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[1]. Rheniumpentacarbonyl bromide was prepared from dirhenium decacarbonyl[2]. Triethyloxonium tetrafluoroborate was prepared according to the method of Meerwein[3].

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_2O_5.

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. ^{1}H and ^{13}C NMR spectra were measured at 300.133 and 75.469 MHz, respectively.

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[1] G. H. Spies, R. J. Angelici; *Organometallics*, **1987**, *6*, 1897–1903
[2] S. P. Schmidt, W. C. Trogler, F. Basolo; *Inorg. Synth.*, **1990**, *28*, 162
[3] 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.

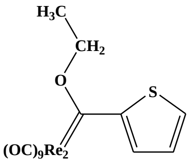
5.2 Synthesis

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

This compound was prepared according to the method of Choi *et al*[4].

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 attach 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.

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[4] 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 α–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°C (from 0°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°C before the metal complex is added, by placing it in an acetone/dry ice bath.

$[Re(CO)_5Br]$ (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 Et_3OBF_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 Et_3OBF_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°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 $C_{16}H_8O_{10}SRe_2$ (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. $Re_2(CO)_{10}$ (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°C and addition of an appropriate volume of a dichloromethane Et_3OBF_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 ($Re_2(CO)_{10}$) 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.

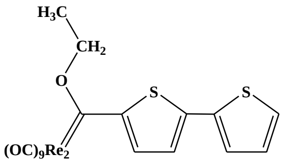
The THF was removed and the residue dissolved in distilled deoxygenated water (O_2 was removed from the water by repeated (3 times) heating and cooling cycles, whilst passing N_2 (g) through the solution). The water solution was orange–brown.

The water was quickly layered with 20 ml diethyl ether and a portion of Et_3OBF_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 Na_2SO_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$_4$H$_2$S–C$_4$H$_3$S}]*



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°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°C. The solution attained a clear red–brown colour.

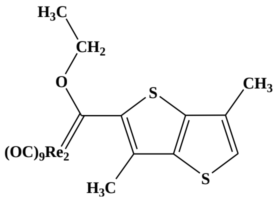
The Schlenk tube with the solution was transferred to an acetone/dry ice bath at –78°C. Re$_2$(CO)$_{10}$ (0.65 g, 1.0 mmol) was added, and the colour of the solution was observed to immediately become deep red. The solution was stirred for 30 min., after which it was removed from the cold bath and the 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_3OBF_4 solution in DCM was obtained as before. An appropriate volume (corresponding to 1 mmol Et_3OBF_4) 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 $C_{20}H_{10}O_{10}S_2Re_2$ (846.6): C 28.37, H 1.19%; Found: C 28.51, H 1.23%

*5.2.2.3 Complex **3** – [$Re_2(CO)_9\{C(OEt)C_8H_7S_2\}$]*



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°C and *n*–BuLi (0.0.75 ml, 1.2 mmol) was added. Stirring was continued for 2 hours at –10°C. A white suspension was observed.

The solution was cooled down to –70°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.

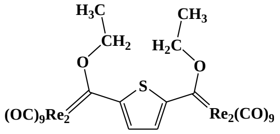
The THF was removed and the residue was dissolved in a minimum dichloromethane. Et_3OBF_4 was measured out and dissolved in dichloromethane. A volume equivalent to 1 mmol (0.2 g, 1.0 mmol) was added at –30°C. The solution was allowed to warm to room temperature and was stirred for 30 min. The colour 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 $C_{20}H_{12}O_{10}S_2Re_2$ (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°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°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°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**.

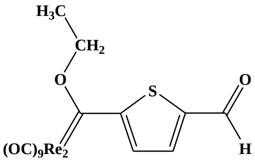
The complex is a light red solid.
5% (0.07 g) of the biscarbene complex was isolated.
The complex is unstable and the melting point was not determined.
Anal. calcd. for $C_{28}H_{12}O_{20}SRe_4$ (1445.3): C 23.27, H 0.84%; Found: C 23.87, H 0.97%

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.

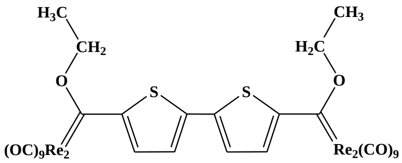
5.2.2.5 Further product isolated: ***12***

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°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°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°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°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.

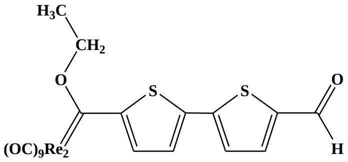
As a final step, the reaction solution was passed through a silica gel filter to remove the salts. The DCM was removed *in vacuo*.

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.

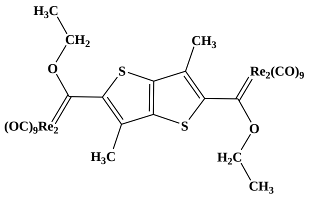
The complex could be purified by recrystallization from a hexane dichloromethane mixture and a crystal structure was determined of the complex.

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.

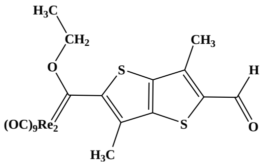
The reaction solution was passed through a silica gel filter to remove the salts. The DCM was removed *in vacuo*.

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 $C_{32}H_{16}O_{20}S_2Re_4$ (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*** *– [$Re_2(CO)_9\{(C(OEt))C_8H_6S_2–C(O)H\}$]*



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_2SO_4 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.

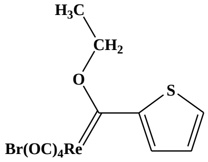
Procedure 1

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.

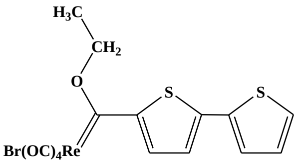
Complex **4** was obtained by decanting the hexane solution (in the case of bromination via the second procedure), which still contained some uncleaved monocarbene complex.

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)$_5$Br] 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]*



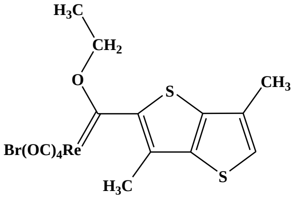
This complex was prepared by both of the procedures described for the preparation of **4**.

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)$_5$Br] 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]*

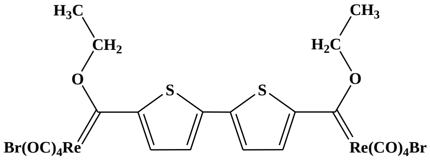


This complex was brominated by following procedure 2, as detailed in section 5.3.

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*** *–* $[Re(CO)_4Br\{(C(OEt)C_4H_2S–C_4H_2SC(OEt))\}Re_2(CO)_9]$



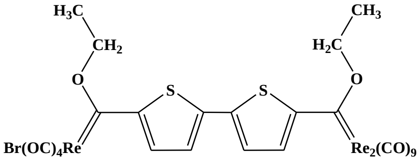
Complex **5** (0.76 g, 0.5 mmol) was dissolved in 40 ml hexane, giving a deep red solution. Bromine (3.11 g/ml, 0.026 ml, 0.5 mmol) was added carefully while stirring was maintained. Only one equivalent of bromine was added, because the intention was to only cleave the rhenium–rhenium bond of one of 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)

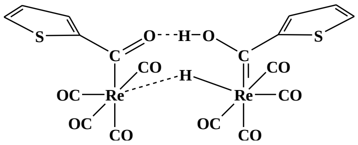
Anal. calcd. for $C_{22}H_{14}Br_2O_{10}S_2Re_2$ (1034.7): C 25.54, H 1.36%; Found: C 25.88, H 1.48%



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** – $[Re(CO)_4\{\mu\text{–}H\}\{C(OH)C_4H_3S\}\text{–}Re(CO)_4\{C(O)C_4H_3S\}]$



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°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°C (dry ice/acetone) and [$Re(CO)_5Br$] (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 °C and alkylating agent Et_3OBF_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.

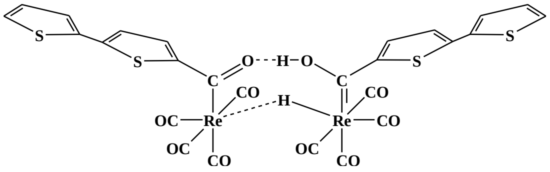
In the second and third preparations, magic methyl (CF_3SO_3Me; 0.16 g, 1.0 mmol) and HBF_4 (0.2 ml, 1.0 mmol) were used, respectively.

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 $C_{18}H_8O_{10}S_2Re_2$ (820.8): C 26.34, H 0.98%; Found: C 26.51, H 1.01%

*5.2.4.2 Complex **16** – [Re(CO)$_4${μ–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°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°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°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°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 [$Re_2(CO)_{10}$] (0.65 g, 1.0 mmol) and thereafter reacting with HBF_4 (0.2 ml, 1.0 mmol).

Yield of complex **16**: 15 % (0.15 g)