# 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.
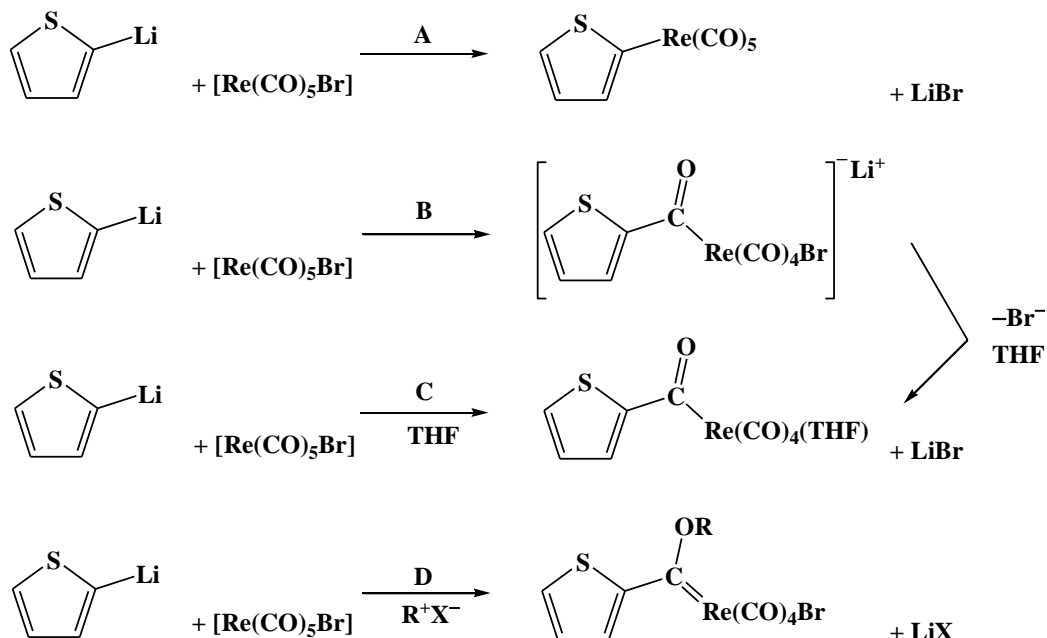
Scheme 2.1: Possible reactions of $[Re(CO)_5Br]$ with 2–lithiumthienyl

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[1].

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[2]. However, if the bromo–ligand were to be eliminated as Br⁻, as indicated in path C, a neutral acyl complex is obtained. Rhenium acyl complexes are well–known[3] 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 σ, π–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)[4].

[1] (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

[2] (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

[3] 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

[4] T. A. Waldbach, R. van Eldik, P. H. van Rooyen, S. Lotz; *Organometallics*, **1997**, *16*, 4056–4070
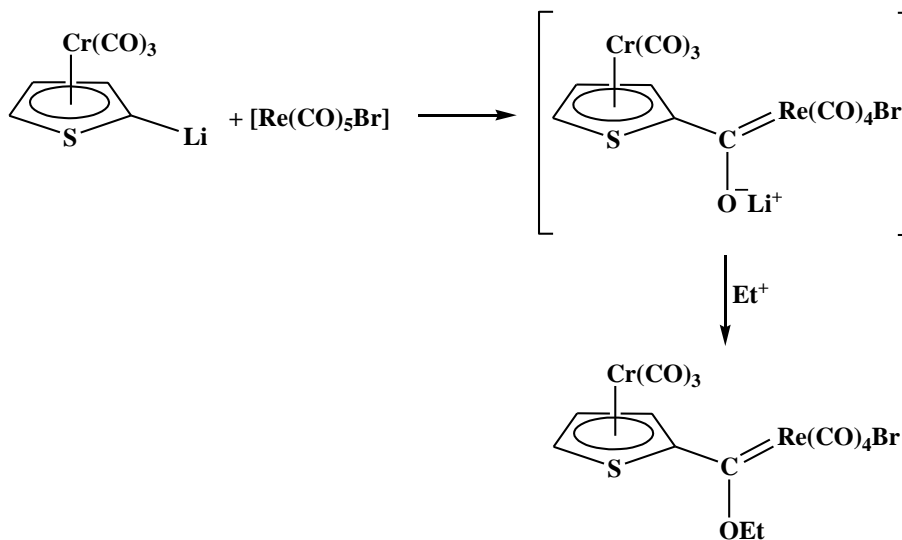
Scheme 2.2: Preparation of a rhenium Fischer carbene complex

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)$_5$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$_3$OBF$_4$) 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)$_5$" – has taken the place of the bromo ligand.

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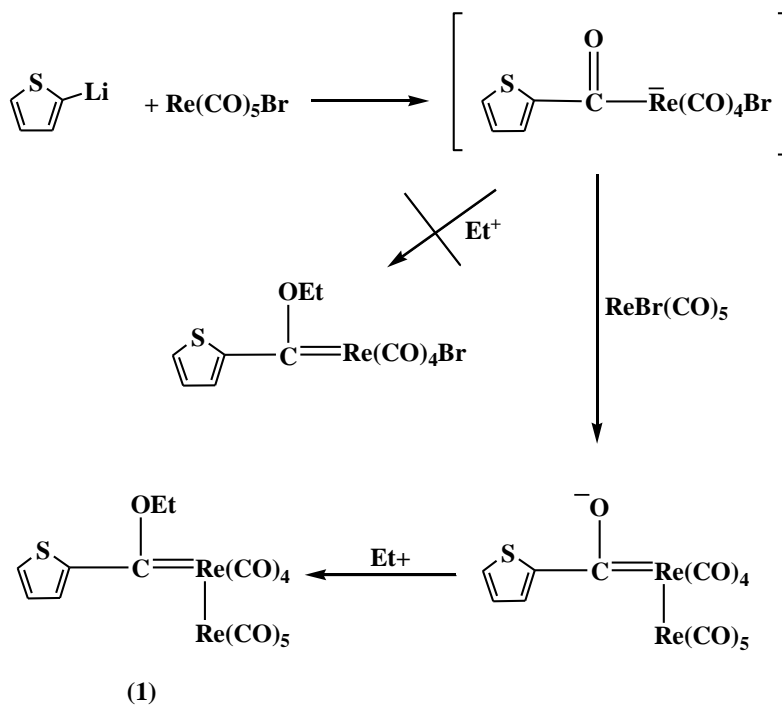

Scheme 2.3: 2–Lithiumthienyl reaction with [Re(CO)$_5$Br]

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 [Re$_2$(CO)$_{10}$] and 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.
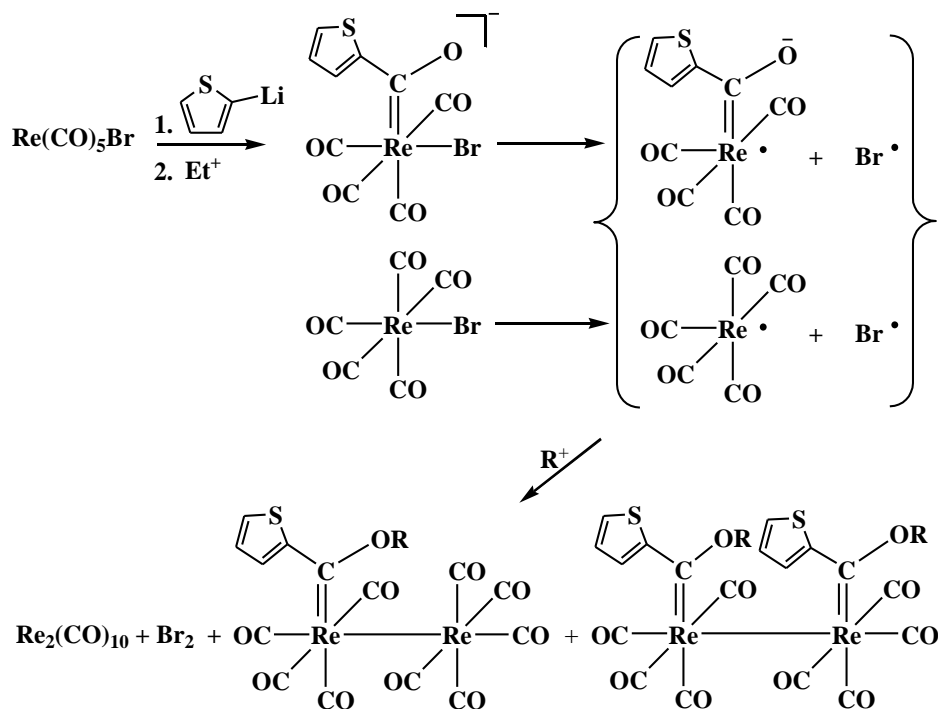
Scheme 2.4: Homolytic cleavage of Br ligand as Br$^{\bullet}$ and expected products

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 (Br$^-$) may have been eliminated to alleviate the problem of having two X–type ligands bound to the metal in an acyl anionic intermediate.
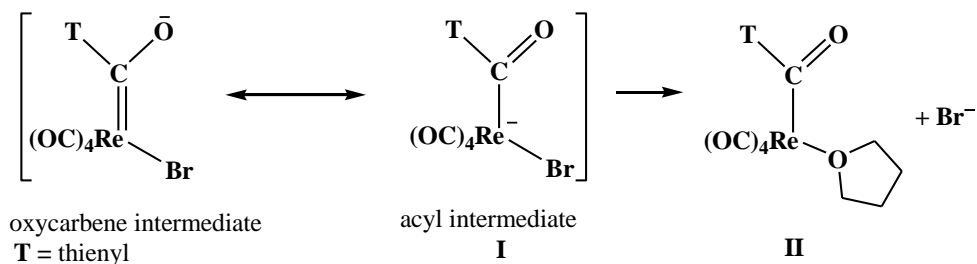
Scheme 2.5: Acylate and rhenate structures

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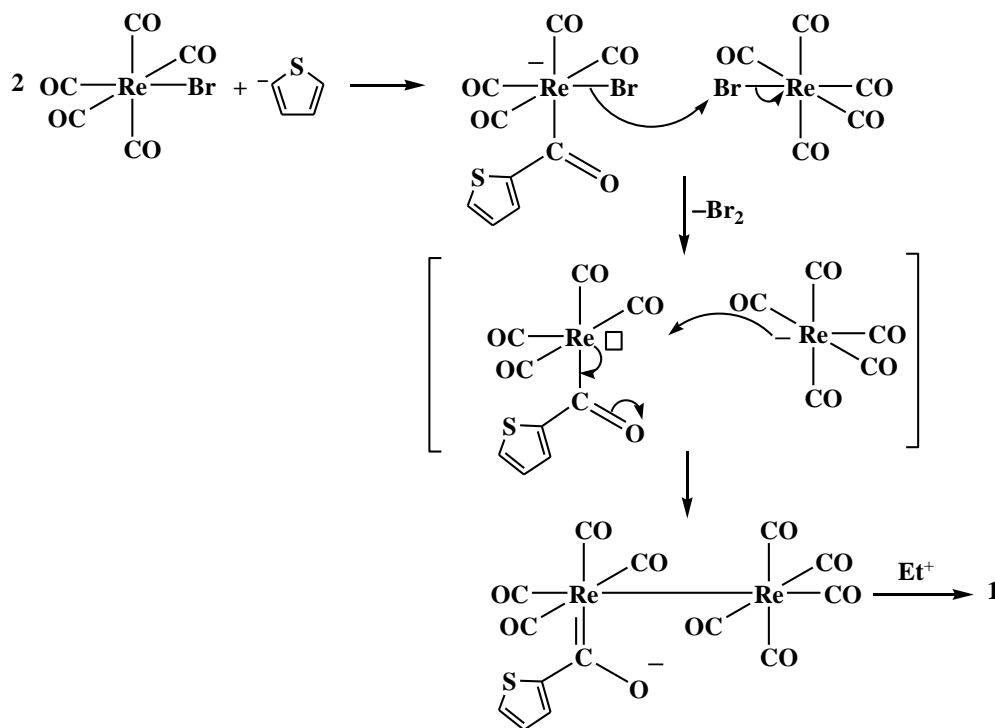
Scheme 2.6: Postulated mechanism for the formation of complex **1**

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 $[Re(CO)_5]^-$. 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[5]. The formation of [Re(CO)$_4${C(OEt)thienyl}Br] from [Re(CO)$_5$Br] and 2–lithiumthienyl was not found.

2.3 Reaction of 2–lithiumthienyl derivatives with [Re$_2$(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 [Re(CO)$_5$Br] system and the low yield of the above reaction to make **1**, it was decided to rather use [Re$_2$(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[6]. 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 {Re(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 [Re$_2$(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 [Re$_2$(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

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

[6] 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)$_5$ substituent is a very bulky ligand compared to a CO ligand. Work done by Bezuidenhout[7], in our laboratories has shown the electronic preference for the equatorial position in manganese carbonyl complexes. The aminolysis of *ax*–[Mn$_2$(CO)$_9${C(OEt)C$_4$H$_3$S}] with NH$_3$ afforded an *eq*–[Mn$_2$(CO)$_9${C(NH$_2$)C$_4$H$_3$S}] whereas the more bulky amine, HN^{i}Pr$_2$, afforded an *ax*–[Mn$_2$(CO)$_9${C(N^{i}Pr$_2$)C$_4$H$_3$S}], emphasizing the steric influence of the modified ligands.
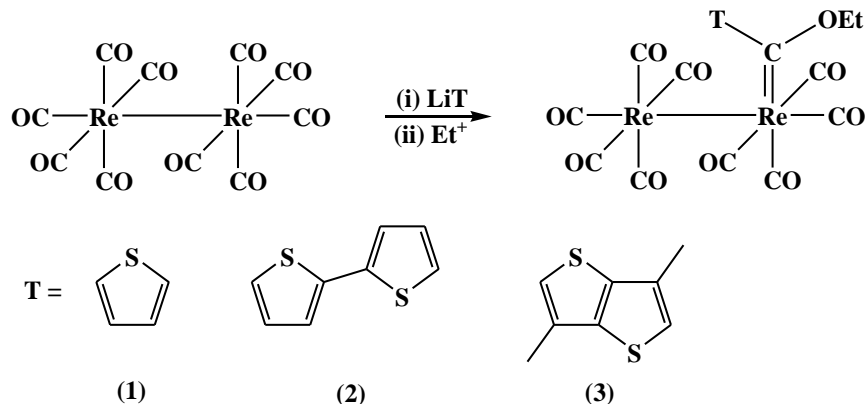
Scheme 2.7: Preparation of dirhenium monocarbene complexes

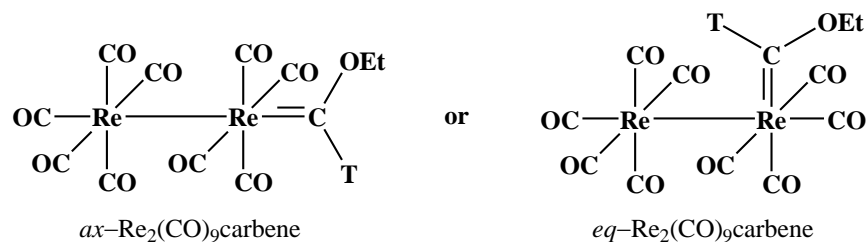*ax*–Re$_2$(CO)$_9$carbene   *eq*–Re$_2$(CO)$_9$carbene

Figure 2.1: Axial and equatorial substituted carbene ligands

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[7] 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 [Re(CO)$_5$Br] route, but the successful synthesis of the dirhenium monocarbene complexes opened the possibility to cleave the Re–Re bond with Br$_2$ to generate [Re(CO)$_5$Br] and the desired complex [Re(CO)$_4$(carbene)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 [M$_2$(CO)$_{10}$] (M = Mn/Re) by bromine, affording [M(CO)$_5$Br], is well–documented[8]. The prepared dirhenium carbene complexes **1**–**3** were reacted with 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**.

T = thiophene (**4**)
5,6–bithiophene (**5**)
3,6–dimethylthieno[3,2–*b*]thiophene (**6**)
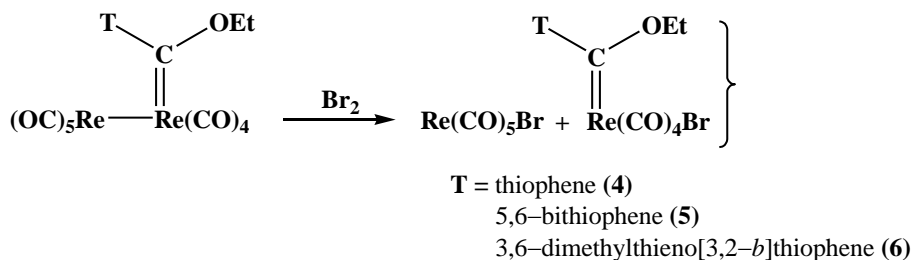
**Scheme 2.8**: Bromine–cleaving of Re–Re bonds in monocarbene complexes

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[9] and bromine adds to the double bond by first association of Br$^+$. For instance, nucleophilic attack of an aromatic ring is by one of the aromatic ring's double bonds on Br$_2$[10] (into an empty d–

[8] S. P. Schmidt, W. C. Trogler, F. Basolo; *Inorg. Synth.*, **1990**, *28*, 162
[9] (a) S. R. Merrigan, D. A. Singleton; *Org. Lett.*, **1999**, *1*, 327–329; (b) R. S. Brown; *Acc. Chem. Res.*, **1997**, *30*, 131–137
[10] 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[11] have shown that a similar halonium intermediate may be involved in the halogenation of $[Mn_2(CO)_{10}]$ and $[Re_2(CO)_{10}]$. A free halide ion is generated in the reaction and is suggested to nucleophilically attack on and open the bridged intermediate.
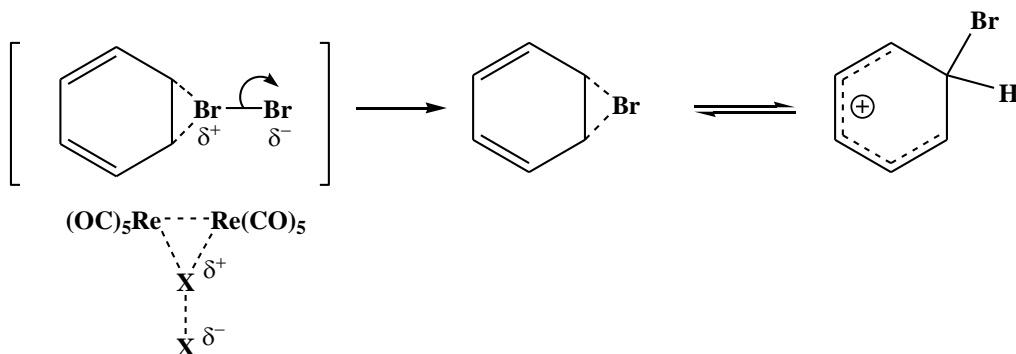
Scheme 2.9: Bromine addition to metal–metal bond

The same reactions with electron–poorer alkenes[12] require strongly electrophilic Br^+ or polarized Br–X bonds and they are more likely to undergo radical reactions[13]. Metal–carbene bonds have been used in reactions to bond to transition metals with vacant coordination sites[14]. These bonds are not as electron–rich as olefinic bonds and reaction with 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[15].

The Fischer group[16] reported that in the reaction between a chromium Fischer carbene complex and HBr, the electrophilic chromium carbene carbon was attacked by 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

[11] S. P. Schmidt, W. C. Trogler, F. Basolo; *J. Am. Chem. Soc.*, **1984**, *106*, 1308–1313

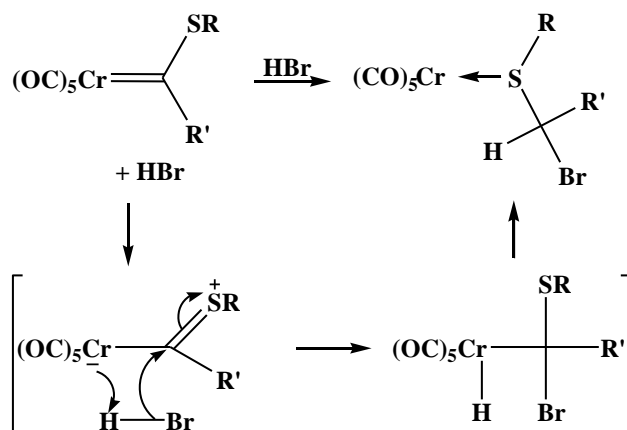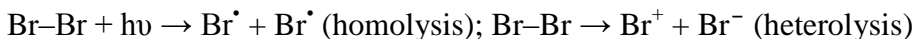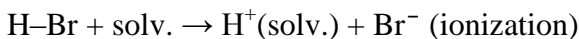[12] V.A. Petrov, C.G. Krespan; *J. Org. Chem.*, **1996**, *61*, 9605–9607

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

[14] (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

[15] J. Ushio, H. Nakatsuji, T. Yonezawa; *J. Am. Chem. Soc.*, **1984**, *106*, 5892–5901

[16] (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_2 differ though, the former is a polar substrate and the latter a non–polar substrate:

H–Br + solv. → H^+(solv.) + Br^- (ionization)

Br–Br + hυ → $Br^{\bullet}$ + $Br^{\bullet}$ (homolysis); Br–Br → Br^+ + Br^- (heterolysis)

Scheme 2.10: Reaction of a chromium carbene complex with HBr

The M–M bond energy ($Mn(CO)_5$–$Mn(CO)_5$ ≈ 170 kJ/mol[17]; $Re(CO)_5$–$Re(CO)_5$ ≈ 213 kJ/mol[18]) is approximately half as strong as a similar carbon–carbon (C–C ≈ 350 kJ/mol)[19] bond in organic chemistry. Homolysis of the weaker Re–Re and the Br_2 bonds produces isolobal fragments which can exchange and afford the final cleaved products.
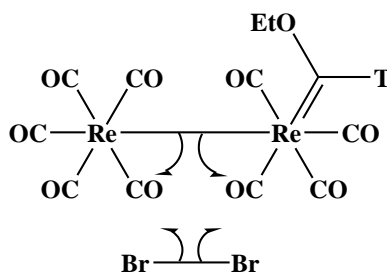

Figure 2.2: Radical cleaving of Re–Re bond by Br_2

[17] E. Folga, T. Ziegler; *J. Am. Chem. Soc.*, **1993**, *115*, 5169–5176
[18] B. C. Gilbert, A. F. Parsons; *J. Chem. Soc., Perkin Trans.*, **2002**, 367–387
[19] *Advanced Organic Chemistry, 4th Ed.*, John Wiley & Sons, Editor: J. March; 24 (Table 1.7)

Although it is possible to synthesize [Re(CO)$_4${C(OEt)R}Br] complexes along this route, one half of the starting complex is lost as [Re(CO)$_5$Br]. One would ideally have liked to start with [{Re(CO)$_4${C(OEt)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[20]. 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 [Re$_2$(CO)$_{10}$], and thereafter adding two equivalents Et$_3$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).

7–9

T = thiophene (**7**) / 5,5'–bithiophene (**8**) / 3,6–dimethylthieno[3,2–*b*]thiophene (**9**)
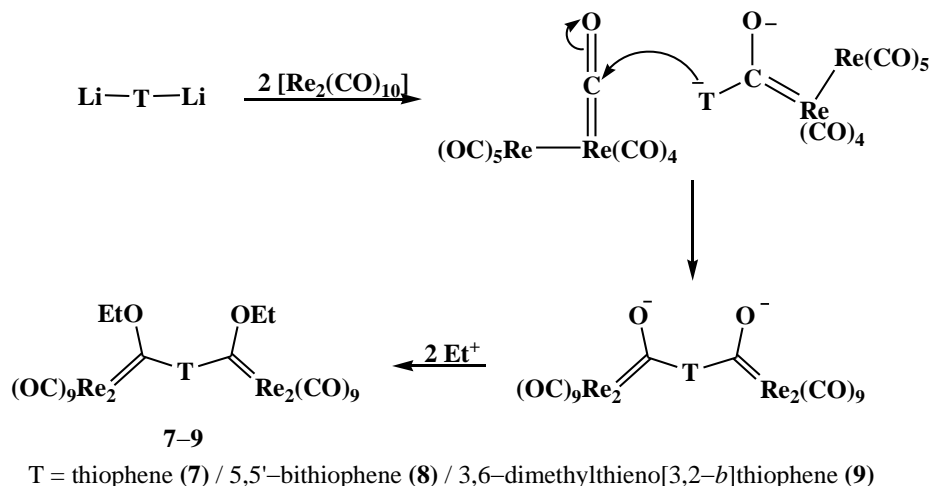
Scheme 2.11: Preparation of complexes **7–9**

[20] (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 $[Re_2(CO)_{10}]$ 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}H NMR spectroscopy.

T = bithiophene
**X** = Re(CO)$_5$ (**10**) / Br (**11**)
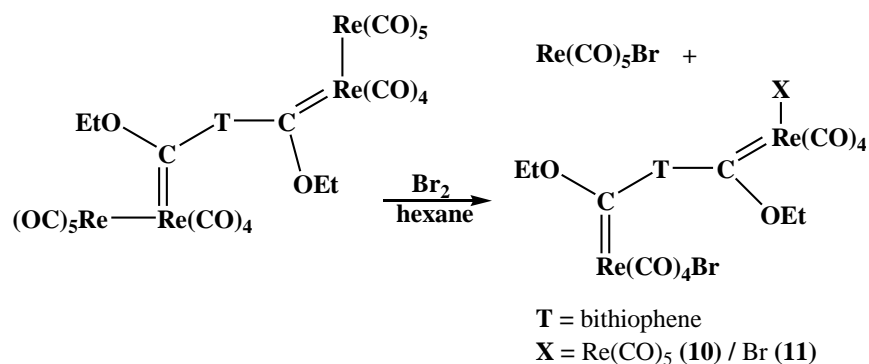
Scheme 2.12: Bromine–cleaving of Re–Re bonds in tetrametal biscarbene complexes

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.
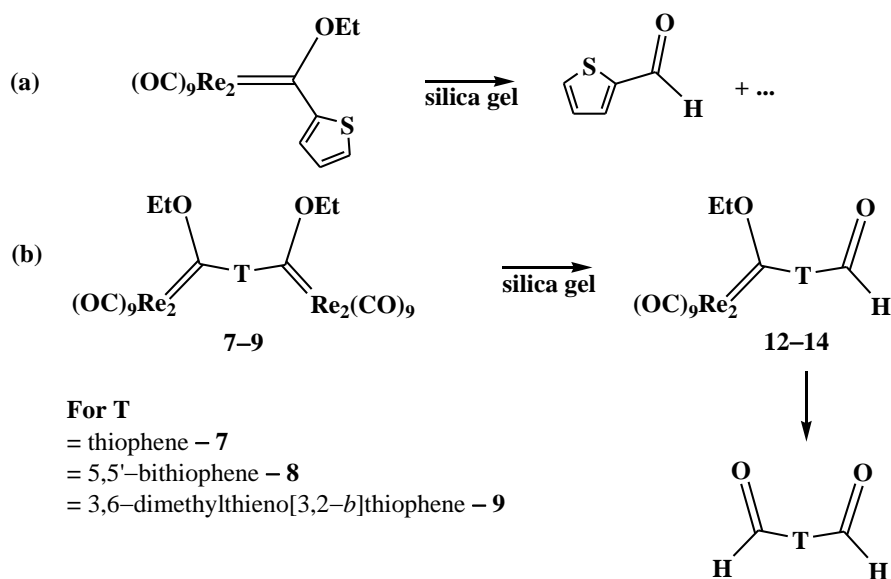
Scheme 2.13: Formation of aldehyde species

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_2–group attached to oxygen could generate an acyl radical that reacts to give, amongst others, aldehydes[21] (Scheme 2.14).
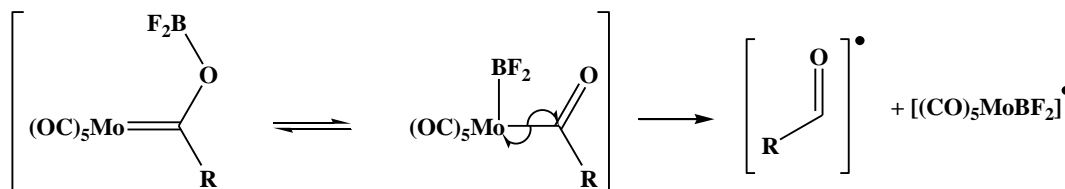
Scheme 2.14: Ligand decomplexation to give acyl synthons

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[22]. Hydroxycarbene complexes are usually stabilized in the solid state through hydrogen–bonding[23].

[21] J. Barluenga, F. Rodríguez, F. J. Fañanás; *Chem. Eur. J.*, **2000**, *6*, 1930–1937

[22] (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

[23] (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_4. 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[24].
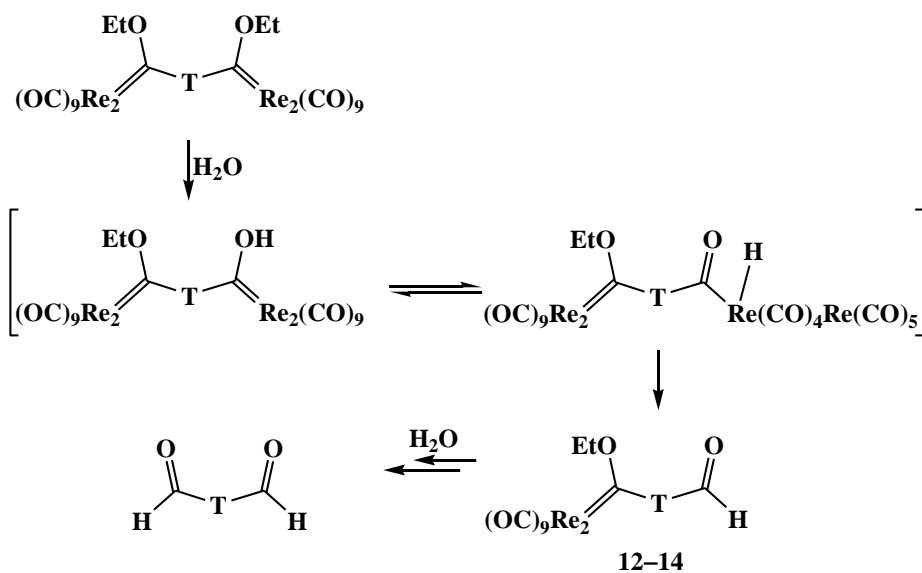
The hydroxycarbene complex is convertible into a very reactive hydrido–acyl complex[25]. As Schemes 2.15 and 2.16 shows, the aldehyde is obtained by reductive elimination of the hydride and acyl ligand.
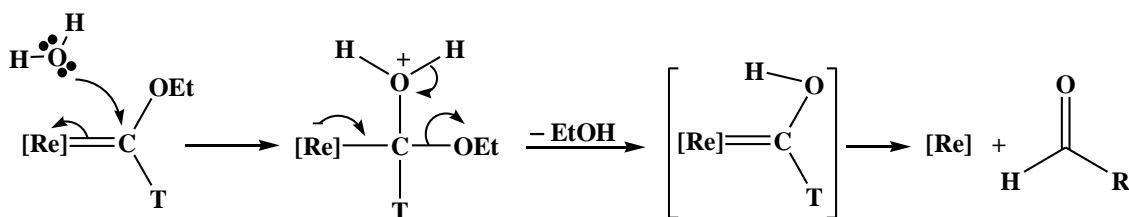
Scheme 2.15: Hydroxycarbene intermediates

[24] (a) C. F. Bernasconi, M. Pérez–Lorenzo, S. J. Codding; *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
[25] C. P. Casey, C. J. Czerwinski, R. K. Hayashi; *J. Am. Chem. Soc.*, **1995**, *117*, 4189–4190

EtO   OEt

(OC)$_9$Re$_2$ — T — Re$_2$(CO)$_9$

↓ H$_2$O

[EtO   OH   EtO   O   H
  (OC)$_9$Re$_2$ — T — Re$_2$(CO)$_9$ ⇌ (OC)$_9$Re$_2$ — T — Re(CO)$_4$Re(CO)$_5$]

↓

O   O   H$_2$O   EtO   O
H — T — H   ⟵   (OC)$_9$Re$_2$ — T — H

12–14

T = thiophene **(12)** / 5,6–bithiophene **(13)** / 3,6–dimethylthieno[3,2–*b*]thiophene **(14)**

**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. [Re$_2$(CO)$_{10}$] and [Re(CO)$_5$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 HBF$_4$ and the solvents removed for ^{1}H NMR studies of the mixtures.

For the reaction of [Re(CO)$_5$Br] with protonation in THF, a single major product was indicated by ^{1}H NMR spectroscopy. The NMR data of this compound was consistent with a hydroxycarbene complex, [Re(CO)$_4${C(OH)C$_4$H$_3$S}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}H NMR spectroscopy for the water fraction. $[Re(CO)_5\{C(O)C_4H_3S\}]$ 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 $[Re(CO)_5\{C(O)C_4H_3S\}]$ was prepared by reacting the rhenium carbonyl anion $[Re(CO)_5]^-$ with 2–thienyl acetylchloride (it was previously prepared by Rauchfuss *et al*[1a] by a different method). $[Re(CO)_5\{C(O)C_4H_3S\}]$ shows thienyl signals in the ^{1}H NMR spectrum at 7.97 (dd), 7.72 (dd) and 7.18 ppm (dd). Both preparative methods are shown below:
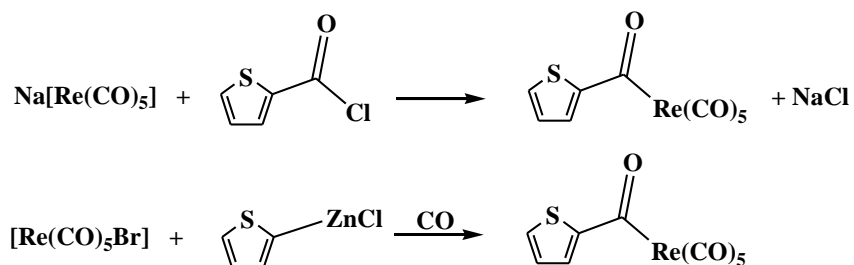
Scheme 2.17: $[Re(CO)_5\{C(O)C_4H_3S\}]$ synthesis

The reaction with $[Re_2(CO)_{10}]$ afforded various products and not all could be identified. Importantly, NMR bands belonging to $[Re_2(CO)_9\{C(OH)C_4H_3S\}]$, 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 $[Re_2(CO)_{10}]$ 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. $[Re(CO)_5]^-$ can be alkylated (Et$^+$) and after β–H elimination again give

[Re(CO)$_5$H], with a Re–H ^{1}H NMR chemical shift value recorded at –5.7 ppm[26]. [Re(CO)$_5$H] coordinates through the Re–H bond to a coordinatively unsaturated Re– intermediate to give E (–15.2 ppm)[27]. The formation of [Re(CO)$_5$H] and hydride complexes are shown below in Scheme 2.18:
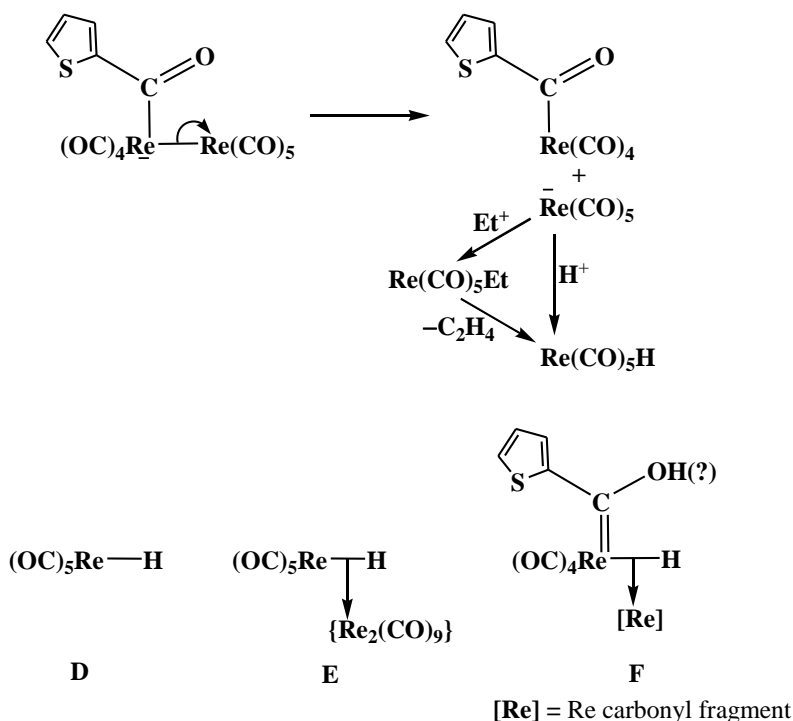
Scheme 2.18: Formation of [Re(CO)$_5$H] and other hydride complexes

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.

[26] I. del Rosal, L. Maron, R. Poteau, F. Jolibois; *Dalton Trans.*, **2008**, 3959–3970
[27] 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 $[Re(CO)_5Br]$ and 2–lithiumthienyl, and subsequent alkylation with Et_3OBF_4 or protonation with 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.
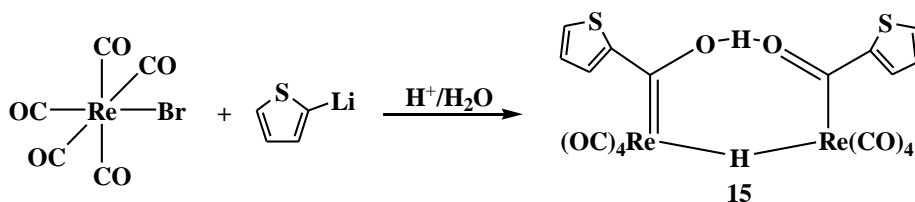

Scheme 2.19: Complex **15** formation

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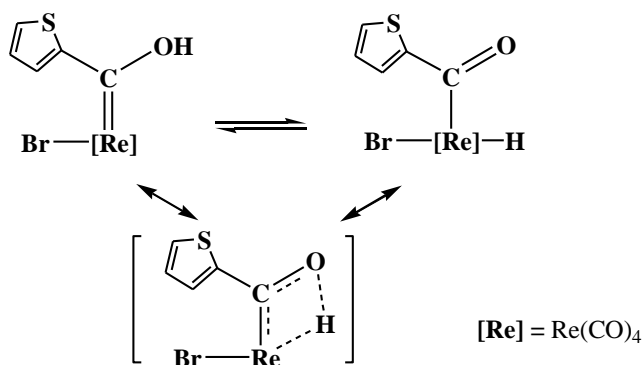
**Scheme 2.20**: Proposed metal–to–oxygen migration of a hydrogen atom

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[28], also shown in the scheme, display these two functionalities on one rhenium atom, in **15** they are found on two separate rhenium atoms.

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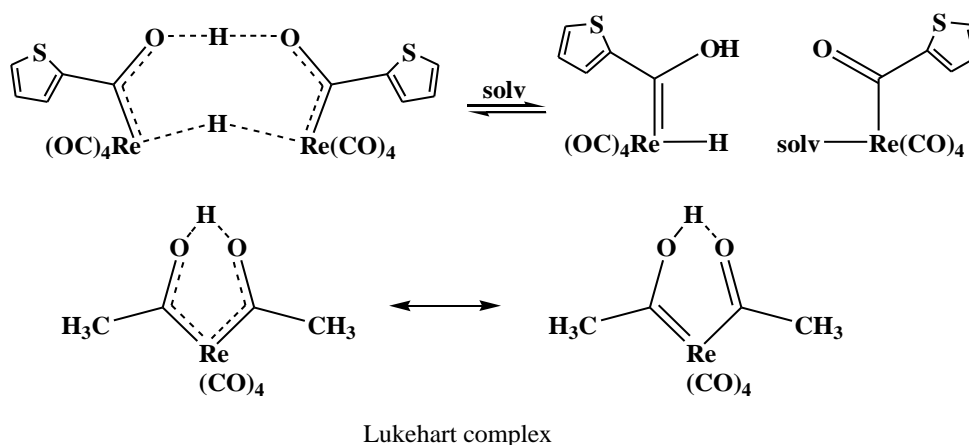
Scheme 2.21: Fragments of complex **15**

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.

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[28] (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
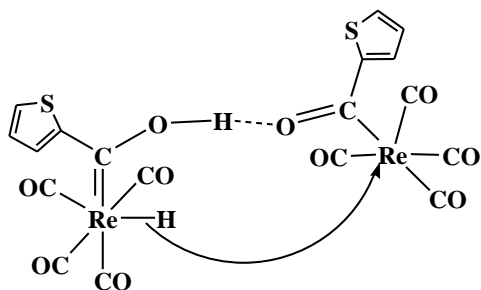
Scheme 2.22: Attachment of two rhenium species through hydrogen bonding

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 $[Re(CO)_5H]$ formed *in situ* (Scheme 2.18). When the preparation was repeated, adding either HBF_4 or magic methyl, instead of Et_3OBF_4, the same complex was obtained.

2–Lithiumthienyl attacks on a carbonyl ligand of $[Re(CO)_5Br]$ 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[29]. Complex **15** is suggested to have formed from such a species, as is shown in Scheme 2.23.

The $Re(CO)_5$–H bond strength is 310 kJ/mol[30]. Unfortunately no bond energy of $Re(CO)_5$–Br data could be found in literature, but the ordering of Mn–X bond dissociation energies follows the following pattern[31]:

$(CO)_5Mn$–X (Δ(Mn–X), kJ/mol)

[29] K. P. Darst, C. M. Lukehart; *J. Organomet. Chem.*, **1979**, *17*, 65–71

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

[31] (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_3 (sp^3–C) (185) > C(O)CH_3 (165) > $Mn(CO)_5$ (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.


$$X = OH, Re(CO)_5$$
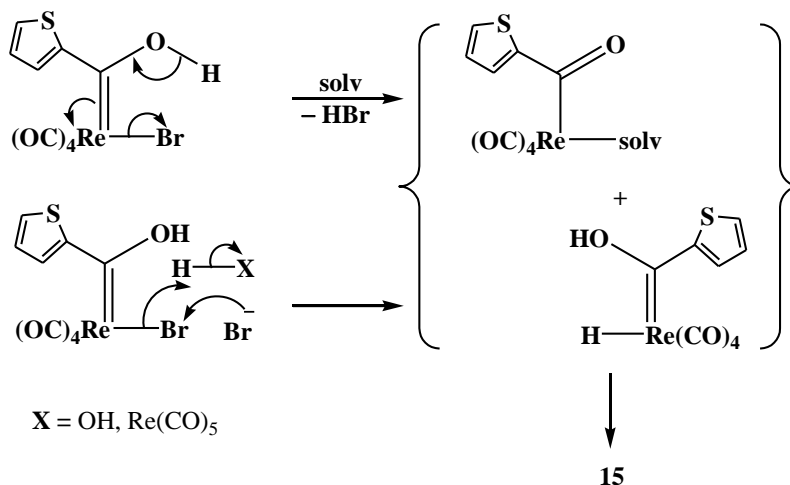
Scheme 2.23: Possible reaction route to **15**

The reaction of 2–lithiumthienyl or 5–lithium–2,2′–bithienyl with $[Re_2(CO)_{10}]$ 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[32], 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

[32] (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.
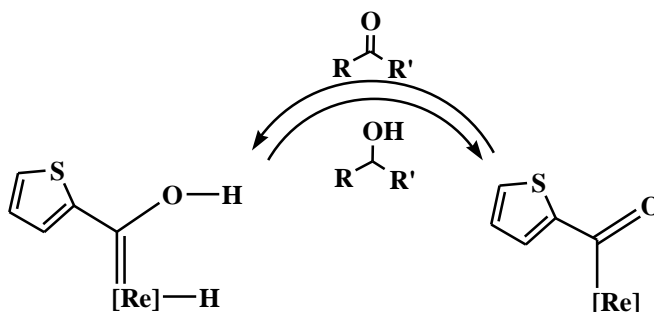
Scheme 2.24: Proposed activity of complex **15**

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}H NMR spectrum. The recognition of the signal of the hydroxycarbene proton is elusive on the ^{1}H NMR spectrum. No signal was observed that may belong to this hydrogen. Evidence of acyl and aldehyde formation was found in the ^{1}H NMR spectrum of a decomposition mixture of **15**. Although this is not conclusive, it may show that the complex has lost 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.