

4 Bimetallic π -bonded Benzo[*b*]thienylcarbene Complexes

1. Introduction

Coordination through the π -cloud of aromatic molecules causes a localization of the double bonds leading to an electron deficiency of the rings of arene-transition metal complexes that was already recognised in the 1950s.¹ This property aids in the addition of nucleophiles to the arene ligand and deprotonation of acidic arene protons. Several reasons exist for the interest in investigating arene complexes of transition elements. The arene ligand is uncharged and because it can donate an even number of electrons will thus not affect the charge of the complex. The creation of vacant coordination positions can be achieved more easily than in the case of negatively charged ligands e.g. cyclopentadienyl. The hapticity of the arene ligand can be varied e.g. $\eta^6 \rightarrow \eta^4 \rightarrow \eta^2$, by changing or adding additional ligands, this property empowers these complexes to vacate coordination sites and to act as precursors for catalysts in e.g. hydrogenation or polymerization processes.²⁻⁵

An important feature of heteroarene metal complexes is the competition between heteroatom-metal σ bonds and arene-metal π bonds. A possible explanation for σ -bond formation in pyrroles and pyridines is attributed to the lower ionization energies of unbonded electron pairs of the heteroatom compared to the π -electrons of the arene ring. Thus, the unbonded electron pairs are more accessible for bonding than the electrons in the π -system. Another trait of π -heteroarene complexes is their stability relative to their carbocyclic analogues. In general, the more electronegative atoms such as N and S form π -heteroarene complexes that tend to be more air sensitive.^{6,7} Modification of the chemical and physical properties of the metal centre upon coordination to the heteroarene ligand can occur.

The first example⁸ of the synthesis of heterodimetallic carbene complexes following the route depicted in Scheme 4.1 (*vide infra*) was the addition of ferrocenyl lithium (FcLi) to $[M(CO)_6]$ ($M = Cr, W$) to yield the ate complexes that were alkylated with $[Me_3O]BF_4$ or $[Et_3O]BF_4$ to yield complexes $[(CO)_5M=C(OR)Fc]$ ($R = Me$ or Et). Other examples of bimetallic complexes of the type $[(CO)_5M=C(OEt)C_6H_5Cr(CO)_3]$ ($M = Cr, W$) were synthesized by Fischer in 1980.⁹ More related to the work of this study is $(\eta^6\text{-benzo}[b]\text{thiophene})\text{-tricarbonylchromium}(0)$ complexes, of which complex **5** was already synthesised in our laboratories during preliminary investigations.¹⁰

The η^5 -heterocyclic metal carbonyl complexes e.g. with η^5 -thiophene¹¹ and η^5 -pyrrole¹² rings have been studied thoroughly. More recently the interest shifted to the benzannulated derivatives of these five membered monoheterocycles, e.g. benzo[*b*]thiophene (BT) and indole,¹² which were π -coordinated to transition metals. In these cases coordination of the benzene ring takes preference to coordination of the heteroarene ring (Figure 4.1). $Li[Cr(\eta^5\text{-thienyl})(CO)_3]$ reacts with $[M(CO)_6]$ ($M = Cr, W$) and $[Re(CO)_5Br]$ to yield after subsequent alkylation with $[Et_3O]BF_4$, the carbene complexes $[M(CO)_5\{C(OEt)\eta^5\text{-thienylCr(CO)}_3\}]^{13}$ and $[Re(CO)_4(Br)\{C(OEt)\eta^5\text{-thienylCr(CO)}_3\}]^{14}$ respectively. The synthesis of these tricarbonylchromium compounds are known and these complexes were fully characterized by Fischer *et al.*¹⁵ In addition BT is known to coordinate through the sulphur atom, as seen for $Cp(CO)_2Re(BT)$,¹⁶ or through the 2,3-double bond, e.g. $(\eta^2\text{-}2,3\text{-BT})ReCp(CO)_2$.¹⁷

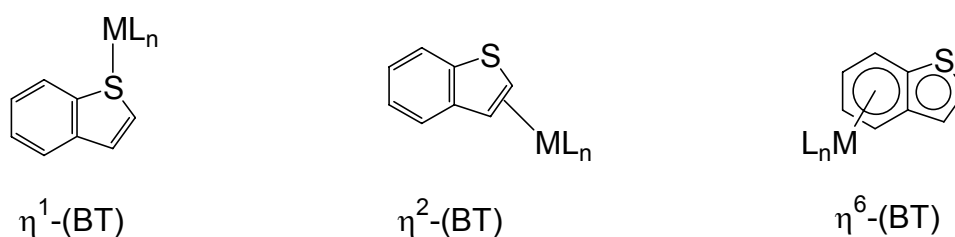


Figure 4.1 Bonding modes of benzo[*b*]thiophene

In this study the synthesis of new bimetallic carbene complexes were investigated by making use of π -coordinated tricarbonylchromium complexes of BT. Bimetallic carbene complexes **5** and **6** were synthesized to study the effect of π -bonded benzo[*b*]thiophene as a carbene substituent.

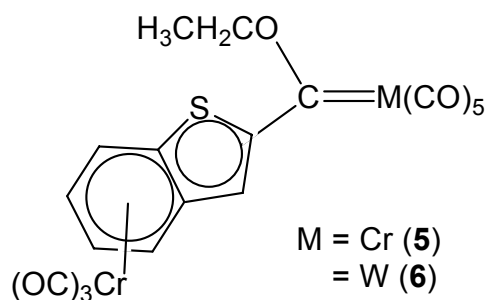


Figure 4.2 Bimetallic π -bonded BT carbene complexes synthesized in this chapter

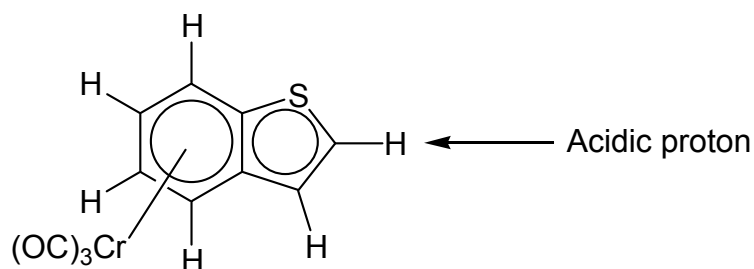
To focus on the electronic and steric properties of this substituent, alkylation was achieved by using $[\text{Et}_3\text{O}]\text{BF}_4$. Comparison with **1** and **2** in Chapter 2 will reveal the effect of π -coordination of BT by $\text{Cr}(\text{CO})_3$ on the carbene carbon atom. It is anticipated that the $\text{Cr}(\text{CO})_3$ unit will remove electron density from the BT ring, disrupt the conjugation of double bonds in BT and decrease the amount of electron density available to stabilize the carbene carbon atom.

2. Synthesis

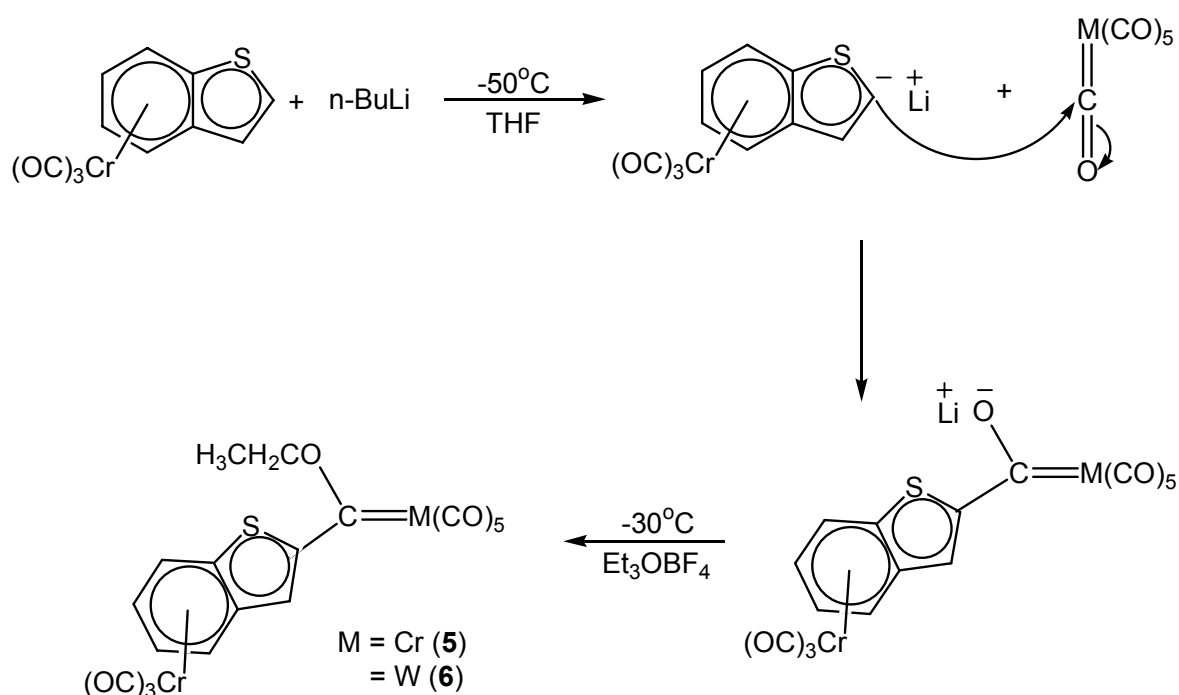
The (η^6 -benzo[*b*]thiophene)tricarbonylchromium(0) precursor was prepared according to known literature methods.¹⁸ The preparation involved the displacement of the amine-ligands in the complex $[\text{Cr}(\text{NH}_3)_3(\text{CO})_3]$ by the heteroarene in the presence of boron trifluoride diethyl etherate in boiling dibutyl ether. The harder ammonia base will preferentially coordinate to the harder Lewis acid BF_3 , thereby facilitating its substitution and the coordination of the heteroarene.



The coordination of a transition metal to an arene ligand in a π -complex modifies the reactivity of the arene ligand. A definite result is the acidification of the ring protons, which allows direct proton abstraction from the ring. The first observation of metallation of arene ligands was reported in 1968¹⁹ and the first examples with chromiumtricarbonyl activation followed soon afterwards.²⁰ An important property of (π -arene)tricarbonylchromium complexes is the displacement of the arene hydrogens under mild conditions. Despite the fact that the tricarbonylchromium moiety is coordinated to the benzene ring in the π -complex of BT, the α -proton on the thiophene ring remains the most acidic.²¹



Deprotonation of the (π -benzo[*b*]thiophene)tricarbonylchromium(0) complex is accomplished by the use of a strong base ($\text{pK}_a > 20$) e.g. *n*-butyllithium and hydrogen-metal exchange occurs under conditions where the uncoordinated substrate is still not reactive.



Scheme 4.1

The desired products **5** (red-pink) and **6** (red-orange) were obtained in high yields after purification using column chromatography with silica gel as stationary phase. The $\text{Cr}(\text{CO})_3$ and $\text{Cr}(\text{CO})_5$ metal fragments can communicate electronically *via* a connecting conjugated π -system in the bridging BT-carbene ligand. It is possible from spectroscopic measurements to look at the role of each substituent to stabilize the carbene carbon atom in the complex. Also, the introduction of a π -bonded $\text{Cr}(\text{CO})_3$ fragment on the BT substituent will introduce additional steric strain to the bimetallic carbene complex compared to the complexes **1** and **2** in Chapter 2.

3. Spectroscopic characterization

3.1 NMR Spectroscopy

π -Coordination of an arene ring to a $\text{Cr}(\text{CO})_3$ fragment leads to the localization of the double bonds and the disruption of the aromaticity of the ring. The ring current, the induced magnetic lines of force that result from the flow of charge, is destroyed and the result is a significant upfield change in chemical shift. The reactivity and aromaticity of heteroaromatic compounds can be studied by nuclear resonance spectroscopy by measuring the chemical shifts and coupling constants of the arene protons and carbons.

All ^1H NMR spectra were recorded in CDCl_3 and in C_6D_6 . ^{13}C NMR spectra were only recorded in CDCl_3 due to their poor solubility in C_6D_6 and the only useful ^{13}C NMR spectrum was obtained for **5**.

^1H NMR Spectroscopy

The signals of the protons of $(\eta^6\text{-benzo}[b]\text{thiophene})\text{tricarboylchromium}(0)$ in deuterated chloroform are given in Figure 4.3. The same system of numbering of the protons and carbon atoms was used as before. The ^1H NMR data of complexes **5** and **6** are summarized in Table 4.1. Figure 4.4 represents the ^1H NMR spectrum of **5**.

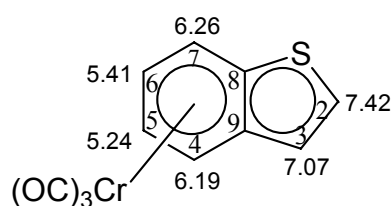


Figure 4.3 Chemical shifts of the protons of $(\eta^6\text{-benzo}[b]\text{thiophene})\text{tricarboylchromium}(0)$.²²

Two important observations of the chemical shifts in the ^1H NMR spectra of **5** and **6** are seen when compared to the corresponding complexes **3** and **4** in Chapter 3. The spectra display an upfield shift of almost 2.0 ppm for the benzene protons because of the π -coordination to the $\text{Cr}(\text{CO})_3$ -fragment and also an upfield shift for H3 of around 0.3 ppm in C_6D_6 and 0.6 ppm in CDCl_3 . The latter is still 1.0 ppm downfield from the same resonance

in uncoordinated BT emphasizing deshielding at C3 caused by the electron-withdrawing effect of the carbene carbon atom. This effect, however, is less important in these compounds. The same observations were recognised when comparing **5** and **6** with **1** and **2** in chapter 2. An overall upfield shift is observed, for the benzene protons once again a shift of about 2.0 ppm can be seen and the upfield shift for H3 is around 0.5 ppm.

For complex **5** in C₆D₆, the coupling constant of the CH₂ group could not be resolved from the CH₂ signal, due to the overlap of signals with the H6 resonances. Coupling constants was obtained from the H4 and H7 resonances.

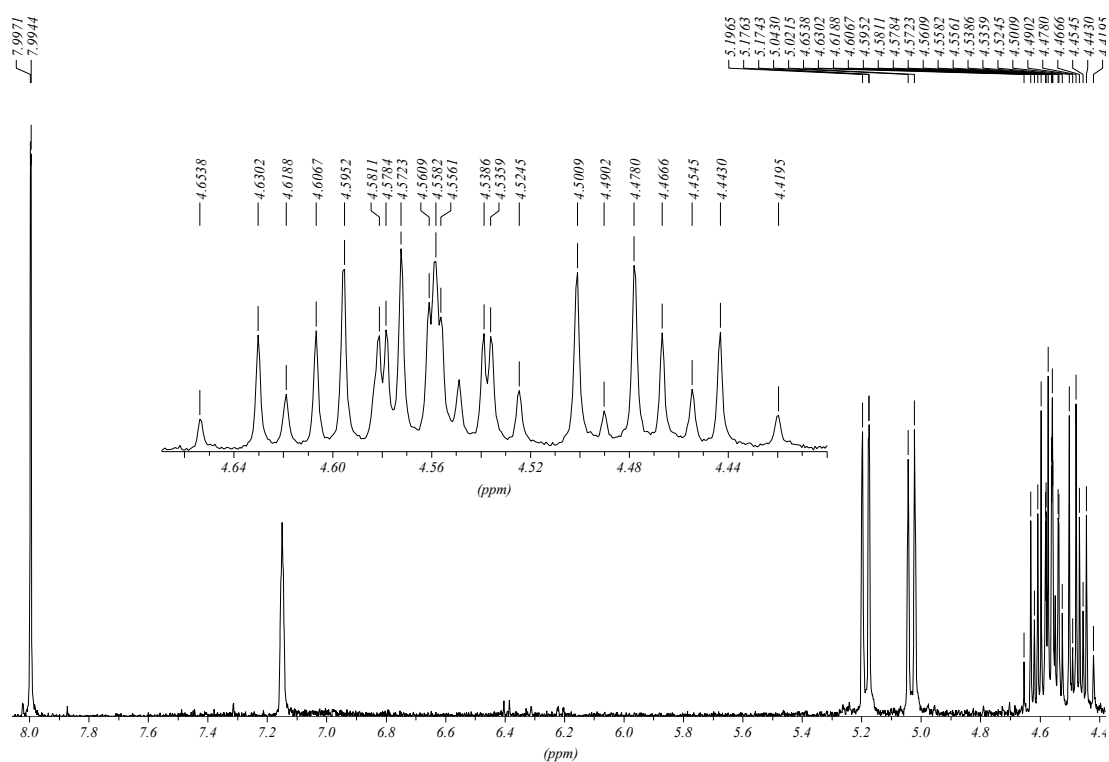
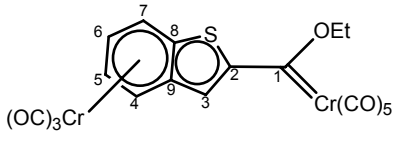
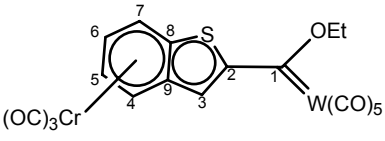


Figure 4.4 ¹H NMR spectrum of complex **5** in C₆D₆, in the region for the ring protons

Table 4.1 ¹H NMR data of complexes **5** and **6**

Assignment	Complexes				
	Chemical shifts (δ , ppm) and coupling constants (J, Hz)				
	 5			 6	
Proton		$^3J_{H-H}$	$^4J_{H-H}$	$^3J_{H-H}$	
H3 ^a	8.13 (s)	-	-	8.05 (d)	-
H4	6.07 (d)	6.8	-	6.07 (d)	6.7
H5	5.61 (m)	6.8	0.9	5.64 (m)	6.7
H6	5.26 (m)	6.6	-	5.25 (m)	6.5
H7	6.29 (d)	6.6	0.9	6.29 (dd)	6.5
-CH ₂	5.19 (q)	7.0	-	4.98 (q)	7.1
-CH ₃	1.69 (t)	7.0	-	1.67 (t)	7.1
H3 ^b	8.00 (d)	-	0.8	7.91 (s)	-
H4	5.03 (d)	6.5	0.8	5.00 (d)	7.0
H5	4.56 (m)	6.5	0.6	4.56 (m)	7.0
H6	4.19 (m)	6.7	-	4.17 (m)	6.5
H7	5.19 (dd)	6.7	0.6	5.14 (d)	6.5
-CH ₂ -	4.54 (q)	-	-	4.34 (q)	-
-CH ₃	0.97 (t)	7.0	7.0	0.94 (t)	7.0

^a recorded in CDCl₃, ^b spectrum was recorded in C₆D₆,

¹³C NMR spectroscopy

^{13}C NMR chemical shift values for $(\eta^6\text{-benzo}[b]\text{thiophene})\text{tricarboonylchromium}(0)$ are captured in Figure 4.5 and the ^{13}C NMR spectrum for **5** was measured in deuterated chloroform (Figure 4.6). It was not possible to obtain a useful spectrum for **6** due to poor solubility and decomposition of the compound during measurements.

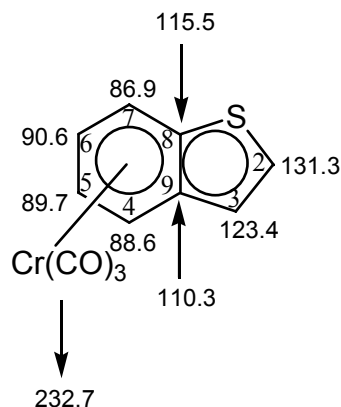


Figure 4.5 Chemical shifts of the carbons of $(\eta^6\text{-benzo}[b]\text{thiophene})\text{tricarboonylchromium}$

Chemical shifts (δ , ppm, CDCl_3) of **5**: 318.2 (C1), 231.4 ($\text{Cr}(\text{CO})_3$), 223.4 (trans) and 216.5 (cis) ($\text{Cr}(\text{CO})_5$), 155.6 (C2), 138.2 (C3), 88.9 (C4), 89.8 (C5), 92.2 (C6), 84.3 (C7), 118.1 and 126.6 (C8, C9), 76.8 (CH_2), 15.0 (CH_3).

The signals in the ^{13}C NMR spectrum of **5** follow the same pattern as the signals of the ^1H NMR and display upfield changes in chemical shift of approximately 30 ppm for the benzene protons because of π -coordination to the $\text{Cr}(\text{CO})_3$ -fragment. The shifts of the thienyl carbons are downfield from those observed in $[\text{Cr}(\eta^6\text{-BT})(\text{CO})_3]$ due to attachment to the carbene carbon atom. When comparing C2 of **1** and **3** with C2 of **5**, a large downfield shift is observed in **5** in comparison with **1** $\Delta\delta = 16.4$ ppm and **3** $\Delta\delta = 35.4$ ppm, at the same time an upfield shift is observed when comparing chemical shifts of C3, in comparison with **1** $\Delta\delta = 0.5$ ppm and **3** $\Delta\delta = 1.3$ ppm. The carbonyl resonances of $\text{Cr}(\text{CO})_3$ are the same as in $[\text{Cr}(\eta^6\text{-BT})(\text{CO})_3]$ and those of $\text{Cr}(\text{CO})_5$ the same as in **3**.

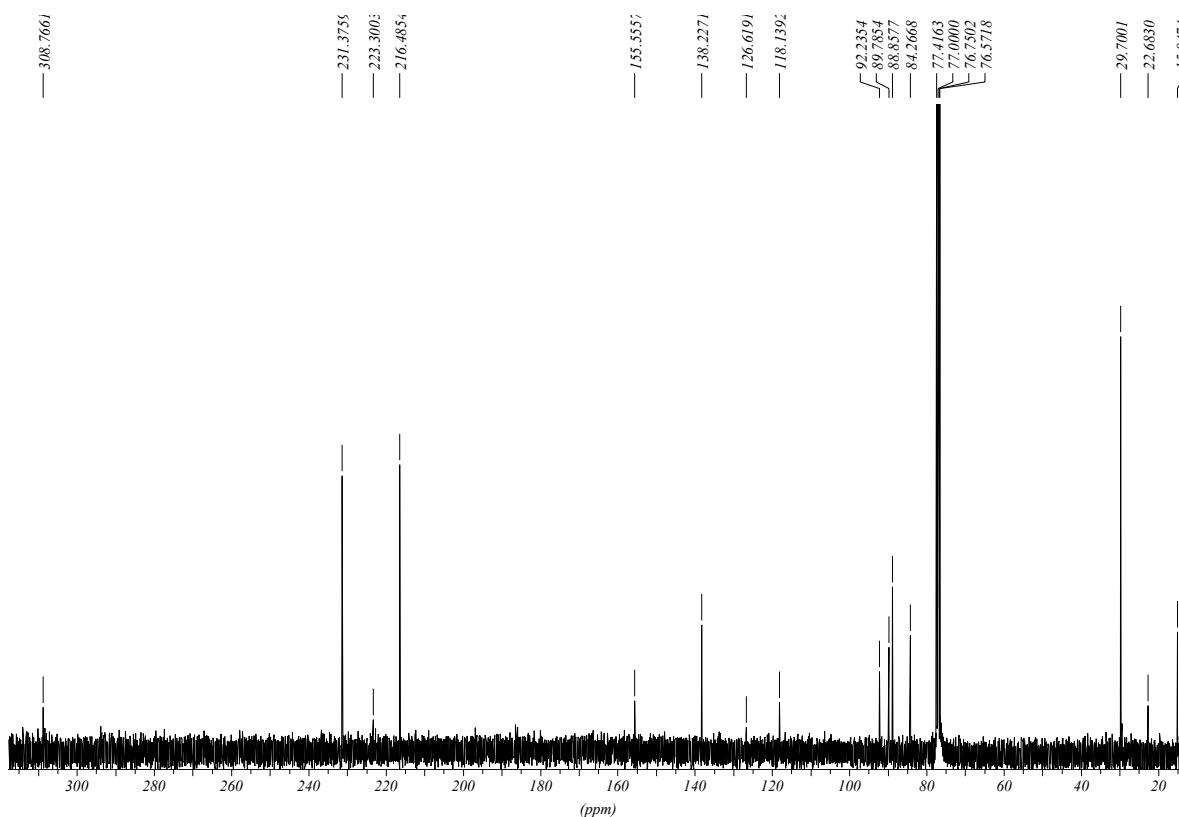


Figure 4.6 ^{13}C NMR spectrum of complex **5** in CDCl_3

3.2 Infrared Spectroscopy

Distinct patterns are observed for the bands of the different metal carbonyl fragments. The number, intensities and region of the bands in the spectrum is a valuable aid for the characterization of the products. The individual vibrational modes are assigned to specific bands by taking a local symmetry of the carbonyls into consideration. Since complexes of the general composition $\text{ML}_3(\text{CO})_3$ belong to the symmetry group C_{3v} , two IR-active bands are observed in the spectrum, they correspond to the A_1 and the E vibrational modes. The first sharp A_1 band is observed at higher wavenumbers than the stronger E band and is associated with the symmetrical stretching vibrations while the E band, at lower wavenumbers, is associated with the unsymmetrical stretching vibrations in the molecule. Aspects related to the vibrational modes of a metalpentacarbonyl fragment were discussed in Chapter 2.

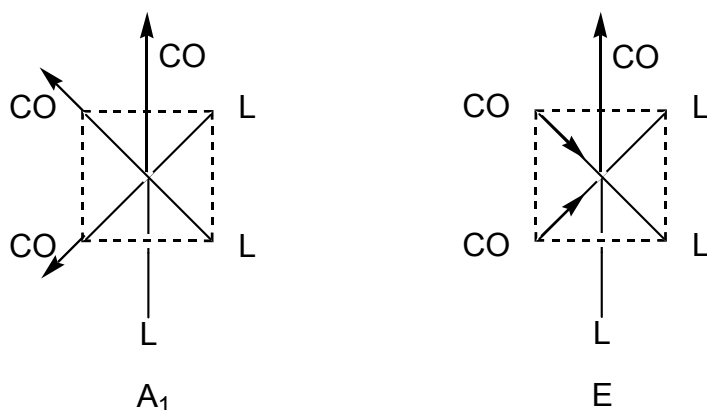


Figure 4.7 Stretching vibrational modes of $M(CO)_3L_3$

All IR spectra were recorded in hexane and dichloromethane.

The wavenumbers of the carbonyl bands for compounds **5** and **6** lie between 1900 and 2070 cm^{-1} , which indicate the presence of terminal carbonyl groups only. Because of the overlap of the pentacarbonyl and the tricarbonyl moieties in these compounds, it was almost impossible to unambiguously allocate a specific wavenumber to the A_1 band of the Cr(CO)_3 -fragment in compound **6**.

Table 4.3 IR-data in the carbonyl region of complex **5** and **6**

Complex	Carbonyl vibrating frequencies (ν_{CO} , cm^{-1})					
	Cr(CO)_3		Cr(CO)_5			
	A_1	E	$A_1^{(1)}$	B_1	$A_1^{(2)}$	E
5 ^a	1928m	1905s 1914s	2059m	1989vw	1950*vs	1950vs
5 ^b	1947s	1901m	2060m-s	-	1969vs	1947s
6 ^a	1945vs	-	2067w	1980vw	1954m ^c	1945vs
6 ^b	1942vs	1903w	2068m-s	-	1969s	1942vs

^a Hexane as solvent, ^b Dichloromethane as solvent, ^c observed as a shoulder,

* $A_1^{(2)}$ and E overlap

3.3 X-ray Crystallography

Final confirmation of the structures of **5** and **6** was obtained from single crystal X-ray diffraction studies. The complexes were crystallised from a layered 1:1 dichloromethane:hexane solution. This method gave dark purple crystals of good quality for both complexes. Figures 4.8 and 4.9 represent the ORTEP²³ + POV-Ray²⁴ plots of the geometry of **5** and **6**, which also indicate the atom numbering scheme that was used for the structural data. Compound **5** crystallized in the space group $P\bar{1}$ with $a = 8.3523(11)$, $b = 10.7547(15)$, $c = 13.0118(17)$ Å, $Z = 2$, compound **6** crystallized in the space group $P\bar{1}$ with $a = 8.4597(6)$, $b = 10.8010(8)$, $c = 13.1159(10)$ Å, $Z = 2$. The most important bond lengths and angles are listed in Table 4.4. Other structural information is captured on the supplementary CD.

An important feature of the structures of **5** and **6** that differentiate them from the structures in the previous chapters are the two possible positions of the sulphur atom in the thienyl ring with respect to the ethoxy substituent and the C9-C10 bond. The major isomer (Cr 88.0 %, W 84.4 %) is the one with the sulphur on the same side as the ethoxy substituent, similar to the structures of **1** and **2** and the same arguments used in Chapter 2 may be valid. The question to answer is why does a second, minor isomer (Cr 12 %, W 15.6 %) exist with the sulphur on the opposite side of the ethoxy substituent. The existence of the second isomer can be explained by placing the $\text{Cr}(\text{CO})_3$ fragment on one of two different sides of the flat benzene ring when the ring is attached to a substituent in the 2-position. Rotation round this C2-substituent bond to get the $\text{Cr}(\text{CO})_3$ fragment on the same side for both isomers, will mean that the sulphur will have to move to the other side of the molecule (Figure 4.8).²⁵

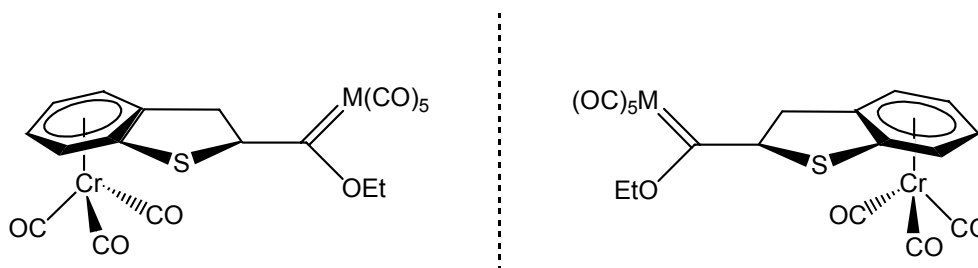


Figure 4.7 Planar chirality in π -BT carbene complexes

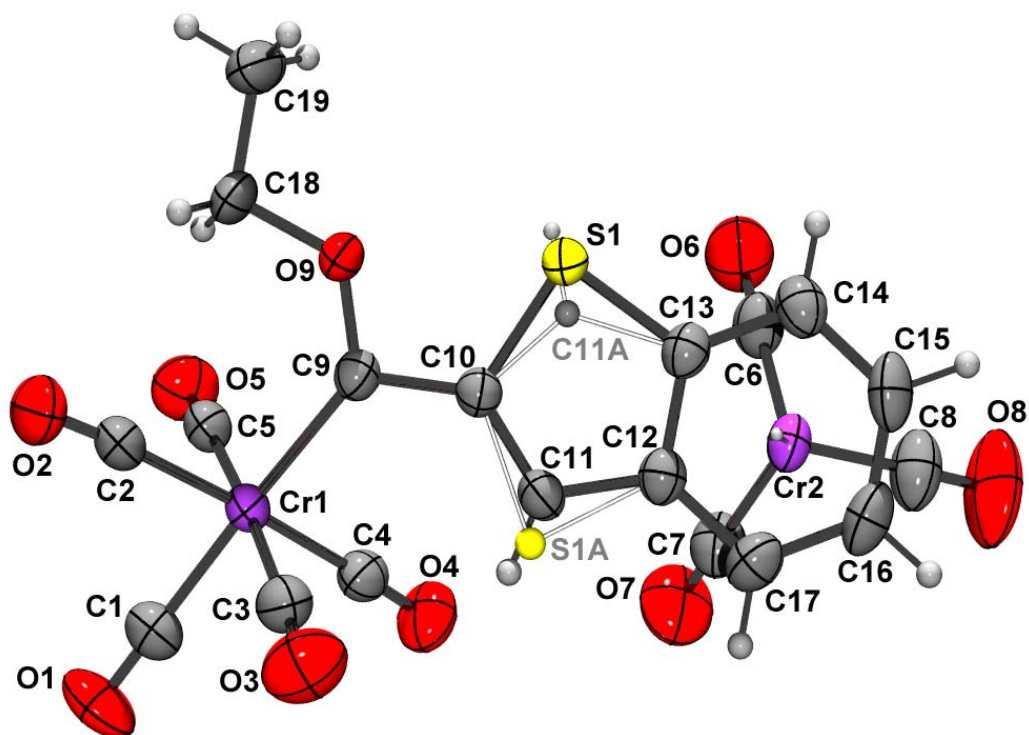


Figure 4.8 ORTEP + POV-Ray plot of the geometry of complex 5

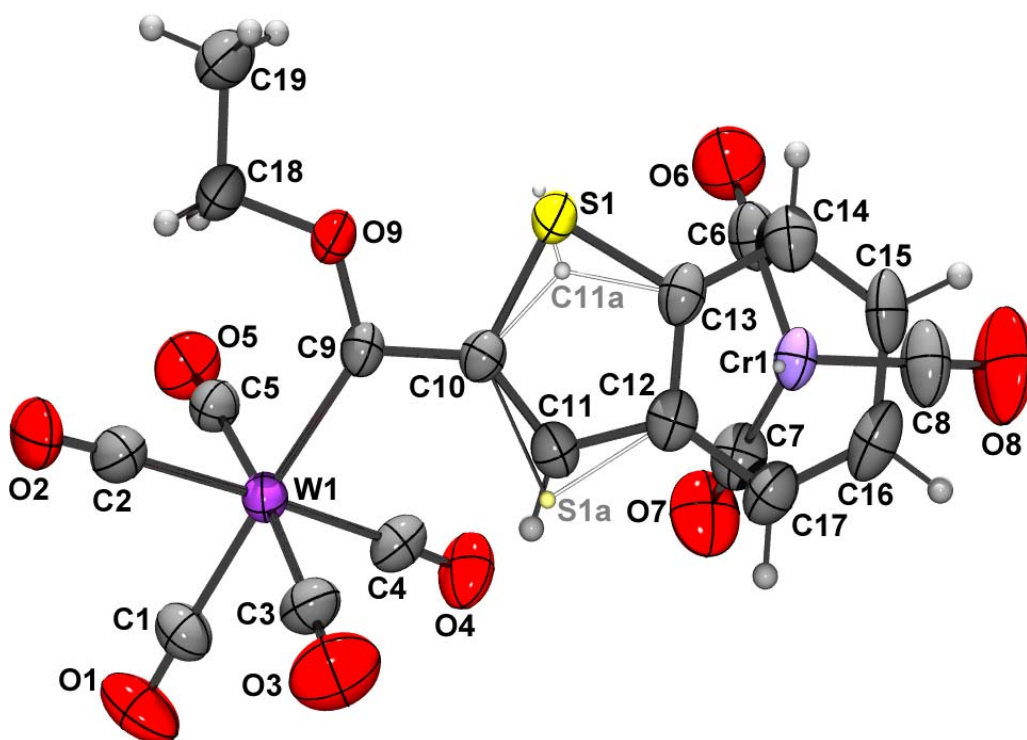


Figure 4.9 ORTEP + POV-Ray plot of the geometry of complex 6

This phenomenon, described as planar chirality,²⁵ has been described before in literature and is relevant for asymmetrically substituted π -arene complexes. Assuming that the attack on the carbonyl is such that both isomers will form it is not clear on steric grounds why the sulphur is not in the normal position and the $\text{Cr}(\text{CO})_3$ fragment on both sides of the benzene ring. This again raises the question whether free rotation exists around the C9-C10 bond in solution, and not in the solid state.

Table 4.4 Selected bond lengths and angles of **5** and **6**

Bond	Bond Lengths (Å)		Bond	Bond angles (°)	
	5 (M = Cr)	6 (M = W)		5 (M = Cr)	6 (M = W)
M(1)-C(9)	2.050(2)	2.179(7)	C(1)-M(1)-C(9)	177.75(10)	177.4(2)
C(9)-O(9)	1.324(3)	1.318(8)	O(9)-C(9)-C(10)	104.52(18)	105.5(5)
C(9)-C(10)	1.472(3)	1.471(8)	O(9)-C(9)-M(1)	130.04(15)	130.0(4)
O(9)-C(18)	1.453(3)	1.458(7)	C(10)-C(9)-M(1)	125.36(15)	124.4(4)
M(1)-C(1)	1.884(3)	2.011(7)	C(9)-O(9)-C(18)	124.28(18)	123.3(5)
M(1)-C(2,3,4,5) ^a	1.905(3)	2.058(8)	C(9)-C(10)-S(1)	117.69(15)	117.0(4)
C(10)-C(11)	1.354(4)	1.353(9)	C(9)-C(10)-S(1A)	118.4(2)	118.8(5)
C(11)-C(12)	1.439(3)	1.441(9)			
C(12)-C(13)	1.408(3)	1.399(8)			
C(13)-S(1)	1.726(2)	1.735(6)			
C(10)-S(1)	1.763(2)	1.778(5)			
C(10)-C(11A) ^m	1.356(9)	1.355(9)			
C(11A)-C(13) ^m	1.455(9)	1.449(9)			
C(12)-S(1A) ^m	1.707(5)	1.725(6)			
C(10)-S(1A) ^m	1.782(4)	1.776(5)			

^a mean value

^m minor product

Table 4.5 Selected torsion angles of **5** and **6**

Bond	Torsion angle (°)	
	5 (M = W)	6 (M = W)
C(2)-M(1)-C(9)-O(9)	-42.0(2)	-41.3(6)
M(1)-C(9)-O(4)-C(18)	3.5(4)	2.1(9)
O(9)-C(9)-C(10)-S(1)	-8.2(2)	-8.2(6)
O(9)-C(9)-C(10)-S(1A) ^m	169.5(3)	169.5(5)
O(9)-C(9)-C(10)-C(11)	174.7(3)	175.3(6)
O(9)-C(9)-C(10)-C(11A) ^m	-10.5(13)	-11(2)
M(1)-C(9)-C(10)-S(1)	168.59(11)	169.7(3)
M(1)-C(9)-C(10)-S(1A) ^m	-13.7(3)	-12.7(7)
C(10)C(11)-C(12)-C(17)	-179.2(2)	-178.8(6)
C(10)-S(1A)-C(12)-C(17) ^m	-177.4(2)	-176.9(5)

^m minor isomer

Structural information shows that the carbene ligand in the complexes **5** and **6** does not lie in a flat plane, one can see this by looking at the torsion angles O(9)-C(9)-C(10)-S(1) (**5** = -8.2(2) and **6** = -8.2(6)) for the major isomer and O(9)-C(9)-C(10)-S(1A) (**5** = 169.5(3) and **6** = 169.5(5)) for the minor isomer, in the solid state. The BT rings in both complexes, including the major and minor isomers, may be considered as flat, since the minimal distortion is present (all torsion angles are smaller than 2°). There is believed to be little steric hindrance in these complexes, since the etoxy group is a lot smaller than the titanoxo group in complex **4** and the O(9)-C(9)-C(10) angles are around 105° and similar to the corresponding angles in **1** and **2** in Chapter 2. In these complexes two of the four carbonyls bend away from the carbene carbon, towards the trans carbonyl as seen by looking at C(9)-M(1)-C(2) (**5** = 94.17(9)° and **6** = 94.7(3)°) and C(9)-M(1)-C(5) (**5** = 93.18(9)° and **6** = 93.6(3)°). Furthermore, it was observed that the major isomer has less distortion overall in comparison with the minor isomer.

The carbonyl conformations in (η^6 -arene)Cr(CO)₃ complexes were studied and it was concluded that the conformation of the arene ligand is dependent on the electronic characteristics of the arene ligand.^{26,27} As shown in Figure 4.7, the ML₃ fragment of a condensed aromatic ligand can adopt one of three orientations within the *ortho*

substitution. The three different orientations are known as the E orientation in which three ring carbon atoms and the three ligands, L, are eclipsed (a) and the S orientation in which the ring carbon atoms are staggered with respect to the ligands, L, and an M-L bond does not project onto the C-C bond containing S1 and S2 (b).

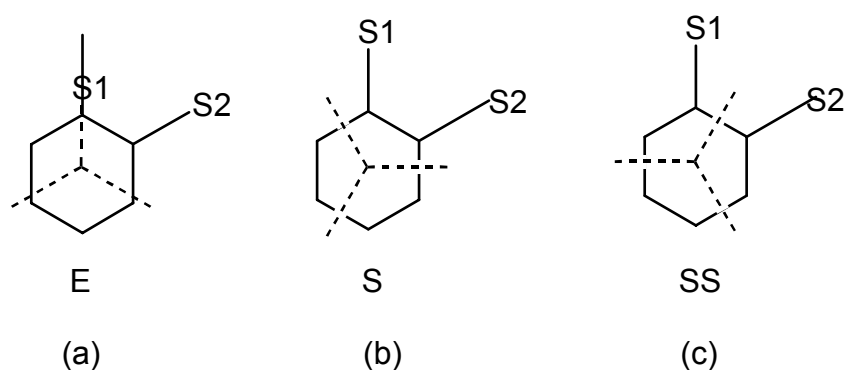


Figure 4.10 Conformational possibilities for disubstituted η^6 -arene- ML_3 complexes²⁷

Among the *ortho*-substituted-arene- ML_3 structures that exhibit the E orientation, the more electron-donating substituent is eclipsed while the more electron-withdrawing substituent is not eclipsed, as would be expected, based on electronic arguments found in literature.²⁷ When looking at the crystal structures of **5** and **6**, it is clear that the two complexes also took on the expected staggered (b) conformation since the carbene carbon *via* the condensed thiophene ring (S1, S2) is electron withdrawing.

When comparing the metal-carbene bond lengths obtained for complexes **5** and **6** with the distances in Chapter 2, the Cr-C(carbene) distances are the same but the W-C(carbene) is significantly shorter in **6**. For the thiophene ring the bond C(10)-C(11) for the major products as well as that of the minor products is shorter than that of free thiophene and the C(11)-C(12) bonds are longer than that of free thiophene. This indicates the disruption of the delocalization of electron density within the thiophene ring itself, π -coordination of benzene in BT eliminates one of the double bonds of thiophene and results in only one olefinic bond in thiophene and no conjugated π -system. Both the C-S bonds in **5** and **6** for the major and minor products are longer than that of free thiophene (except for the S(1A)-C(12) bond of complex **5**). This can be explained by looking at the localization of the benzene protons, since the $Cr(CO)_3$ -fragment will cause this phenomenon. Thus,

stabilization of the carbene carbon can only be supported by the thiophene ring (Figure 4.11), and no longer by the benzene ring as seen for complexes 1-4 (Figure 3.3).

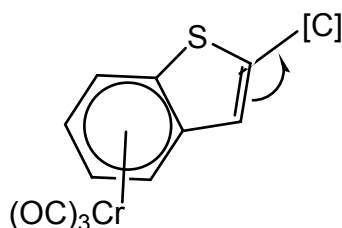


Figure 4.11 Stabilization of the carbene carbon by the thiophene ring

4. References

1. H.H.Zeiss, P.J.Wheatly, H.J.S.Winkler, *Benzenoid-Metal Complexes*, Ronald Press, New York **1966**.
2. M.Y.Darensbourg, El.Muetterties, *J. Am. Chem. Soc.* **1978**, *100* 7425.
3. T.W.Bell, M.Helliwell, M.G.Partridge, R.N.Perutz, *Organometallics* **1992**, *11* 1922.
4. A.M.Morken, D.P.Eyman, M.A.Wolff, S.J.Schauer, *Organometallics* **1993**, *12* 725.
5. C.Pellecchia, A.Grazzi, A.Immirizi, *J. Am. Chem. Soc.* **1993**, *115* 1160.
6. M.Novi, G.Giuseppe, C.Dell'Erba, *J. Heterocycl. Chem.* **1975**, *12* 1055.
7. G.E.Herberich, J.Hengesback, V.Kolle, W.Oschmann, *Angew. Chem., Int. Ed. Engl.* **1977**, *16* 42.
8. J.A.Connor, J.P.Lloyd, *J. Chem. Soc., Dalton Trans.* **1972**, 1470.
9. E.O.Fischer, F.J.Gammel, D.Neugenberger, *Chem. Ber.* **1980**, *113* 1010.
10. M.A.Sierra, *Chem. Rev.* **2000**, *100* 3591.
11. C.H.Langford, *Inorg. Chem.* **1965**, *4* 326.
12. K.K.Joshi, P.L.Pauson, *Proc. Chem. Soc.* **1962**, 326.
13. Y.M.Terblans, S.Lotz, *J. Chem. Soc., Dalton Trans.* **1997**, 2177.
14. T.A.Waldbach, R.van Eldik, P.H.van Rooyen, S.Lotz, *Organometallics* **1997**, *16* 4056.

15. E.O.Fischer, H.A.Goodwin, C.G.Kreiter, H.D.Simmons, K.Sonogashira, S.B.Wild, *J. Organomet. Chem.* **1968**, *14* 359.
16. K.Choi, R.J.Angelici, *Organometallics* **1992**, *11* 330.
17. J.A.Rudd, R.J.Angelici, *Inorg. Chim. Acta* **1995**, *240* 393.
18. M.Novi, G.Guanti, *J. Heterocycl. Chem.* **1975**, *12* 1055.
19. C.Elschenbroich, *J. Organomet. Chem.* **1968**, *14* 157.
20. M.D.Rausch, *Pure Appl. Chem.* **1972**, *30* 523.
21. J.Davidson, H.Patel, P.Preston, *J. Organomet. Chem.* **1987**, *336* C44.
22. M.Landman, Novel heteroarene complexes of chromium(0), MSc dissertation, University of Pretoria **1997**, p76.
23. L.J.Farrugia, *J. Appl. Crystallogr.* **1997**, *30* 565.
24. The POV-Ray Team, POV-Ray 2004 . URL: <http://www.povray.org/download/>.
25. K.Schlögl, *J. Organomet. Chem.* **1986**, *300* 219.
26. G.Erker, R.Schlund, C.J.Krüger, *J. Organomet. Chem.* **1988**, *338* C4.
27. E.L.Muetterties, J.R.Bleeke, E.J.Wuckerer, T.A.Albright, *Chem. Rev.* **1982**, *82* 499.