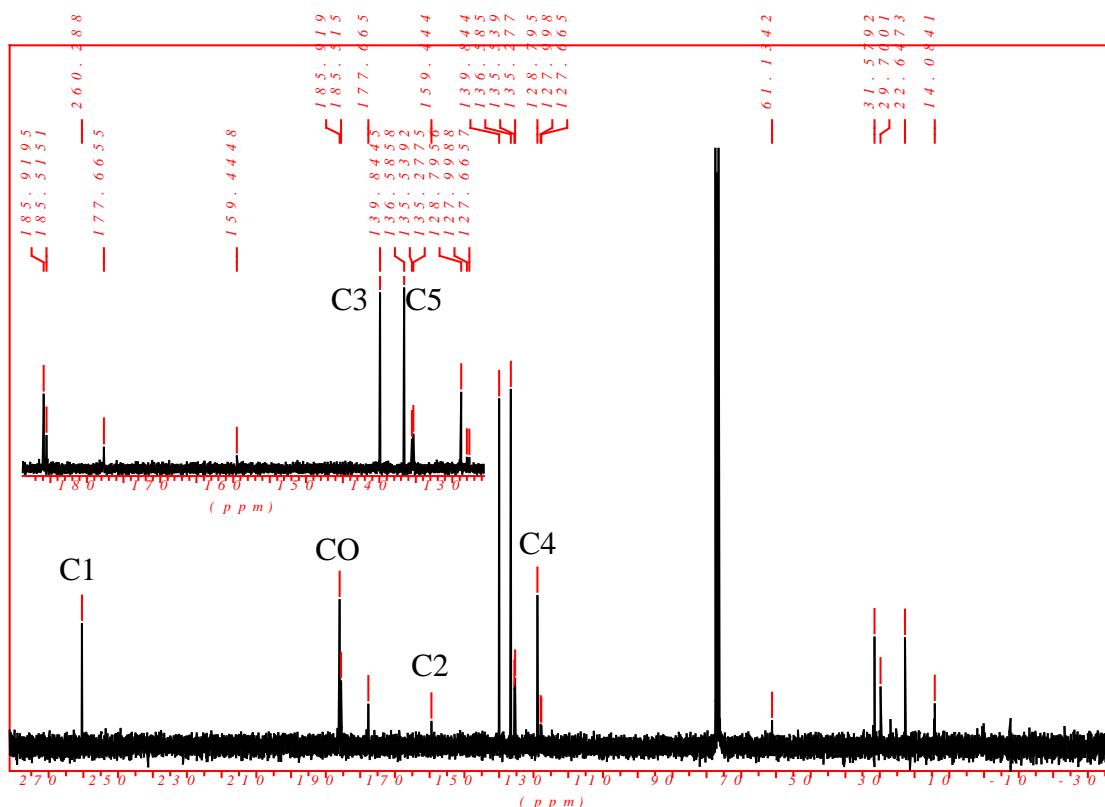
Complex	$^{13}\text{C}$ NMR bands (ppm)
 <p><b>4</b></p>	260.4 (carbene); CO not observed; 137.3 (C2); 134.7 (C3); 128.5 (C4); 138.3 (C5); 77.2 ( $\text{OCH}_2\text{CH}_3$ ); 14.5 ( $\text{OCH}_2\text{CH}_3$ )
 <p><b>5</b></p>	268.0 (carbene); 192 (CO); 152.8 (C2); 135.7 (C5); 148.6 (C3); 131.8 (C6); 129.0 (C9); 128.8, 127.6 (C4, C7); 125.7 (C8); 78.8 ( $\text{OCH}_2\text{CH}_3$ ); 15.1 ( $\text{OCH}_2\text{CH}_3$ )
 <p><b>6</b></p>	272.1 (carbene); 186.0; 184.3 (CO); 151.0 (C2); 146, 151.0 (C4, C5); 137.2 (C3); 131.2 (C6, C7); 31.6, 32.0 (Me3, Me6) 79.7 ( $\text{OCH}_2\text{CH}_3$ ); 15.7 ( $\text{OCH}_2\text{CH}_3$ );

The value of C2 of thiophene (**4**) differs a lot from that of C2 in the other two complexes – it appears at much higher field strength. The ethoxy groups' carbon signals are roughly the same, so the extra density (for carbene stabilization) has to come from the metal. If the metal donates more electron density to the carbene carbon, there is less electron-density left on the metal to donate to the carbonyl ligands.

### 3.2.4 Complex 15 and 16

The  $^{13}\text{C}$  NMR spectrum of **15** is given below in Figure 3.13. The signals of the carbene carbon, the carbonyl ligands and the thiophene carbon atoms are all observed. There are some small unidentified peaks in the spectrum, which may belong to a dissociation product. It is also possible that, in solution, this complex breaks up into a 16-electron and the 18-electron complex and that one sees signals for these two different fragment complexes.

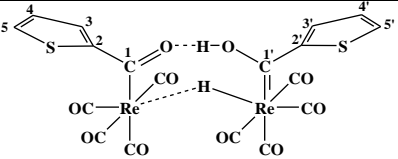
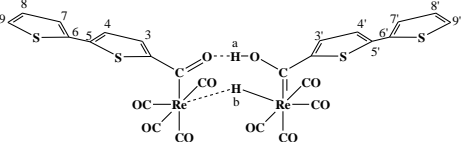
The carbene carbon signal at 260.3 ppm lies at about the same location in the spectrum as do the carbene carbon signal of **7**, showing that these two carbon atoms are similarly shielded. The carbene carbon atom of this complex is presumed to have some acyl character and there is expected to be a degree of double bonding between it and the oxygen atom.



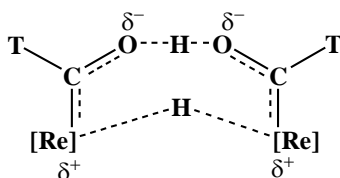
**Figure 3.13:**  $^{13}\text{C}$  NMR spectrum of **15** in  $\text{CDCl}_3$

In the spectrum there are three signals that might be assigned to the carbonyl carbon atoms. They are well-resolved and located at 185.9, 185.5 and 177.7 ppm. It is presumed that the last would belong to the carbonyl carbon atom that is *trans* to the carbene (acyl) ligand or *trans* to the hydride ligand. The signal at 185.5 ppm likely belongs to the two equivalent equatorial carbonyl ligands that are *cis* to the carbene (acyl) ligand.

**Table 3.11:**  $^{13}\text{C}$  NMR spectral data for **15** and **16**

Complex	$^{13}\text{C}$ NMR bands (ppm)
	260.3 (carbene); 185.9, 185.5, 177.7 (CO); 159.5 (C2); 139.8 (C3); 128.8 (C4); 136.6 (C5)
	259.0 (carbene); 193 (br, CO); 152.5 (C2); 141.1, 134.9, 126.5, 125.9, 124.0 (C3, C4, C7, C8, C9); C5, C6 not observed.

As was also observed with proton NMR spectroscopy, the two sides of the molecule (equivalent carbon atoms) give coinciding signals in the  $^{13}\text{C}$  NMR spectrum. The carbene/acyl-carbon atom signal is shifted upfield significantly for **15** and **16** from the carbene carbon atom of **1** and **2**, respectively, which we ascribe to greater acyl character. Electron delocalization over the 8-membered ring is shown in Figure 3.14.

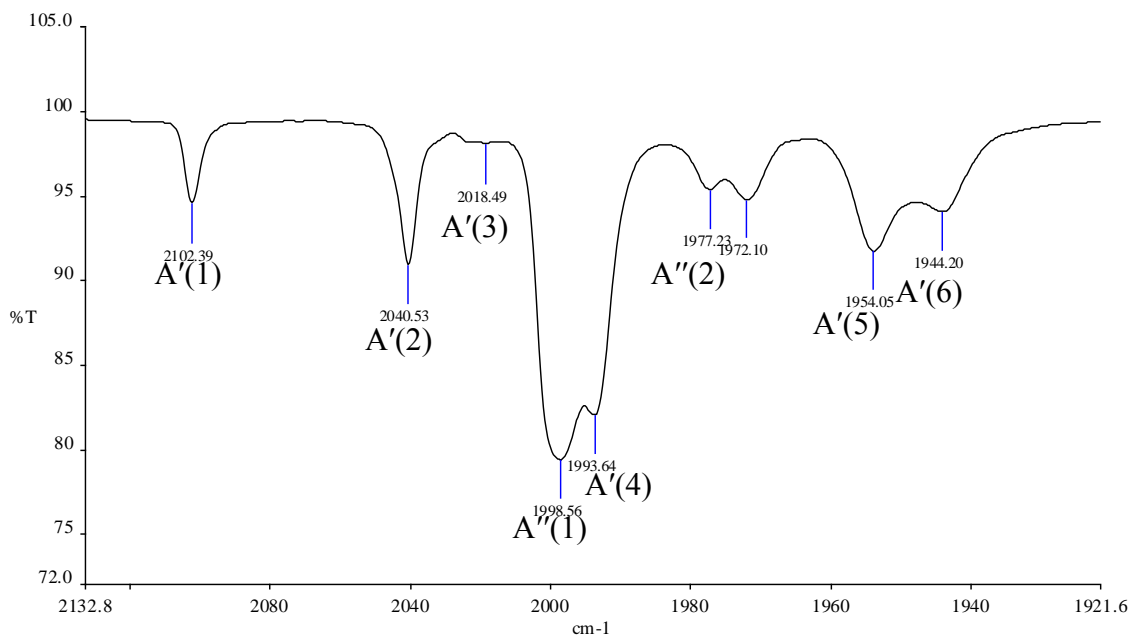


**Figure 3.14:** Electron delocalization in complexes **15** and **16** over the cyclic 8-membered ring

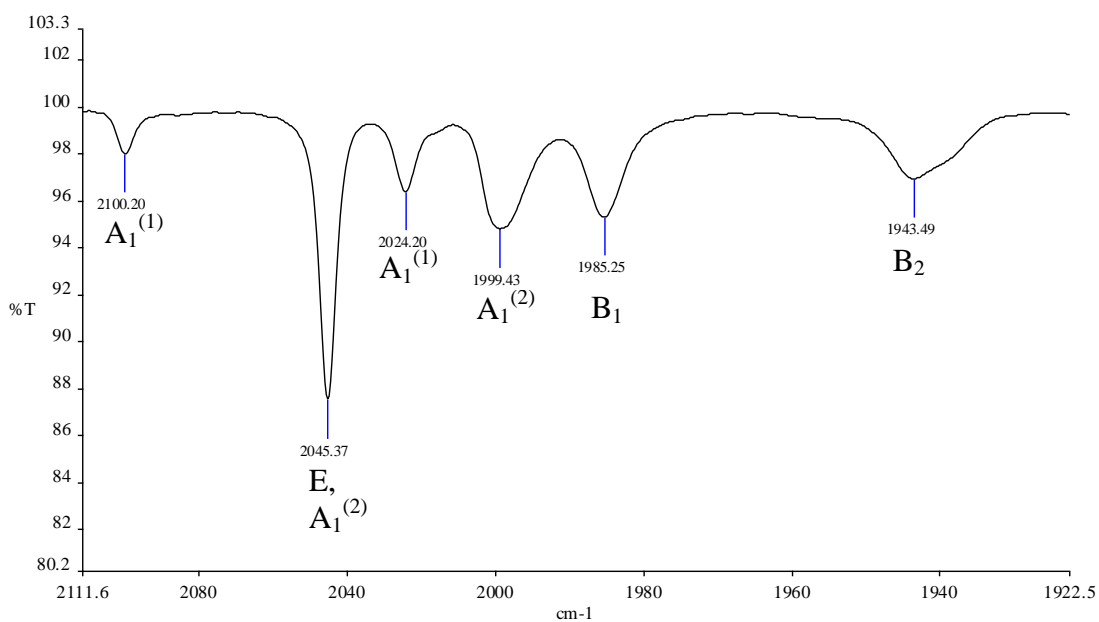
### 3.3 IR spectroscopy data

The vibrational spectra of all the complexes were determined in hexane by infrared spectroscopy. The carbonyl region of the spectra was studied. In Figure 3.15, the infrared spectra of complexes **2**, **5** and **15** are shown. The infrared spectrum of **5** also contains signals of  $[\text{Re}(\text{CO})_5\text{Br}]$  ( $2100, 2045\text{ cm}^{-1}$ ), the other product of Re-Re bond cleaving.

The infrared spectrum of **15** was examined and no acyl signal was observed in the acyl region.

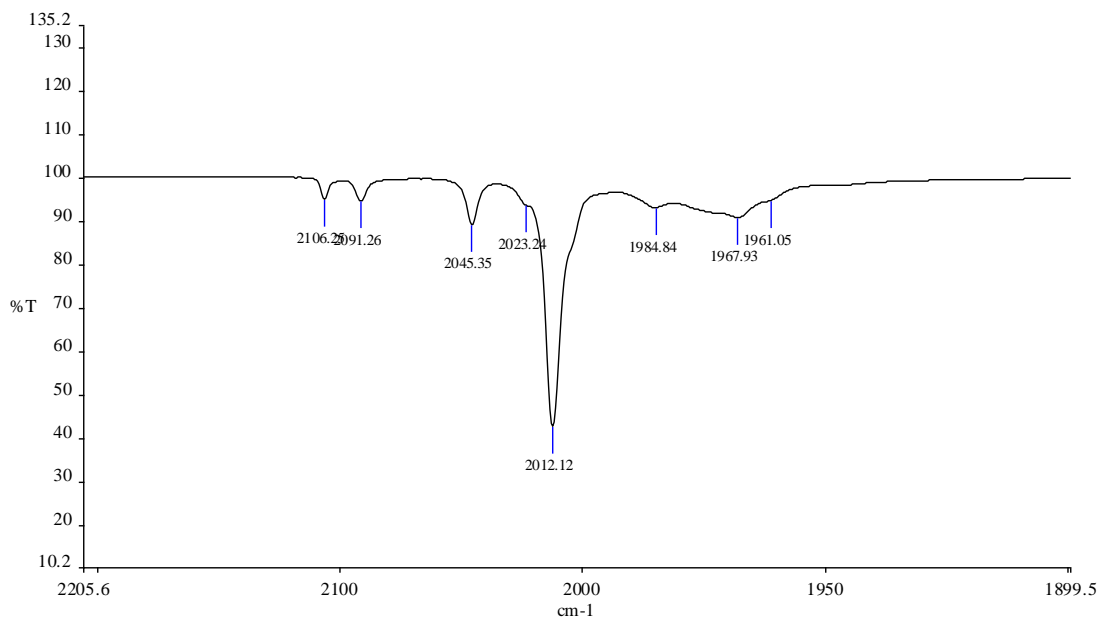


### Complex 2



### Complex 5





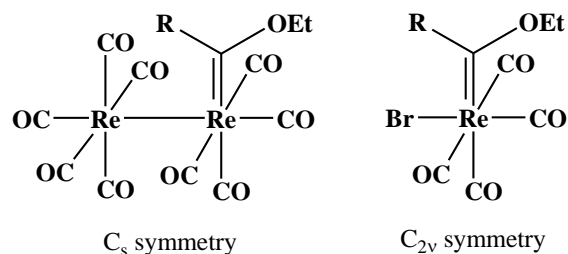
### Complex 15

**Figure 3.15:** IR spectra ( $\nu_{\text{CO}}$ -region,  $\text{cm}^{-1}$ ) of complexes **2**, **5** and **15**

Infrared spectroscopy was used to primarily determine whether the complex was a monorhenium monocarbene carbonyl complex, *cis*- $\text{Re}(\text{CO})_4$  ( $\text{C}_{2v}$ ), or a dirhenium monocarbene complex, *eq*- $\text{Re}_2(\text{CO})_9$  ( $\text{C}_s$ ). One can also deduce from the pattern of bands whether the complex is a monocarbene or a biscarbene (or even more carbene ligands) dirhenium complex.

In all cases it was found that there is only one carbene ligand per dirhenium or rhenium unit. Infrared spectroscopy confirmed this, as well as giving information of the specific stereoisomer of the complex. The IR spectroscopy data of the complexes are given in Tables 3.12, 3.13 and 3.14.

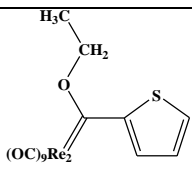
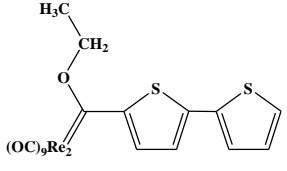
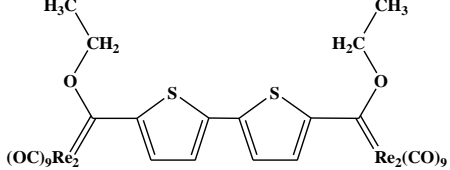
The complexes in Table 3.12 have equatorial carbene ligands of dirhenium nonacarbonyl units. One finds  $\text{C}_s$  symmetry and 9 infrared signals for these types of complexes, Figure 3.16. An axial dirhenium nonacarbonyl complex ( $\text{C}_{4v}$ ) will display five bands.



**Figure 3.16:** Symmetry of monocarbene complexes

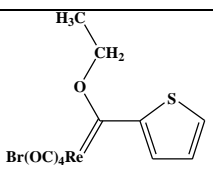
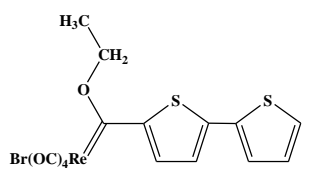
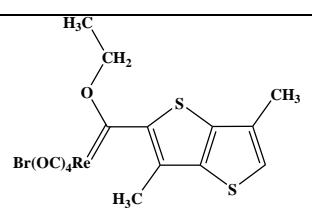
Comparing the spectra of the uncleaved complexes with that of the cleaved complexes, one clearly sees the difference between a dirhenium 9-carbonyl complex and a single metal four-carbonyl complex. There are only 4 signals in the infrared spectrum of the cleaved Re-bromide carbene complexes.

**Table 3.12:** IR spectroscopy data ( $\nu_{\text{CO}}$ -region,  $\text{cm}^{-1}$ ) of uncleaved complexes

Complex	Structure	Bands <sup>a</sup> ( $\text{cm}^{-1}$ )
<b>1</b>		2103 (w); 2071 (w); 2042 (m); 2015 (vs); 2002 (s); 1994 (s); 1977 (s); 1955 (m); 1945 (w)
<b>2</b>		2102 (w); 2041 (m); 2018 (s); 1999 (vs); 1994 (vs); 1977 (w); 1972 (w); 1954 (m); 1944 (w)
<b>8</b>		2102 (w); 2045 (s); 2029 (m); 2012 (w); 2001 (vs); 1994 (vs); 1983 (m); 1954 (m)

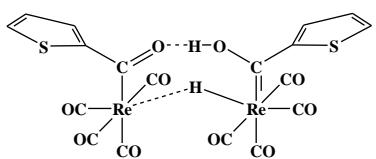
<sup>a</sup>Signals can range from very weak to very strong and it is indicated by: vw = very weak; w = weak; m = medium; s = strong; vs = very strong.

**Table 3.13:** IR spectroscopy data of cleaved carbene complexes (carbonyl region)

Complex	Structure	Bands (cm <sup>-1</sup> )
<b>4</b>		2071 (s); 2015 (s); 2004 (s); 1977 (s)
<b>5</b>		2024 (m); 1999 (s); 1985 (s); 1943 (m)
<b>6</b>		2046 (s); 1999 (vs); 1985 (m); 1947 (w)

The carbonyl stretching frequencies of **4** are at significantly higher wavenumbers than those of the other two monocarbene complexes. This is in agreement with the NMR data of the thiophene monocarbene complex versus the other two monocarbene complexes. Less back-bonding to CO ligands means stronger C–O bonds and higher wavenumbers.

**Table 3.14:** Infrared spectrum of complex **15** (carbonyl region)

Complex	Structure	Bands (cm <sup>-1</sup> )
<b>15</b>		2106 (w); 2091 (w); 2045 (m); 2023 (w); 2012 (vs); 1985 (w); 1968 (w); 1961 (w)

It seems puzzling that complex **15** should have so many carbonyl bands in the infrared spectrum. As each rhenium atom has four CO ligands one would expect a CO band pattern that is similar to other O<sub>h</sub> complexes with four CO ligands and one would also

expect that the carbonyl ligands on the two metal fragments should give coinciding infrared signals, as was the case with the NMR data. Seemingly the two fragments' CO ligands absorb at different wavelengths and signals are duplicated. Infrared and NMR spectroscopy have very different time-domains, with the former being faster than the latter by a factor of about  $10^{10}$ . This would suggest that the species are quickly interconverting and this is observed with IR spectroscopy, where NMR spectroscopy only shows a time-averaged structure.

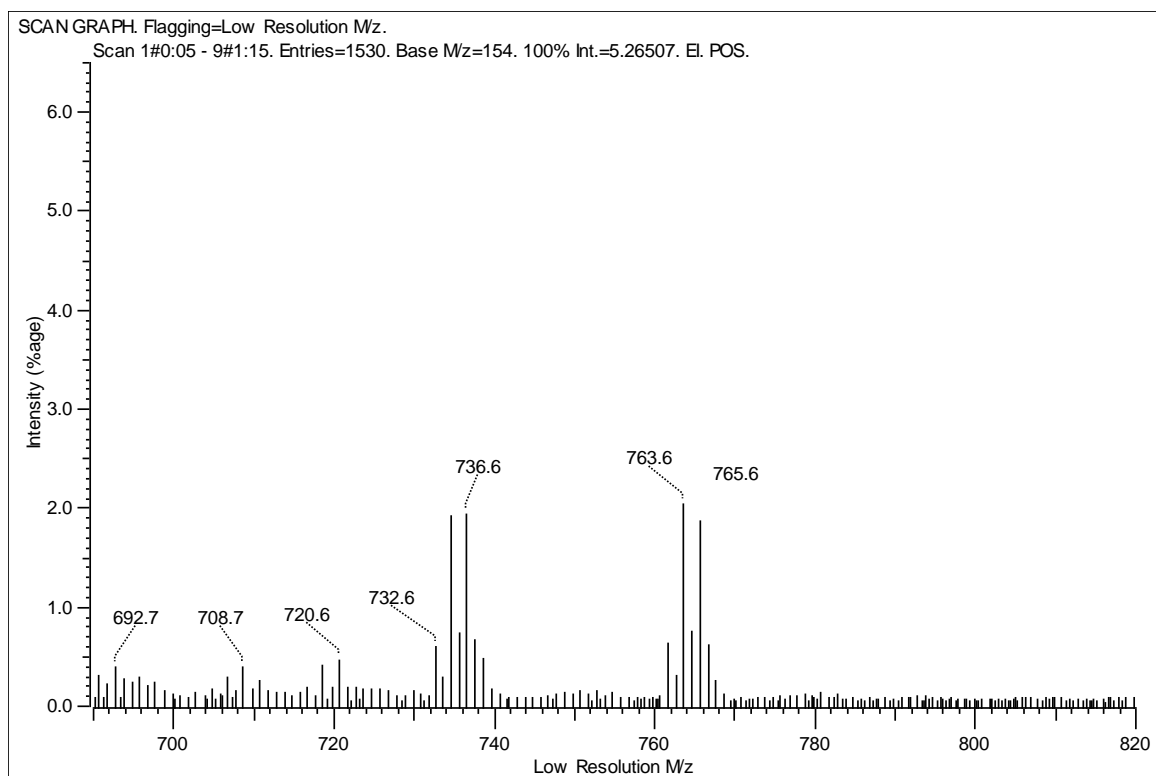
There is the possibility that the complex dissociates in solution into its two fragments. The signal of the carbene-oxygen may also appear in this area, as it was not observed in the typical region where one observes acyl ligand C-O vibrational absorptions.

### **3.4. Mass spectrometry data**

#### **3.4.1 Complex 1**

A part of the mass spectrum of **1** is shown in Figure 3.17 (showing the  $M^+$  peaks) and the whole spectrum in Figure 3.19. The fragmentation data of complex **1** is given in Table 3.15.

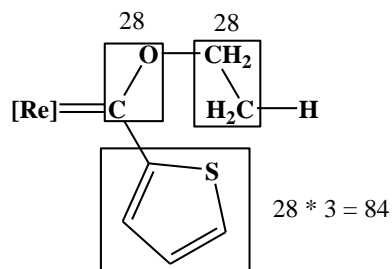
Rhenium occurs in nature in two isotopic forms:  $^{185}\text{Re}$  (37%) and  $^{187}\text{Re}$  (63%). In the mass spectrum, one observes peak groupings and these correspond to specific molecular ions. The  $M^+$  molecular ion peak is observed at  $m/z = 763.6/765.6$  (two values for two rhenium isotopes).



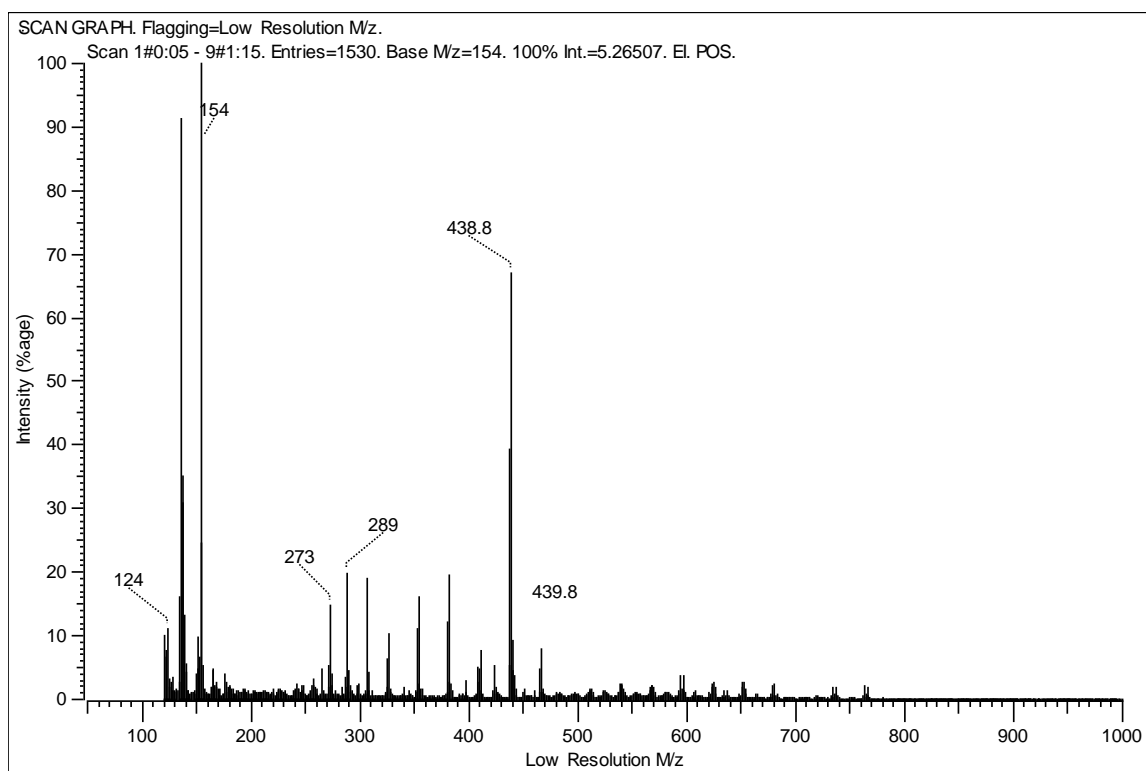
**Figure 3.17:** Part of the mass spectrum of **1**

It can be seen on Figure 3.19 that the peaks in the range from 500 to 800  $m/z$  are all small peaks. This would indicate a rapid loss of all carbonyl ligands. The first strong peak is at  $m/z = 439.8$  (68%), which corresponds to the  $M^+ - \text{Re}(\text{CO})_5$  ion. The peak at  $m/z = 327$ , which represents  $\text{Re}(\text{CO})_5^+$ , is much weaker, indicating fragmentation pathways that show an initial rhenium–rhenium bond cleavage as well as the elimination of carbonyl ligands. The principle ion is at  $m/z = 154$ . This corresponds to an unknown molecular ion without Re. There are also peaks at  $m/z = 273$ , 289 and 307 that seem to belong to species without a Re atom (only single peaks). They are difficult to identify.

Assignment of fragment ions are unsubstantiated and more than one fragment ion is possible for a given  $m/z$  value. For example, the carbene ligand may fragment in various ways giving fragments corresponding to 28 or multiples thereof, see Figure 3.18.

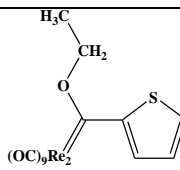


**Figure 3.18:** Fragments of carbene ligand that displays  $m/z = 28$  units



**Figure 3.19:** Mass spectrum of **1**

**Table 3.15:** Fragmentation data of **1**

		
$m/z$	Intensity (%)	Molecular ion
763.6; 765.6	2.1	$M^+$
734.6; 736.6	2.0	$M^+ - CH_2CH_3$
678.7; 680.7	2.4	$M^+ - CH_2CH_3 - 2CO$
650.7; 652.7	2.8	$M^+ - CH_2CH_3 - 3CO$
622.7; 624.7	2.7	$M^+ - CH_2CH_3 - 4CO$
594.7; 596.7	3.7	$M^+ - CH_2CH_3 - 5CO$
567.8; 568.8	2.2	$M^+ - CH_2CH_3 - 6CO$
538.8; 540.8	2.5	$M^+ - CH_2CH_3 - 7CO$
510.8; 512.8	1.7	$M^+ - CH_2CH_3 - 8CO$
464.8; 466.8	8.5	$[Re(CO)_5\{C(OEt)C_4H_3S\}]^+$
436.8; 438.8	68	$M^+ - Re(CO)_5$
354.8; 355.8	16	$[Re(CO)_6]^+$
326.8; 327.8	11	$[Re(CO)_5]^+$

### 3.4.2 Complex 2

The molecular ion,  $m/z = 845.4$  ( $M^+$ ), was observed for complex **2**. The first peak of high intensity one finds at  $m/z = 548.6$ . Again this ion represents the fragment ion  $M^+ - Re(CO)_5$  which emphasized the weakness of the Re–Re bond. In both cases a fragment ion, corresponding to the uptake of a carbonyl i.e.  $Re(CO)_6^+$  and  $Re(CO)_5(\text{carbene})^+$ , is observed. Fragmentation data of the complex is given in Table 3.16.

The higher  $m/z$  values of the mass spectrum of this complex, also features a lot of peaks of low intensity, similar to the spectrum of **1**. This would suggest the rapid loss of  $CH_2CH_3$  and carbonyl ligands.

**Table 3.16:** Fragmentation data of **2**

$m/z$	Intensity (%)	Molecular ion
845.4; 847.4	2.5	$M^+$
816.4; 818.3	2.3	$M^+ - CH_2CH_3$
760.4; 762.4	2.0	$M^+ - CH_2CH_3 - 2CO$
732.4; 734.4	2.0	$M^+ - CH_2CH_3 - 3CO$
704.5; 706.5	2.6	$M^+ - CH_2CH_3 - 4CO$
676.5; 678.5	1.9	$M^+ - CH_2CH_3 - 5CO$
648.5; 650.5	2.2	$M^+ - CH_2CH_3 - 6CO$
620.6; 622.6	3.0	$M^+ - CH_2CH_3 - 7CO$
546.6; 548.6	38	$[Re(CO)_5\{C(OEt)C_8H_5S\}]^+$
518.6; 520.6	85	$M^+ - Re(CO)_5$ or $[Re(CO)_4\{C(OEt)C_8H_5S\}]^+$
353.8; 355.8	7	$Re(CO)_6^+$
325.8; 327.8	8	$Re(CO)_5^+$

### 3.4.3 Complex 3

The  $M^+$  peak ( $m/z = 848, 846$ ) was observed and is of low intensity, as is also the case for complexes **1** and **2**. The fragmentation data of complex **3** is given in Table 3.17 and a similar pattern of fragmentation than those of complexes **1** and **2** was observed.

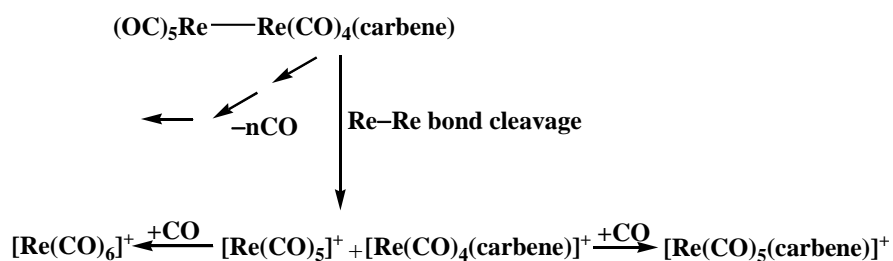
The largest peak corresponds to the loss of  $Re(CO)_5$  from **3**:  $848.4 \rightarrow 522.6$ . There is also evidence for step by step CO loss from the complex, but it seems that the loss of  $Re(CO)_5$  is preferred.



**Table 3.17:** Fragmentation data of complex **3**

$m/z$	Intensity (%)	Molecular ion
848.4; 846.4	0.6	$M^+$
818.3; 820.3	0.4	$M^+ - CO$
762.4; 764.4	1.0	$M^+ - 3CO$
734.4; 736.4	1.1	$M^+ - 4CO$
706.5; 708.5	1.0	$M^+ - 5CO$
520.6; 522.6	62	$M^+ - Re(CO)_5 /$ $[Re(CO)_4\{C(OEt)C_8H_7S_2\}]^+$
492.6; 494.6	24	$[Re(CO)_3\{C(OEt)C_8H_7S_2\}]^+$
353; 355	7	$Re(CO)_6^+$

The following scheme represents a summary of the fragmentation observed for the complexes **1–3**.



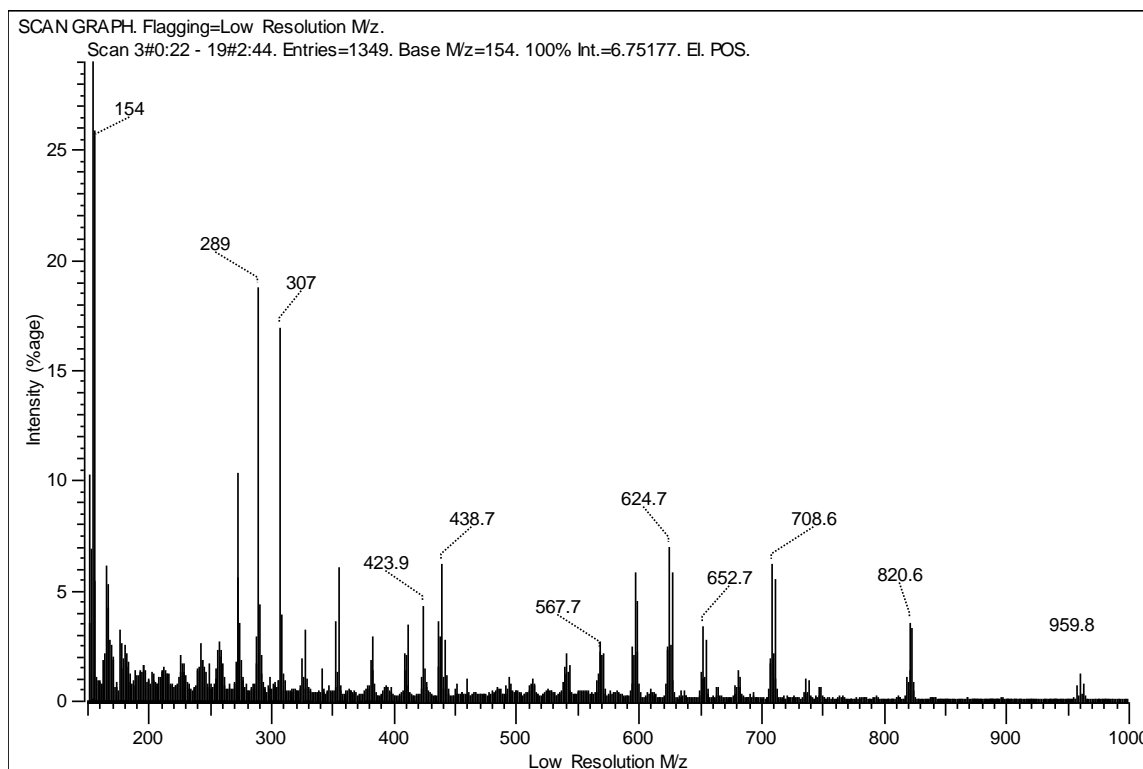
**Scheme 3.5:** Fragmentation pathway for **1–3**

### 3.4.4 Complexes **8** and **10**

No  $M^+$  peak was observed at  $m/z = 1527$  (**8**) and  $1035$  (**10**), respectively. The highest peak observed for **8** is 50 mass units lower at  $m/z = 1477$ . It is not clear which fragment this represents. There is a signal of high intensity at  $m/z = 959.1$ , corresponding to the loss of two rhenium atoms and seven carbonyl ligands.

### 3.4.5 Complex **15**

The mass spectrum of **15** is shown in Figure 3.20 and the fragmentation data in Table 3.18. The  $M^+$  is observed at  $m/z = 820.8$  and an interesting signal is also seen at the higher value of  $m/z = 959.8$ . This higher peak shows that the complex combined with another fragment to give a higher-mass molecular cation, but it could not be identified.

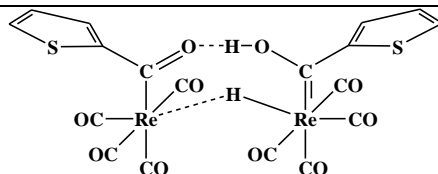


**Figure 3.20:** Mass spectrum of **15**

It is very insightful that the data shows loss of ten carbonyl groups, where the complex only has eight. This suggests that the CO groups of the acyl/carbene ligands are lost with the other carbonyl ligands.

**Table 3.18:** Fragmentation data of **15**

<i>m/z</i>	Intensity (%)	Molecular ion
820.6; 822.6	4.0	M <sup>+</sup>
708.6; 710.6	6.4	M <sup>+</sup> – 4CO
652.7; 654.7	3.4	M <sup>+</sup> – 6CO
624.7; 626.7	7.2	M <sup>+</sup> – 7CO
596.7; 598.7	6.0	M <sup>+</sup> – 8CO
568.7; 570.7	3.0	M <sup>+</sup> – 9CO
540.7	2.1	M <sup>+</sup> – 10CO



## Chapter 4: Structural features of rhenium carbene complexes

### 4.1 Introduction

Because neutral monorhenium carbonyl complexes require one X-type ligand, which can be a second rhenium carbonyl fragment, many structural variations and conformers are possible in the solid state. In addition, carbene ligands have planar  $sp^2$ -carbons with directional properties attached to substituents such as hetero-arenes, which are also planar rings, atoms with lone pairs (oxygen, Fischer carbenes) and low oxidation-state transition metals, all contributing to various structural features. It is important to remember for the discussion of the crystal structures that the carbene carbon is  $sp^2$  hybridized and that a plane is defined by the carbene carbon and the three atoms that are bound to the carbene carbon atom, i.e. Re, O and C(thienyl). This plane will be referred to as the carbene plane.

General structural features of such complexes that are important, and may vary, are listed below. These include the following positions and orientations affected by the carbene ligand.

1. Positions of ligands coordinated to rhenium
  - a. The carbene ligand is expected to be *cis* (in an equatorial position) to the X-type ligand<sup>1</sup>.
  - b. Equatorial carbonyl ligands on two rhenium atoms in  $Re(CO)_5-Re(CO)_4-L$  are expected to be staggered viewed along the metal-metal bond.
2. The rhenium-carbene bond normally displays double bond character and is expected to be shorter than a rhenium-carbon single bond.
3. Orientation of carbene substituents
  - a. The heteroarene substituent is expected to have the sulfur atom orientated towards the ethoxy side of the carbene<sup>2</sup>.

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<sup>1</sup> (a) E. O. Fischer, E. Offhaus, J. Müller, D Nöthe; *Chem. Ber.*, **1972**, 105, 3027–3035; (b) E. W. Post, K. L. Watters; *Inorg. Chim. Acta*, **1978**, 26, 29–36

- b. Position of the ethyl of the ethoxy substituent with respect to the other metal ligands<sup>3</sup>.
4. Conjugation between the two planar rings of bithiophene complexes should make them coplanar, but the relative positions of the heteroatoms may differ.

The structures of carbene complexes were determined by X-ray diffraction studies of single crystals and support conclusions drawn from spectroscopic data. The structures consist of monorhenium and dirhenium monocarbene complexes and tetrarhenium biscarbene complexes. The final structure to be discussed displays ligands that are intermediate between carbene and acyl ligands.

## **4.2 Dirhenium monocarbene complexes**

### **4.2.1 Complex 1**

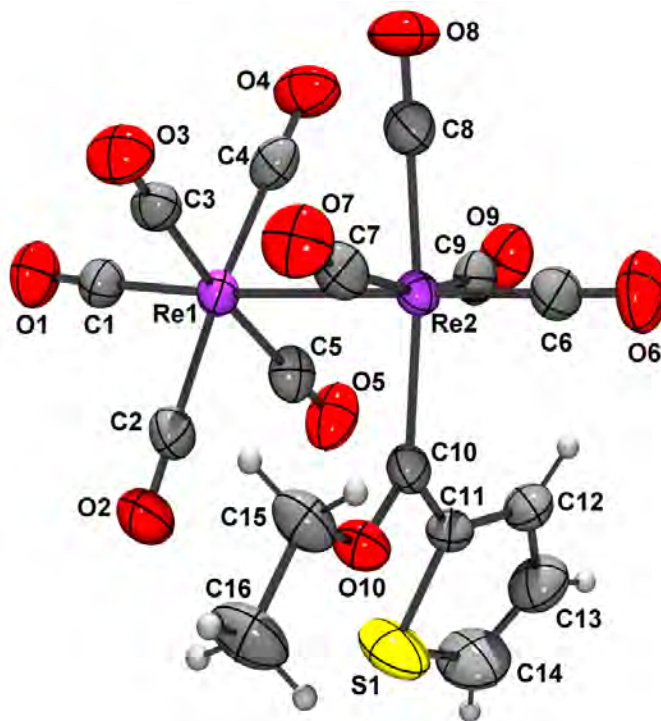
The structure consists of two Re-fragments,  $\{\text{Re}(\text{CO})_5\}$  and  $\{\text{Re}(\text{CO})_4(\text{carbene})\}$  held together by a metal-metal bond. Both metals have an octahedral ligand environment and  $\text{Re}(\text{CO})_5$  is seen as the X-type ligand. The structure confirms that the carbene is an equatorial ligand in the structure. The other ligands of the metals are carbonyl ligands and they are in the staggered conformation with respect to each other, viewed along the metal-metal bond. The carbene carbon has three substituents, an aromatic 5-membered ring (thienyl), a dirhenium carbonyl unit and the  $\text{OCH}_2\text{CH}_3$  group. In Figure 4.1 the structure is shown and selected bond lengths and angles are given in Tables 4.1a and 4.1b.

The carbene environment, i.e. the carbene carbon-to-substituent bond lengths and the bond angles around the carbene carbon will be compared and discussed at the end of this chapter.

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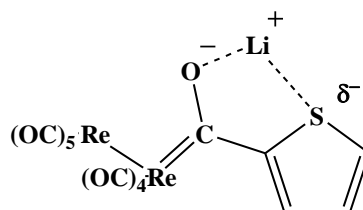
<sup>2</sup> D. C. Liles, S. Lotz; *Acta Cryst.*, **2006**, E62, m331–m334

<sup>3</sup> D. M. Andrada, M. E. Zoloff Michoff, I. Fernandez, A. M. Granados, M. A. Sierra; *Organometallics*, **2007**, 26, 5854–5858



**Figure 4.1:** Molecular structure of **1**

The ethoxy carbene–substituent is orientated to the sulfur side of the thiophene and the dirhenium fragment to the other side of the thiophene ring. It is anticipated that the metalate intermediate (formed after nucleophilic attack on the carbonyl carbon atom) may be conformation–locked because of a five–membered ring that forms (shown in Figure 4.2). Then after alkylation, carbene–stabilization from the thienyl ring by  $\pi$ –conjugation and steric bulkiness (lack of rotation) around the carbene carbon atom may restrict rotation and lock the carbene substituents in these positions.



**Figure 4.2:** A five–membered intermediate complex ring

**Table 4.1a:** Selected bond lengths of **1** (Å)

Carbene bond lengths			
C10–Re2	2.125 (5)	C10–C11	1.461 (7)
C10–O10	1.335 (6)		
Thienyl bond lengths			
C11–C12	1.400 (8)	C11–S	1.723 (5)
C12–C13	1.403 (8)	C14–S1	1.695 (8)
C13–C14	1.326 (11)		
Re–CO bond lengths			
Re–CO <sub>avg</sub> of Re(CO) <sub>5</sub> <i>eq</i> –CO ligands	1.988 (6)	Re–CO <sub>avg</sub> of Re(CO) <sub>4</sub> <i>eq</i> –CO ligands	1.983 (6)
<i>ax</i> –CO of Re(CO) <sub>5</sub>	1.928 (6)	<i>ax</i> –CO of Re(CO) <sub>4</sub>	1.923 (6)
Re(CO) <i>trans</i> carbene	1.982 (6)		
Other bond lengths			
O10–CH <sub>2</sub>	1.434 (7)	Re1–Re2	3.0899 (3)
CH <sub>2</sub> –CH <sub>3</sub>	1.514 (8)		

Bond distances and angles for thiophene were determined by the technique of microwave spectroscopy<sup>4</sup>. The values are S–C<sub>α</sub> = 1.714 (1) Å, C<sub>α</sub>–C<sub>β</sub> = 1.370 (2) Å and C<sub>α</sub>–C<sub>β</sub> = 1.424 (2) Å. The values of the bond distances correspond to mean values for thiophene of 1.712, 1.362 and 1.424 Å<sup>5</sup>. The internal bond angles centred on S, C<sub>α</sub> and C<sub>β</sub> are respectively 92.2 (1), 111.5 (3) and 112.5 (3) °.

As electron density is drawn out of the thienyl ring to stabilize the carbene carbon atom, the closest ring double bond, to the carbene, is expected to be lengthened and become

<sup>4</sup> R. J. Angelici; *Coord. Chem. Rev.*, **1990**, *105*, 61–76

<sup>5</sup> F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor; *J. Chem. Soc. Perkin Trans. 2*, **1987**, S1–S19

more single in bond nature. The examination of C–C bonds of the thienyl ring supports this conclusion. Formally double, bond C11–C12 is the same length as the ‘single’ bond C12–C13 and both are significantly longer than the shortest C–C bond length C13–C14. C11–C12 is also longer than the thiophene mean C2–C3 bond length of 1.362 Å and also longer than the value of 1.370 (2) Å determined for this bond of thiophene. Resonance delocalization of electron–density from the ring double bonds to the carbene–carbon atom was used to explain the NMR shifts of the ring protons. That reasoning is now supported by structural evidence as well.

The bond between the carbene carbon and the ring carbon atom C10–C11 is longer than C13–C14, which is believed to still have a lot of double bond character. A single carbon–carbon bond in complex **1** is that between the carbon atoms of the ethoxy substituent, and the length of this bond is 1.514 (8) Å. C10–C11 is much shorter than this bond. One should perhaps not draw too much from this data, as the carbon atoms have different hybridizations and are not directly comparable, but it seems clear that there is a degree of double bonding between the carbene carbon and the thienyl ring carbon.

Because the ethoxy oxygen atom is bonded to the  $sp^2$  hybridized carbene carbon atom and to a  $sp^3$  carbon atom of the ethyl group, a comparison of these two bond distances could provide some insight into the degree by which the oxygen atom stabilizes the carbene carbon. Both are single bonds, formally, but the bond between the carbene and the oxygen may contain some double bond character. The mean value for a  $Csp^2$ –O bond in an enol ester is 1.354 Å<sup>5</sup>. These values are: C(carbene)–O = 1.335 (6) Å and O–CH<sub>2</sub> = 1.434 (7) Å. The former is indeed significantly shorter than the latter, by 0.1 Å and closer to the mean C–O bond distance of an enol ester. It should be remembered that a  $sp^2$  orbital contains more s character than a  $sp^3$  orbital, which would make for a shorter bond.

The bond lengths between the rhenium atoms and carbonyl ligands in the complex can be compared to the same distances of  $[Re_2(CO)_{10}]^6$ . The average value of the rhenium–carbonyl bond distances of the two axial carbonyl ligands, of complex **1**, is 1.926 (6) Å

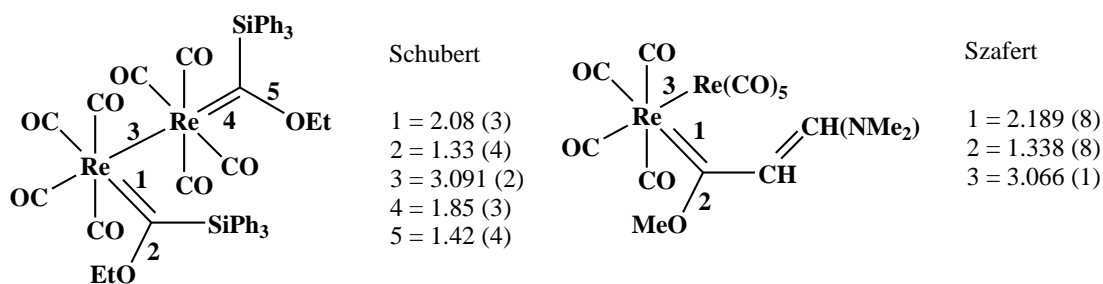
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<sup>6</sup> M. R. Churchill, K. N. Amoh, H. J. Wasserman; *Inorg. Chem.*, **1981**, 20, 1609–1611



and of  $[\text{Re}_2(\text{CO})_{10}]$  is 1.927 (7) Å, which is the same. The average Re–C distance values for the equatorial carbonyl ligands of the two rhenium fragments are the same within experimental error (for  $[\text{Re}_2(\text{CO})_{10}]$  the average *eq*–CO metal–carbon distance is 1.987 (6) Å). On the  $\{\text{Re}(\text{CO})_4\}$  fragment, that bears the carbene ligand, there are two carbonyl ligands that are *trans* to non–carbonyl ligands: the axial carbonyl ligand and the carbonyl ligand *trans* to carbene ligand. Their respective metal–carbon bond distances are 1.923 (6) Å and 1.982 (6) Å. The latter is comparable to the other equatorial carbonyl ligand–metal bond distances, but the former is significantly shorter. This is because the CO ligand opposite the Re–Re bond is not *trans* to a  $\pi$ –accepting ligand that competes with the carbonyl for electron–density. The Re–carbene value is slightly longer than the mean value for terminal alkoxy-carbenes of 2.098 Å<sup>7</sup>.

The Re–Re bond length of 3.0899 (3) Å, of the complex, is significantly longer than the Re–Re bond length of  $[\text{Re}_2(\text{CO})_{10}]$ , which is 3.041 (1) Å. Two dirhenium carbene complexes from literature are shown below and it can be seen that the Re–Re distance for **1** falls in the range of a typical complex. The two complexes were reported by Schubert<sup>8</sup> and Szafert<sup>9</sup>. In the dirhenium biscarbene complex with an equatorial and axial carbene ligand, one notes that the axial metal–carbene bond length is shorter than the equatorial one. The Re–carbene bond distance of **1** is even longer than the latter and closer to the value of the Szafert dirhenium monocarbene complex.



**Figure 4.3:** Bond distances in (Å) of rhenium carbene complexes

<sup>7</sup> A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson, R. Taylor; *J. Chem. Soc. Dalton Trans.*, **1989**, S1–S83

<sup>8</sup> U. Schubert, K. Ackermann, P. Rustemeyer; *J. Organomet. Chem.*, **1982**, 232, 323–334

<sup>9</sup> K. Osowska, K. Mierzwicki, S. Szafert; *Organometallics*, **2006**, 25, 3544–3547

**Table 4.1b:** Torsion angles of complex **1** (°)

Carbene plane deviation relative to cis equatorial CO ligands			
C11–C10–Re2–C7	0.2 (5)	O10–C10–Re2–C7	3.2 (5)
C11–C10–Re2–C9	6.5 (5)	O10–C10–Re2–C9	9.5 (5)
Thienyl twist out of the carbene plane			
S1–C11–C10–Re2	28.5 (3)	C12–C11–C10–Re2	27.7 (9)
S1–C11–C10–O10	26.1 (6)	C12–C11–C10–O10	25.3 (6)
Ethoxy twist out of the carbene plane			
C15–O10–C10–Re2	2.4 (8)	C15–O10–C10–C11	0.1 (5)
Ethoxy planarity			
C10–O10–C15–C16	5.8 (5)		

Because the carbene ligand requires more space than a carbonyl ligand and because of the difference in their bonding properties, the two carbonyl ligands C7–O7 and C9–O9 are bent away from the carbene substituents and the octahedral ligand environment around this rhenium is distorted. This bending from linearity is roughly 10 degrees for the two carbonyl ligands.

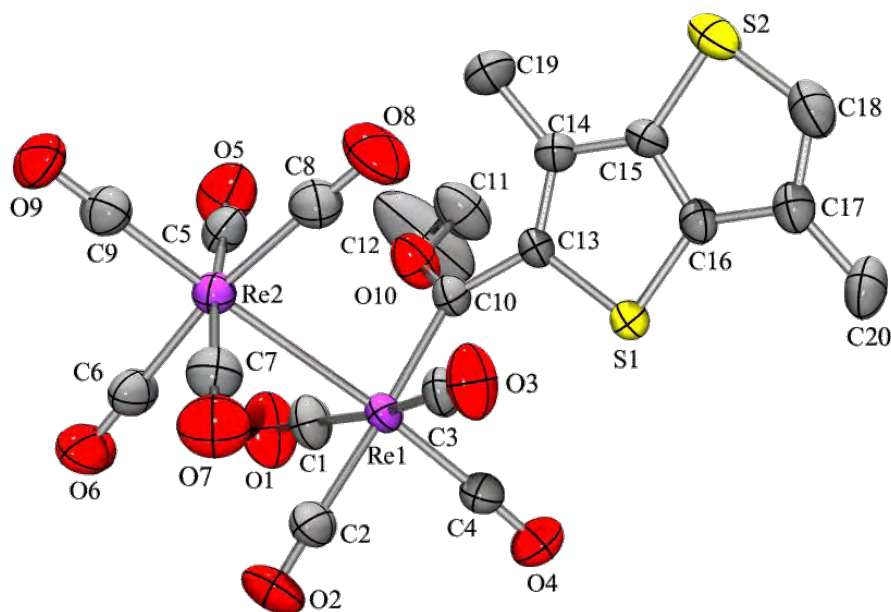
From torsional twist angles it can be seen that the ethoxy substituent of the carbene ligand and the C7–O7 carbonyl ligand are only slightly twisted away from each other (away from a fully eclipsed conformation). The thienyl carbene substituent is on the C9–O9 carbonyl ligand side and the deviation away from a fully eclipsed conformation is larger.

#### 4.2.2 Complex 3

The structural features of **3** are similar to those of **1**. Complex **3** has a 3,6-dimethylthieno[3,2-*b*]thiophene carbene substituent. The structure confirms that the carbene ligand in this complex is also equatorial and the carbonyl ligands of the two

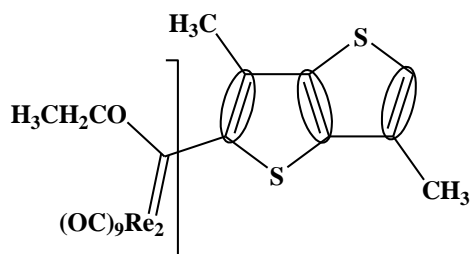
equatorial plains are again staggered (viewed along the metal–metal bond). The structure is shown in Figure 4.4 and selected bond–lengths and angles are given in Tables 4.2a and 4.2b.

All the carbon–sulfur bond lengths of the thiophene rings follow the same pattern. The C–S bond distances closest to the carbene ligand is marginally shorter compared to the distant C–S distance.



**Figure 4.4:** Molecular structure of **3**

Within experimental error the three C–C bond distances of the thienyl rings indicated in Figure 4.5 are the same length, with the exception of C17–C18, which is shorter. Double bond delocalization in the rings (which causes the lengthening of the double bonds) is limited because of the twist of the thienyl group with respect to the carbene plane. The torsion angle Re1–C10–C13–C14 is 47°, representing a large deviation of the plane of the thienyl rings and the carbene plane.



**Figure 4.5:** Localized longer (single) and shorter (double) bonds

**Table 4.2a:** Selected bond lengths of **3** (Å)

Carbene bond lengths			
C10–Re1	2.098 (6)	C10–C13	1.466 (8)
C10–O10	1.326 (8)		
Thienyl bond lengths			
C13–C14	1.379 (8)	C17–C20	1.498 (10)
C14–C15	1.396 (8)	C13–S1	1.739 (6)
C14–C19	1.496 (9)	C16–S1	1.721 (5)
C15–C16	1.378 (8)	C15–S2	1.727 (6)
C16–C17	1.411 (8)	C18–S2	1.719 (8)
C17–C18	1.358 (9)		
Other bond lengths			
O10–C11	1.429 (9)	Re1–Re2	3.0468 (4)
C11–C12	1.451 (13)		
Re–CO bond lengths			
Re–CO <sub>avg</sub> of Re(CO) <sub>5</sub> <i>eq</i> –CO ligands	1.986 (8)	Re–CO <sub>avg</sub> of Re(CO) <sub>4</sub> <i>eq</i> –CO ligands	1.974 (7)
<i>ax</i> –CO of Re(CO) <sub>5</sub>	1.927 (7)	<i>ax</i> –CO of Re(CO) <sub>4</sub>	1.910 (7)
Re(CO) <i>trans</i> carbene	1.993 (7)		

The Re–Re bond distance of this complex is less than the Re–Re bond of complex **1** and this means the carbonyl ligands being closer to one another. It was noticed with complex **1** that the carbonyl ligands are staggered, but not perfectly so (meaning that the torsional angles between two CO ligands next to each other is 45 degrees). Instead, for complex **1** it is measured at 32.9° for two CO ligands and for this complex the same measurement comes to 40.9°.

The average value of the rhenium–carbonyl bond distances of the two axial carbonyl ligands is 1.919 (6) Å and not different from the corresponding distances of [Re<sub>2</sub>(CO)<sub>10</sub>]. The average Re–C distances of the equatorial carbonyl ligands of the two rhenium fragments are also the same as the equatorial carbonyl ligands of [Re<sub>2</sub>(CO)<sub>10</sub>]. The axial carbonyl ligand–Re bond distances are the shortest of all the metal–carbonyl bond distances.

**Table 4.2b:** Selected dihedral angles of **3** (°)

Carbene plane deviation relative to equatorial CO ligands			
C13–C10–Re1–C10	20.6 (5)	O10–C10–Re1–C1	20.1 (5)
C13–C10–Re1–C3	10.9 (5)	O10–C10–Re1–C3	11.3 (5)
Thienyl deviation out of the carbene plane			
S1–C13–C10–O10	42.0 (5)	S1–C13–C10–Re1	42.3 (7)
C14–C13–C10–O10	46.5 (10)	C12–C13–C10–Re1	47.0 (6)
Ethoxy twist out of the carbene plane			
C17–O10–C10–Re1	24.0 (6)	C17–O10–C10–C11	24.2 (10)
Ethoxy planarity			
C10–O10–C17–C18	33.9 (11)		

It can be seen that the aromatic substituent is twisted with respect to the carbene plane more than the ethoxy substituent, almost twice as much (C13–C10–Re1–C3 = 10.9°, O10–C10–Re1–C1 = 20.1°). It is interesting to note that the ethoxy and the aromatic carbene substituents (O10–C10–C11–S1) are twisted 47° with respect to each other. A

five-membered intermediate, like that shown in Figure 4.4, may have formed. After alkylation, deformation of the whole structure may have occurred, due to restricted rotation around the C10–C13 bond and packing forces.

In the thienyl substituent (3,6-dimethylthieno[3,2-*b*]thiophene) of complex **3** the closest ring is defined by carbon atoms C13–C16 and S1. One might compare this ring to the thienyl ring of complex **1**, although it has a methyl at ring position 3 and another ring fused to it. The following bond length and internal angle data provides for a comparison between the two thiophene rings of complexes **1** and **3** (ring carbon atoms are numbered as 2 (attached to carbene carbon), 3, 4 and 5):

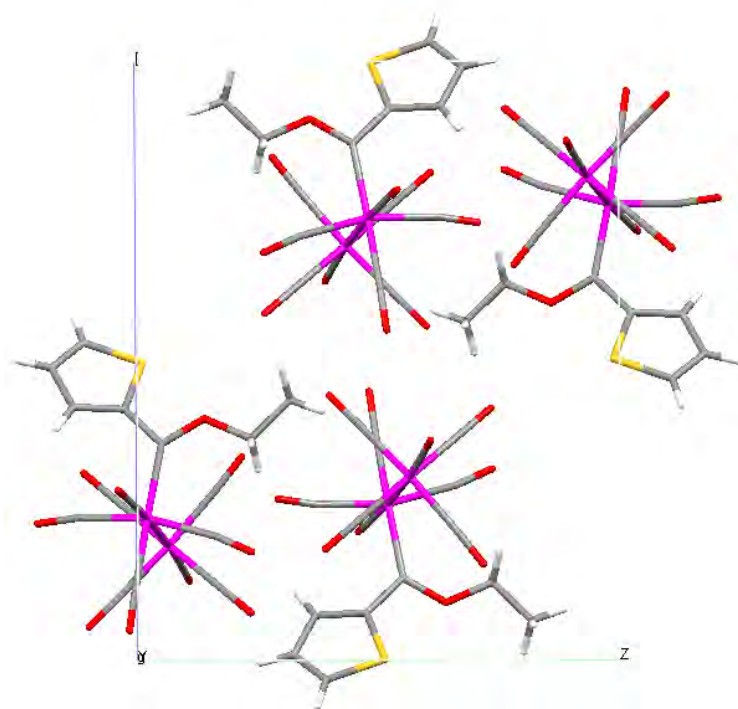
**Table 4.3:** Thienyl ring comparisons between complexes **1** and **3**

Complexes	<b>1</b>	<b>3</b>
Bonds distances (Å)		
C2–C3	1.400 (8)	1.379 (8)
C3–C4	1.403 (8)	1.396 (8)
C4–C5	1.326 (11)	1.378 (8)
C2–S	1.723 (5)	1.739 (6)
C5–S	1.695 (8)	1.721 (5)
Ring internal angles (angles centered on named atoms) (°)		
C2	110.2 (4)	112.7 (4)
C3	111.9 (6)	110.1 (5)
C4	113.0 (6)	115.8 (5)
C5	113.6 (5)	110.1 (4)
S	91.3 (3)	91.2 (3)

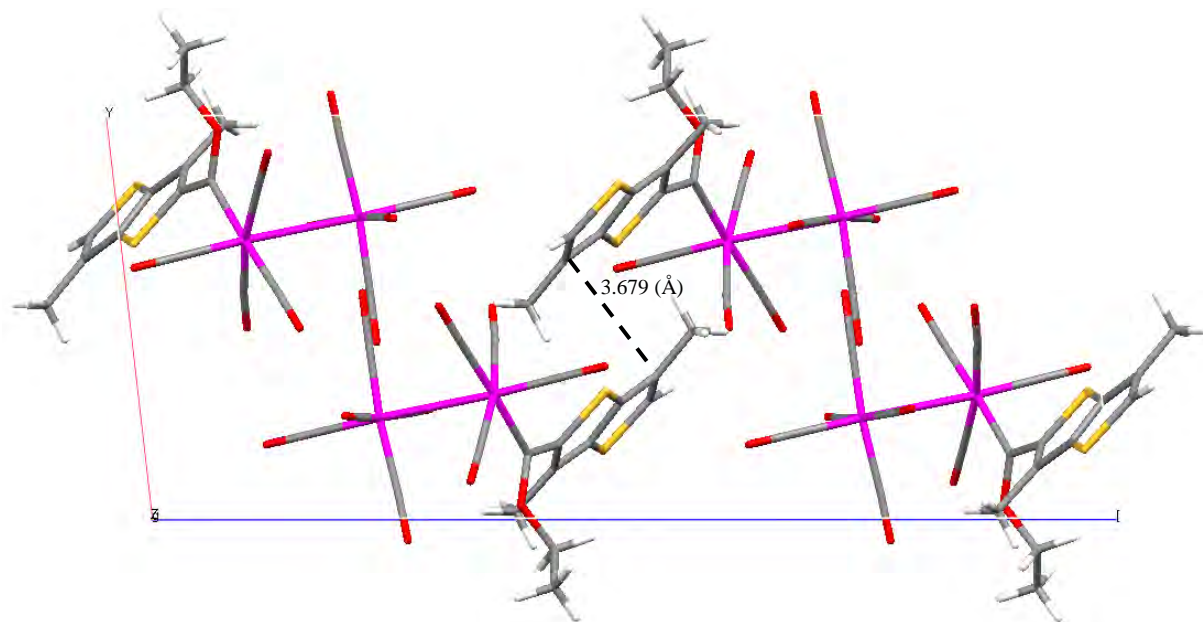
A comparison of the internal angles of the thiophene substituent of complex **1** show that the angles centered on C2 and C5 do have a significant difference from the values determined for thiophene by microwave spectroscopy. Even though they are in most cases not significantly different, taken into account the experimental errors of the

measurements, the ring C–C bonds in **3** are marginally shorter than the corresponding distances in **1**. There are also small differences in corresponding angles between the two thiophene rings of the substituents of complex **3** and the differences are assumed to have little significance.

An examination of the packing of these two complexes (Figure 4.6) does not indicate that hydrogen–bonding plays a role in determining the packing. With complex **1**, the thiophene substituents are placed far apart. The positioning of the individual molecules in **3** suggests possible  $\pi$ –interaction, with a distance of 3.7 Å between closest ring carbon atoms of two 3,6–dimethylthieno[3,2-*b*]thiophene substituents.



Complex 1



Complex 3

**Figure 4.6:** Crystal packing for **1** and **3**

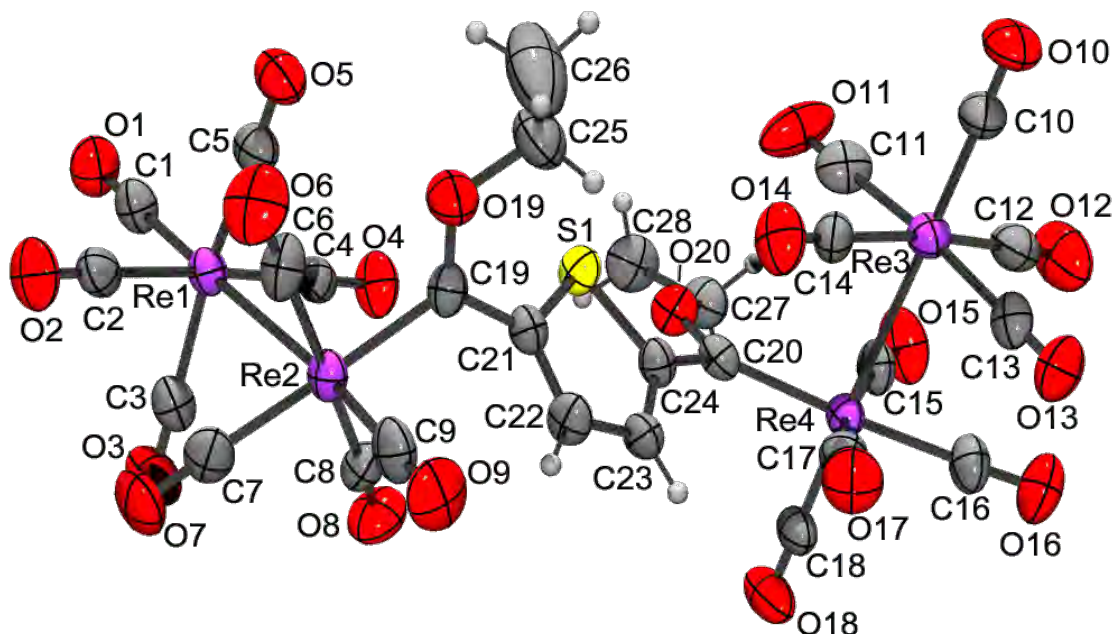
### **4.3 Tetrarhenium biscarbene complexes**

#### **4.3.1 Complex 7**

The molecule consists of two Fischer carbene ligands attached at both ends of a linking thiophene bridge. The carbene ligands then both have  $\{\text{OCH}_2\text{CH}_3\}$  and  $\{\text{Re}_2(\text{CO})_9\}$  fragments bonded to them. The complex structure is shown in Figure 4.7.

The metal fragments are directed away from the sulfur atom of the thiophene ring and the ethoxy carbene substituents are on the same side of the sulfur atom of the aromatic ring. The equatorial carbonyls of the two metal fragments are again staggered and both carbene ligands are found in equatorial positions. Selected bond distance and bond angle data are given in Table 4.4a and 4.4b.

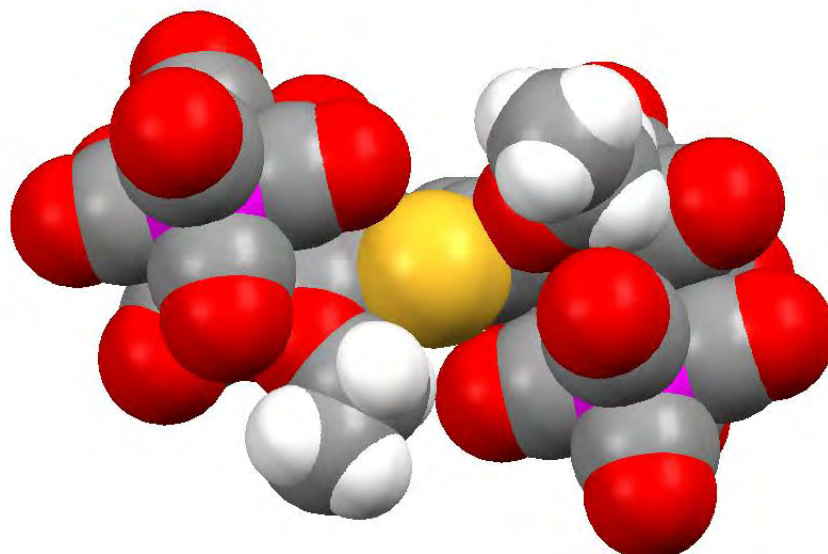




**Figure 4.7:** Molecular structure of **7**

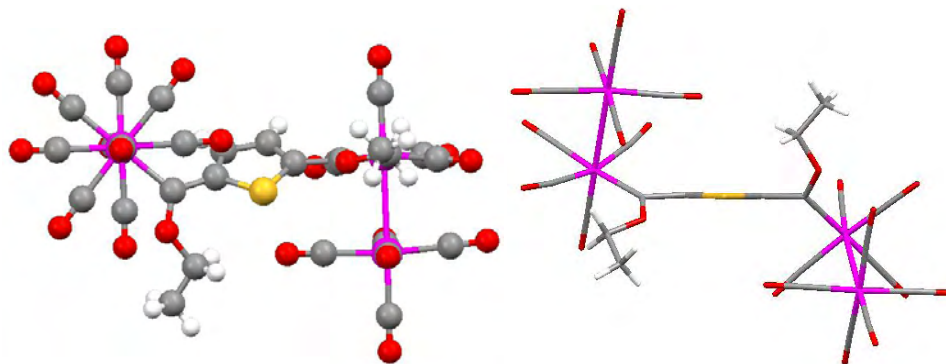
The first impression when looking at the image of the molecule is that the carbene substituents of this complex are sterically constrained. In the planar thiophene biscarbene arrangement the ethoxy groups in the complex can interfere with each other across the ring, and as a result the one lies above and one below the plane of the thiophene ring (Figure 4.8).

The molecule seems to be twisted “out of shape”. The two sides are non-equivalent in terms of angles and bond distances. The Re–Re bonds of the two fragments are not the same length, evidence of the inner strain present in the molecule. The shorter one is comparable to the Re–Re bond of **3**.



**Figure 4.8:** Ethoxy groups are orientated to the opposite sides of the thiophene ring (central)

If one were to draw lines along the Re–Re bonds, the two lines would, by rough estimation, be perpendicular to each other, which are shown in Figure 4.9. In fact – the torsional angle between them is  $95^\circ$ . The image also shows that the CO ligands of the two metals are in the staggered conformation, when viewed along the metal–metal bonds. The second carbene ethoxy substituent is almost co-planar to the Re–Re bond of the first carbene ligand and *vice versa*. The dihedral angle between the two ethoxy groups is  $78^\circ$  (O–C1–C1'–O).



**Figure 4.9:** Lines along Re–Re bonds are perpendicular

**Table 4.4a:** Selected bond lengths of **7** (Å)

Carbene bond lengths			
C19–Re2	2.093 (10)	C20–Re4	2.076 (10)
C19–O19	1.303 (13)	C20–O20	1.338 (12)
C19–C21	1.476 (14)	C20–C24	1.480 (12)
Thienyl bond lengths			
C21–C22	1.363 (14)	C23–C24	1.347 (13)
C22–C23	1.421 (14)		
Ethoxy bond lengths			
O19–C25	1.465 (15)	O20–C27	1.438 (13)
C25–C26	1.39 (2)	C27–C28	1.511 (17)
Re–Re bond lengths			
Re1–Re2	3.0434 (6)	Re3–Re4	3.0569 (7)
Re–CO bond lengths (Re1, Re2)			
Re–CO <sub>avg</sub> of <i>eq</i> – Re(CO) <sub>5</sub>	1.989 (12)	Re–CO <sub>avg</sub> (Re(CO) <sub>4</sub> <i>trans</i> –CO carbonyls)	1.994 (12)
<i>ax</i> –CO of Re(CO) <sub>5</sub>	1.934 (11)	<i>ax</i> –CO of Re(CO) <sub>4</sub>	1.907 (13)
Re(CO) <i>trans</i> carbene	1.984 (12)		
Re–CO bond lengths (Re3, Re4)			
Re–CO <sub>avg</sub> of <i>eq</i> – Re(CO) <sub>5</sub>	1.988 (14)	Re–CO <sub>avg</sub> (Re(CO) <sub>4</sub> <i>trans</i> –CO carbonyls)	1.983 (12)
<i>ax</i> –CO of Re(CO) <sub>5</sub>	1.952 (11)	<i>ax</i> –CO of Re(CO) <sub>4</sub>	1.942 (11)
Re(CO) <i>trans</i> to carbene	1.993 (12)		

**Table 4.4b:** Bond and torsion angles for complex **7** (°)

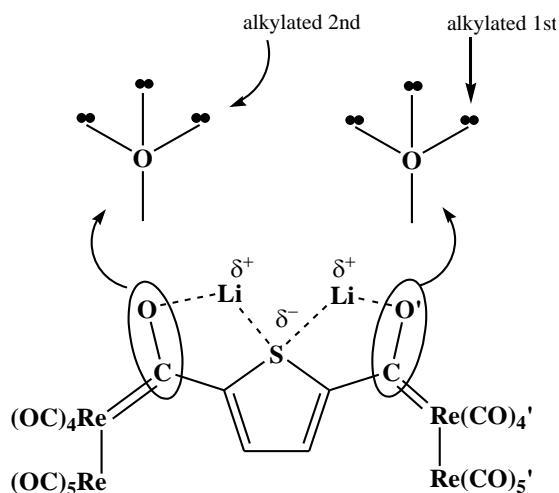
Carbene ligand angle to <i>cis</i> carbonyl ligands			
C19–Re2–C6	88.5 (4)	C20–Re4–C17	92.9 (4)
C19–Re2–C8	90.2 (4)	C20–Re4–C15	97.2 (4)
Deviation relative to equatorial CO ligands because of carbene ligand			
O19–C19–Re2–C6	9.7 (8)	O20–C20–Re4–C15	5.1 (9)
O19–C19–Re2–C8	17.7 (8)	O20–C20–Re4–C17	5.2 (9)
C21–C19–Re2–C6	13.6 (8)	C24–C20–Re4–C15	4.6 (8)
C21–C19–Re2–C8	21.6 (8)	C24–C20–Re4–C17	5.7 (8)
Thienyl twist out of the carbene plane			
S1–C21–C19–Re2	46.3 (7)	S1–C24–C20–Re4	30.2 (5)
S1–C21–C19–O19	50.2 (13)	S1–C24–C20–O20	30.7 (10)
C22–C21–C19–Re2	44.2 (14)	C23–C24–C20–Re4	36.7 (14)
C22–C21–C19–O19	48.0 (11)	C23–C24–C20–O20	37.1 (11)
Ethoxy substituent twist out of the carbene plane			
C19–O19–C25–C26	33.1 (17)	C20–O20–C27–C28	10.4 (9)

The carbene ligand with its substituents causes a large deviation of the two *cis* equatorial carbonyl ligands from linearity. This applies to both of the carbenes. The two *cis* carbonyl ligands are again bent away from the carbene ligand (except for C6–O6, which is slightly bent towards the carbene ligand), as was the case for **1** and **3**. This deviation is given in Table 4.4b.

The ethoxy groups of the carbene ligands are oppositely orientated relative to their metals. Notably the oxygen–lone pairs of one are towards the ring and of the other towards the metals. Sierra<sup>3</sup> reported a favoured positioning of the oxygen lone pairs away from the metal carbonyl fragment in monocarbene complexes to minimize interaction of the lone pairs with the “carbonyl wall”. The ethoxy group C19–O19–C25–C26 has the lone–pair towards the metal substituent and is bent by 33° out of the carbene plane, while

the other one (C20–O20–C27–C28) has the lone-pairs away from the metal and is only bent by 10 degrees out of the carbene plane.

If one assumes the alkylation is a stepwise process, one could start by alkylating the first oxygen according to the Sierra favoured position with the lone-pairs in a position away from the metal. The presence of a second metal with carbonyls, in close proximity, could change the alkylation site of the second alkylation. This seems to be the case as the other ethyl group is orientated with the lone-pairs towards the second metal fragment. Arguably the intermediate pre-alkylation complex (Figure 4.10) was more planar than the final complex. This argument relies on the assumption that the largest steric hindrance in the molecule comes from the two ethoxy carbene substituents that can interfere with each other across the thiophene ring. The first alkylation then proceeded in such a way that the  $\text{Et}^+$  attached from the thiophene side so that it points ‘towards’ the metals (the oxygen lone pairs are over the ring), as is observed in the conformation of the monocarbene complex **1**. This is then ethoxy group C20–O20–C27–C28, which also happens to be more planar than ethoxy group C19–O19–C25–C26, which is perceived to have been alkylated afterwards.



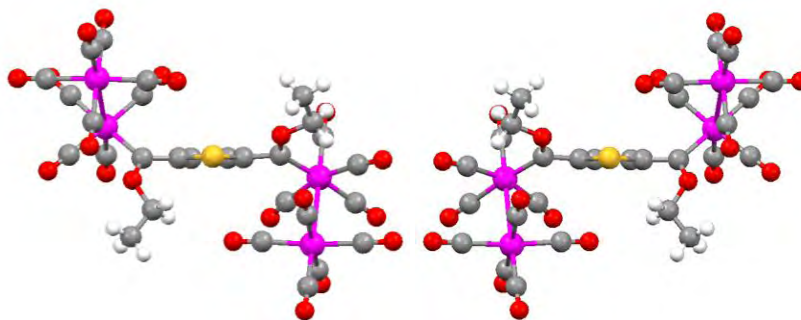
**Figure 4.10:** Visualization of intermediate state of **7**

A comparison of the bond lengths and internal angles of the thienyl ring of **7** with those of complex **1** provides insight (Table 4.5). Unfortunately the larger experimental error of structure **7** limits the potential for meaningful comparison. Based on the values, with experimental error taken into account, one cannot say that the two thiophene rings of the two complexes are different in terms of bond lengths. The differences in inner bond angles between the rings of the two complexes are also small. It is interesting to note that the thiophene ring with two carbenes attached (**7**) is more symmetrical than the thiophene ring of **1**. The carbene carbon atoms of complex **7** are linked by a  $\pi$ -conjugated link through the thiophene ring. As a result of this they compete for electron density equally well from the ring and the ring displays localized single and double bonds. The more distorted thiophene ring of complex **1** also differs more from the mean values of thiophene in terms of bond length.

**Table 4.5:** Comparison of bond distances (Å) and angles (°) of thienyl rings of **1** and **7**

	<b>1</b>	<b>7</b>
Bonds distances (Å)		
C2–C3	1.400 (8)	1.363 (14)
C3–C4	1.403 (8)	1.421 (14)
C4–C5	1.326 (11)	1.347 (13)
C2–S	1.723 (5)	1.736 (10)
C5–S	1.695 (8)	1.744 (10)
Ring internal angles, centered on named atoms (°)		
C2	110.2 (4)	110.1 (7)
C3	111.9 (6)	113.7 (9)
C4	113.0 (6)	113.3 (9)
C5	113.6 (5)	110.8 (7)
S	91.3 (3)	92.0 (5)

Finally, the complex is enantiomeric. In Figure 4.11 the complex and its mirror image is shown. The two are non-super-imposable.



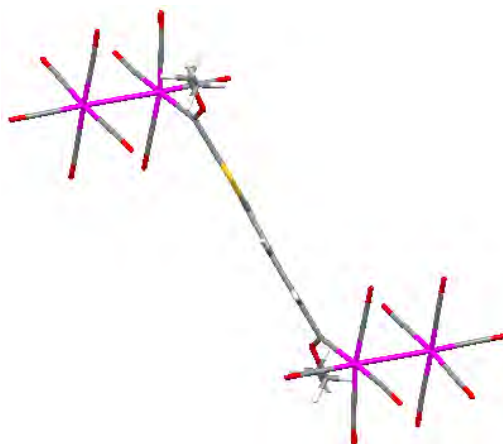
**Figure 4.11:** Stereo-isomers of **7**

The packing observed for this complex has the aromatic thiophene bridges of the biscarbene complexes far apart and  $\pi$ -stacking does not play a role.

#### 4.3.2 Complex 8

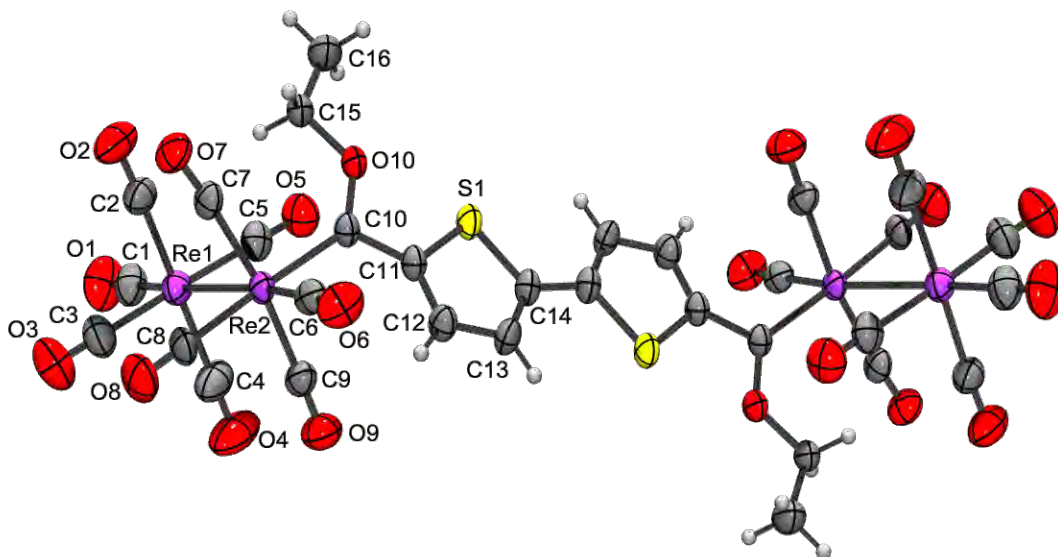
Complex **8** displays two carbene carbon atoms attached to the two sides of a bithiophene bridge. The composition of the complex is similar to **7**, but with a bithiophene, rather than a thiophene, bridge there is far more free space between the  $\{\text{Re}_2(\text{CO})_9\}$  and ethoxy fragments. The molecule has a centre of symmetry and the two sides are identical. The carbene ligands are equatorial ligands and the ethoxy groups are orientated on the same side as the sulfur atoms of the rings. They also have the electron-pairs of the oxygen atoms directed towards the rings.

A view of the complex is given below in Figure 4.12. In this view one observes the bithiophene side-on. With the space afforded by the bithiophene, one could also have expected a complex where the two  $\{\text{Re}_2(\text{CO})_9\}$  fragments are on the same side of the bithiophene plane. A rotation around the carbene-ring carbon bond would place them on the same side, but then the ethoxy substituent would not be on the sulfur side of the ring any more.



**Figure 4.12:** Complex view: end-on view of bithiophene carbene substituent

The structure of **8** is shown in Figure 4.13 and crystal data for this complex is given in Table 4.6a and 4.6b.



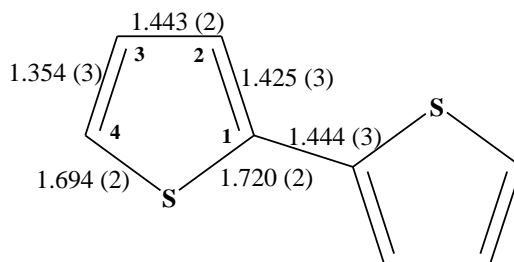
**Figure 4.13:** Molecular structure of **8**



**Table 4.6a:** Complex **8** bond lengths (Å)

Carbene distances			
C10–Re2	2.121 (5)	C10–C11	1.470 (6)
C10–O10	1.319 (6)		
Thienyl bond distances			
C11–C12	1.359 (7)	C13–C14	1.360 (7)
C12–C13	1.398 (7)	C14–C14'	1.452 (9)
Other bonds			
O10–C15	1.440 (5)	Re1–Re2	3.1422 (4)
C15–C16	1.491 (7)		
Re–CO bond lengths			
Re–CO <sub>avg</sub> of <i>eq</i> – Re(CO) <sub>5</sub>	1.990 (7)	Re–CO <sub>avg</sub> (Re(CO) <sub>4</sub> <i>trans</i> –CO carbonyls)	1.989 (6)
<i>ax</i> –CO of Re(CO) <sub>5</sub>	1.938 (6)	<i>ax</i> –CO of Re(CO) <sub>4</sub>	1.908 (5)
Re(CO) <i>trans</i> carbene	1.991 (5)		

The structure of bithiophene was determined<sup>10</sup> and the values are shown below. It has a predominantly transoid structure and the long C1–C2 bond is an artifact of disorder. The two rings are planar.



**Figure 4.14:** Bond distances of 2,2'-bithiophene (Å)

<sup>10</sup> P. A. Chaloner, S. R. Gunatunga, P. B. Hitchcock; *Acta Cryst.*, **1994**, C50, 1941–1942

The bithiophene substituent in this complex has a C12–C13 bond that is significantly shorter than the equivalent bond in bithiophene, which indicates that there is more electron density in the bond.

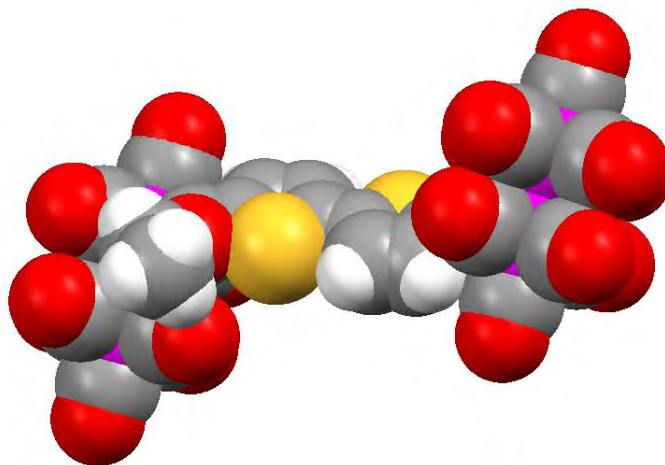
The internal ring bond angles centered on the atoms are: S (92.20 (9)°), C1 (112.3 (1)°), C2 (108.3 (2)°), C3 (114.8 (2)°) and C4 (112.4 (1)°) and for the ring with the carbene the equivalent internal angles in complex **8** are 91.5 (2)°, 111.1 (3)°, 113.1 (5)°, 114.0 (4)°, 110.2 (3)°, respectively. It can be seen that some of the angles are significantly distorted.

**Table 4.6b:** Torsional angles of **8** (°)

Carbene plane twist relative to equatorial CO ligands			
O10–C10–Re2–C7	20.0 (5)	C11–C10–Re2–C7	22.4 (4)
O10–C10–Re2–C9	26.4 (5)	C11–C10–Re2–C9	28.8 (4)
Thienyl rings deviation out of the carbene plane			
S1–C11–C10–Re2	18.6 (2)	C12–C11–C10–Re2	19.9 (7)
S1–C11–C10–O10	20.4 (5)	C12–C11–C10–O10	21.7 (5)
Ethoxy twist out of the carbene plane			
C15–O10–C10–Re2	4.6 (7)	C15–O10–C10–C11	2.5 (4)
Ethoxy with respect to thienyl substituent			
O10–C10–C11–S1	20.4 (5)	O10–C10–C11–C12	21.7 (5)

The complex differs from **7** in a few aspects. Primarily, the two sides of the complex are identical. If lines were drawn along the Re–Re bonds, they would be parallel. The image in Figure 4.15 illustrates the orientation of the {Re<sub>2</sub>(CO)<sub>9</sub>} fragments. The equatorial carbonyl ligands of the dirhenium parts eclipse each other (as viewed along the metal–metal bonds). It is rare for {Re<sub>2</sub>(CO)<sub>9</sub>} complexes and is a higher–energy conformation for carbonyl ligands to adopt. As a consequence a Re–Re bond lengthening was observed. From the structure it is clear that this unfavourable conformation results from the ethyl groups that wedge into the open space between the equatorial carbonyls of two rhenium atoms. This can be seen more clearly from the space–filled representation of the

structure shown in Figure 4.15. Other conformational features associated with the ethoxy substituents place them in ideal positions.



**Figure 4.15:** View of **8** showing carbonyl orientations

The extra thiophene ring places the metal–carbonyl fragments farther apart and creates more space for the carbene substituents. One can see in this complex (**8**) that the two ethoxy carbene substituents are more coplanar with the bithiophene than the ethoxy groups of **7** are in the plane of the thiophene.

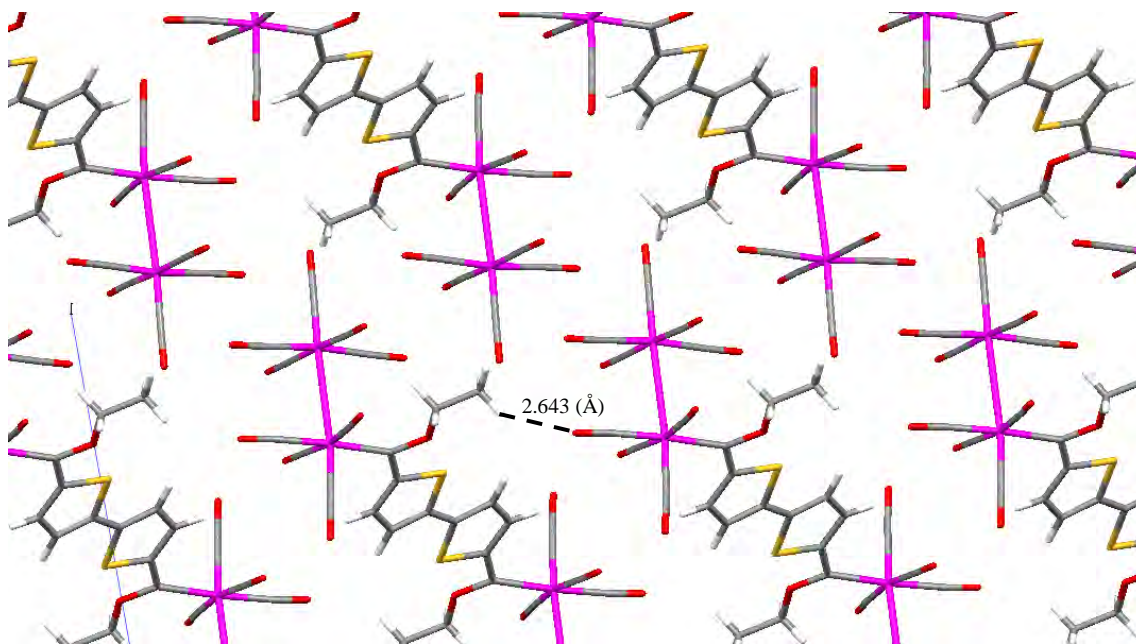
Torsional angle data show that the carbene with its substituents is twisted with respect to the equatorial carbonyl ligands that are *cis* to it by an angle of 20 to 29°. The thienyl substituent is twisted with respect to the carbene plane by an angle of about 20° and the ethoxy substituent is more in the plane of the carbene ligand. It is internally twisted by 17°.

The complex has the longest Re–Re bond length of **1**, **3**, **7** and **8** and therefore the equatorial carbonyl ligands on the two rhenium atoms are farther apart from each other, in this complex than in the other complexes. This would reduce their steric conflict of being in the eclipsed conformation.

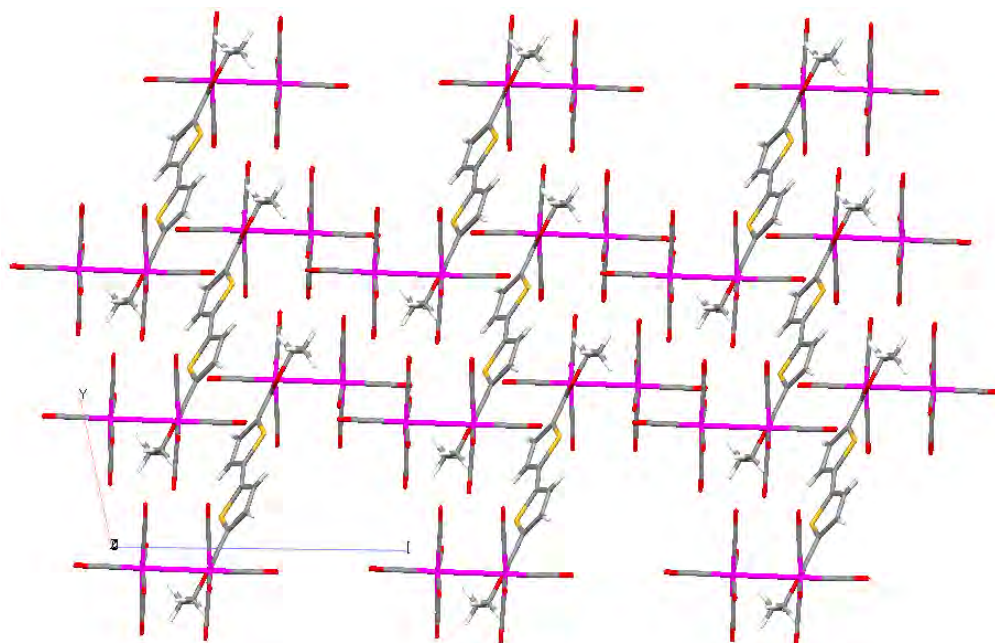
The Re–C bond lengths of the equatorial carbonyl ligands of the complex are all the same length, within experimental error. The axial CO ligands have shorter Re–C bond lengths and the shortest of all is the Re–CO<sub>ax</sub> bond of the fragment bearing the carbene ligand.

The closest atoms of the bithiophene bridges are separated from each other in the crystal by about 4 Å (C2–S) and  $\pi$ -stacking is not a determining factor in the packing of the complex molecules. This complex is unique in that the carbonyl ligands on the rhenium atoms are eclipsed. The positioning of the ethoxy group may also be supported by hydrogen-bonding interaction with a neighbouring complex molecule in the crystal structure. One of the ethoxy CH<sub>3</sub> hydrogen atoms is 2.64 Å from the carbonyl ligand oxygen atom on a neighbouring molecule (the carbonyl that is *trans* to the carbene carbon atom). The crystal packing, as viewed along the three axes, is shown below:

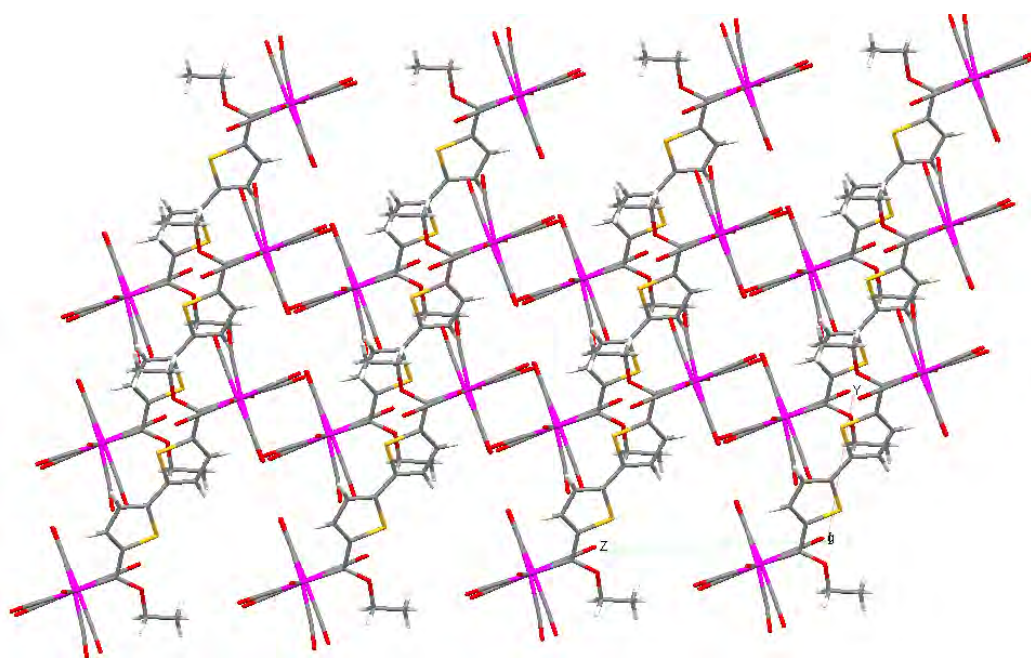
(a)



(b)



(c)



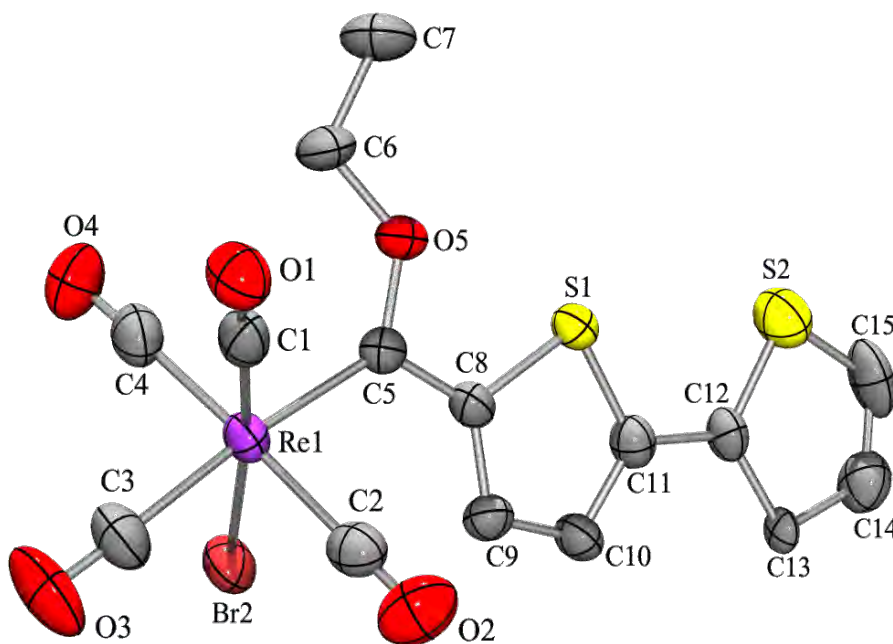
**Figure 4.16:** Packing of **8** observed along a, b and c axes

## 4.4 Monorhenium monocarbene complexes

### 4.4.1 Complex 5

The structure features a carbene carbon with three attached groups – a  $\{\text{Re}(\text{CO})_4\text{Br}\}$  metal fragment, an ethoxy substituent and a bithienyl aromatic substituent. The ethoxy substituent is orientated to the sulfur side of the ring and it is situated with the oxygen lone pairs directed towards the ring.

An interesting feature of the complex is the thienyl rings of the bithiophene substituent which are orientated with the sulfur atoms on the same side. However, there is uncertainty about the positioning of the second ring. The second (“S2”) ring is disordered. Its site occupation factors are 78.0(6) % and 22.0(6) %. The minor orientation of the ring represents a rotation of approximately  $180^\circ$  around the external C–C bond. The crystal structure of the complex is shown in Figure 4.17 and some of the bond distances and angles for the complex are given in Tables 4.7a and 4.7b.



**Figure 4.17:** Molecular structure of **5**

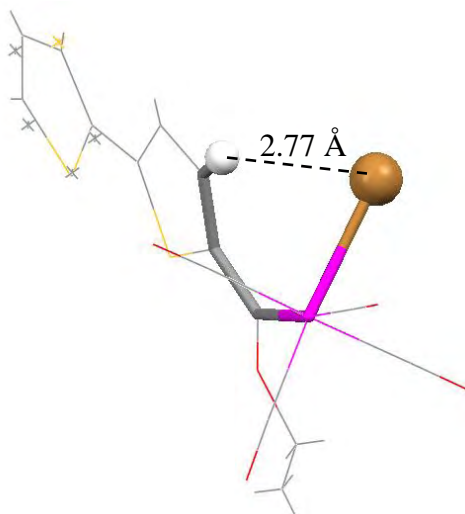
The C–C bond lengths of the thienyl ring with the carbene attached are the same lengths, within experimental error. This bond–equalization is due to delocalization of electron density. For the second thienyl ring it is only the C14–C15 bond that displays a significantly longer value, but this distance is the same as the corresponding distance C10–C11 in the first ring. The C8–C9 and C10–C11 distance is between the corresponding values for 2,2′–bithiophene and 5–formyl–2,2′–bithiophene.

**Table 4.7a:** Complex **5** bond lengths (Å)

Carbene bond distances			
C5–Re1	2.164 (4)	C5–C8	1.434 (6)
C5–O5	1.328 (4)		
Thienyl bond distances			
C8–S1	1.745 (4)	C12–S2	1.7466
C8–C9	1.383 (5)	C12–C13	1.3774
C9–C10	1.380 (5)	C13–C14	1.3770
C10–C11	1.392 (5)	C14–C15	1.3970
C11–S1	1.709 (4)	C15–S2	1.7038
C11–C12	1.444 (6)		
Other bond distances			
O5–C6	1.435 (5)	Re1–Br2	2.6365 (5)
Re–CO bond lengths			
Re–CO <sub>avg</sub> ( <i>trans</i> to CO)	2.005 (5)	Re–CO <sub><i>trans</i>–Br</sub>	1.924 (5)
Re–CO <sub><i>trans</i>–carbene</sub>	2.000 (5)		

The carbonyl ligands are all equally far from the metal, except for the carbonyl ligand that is *trans* to the bromide ligand, which has a shorter Re–C bond distance than the others in **5**. Its value is closer to the mean value for a terminal CO ligand (1.936 Å).

There is a possibility of hydrogen bonding to the bromo ligand from the hydrogen atom at position 3 of the bithiophene ring. The non-bonding H3–Br distance is 2.77 Å, a value that falls in the range of a hydrogen bond.



**Figure 4.18:** Hydrogen bonding between H3 and bromo ligand

The Re–Br distance of 2.6365 (5) Å is longer than the mean value of 2.573 Å<sup>7</sup> and also longer than the Re–Br bond (2.606 (2) Å) of an equivalent cyclic dioxycarbene complex prepared by Angelici<sup>11</sup>.

Unfortunately, suitable crystals could not be obtained for a structure determination of uncleaved complex **2**. One could speculate about the structure of complex **2** – and assume that the two complexes look very similar except that **2** has a {Re(CO)<sub>5</sub>} ligand, where **5** has a bromo ligand. It is likely that the bithiophene substituent lies at the same place than it does in this complex, but that it is more twisted out of the carbene plane (see next structure discussion for details). The loss of a bulky Re(CO)<sub>5</sub> group allows for better positioning of the hetero–aromatic ring, in a way that promotes conjugation. Therefore the substituent can contribute more to carbene stabilization and therefore a more shielded

<sup>11</sup> G. L. Miessler, S. Kim, R. A. Jacobson, R. J. Angelici; *Inorg. Chem.*, **1987**, 26, 1690–1695



carbene carbon atom and a shift to higher field strength in the  $^1\text{H}$  NMR spectrum is observed (Tables 3.1 and 3.3).

**Table 4.7b:** Torsional angles of **5** ( $^\circ$ )

Carbene plane deviation relative to equatorial CO ligands			
O5–C5–Re1–C2	45.5 (3)	C8–C5–Re1–C2	43.0 (3)
O5–C5–Re1–C4	46.4 (3)	C8–C5–Re1–C4	43.9 (3)
Thienyl twist out of the carbene plane			
S1–C8–C5–Re1	5.0 (19)	C9–C8–C5–Re1	8.3 (6)
S1–C8–C5–O5	2.9 (4)	C9–C8–C5–O5	6.2 (4)
Ethoxy twist out of the carbene plane			
C6–O5–C5–Re1	4.0 (5)	C6–O5–C5–C8	1.8 (4)
Ethoxy with respect to thienyl substituent			
S1–C8–C5–O5	2.9 (4)	C9–C8–C5–O5	6.2 (4)
Ethoxy twist			
C5–O5–C6–C7	0.9 (4)		
Planarity of the thiophene rings			
S1–C11–C12–S2	3.3 (8)	S2–C12–C11–C10	2.9 (4)
S1–C11–C12–C13	1.5 (3)	C10–C11–C12–C13	1.1 (8)

As was the case for most of the other structures, the orientation of the ethoxy group is such that the two lone pairs of the oxygen are orientated away from the metal towards the thienyl group. The ethoxy carbene substituent is almost completely flat, being internally bent by an angle of less than  $1^\circ$ . This contrasts with what was seen with the other complexes' (that have been discussed) ethoxy substituents and suggests a sterically less hindered situation.

The orientation of the carbene ligand is shown below. In the Angelici cyclic dioxycarbene complex the carbene ligand is twisted with respect to the plane defined by

the carbonyl ligands *cis* to the bromo ligand by an angle of 51.8 °. The two rings of the bithienyl substituent are coplanar.

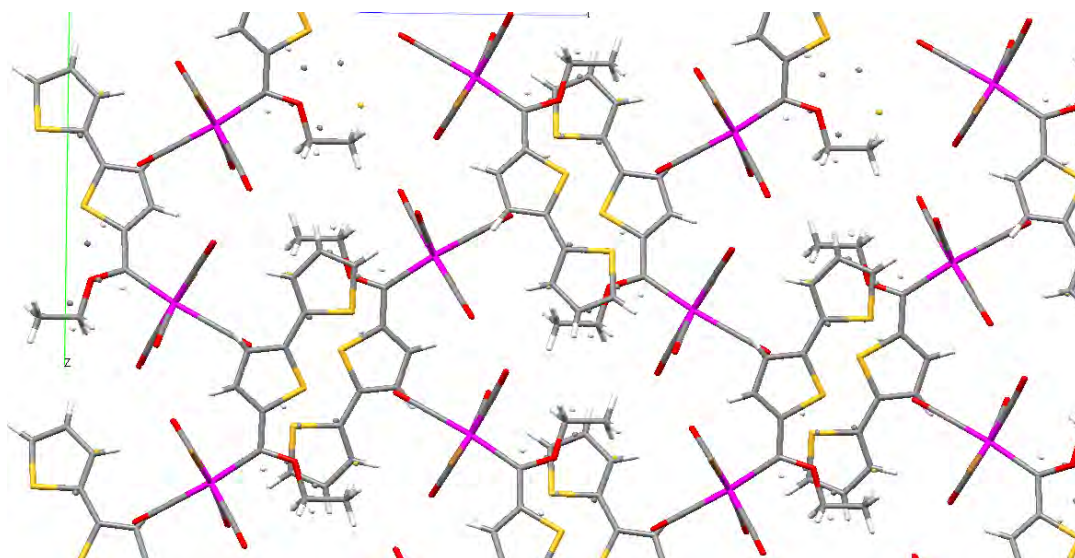


**Figure 4.19:** Carbene orientation with respect to the carbonyl ligands

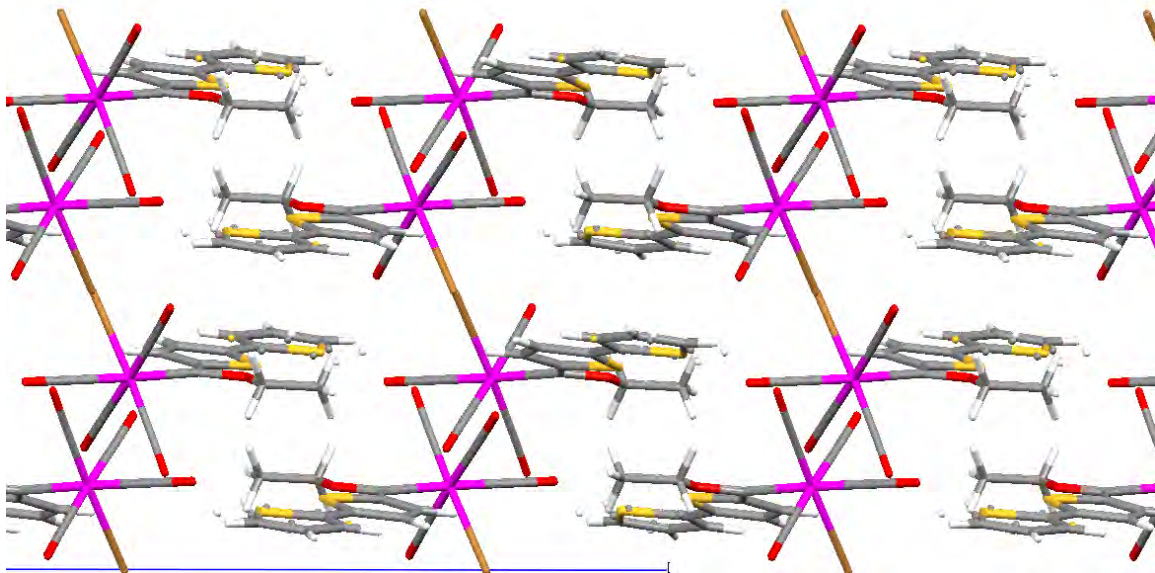
Internal angles of the thiophene ring with the carbene attached are 91.99 (18)° (S1), 109.6 (3)° (C8), 114.4 (3)° (C9), 112.5 (4)° (C10) and 111.5 (3)° (C11). There is a slight distortion within the ring.

In the following figure the views of the molecular packing in the crystal is provided.

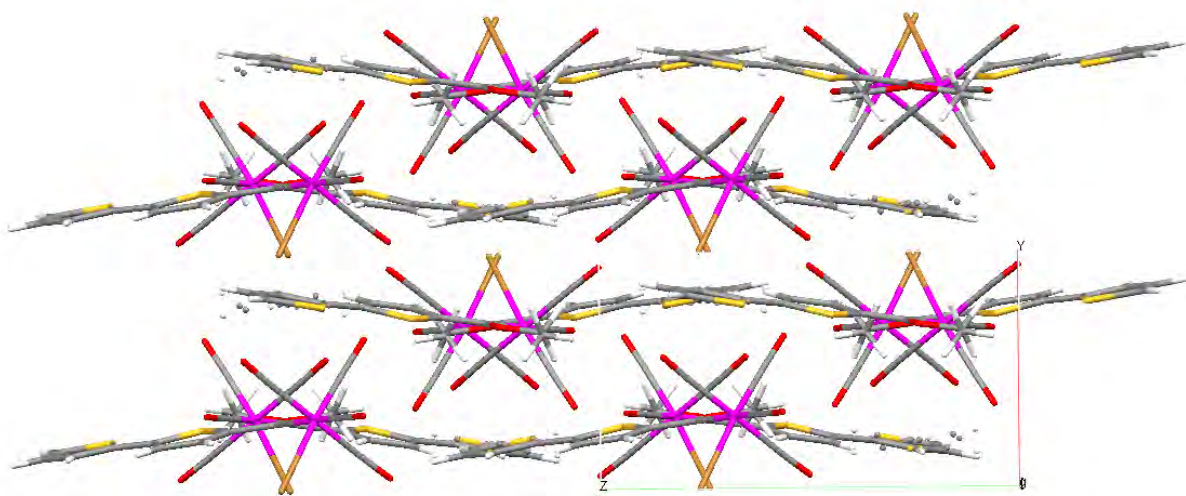
(a)



(b)



(c)



**Figure 4.20:** Packing of 5 observed along a, b and c axes

Distances between ring atoms of the thienyl substituents of complexes that lie next to each other in the crystal are quite large and indicate that  $\pi$ -stacking is not important in determining the packing of the molecules.

#### 4.4.2 Complex 6

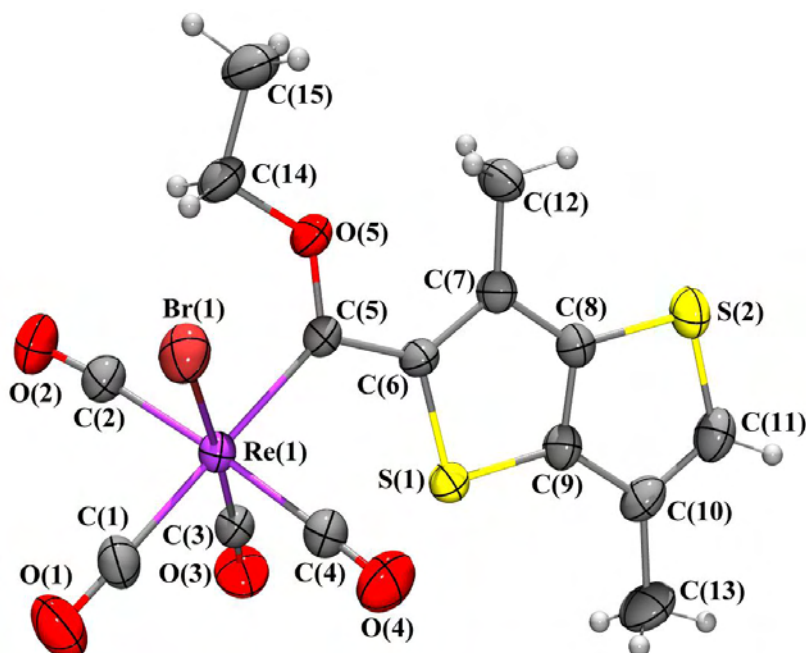
The complex consists of a carbene carbon with these three groups attached:  $\{\text{ReBr}(\text{CO})_4\}$ , 3,6-dimethylthieno[3,2-*b*]thiophene and  $\{\text{OCH}_2\text{CH}_3\}$ . The bromo ligand is *cis* to the carbene ligand with little distortion of the octahedral arrangement of ligands.

Interestingly, the ethoxy substituent in this complex is situated on the opposite side of the ring, away from the sulfur atom of the ring and one can ascribe this to less steric hindrance between the substituent and the ring methyl (C12) than there would be between the metal fragment and the ring methyl. This complex is similar to a chromium complex prepared by Landman et al<sup>12</sup>. In this complex of 3,6-dimethylthieno[3,2-*b*]thiophene, the ethoxy substituent assumes a similar position (on the side of the methyl of the ring) and the ethyl part is also positioned away from the methyl, as in this complex. The structure of the complex is shown in Figure 4.21 and some bond distances and angles are given in Tables 4.8a and 4.8b.

The carbene–O bond is significantly shorter than the ethoxy O–CH<sub>2</sub> bond (1.456 (6) Å), once again pointing to a degree of double bonding between the carbene and the oxygen atom. The bond between the carbene and the carbon of the thienyl substituent (C5–C6) is slightly shorter than the bonds between the ring methyls and the carbon atoms (C7–C12, C10–C13) to which they are attached. This seems to suggest that the bond between the carbene and the aromatic substituent displays some double bond character but is mostly a single bond, based on bond length. The CH<sub>2</sub>–CH<sub>3</sub> bond length of the ethoxy substituent is 1.502 (8) Å, making the three C–C single bonds of the complex (the other two are the ring–methyl bonds) all the same length, within experimental error.

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<sup>12</sup> M. Landman, H. Görls, S. Lotz; *Eur. J. Inorg. Chem.*, **2001**, 233–238



**Figure 4.21:** Molecular structure of **6**

All the C–C bonds of the aromatic rings are shorter than the C5–C6 bond, and the shortest of them is C10–C11, which is the double bond farthest away from the carbene. The longest distance in the thienyl rings is between C9 and C10. The second thienyl ring is more typical – with a shorter and a longer bond. It is interesting to see that not all of the ring carbon–sulfur bonds are the same length. The inner C–S bonds C4–S2 and C5–S1 are the shortest and the longest is C2–S1. It is assumed that the carbene takes electron density out of the C2–S1 bond, causing it to be lengthened. The bond lengths of the thienyl substituents of complex **3** and **6** are very similar.

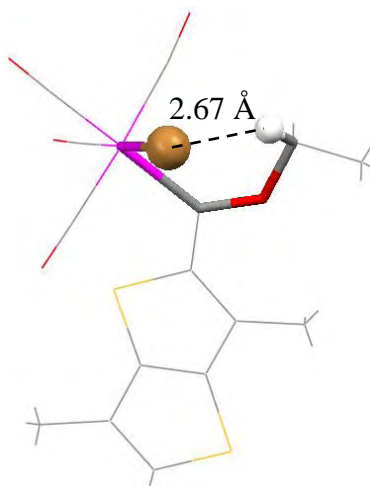
The Re–Br bond of 2.6383 (5) Å is slightly longer than the Re–Br bond of complex **5**. The Re–C bond distance *trans* to the bromide ligand, is significantly shorter (1.914 (5) Å) than the corresponding distance (2.000 (5) Å; average) of rhenium carbonyl ligands *trans* to carbonyls. It shows that the metal back–donates more electron density into the  $\pi^*$  orbital of this ligand (the bromide ligand is not a  $\pi$ –acceptor and does not compete with the CO ligand for electron density). The Re–C bond distance of the carbonyl ligand that

is *trans* to the carbene ligand is slightly shorter (1.980 (6) Å) than the Re–C distance of carbonyl ligands *trans* to a carbonyl ligand.

**Table 4.8a:** Complex **6** bond lengths (Å)

Carbene bond distances			
C5–Re1	2.166 (5)	C5–C6	1.447 (6)
C5–O5	1.319 (6)		
Thienyl bond distances			
C6–S1	1.757 (4)	C8–S2	1.725 (5)
C6–C7	1.403 (6)	C9–C10	1.423 (6)
C7–C8	1.402 (6)	C10–C11	1.348 (8)
C7–C12	1.490 (6)	C10–C13	1.498 (8)
C8–C9	1.385 (7)	C11–S2	1.731 (6)
C9–S1	1.716 (5)		
Metal–ligand bond distances			
Re–Br	2.6383 (5)		
Re–CO bond lengths			
Re–CO <sub>avg</sub> ( <i>trans</i> to CO)	2.000 (5)	Re–CO <sub><i>trans</i>-Br</sub>	1.914 (5)
Re–CO <sub><i>trans</i>-carbene</sub>	1.980 (6)		

There is a possibility of hydrogen bonding between the bromo ligand and a hydrogen atom of the ethoxy substituent. The distance between them is only 2.67 Å and is shown in Figure 4.22. This hydrogen bonding would also contribute to the positioning taken by the ethoxy substituent.



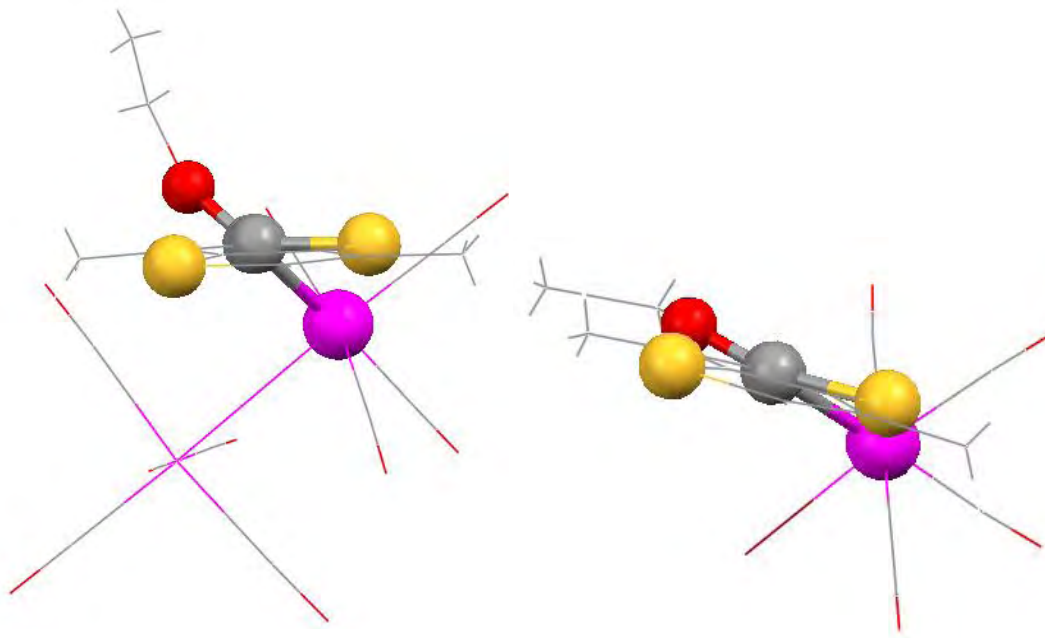
**Figure 4.22:** Hydrogen bonding between H14 and bromo ligand

**Table 4.8b:** Torsion angles of **6** (°)

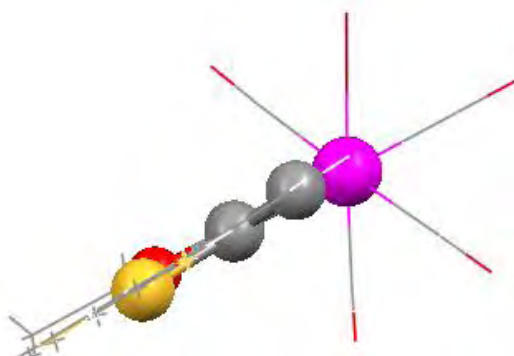
Carbene plane deviation relative to cis equatorial CO ligands			
O5–C5–Re1–C2	36.5 (5)	C6–C5–Re1–C2	34.1 (4)
O5–C5–Re1–C4	41.4 (4)	C6–C5–Re1–C4	39.0 (4)
Thienyl twist out of the carbene plane			
S1–C6–C5–Re1	16.5 (6)	C7–C6–C5–Re1	19.3 (4)
S1–C6–C5–O5	14.5 (3)	C7–C6–C5–O5	17.3 (7)
Ethoxy twist out of the carbene plane			
C14–O5–C5–Re1	2.2 (7)	C14–O5–C5–C6	0.1 (4)
Ethoxy substituent with respect to thienyl substituent			
O5–C5–C6–S1	14.5 (3)	O5–C5–C6–C7	17.3 (7)
Ethoxy substituent twist			
C5–O5–C14–C15	20.2 (5)		

In Figure 4.23, the deviations of the thienyl plane out of the carbene plane (defined by the oxygen of the ethoxy substituent and the metal) can clearly be seen. The oxygen lies above and the rhenium below this plane, with the aromatic substituent in front, as viewed. The aromatic ring substituent deviates more out of the carbene plane in the case of

uncleaved complex **3** than in the case of **6**. For bithiophene complex **5** the correspondence is even closer, as is shown below – Figure 4.24.



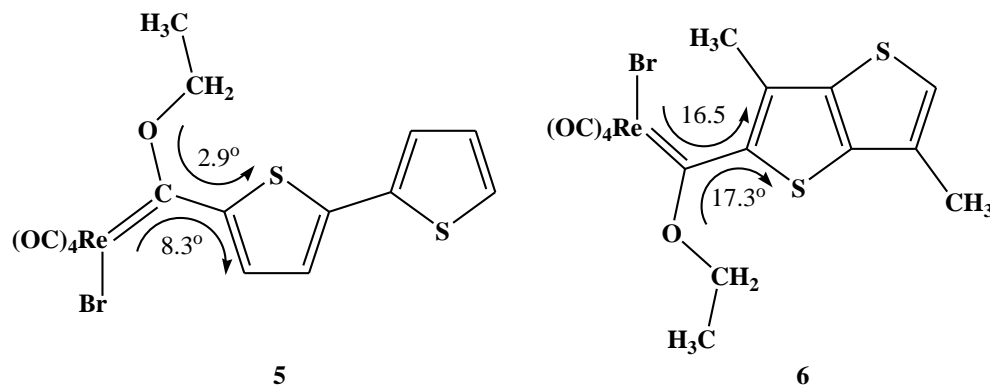
**Figure 4.23:** Showing twist angle of aromatic substituent in **3** and **6**



**Figure 4.24:** Showing twist angle of aromatic substituent in complex **5**

The difference in the relative twist can also be seen from the dihedral angles of **5** and **6**, shown in Figure 4.25.





**Figure 4.25:** The carbene substituents in **5** are closer to coplanarity than those of **6**

The packing of the molecules in the crystal of **6** are different from the packing of **3**. With the molecules of this complex – in the crystal – the thienyl substituents are too far apart to consider  $\pi$ -stacking as a determining factor in how the complex molecules have assembled. No atoms that could hydrogen-bond to each other are close enough for such bonding.

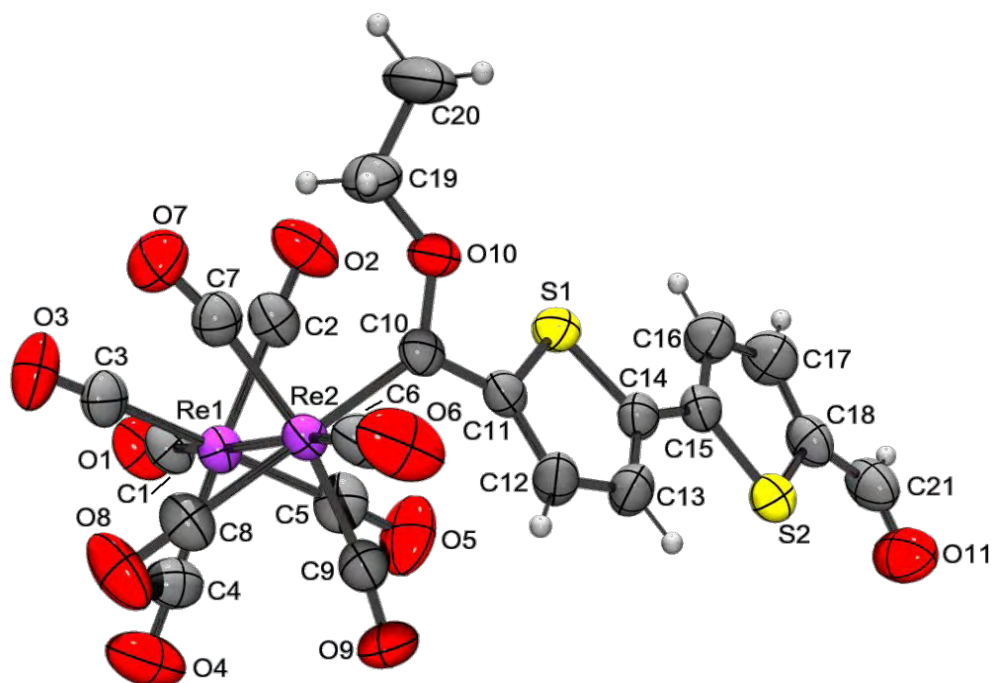
## 4.5 Dirhenium monocarbene aldehyde complex

### 4.5.1 Complex 13

The complex displays a carbene carbon atom with dirhenium nonacarbonyl, an ethoxy and the 9-formyl-bithiophene substituent attached to it. The carbonyl ligands in the equatorial planes of the two rhenium atoms are in the favoured staggered conformation. The ethoxy substituent is on the side of the sulfur atom of the thienyl ring as is found for most complexes of this kind<sup>13</sup>. The metals have an octahedral arrangement of ligands with the greatest deviation from linearity by the two carbonyls *cis* to the carbene ligand ( $C6-Re2-C7 = 92.6 (2)^\circ$ ;  $C6-Re2-C9 = 93.6 (2)^\circ$ ).

The structure is shown in Figure 4.26 and the data given in Tables 4.9a and 4.9b.

<sup>13</sup> S. Lotz, C. Crause, A. J. Olivier, D. C. Liles, H. Görls, M. Landman, D. I. Bezuidenhout; *Dalton Trans.*, **2009**, 697–710



**Figure 4.26:** Crystal structure of **13**

The carbon–carbon bonds of the first ring are not all the same length – C11–C12 and C13–C14 are shorter than C12–C13. The carbon–carbon bonds are for the second ring, however, all the same length, within experimental error. The carbon–sulfur bonds of the rings are the same length within experimental error, except for C11–S1, which is longer than the other C–S bonds.

The rhenium–rhenium bond is shorter than the Re–Re bond of complex **8** (from which this complex derives) and about the same as the rhenium–rhenium bond of the other complexes. All the equatorial carbonyl ligand metal–carbon bonds are the same length. The axial carbonyl ligands’ Re–C bonds are shorter, with the axial carbonyl of the metal fragment that also bears the carbene ligand, having the shortest bond.

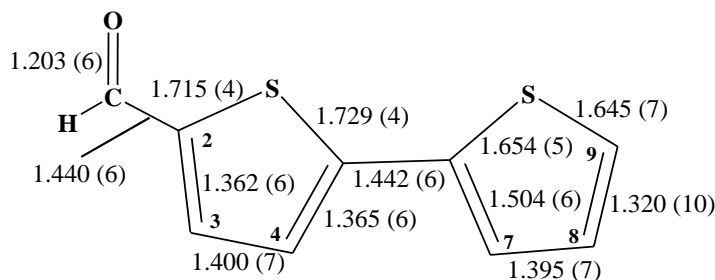
**Table 4.9a:** Complex **13** bond lengths (Å)

Carbene bond distances			
C10–Re2	2.117 (4)	C10–C11	1.460 (6)
C10–O10	1.323 (5)		
Aldehyde functionality bond distances			
C21–O11	1.186(7)	C18–C21	1.456 (7)
Aromatic substituent C–C bond distances			
C11–C12	1.373 (6)	C15–C16	1.370 (6)
C12–C13	1.400 (7)	C16–C17	1.387 (7)
C13–C14	1.360 (6)	C17–C18	1.374 (8)
C14–C15	1.453 (6)		
Carbon–sulfur bond distances			
C11–S1	1.737 (4)	C15–S2	1.712 (5)
C14–S1	1.716 (4)	C18–S2	1.715 (5)
Ethoxy substituent bonds			
O10–C19	1.445 (6)	C19–C20	1.513 (7)
Metal–metal bond			
Re1–Re2	3.0770 (3)		
Re–CO bond distances			
Re–CO <sub>avg</sub> of eq– Re(CO) <sub>5</sub>		Re–CO <sub>avg</sub> (Re(CO) <sub>4</sub> <i>trans</i> –CO carbonyls)	1.983 (5)
ax–CO of Re(CO) <sub>5</sub>	1.934 (5)	ax–CO of Re(CO) <sub>4</sub>	1.917 (5)
Re–CO <sub><i>trans</i></sub> –carbene	1.978 (5)		

The structure of 5–formyl–2,2′–bithiophene was determined<sup>14</sup> and the bond distances are shown below. The molecule has a predominantly *cisoid* structure and the two rings and aldehyde are almost coplanar. In complex **13**, the bond lengths of the ring with the

<sup>14</sup> S. P. Armes, P. A. Chaloner, P. B. Hitchcock, M. R. Simmons; *Acta Cryst.*, **1994**, C50, 1945–1947

aldehyde are not meaningfully different from the analogous bonds of the thiophene ring with the aldehyde of 5-formyl-2,2'-bithiophene. The aldehyde functionality of 5-formyl-2,2'-bithiophene also causes a distortion of the ring bond lengths of the ring to which it is attached (compared to bithiophene). The same was seen in the case of bithiophene monocarbene complex **5**, which is also predominantly cisoid.



**Figure 4.27:** Bond distances of 5-formyl-2,2'-bithiophene (Å)

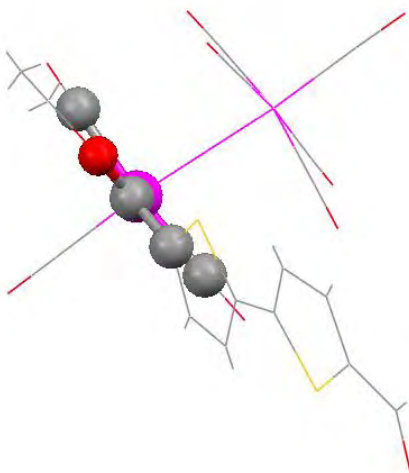
Three connecting carbon-carbon bonds can be seen in **13**, they are the bonds between the two rings and between the pendant carbene and aldehyde functions on the rings. These bonds are remarkably similar in bond length. Furthermore, the carbon-carbon bond lengths of the ring with the aldehyde attached are the same as the equivalent bonds of the ring with the carbene attached.

The double bonding between the carbene carbon atom and the oxygen and the aldehyde carbon atom and oxygen atom is clearly seen upon comparing C10-O10 (1.323 (5) Å) and C21-O11 (1.186 (7) Å) – the latter bond is shorter. This bond length does not differ significantly from the aldehyde C-O bond length of 5-formyl-2,2'-bithiophene or from the mean value for this type of bond: 1.192 Å<sup>5</sup>. Looking at the two bonds of the ethoxy oxygen atom, one sees that the carbene-O bond is definitely shorter than the O-CH<sub>2</sub>CH<sub>3</sub> bond (1.445 (6) Å). It was also observed for the other complexes.

**Table 4.9b:** Selected bond torsion angles of **13** (°)

Carbene plane twist relative to cis equatorial CO ligands			
O10–C10–Re2–C7	2.8 (4)	C11–C10–Re2–C7	6.7 (4)
O10–C10–Re2–C9	4.0 (4)	C11–C10–Re2–C9	0.1 (4)
Thienyl twist out of the carbene plane			
S1–C11–C10–Re2	30.8 (2)	C12–C11–C10–Re2	35.1 (6)
S1–C11–C10–O10	27.8 (4)	C12–C11–C10–O10	32.1 (5)
Ethoxy twist out of the carbene plane			
C19–O10–C10–Re2	7.3 (7)	C19–O10–C10–C11	3.9 (4)
Ethoxy with respect to thienyl			
O10–C10–C11–S1	27.8 (4)	O10–C10–C11–C12	32.1 (5)
Aldehyde twist with respect to thienyl substituent			
O11–C21–C18–S2	5.0 (8)	O11–C21–C18–C17	3.4 (6)
Ethoxy internal twist			
C10–O10–C19–C20	3.4 (5)		

The carbene plane is close to being coplanar with the plane of the other equatorial ligands of the rhenium (the one of which the carbene is a ligand – see Figure 4.28).

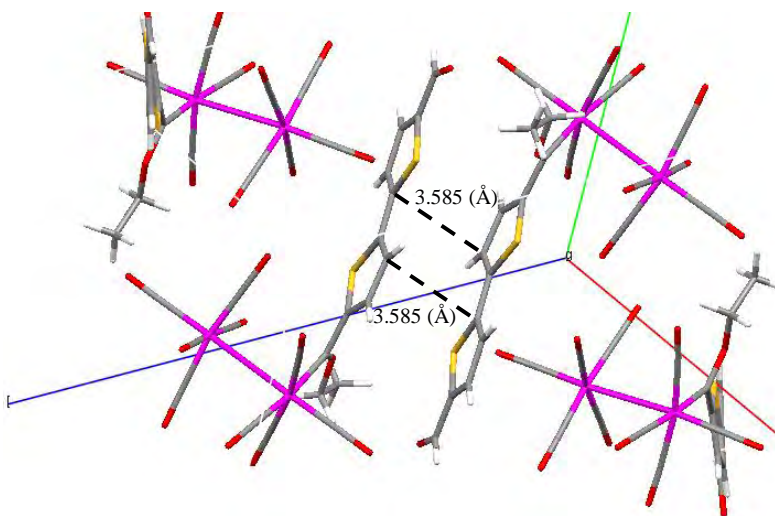


**Figure 4.28:** Coplanarity of carbene plane with equatorial ligands' plane

The two aromatic rings (they are coplanar) are twisted around the bond to the carbene and the angle between their plane and that of the carbene is roughly  $30^\circ$ . The ethoxy group is close to being coplanar with the carbene plane and is only slightly twisted out of the carbene plane.

The carbonyl ligand that is next to the ethoxycarbene substituent is pushed away by  $\sim 10^\circ$ . The other one has more space (bithiophene rings are twisted out of the carbene plane) and is twisted away by only  $\sim 7.5^\circ$ . The axial carbonyl ligand is almost straight. Besides steric crowding, there is also an electronic reason for these two carbonyl ligands to be bent – the carbene ligand  $\pi$ -interacts with one of the two d-orbitals that  $\pi$ -interacts with the two *cis* carbonyl ligands causing an imbalance in charge distribution.

There is an indication that  $\pi$ -stacking played a determining factor in how the complex **13** molecules packed in the crystal structure. As the following image shows, the thiophene rings of the thienyl substituent lie approximately over each other and distances of about 3.5–3.7 Å are measured between closest ring carbon atoms. Hydrogen-bonding is not believed to have played a significant role in the crystal packing.

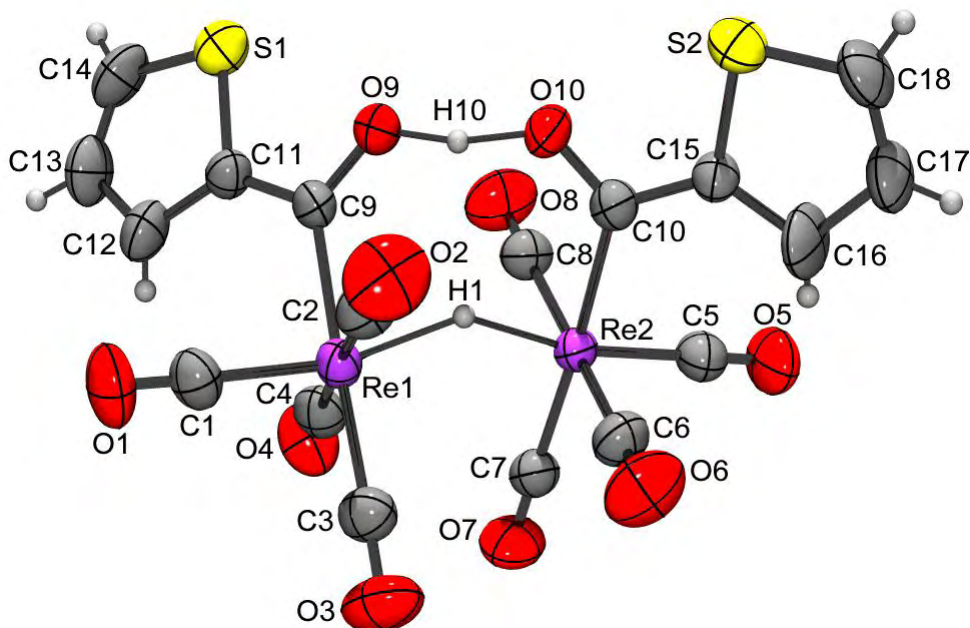


**Figure 4.29:** Crystal packing in **13**

## 4.6 Dirhenium bis-carbene/acyl complex

### 4.6.1 Complex 15

In this complex there are two rhenium atoms, each with one carbene/acyl-intermediate ligand. The rhenium atoms have only four other carbonyl ligands. The carbene/acyl ligands lie next to each other. The two fragments of the molecule are held together by bonds to two hydrogen atoms. One is located between the oxygen atoms of the carbene/acyl ligands. The other is located between the two rhenium atoms. An eight-membered ring, dirhenium metalla-cycle, is formed by the two metal atoms, the carbene acyl moieties/ligands and the bridging hydrogen atoms. The bridging hydrogen atoms place the acyl and carbene ligands in the same plane (C9–Re1–Re2–C10). The sulfur atoms of the thienyl rings are on the same side as the oxygen atoms of the acyl and hydroxycarbene ligands. The structure is shown in Figure 4.30 and the data of the complex is in Tables 4.10a and 4.10b.



**Figure 4.30:** Crystal structure of complex 15

**Table 4.10a:** Selected bond lengths of **15** (Å)

Carbene/acyl ligand bond distances			
C9–Re1	2.159 (4)	C10–Re2	2.173 (4)
C9–O9	1.271 (4)	C10–O10	1.283 (4)
C9–C11	1.456 (5)	C10–C15	1.444 (6)
Thienyl bond lengths			
C11–C12	1.429 (11)	C15–C16	1.414 (13)
C12–C13	1.392 (10)	C16–C17	1.440 (13)
C13–C14	1.322 (8)	C17–C18	1.310 (8)
C11–S1	1.739 (4)	C15–S2	1.722 (4)
C14–S1	1.671 (7)	C18–S2	1.687 (7)
O–H bond lengths			
O9–H10	1.19 (7)	O10–H10	1.26 (7)
Re–ligand bond lengths			
Re1–Re2	3.3622 (2)	Re2–H1	1.79 (4)
Re1–H1	1.77 (4)		
Re–CO bond distances			
Re–CO <sub>avg</sub> ( <i>trans</i> CO)	1.989 (5)	Re2–CO <sub>avg</sub> ( <i>trans</i> CO)	1.992 (4)
Re1–CO <sub>trans</sub> –carbene	1.977 (4)	Re2–CO <sub>trans</sub> –carbene	1.971 (4)
Re1–CO <sub>trans</sub> –hydride	1.926 (4)	Re2–CO <sub>trans</sub> –hydride	1.937 (4)

Both of the thiophene rings are disordered, but the “S1” ring is disordered only to a very small extent (major orientation: 94.3 (6) %). For the “S2” ring it is 88.3 (6) % (major orientation) and 11.7 (6) % (minor orientation).

The two Re–C (carbene, acyl) bonds are the same length, within experimental error. The same applies to the carbene (acyl) – oxygen bonds and also to the bonds to the bridging hydrogen atoms (the hydrogen atoms could be located). This shows that, even though the two components are regarded as an 18–electron hydroxycarbene hydride complex and a



16-electron acyl carbonyl complex, in this complex there are two resonance structures of equal importance.

The carbene–rhenium bond length of **1** is 2.125 (5) Å, a shorter bond than the rhenium–carbon (carbene, acyl) bonds of 2.159 (4) Å and 2.173 Å for **15**. On the other hand, the carbene/acyl–oxygen bonds of this complex are much shorter than the carbene–oxygen bond of complex **1**. The bonds to the thienyl ring are the same for the two complexes **1** and **15**.

The distance between the two rhenium atoms is longer than the Re–Re bond distance of complex **1** (3.0899 (3) Å) by about 0.27 Å. Formally there is no bond between the two metals. The 16-electron [Re(CO)<sub>4</sub>{C(O)T}] fragment receives electron density from the other rhenium and the hydrogen (hydride). This represents a three-center, two-electron bond. The other Re fragment is an 18-electron species: [Re(CO)<sub>4</sub>H{C(OH)T}] and do not require a bond to another Re atom.

Even though the determination of the bond lengths to the bridging hydrogen atoms H1 and H10 is not precise, one can still see that the distances between the oxygen atoms and H10 is shorter than the distances between the rhenium atoms and bridging hydride H1. This is due to rhenium being bigger than oxygen. Due to experimental error one cannot say conclusively that the Re–H bonds are shorter than the mean value of 1.832 Å<sup>7</sup>.

Of all the carbonyl ligands of Re1, the one that is *trans* to the hydride ligand is significantly closer to the rhenium atom than the other carbonyl ligands. With Re2 the situation is the same, but the other carbonyl ligands are not equally close to the metal. Re2–C7O7 (*trans* to carbene) is shorter than Re2–C6O6 (*trans* to carbonyl).

The thiophene rings are close to being coplanar with the carbene planes, thus maximizing delocalization potential. Ring S2–C15–C16–C17–C18 is twisted slightly more out of the carbene plane than ring S1–C11–C12–C13–C14.

**Table 4.10b:** Selected torsion angles of **15** (°)


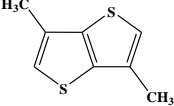

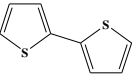
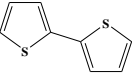
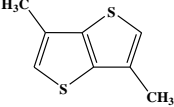
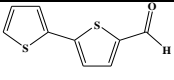

Carbene plane deviation relative to equatorial CO ligands			
O9–C9–Re1–C1	35.9 (3)	O10–C10–Re2–C5	34.5 (3)
C11–C9–Re1–C1	38.7 (3)	C15–C10–Re2–C5	32.3 (4)
Thienyl twist out of the carbene plane			
S1–C11–C9–Re1	0.3 (2)	S2–C15–C10–Re2	8.2 (2)
C12–C11–C9–Re1	0.6 (8)	C16–C15–C10–Re2	7.2 (11)
S1–C11–C9–O9	2.7 (5)	S2–C15–C10–O10	6.2 (5)
C12–C11–C9–O9	1.8 (7)	C16–C15–C10–O10	5.2 (9)
Hydroxy twist out of the carbene plane			
H10–O9–C9–Re1	3.1 (5)	H10–O10–C10–Re2	0.3 (9)
H10–O9–C9–C11	5.5 (7)	H10–O10–C10–C15	1.6 (11)

#### **4.7 Summary of bond parameters around the carbene carbon atoms for the complexes**

This section provides an overview of the structural features of the complexes.

In Table 4.11 the carbene–substituent bond lengths are given for the complexes. The first seven complexes that were discussed are all ethoxy carbene complexes and the carbene–OCH<sub>2</sub>CH<sub>3</sub> bonds are all the same length, within experimental error. Complex **15** has the shortest carbene–oxygen bonds, as expected as it represents the average of a C–O double bond (acyl) and a C–O (carbene) bond. These ligands of complex **15** have a dual nature, i.e. that of an acyl and a hydroxycarbene ligand. The carbene–C (thienyl) bonds of the eight complexes are also all the same length.

**Table 4.11:** Carbene–substituent bonds lengths (Å) and angles (°)

	R–group	Re=[C] <sup>*</sup> (Å) <i>Re–[C]–O</i> (°)	O–[C] (Å) <i>O–[C]–R</i> (°)	R–[C] (Å) <i>R–[C]–Re</i> (°)	Re–Re / Re–Br
<b>1</b>		2.125 <i>129.9 (4)</i>	1.335 <i>105.2 (4)</i>	1.461 <i>124.9 (4)</i>	3.0899 (3)
<b>3</b>		2.098 <i>117.4 (4)</i>	1.326 <i>116.4 (5)</i>	1.466 <i>126.1 (4)</i>	3.0468 (4)
<b>7</b>		2.093 <i>119.1 (7)</i>	1.303 <i>118.2 (9)</i>	1.476 <i>122.7 (7)</i>	3.0434 (6)
		2.076 <i>131.5 (6)</i>	1.338 <i>104.5 (8)</i>	1.480 <i>124.1 (7)</i>	3.0569 (7)
<b>8</b>		2.121 <i>131.8 (3)</i>	1.319 <i>105.6 (4)</i>	1.470 <i>122.6 (3)</i>	3.1422 (4)
<b>5</b>		2.164 <i>128.4 (3)</i>	1.328 <i>106.8 (3)</i>	1.434 <i>124.8 (2)</i>	2.6365 (5)
<b>6</b>		2.166 <i>128.0 (3)</i>	1.319 <i>106.5 (4)</i>	1.447 <i>125.4 (3)</i>	2.6383 (5)
<b>13</b>		2.117 <i>130.9 (3)</i>	1.323 <i>104.1 (3)</i>	1.460 <i>125.0 (3)</i>	3.0770 (3)
<b>15</b>		2.173 <i>122.1 (3)</i>	1.283 <i>113.1 (3)</i>	1.444 <i>124.8 (3)</i>	3.3622 (2)
		2.159 <i>123.6 (3)</i>	1.271 <i>111.9 (3)</i>	1.456 <i>124.4 (3)</i>	

\* [C] represents the carbene carbon atom

The metal–carbene bond lengths of the complexes are not all the same length. The Re–C (carbene) distances all fall in the range 2.076–2.166 Å. Some are shorter and some are longer than the mean value for an alkoxycarbene complex of rhenium – 2.098 Å. The

rhenium–carbene bond lengths of the [Re]Br complexes, and of the dirhenium hydride–bridged complex, are longer than that of the other carbene complexes. A possible explanation for this, in the case of the rhenium–bromo carbene complexes, may be that the other two carbene substituents are more involved in carbene stabilization and the metal is less involved (smaller  $\pi$ –back bonding makes for a longer Re–C bond). As representative examples, consider complexes **3** and **6**. In **15** we find longer Re–C (carbene) and shorter C (carbene)–O lengths, due to the ligand being intermediate between an acyl and a carbene ligand.

In a Re(V) dioxo complex with four equivalent N–heterocyclic carbene ligands, which is representative of a long Re–carbene distance, the lengths of the bonds between the carbon atoms and the metal are 2.22–2.23 Å<sup>15</sup>.  $\sigma$ –Bonding dominates the bonding between the metal and the carbene ligands since the metal doesn't have any electrons to  $\pi$ –donate. The bonds of the complexes discussed here are all significantly shorter than that, evidence for the existence of  $\pi$ –bonding.

There is a fine balance of energetically most favoured conformation between ring planarity, carbene planarity and orientation of carbonyl ligands and electronic factors are readily influenced by steric constraints in the molecule.

If one considers the angles around the carbene carbon atom, you see that the angle made by the R substituent, the carbene and the metal are for all the complexes roughly the same, falling in the range of 122–127°. The ethoxy group is more variable in its position, as can be seen by looking at the values for the R–C–O and M–C–O bond angles. Because of the sp<sup>3</sup>–carbons it is more flexible. The complexes that show the largest strain are again **3** and **7** (only one of the two ethoxy substituents is very twisted). Complexes with flat ethoxy groups are **5**, **13** and **1**.

Of the eight complexes, complexes **3** and **7** show the largest torsional twist between the thienyl substituent and the carbene plane. The thienyl substituent of complex **3** is 3,6–

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<sup>15</sup> H. Braband, T. I. Zahn, U. Abram; *Inorg. Chem.* **2003**, *42*, 6160–6162

dimethylthieno[3,2-*b*]thiophene. Steric hindrance between the pendant methyl at ring position 3 and carbonyl ligands may be responsible for the large twisting. The ethoxy groups of **7** interfere with each other across the thiophene bridge. Complexes **5** and **15**, on the other hand have thienyl substituents that are almost coplanar with the carbene plane.

## Chapter 5: Experimental

### 5.1 General

Dirhenium decacarbonyl, 2,2'-bithiophene, thiophene and *n*-BuLi were purchased from commercial suppliers. 3,6-dimethylthieno[3,2-*b*]thiophene was prepared in our laboratories. Bithiophene was used as obtained, but thiophene was purified according to the method of Angelici<sup>1</sup>. Rheniumpentacarbonyl bromide was prepared from dirhenium decacarbonyl<sup>2</sup>. Triethyloxonium tetrafluoroborate was prepared according to the method of Meerwein<sup>3</sup>.

Solvents were dried and distilled under an atmosphere of nitrogen before use. THF, ether (a small quantity of benzophenone was used as indicator for ethers – a deep blue colour was indication that the ether was dry) and hexane were distilled from sodium metal. Dichloromethane was distilled from P<sub>2</sub>O<sub>5</sub>.

All reactions were performed in an inert atmosphere of either nitrogen or argon by using standard Schlenk and vacuum-line techniques. Glassware was thoroughly cleaned and dried before use. All reactions were performed in the fume hood.

Column chromatography, for separation of products, was carried out under an argon atmosphere using silica gel (particle size 0.063–0.200 nm) as stationary phase. Products were separated by using a mixture of solvents (normally DCM and hexane) and a concentration gradient.

All NMR spectra were recorded in degassed deuterated chloroform on a Bruker ARX-300 spectrometer. The chloroform peak was used as the reference peak. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured at 300.133 and 75.469 MHz, respectively.

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<sup>1</sup> G. H. Spies, R. J. Angelici; *Organometallics*, **1987**, 6, 1897–1903

<sup>2</sup> S. P. Schmidt, W. C. Trogler, F. Basolo; *Inorg. Synth.*, **1990**, 28, 162

<sup>3</sup> H. Meerwein, *Org. Synth.*, **1966**, 46, 113–114

Infrared spectra were recorded on a Perkin–Elmer Spectrum RX1 FT–IR spectrophotometer with a NaCl cell, using hexane as solvent.

Mass spectrometry was done on a Finnigan MAT 8200 instrument at ca. 70 eV using the electron impact method.

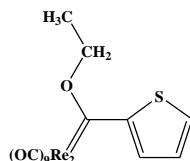
## 5.2 Synthesis

### 5.2.1 Preparation of 3,6–dimethylthieno[3,2–*b*]thiophene

This compound was prepared according to the method of Choi *et al*<sup>4</sup>.

### 5.2.2 Preparation of dirhenium complexes

#### 5.2.2.1 Complex **1** – $[Re_2(CO)_9\{C(OEt)C_4H_3S\}]$



Three different procedures all yielded the thiophene ethoxy monocarbene complex **1**. The general approach is similar for all: nucleophilic attack by lithiated thienyl nucleophile on metal reagent complex initiates the process.

#### *Lithiation*

The lithiation procedure followed for the three preparations of **1** by the different methods all involved initial monolithiation of thiophene. Lithiated thienyl species were always prepared prior to use.

<sup>4</sup> K. S. Choi, K. Sawada, H. Dong, M. Hoshino, J. Nakayama; *Heterocycles*, **1994**, 38, 143–149

The strong base *n*-BuLi (1.6 M; 0.70 ml, 1.1 mmol) is used for the purpose of lithiation. It removes the  $\alpha$ -hydrogen atoms of thiophene. For the monolithiation of thiophene, one equivalent is used (a slight excess, 10%, ensures maximum yield).

One mmol thiophene (0.079 ml ~ 0.08 ml, 1.0 mmol) was monolithiated by firstly dissolving thiophene in 30 ml freshly distilled dry THF in a schlenk tube. The solution is cooled to  $-10^{\circ}\text{C}$  (from  $0^{\circ}\text{C}$  and up, the *n*-BuLi reacts with THF). *n*-BuLi is added drop-wise and then the reaction mixture is stirred for 30 min. at this temperature. The solution becomes light yellow.

#### 5.2.2.1.1 Method 1

The next step after lithiating the thienyl substituent is reacting it with the metal precursor carbonyl complex – metalation.

Reactions of lithiated reagents with metal carbonyl complexes are vigorous, therefore the temperature of the solution is first cooled down to  $-78^{\circ}\text{C}$  before the metal complex is added, by placing it in an acetone/dry ice bath.

[Re(CO)<sub>5</sub>Br] (0.41 g, 1.0 mmol) was added to the reaction solution. The solution attained a red-brown colour.

However, a determination of the mobility of the product by thin layer chromatography (using polar DCM as eluent) revealed that the product was immobile on silica gel. It was assumed that the product was an anionic species produced by attack of the lithiated thiophene on the carbon atom of a carbonyl ligand and it was decided to alkylate the complex to prepare a neutral carbene complex. The colour of the solution was orange.



### *Alkylation*

For the alkylation, oxonium salt  $\text{Et}_3\text{OBF}_4$  was used. THF was removed under reduced pressure. The residue was dissolved in a minimum of dichloromethane. The colour of the dichloromethane solution is darker and more reddish than the THF solution of the same compounds.

For all alkylations, a procedure was followed whereby a slight excess of alkylating agent is dissolved in a measured amount of dichloromethane – usually 10 ml. A volume was then taken out of the solution corresponding to the correct amount of alkylating agent needed. The amount of alkylating agent taken was different for each reaction and also the volume of solution pipetted out and used for alkylation. Furthermore, alkylations were monitored for completion by inspection with TLC. If needed, more was added. Therefore, no precise volumes will be given.

The  $\text{Et}_3\text{OBF}_4$  is placed in a pre-weighed, empty schlenk tube under argon. The ether is removed under vacuum and the mass of the alkylating agent is determined. The correct volume (corresponding to: 0.20 g, 1.1 mmol) of this solution, needed for the alkylation, was pipetted out and added to the schlenk tube at  $-30^\circ\text{C}$ . After stirring for a few minutes at this temperature the reaction vessel is taken out of the cold bath and allowed to warm up to room temperature and stirring is continued for 30 min. at room temperature.

It was observed with TLC that the product that formed was mobile on silica gel (DCM/hexane eluant mixtures), showing that it is a neutral product.

### *Filtering*

A final step in the experimental procedure of the synthesis is to filter the solution through a short silica gel filter to remove any remaining lithium salts. The dichloromethane was then removed under reduced pressure.

### *Separation*

A silica gel column of about 15 cm in length was prepared under argon in hexane. The products of the reaction were dissolved in a minimum volume of DCM and then an equivalent volume of silica gel is added. The DCM is removed under vacuum, leaving silica gel with the products adsorbed on it. This was placed on top of the column and eluting was commenced with hexane. The different products have different polarities and the polarity of the eluting agent is gradually increased by proportionally using more DCM to hexane.

The monocarbene complex was collected after the unreacted thiophene and the butyl-carbene rhenium complex had eluted with hexane.

### *Characteristics*

The complex is a yellow solid.

0.06 g (8 %) of complex **1** was isolated.

The complex was heated, but turned black around 112°C and did not melt.

Anal. calcd. for C<sub>16</sub>H<sub>8</sub>O<sub>10</sub>SRe<sub>2</sub> (764.7): C 25.13, H 1.05%; Found: C 25.36, H 1.15%

#### *5.2.2.1.2 Method 2*

The monolithiation of thiophene was performed in the same manner as described above, in dry THF.

The reaction mixture was cooled down to -78°C. Re<sub>2</sub>(CO)<sub>10</sub> (0.65 g, 1.0 mmol) was added in small portions. After 30 min. the temperature of the solution was raised to room temperature and the solution was stirred for a further 1 hour. The colour of the solution was observed to change from light yellow to deeper yellow.

Alkylation was done in the same manner as was described for method 1. This involved the removal of the THF, redissolving the products in 30 ml dichloromethane, cooling to  $-30^{\circ}\text{C}$  and addition of an appropriate volume of a dichloromethane  $\text{Et}_3\text{OBF}_4$  solution to the reaction solution. No change in colour was observed. Finally, the solution was filtered through a short silica gel filter to remove any remaining lithium salts. The dichloromethane was removed under reduced pressure.

A separation on a silica gel column was performed as was done in method 1 and the complex was obtained as a slightly polar fraction.

The monocarbene complex was isolated as a yellow solid in 77 % (0.59 g) yield.

#### 5.2.2.1.3 Method 3

The lithiation (thiophene) and the reaction steps ( $\text{Re}_2(\text{CO})_{10}$ ) were done in exactly the same way as is described above for ‘Method 2’. The alkylation was done according to a different procedure and will be discussed below.

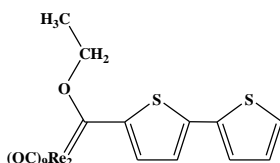
The THF was removed and the residue dissolved in distilled deoxygenated water ( $\text{O}_2$  was removed from the water by repeated (3 times) heating and cooling cycles, whilst passing  $\text{N}_2$  (g) through the solution). The water solution was orange–brown.

The water was quickly layered with 20 ml diethyl ether and a portion of  $\text{Et}_3\text{OBF}_4$  was added to the water fraction (it was scooped out of the round bottom flask with a spatula and dropped into the separation vessel). The water and ether were vigorously mixed by shaking and was then allowed to settle. It was observed that the ether layer had attained an orange colour (the ethoxy carbene complex had formed was extracted into the ether layer). The ether layer on top was carefully removed with a pipette and filtered through anhydrous  $\text{Na}_2\text{SO}_4$  to remove water. 20 ml diethyl ether was added on top and the process of alkylation repeated. The process was repeated until the water fraction was clear and colourless.

All the diethyl ether portions were combined and the diethyl ether was removed under reduced pressure. Complex **1** was obtained in pure form and no further separation was required.

By following this method 69 % (0.53 g) monocarbene complex could be isolated.

#### 5.2.2.2 Complex **2** – $[Re_2(CO)_9\{C(OEt)C_4H_2S-C_4H_3S\}]$



Although the water alkylation procedure was quite useful for the preparation of **1** in pure form (5.2.2.1.3), it was found that the procedure did not yield the analogous bithiophene complex. Instead clay-like yellow product(s) were obtained and no further work-up was performed. The procedure that was followed for the preparation of **2** was the reaction with monolithiated bithiophene in THF and alkylation in DCM.

Bithiophene (0.17 g, 1 mmol) was placed in a Schlenk tube and 30 ml freshly distilled, dry THF was added, giving a clear and colourless solution. The solution was placed in a cold bath at  $-10^{\circ}C$ . *n*-BuLi (1.6M; 0.70 ml, 1.1 mmol) was added drop-wise, whilst the solution was stirred for 30 min. at  $-10^{\circ}C$ . The solution attained a clear red-brown colour.

The Schlenk tube with the solution was transferred to an acetone/dry ice bath at  $-78^{\circ}C$ .  $Re_2(CO)_{10}$  (0.65 g, 1.0 mmol) was added, and the colour of the solution was observed to immediately become deep red. The solution was stirred for 30 min., after which it was removed from the cold bath and the temperature was allowed to increase to room temperature. The solution was stirred at room temperature for a further 1 hour.

The THF was removed under vacuum and the residue dissolved in a minimum of dichloromethane. Et<sub>3</sub>OBF<sub>4</sub> solution in DCM was obtained as before. An appropriate volume (corresponding to 1 mmol Et<sub>3</sub>OBF<sub>4</sub>) was then taken and added to the reaction solution at –30°C. After a few minutes the reaction mixture was warmed to room temperature and allowed to stir at room temperature for a further 30 min. The colour was observed to become slightly darker red upon alkylation of the products. The reaction solution was passed through a silica gel filter to remove the salts. The DCM was removed *in vacuo*.

The reaction products were dissolved in a minimum of DCM and an equivalent volume of dry silica gel was added. The DCM was removed *in vacuo*, leaving the products of the reaction adsorbed on the silica gel. A 15 cm silica gel column was packed in hexane and the silica gel with the products placed on top of the column. Hexane and dichloromethane mixtures were used to elute the products. By starting with non-polar hexane to remove the non-polar substances and gradually increasing the polarity of the eluant (by using proportionally more dichloromethane), complexes of different polarities could be separated on the column. The monocarbene complex is less polar than the biscarbene complex (also formed in very low yield; from double lithiation of bithiophene) and came off the column first.

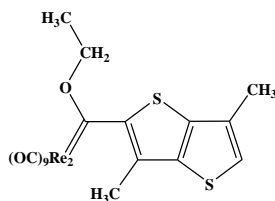
The complex is a red solid.

55 % (0.47 g) of complex **2** was isolated.

The complex was heated, but decomposed around 122°C.

Anal. calcd. for C<sub>20</sub>H<sub>10</sub>O<sub>10</sub>S<sub>2</sub>Re<sub>2</sub> (846.6): C 28.37, H 1.19%; Found: C 28.51, H 1.23%

### 5.2.2.3 Complex **3** – [Re<sub>2</sub>(CO)<sub>9</sub>{C(OEt)C<sub>8</sub>H<sub>7</sub>S<sub>2</sub>}]



3,6-Dimethylthieno[3,2-*b*]thiophene (0.18 g, 1.0 mmol) was dissolved in 30 ml freshly distilled dry THF. The temperature of the solution was brought down to  $-10^{\circ}\text{C}$  and *n*-BuLi (0.0.75 ml, 1.2 mmol) was added. Stirring was continued for 2 hours at  $-10^{\circ}\text{C}$ . A white suspension was observed.

The solution was cooled down to  $-70^{\circ}\text{C}$ . Dirhenium decacarbonyl (0.65 g, 1.0 mmol) was added and the solution left to stir for 15 min. The temperature was raised to room temperature and stirring continued for 1 hour. The solution attained an orange-red colour.

The THF was removed and the residue was dissolved in a minimum dichloromethane.  $\text{Et}_3\text{OBF}_4$  was measured out and dissolved in dichloromethane. A volume equivalent to 1 mmol (0.2 g, 1.0 mmol) was added at  $-30^{\circ}\text{C}$ . The solution was allowed to warm to room temperature and was stirred for 30 min. The colour observed was orange.

As a final step, the reaction solution was passed through a silica gel filter to remove the salts. The DCM was removed *in vacuo*.

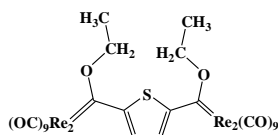
The products of the reaction were adsorbed on silica gel, in a manner as was described above. A 15 cm silica gel column was packed in hexane. The silica gel with the adsorbed compounds was placed on the column and eluting was started with pure hexane. The polarity of the eluting agent was increased gradually by increasing the dichloromethane percentage and compounds of increasing polarity were thus separated off the column. The complex was obtained after organic fractions and the butyl carbene complex were removed from the column.

The complex is an orange solid.

56% (0.48 g) of the monocarbene complex was isolated.

Anal. calcd. for  $\text{C}_{20}\text{H}_{12}\text{O}_{10}\text{S}_2\text{Re}_2$  (848.6): C 28.31, H 1.43%; Found: C 28.54, H 1.56%

5.2.2.4 Complex 7 –  $[Re_2(CO)_9\{C(OEt)C_4H_2SC(OEt)\}Re_2(CO)_9]$



Thiophene (0.079 ml ~ 0.08 ml, 1.0 mmol) was dissolved in 30 ml freshly distilled, dried THF and the solution was cooled to  $-10^{\circ}C$ . *n*-BuLi (1.6M; 1.40 ml, 2.2 mmol) was added and the reaction mixture stirred for 30 min. at this temperature. The solution became light yellow and cloudy.

The reaction solution was cooled down to  $-78^{\circ}C$ .  $[Re_2(CO)_{10}]$  (1.30 g, 2.0 mmol) was added. The colour of the solution changed to darker yellow and eventually became orange. After 30 min. the Schlenk tube was taken out of the cold bath and was allowed to warm to room temperature and stirring was continued for another hour.

The THF was removed *in vacuo* and the residue dissolved in a minimum DCM. The temperature of the solution was lowered to  $-30^{\circ}C$ .  $Et_3OBF_4$  was taken out of the container where it is kept under ether and placed in a clean, dry pre-weighed Schlenk tube. It was dried under vacuum. DCM (10 ml) was added and an appropriate volume of  $Et_3OBF_4$  solution (corresponding to 0.40 g, 2.2 mmol) was pipetted out and added to the reaction solution.

After a few minutes the reaction mixture was allowed to warm to room temperature and stirred at room temperature for another 30 min. Thin layer chromatography was used to monitor the reaction.

The reaction solution was passed through a silica gel filter to remove the salts. The DCM was removed under reduced pressure.

The product was obtained by performing a separation on silica gel in the same way as was described for monocarbene complex **1**. The residue of the reaction was adsorbed on a minimum silica gel (by first dissolving in a minimum of DCM and then adding the same volume of silica gel; removing the DCM) and then placed on top of a 15 cm column that was packed in hexane.

It was reddish in colour and eluted after the monocarbene complex – it is a more polar complex than complex **1**.

The complex is a light red solid.

5% (0.07 g) of the biscarbene complex was isolated.

The complex is unstable and the melting point was not determined.

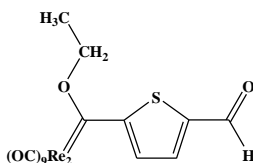
Anal. calcd. for  $C_{28}H_{12}O_{20}SRe_4$  (1445.3): C 23.27, H 0.84%; Found: C 23.87, H 0.97%

### Notes

The method detailed above for the preparation of thiophene biscarbene complex **7** was not useful to prepare a large amount of the complex. In fact, it formed as a byproduct, and the majority product was monocarbene complex **1**. This might indicate that the double lithiation of thiophene is not very successful under these reaction conditions.

#### 5.2.2.5 Further product isolated: **12**

Complex **12** –  $[Re_2(CO)_9\{(C(OEt))C_4H_2S-C(O)H\}]$

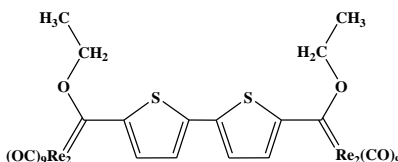


The complex is a yellow solid.

Anal. calcd. for  $C_{17}H_8O_{11}SRe_2$  (792.7): C 25.76, H 1.02%; Found: C 25.88, H 1.14%



5.2.2.6 Complex 8 –  $[Re_2(CO)_9\{C(OEt)C_4H_2S-C_4H_2SC(OEt)\}Re_2(CO)_9]$



This complex was isolated even from the preparation of the monocarbene complex in a not insignificant yield. It was obtained in better yield when bithiophene was doubly lithiated and 2 equivalents of  $[Re_2(CO)_{10}]$  was added.

Bithiophene (0.17 g, 1.0 mmol) was lithiated (1.6M; 1.40 ml, 2.2 mmol) at  $-20^\circ C$  in 30 ml THF. The colour of the solution was red–brown. It was allowed to stir for 30 min., and then the solution was cooled to  $-78^\circ C$  by placing it in an acetone/dry ice bath.

Dirhenium decacarbonyl (1.30 g, 2.0 mmol) was added to the reaction mixture and the solution was left to stir for 15 min. The temperature was raised to  $-40^\circ C$  and after 20 min. raised to room temperature. Stirring was continued for 1.5 hours at room temperature. The solution became deep red in colour.

The solvent was removed under reduced pressure and the residue dissolved in dichloromethane.  $Et_3OBF_4$  (0.40 g, 2.2 mmol) was added at  $-30^\circ C$ . The reaction was allowed to warm to room temperature and stirred for another 30 min. at room temperature. The success of the alkylation step was monitored with thin layer chromatography.

As a final step, the reaction solution was passed through a silica gel filter to remove the salts. The DCM was removed *in vacuo*.

The products were separated by column chromatography. A 15 cm silica gel column was packed in hexane under argon. Hexane dichloromethane solutions were used as eluent of

increasing polarity to bring down from the column products of increasing polarity. Organic fractions without colour were removed first, followed by a small amount of butyl carbene complex and some monocarbene complex **2** (approximately 15%). Thereafter the biscarbene complex was obtained by using a 5:1 hexane to dichloromethane solution to elute.

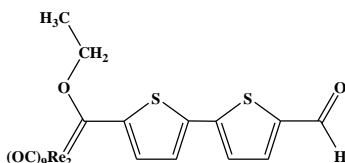
The complex is a dark red solid.

58 % (0.89 g) of the complex was isolated.

Anal. calcd. for  $C_{32}H_{14}O_{20}S_2Re_4$  (1527.4): C 25.16, H 0.92%; Found: C 25.32, H 0.99%

#### 5.2.2.7 Further product isolated: **13**

*Complex 13* –  $[Re_2(CO)_9\{(C(OEt))C_4H_2S-C_4H_2S-C(O)H\}]$



It was noticed that there was still a very polar product or products with red–brown colour on the origin of the column. This band was immobile on the column, even when eluting with clean dichloromethane. It was decided to elute with either high purity acetone or high purity THF (both used directly as is from the supplier). Using these eluents ensured that most compounds still on the column were removed, so often an impure mixture of compounds was obtained. It was necessary to dry the fraction immediately on collection, as THF and acetone are known to bring water down off a silica gel column. The THF or acetone fraction was passed through a  $Na_2SO_4$  filter to remove the water and then the solvent was removed under vacuum.

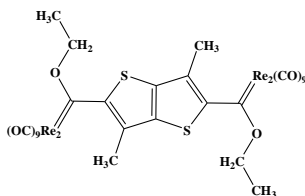
The complex could be purified by recrystallization from a hexane dichloromethane mixture and a crystal structure was determined of the complex.

The complex is a red solid.

Yield of complex = 16% (0.14 g)

Anal. calcd. for  $C_{21}H_{10}O_{11}S_2Re_2$  (874.8): C 28.83, H 1.15%; Found: C 28.96, H 1.22%

5.2.2.8 Complex **9** –  $[Re_2(CO)_9\{C(OEt)C_8H_6S_2C(OEt)\}Re_2(CO)_9]$



The procedure of 3,6–dimethylthieno[3,2–*b*]thiophene double lithiation is a method that has been successfully applied in our laboratories for the double lithiation of this compound. It is similar to the monolithiation of the compound.

Double lithiated 3,6–dimethylthieno[3,2–*b*]thiophene, this thienyl molecule (0.17 g, 1.0 mmol) was dissolved in 30 ml freshly distilled, dried THF. The colourless solution was cooled down to 0°C by placing it in an ice bath. *n*–BuLi (1.6M; 1.40 ml, 2.2 mmol) was added drop–wise. The colour was observed to become yellowish and slightly cloudy.

The solution was cooled down to –78°C (acetone/dry ice bath) and  $[Re_2(CO)_{10}]$  (1.30 g, 2.0 mmol) was added. The solution attained an orange–red colour. After about 20 min. at this temperature, the temperature of the solution was allowed to rise to room temperature. Stirring was continued at room temperature for another 1 hour.

The THF solvent was removed under vacuum and the residue was dissolved in a minimum freshly distilled dichloromethane. 0.6 g  $Et_3OBF_4$  was added by dissolving it in 10 ml dichloromethane and taking a fraction of the solution that corresponds to slightly more than 2 equivalents (0.40 g, 2.2 mmol) of alkylating agent. The colour observed for the solution was orange – an indication that monocarbene complex **3** was the major product.

The reaction solution was passed through a silica gel filter to remove the salts. The DCM was removed *in vacuo*.

Separation was done on a silica gel column by packing a 15 cm column of silica gel under hexane. The reaction products were adsorbed on a minimum silica gel and placed on top of the column and separation was done by starting elution with pure hexane and gradually increasing the polarity of the eluent by using a larger percentage of dichloromethane. A large orange fraction (0.87 g; 57 %) was obtained and was later identified to be the monocarbene complex **3**. A small red fraction was obtained and this was the biscarbene complex **9**.

7 % (0.11 g) of the complex was isolated.

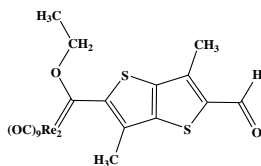
The complex is a red solid.

The complex is unstable and the melting point was not determined.

Anal. calcd. for C<sub>32</sub>H<sub>16</sub>O<sub>20</sub>S<sub>2</sub>Re<sub>4</sub> (1529.4): C 25.13, H 1.05%; Found: C 25.45, H 1.13%

#### 5.2.2.9 Further product isolated: **14**

Complex **14** – [Re<sub>2</sub>(CO)<sub>9</sub>{(C(OEt))C<sub>8</sub>H<sub>6</sub>S<sub>2</sub>–C(O)H}]



A red–brown product on the origin of the column (immobile in DCM) was eluted with THF (used directly from the supplier). Using THF ensured that most compounds still on the column were removed, so an impure mixture of compounds was obtained. The THF fraction was passed through a Na<sub>2</sub>SO<sub>4</sub> filter to remove the water and then the solvent was removed under vacuum to give **13**.

The complex is a red solid.

Yield of complex: 19% (0.17 g)

Anal. calcd. for  $C_{21}H_{12}O_{11}S_2Re_2$  (876.7): C 28.77, H 1.38%; Found: C 29.03, H 1.52%

### 5.2.3 Re–Re bond cleavage by $Br_2$

Bromination of complexes (cleaving of the Re–Re bond of the complexes with  $Br_2(l)$ ) is facile at room temperature in hexane. This was done for complexes **1**, **2**, **3**, and **8** and one or both of the following two procedures were followed.

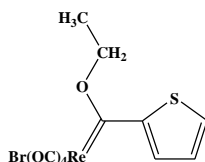
#### *Procedure 1*

A definite, slight excess of  $Br_2(l)$ , is added to the reagent complex in 30 ml hexane. The solution is stirred at room temperature for an hour. The colour of the solution is observed to change – for instance red solutions will become more yellowish and duller. The cleaved complex was then separated from the other complexes and compounds on a silica gel column. This produced variable yields of complex as it was difficult to precisely add the right amount of  $Br_2(l)$  – a very small amount was usually required.

#### *Procedure 2*

This procedure is more effective and involves no further work–up. Complete turn–around is achievable. Small amounts of  $Br_2(l)$  (dissolved in 10 ml hexane) is added drop–wise to a hexane solution of the uncleaved starting complex. The solution is stirred. The more polar cleaved product dissolves poorly in hexane and falls out of solution. In this way it is possible to monitor the reaction for completion. Furthermore, the hexane part losing its colour shows that there is no more uncleaved complex left. The hexane is poured off and the precipitate is washed with hexane. Good yields of cleaved complex could be obtained in this way.

5.2.3.1 Complex 4 –  $[Re(CO)_4\{C(OEt)C_4H_3S\}Br]$



Monocarbene complex **1** (0.38 g, 0.5 mmol) was dissolved in approximately 40 ml hexane – hexane was added until the entire batch of monocarbene complex was dissolved. The solution was yellow. Bromine (3.11 g/ml, 0.026 ml, 0.5 mmol) was added carefully while stirring was maintained. The solution changed colour from yellow to greyish yellow and a precipitate formed.

Complex **4** was obtained by decanting the hexane solution (in the case of bromination via the second procedure), which still contained some uncleaved monocarbene complex.

Separation was necessary when procedure 1 was followed for bromination. A 10 cm silica gel column was packed under argon in hexane. The residue of the reaction was adsorbed on silica gel. The silica gel with the adsorbed compounds was placed on top of the column.

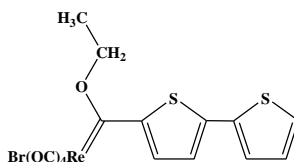
First hexane was used to elute, although there were not many organic compounds. The polarity was increased by using proportionally more dichloromethane and the uncleaved complex was removed from the column first. The polarity had to be increased to get the cleaved complexes  $[Re(CO)_5Br]$  and complex **4** off the column. No further products were isolated.

The complex is a whitish yellow solid.

Yield of complex **4**: 60% (0.31 g; procedure 1) and 81% (0.42 g; procedure 2)

Anal. calcd. for  $C_{11}H_8BrO_5SRe$  (518.4): C 25.49, H 1.56%; Found: C 25.64, H 1.78%

5.2.3.2 Complex **5** –  $[Re(CO)_4\{C(OEt)C_4H_2S-C_4H_3S\}Br]$



This complex was prepared by both of the procedures described for the preparation of **4**.

Monocarbene complex **2** (0.43 g, 0.5 mmol) was dissolved in approximately 40 ml hexane – enough hexane was added to dissolve all of complex **2**. The solution was red. Bromine (3.11 g/ml, 0.026 ml, 0.5 mmol) was added while stirring was maintained. The hexane solution gradually became more yellow in colour and a precipitate formed.

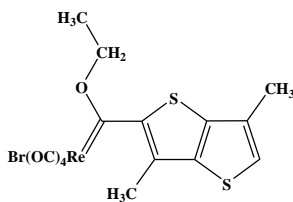
In the case of bromination by the first procedure, the separation was done by column chromatography. A 10 cm silica gel column was packed under argon in hexane. The residue of the reaction was adsorbed on silica gel. The silica gel with the adsorbed compounds was placed on top of the column. Eluting was commenced with hexane. The polarity was increased by using proportionally more dichloromethane and the unreacted complex **2** was removed first. The polarity had to be increased to remove the cleaved complexes  $[Re(CO)_5Br]$  and **5** which separated from the column.

The complex is a yellowish red solid.

Yield of complex **5**: 58% (0.35 g; procedure 1) and 73% (0.44 g; procedure 2)

Anal. calcd. for  $C_{15}H_{10}BrO_5S_2Re$  (600.5): C 30.00, H 1.68%; Found: C 30.34, H 1.87%

5.2.3.3 Complex **6** –  $[Re(CO)_4\{C(OEt)C_8H_7S_2\}Br]$



This complex was brominated by following procedure 2, as detailed in section 5.3.

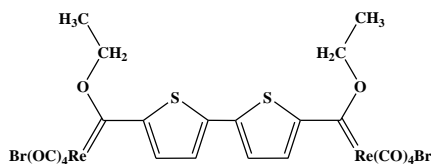
Complex **3** (0.43 g, 0.5 mmol) was completely dissolved in 40 ml hexane. Bromine (3.11 g/ml, 0.026 ml, 0.5 mmol) was added while stirring was maintained. The procedure for bromination was to first add 0.26 ml bromine to 10 ml hexane and then take 1 ml of the solution and add it to the reaction mixture. Alternatively, one could take < 1ml of bromine and add it drop-wise to the solution (while maintaining stirring) and repeat the process until the hexane is almost colourless. It was observed that the product fell out of solution as a yellowish white precipitate. The remaining hexane was decanted and the precipitate washed with 10 ml hexane. The hexane was removed under reduced pressure.

The product is a yellowish white solid.

Yield of complex **6**: 0.23 g (75%)

Anal. calcd. for  $C_{15}H_{12}BrO_5S_2Re$  (602.5): C 29.90, H 2.01%; Found: C 30.01, H 2.21%

5.2.3.4 Complexes **10** –  $[Re(CO)_4Br\{C(OEt)C_4H_2S-C_4H_2SC(OEt)\}Re(CO)_4Br]$  – and **11** –  $[Re(CO)_4Br\{(C(OEt)C_4H_2S-C_4H_2SC(OEt)\}Re_2(CO)_9]$



Complex **5** (0.76 g, 0.5 mmol) was dissolved in 40 ml hexane, giving a deep red solution. Bromine (3.11 g/ml, 0.026 ml, 0.5 mmol) was added carefully while stirring was maintained. Only one equivalent of bromine was added, because the intention was to only cleave the rhenium–rhenium bond of one of the complex’s carbenes. The solution became lighter and duller in colour and a precipitate formed.

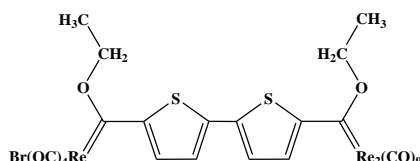


The hexane was decanted once the further addition of bromine did not produce more precipitate. The products were washed with 10 ml clean hexane and then the hexane was removed under reduced pressure.

The product is a rose solid.

Yield of complex **10**: 40 % (0.21 g)

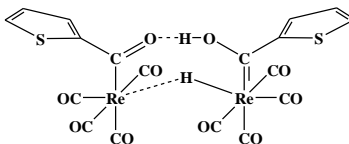
Anal. calcd. for  $C_{22}H_{14}Br_2O_{10}S_2Re_2$  (1034.7): C 25.54, H 1.36%; Found: C 25.88, H 1.48%



A very small amount of complex, **11** – 5% (0.06 g) was obtained, showing that the bromination of both sides of the molecule is favoured and the reaction proceeded in a stepwise manner.

## 5.2.4 Hydrogen-bridged complexes

### 5.2.4.1 Complex **15** – $[Re(CO)_4\{\mu-H\}\{C(OH)C_4H_3S\}-Re(CO)_4\{C(O)C_4H_3S\}]$



Thiophene (0.079 ml ~ 0.08 ml, 1.0 mmol) was dissolved in 30 ml freshly distilled THF in a Schlenk tube. The solution is cooled to  $-10^\circ C$  and *n*-BuLi (1.6M; 0.70 ml, 1.1 mmol) was added drop-wise whilst the solution was stirred. Stirring is continued for 30 min. at this temperature.

The solution was cooled down to  $-78^{\circ}\text{C}$  (dry ice/acetone) and  $[\text{Re}(\text{CO})_5\text{Br}]$  (0.41 g, 1.0 mmol) was added. The solution attained a red–brown colour. Stirring was continued at this temperature for 30 min. The solution was allowed to warm to room temperature and stirring was continued for another two hours. The solution had a dark yellow colour.

The THF was removed under reduced pressure and the residue was dissolved in 30 ml dichloromethane. The complex was successfully prepared thrice, each time using a different agent to neutralize the complex. In the first preparation the solution was cooled down to  $-40^{\circ}\text{C}$  and alkylating agent  $\text{Et}_3\text{OBF}_4$  (0.2 g 1.0 mmol) was added. After a few minutes the temperature of the solution was allowed to rise to room temperature and stirring was continued at room temperature for another 30 min.

In the second and third preparations, magic methyl ( $\text{CF}_3\text{SO}_3\text{Me}$ ; 0.16 g, 1.0 mmol) and  $\text{HBF}_4$  (0.2 ml, 1.0 mmol) were used, respectively.

The complex was purified by column chromatography with hexane/dichloromethane mixtures. By gradually increasing the polarity of the eluent (using proportionally more dichloromethane) products of increasing polarity could be brought down off the column. The complex was obtained as a polar complex, washed down with a strongly polar eluent (1:1 dichloromethane: hexane), and obtained as the fifth compound off the column.

The complex was crystallized from a dichloromethane hexane solution and gave good crystals, allowing for a high quality crystal structure where even the bridging hydrogen atoms could be located.

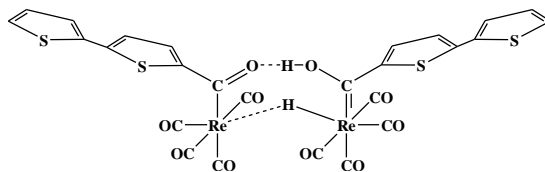
The product is a light yellow solid.

Yield of complex **15**: 65 % (0.53 g)

The melting point could not be determined as the complex slowly decomposed on heating.

Anal. calcd. for  $\text{C}_{18}\text{H}_8\text{O}_{10}\text{S}_2\text{Re}_2$  (820.8): C 26.34, H 0.98%; Found: C 26.51, H 1.01%

5.2.4.2 Complex **16** –  $[Re(CO)_4\{\mu-H\}\{C(OH)C_8H_5S_2\}-Re(CO)_4\{C(O)C_8H_5S_2\}]$



The reaction was not optimized for a higher yield synthesis of this complex and was isolated from the synthesis for biscarbenes (double lithiation of bithiophene) as a byproduct. Bithiophene (0.17 g, 1.0 mmol) was lithiated (1.6M; 1.40 ml, 2.2 mmol) at  $-20^{\circ}\text{C}$  in 30 ml THF. The colour of the solution was red–brown. It was allowed to stir for 30 min., and then the solution was cooled to  $-78^{\circ}\text{C}$ .

Dirhenium decacarbonyl (1.30 g, 2.0 mmol) was added to the reaction mixture and the solution was left to stir for 15 min. The temperature was raised to  $-40^{\circ}\text{C}$  and after 20 min. raised to room temperature. Stirring was continued for 1.5 hours at room temperature. The solution became deep red in colour. The solvent was removed under reduced pressure and the residue dissolved in dichloromethane.  $\text{Et}_3\text{OBF}_4$  (0.40 g, 2.2 mmol) was added at  $-30^{\circ}\text{C}$ . The reaction was allowed to warm to room temperature and stirred for another 30 min. at room temperature. The reaction solution was lastly filtered through silica gel and the DCM removed *in vacuo*.

The complex was obtained as a very polar fraction from the column separation of reaction products on a silica gel column with hexane/dichloromethane mixtures as eluents.

The formation of **16** was observed, but it was not isolated. Higher yields of the complex was achieved by reacting 1 mmol of 5–lithium–2,2'–bithienyl (prepared as prescribed in section 5.2.2.2), with one equivalent of  $[\text{Re}_2(\text{CO})_{10}]$  (0.65 g, 1.0 mmol) and thereafter reacting with  $\text{HBF}_4$  (0.2 ml, 1.0 mmol).

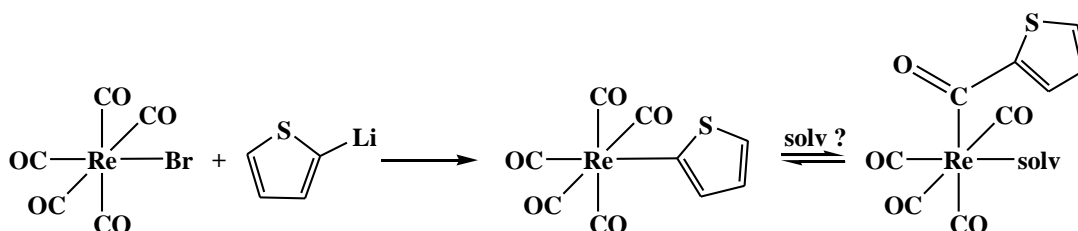
Yield of complex **16**: 15 % (0.15 g)

## Chapter 6: Concluding comments

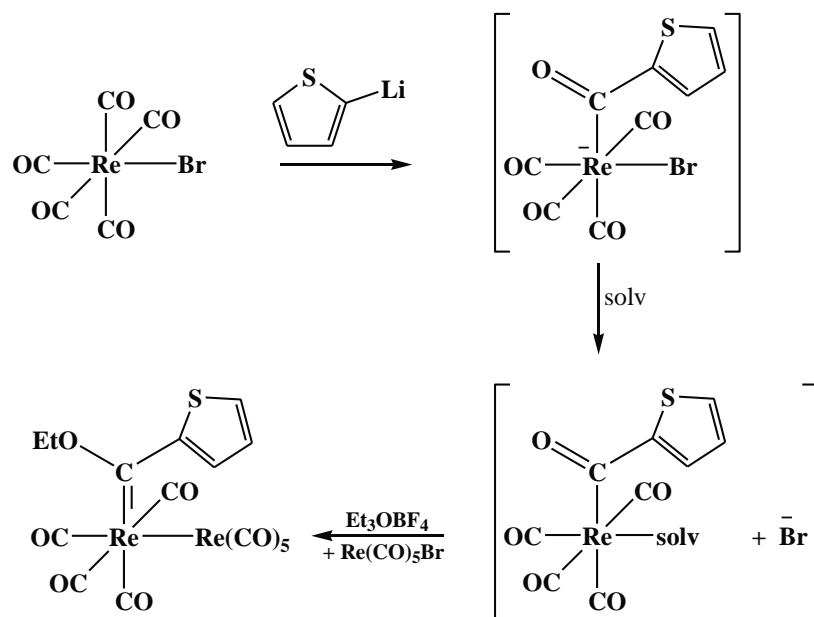
### 6.1 Summary

In this study it was seen that rhenium carbonyl complexes, one of the lesser studied transition metals, has a rich chemistry when reacted with nucleophiles. The rhenium atoms of the chosen starting complexes ( $[\text{Re}_2(\text{CO})_{10}]$ ,  $[\text{Re}(\text{CO})_5\text{Br}]$ ) have predominantly L-type carbon-bonded ligands with one X-type ligand (Br,  $\text{Re}(\text{CO})_5$ ).

The bromo ligand of rheniumpentacarbonyl bromide was anticipated to be labile, easily replaceable from the metal by another nucleophile. Lithiated thienyl derivatives were used as nucleophiles. The synthesis of a complex with a thienyl ligand was attempted by reacting lithiated thienyl with rheniumpentacarbonyl bromide.

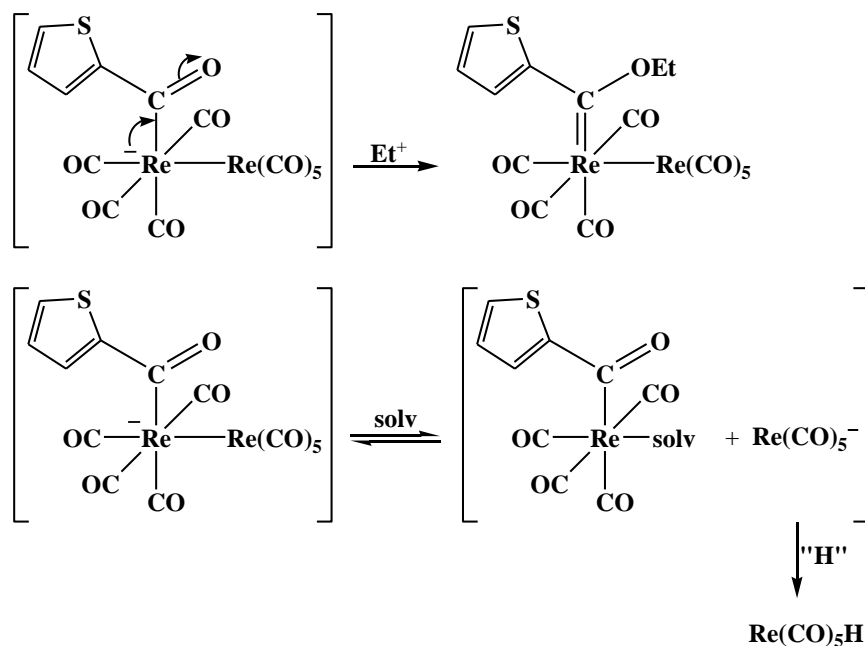


Lithiated thienyl did not substitute the bromo ligand in  $[\text{Re}(\text{CO})_5\text{Br}]$ , but the reaction produced a charged intermediate (immobile on silica) and it was understood that the nucleophile had attacked a carbonyl ligand. A carbene precursor compound (metalate) had thus formed and accordingly, alkylation with oxonium salt  $\text{Et}_3\text{OBF}_4$  yielded a neutral complex. However, the complex that was isolated by column chromatography was found to be the dirhenium monocarbene complex.

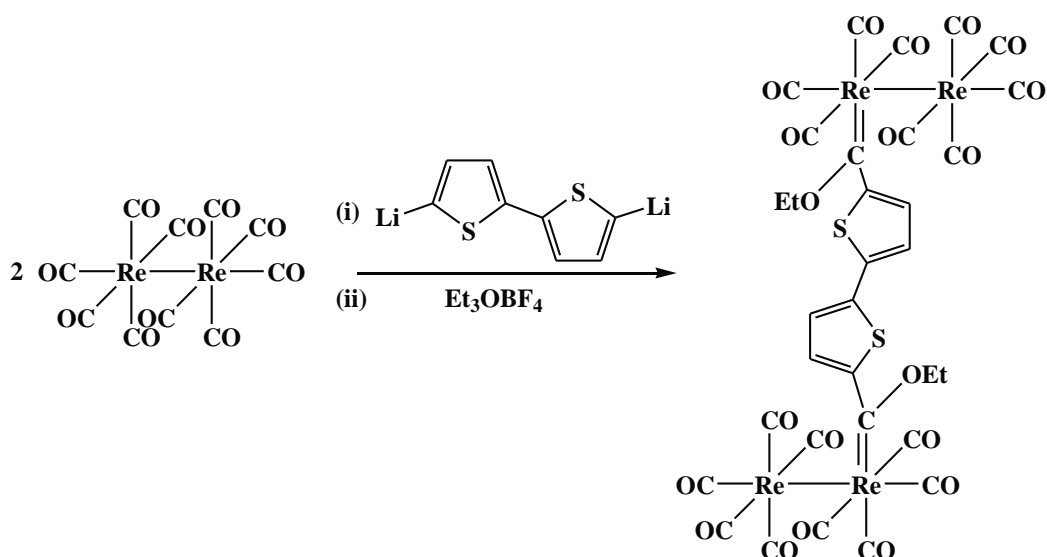


Instead of bromo–ligand substitution, the 2–lithiumthienyl had bonded to the carbon atom of a carbonyl ligand and triggered a series of conversions. The intermediate anionic metalate presumably eliminated its bromo–ligand, as bromide, and a neutral rhenium species with a vacant coordination site was left behind, an important species. Also with  $[\text{Re}_2(\text{CO})_{10}]$  the release of  $[\text{Re}(\text{CO})_5]^-$  was evident as the same intermediate and final product were formed as well as rhenium carbonyl hydrides. Where the goal had been to start with a complex with a vacant coordination site, it seems that such a complex had indeed formed as intermediate species.

In the first case, the released  $\text{Br}^-$  may then have removed the bromo ligand of  $[\text{Re}(\text{CO})_5\text{Br}]$ , with formation of  $[\text{Re}(\text{CO})_5]^-$  and this rheniumpentacarbonyl then bonded to the other species with the vacant coordination site forming a Re–Re bond. The dirhenium thiophene monocarbene complex along this route was isolated in low yield. In the second case the neutral, solvated rhenium acyl intermediate was again formed and the release of  $[\text{Re}(\text{CO})_5]^-$  was evident from the formation of  $[\text{Re}(\text{CO})_5\text{H}]$  on protonation or alkylation. The existence of the anionic intermediate  $[\text{Re}(\text{CO})_4\{\text{C}(\text{O})\text{thienyl}\}\text{X}]^-$  ( $\text{X} = \text{Br}, \text{Re}(\text{CO})_5$ ) is speculative. In the last step alkylation of the dirhenium intermediate will afford the dirhenium carbene complex **1**.

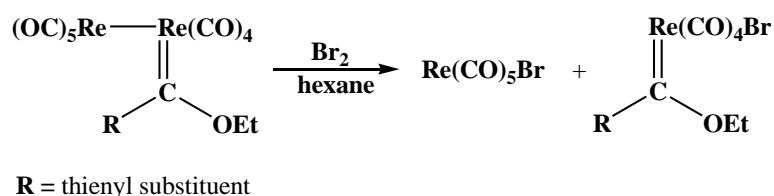


It was decided that, for the thienyl substrates 2,2'-bithiophene and 3,6-dimethylthieno[3,2-*b*]thiophene, the desired dirhenium carbene complexes would be better prepared with  $[\text{Re}_2(\text{CO})_{10}]$  as precursor reagent and not  $[\text{Re}(\text{CO})_5\text{Br}]$ . Monocarbene and biscarbene complexes (double lithiation of the aromatic molecules and their reaction with two equivalents of  $[\text{Re}_2(\text{CO})_{10}]$ ) were prepared and isolated as major products. The reaction for the preparation of the bithiophene biscarbene complex **8** is shown below.



In each case it was found that an equatorial carbonyl ligand had been transformed into a carbene ligand by application of the Fischer carbene synthesis method. No products were isolated where the carbene was located in an axial location. Dirhenium decacarbonyl has ten carbonyl ligands, two axial and eight equatorial. The question was raised whether more than one of the carbonyl ligands could be transformed into a carbene ligand? However, it was found that the addition of large excesses of lithiated thiophene or thienyl precursors did not yield any products of multiple carbonyl attack. The question that was asked next was how one could prepare monorhenium carbene complexes.

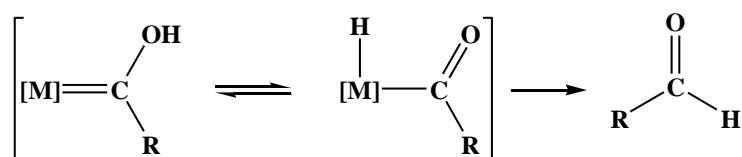
Hence, it was investigated whether the Re–Re bonds of the complexes that were prepared could be cleaved with bromine without affecting the carbene ligand. These reactions proved to be successful and the carbene ligand itself was not altered by the added bromine during the reaction. In this way it was possible to obtain a monorhenium bromo–carbene complex, which was not obtainable from the application of the Fischer carbene synthesis method to rheniumpentacarbonyl bromide.



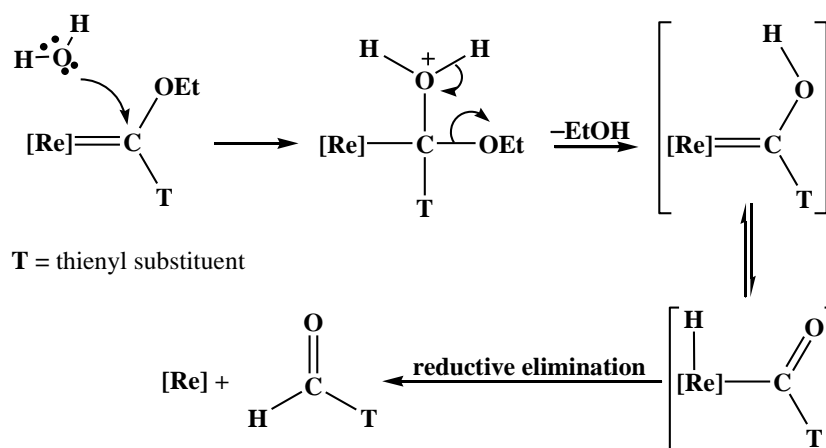
The reverse action of the shown reaction is rhenium–rhenium bond formation or Re(CO)<sub>5</sub> and Br exchange. This implies forming a weaker Re–Re bond by breaking stronger Re–Br bonds.

The dirhenium carbene complexes that were synthesized from dirhenium decacarbonyl, according to the Fischer method, had to be purified by column chromatography. Silica gel columns were prepared for the separations and hexane/dichloromethane mixtures used as eluent. The carbene complexes were isolated and along with them by-products that formed during workup such as aldehydes. Biscarbene complexes yielded monocarbene aldehyde complexes and dialdehyde species by modification of the carbene ligands. From the

monocarbene complexes, monoaldehydes were obtained. It was clear that the carbene ligands of the complexes had been transformed into aldehydes. Water was presumed to be responsible for transforming a carbene ligand into an aldehyde and initially to have come from the silica gel during column chromatography. Hydroxycarbene ligands have been shown to be in equilibrium with acyl-hydrido complexes, which could be the precursor for an aldehyde formation.



To explain the formation of aldehydes from ethoxycarbene precursors, the substitution of OEt by OH is a prerequisite. It was shown that water reacts with the carbene ligand presumably in a similar fashion as primary amines to afford hydroxycarbene ligands.

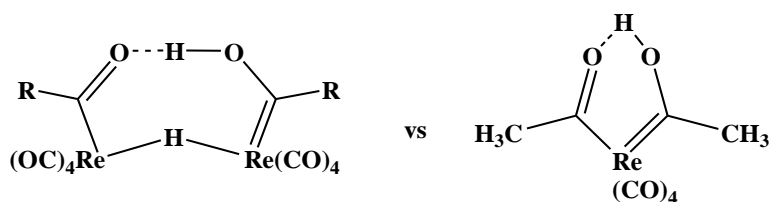


The reactive hydroxycarbene species could not be isolated. Another way for a hydroxycarbene species to have formed would be by the direct protonation of the metal acylate. Reaction of biscarbene dirhenium complexes with water yielded stable intermediate carbene-aldehyde complexes that could be isolated and studied. This complex represents an intermediate complex in the conversion of biscarbene complexes to dialdehydes.



Dirheniumdecarbonyl was reacted with lithiated thiophene and then the intermediates were protonated. Reaction mixtures indicated the presence of Re–H species which were observed spectroscopically and assigned to known hydride complexes. The Re–H bond strength is comparable with Re–Br bond strength and much stronger than a Re–Re bond. Re–Re bonds are readily formed or cleaved in reactions. Attempts to prepare hydroxycarbene complexes by the above method (with protonation instead of alkylation) proved less successful. The weakness of the rhenium–rhenium bond and the instability of the hydroxycarbene complexes yielded hydride species and aldehydes.

According to proton NMR data, a bromo–hydroxycarbene complex was stable to a degree. However, it had also been ascertained that the bromo ligand could be lost and rhenium–rhenium bond formation could occur. Finally, with hydroxycarbene complexes of rhenium, it should always be considered that a hydride–acyl species can form. The two unique complexes **15** and **16** admirably illustrate all of these phenomena in one complex. This dirhenium carbene–acyl complex can be compared with the monorhenium carbene–acyl complex reported by Lukehart.



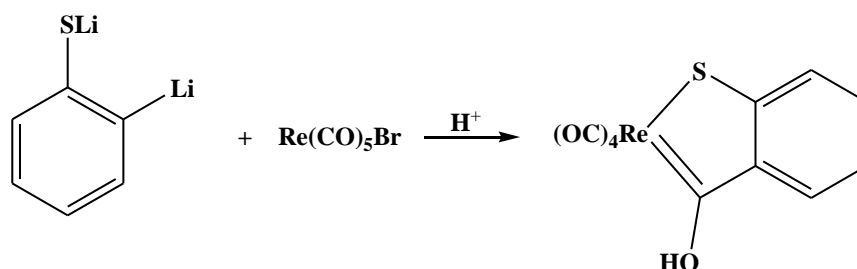
These complexes display both an acyl and a hydroxycarbene fragment and represent important intermediates discussed above. The complexes have the potential to be hydrogenation catalysts. Two rhenium fragments, each having a ligand which is intermediate between a carbene and an acyl ligand – are held together by bonding to two hydrogen atoms. This can be seen as the trapping and stabilization of a hydroxycarbene complex by an acyl complex through hydrogen bonding.

## 6.2 Future work

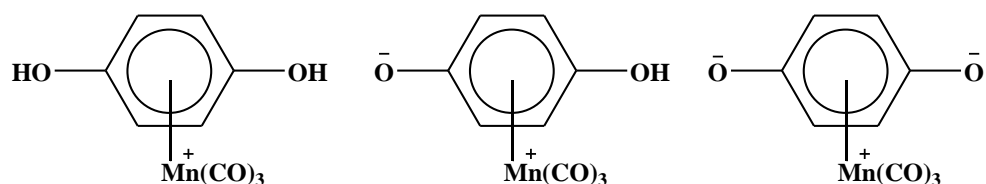
The following questions arose from this work and are worth looking at in future research:

- (i) The mechanism of the aldehyde formation warrants further investigation. Of great importance in such a study is the source of hydrogen atoms and how they add to the carbonyl. Two obvious pathways follow from this study, i.e. the formation of an acyl–hydrido intermediate, either by direct protonation of the metalate or by transfer of a hydrogen from a hydroxycarbene ligand to the metal. In both instances the formation of the aldehyde could be achieved by a reductive elimination reaction if the same rhenium centre is involved. A second pathway is the transfer of a hydride from a rhenium hydride complex to the carbonyl carbon of a second species containing an acyl ligand.
- (ii) The potential catalytic properties of complexes **15** and **16** could lead to exciting new possible applications of hydroxycarbene complexes in template reactions or in catalysis. The same features that make the Shvo catalyst such a diverse and excellent catalyst for the hydrogenation of unsaturated carbon–heteroatom bonds are present in these complexes. However, instead of being part of a  $\pi$ -bonded cyclopentadienyl ligand (Shvo), in **15** and **16** it represents an acyl–carbene/hydrido ligand. The availability of a protonic and a hydridic proton represents the key components for hydrogenation reactions. The composition of the complexes, may make them suitable for hydrogenations in a template–type reaction and the regeneration of the initial catalyst unlikely (uptake of  $H_2$ )
- (iii) Fischer–type cationic monorhenium carbene complexes are scarce in literature and could be studied more extensively. In this study it was found that dirhenium monocarbene complexes could be readily synthesized and cleaved by halogens, affording neutral monorhenium carbene complexes. Removal in coordinating solvents of the halide is a route to cationic rhenium Fischer type carbene complexes which can be investigated for their reactivity and chemical behaviour.
- (iv) The stabilization of hydroxycarbene complexes into useful precursor complexes is another area that warrants investigation. Replacement of lithiated thiophenes by lithiated heteroaromatic precursors that contain a second heteroatom (P, S, N) capable of coordinating to the metal and forming a chelate ring (L–X) is a possible

entry into stable hydroxycarbene complexes. A possible example is shown below and involve the doubly lithiated thiophenol:



- (v) The intermolecular stabilization of hydroxycarbene complexes by intermediate hydrogen bonding of various OH/F substrates and organometallic hydroquinone complexes of manganese.



- (vi) Synthesis of Organometallic frameworks with carbene ligands by attaching biscarbene rods in 2- and 3-dimensional frameworks.

## Appendix: Crystal structure data

Included on the cd is the measurement and structural data for all the crystal structures (doc and cif files) reported herein, including:

