

# Cleaving of Metal-Metal

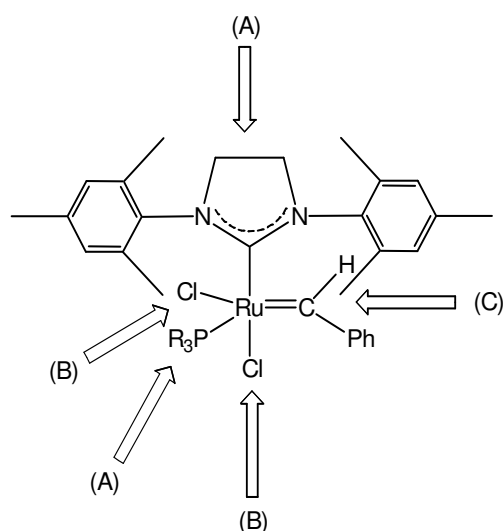
# 3 Bonds: Monomanganese

# Monocarbene Complexes

## 3.1 Background

### 3.1.1 Overview

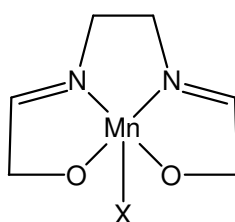
In 1998, the Schrock-type carbene complex, the so-called Grubbs carbene  $[\text{Ru}(\text{PR}_3)_2(\text{carbene})\text{Cl}_2]$  was awarded the title "reagent of the year" for the success it exhibited as ring-closing metathesis catalyst<sup>[1]</sup>. Such was the impact of this work that Schrock, Grubbs and Chauvin were awarded the Nobel Prize for Chemistry in 2005.



**Figure 3.1** Assembly of the second generation Grubbs ruthenium catalyst

The catalyst system (Figure 3.1) consists of a ruthenium metal centre, bulky ligands to protect the reaction centre (A), X-type halide ligands to support alkyl binding (B), and the carbene ligand (C) to initiate metathesis.

For Group VII transition metals, specifically manganese, low oxidation state catalysts are fairly unknown. Perhaps the best known example of this transition metal as high-valent catalyst is the Mn(III)-salen complexes catalysing epoxidation reactions<sup>[2]</sup>.

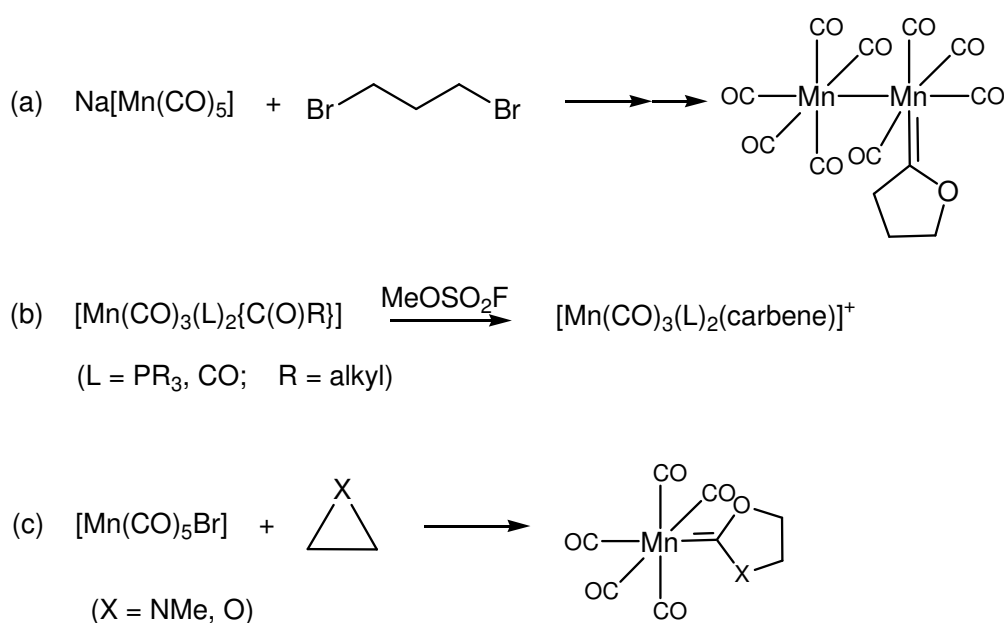


**Figure 3.2** General structure of the Mn(III)-salen complexes

The chemistry of Group VII transition metal carbonyl complexes containing both Fischer carbene and halogen ligands,  $[\text{Mn}(\text{CO})_4(\text{carbene})\text{X}]$  (X = halogens), has been neglected due to the difficulties associated with the synthesis of such compounds<sup>[3-6]</sup>.

The King compound,  $[\text{Mn}_2(\text{CO})_9(\overline{\text{COCH}_2\text{CH}_2\text{CH}_2})]$ , that was initially assigned an incorrect structure without a carbene ligand  $[\text{Mn}_2(\text{CO})_{10}(\text{CH}_2)_3]$ <sup>[7]</sup>, sparked interest in the challenges associated with the synthesis of  $[\text{M}(\text{CO})_4(\text{carbene})\text{X}]$  (M = Mn, Re; X = halogens) complexes. The isolation of binuclear monocarbene complexes of Group VII transition metals,  $[\text{Mn}_2(\text{CO})_9\{\text{C}(\text{OR})\text{R}\}]$ , (R = alkyl) prepared from  $\text{Na}[\text{Mn}(\text{CO})_5]$  and 1,3-dihaloalkanes was reinvestigated and resulted in detailed mechanistic studies of the reactions of  $\text{Na}[\text{M}(\text{CO})_5]$  (M = Mn, Re) with dihaloalkanes<sup>[8-11]</sup>. By using different dihaloalkanes, a number of complexes similar to the King compound containing a cyclic carbene ligand were synthesized and characterized<sup>[12;13]</sup>. In a few instances, with more sophisticated chloro precursors, cationic

mononuclear carbene complexes  $[\text{Mn}(\text{CO})_3(\text{L})_2(\text{carbene})]^+$  ( $\text{L} = \text{phosphine or CO}$ ) could be obtained, which after subsequent treatment with halides, afforded the desired neutral halo-carbene complexes  $[\text{M}(\text{CO})_4(\text{carbene})\text{X}]^{[14-19]}$  (Scheme 3.1, (a)). However, the complexes  $[\text{Mn}(\text{CO})_3(\text{L})_2(\text{carbene})]^+$  ( $\text{L} = \text{PR}_3$  or  $\text{CO}$ ) could be afforded by employing the alkylation of  $[\text{Mn}(\text{CO})_3(\text{L})_2\{\text{C}(\text{O})\text{R}\}]$  with the strong alkylating agent  $\text{MeOSO}_2\text{F}^{[20]}$  (Scheme 3.1, (b)). These contributions to this field of the carbene chemistry of Group VII transition metals are illustrated in Scheme 3.1.

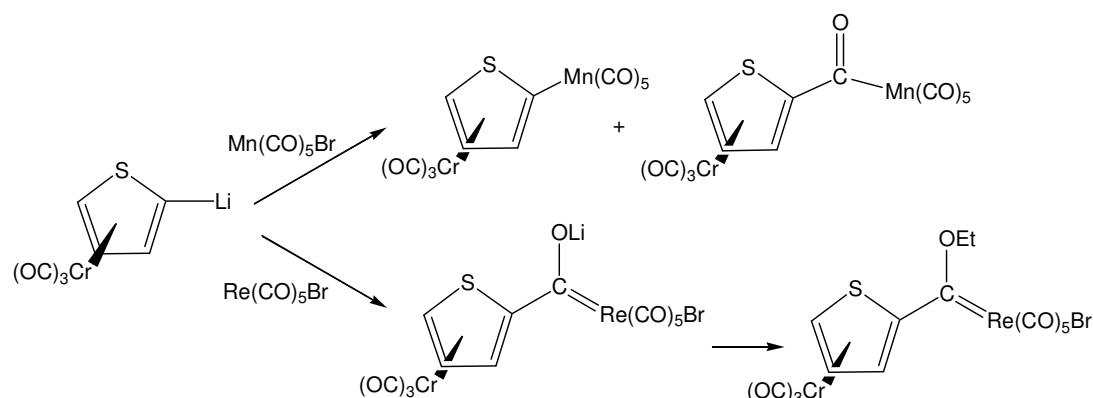


### Scheme 3.1 Preparatory pathways of manganese carbene complexes

A major contribution came from the work done by Angelici and his group<sup>[21-23]</sup>. Strained 3-membered heterocyclic substrates (oxirane, aziridine) with  $[\text{M}(\text{CO})_5\text{X}]$  ( $\text{M} = \text{Mn}, \text{Re}; \text{X} = \text{Br}, \text{Cl}$ ) afforded neutral cyclic aminoxy and dioxy carbene complexes also containing a halogen ligand (Scheme 3.1, (c)). This reaction could also be applied to  $[\text{M}_2(\text{CO})_{10}]$  ( $\text{M} = \text{Mn}, \text{Re}$ ) for oxirane<sup>[22]</sup>.

Reaction of the lithiated  $[(\eta^5\text{-thiophene})\text{Cr}(\text{CO})_3]$  or the analogous lithiated  $[(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3]$  with  $[\text{Mn}(\text{CO})_5\text{Br}]$  involved attack either on the metal centre or on a carbonyl ligand with elimination of bromide and yielded for the thiophene precursor the binuclear complexes  $[(\eta^1, \eta^5\text{-thienyl-}$

$\text{Mn}(\text{CO})_5\text{Cr}(\text{CO})_3$  and  $[\{\eta^1, \eta^5\text{-thienyl-C}(\text{O})\text{Mn}(\text{CO})_5\}\text{Cr}(\text{CO})_3]$  (Scheme 3.2)<sup>[24-28]</sup>.



**Scheme 3.2** Different reaction routes of  $[\text{M}(\text{CO})_5\text{Br}]$  with lithiated  $[\{\eta^5\text{-thiophene}\}\text{Cr}(\text{CO})_3]$  ( $\text{M} = \text{Mn}, \text{Re}$ )

By contrast, the corresponding reaction with  $[\text{Re}(\text{CO})_5\text{Br}]$  involved attack on a carbonyl ligand without the elimination of bromide. Subsequent alkylation of the latter with  $[\text{Et}_3\text{OBF}_4]$  yielded the binuclear carbene complex  $[\{\eta^1, \eta^5\text{-thienyl-C}(\text{OEt})\text{Re}(\text{CO})_4\text{Br}\}\text{Cr}(\text{CO})_3]$  (Scheme 3.2).

This prompted the investigation of the reaction of  $[\text{Re}(\text{CO})_5\text{Br}]$  with lithiated thiophene to assess the role, if any, of the  $\text{Cr}(\text{CO})_3$ -fragment. Although not reacting smoothly, it was possible, after subsequent alkylation with  $[\text{Et}_3\text{OBF}_4]$ , to isolate and characterize the monocarbene dirhenium nonacarbonyl complex,  $[\text{Re}_2(\text{CO})_9\{\text{C}(\text{OEt})\text{thienyl}\}]$ <sup>[29]</sup>. This reaction showed that it was possible to eliminate a bromide from  $[\text{Re}(\text{CO})_5\text{Br}]$  during a Fischer carbene synthesis procedure ( $\text{Li-thienyl}/\text{Et}_3\text{OBF}_4$ ) and replace it with the isolobal fragment  $\text{Re}(\text{CO})_5$  to give  $[\text{Re}_2(\text{CO})_9\{\text{C}(\text{OEt})\text{thienyl}\}]$ .

In contrast, reactions of lithiated thiophene with  $[\text{Mn}(\text{CO})_5\text{Br}]$  afforded a number of unstable compounds that could not be characterized unambiguously<sup>[29]</sup>.

We envisaged that the reverse reaction of cleaving the manganese-manganese bond in the binuclear carbene complexes could be applied, provided the carbene ligand would not be affected by the oxidant.

### 3.1.2 Cleaving of metal-metal bonds

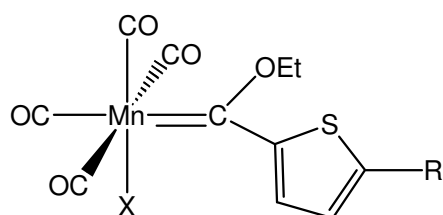
The metal-metal bond in  $[\text{Mn}_2(\text{CO})_{10}]$  can easily be cleaved reductively by sodium, affording the anionic sodium salt  $\text{Na}[\text{Mn}(\text{CO})_5]^{[30]}$ . On the other hand the metal-metal bond can also be cleaved oxidatively with halogens to give neutral metal carbonyl halides,  $[\text{Mn}(\text{CO})_5\text{X}]$  ( $\text{X} = \text{halogens}$ )<sup>[31]</sup>. The reductive cleavage of the Mn-Mn bond of  $[\text{Mn}_2(\text{CO})_9\{\text{C}(\text{OR})\text{Me}\}]$  with sodium in THF was attempted by Fischer and co-workers, but only  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Na}[\text{Mn}(\text{CO})_5\text{X}]$  were observed to have formed<sup>[32]</sup>.

Oxidation of the metal results either in the loss of the carbene ligand or the coordination of the products of the oxidizing agent to the metal. Biscarbene complexes of Group VII transition metals are readily oxidized by trace amounts of oxygen to give monocarbene-ester products<sup>[33;34]</sup>, while diaminecarbene complexes of tungsten could be oxidized with iodine to yield  $[\text{W}(\text{CO})_4(\text{I})_2(\text{carbene})]^{[35]}$ . Although largely unnoticed in later work, the cleavage of the metal-metal bond of the dioxy carbene by bromine was reported by Angelici<sup>[22]</sup>. Nevertheless, very few examples exist where the ligand in  $[\text{M}(\text{CO})_4(\text{carbene})\text{X}]$  ( $\text{M} = \text{Mn}$ ,  $\text{X} = \text{halogen}$ ) complexes is not a cyclic alkoxy carbene.

### 3.1.3 Focus of this study

The object of this chapter was to synthesize low valent mononuclear manganese carbene complexes. After some modification these complexes could serve as precursors with potential catalytic properties. The assembly of the complexes should contain both an X-type ligand to support alkyl-binding,

bulky ligands to protect the reaction site, and carbene ligands, which could initiate carbon-carbon coupling and carbonyl insertion reactions.



**6** X = Br, R = thienyl

**7** X = I, R = H

**Figure 3.3** Mononuclear manganese carbene complexes

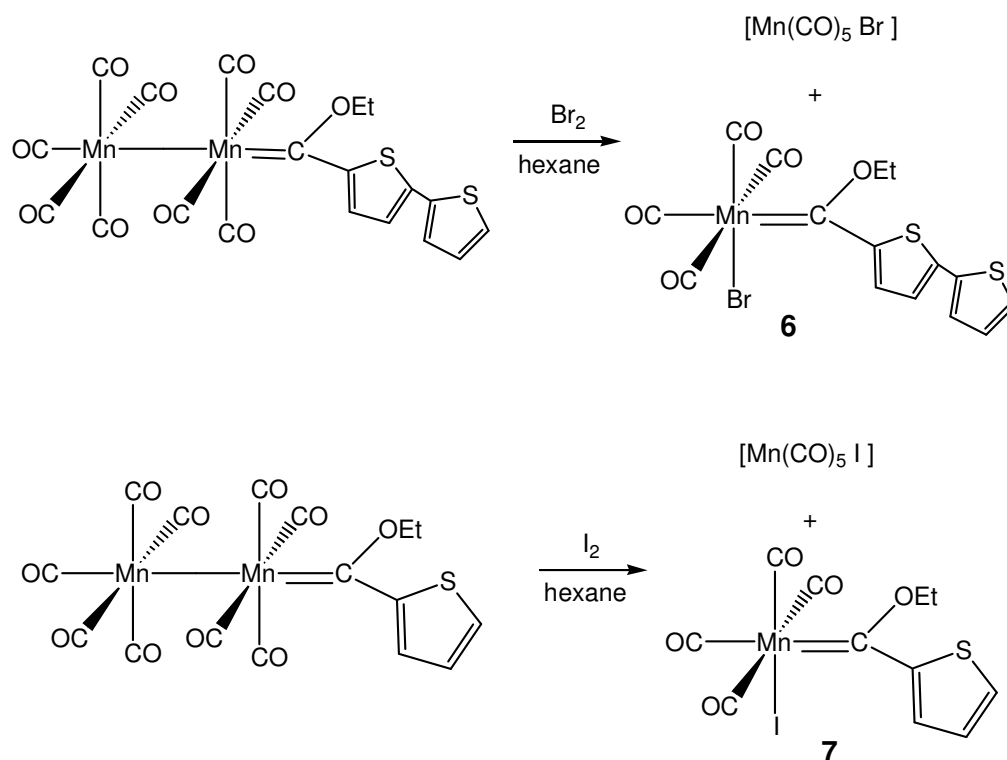
The synthesis of these complexes was afforded by the oxidative metal-metal bond cleavage by halogens of the binuclear monocarbene precursor complexes synthesized in Chapter 2.

## 3.2 Synthesis

The bimetallic carbene complex is dissolved in a small volume hexane and a stoichiometric amount of halogen, also dissolved in a minimum volume of hexane, was added dropwise under vigorous stirring. A red-orange precipitate immediately started forming and stirring was continued until the solution became clear. The solvent and unreacted halogen were removed under reduced pressure and the products were purified by column chromatography on silica gel for **6** and aluminium oxide for **7**.

The reaction of the bithiophene monocarbene complex and bromine did not proceed smoothly and only 21% of complex **6** (dark red) and 41% of  $[\text{Mn}(\text{CO})_5\text{Br}]$  could be isolated. By changing the solvent to  $\text{CS}_2$ , a solvent generally used to cleave  $[\text{Mn}_2(\text{CO})_{10}]$ <sup>[28]</sup>, only reactions leading to the

decomposition of the complex and elimination of the carbene ligand with the formation of  $\text{Mn}_2(\text{CO})_{10}$  were observed. Replacing the bromine with iodine and using the minimum amount of hexane as solvent, gave 43% of complex **7** (red) after purification.

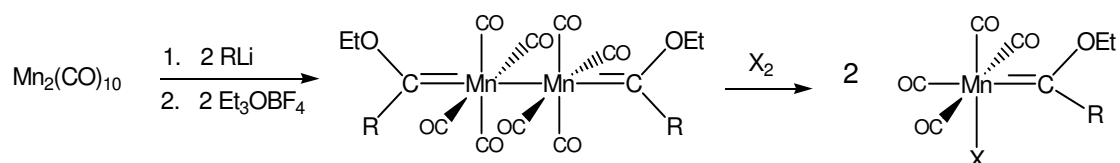


**Scheme 3.3** Synthesis of **6** and **7**

Substitution kinetics of carbonyl ligands in  $[\text{Mn}(\text{CO})_5\text{halides}]$  revealed that rates increased with decreasing atomic number for the halides<sup>[36]</sup>. Based on this result it can be concluded that the bromo-carbene complex of manganese is less stable in the reaction medium compared to the analogous iodo-carbene complex of manganese.

During the synthesis of the  $[\text{Mn}(\text{CO})_4(\text{carbene})\text{X}]$  complexes, 50% of the transition metal manganese is lost as  $[\text{Mn}(\text{CO})_5\text{X}]$ . In an effort to increase the yields of the desired mononuclear manganese carbene complexes with halide ligands, the synthesis of binuclear biscarbenes were attempted as illustrated in Scheme 3.4. If synthesis of biscarbene complexes proved possible, then subsequent cleaving of the Mn-Mn bond would double yields of the halo-

carbene complex. The synthesis of biscarbene was attempted by addition of two equivalents of lithiated heteroarene in a one-pot Fischer reaction, as well as the stepwise addition of two equivalents of lithiated reagent as described by Brandsma<sup>[37]</sup>. However, it was not possible to isolate biscarbene complexes prepared by either method.



**Scheme 3.4** Proposed synthesis of biscarbene complexes

### 3.3 Characterisation

Compositions of products were established by spectroscopic methods and mass spectrometry and final confirmation of the structures came from a single crystal X-ray diffraction study of **7**.

#### 3.3.1 NMR Spectroscopy

The NMR spectra of complex **6** were recorded in  $\text{CDCl}_3$ , but better resolution was achieved by recording the spectra of **7** in deuterated acetone. The same system of numbering of the carbon atoms and protons of the heteroarene substituents used in Chapter 2 was applied.

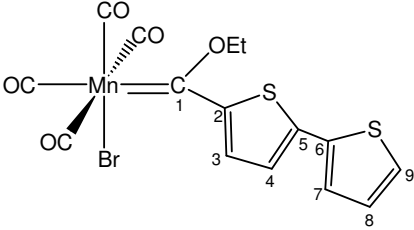
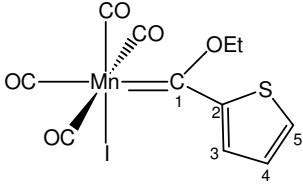
##### 3.3.1.1 $^1\text{H}$ NMR Spectroscopy

The  $^1\text{H}$  NMR data of **6** and **7** are summarized in Table 3.1. When comparing chemical shift values of **6** and **7** with that of **1** and **2** in Chapter 2, a downfield



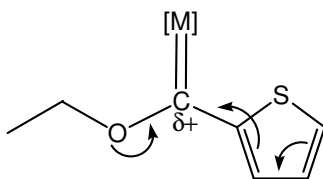
shift of  $\Delta\delta > 0.2$  ppm is observed for the methylene protons, and the ring protons show a downfield shift varying between  $\Delta\delta = 0.1 - 0.3$  ppm. This can be ascribed to the change of oxidation state of the manganese metal centre: the oxidative cleavage causes the binuclear Mn(0) carbene complexes to be oxidized to the monocuclear Mn(I) carbene complexes containing a halide ligand. The manganese atom therefore has less electron density for back donation to the electrophilic carbene carbon. The electrophilic carbene carbon then has to be stabilized by even more electron donation from the ethoxy and heteroarene substituents, as illustrated in Figure 3.4.

**Table 3.1**  $^1\text{H}$  NMR data of complexes **6** and **7**

Assignment	Complexes			
	Chemical shifts ( $\delta$ , ppm) and coupling constants ( $J$ , Hz)			
	 <b>6</b>		 <b>7</b>	
Proton	$\delta^a$	$J$	$\delta^b$	$J$
H3	8.53	n.o.	8.74 (dd)	4.1, 1.1
H4	7.72	n.o.	7.49 (dd)	4.9, 4.1
H5	-	-	8.29 (dd)	4.9, 1.1
H7	7.80	n.o.	-	-
H8	7.49	n.o.	-	-
H9	7.90	n.o.	-	-
-OCH <sub>2</sub> CH <sub>3</sub>	5.53 (q)	7.0	5.67 (q)	7.0
-OCH <sub>2</sub> CH <sub>3</sub>	2.02 (t)	7.0	1.72 (t)	7.0

a) Spectrum recorded in CDCl<sub>3</sub>

b) Spectrum recorded in acetone-d<sub>6</sub>



**Figure 3.4** Electron donation by carbene substituents

### 3.3.1.2 $^{13}\text{C}$ NMR Spectroscopy

The  $^{13}\text{C}$  NMR data of **6** and **7** are reported in Table 3.2. In the spectrum of **6** recorded in  $\text{CDCl}_3$ , the signals of the carbene carbon and the carbonyl ligands were not observed. An improved spectrum was obtained for **7** in acetone- $d_6$ . In contrast with the data obtained for  $^1\text{H}$  NMR, no consistent downfield shift of the signals was observed in the  $^{13}\text{C}$  NMR spectra.

**Table 3.2**  $^{13}\text{C}$  NMR data of complexes **6** and **7**

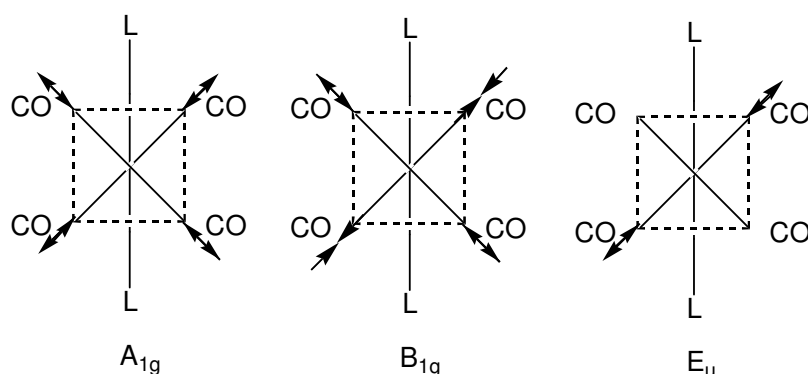
Assignment	Complexes	
	<b>6</b>	<b>7</b>
Carbon	$\delta^a$ (ppm)	$\delta^b$ (ppm)
C1	n.o.	296.4
C2	162.3	144.9
C3	134.4	138.0
C4	124.4	129.4
C5	134.6	143.6
C6	133.5	-
C7	127.3	-
C8	131.3	-
C9	125.6	-
CO (trans)	n.o.	217.6
CO ( <i>cis</i> )	n.o.	211.9
-OCH <sub>2</sub> CH <sub>3</sub>	76.2	79.6
-OCH <sub>2</sub> CH <sub>3</sub>	14.7	14.9

a) Spectrum recorded in  $\text{CDCl}_3$

b) Spectrum recorded in acetone- $d_6$

### 3.3.2 Infrared Spectroscopy

For an octahedral  $[M(\text{CO})_4\text{L}_2]$  complex, the two non-carbonyl ligands, L, can either be *cis* or *trans* substituted. To distinguish between these two possibilities, the infrared spectrum of the carbonyl stretching region can be inspected. For a *trans*- $[M(\text{CO})_4\text{L}_2]$  complex, a single intense band can be observed, which is assigned to the IR-active  $E_u$ -mode<sup>[38]</sup>. In some cases, much weaker high-frequency satellites have been observed which could be assigned to the Raman-active  $A_{1g}$  and  $B_{1g}$  modes (Figure 3.5). The order of the frequencies for this symmetry must be  $A_{1g} > B_{1g} > E_u$ .

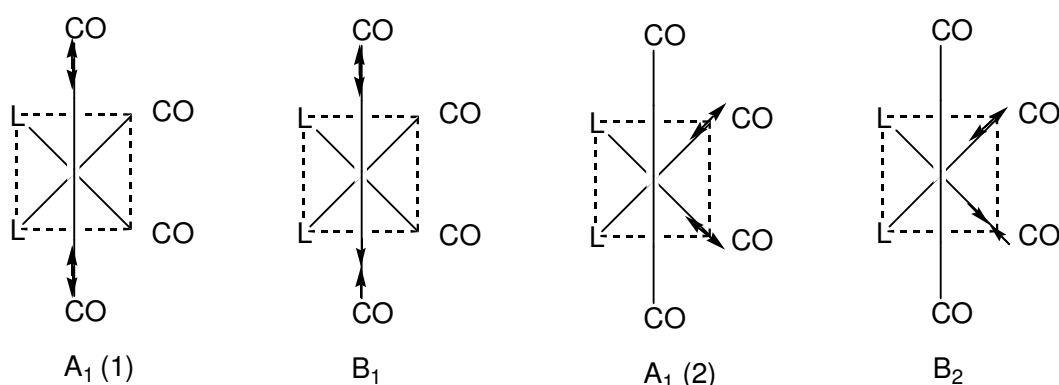


**Figure 3.5** IR- and Raman -active modes observed for *trans*- $[M(\text{CO})_4\text{L}_2]$

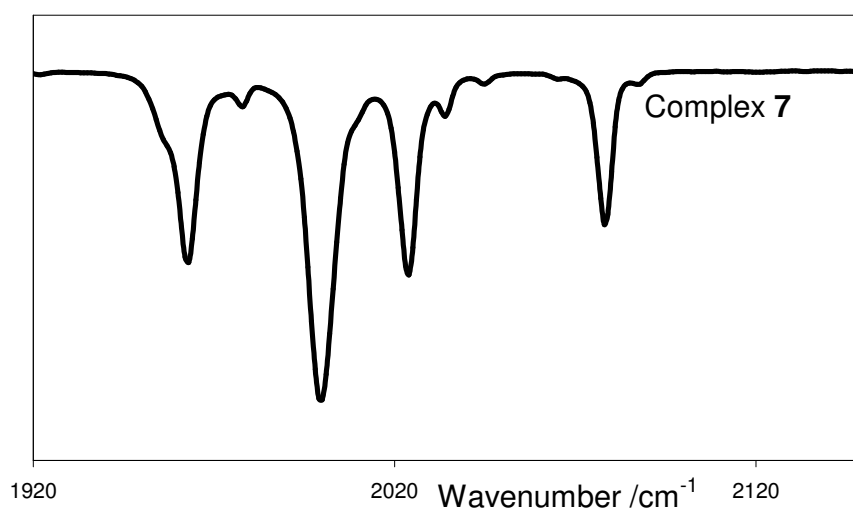
On the other hand, there are four IR-active normal modes (Figure 3.6) for the *cis*-substituted  $[M(\text{CO})_4\text{L}_2]$  complexes, with the following order:  $A_1(1) > A_1(2) > B_1 > B_2$ <sup>[38]</sup>. The characteristic  $\nu(\text{CO})$  pattern is a sharp  $A_1(1)$  mode of medium intensity followed by the intense  $A_1(2)$  band, and then the  $B_1$  and  $B_2$  bands.

When the infrared spectra of **6** and **7** were recorded in hexane, four bands were seen in the carbonyl region, as seen in Figure 3.7. The infrared data is summarized and the assignments of the observed bands are given in Table 3.4. It was therefore concluded that the cleaved product is *cis*-substituted, even although the binuclear precursor was axially substituted. When comparing these manganese complexes with their rhenium analogues recently synthesized in our laboratories<sup>[29]</sup>, it is clear that the cleaved product

is always *cis*-[M(CO)<sub>4</sub>(carbene)X], regardless of whether or not the starting material was the equatorially coordinated dirhenium monocarbene or the axially coordinated dimanganese monocarbene. This information would suggest a dissociative reaction mechanism, although no further studies were done in this project on the reaction mechanism of the cleaving of the binuclear monocarbene complexes with halogens.



**Figure 3.6** IR-active normal modes for *cis*-[M(CO)<sub>4</sub>L<sub>2</sub>]



**Figure 3.7** Infrared spectrum of 7 in the carbonyl region

**Table 3.3** IR-data in the carbonyl region of complex **6** and **7**<sup>a</sup>

Complex	Carbonyl stretching frequencies ( $\nu_{\text{CO}}$ , $\text{cm}^{-1}$ ) for <i>cis</i> -[Mn(CO) <sub>4</sub> (carbene)(halogen)]			
	A <sub>1</sub> (1)	A <sub>1</sub> (2)	B <sub>1</sub>	B <sub>2</sub>
<b>6</b>	2089 (m)	2009 (m)	1996 (vs)	1975 (m)
<b>7</b>	2090 (m)	2010 (m)	1996 (vs)	1975 (m)

a) Spectra recorded in hexane

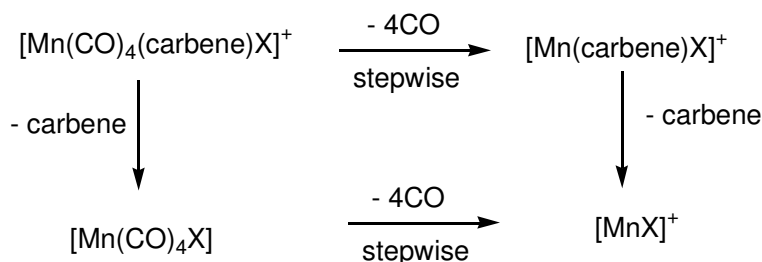
### 3.3.3 Mass Spectrometry

A molecular ion peak,  $M^+$ , was observed in the mass spectra for complexes **6** and **7**, and in contrast to the mass spectral data observed for complexes **1** - **5** in Chapter 2, a more consistent fragmentation pattern was observed. The identified fragment ions are summarized in Table 3.4.

**Table 3.4** Mass spectral data of cleaved monocarbene halide complexes

Complex	m/z	Intensity (%)	Fragment ion
<b>6</b>	469	2	$[M]^+$
	441	9	$[M - \text{CO}]^+$
	385	15	$[M - 3\text{CO}]^+$
	357	4	$[M - 4\text{CO}]^+$
	247	11	$[M - (\text{carbene})]^+$
<b>7</b>	434	36	$[M]^+$
	350	4	$[M - 3\text{CO}]^+$
	322	21	$[M - 4\text{CO}]^+$
	294	7	$[M - (\text{carbene})]^+$
	138	69	$[M - \text{CO} - (\text{carbene}) - \text{I}]^+$

The fragmentation pattern deduced from the fragment ions observed (and tabulated in Table 3.4) indicates that two routes exist (Scheme 3.4). In the first, the carbonyl ligands were lost sequentially, followed by the loss of the carbene ligand and then the halide ligand. In the second unexpected route, the carbene ligand is fragmented before stepwise loss of carbonyl ligands.

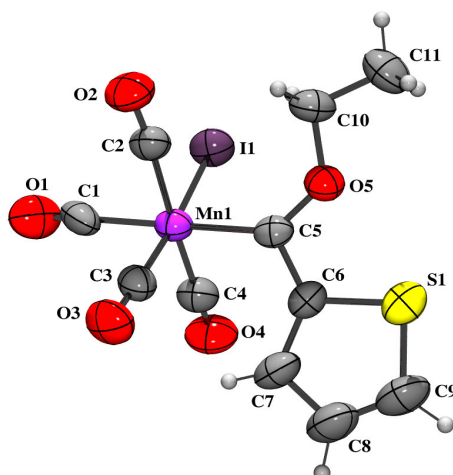


**Scheme 3.4** Fragmentation routes for  $[\text{Mn}(\text{CO})_4(\text{carbene})\text{X}]^+$

### 3.3.4 X-Ray Crystallography

No suitable crystals could be obtained for complex **6**, but solvent layering of hexane:dichloromethane (3:1) yielded dark-red crystals of good quality for complex **7**, and final confirmation of the molecular structure of this complex was obtained using X-ray crystallography. Figure 3.8 represents the ORTEP<sup>[39]</sup> + POV-Ray<sup>[40]</sup> plot of the geometry of **7**, while Table 3.5 gives a summation of the most important bond lengths, angles and torsion angles. The complete set of crystallographic information of **7** is given in Appendix 4.

Complex **7** crystallized in the tetragonal system, space group  $I4_1/a$  with sixteen molecules in the unit cell. The coordination of the manganese atom is octahedral and a *cis*-arrangement of non-carbonyl ligands, already deduced from the infrared spectrum of the molecule, was confirmed.



**Figure 3.8** ORTEP + POV-Ray plot of the geometry of complex **7** with atom numbering

The dihedral angle between the least-squares planes through (S(1), C(6), C(7), C(8) and C(9)) and through (C(5), C(6), O(5) and Mn(1)) is  $8.0(6)^\circ$ . The plane of the carbene carbon, thienyl ring and oxygen atom is again approximately perpendicular to the equatorial plane of the *cis* carbonyl; this is demonstrated by the angles (C(5)-Mn(1)-C(carbonyl))  $90 - 93^\circ$ , C(5)-Mn(1)-I(1)  $95.4(3)^\circ$  and is positioned approximately intermediately between the equatorial ligands around Mn(1), as is evident from the torsion angles of  $-38.9(7)^\circ$  and  $51.4(7)^\circ$  for C(2)-Mn(1)-C(5)-O(5) and I(1)-Mn(1)-C(5)-O(5), respectively (Table 3.5).

The same disorder of the ethoxy-thien-2-yl-methylidene ligand as that described for **2** (Chapter 2) was also observed in **7**. Figure 3.8 shows the major orientation ( $85.9(5)\%$ ).

The carbene ligand is again in the *trans*-configuration about the C-O bond (C(6)-C(5)-O(5)-C(10)  $-173.8(6)^\circ$ ) - as expected when the thienyl ring is close to being coplanar with the plane of the bonding geometry about the carbene carbon as this prevents a *cis*-configuration being adopted. The metal carbon bond distance *trans* to the iodide ligand is significantly shorter than the Mn-CO

distances opposite carbonyl ligands, reflecting the poor  $\pi$ -acceptor properties of an iodide ligand. The Mn-carbon distances observed for the carbene and the carbonyl ligand *trans* to the carbene are almost the same corresponding to a very long metal-carbonyl bond distance.

The bond angles of the thienyl ring (Table 3.5) are distorted even more severely than that of **2** compared to the bond angles of free thiophene<sup>[41]</sup>, indicating an even greater ring involvement in stabilizing the carbene carbon atom of the oxidized manganese carbene complex than was exhibited by **2** (Chapter 2).

**Table 3.5** Selected bond lengths, bond angles and torsion angles of **7**

Atoms	Bond Lengths (Å)	Atoms	Bond Angles (°)
Mn(1)-C(1)	1.949(10)	Mn(1)-C(5)-O(5)	132.8(6)
Mean Mn(1)-C(x) (x=2,4)	1.857(6)	O(5)-C(5)-C(6)	105.2(6)
Mn(1)-C(5)	1.986(8)	C(6)-C(5)-Mn(1)	122.0(6)
C(5)-O(5)	1.318(8)	S(1)-C(6)-C(7)	130.7(7)
C(5)-C(6)	1.437(9)	C(6)-S(1)-C(9)	92.5(5)
C(6)-C(7)	1.411(10)	C(7)-C(8)-C(9)	116.0(9)
C(7)-C(8)	1.414(13)	Atoms	Torsion Angles (°)
C(8)-C(9)	1.364(15)		
Mn(1)-C(3)	1.784(6)	I(1)-Mn(1)-C(5)-O(5)	51.4(7)
Mn(1)-I(1)	2.709(1)	C(2)-Mn(1)-C(5)-O(5)	-38.9(7)

A comparison of the structure of **7** with the complex *cis*-[Mn(CO)<sub>4</sub>(COCH<sub>2</sub>CH<sub>2</sub>O)Cl], synthesized by Moss and co-workers<sup>[16]</sup>, can be done. For both these complexes, the manganese atom is in a slightly distorted



octahedral environment (angles at Mn 87 - 93°), although the angle (49°) between the mean plane of the carbene carbon atom and the two oxygen atoms in the ring, and which encompassed Mn(1), C(1), C(5), C(4) and C(2) is distinctly different from the almost planar arrangement found for **7** (8.0(6)°). The Mn-C(carbene) bond lengths are very similar (1.986(8)Å for **7** and 1.96Å for the chloro-carbene). The arrangement around the central manganese atom is therefore similar in both cases, but the cyclic carbene of the chloro-carbene complex is not co-planar as is found for the carbene ligand of **7** with the ethoxy- and thienyl-substituents.

### 3.4 Conclusions

The oxidative cleavage of the manganese-manganese bond in binuclear monocarbene complexes with halogens, without affecting the carbene ligand, proved successful. The resulting products had manganese metal centres in oxidation state +1, which means that less back bonding from the metal to the electrophilic carbene carbon atom is evident. The change in oxidation state is compensated for by the electron donation of the ethoxy and heteroarene substituents on the carbene ligand, as seen by the downfield shift of these protons in the <sup>1</sup>H NMR spectra and the distortion of the thienyl ring in the crystal structure obtained for **7**. The cleaved products exhibit a *cis*-configuration, even although the binuclear carbene precursors were axially substituted.

Future work would include investigating the modification of the carbene by replacing the alkoxy substituent. This would transform the Fischer carbene complexes to Schrock carbenes. A possible route to achieve this is by reacting the carbene ligand with a Lewis acid such as a BX<sub>3</sub> reagent to form a carbyne with elimination of the ethoxy group, followed by an attack of a hydride to insert a hydrogen as substituent on the carbene ligand<sup>[42]</sup>. Schrock carbene complexes show higher reactivity as catalysts towards carbon-carbon coupling reactions.

### 3.5 References

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