

Chapter 4

Rhenium(I) complexes with thiophene-containing ligands

4.1 Introduction

Organometallic liquid crystals have only recently come to the foreground and various metals such as Fe¹⁻⁷, Rh⁸, Mn^{9,10}, Pt¹¹, Pd^{11,12}, etc. have been studied and displayed liquid crystalline properties. Problems associated with organic ligands are often the lability and instability of the metal carbon bond under thermal conditions. Planar or linear complexes are favoured as they could be used to mimic anisotropic rods or discs. In some instances the chains will be attached to a π -bonded arene ligand and in other examples to metal carbon bonds (Figure 4.1).

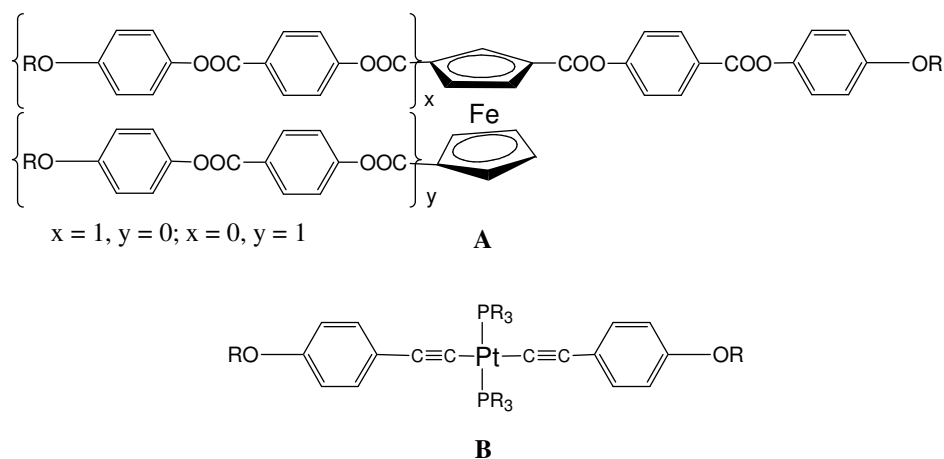


Figure 4.1 Calamitic organometallic liquid crystals

In the previous chapters' synthesis of nickel and zinc complexes, classical examples of inorganic compounds were discussed. In this section examples of

organometallic compounds of rhenium(I) with the same type of ligands were investigated. The coordination environment of ligands at the metal centre for nickel and zinc complexes is either square-planar or tetrahedral/trigonal bipyramidal. For many years, the mesomorphic properties of calamitic metal-containing liquid crystals¹³ have mostly been associated with square planar or linear coordination at the metal centre. Thermotropic, calamitic mesophases of manganese(I) and rhenium(I) complexes of orthometalated imines were observed for the first time in 1994 by Bruce and co-workers¹⁴. The coordination geometry at the metal centre of these complexes was octahedral. It was reported that at least four aromatic rings in the organic backbone were necessary to preserve the overall molecular anisotropy to obtain the calamitic mesophases. Other orthometallated complexes of Mn(I) and Re(I) reported recently are with diazabutadiene^{9,10,15,16} and 2,2'-bipyridine^{14,17}. The carbonyl ligands have been omitted in Figure 4.2.

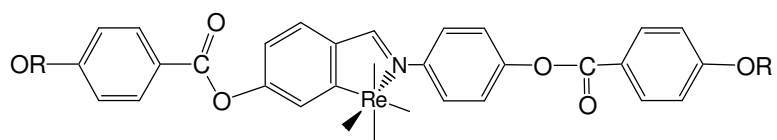


Figure 4.2 Orthometallated imine complexes of rhenium

Liquid crystals rely on the presence of anisotropic dispersion forces to stabilize their mesophases, and these arise from a shape anisotropy of the molecules, generally coupled with a significant anisotropy of polarisability. The addition of two extra ligands to the highly anisotropic coordinated planar, four-coordinate metal centre may generate octahedral coordination with reduced overall anisotropy¹⁸. In these complexes the rhenium is anchored in the centre of the

molecule by two nitrogen donor ligands and with the chain structure extending on both sides. The carbonyl ligands are omitted in Figure 4.3.

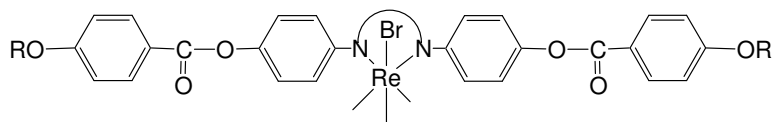


Figure 4.3 Diazabutadiene and bipyridine complexes of rhenium

Halotricarbonyl(α -diimine)rhenium complexes have been reported as efficient photosensitizers for energy and electron transfer¹⁹. Luminescence properties have been detected in *fac*-[ReX(α -diimine)(CO)₃] complexes where X can be varied from the simple halo and cyano group to organic ligands such as pyridine and acetylide^{19,20}. Complexes of diazabutadienes with ReBr(CO)₃ have been reported as luminescent organometallic liquid crystals²¹. Binnemans and his co-workers synthesized the bromotricarbonyl rhenium(I) complexes by coupling mesogenic 4-cyanobiphenyl groups with a long alkyl spacer to a substituted imidazo[4,5-f]-1,10-phenanthroline, which acts as the coordinating group²². The mesophases of the complexes were nematic, smectic or lamello-columnar phases, depending on the position and number of 4-cyanobiphenyl groups.

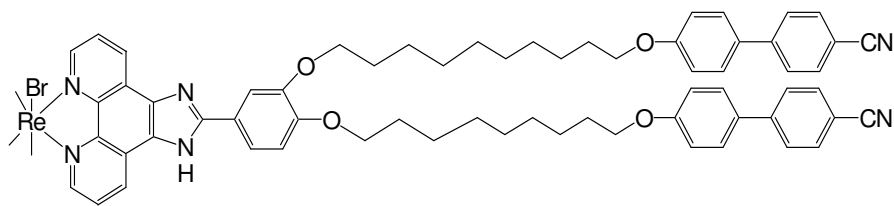


Figure 4.4 Luminescent rhenium(I) liquid crystals

The rhenium(I)-containing metallomesogens showed moderate transition temperatures and they were strongly luminescent, both in the solid state and in solution. In these complexes the rhenium is on one side of the chain structure.

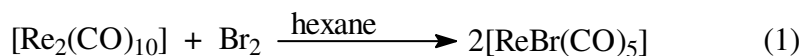
In this study, 5-alkyl-2-thiophene- or bithiophenedithiocarboxylate complexes of rhenium(I) tetracarbonyl were synthesized and their structural features and potential liquid-crystalline properties investigated. Instead of arene rings thiophene rings are incorporated with the idea of modifying the structural features slightly and facilitating charge transfer processes and polarization effects.

4.2 Results and discussion

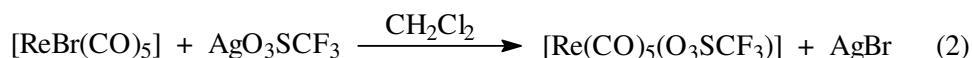
4.2.1 Synthesis and characterization

Complexes of the type $[\text{Re}(\text{CO})_4(\text{S}_2\text{CTR})]$ (where R = H, T = thiophene (**12**), R = CH_3 , T = bithiophene (**13**), R = $\text{C}_{14}\text{H}_{29}$, T = thiophene (**14a**), R = $\text{C}_{14}\text{H}_{29}$, T = bithiophene (**14b**)) were synthesized via a three-step reaction sequence.

During the first-step bromopentacarbonylrhenium, $[\text{ReBr}(\text{CO})_5]$ was prepared by the reaction of dirheniumdecacarbonyl, $[\text{Re}_2(\text{CO})_{10}]$ with bromine under a stream of nitrogen at room temperature (equation (1))²³.

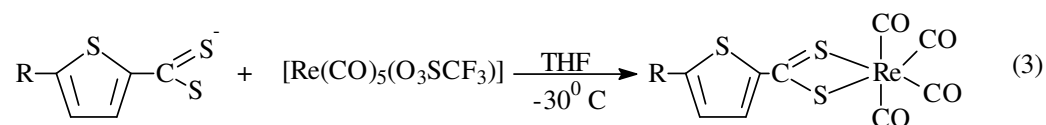


In the second step pentacarbonyl(trifluoromethanesulfonato)rhenium(I), $[\text{Re}(\text{CO})_5(\text{O}_3\text{SCF}_3)]$ was prepared from $[\text{ReBr}(\text{CO})_5]$ (equation (2))²⁴.



Silver(I) trifluoromethanesulfonate, $\text{Ag}(\text{O}_3\text{SCF}_3)$ was added to a dichloromethane solution containing $[\text{ReBr}(\text{CO})_5]$ and stirring continued for 2 hours at room temperature. The fluffy AgBr precipitate was removed by filtration through a fine Schlenk frit to yield a clear solution. The volume of the solution was reduced under vacuum, allowed to warm to room temperature and freshly distilled hexane was added and the solvents were removed slowly in vacuum to precipitate $[\text{Re}(\text{CO})_5(\text{O}_3\text{SCF}_3)]$ as a white powder.

In the third step, the 5-alkyl-2-thiophenedithiocarboxylate ion was prepared *in situ*, as described²⁵ in the previous chapter, and $[\text{Re}(\text{CO})_5(\text{O}_3\text{SCF}_3)]$ added (equation (3)).



The colour of the mixture turned red, solvents were removed and the purification was done on a silica gel column. The complexes were characterized by NMR and IR spectroscopy and the data confirmed the assigned structures of the complexes.

The ^1H NMR spectrum of $[\text{Re}(\text{CO})_4(\text{S}_2\text{CC}_4\text{H}_2\text{SCH}_3)]$, **13** (Figure 4.5) showed two signals in the arene region of the spectrum, a doublet at 7.63 ppm and a multiplet at 6.82 ppm. Both integrated for one proton (the signal at 5.27 ppm should be discarded as it represents some dichloromethane in the sample).

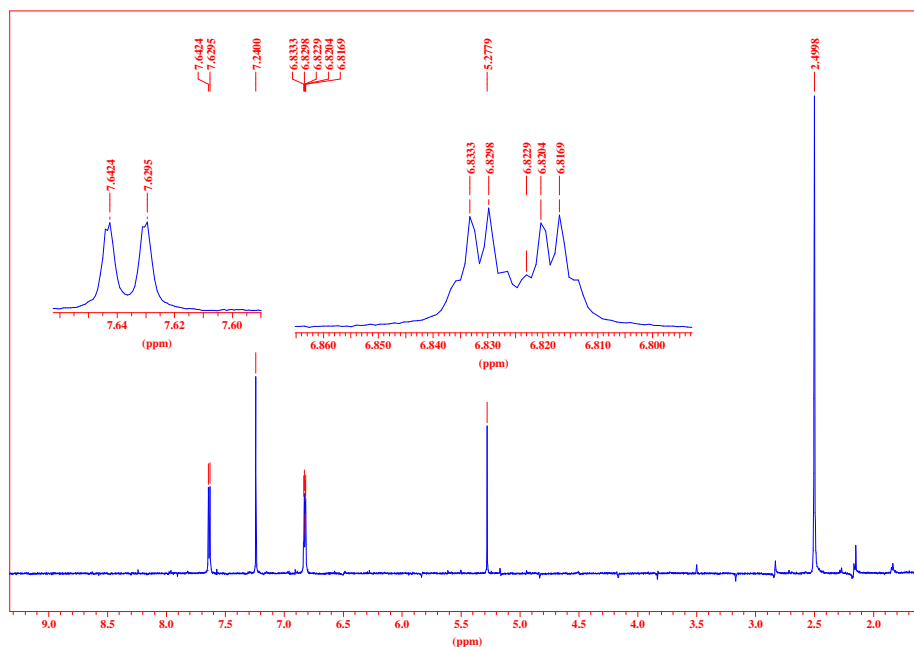


Figure 4.5 ^1H NMR spectrum of $[\text{Re}(\text{CO})_4(\text{S}_2\text{CTCH}_3)]$ (**13**)

These protons, H3 and H4, are assigned to the protons of the thiophene ring. The resonances at 6.82 ppm is broadened because of the J_4 coupling with the protons of the methyl group. A singlet at 2.50 ppm, integrating for three protons, was assigned to the methyl group attached to the thiophene ring. Assignments of the protons in **12** were not unambiguous because of signals overlapping.

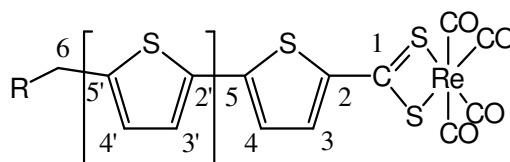


Figure 4.6 Structure of complexes with atomic numbering scheme used

The ^{13}C NMR of **14b** showed signals for all the carbon atoms in the structure and is depicted in Figure 4.7. The peak at 242.6 ppm in **13** was assigned to the carbons

of the carbonyl ligands, but was not observed in the spectra of **14a** and **14b**. The signal at 185.5 ppm is assigned to the CS₂ carbon, C1 and is close to the value reported for CS₂ carbon at 192.3 ppm in the solvent CS₂²⁶. The thiophene carbons are readily assigned both from signal intensity and their chemical shift values at 152.7, 151.7, 128.6 and 127.5 ppm, respectively. Whereas the methyl carbon C6 in **13** is at 16.2 ppm, eleven chemical shift values of the total of fourteen carbons in the chain of **14b** were resolved. It is clear from the spectrum that overlapping of signals occurred in the 29.7 ppm region. The spectral data of **12**, **13**, **14a** and **14b** are summarized in Table 4.1.

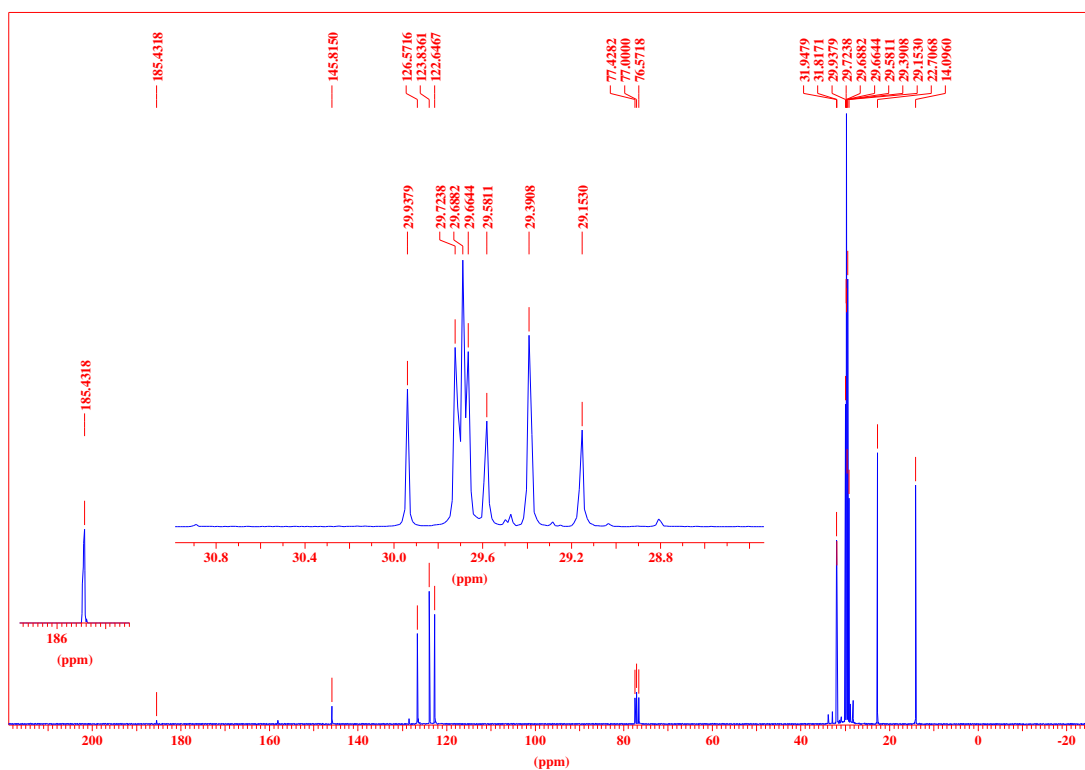


Figure 4.7 ¹³C NMR spectrum of [Re(CO)₄(S₂CTTC₁₄H₂₉)] (**14b**)

Table 4.1 NMR and IR data of complexes **12-14**

Complex	¹ H NMR (δ/ppm and <i>J</i> /Hz in CDCl ₃)	¹³ C NMR (δ/ppm in CDCl ₃)	IR ^a (ν/cm ⁻¹ in hexane)
12	7.16 (d, 2H, H3 and H4, <i>J</i> = 4.0), 7.14 (d, 2H, H3' and H4', <i>J</i> = 4.0), 6.97 (d, 1H, H5', <i>J</i> = 4.4)	240.0 (C=O), 185.6 (CS ₂), 141.1, 137.9 (C2, C5), 128.2 (C2' and C5'), 124.8 (C3 and C4), 124.2 (C3' and C4').	2099 (m), 2007 (s), 1995 (s), 1961 (s).
13	7.63 (d, 1H, H3, <i>J</i> = 3.9), 6.82 (m, 1H, H4), 2.5 (s, 3H, H6).	242.6 (C=O), 185.5 (CS ₂), 152.7 (C2), 151.7 (C5), 128.6 (C3), 127.5 (C4), 16.2 (C6)	2104 (m), 2010 (s), 1996 (s), 1959 (s).
14a	7.1 (d, 1H, H3 <i>J</i> = 4.0), 6.79 (m, 1H, H4), 2.84 (t, 2H, CH ₂ , H6, <i>J</i> = 7.5), 1.73 (m, 2H, H7), 1.32 (m, 22H, H8-H18), 0.92 (t, 3H, H19, <i>J</i> = 7.2).	CO*, 185.4 (CS ₂), 145.8 (C2), 126.6, 123.8 and 122.6 (C3-C5), 31.9 (C6), 21.8, 29.9, 29.7, 29.6, 29.5, 29.4, 29.2 and 22.7 (C7-C18), 14.1 (C19)	2101 (m), 2007 (s), 1995 (s), 1961 (s).
14b	7.71 (d, 1H, H3, <i>J</i> = 4.1), 7.36 (d, 1H, H4, <i>J</i> = 4.4), 7.19 (d, 1H, H3', <i>J</i> = 4.1), 7.06 (t, 1H, H4', <i>J</i> = 4.4),), 2.84 (t, 2H, CH ₂ , H6, <i>J</i> = 7.5), 1.73 (m, 2H, H7), 1.32 (m, 22H, H8-H18), 0.92 (t, 3H, H19, <i>J</i> = 7.2).	CO*, 185.6 (CS ₂ , C5), 156.5 (C2), 153.4 (C5), 146.9 (C2'), 129.0 (C5'), 128.5, 127.6, 126.4, 124.7 (C3, C4, C3', C4'), 41.4 (C6), 31.9, 31.8, 29.9, 29.7, 29.6, 29.6, 29.4, 29.2, 22.7 (C7-C18), 14.1 (C19).	2101 (m), 2007 (s), 1996 (s), 1960 (s).

* not observed

The infrared spectra of the complexes have the typical pattern of four carbonyl ligands displaying C_{2v} symmetry and are representative of *cis*-[M(CO)₄L₂] complexes. The spectrum of **13** (Figure 4.8) showed peaks at 2104 (A₁⁽¹⁾), 2010 (A₁⁽²⁾), 1996 (B₁) and 1959 B₂) cm⁻¹ of similar intensities.

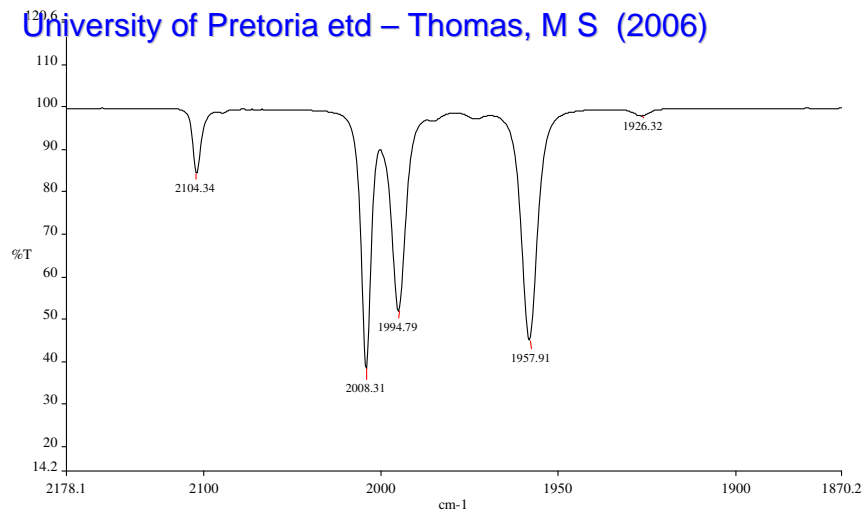


Figure 4.8 IR spectrum of $[\text{Re}(\text{CO})_4(\text{S}_2\text{CTCH}_3)]$ (**13**)

4.2.3 Molecular Structure

The molecular structure of **12** was determined by single crystal X-ray crystallography and confirmed to have a *cis*- $[\text{Re}(\text{S}_2\text{CTR})(\text{CO})_4]$ arrangement of ligands. Single crystals suitable for crystal structural determination were obtained by slow diffusion of hexane into a dichloromethane solution of **12** at room temperature. The structure of **12** supported the spectroscopic data. The molecular structure of **12** is shown in Figure 4.9.

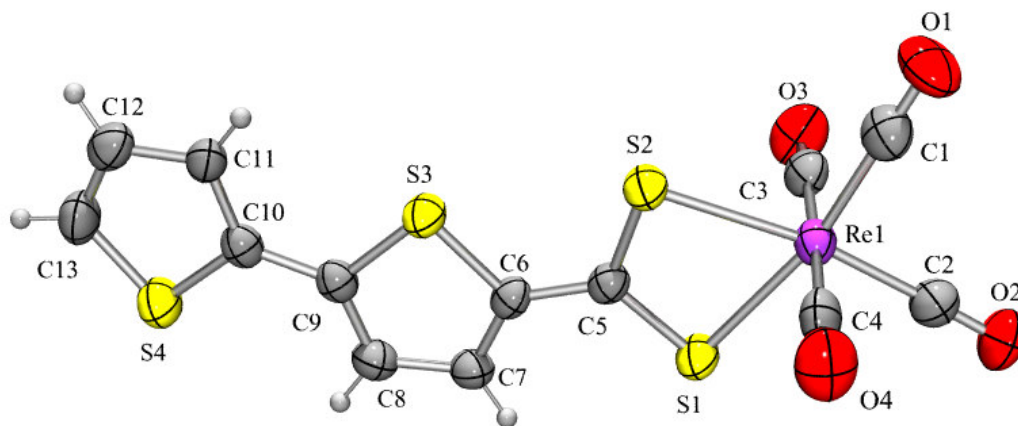


Figure 4.9 An ORTEP²⁷+ POV-Ray²⁸ plot of the geometry of **12**

The Re-S distances are almost the same. Re(1)-S(1) is 2.512 Å whereas Re(1)-S(2) is 2.497 Å. This is also true for the C-S bond lengths of the carbon disulfide moiety, indicating delocalization of electron density over the chelate ring. The Re-C bond distances of the carbonyl ligands *trans* to the sulfur donor atoms are the same and significantly shorter than the other Re-C (carbonyl) distances. This is indicative of the poorer π -acceptor properties of the sulfur ligands compared to the carbonyl ligands. Selected bond lengths and angles are given in Table 4.2 and 4.3 respectively. The sulfur atoms in the thiophene rings of bithiophene are on opposite sides with respect to one another in the dithiocarboxylate ligand. Compared to bond distances of free thiophene (see chapter 3) the C-S distances are longer and represent less π -delocalization in the thiophene ring. Delocalization towards the coordinating CS₂ moiety on the outside of the ring is also important. Interestingly, the formal single bond in the thiophene rings in **12** is shorter than normal C-C single bonds or the corresponding distance in the free thiophene.

Table 4.2 Selected bond lengths for **12**

Atoms	Bond length (Å)	Atoms	Bond length (Å)
Re(1)-C(1)	1.942(6)	Re(1)-C(2)	1.943(6)
Re(1)-C(3)	1.993(6)	Re(1)-C(4)	1.998(6)
Re(1)-S(1)	2.512(1)	Re(1)-S(2)	2.497(1)
S(1)-C(5)	1.701(4)	S(2)-C(5)	1.692(5)
C(5)-C(6)	1.435(6)	C(9)-C(10)	1.437(7)
C(6)-S(3)	1.733(4)	C(10)-S(4)	1.721(5)
C(9)-S(3)	1.729(5)	C(13)-S(4)	1.693(6)

C(6)-C(7)	1.368(6)	C(10)-C(11)	1.398(7)
C(7)-C(8)	1.409(7)	C(11)-C(12)	1.429(8)
C(8)-C(9)	1.374(6)	C(12)-C(13)	1.348(8)

Table 4.3 Selected bond angles for **12**

Atoms	Bond angle (°)	Atoms	Bond angle (°)
C(1)-Re(1)-C(2)	91.5(2)	C(1)-Re(1)-C(3)	89.6(2)
C(1)-Re(1)-C(4)	91.9(2)	C(2)-Re(1)-C(3)	91.2(2)
C(2)-Re(1)-C(4)	89.9(2)	C(3)-Re(1)-C(4)	178.1(2)
O(1)-C(1)-Re(1)	178.5(6)	O(2)-C(2)-Re(1)	178.4(6)
O(3)-C(3)-Re(1)	178.2(5)	O(4)-C(4)-Re(1)	177.4(6)

4.2.2 Thermal properties

Thermal properties of the complexes were studied by using thermo-gravimetric analysis, TGA. All the complexes **12**, **13**, **14a** and **14b** decomposed before melting. The TGA spectrum of **12** (Figure 4.10) showed some decomposition between 155-160°C, that is ascribed to the elimination of carbonyl ligands. As a result no mesophases were present in any of the compounds.

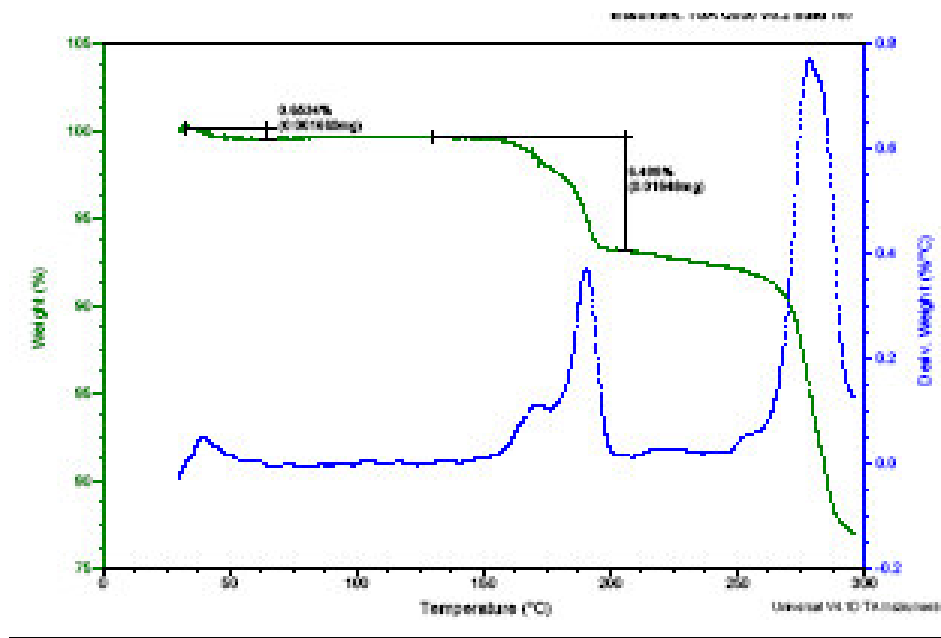


Figure 4.10 TGA spectrum of 12

4.3 Experimental Section

General

Hexane and tetrahydrofuran were distilled over sodium and benzophenone prior to use, and dichloromethane was stored over calcium chloride. All chemicals were used as received unless otherwise specified. All reactions were performed in an inert atmosphere of either nitrogen or argon by using Schlenk techniques and vacuum-line. Column chromatography was carried out using silica gel.

Infrared spectra were recorded on a Perkin Elmer Spectrum 1000 FT-IR spectrometer. All NMR spectra were recorded in deuterated chloroform using the chloroform peak as standard on a Bruker ARX-300 spectrometer.

Thermal properties were studied on thermogravimetric analysis instrument TGA.

A crystal of size 0.34 x 0.10 x 0.06 mm³ of **12** was mounted in a sealed capillary tube for data collection. All geometric and intensity data were collected on a Siemens SMART diffractometer with a CCD detector.

4.3.1 Synthesis

All the complexes were synthesized via a three-step reaction in a similar manner. A typical procedure for complex **13** is described.

Preparation of bromopentacarbonylrhenium, [ReBr(CO)₅]

Hexane (30.0 ml freshly distilled) was transferred to a 50.0 ml Schlenk flask equipped with a Teflon-coated stir bar. Dirheniumdeccacarbonyl, [Re₂(CO)₁₀] (6.50 g, 10.0 mmol) was added under a stream of N₂, and bromine (1.70 g, 11.0 mmol) was added to the solution by means of a syringe and immediately a precipitate was formed in the flask. Stirring was continued for 30 min, and almost all of the orange colour disappeared. Volatiles were removed under continuous vacuum at room temperature and a white powder was obtained. The white powder was transferred to a sublimator and sublimed at 85-90°C. Yield = 3.65 g (90.0%).

Preparation of pentacarbonyl(trifluoromethanesulfonato)-rhenium(I), [Re(CO)₅(O₃SCF₃)]

Freshly sublimed bromopentacarbonylrhenium (3.25 g, 8.0 mmol) was placed in a 50.0 ml Schlenk flask along with a Teflon-coated stirring bar under an atmosphere of nitrogen. Dichloromethane (40.0 ml freshly distilled from P₄O₁₀ under nitrogen) was added through a septum by syringe, and the solution was stirred

until all the $\text{Re}(\text{CO})_5\text{Br}$ was dissolved. From a Schlenk addition tube 2.31 g (9.0 mmol) of $\text{Ag}(\text{O}_3\text{SCF}_3)$ was added under a purge of N_2 , and stirring was continued for 2 hours at room temperature. The $\text{Ag}(\text{O}_3\text{SCF}_3)$ was weighed under subdued light and the reaction flask was wrapped with foil to exclude room light just before the addition of silver triflate. The fluffy AgBr precipitate was formed and removed by filtration through a fine Schlenk frit to yield a clear solution. The volume of the solution was reduced under vacuum, allowed to warm to room temperature and freshly distilled hexane was added and the solvents were removed slowly in vacuum to precipitate $[\text{Re}(\text{CO})_5(\text{O}_3\text{SCF}_3)]$ as a white powder. Yield = 3.17 g (78%).

Preparation of tetracarbonyl-5-methyl-2-thiophenedithiocarboxylatorhenium(I)
 $[(\text{CO})_4\text{Re}(\text{S}_2\text{CC}_4\text{H}_2\text{SCH}_3)]$

In the third step the 5-methyl-2-thiophenedithiocarboxylate ion was prepared in situ as described by Brandsma²⁵ in the previous chapter. A hexane solution which contained 0.32 g (2.0 mmol) of the 5-methyl-2-thiophenedithiocarboxylate ion was cooled to -30°C and 0.95 g (2.0 mmol) of $[\text{Re}(\text{CO})_5(\text{O}_3\text{SCF}_3)]$ was added. The cold bath was removed and the mixture was left stirring for 2 hours. The colour of the mixture turned red. Solvents were removed and the purification was done on a silica gel column and the product was extracted with hexane/dichloromethane 4:1 as the eluent. Yield = 0.52 g (55%). The complexes **12**, **14a** and **14b** were prepared similarly. See Table 4.4.

Table 4.4 Experimental results of **12-14** complexes

Complex	Colour	Mass (g)	Yield (%)
12	Red	0.67	62
13	Orange	0.52	55
14a	Orange	0.56	43
14b	Red	0.68	46

4.4 Conclusion

The complexes are not suitable as liquid crystals since the complexes decomposed before melting. From the TGA studies, it is clear that the carbonyl ligands are eliminated at lower temperatures.

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