

## Chapter 5

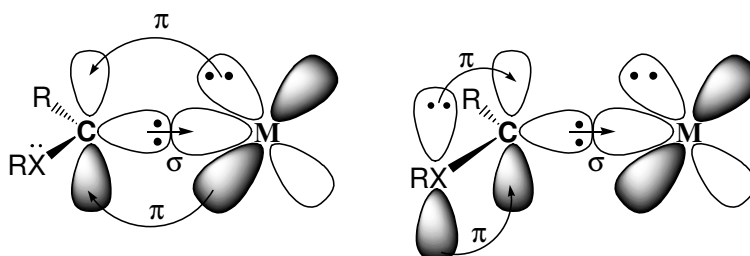
# Carbene complexes of Manganese(I) with thiophene-containing ligands

### 5.1 Introduction

Complexes containing metal-carbon double bonds are generally referred to as metal-carbene or metal-alkylidene complexes<sup>1-3</sup>. Applications of carbene complexes in organic syntheses have been widely employed and recognized for their usefulness<sup>4-10</sup>, but very few studies directed towards material properties of carbene complexes have been recorded. The reason for this is that carbene complexes were traditionally seen as very unstable compounds and researchers rather looked at them as reaction intermediates. Today we know that many carbene complexes in transition metal chemistry are as stable as their counterparts displaying phosphine or other classical inorganic ligands. They have an additional advantage as they possess the capability of bringing in electronic contact the transition metal with a conjugated fragment that forms part of a substituent on the carbene carbon atom. Binuclear organometallic complexes in which the metal centres are connected by a conjugated bridge have attracted a lot of interest as potential molecular wires<sup>11,12</sup>. The only drawback to this approach is that connecting chains of carbon tend to be unstable at the sites of bond unsaturation. Thiophene and polythiophenes or their derivatives, on the other hand, have been identified as molecules with potential electro-optical properties and form part of some of the most stable molecular switching devices discovered to date<sup>13</sup>. For many years we have pursued the chemistry of mono- or binuclear transition metal carbene complexes where one of the substituents would contain a thiophene or

thiophene derivative<sup>14-17</sup>. One of the obvious possible applications for carbene complexes with thiophene derivatives is constructing materials with non-linear optical and liquid crystalline properties<sup>18</sup>.

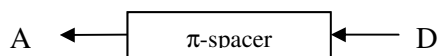
Among the stable and isolable organometallic compounds containing transition metals, Fischer-type carbene complexes have recently become very popular<sup>19</sup>. In Fischer carbene complexes at least one of the organic substituents will have a heteroatom with lone pair electrons. The carbene carbon atom is strongly electrophilic and will use the transition metal and/or the heteroatom to stabilize this center.



**Figure 5.1** Electron distribution and bonding in Fischer carbene complexes

Fischer carbene ligands have empty p-orbitals perpendicular to the plane of the  $sp^2$ -orbitals and as a result, can act as a connector of  $\pi$ -electron conjugation from the metal to a conjugated chain or unit via the carbene carbon. Charge transfer is possible in a large segment of the complex and can be fine-tuned by carefully selecting the transition metal and the conjugated substituent on the carbene carbon. Molecules with large  $\pi$  systems and, in particular, organometallic complexes have been extensively used in attempts to obtain materials with non-linear optical (NLO) properties. It has been shown that organometallic complexes that contain thiophene moieties contribute to the enhancement of such properties<sup>20-27</sup>. Attention in this field has more recently been directed to “push-pull” molecules because transition metals introduce new

variables such as their different oxidation states, differences in the nature and number of the ligands that allow the modulation of their electron-withdrawing or releasing properties and optimization of their interaction with the  $\pi$ -spacer in order to create the best non-linear response<sup>28</sup>.



**Figure 5.2** Push-Pull structures

Non centro-symmetric molecules are good candidates for second order non-linear activity and, in particular, large first  $\beta$  hyperpolarisability can be observed in conjugated poly-unsaturated organic molecules in which a  $\pi$ -system connects electron-donating **D** to accepting **A** groups. Fischer-type carbene complexes have recently become serious contenders as compounds exhibiting NLO-properties (Figure 5.2). Licandro and coworkers<sup>29</sup> reported and exploited the push-pull nature of pentacarbonyl(metal) carbene complexes. The  $M(CO)_5(\text{carbene-carbon})$  moiety behaved as a strong electron-withdrawing group that is similar to a Lewis acid leading to polarization in the carbene substituent.

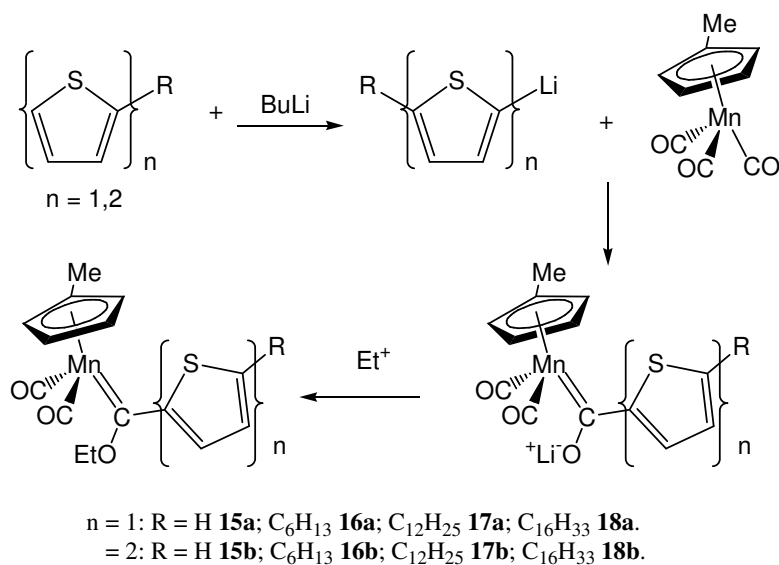
The aim was to synthesize carbene complexes of manganese(I) with thiophene or bithiophene containing-ligands and to test their liquid crystalline properties. We chose  $[Mn(\eta^5-C_5H_5)(CO)_2(\text{carbene})]$  as our model compound as it is known to give very stable carbene complexes<sup>30</sup>. Important is the limiting of the number of carbonyl ligands as they could affect the melting behaviour of the compound adversely. We selected to use methylcyclopentadienyl instead of cyclopentadienyl as ligand that will lower and affect the temperature range of the melting process. The geometry around

the metal centre is pseudo tetrahedral, but diamagnetic which could also be of interest. Incorporation of a polarizable component is achieved by using 2-alkyl substituted thiophene carbene substituents. In 1994 Bruce<sup>31</sup> reported the liquid crystalline complexes of octahedral manganese(I). The complexes described were the first examples of calamitic (rod-like) liquid crystalline metal complexes containing manganese with octahedral coordination.

## 5.2 Results and discussion

### 5.2.1 Synthesis and characterization

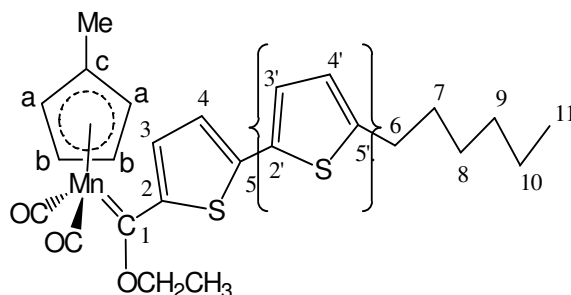
Carbene complexes of manganese(I), of the type  $[\text{MnMeCp}(\text{CO})_2\{\text{C}(\text{OEt})\text{TR}\}]$  (where T = 2,5-disubstituted thiophene,  $\text{C}_4\text{H}_2\text{S}$  (**a**) or bithiophene,  $\text{C}_8\text{H}_4\text{S}_2$  (**b**) and R = H (**15**),  $\text{C}_6\text{H}_{13}$  (**16**),  $\text{C}_{12}\text{H}_{25}$  (**17**),  $\text{C}_{16}\text{H}_{33}$  (**18**)) have been prepared.



**Scheme 5.1**

Alkyl thiophene or bithiophene derivatives were dissolved in THF and reacted in the cold under argon-atmosphere with BuLi dissolved in hexane. After the reaction

mixture was cooled to  $-40^{\circ}\text{C}$ ,  $[\text{MnMeCp}(\text{CO})_3]$  was added. The mixture was first stirred in the cold and then for a further period at room temperature. The solvent was removed from the dark-red solution and the residue was re-dissolved in dichloromethane and alkylated in the cold with a solution of  $\text{Et}_3\text{OBF}_4$ . The reaction mixture was filtered through a plug of silica gel and thereafter chromatographed on silica gel by using hexane/dichloromethane (4:1) solution. The first yellow band was unreacted alkyl thiophene followed by a red-brown band, the desired product. The product was recovered from the solvent in high yield (about 70%). The complexes **15a-17a** were oils, whereas complex **18a** was a solid with melting point  $31\text{-}32^{\circ}\text{C}$ . The complexes **15b-17b** were solids, but **18b** was an oil. Once purified, NMR and IR spectroscopy and mass spectrometry were used to characterize the complexes **15a-18a** and **15b-18b**.



**Figure 5.3** Atomic numbering of **16a/b**

In this chapter Figure 5.3 shows how the different atoms are numbered in the text for the different compounds. The cyclopentadienyl carbons are indicated by a, b and c, the second thiophene ring in the bithiophene complexes takes the same numbering sequence than the thiophene complexes but with primed numbers and the alkyl chains are numbered starting with carbon 6 and following the numerical order.

The  $^1\text{H}$  NMR spectra of the thiophene (T) complexes **15a-18a** displayed resonances of much poorer resolution compared to the bithiophene (TT) analogues **15b-18b** and

it was not possible to get good coupling data for the thiophene complexes. The complex  $[\text{MnMeCp}(\text{CO})_2\{\text{C}(\text{OEt})\text{TC}_6\text{H}_{13}\}]$  (T = thiophene,  $\text{C}_4\text{H}_2\text{S}$ ) (**16a**) showed two broad singlets at 7.70 and 6.73 ppm for the two protons H3 and H4 of the thiophene ring. By contrast the spectrum of **17b** shown in Figure 5.4 displayed four well-resolved doublets (7.81, 7.12, 6.94 and 6.69 ppm) in the arene region. These patterns of chemical shifts for **16a-18a** and **16b-18b** are expected for 2,5-disubstituted thiophene and 2,5'-disubstituted bithiophene complexes, respectively. The carbene carbon in the 2-position is a strong electron-withdrawing substituent and H3/H3' will be shifted downfield compared to an alkyl chain, which is electron-donating on the other side of the thiophene ring, and H4/H4' will appear upfield. Compared to uncoordinated thiophene where H3 and H4 are found at chemical shift values of 6.96 ppm (chapter 2), H3 in the carbene complexes is downfield by *ca* 0.7 ppm and H4 upfield by *ca* 0.2 ppm.

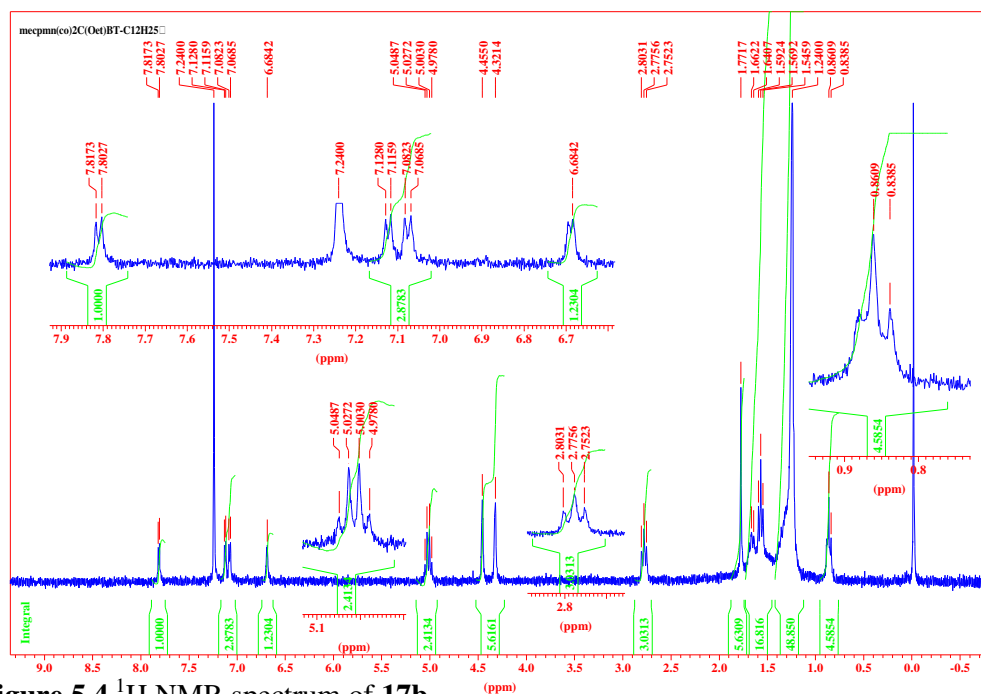
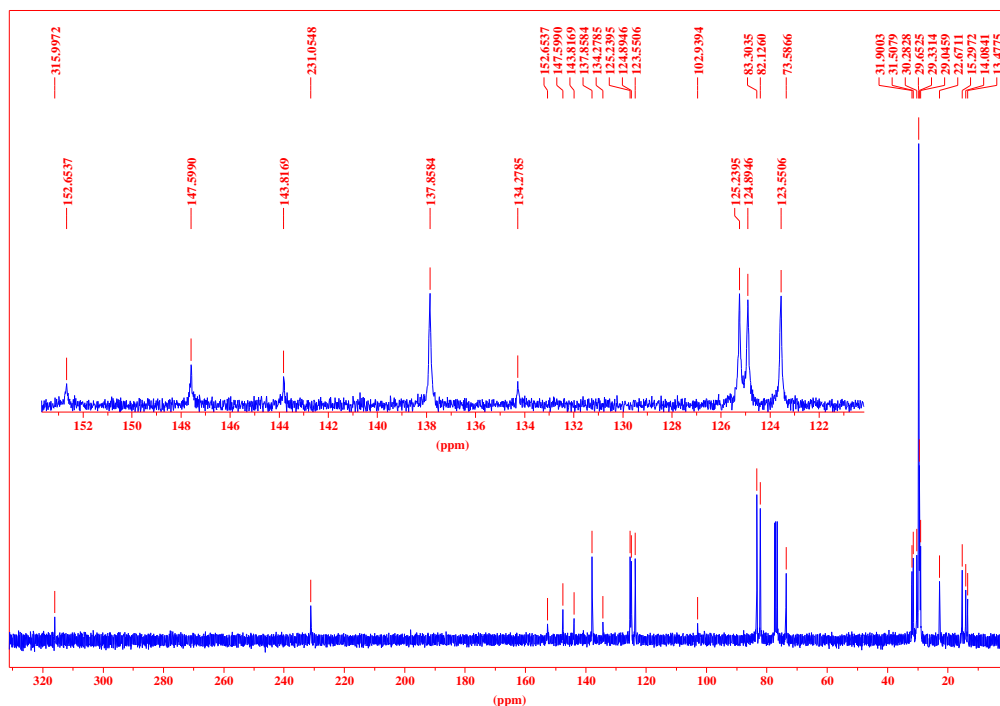


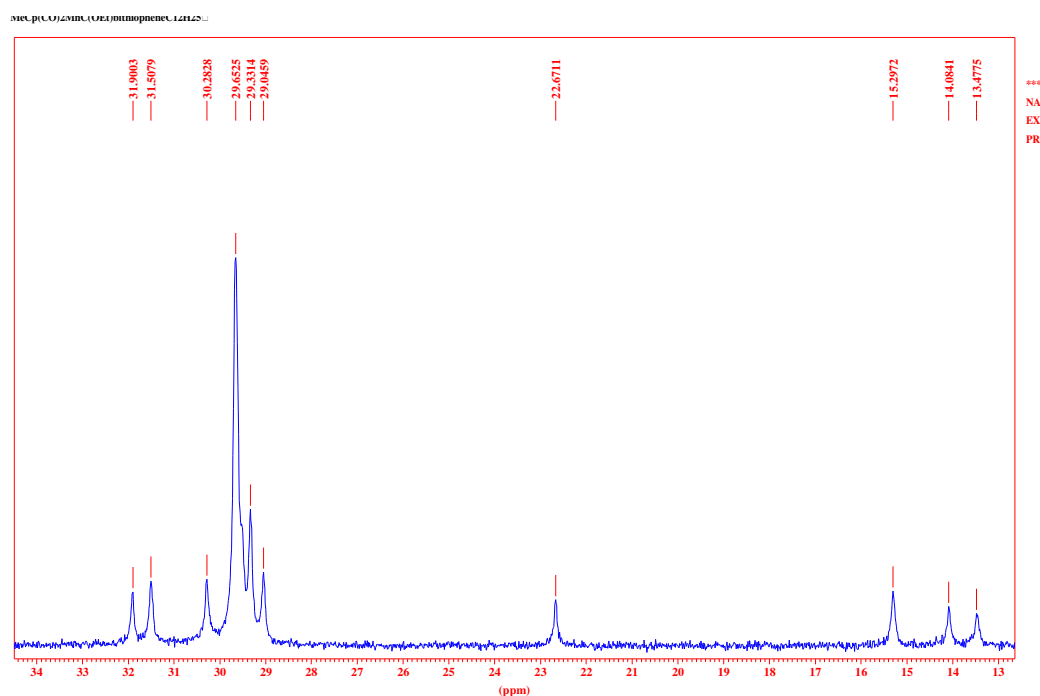
Figure 5.4  $^1\text{H}$  NMR spectrum of **17b**

The NMR data of the complexes are summarized in Tables 5.1 and 5.2. The chemical shifts of the methylene resonances of the ethoxy substituents of the carbene ligands afford characteristic quartets at 5.0 ppm, which compare well with values reported in the literature<sup>14</sup>. The resonances of the cyclopentadienyl protons a and b appear as two singlets around 4.4 ppm in the spectra and the alkyl chains start downfield for H6 as a triplet at *ca* 2.8 ppm (H6), then shows a broadened quintet at *ca* 1.65 ppm (H7, not always resolved) slightly upfield from the Cp methyl substituent at *ca* 1.75 ppm. The methyl group of the ethoxy substituent is next around 1.6 ppm followed by a strong multiplet at 1.5-1.2 ppm representing the rest of the alkyl chain which ends with a triplet for the last carbon of the chain at *ca* 0.85 ppm.



**Figure 5.5**  $^{13}\text{C}$  NMR spectrum of **17b** with an expanded view of the bithiophene region

The  $^{13}\text{C}$  NMR spectrum of **17b** (Figure 5.6) clearly indicated the carbene carbon, the carbonyl ligands, the carbons of the bithiophene ring and also accounts for all the other carbon atoms in the structure. The spectrum depicted the carbene carbon C1 at 316.0 ppm and  $\text{Mn}(\text{CO})_2$  at 231.1 ppm, respectively. In the bithiophene region all eight signals were resolved and from peak intensities it is possible to divide the chemical shifts in four quaternary and four CH resonances (see expansion in Figure 5.6). Moving further upfield, one could readily assign the c and a chemical shifts (figure 5.3) of the cyclopentadienyl ring and the carbene methylene carbon of the ethoxy substituent moved slightly upfield from the deuterated solvent resonances.



**Figure 5.6**  $^{13}\text{C}$  NMR spectrum of **17b** in the alkyl region

The alkyl chain is represented by 8 signals for the 12 carbon atoms with some overlapping at 29.0 ppm. The sequence for the methyl chemical shifts (ppm) is: EtO of carbene > Alkyl chain end > Cp substituent, based on the results of the  $^{13}\text{C}$  NMR



spectra of  $[\text{Mn}(\text{MeCp})(\text{CO})_3]$ , ethoxy carbene complexes<sup>32</sup> and the alkylthiophene substrates.

**Table 5.1** Spectral data for the thiophene complexes, **15a-18a**

Complex	<sup>1</sup> H NMR ( $\delta$ /ppm and $J$ /Hz in $\text{CDCl}_3$ )	<sup>13</sup> C NMR ( $\delta$ /ppm in $\text{CDCl}_3$ )	IR <sup>a</sup> ( $\text{v}/\text{cm}^{-1}$ in hexane) $\text{M}(\text{CO})_2$
<b>15a</b>	8.03 (s, 1H, H3), 7.26 (s, 2H, H4 and H5), 5.22 (s, 2H, $\text{OCH}_2$ ), 4.63 (s, 2H, Hb (Cp)), 4.56 (s, 2H, Ha (Cp)), 1.98 (t, 3H, Cp- $\text{CH}_3$ $J = 7.0$ ), 1.78 (t, 3H, $\text{CH}_3$ (OEt)), $J = 7.2$ .	319.2 (C1, carbene), 231 (CO-Mn), 156.0 (C2), 135.9 (C5), 132.5 (C3), 128.0 (C4), 103.3 (Cc (Cp)), 84.0, 82.8 (Cb and Ca (Cp)), 75.2, 15.8 ( $\text{OCH}_2\text{CH}_3$ ) 13.5 (Cp- $\text{CH}_3$ ).	1947 (vs), 1889 (vs)
<b>16a</b>	7.78 (s, 1H, H3), 6.81 (s, 1H, H4), 5.02 (s, 2H, $\text{OCH}_2$ ), 4.48 (s, 2H, Hb of Cp) 4.35 (s, 2H, Ha of Cp) 2.78 (t, 2H, H6, $J = 7.0$ ), 1.60 (s, 6H, Cp- $\text{CH}_3$ and $\text{CH}_3$ (OEt)), 1.33 (m, 10H, H7-H10), 0.90 (t, 3H, H11, $J = 7.2$ ).	317.4 (C1, carbene), 231.2 (CO-Mn), 153.4 (C2), 137.3 (C5), 125.6 (C3), 125.0 (C4), 102.6 (Cc (Cp)), 83.2, 82.8 (Cb and Ca (Cp)), 73.5, 15.3 ( $\text{OCH}_2\text{CH}_3$ ), 13.5 (Cp- $\text{CH}_3$ ), 31.5, 31.2, 30.6, 28.8, 22.5, 14.2 (C6-C11).	1943 (vs), 1886 (vs)
<b>17a</b>	7.77 (s, 1H, H3), 6.81 (s, 1H, H4), 5.03 (s, 2H, $\text{OCH}_2$ ), 4.48 (s, 2H, Hb (Cp)), 4.36 (s, 2H, Ha (Cp)), 2.80 (t, 2H, H6, $J = 7.0$ ), 2.20 (s, 3H, Cp- $\text{CH}_3$ ), 1.62 (t, 3H, $\text{CH}_3$ (OEt) $J = 7.0$ ), 1.32 (m, 20H, H7-H16), 0.97 (t, 3H, H17, $J = 7.2$ ).	317.4 (C1, carbene), 231.4 (CO-Mn), 153.9 (C2), 137.73 (C5), 126.1 (C3), 125.7 (C4), 102.8 (Cc (Cp)), 83.6, 82.4 (Cb and Ca (Cp)), 73.9, 15.7 ( $\text{OCH}_2\text{CH}_3$ ), 14.1 (Cp- $\text{CH}_3$ ), 32.3, 31.7, 30.9, 30.0 (vs), 23.1, 14.4 (C6-C17).	1943 (vs), 1886 (vs)
<b>18a</b>	7.79 (s, 1H, H3), 6.80 (s, 1H, H4), 5.02 (s, 2H, $\text{OCH}_2$ ), 4.45 (s, 2H, Hb (Cp)), 4.33 (s, 2H, Ha (Cp)), 2.77 (s, 2H, H6), 1.79 (s, 3H, Cp- $\text{CH}_3$ ), 1.67 (s, 2H, H7), 1.57 (t, 3H, $\text{CH}_3$ (OEt)), 1.27 (m, 26H, H8-H20), 0.89 (t, 3H, H21,	317.6 (C1, carbene), 231.2 (CO-Mn), 153.5 (C2), 137.3 (C5), 126.2 (C4), 125.6 (C3), 102.7 (Cc (Cp)), 83.2, 82.0 (Cb and Ca (Cp)), 73.5, 15.5 ( $\text{OCH}_2\text{CH}_3$ ), 13.5 (Cp- $\text{CH}_3$ ), 31.9, 31.2, 30.5, 29.6	1943 (vs), 1886 (vs)

	$J = 7.2$	(vs), 22.6, 14.4 (C6-C21).	
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<sup>a</sup> carbonyl region

**Table 5.2** Spectral data for the bithiophene complexes, **15b-18b**

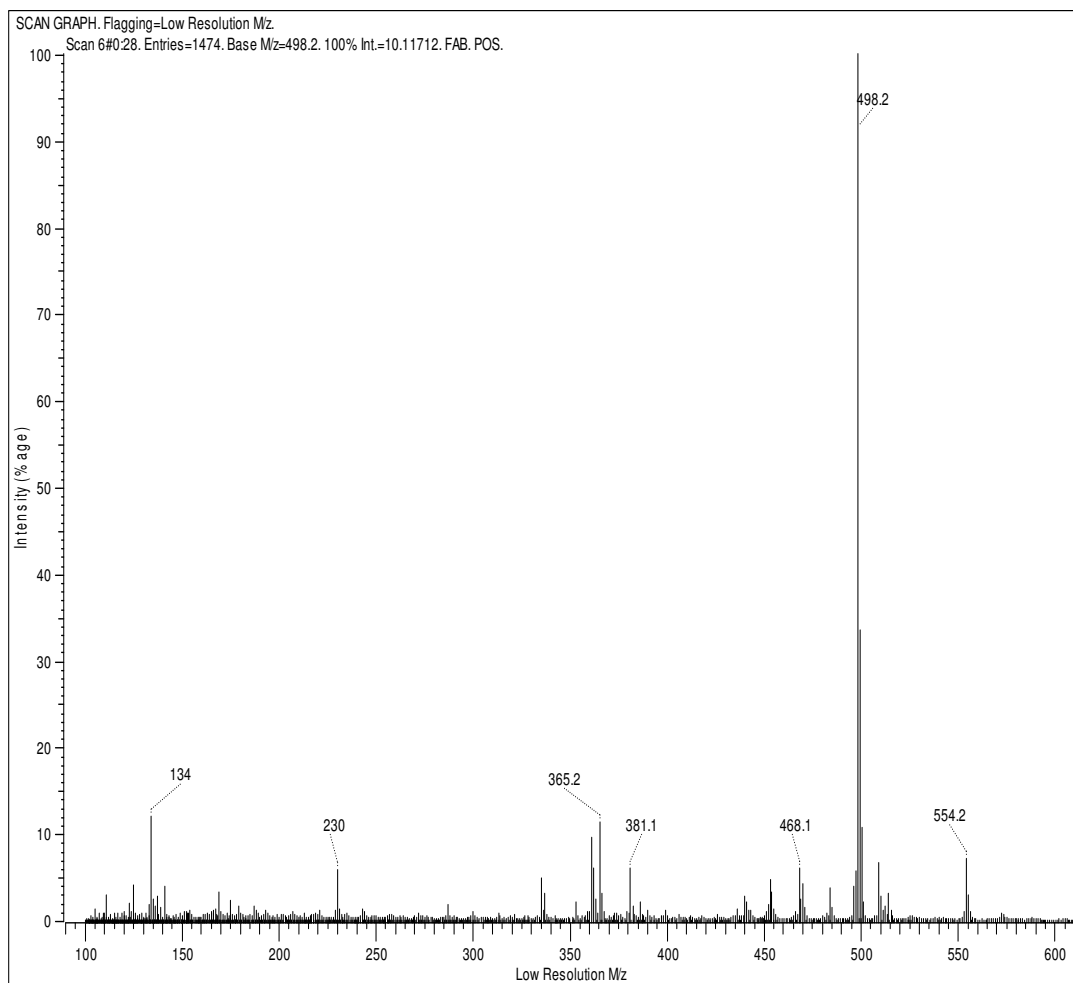
Complex	<sup>1</sup> H NMR ( $\delta$ /ppm and $J$ /Hz in CDCl <sub>3</sub> )	<sup>13</sup> C NMR ( $\delta$ /ppm in CDCl <sub>3</sub> )	IR <sup>a</sup> (v/cm <sup>-1</sup> in hexane)
<b>15b</b>	7.81 (d, 1H, H3, $J = 4.3$ ), 7.29 (d, 1H, H4, $J = 3.6$ ), 7.14 (s, 2H, H3' and H4'), 7.02 (d, 1H, H5', $J = 3.6$ ), 5.02 (s, 2H, OCH <sub>2</sub> ), 4.46 (s, 2H, Hb (Cp)), 4.33 (s, 2H, Ha (Cp)), 1.78 (s, 3H, Cp-CH <sub>3</sub> ), 1.57 (s, 3H, CH <sub>3</sub> (OEt)).	319.4 (C1, carbene), 230.7 (CO-Mn), 157.3 (C2), 137.5 (C3), 145.8 (C5), 143.3 (C2'), 128.2 (C5'), 126.1 (C3'), 125.0 (C4), 124.3 (C4'), 97.5 (Cc (Cp)), 83.4 (Cb (Cp)), 82.3 (Ca (Cp)), 73.7 (OCH <sub>2</sub> ), 15.3 (CH <sub>3</sub> (OEt)), 13.5 (Cp-CH <sub>3</sub> )	1945 (vs), 1888 (vs)
<b>16b</b>	7.81 (d, 1H, H3, $J = 4.2$ ), 7.12 (d, 1H, H4, $J = 3.6$ ), 6.94 (d, 1H, H3', $J = 4.2$ ), 6.69 (d, 1H, H4', $J = 3.6$ ), 5.02, d, 2H, OCH <sub>2</sub> , $J = 7.2$ ), 4.46 (s, 2H, Hb (Cp)), 4.33 (s, 2H, Ha (Cp)), 2.78 (t, 2H, H6, $J = 7.0$ ), 2.29 (t, 3H, Cp-CH <sub>3</sub> , $J = 7.0$ ), 1.67 (t, 3H, CH <sub>3</sub> (OEt), $J = 7.0$ ), 1.25 (m, 8H, H7-H10), 0.87 (t, 3H, H11, $J = 6.7$ ).	317.1 (C1, carbene), 231.0 (CO-Mn), 143.8 (C2), 137.9 (C5), 124.9 (C4), 129.9 (C2'), 128.9 (C5), 126.0 (C3'), 125.3 (C5'), 123.6 (C4'), 103.0 (Cc (Cp)), 83.7 (Cb (Cp)), 82.5 (Ca (Cp)), 73.9 (OCH <sub>2</sub> ), 15.6 (CH <sub>3</sub> (OEt)), 13.4 (Cp-CH <sub>3</sub> ), 31.9, 31.5, 30.3, 28.7, 22.6, 14.5 (C6-C11).	1944 (vs), 1887 (vs).
<b>17b</b>	7.81 (d, 1H, H3, $J = 4.4$ ), 7.11 (d, 1H, H4, $J = 3.6$ ), 7.07 (d, 1H, H3', $J = 4.2$ ), 6.68 (d, 1H, H4', $J = 3.6$ ), 5.02 (s, 2H, OCH <sub>2</sub> , $J = 7.0$ ), 4.45 (s, 2H, Hb (Cp)), 4.32 (s, 2H, Ha (Cp)), 2.77 (t, 2H, H6, $J = 7.0$ ), 1.77 (s, 3H, Cp-CH <sub>3</sub> ), 1.56 (t, 3H, CH <sub>3</sub> (OEt), $J = 7.0$ ), 1.24 (m, 20H, H7-H16), 0.85 (t, 3H, H17, $J = 6.7$ ).	316.0 (C1, carbene), 231.1 (CO-Mn), 152.7 (C2), 147.6 (C5), 143.8 (C2'), 137.9 (C3), 134.3 (C5'), 125.2 (C4), 124.9 (C3'), 123.9 (C4'), 102.9 (Cc (Cp)), 83.3, (Cb (Cp)), 82.1 (Ca (Cp)), 73.5 (OCH <sub>2</sub> ), 15.3 (CH <sub>3</sub> (OEt)), 13.5 (Cp-CH <sub>3</sub> ), 31.9, 31.5, 30.3, 29.7, 29.3, 29.0, 22.7, 14.1 (C6-C17).	1944 (vs), 1887 (vs).
<b>18b</b>	7.81 (d, 1H, H3, $J = 3.9$ ), 7.12 (d,	317.7 (C1, carbene), 231.7	1943 (vs), 1887

1H, H4, $J = 3.6$ ), 7.07 (d, 1H, H3', $J = 4.0$ ), 6.69 (d, 1H, H4', $J = 3.6$ ), 5.02 (s, 2H, OCH <sub>2</sub> , $J = 7.7$ ), 4.46 (s, 2H, Hb (Cp)), 4.32 (s, 2H, Ha (Cp)), 2.78 (t, 2H, H6, $J = 7.0$ ), 1.77 (s, 3H, Cp-CH <sub>3</sub> ), 1.65 (t, 3H, CH <sub>3</sub> (OEt), $J = 7.7$ ) 1.28 (m, 28H, H7- H20), 0.86 (t, 3H, H21, $J = 6.7$ ).	(CO-Mn), 153.2 (C2), 152.9 (C5), 144.8 (C2'), 137.6 (C3), 135.3 (C5'), 125.1 (C4), 124.7 (C3'), 123.6 (C4'), 102.5 (Cc (Cp)), 83.3 (Cb (Cp)), 82.1 (Ca (Cp)), 76.6 (OCH <sub>2</sub> ), 15.4 (CH <sub>3</sub> (OEt)), 13.7 (Cp-CH <sub>3</sub> ), 31.9, 31.6, 31.5, 30.3, 30.1, 29.7, 29.6, 29.5, 29.4, 28.7, 22.7, 22.6, 14.1 (C6-C21).	(vs).
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<sup>a</sup> carbonyl region

The IR spectrum of **16a** showed two very strong bands at 1943 and 1886 cm<sup>-1</sup> for the terminal CO ligands. This corresponds to the two infrared vibrations,  $\nu_{\text{sym}}$  and  $\nu_{\text{asym}}$  of the M(CO)<sub>2</sub> class of carbonyl complexes. The <sup>13</sup>C NMR chemical shifts for the carbons of the carbonyl ligands are typical for cyclopentadienylmanganese complexes with two carbonyl ligands<sup>33</sup>.

The complexes were also studied by fast atom bombardment (FAB) mass spectrometry. All the spectra of the complexes showed a peak corresponding to the m/z-value of the molecular ion (M<sup>+</sup>). The parent peak in FAB-MS of **18a** was m/z = 554 (7.5%). The m/z = 498 (100%) peak corresponding to M<sup>+</sup>-2CO is the principal ion peak in the spectra. Fragment ions with m/z-values corresponding to [M(MeCp)]<sup>+</sup> and [M(MeCp)(carbene)]<sup>+</sup> are present in most spectra whereas [M(carbene)]<sup>+</sup> and [M(CO)<sub>2</sub>]<sup>+</sup> are not represented. The fragmentation of parts of the carbene ligand was also observed. Based on these observations it is possible to assign a general fragmentation route for the complexes.



**Figure 5.7** Mass spectrum of **18a**

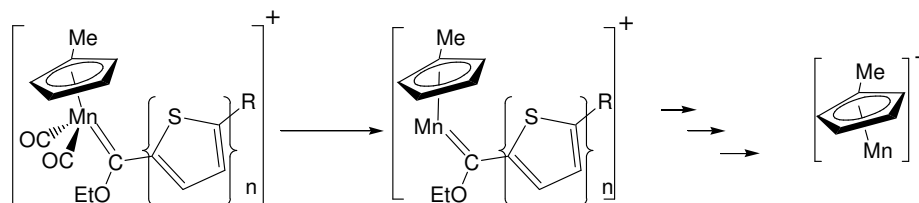
All the other complexes fragmented in a similar manner. The mass spectral data of the complexes **15a-18a** are given in Table 5.3.

**Table 5.3** Mass spectral data of **15a-18a** and **15b-18b**

Complex	Molecular formula	Parent peak (M <sup>+</sup> )	Principal peak (M <sup>+</sup> -2CO)	[MnMeCp] <sup>+</sup> fragment (134)
<b>15a</b>	MnC <sub>15</sub> H <sub>15</sub> O <sub>3</sub> S	330 (30%)	274 (100%)	134 (13%)
<b>16a</b>	MnC <sub>21</sub> H <sub>27</sub> O <sub>3</sub> S	414 (18%)	358 (100%)	134 (9%)
<b>17a</b>	MnC <sub>27</sub> H <sub>39</sub> O <sub>3</sub> S	498 (12%)	442 (100%)	134 (8%)
<b>18a</b>	MnC <sub>31</sub> H <sub>47</sub> O <sub>3</sub> S	554 (7.5%)	498 (100%)	134 (13%)

<b>15b</b>	$\text{MnC}_{19}\text{H}_{17}\text{O}_3\text{S}_2$	412 (20%)	356 (100%)	134 (12%)
<b>16b</b>	$\text{MnC}_{25}\text{H}_{29}\text{O}_3\text{S}_2$	n.o. <sup>a</sup>	440 (4%)	134 (9%)
<b>17b</b>	$\text{MnC}_{31}\text{H}_{41}\text{O}_3\text{S}_2$	580 (13%)	524 (100%)	134 (7%)
<b>18b</b>	$\text{MnC}_{35}\text{H}_{49}\text{O}_3\text{S}_2$	636 (8%)	580 (100%)	134 (8%)

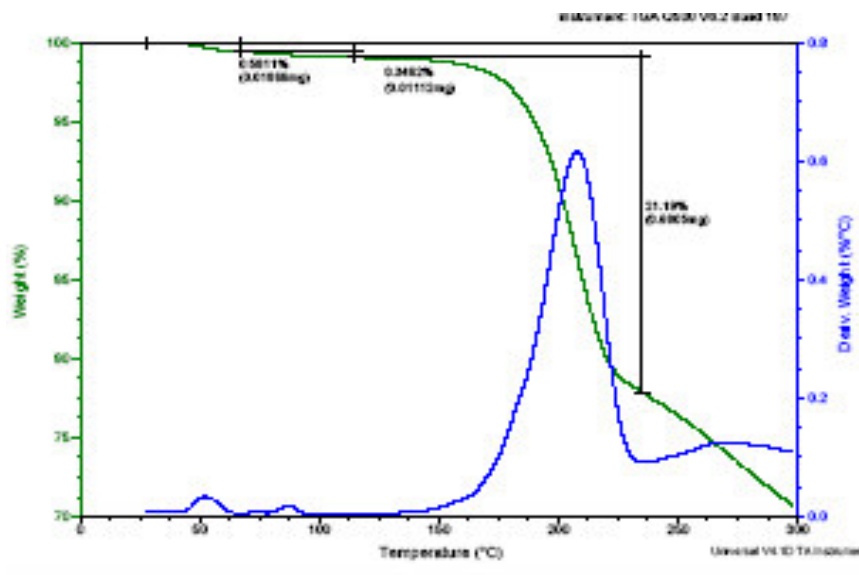
<sup>a</sup>n.o. not observed.



**Figure 5.8** important fragmentations of ions in mass spectra

### 5.2.2 Thermal properties

The TGA measurements showed a decrease (weight loss) at about 50°C, indicating the loss of CO groups from the complex. Therefore the complexes are not stable at moderate temperatures and are not suitable for testing the liquid-crystalline properties.



**Figure 5.9** TGA spectrum of **18a**

### 5.3 Experimental Section

Thiophene and bithiophene were lithiated according to the procedure reported by Brandsma<sup>33</sup>.

#### Synthesis

*A general procedure for all the reactions in a general format is given.*

2.0 mmol of the thiophene, alkylthiophene, bithiophene or alkylbithiophene was dissolved in THF (30.0 ml) and cooled to  $-15^{\circ}\text{C}$  under Argon atmosphere. 1.60 M solution of butyl lithium (1.25 ml, 2.0 mmol) in hexane was added and the mixture stirred for 40 minutes. The reaction was cooled to  $-40^{\circ}\text{C}$  and  $[\text{MnMeCp}(\text{CO})_3]$  (0.44 g, 2.0 mmol) was added. The mixture was stirred in the cold for 30 minutes and for a further 1 hour at room temperature during which the colour of the solution changed from light orange to dark red. The solvent was removed under reduced pressure. The residue was re-dissolved in dichloromethane (30.0 ml), cooled to  $-30^{\circ}\text{C}$  and alkylated with a dichloromethane solution of  $\text{Et}_3\text{OBF}_4$  (0.38 g, 2.0 mmol). The solution was stirred for 30 minutes in the cold and for a further 1 hour at room temperature. The reaction mixture was filtered through a plug of silica gel and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel by using hexane/dichloromethane (4:1) solution. The first yellow band was unreacted thiophene, alkylthiophene, bithiophene or alkylbithiophene, followed by the brown band, which contained the major product. On evaporation of the solvent, the product was obtained and for the solids, recrystallization from dichloromethane-hexane mixtures, pure complexes could be obtained.

**Table 5.4** Experimental results of **15a-18a** and **15b-18b**

Complex	Mass of 2 mmol substrate (g)	State of the product	Melting point (°C)	Mass product(g)	Yield (%)
<b>15a</b>	0.17	Oil	-----	0.51	78
<b>16a</b>	0.34	Oil	-----	0.56	68
<b>17a</b>	0.50	Oil	-----	0.54	55
<b>18a</b>	0.62	Solid	31-32	0.72	65
<b>15b</b>	0.33	Solid	63-65	0.53	65
<b>16b</b>	0.50	Solid	57-59	0.39	40
<b>17b</b>	0.67	Solid	48-49	0.56	48
<b>18b</b>	0.78	Oil	-----	0.58	46

## 5.4 Conclusion

The complexes showed a weight loss before reaching their melting points. Therefore the complexes are not suitable for testing their liquid crystalline properties.

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