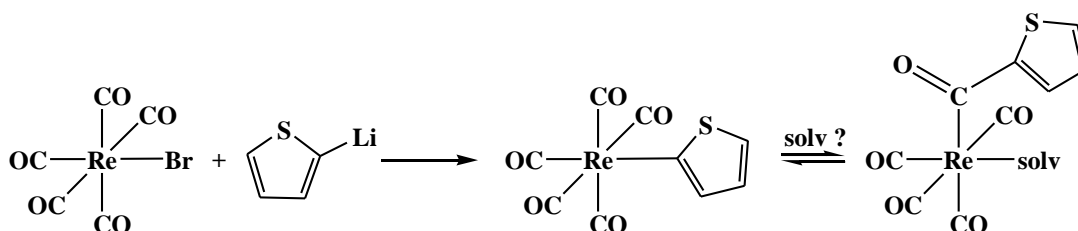


## Chapter 6: Concluding comments

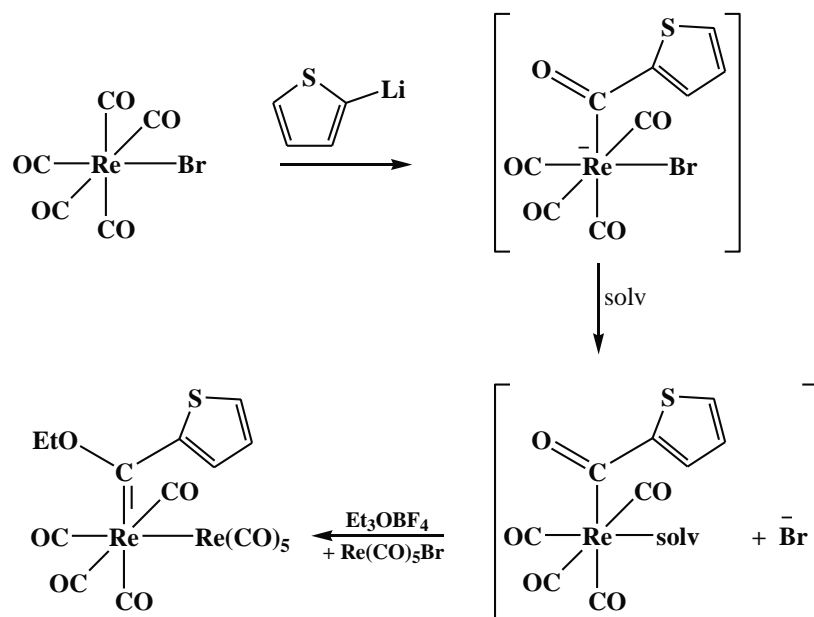
### 6.1 Summary

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.

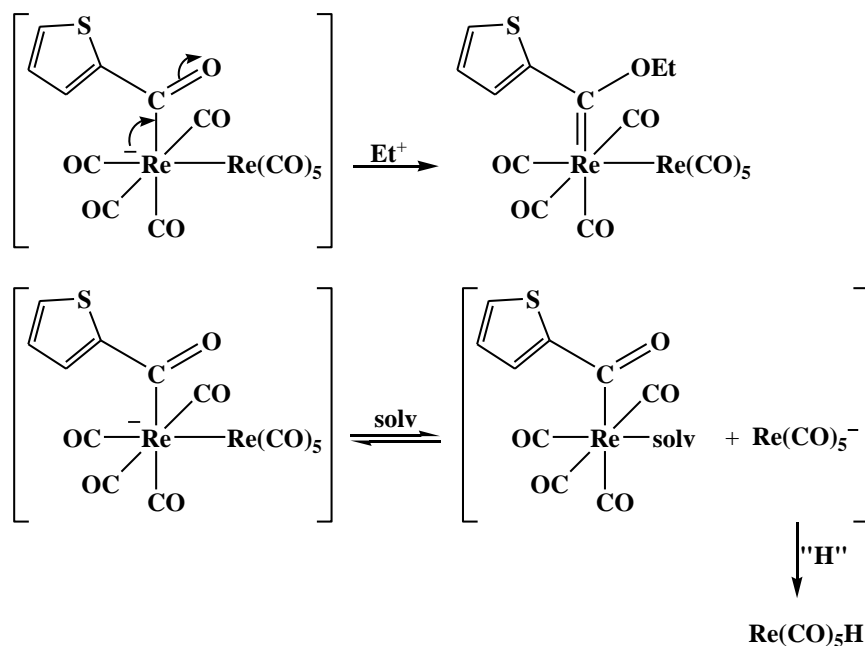


Lithiated thienyl did not substitute the bromo ligand in  $[\text{Re}(\text{CO})_5\text{Br}]$ , but the reaction produced a charged intermediate (immobile on silica) and it was understood that the nucleophile had attacked a carbonyl ligand. A carbene precursor compound (metalate) had thus formed and 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.

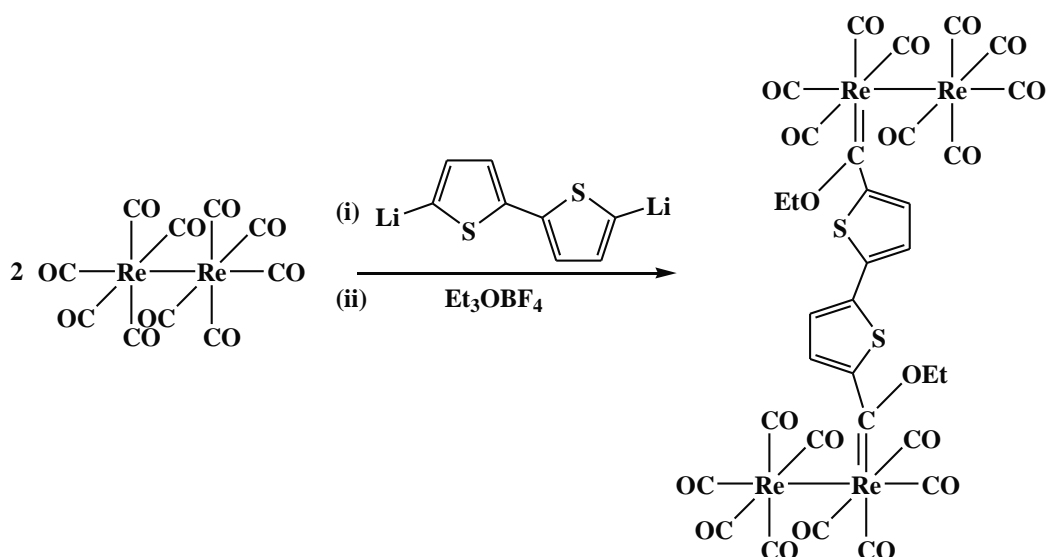


Instead of bromo–ligand substitution, the 2–lithiumthienyl had bonded to the carbon atom of a carbonyl ligand and triggered a series of conversions. The intermediate anionic metalate presumably eliminated its bromo–ligand, as bromide, and a neutral rhenium species with a vacant coordination site was 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**.

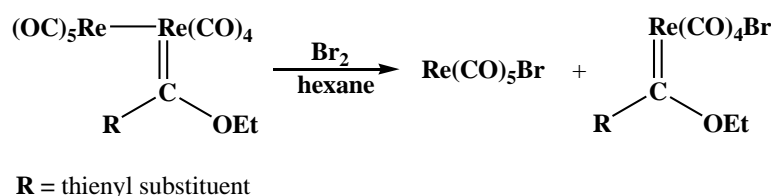


It was decided that, for the thienyl substrates 2,2'-bithiophene and 3,6-dimethylthieno[3,2-*b*]thiophene, the desired dirhenium carbene complexes would be better prepared with  $[\text{Re}_2(\text{CO})_{10}]$  as precursor reagent and not  $[\text{Re}(\text{CO})_5\text{Br}]$ . Monocarbene and biscarbene 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.

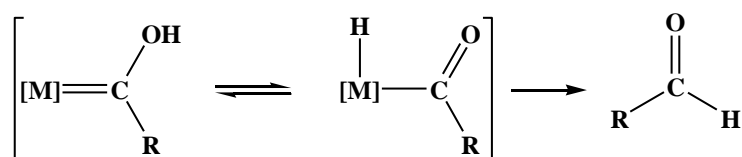
Hence, it was investigated whether the Re–Re bonds of the complexes that were prepared could be cleaved with bromine without affecting the carbene ligand. These reactions proved to be successful and the carbene ligand itself was not altered by the added bromine during the reaction. In this way it was possible to obtain a monorhenium bromo–carbene complex, which was not obtainable from the application of the Fischer carbene synthesis method to rheniumpentacarbonyl bromide.



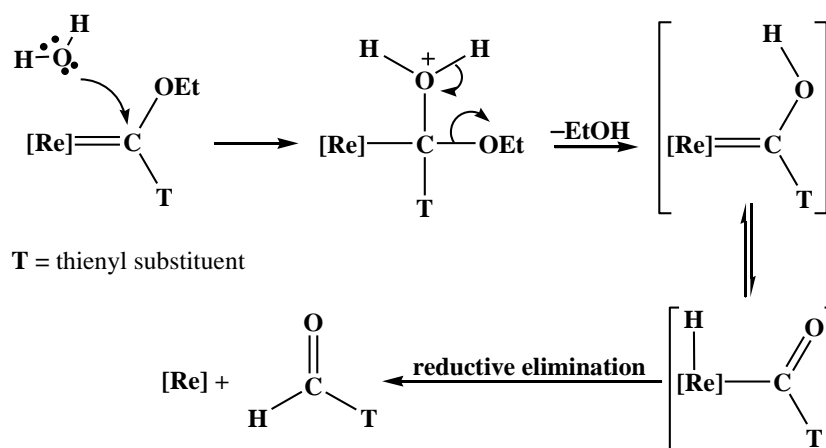
The reverse action of the shown reaction is rhenium–rhenium bond formation or Re(CO)<sub>5</sub> and Br exchange. This implies forming a weaker Re–Re bond by breaking stronger Re–Br bonds.

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.



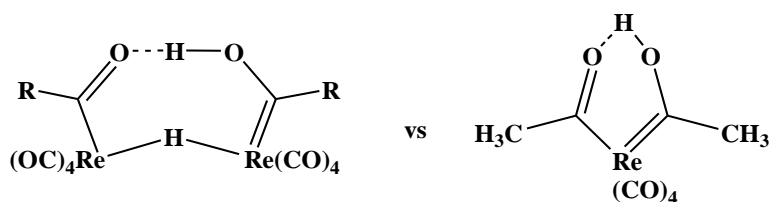
To explain the formation of aldehydes from ethoxycarbene precursors, the substitution of OEt by OH is a prerequisite. It was shown that water reacts with the carbene ligand presumably in a similar fashion as primary amines to afford hydroxycarbene ligands.



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.



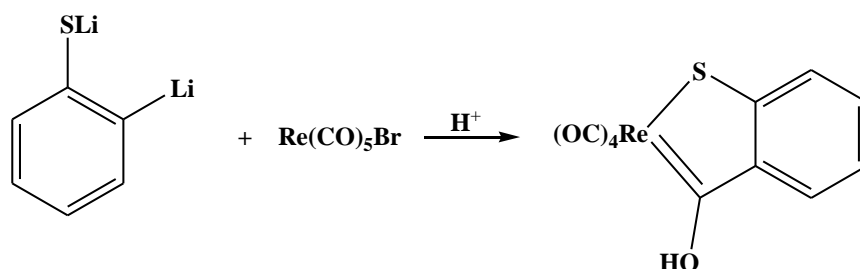
These complexes display both an acyl and a hydroxycarbene fragment and represent important intermediates discussed above. The complexes have the potential to be hydrogenation catalysts. Two rhenium fragments, each having a ligand which is intermediate between a carbene and an acyl ligand – are held together 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

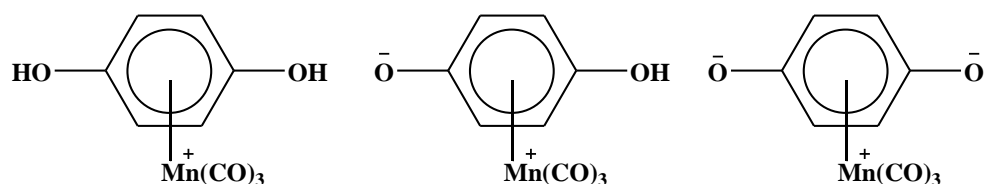
The following questions arose from this work and are worth looking at in future research:

- (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.