

5 Trimetallic Titanoxy-Benzo[b]-thienylcarbene Complexes

1. Introduction

In the previous chapters, a lot of attention was drawn to Fischer carbene complexes, containing one or two metal fragments. As discussed, a number of other examples of these types of complexes exist. In this chapter however, the focus will be on Fischer carbene complexes containing three metal fragments attached to the carbene carbon atom. Examples of polymetallic Fischer carbene complexes are found in literature,¹ and these were obtained by different synthetic routes. Trinuclear complexes are only one example of a polymetallic carbene complex but the ratio of carbene ligand to metal fragment is 1:1. There is no electronic contact between the metals and this type of complex can better be described by a chain of monocarbene complexes.

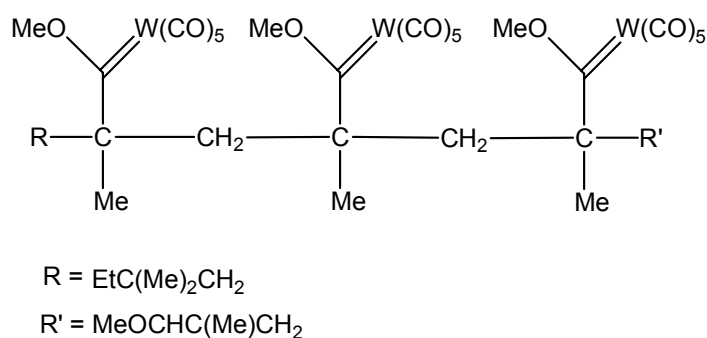


Figure 5.1 Trinuclear tris carbene complex²

Examples exist in literature where all carbene substituents contain a transition metal unit, but two substituents will form part of a ring system in heterodimetallic carbene complexes.^{1,3-5}

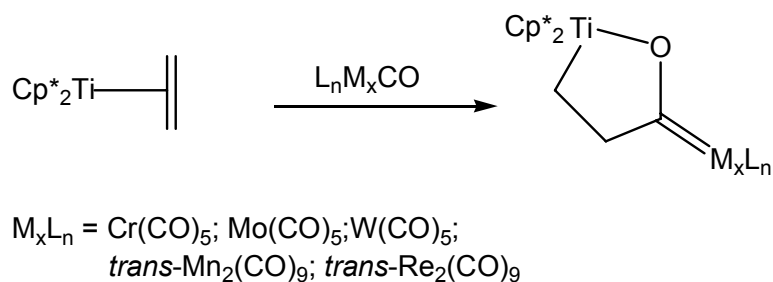


Figure 5.2 Example of cyclic heterodimetallic carbene complexes

The metalloxycarbene complexes can be prepared without a nucleophilic addition to a metal carbonyl by using very reactive η^2 -olefin precursors.

Similarly the reaction of η^4 -coordinated dienes with metal carbonyls afford dimetallic η^3 -allyl metalloxycarbene complexes (Figure 5.3).^{1,3,4}

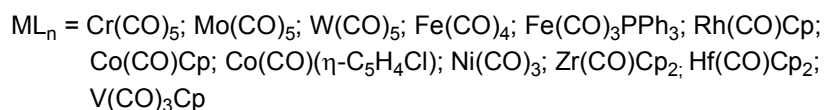
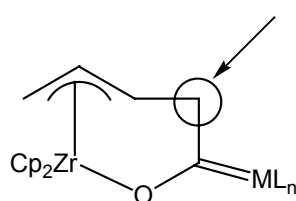


Figure 5.3 Example of dimetallic metalloxycarbenes

The Cp_2Zr fragment acts as a link between two carbene substituents, but these complexes differ in two ways from the complexes discussed in this chapter. Although Zr is π -bonded to an allyl, no electronic connection exists with ML_n because of a CH_2 -unit in this substituent (as indicated by the arrow in Figure 5.3). Secondly the same fragment Cp_2Zr is the metal containing fragment of two substituents and forms part of a metallocycle.

On the other hand, electronic communication through the π -system of the bridging ligand exists in the product obtained starting with a reactive aryne precursor (Figure 5.4).¹ These complexes have all the features and requirements of metal-metal communication but have only two metals as one of them links two substituents of the carbene in a five membered ring.

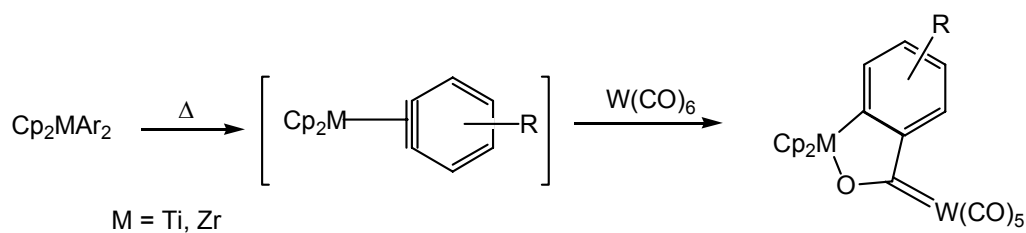


Figure 5.4 Example of metallocyclopentadienylidene complexes with electronic communication

Our purpose was to "surround" a single carbene carbon with three transition metal fragments as depicted in Chapter 1 (Scheme 1.2, structure **J**). This makes the complexes discussed in this chapter unique from the examples found in literature and represents the one type of a Fischer carbene complex without a precedent in literature. Not only was it possible to obtain stable complexes but also to record some reasonable spectra and manage to isolate crystals for crystal structure determinations of both **7** and **8**. An important fact of the complexes obtained in this chapter, is the different metal substituents attached to the carbene carbon, especially in **8** where all the transition metals contained in the fragments attached to the carbene carbon are unique, in **7** Cr appears twice.

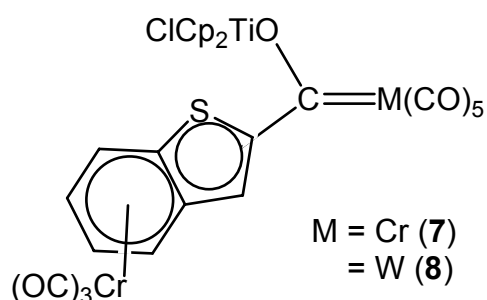
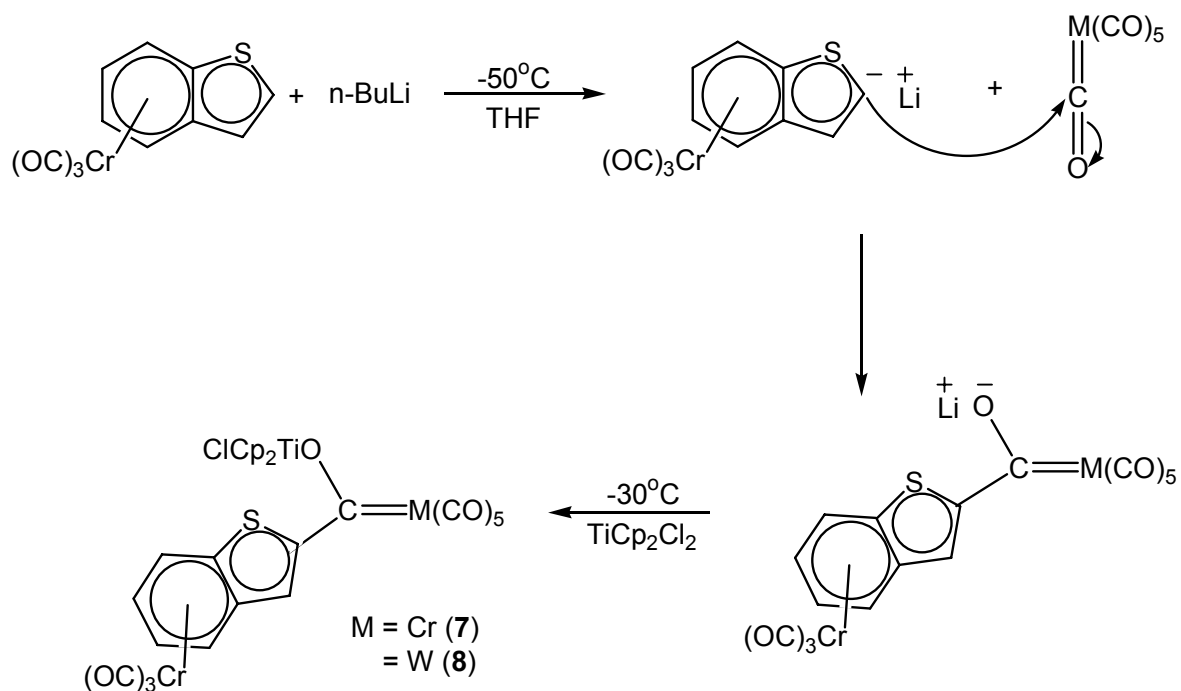


Figure 5.5 Complexes **7** and **8**, showing the three metal fragments that surround a carbene carbon

2. Synthesis

The same procedure was followed as described in Chapter 4. In this instance titanocene dichloride was added instead of triethyloxonium tetrafluoroborate to the metal acylate, and the neutral trimetallic carbene complexes formed.



Scheme 5.1

The desired products **7** (dark purple) and **8** (dark purple) were obtained after purification using column chromatography with aluminium oxide as stationary phase. It was found that the complexes were more stable on alox compared to silica gel during purification. The $Cr(CO)_3$, $Cr(CO)_5$ and the Ti-metal fragments can communicate electronically *via* a connecting conjugated π -system. The π -conjugated linker includes the BT-substituent, the carbene carbon atom and the oxygen as heteroatom. It is possible from spectroscopic measurements to look at the role of each substituent to stabilize the carbene carbon atom and the complex. Also, the introduction of a bulky $TiCp_2Cl$ fragment on the oxygen substituent will introduce additional steric strain within the trimetallic carbene complex.

3. Spectroscopic characterization

1H NMR Spectroscopy

All 1H NMR spectra were recorded in C_6D_6 only, due to decomposition in $CDCl_3$, which is an indication of the poor stability of these complexes in solution. No ^{13}C NMR spectra were obtainable due to poor solubility in C_6D_6 .

A spectrum of poor quality was obtained for complex **7**, and no coupling constants could be calculated. The spectrum obtained for complex **8** shows fully resolved resonances and can be seen in Figure 5.6.

Chemical shifts (δ , ppm, C_6D_6) of **8**: 7.95 (d) (H3) with 0.8 ($^4J_{H-H}$), 5.11 (d) (H4) with 6.7 ($^3J_{H-H}$), 4.57 (m) (H5), 4.15 (m) (H6), 5.21 (dd) (H7) with 6.7 ($^3J_{H-H}$) and 0.8 ($^4J_{H-H}$) and 5.88 and 5.85 (Cp's).

When comparing the chemical shifts of **8** with the analogous **6**, it is clear that H3 in these complexes is very similar ($\Delta\delta = 0.04$). This can be ascribed to a dominating electron withdrawing effect of the $Cr(CO)_3$ fragment that controls the electron density on the BT ring without much interference from the carbene carbon, whilst the ethoxy group in the prior complexes (**5** and **6**) was electron donating, rather than withdrawing. An interesting observation for **8** is that there are two resonance signals for the Cp rings attached to the titanium, indicating that the two rings are in different electronic environments. This was not observed in **4**, which is ascribed to a more sterically crowded complex for **8** with restricted rotation around the Ti-O bond. Hence although the rings can rotate freely (sharp singlet), they are locked in a specific region of space because of the bulkiness of the π -BT substituent. The Cp-rings in **8**, again show a more electron positive titanium centre similarly to complex **4** in Figure 3.4³ because of the down field shift compared to $TiCp_2Cl_2$ (experimentally determined in $CDCl_3$ has a value of 6.57 ppm).

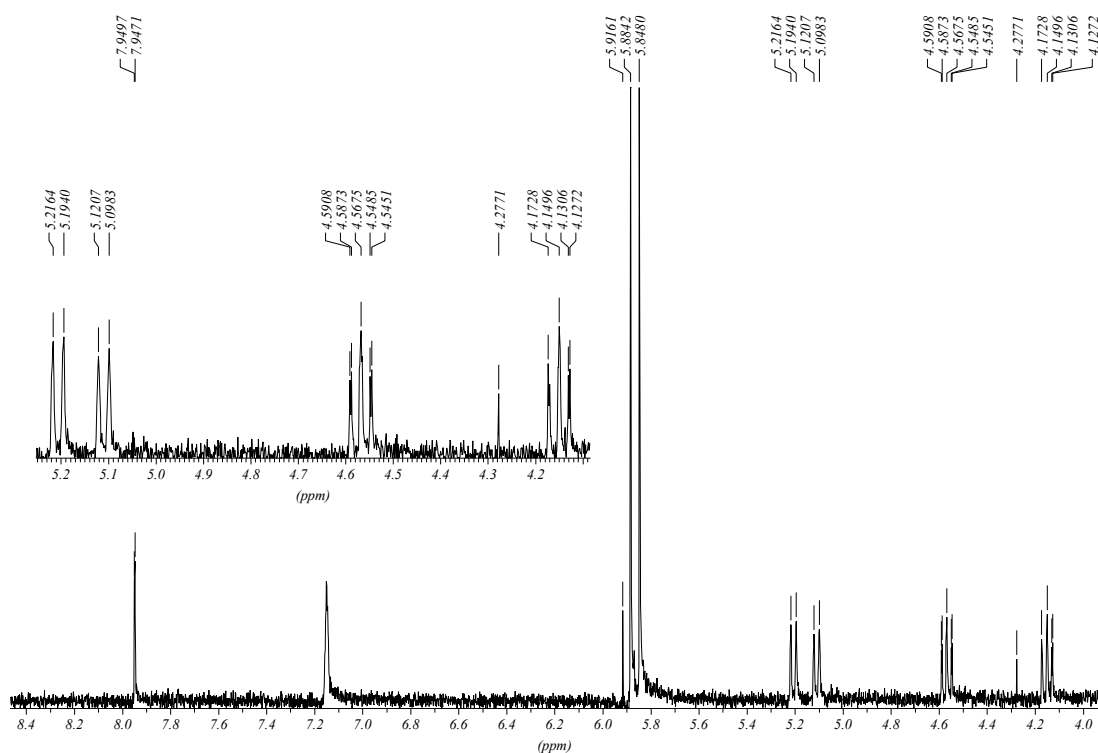


Figure 5.6 ^1H NMR spectrum of complex **8** in C_6D_6

3.2 Infrared Spectroscopy

The carbonyl data of the infrared spectra of complexes **7** and **8** are summarized in Table 5.1, the spectra of the compounds were recorded in dichloromethane due to not being soluble in hexane.

Complexes **7** and **8** contain metalpentacarbonyl and metaltricarbonyl fragments, aspects related to these metal fragments were discussed in Chapters 2 and 4. Due to the overlap of bands of the pentacarbonyl and tricarbonyl moieties in these compounds, it was difficult to unambiguously assign a specific wavenumber to the A_1 band of the $\text{Cr}(\text{CO})_3$ -fragment of both complexes. The spectra are also indicative of large distortions in the complexes and a lowering of the carbonyl symmetry even though bands are broadened because of interaction with the polar solvent.

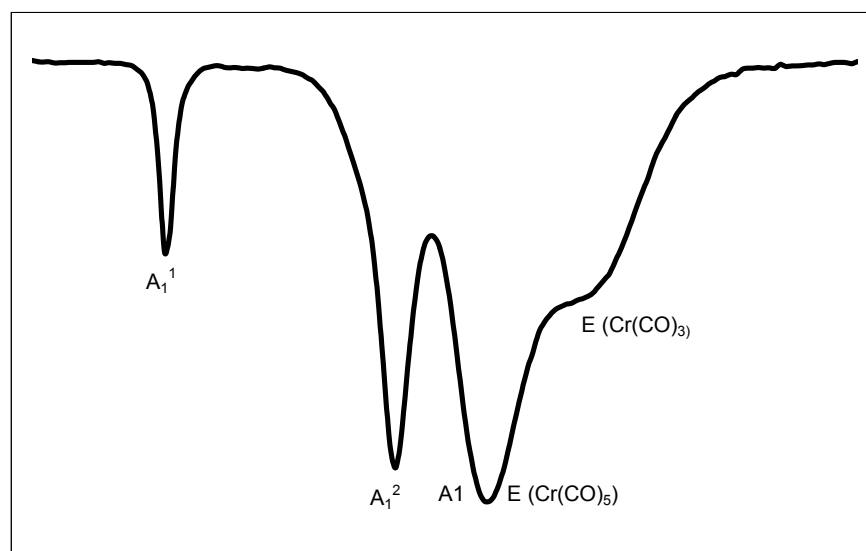


Figure 5.7 Infrared spectrum of **7** in the carbonyl region

Table 5.1 IR-data^b of complex **7** and **8**

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
7	1935*vs	1895m ^c	2052m	-	1968s	1935*vs
8	1930*vs	-	2060m	-	1969s	1930*vs

^b Dichloromethane as solvent *A₁ (Cr(CO)₃) and E (Cr(CO)₅) overlap

^c observed as a shoulder

3.3 X-ray Crystallography

Final confirmation of the structures of **7** and **8** 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 5.8 and 5.9 represent the ORTEP⁶ + POV-Ray⁷ plot of the geometry of **7** and **8**, which also indicates the atom numbering scheme that was used for the structural data. Compound **7** crystallized in the space group P 21/c with $a = 11.260(2)$, $b = 12.083(2)$, $c = 23.804(4)$ Å, $Z = 4$, compound **8** crystallized in the space group P2₁/c with $a = 11.2280(5)$, $b = 12.2398(5)$, $c = 23.9446(11)$ Å, $Z = 4$. The most important bond lengths and angles are listed in Table 5.2, whilst the most important torsion angles

involving the carbene ligand are listed in Table 5.3. Other structural information is captured on the supplementary CD.

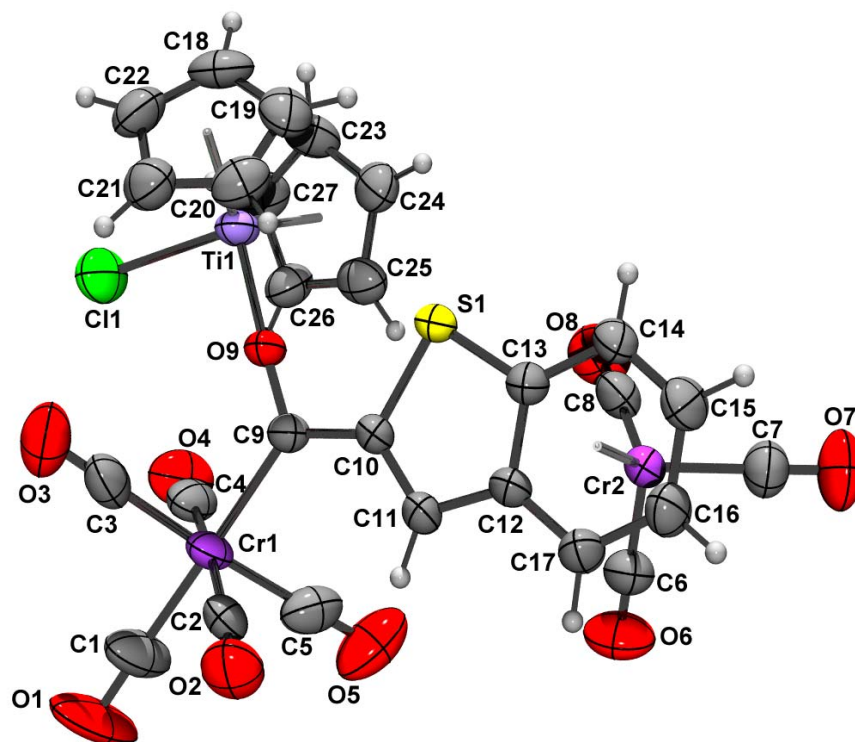


Figure 5.8 ORTEP + POV-Ray plot of the geometry of complex 7

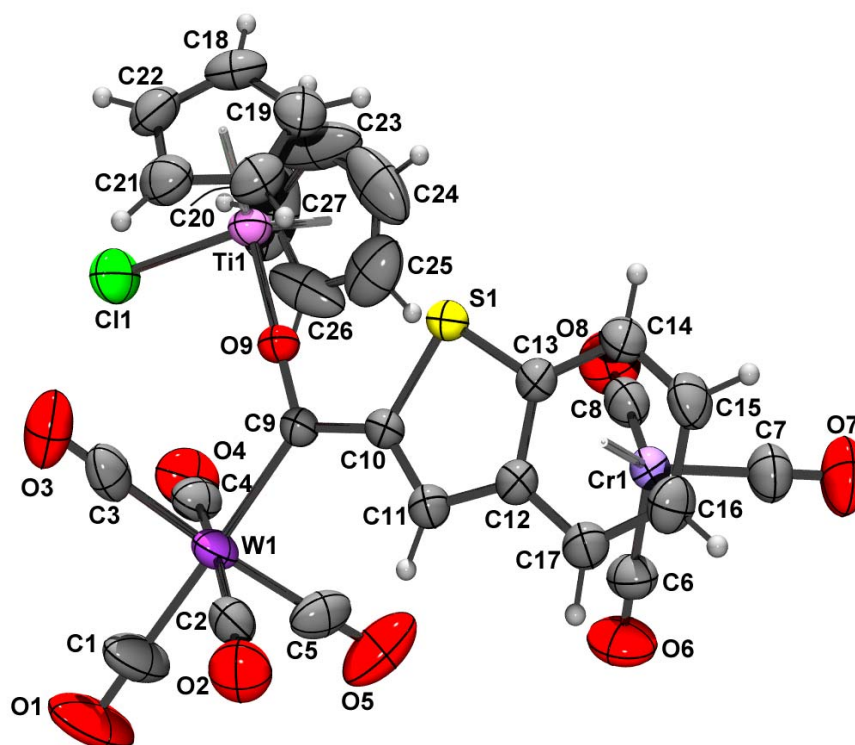


Figure 5.9 ORTEP + POV-Ray plot of the geometry of complex 8

Table 5.2 Selected bond lengths and angles of **7** and **8**

Bond	Bond Lengths (Å)		Bond	Bond angles (°)	
	7 (M = Cr)	8 (M = W)		7 (M = Cr)	8 (M = W)
M(1)-C(9)	2.077(4)	2.207(4)	C(1)-M(1)-C(9)	178.0(3)	177.2(3)
C(9)-O(9)	1.285(5)	1.280(5)	O(9)-C(9)-C(10)	112.7(4)	112.5(3)
C(9)-C(10)	1.463(6)	1.461(6)	O(9)-C(9)-M(1)	120.9(3)	121.4(3)
O(9)-Ti(1)	1.925(3)	1.921(3)	C(10)-C(9)-M(1)	126.4(3)	126.1(3)
M(1)-C(1)	1.859(6)	2.000(6)	C(9)-O(9)-Ti(1)	174.0(3)	174.6(3)
M(1)-C(2,3,4,5) ^a	1.897(7)	2.074(7)	C(9)-C(10)-S(1)	119.8(3)	119.7(3)
C(10)-C(11)	1.363(6)	1.361(6)			
C(11)-C(12)	1.438(6)	1.440(6)			
C(12)-C(13)	1.414(6)	1.424(6)			
C(13)-S(1)	1.724(5)	1.723(4)			
C(10)-S(1)	1.770(4)	1.775(4)			

^a mean value**Table 5.3** Selected torsion angles of **7** and **8**

Bond	Torsion angle (°)	
	7 (M = Cr)	8 (M = W)
C(4)-M(1)-C(9)-O(9)	42.1(4)	40.9(4)
O(9)-C(9)-C(10)-C(11)	-179.5(4)	179.9(4)
O(9)-C(9)-C(10)-S(1)	-1.7(5)	-1.3(5)
M(1)-C(9)-C(10)-S(1)	178.8(2)	177.6(2)

Structural information shows that the carbene ligand of the complexes **7** and **8** lies in a flat plane. One can see this by looking at the torsion angles given in Table 5.5 i.e, O(9)-C(9)-C(10)-S(1) (**7** = -1.7(5) and **8** = -1.3(5)) and M(1)-C(9)-C(10)-S(1) (**7** = 178.8(2) and **8** = 177.6(2)). The plane of the carbene ligand bisects two *cis* carbonyl ligands. These angles are much smaller than those of complexes **4**, **5** and **6**. The BT ligand in both complexes may be considered as flat, since distortion (torsion angles < 1°) is minimal. In these complexes two of the four carbonyls bend away from the carbene carbon, towards the *trans* carbonyl as seen by looking at C(3)-M(1)-C(9) (**7** = 87.5(2) and **8** = 87.01(18)) and C(5)-M(1)-C(9) (**7** = 89.2(2) and **8** = 89.5(2)).

Looking at the crystal structures of **7** and **8** the expected conformation for the $\text{Cr}(\text{CO})_3$ -fragment was obtained as indicated in Chapter 4, the $\text{Cr}(\text{CO})_3$ fragment, once again took on a staggered conformation (Figure 4.10), since this is the energetically favoured conformation.

When comparing the bond lengths obtained for complexes **7** and **8** with known distances from literature⁸ and those discussed in Chapter 2-4, some delocalization of electron density is observed since the C(9)-O(9) (**7** = 1.285(5); **8** = 1.280(5) Å) and C(9)-C(10) (**7** = 1.463(6); **8** = 1.461(6)Å) bonds are shorter than those of single bonds ($\text{Csp}^2\text{-O}(2)$ in enol esters: $\text{C}=\text{C}-\text{O}-\text{C}^* = 1.354$ Å and $\text{Csp}^2\text{-Car}$ (overall) = 1.483 Å), but still longer than double bonds. For the thiophene ring the bonds C(10)-C(11) (**7** = 1.363(6); **8** = 1.361(6)Å) are in the same range as those of free thiophene (1.362 Å) and the C(11)-C(12) (**7** = 1.438(6); **8** = 1.440(6)Å) bonds are longer than those of free thiophene (1.424 Å). Both the C-S bonds in **7** and **8** are longer than those of free thiophene (1.712Å), this observation can be ascribed to the bulkiness of the carbene substituents and poorer conjugation within the thiophene ring. The C-S bond closer to the carbene carbon (C(10)-S(1)) is much longer than those, on the side of the benzene ring (C(13)-S(1)). This can be ascribed to the fact that the ring protons in the benzene ring are no longer available for delocalization due to the bonded $\text{Cr}(\text{CO})_3$ -fragment, while in complexes **1-4** this was not the case. (See Chapter 4, Figure 4.11)

In Chapter 4 we saw two possible structures for the complexes (**5** and **6**) in the solid state, where the positions for the sulphur atom with respect to the ethoxy substituent differ. This observation was explained by means of planar chirality of the π -BT substituent due to the coordination of the $\text{Cr}(\text{CO})_3$ -group. The ethoxy substituent is relatively small, and both isomers formed. For complexes **7** and **8**, however, only one isomer is observed because of the bulkiness of the titanoxo substituent and this isomer agrees with the main product in Chapter 4.

4. References

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