Chapter 4: Structural features of rhenium carbene complexes

4.1 Introduction

Because neutral monorhenium carbonyl complexes require one X–type ligand, which can be a second rhenium carbonyl fragment, many structural variations and conformers are possible in the solid state. In addition, carbene ligands have planar sp^2–carbons with directional properties attached to substituents such as hetero–arenes, which are also planar rings, atoms with lone pairs (oxygen, Fischer carbenes) and low oxidation–state transition metals, all contributing to various structural features. It is important to remember for the discussion of the crystal structures that the carbene carbon is sp^2 hybridized and that a plane is defined by the carbene carbon and the three atoms that are bound to the carbene carbon atom, i.e. Re, O and C(thienyl). This plane will be referred to as the carbene plane.

General structural features of such complexes that are important, and may vary, are listed below. These include the following positions and orientations affected by the carbene ligand.

1. Positions of ligands coordinated to rhenium
    a. The carbene ligand is expected to be *cis* (in an equatorial position) to the X–type ligand[1].
    b. Equatorial carbonyl ligands on two rhenium atoms in Re(CO)$_5$–Re(CO)$_4$–L are expected to be staggered viewed along the metal–metal bond.
2. The rhenium–carbene bond normally displays double bond character and is expected to be shorter than a rhenium–carbon single bond.
3. Orientation of carbene substituents
    a. The heteroarene substituent is expected to have the sulfur atom orientated towards the ethoxy side of the carbene[2].

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[1] (a) E. O. Fischer, E. Offhaus, J. Müller, D Nöthe; *Chem. Ber.*, **1972**, *105*, 3027–3035; (b) E. W. Post, K. L. Watters; *Inorg. Chim. Acta*, **1978**, *26*, 29–36

   b. Position of the ethyl of the ethoxy substituent with respect to the other metal ligands[3].

4. Conjugation between the two planar rings of bithiophene complexes should make them coplanar, but the relative positions of the heteroatoms may differ.

The structures of carbene complexes were determined by X–ray diffraction studies of single crystals and support conclusions drawn from spectroscopic data. The structures consist of monorhenium and dirhenium monocarbene complexes and tetrarhenium biscarbene complexes. The final structure to be discussed displays ligands that are intermediate between carbene and acyl ligands.

4.2 Dirhenium monocarbene complexes

4.2.1 Complex 1

The structure consists of two Re–fragments, {Re(CO)$_5$} and {Re(CO)$_4$(carbene)} held together by a metal–metal bond. Both metals have an octahedral ligand environment and Re(CO)$_5$ is seen as the X–type ligand. The structure confirms that the carbene is an equatorial ligand in the structure. The other ligands of the metals are carbonyl ligands and they are in the staggered conformation with respect to each other, viewed along the metal–metal bond. The carbene carbon has three substituents, an aromatic 5–membered ring (thienyl), a dirhenium carbonyl unit and the OCH$_2$CH$_3$ group. In Figure 4.1 the structure is shown and selected bond lengths and angles are given in Tables 4.1a and 4.1b.

The carbene environment, i.e. the carbene carbon–to–substituent bond lengths and the bond angles around the carbene carbon will be compared and discussed at the end of this chapter.

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[2] D. C. Liles, S. Lotz; *Acta Cryst.*, **2006**, *E62*, m331–m334

[3] D. M. Andrada, M. E. Zoloff Michoff, I. Fernndez, A. M. Granados, M. A. Sierra; *Organometallics*, **2007**, *26*, 5854–5858

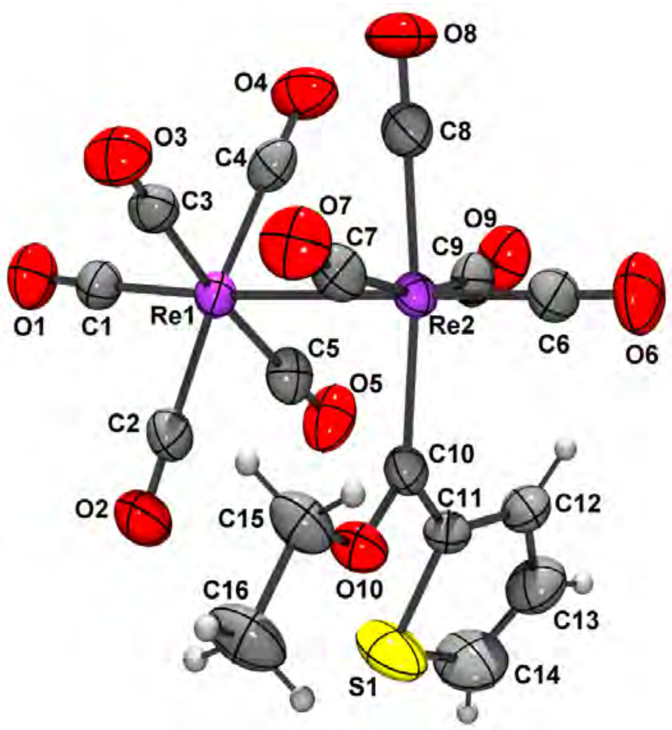

Figure 4.1: Molecular structure of **1**

The ethoxy carbene–substituent is orientated to the sulfur side of the thiophene and the dirhenium fragment to the other side of the thiophene ring. It is anticipated that the metalate intermediate (formed after nucleophilic attack on the carbonyl carbon atom) may be conformation–locked because of a five–membered ring that forms (shown in Figure 4.2). Then after alkylation, carbene–stabilization from the thienyl ring by π–conjugation and steric bulkiness (lack of rotation) around the carbene carbon atom may restrict rotation and lock the carbene substituents in these positions.

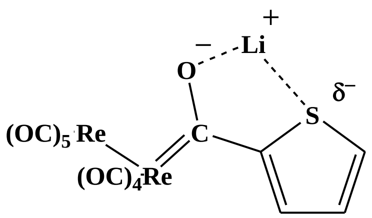

Figure 4.2: A five–membered intermediate complex ring

Table 4.1a: Selected bond lengths of **1** (Å)

Carbene bond lengths			
C10–Re2	2.125 (5)	C10–C11	1.461 (7)
C10–O10	1.335 (6)		
Thienyl bond lengths			
C11–C12	1.400 (8)	C11–S	1.723 (5)
C12–C13	1.403 (8)	C14–S1	1.695 (8)
C13–C14	1.326 (11)		
Re–CO bond lengths			
Re–CO$_{avg}$ of Re(CO)$_5$ *eq*–CO ligands	1.988 (6)	Re–CO$_{avg}$ of Re(CO)$_4$ *eq*–CO ligands	1.983 (6)
ax–CO of Re(CO)$_5$	1.928 (6)	*ax*–CO of Re(CO)$_4$	1.923 (6)
Re(CO) *trans* carbene	1.982 (6)		
Other bond lengths			
O10–CH$_2$	1.434 (7)	Re1–Re2	3.0899 (3)
CH$_2$–CH$_3$	1.514 (8)		

Bond distances and angles for thiophene were determined by the technique of microwave spectroscopy[4]. The values are S–C$_\alpha$ = 1.714 (1) Å, C$_\alpha$–C$_\beta$ = 1.370 (2) Å and C$_\alpha$–C$_\beta$ = 1.424 (2) Å. The values of the bond distances correspond to mean values for thiophene of 1.712, 1.362 and 1.424 Å[5]. The internal bond angles centred on S, C$_\alpha$ and C$_\beta$ are respectively 92.2 (1), 111.5 (3) and 112.5 (3) °.

As electron density is drawn out of the thienyl ring to stabilize the carbene carbon atom, the closest ring double bond, to the carbene, is expected to be lengthened and become

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[4] R. J. Angelici; *Coord. Chem. Rev.*, **1990**, *105*, 61–76

[5] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor; *J. Chem. Soc. Perkin Trans. 2*, **1987**, S1–S19

more single in bond nature. The examination of C–C bonds of the thienyl ring supports this conclusion. Formally double, bond C11–C12 is the same length as the 'single' bond C12–C13 and both are significantly longer than the shortest C–C bond length C13–C14. C11–C12 is also longer than the thiophene mean C2–C3 bond length of 1.362 Å and also longer than the value of 1.370 (2) Å determined for this bond of thiophene. Resonance delocalization of electron–density from the ring double bonds to the carbene–carbon atom was used to explain the NMR shifts of the ring protons. That reasoning is now supported by structural evidence as well.

The bond between the carbene carbon and the ring carbon atom C10–C11 is longer than C13–C14, which is believed to still have a lot of double bond character. A single carbon–carbon bond in complex **1** is that between the carbon atoms of the ethoxy substituent, and the length of this bond is 1.514 (8) Å. C10–C11 is much shorter than this bond. One should perhaps not draw too much from this data, as the carbon atoms have different hybridizations and are not directly comparable, but it seems clear that there is a degree of double bonding between the carbene carbon and the thienyl ring carbon.

Because the ethoxy oxygen atom is bonded to the sp^2 hybridized carbene carbon atom and to a sp^3 carbon atom of the ethyl group, a comparison of these two bond distances could provide some insight into the degree by which the oxygen atom stabilizes the carbene carbon. Both are single bonds, formally, but the bond between the carbene and the oxygen may contain some double bond character. The mean value for a Csp^2–O bond in an enol ester is 1.354 Å[5]. These values are: C(carbene)–O = 1.335 (6) Å and O–CH_2 = 1.434 (7) Å. The former is indeed significantly shorter than the latter, by 0.1 Å and closer to the mean C–O bond distance of an enol ester. It should be remembered that a sp^2 orbital contains more s character than a sp^3 orbital, which would make for a shorter bond.

The bond lengths between the rhenium atoms and carbonyl ligands in the complex can be compared to the same distances of $[Re_2(CO)_{10}]$[6]. The average value of the rhenium–carbonyl bond distances of the two axial carbonyl ligands, of complex **1**, is 1.926 (6) Å

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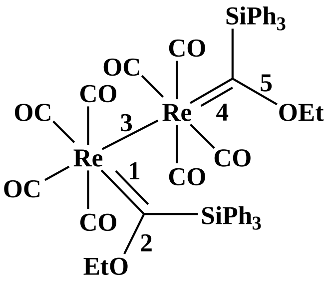
[6] M. R. Churchill, K. N. Amoh, H. J. Wasserman; *Inorg. Chem.*, **1981**, *20*, 1609–1611

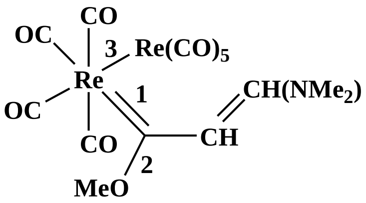
and of [$Re_2(CO)_{10}$] is 1.927 (7) Å, which is the same. The average Re–C distance values for the equatorial carbonyl ligands of the two rhenium fragments are the same within experimental error (for [$Re_2(CO)_{10}$] the average *eq*–CO metal–carbon distance is 1.987 (6) Å). On the {$Re(CO)_4$} fragment, that bears the carbene ligand, there are two carbonyl ligands that are *trans* to non–carbonyl ligands: the axial carbonyl ligand and the carbonyl ligand *trans* to carbene ligand. Their respective metal–carbon bond distances are 1.923 (6) Å and 1.982 (6) Å. The latter is comparable to the other equatorial carbonyl ligand–metal bond distances, but the former is significantly shorter. This is because the CO ligand opposite the Re–Re bond is not *trans* to a π–accepting ligand that competes with the carbonyl for electron–density. The Re–carbene value is slightly longer than the mean value for terminal alkoxycarbenes of 2.098 Å[7].

The Re–Re bond length of 3.0899 (3) Å, of the complex, is significantly longer than the Re–Re bond length of [$Re_2(CO)_{10}$], which is 3.041 (1) Å. Two dirhenium carbene complexes from literature are shown below and it can be seen that the Re–Re distance for **1** falls in the range of a typical complex. The two complexes were reported by Schubert[8] and Szafert[9]. In the dirhenium biscarbene complex with an equatorial and axial carbene ligand, one notes that the axial metal–carbene bond length is shorter than the equatorial one. The Re–carbene bond distance of **1** is even longer than the latter and closer to the value of the Szafert dirhenium monocarbene complex.



Schubert

1 = 2.08 (3)
2 = 1.33 (4)
3 = 3.091 (2)
4 = 1.85 (3)
5 = 1.42 (4)



Szafert

1 = 2.189 (8)
2 = 1.338 (8)
3 = 3.066 (1)

Figure 4.3: Bond distances in (Å) of rhenium carbene complexes

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[7] A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson, R. Taylor; *J. Chem. Soc. Dalton Trans.*, **1989**, S1–S83

[8] U. Schubert, K. Ackermann, P. Rustemeyer; *J. Organomet. Chem.*, **1982**, *232*, 323–334

[9] K. Osowska, K. Mierzwicki, S. Szafert; *Organometallics*, **2006**, *25*, 3544–3547

Table 4.1b: Torsion angles of complex **1** (°)

Carbene plane deviation relative to cis equatorial CO ligands			
C11–C10–Re2–C7	0.2 (5)	O10–C10–Re2–C7	3.2 (5)
C11–C10–Re2–C9	6.5 (5)	O10–C10–Re2–C9	9.5 (5)
Thienyl twist out of the carbene plane			
S1–C11–C10–Re2	28.5 (3)	C12–C11–C10–Re2	27.7 (9)
S1–C11–C10–O10	26.1 (6)	C12–C11–C10–O10	25.3 (6)
Ethoxy twist out of the carbene plane			
C15–O10–C10–Re2	2.4 (8)	C15–O10–C10–C11	0.1 (5)
Ethoxy planarity			
C10–O10–C15–C16	5.8 (5)		

Because the carbene ligand requires more space than a carbonyl ligand and because of the difference in their bonding properties, the two carbonyl ligands C7–O7 and C9–O9 are bent away from the carbene substituents and the octahedral ligand environment around this rhenium is distorted. This bending from linearity is roughly 10 degrees for the two carbonyl ligands.

From torsional twist angles it can be seen that the ethoxy substituent of the carbene ligand and the C7–O7 carbonyl ligand are only slightly twisted away from each other (away from a fully eclipsed conformation). The thienyl carbene substituent is on the C9–O9 carbonyl ligand side and the deviation away from a fully eclipsed conformation is larger.

4.2.2 Complex 3

The structural features of **3** are similar to those of **1**. Complex **3** has a 3,6–dimethylthieno[3,2–*b*]thiophene carbene substituent. The structure confirms that the carbene ligand in this complex is also equatorial and the carbonyl ligands of the two equatorial plains are again staggered (viewed along the metal–metal bond). The structure is shown in Figure 4.4 and selected bond–lengths and angles are given in Tables 4.2a and 4.2b.

All the carbon–sulfur bond lengths of the thiophene rings follow the same pattern. The C–S bond distances closest to the carbene ligand is marginally shorter compared to the distant C–S distance.

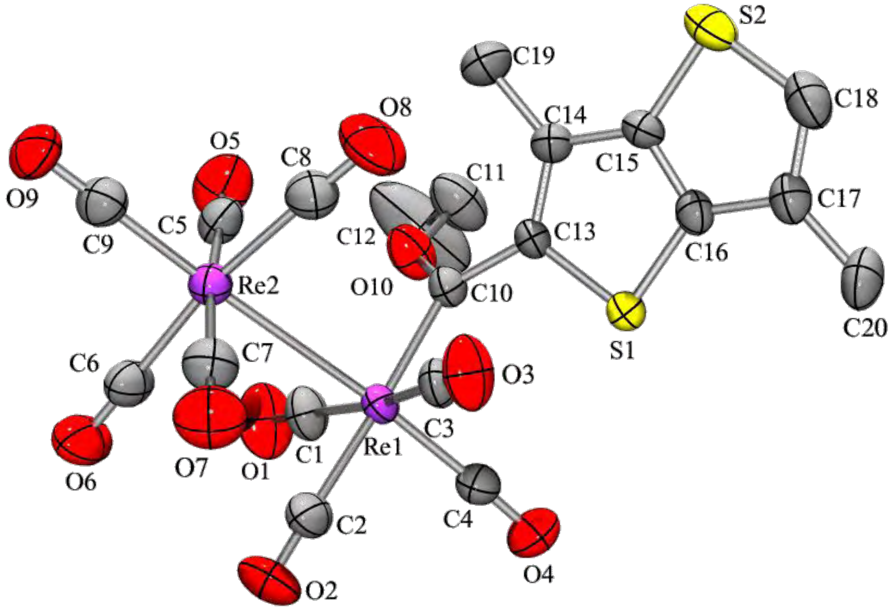


Figure 4.4: Molecular structure of **3**

Within experimental error the three C–C bond distances of the thienyl rings indicated in Figure 4.5 are the same length, with the exception of C17–C18, which is shorter. Double bond delocalization in the rings (which causes the lengthening of the double bonds) is limited because of the twist of the thienyl group with respect to the carbene plane. The torsion angle Re1–C10–C13–C14 is 47°, representing a large deviation of the plane of the thienyl rings and the carbene plane.

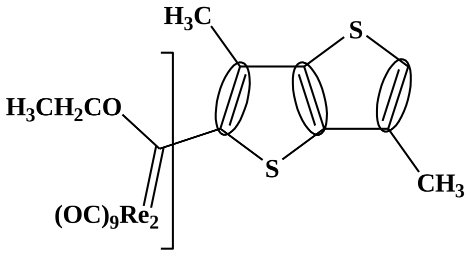


Figure 4.5: Localized longer (single) and shorter (double) bonds

Table 4.2a: Selected bond lengths of **3** (Å)

Carbene bond lengths			
C10–Re1	2.098 (6)	C10–C13	1.466 (8)
C10–O10	1.326 (8)		
Thienyl bond lengths			
C13–C14	1.379 (8)	C17–C20	1.498 (10)
C14–C15	1.396 (8)	C13–S1	1.739 (6)
C14–C19	1.496 (9)	C16–S1	1.721 (5)
C15–C16	1.378 (8)	C15–S2	1.727 (6)
C16–C17	1.411 (8)	C18–S2	1.719 (8)
C17–C18	1.358 (9)		
Other bond lengths			
O10–C11	1.429 (9)	Re1–Re2	3.0468 (4)
C11–C12	1.451 (13)		
Re–CO bond lengths			
Re–CO$_{avg}$ of Re(CO)$_5$ *eq*–CO ligands	1.986 (8)	Re–CO$_{avg}$ of Re(CO)$_4$ *eq*–CO ligands	1.974 (7)
ax–CO of Re(CO)$_5$	1.927 (7)	*ax*–CO of Re(CO)$_4$	1.910 (7)
Re(CO) *trans* carbene	1.993 (7)		

The Re–Re bond distance of this complex is less than the Re–Re bond of complex **1** and this means the carbonyl ligands being closer to one another. It was noticed with complex **1** that the carbonyl ligands are staggered, but not perfectly so (meaning that the torsional angles between two CO ligands next to each other is 45 degrees). Instead, for complex **1** it is measured at 32.9° for two CO ligands and for this complex the same measurement comes to 40.9°.

The average value of the rhenium–carbonyl bond distances of the two axial carbonyl ligands is 1.919 (6) Å and not different from the corresponding distances of $[Re_2(CO)_{10}]$. The average Re–C distances of the equatorial carbonyl ligands of the two rhenium fragments are also the same as the equatorial carbonyl ligands of $[Re_2(CO)_{10}]$. The axial carbonyl ligand–Re bond distances are the shortest of all the metal–carbonyl bond distances.

Table 4.2b: Selected dihedral angles of **3** (°)

Carbene plane deviation relative to equatorial CO ligands			
C13–C10–Re1–C10	20.6 (5)	O10–C10–Re1–C1	20.1 (5)
C13–C10–Re1–C3	10.9 (5)	O10–C10–Re1–C3	11.3 (5)
Thienyl deviation out of the carbene plane			
S1–C13–C10–O10	42.0 (5)	S1–C13–C10–Re1	42.3 (7)
C14–C13–C10–O10	46.5 (10)	C12–C13–C10–Re1	47.0 (6)
Ethoxy twist out of the carbene plane			
C17–O10–C10–Re1	24.0 (6)	C17–O10–C10–C11	24.2 (10)
Ethoxy planarity			
C10–O10–C17–C18	33.9 (11)		

It can be seen that the aromatic substituent is twisted with respect to the carbene plane more than the ethoxy substituent, almost twice as much (C13–C10–Re1–C3 = 10.9°, O10–C10–Re1–C1 = 20.1°). It is interesting to note that the ethoxy and the aromatic carbene substituents (O10–C10–C11–S1) are twisted 47° with respect to each other. A five–membered intermediate, like that shown in Figure 4.4, may have formed. After alkylation, deformation of the whole structure may have occurred, due to restricted rotation around the C10–C13 bond and packing forces.

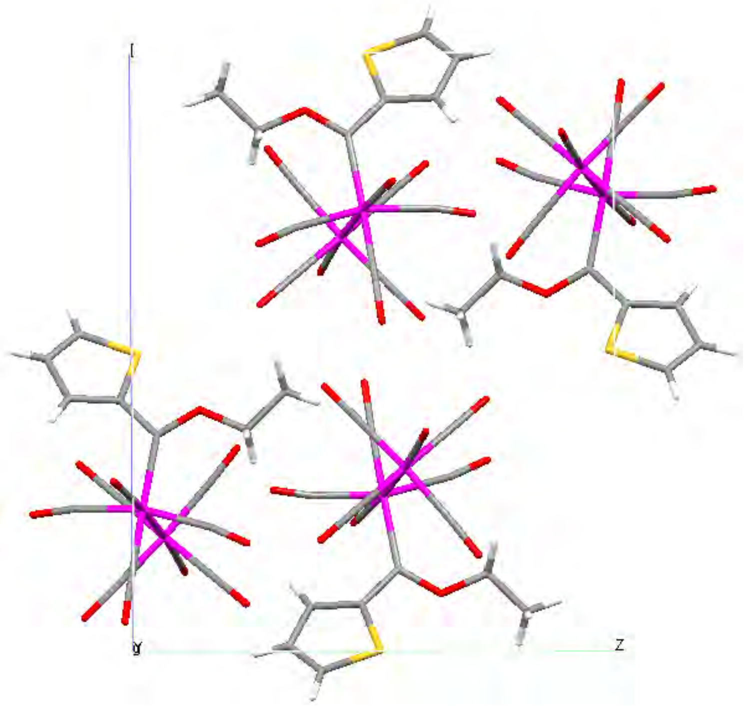
In the thienyl substituent (3,6–dimethylthieno[3,2–*b*]thiophene) of complex **3** the closest ring is defined by carbon atoms C13–C16 and S1. One might compare this ring to the thienyl ring of complex **1**, although it has a methyl at ring position 3 and another ring fused to it. The following bond length and internal angle data provides for a comparison between the two thiophene rings of complexes **1** and **3** (ring carbon atoms are numbered as 2 (attached to carbene carbon), 3, 4 and 5):

Table 4.3: Thienyl ring comparisons between complexes **1** and **3**

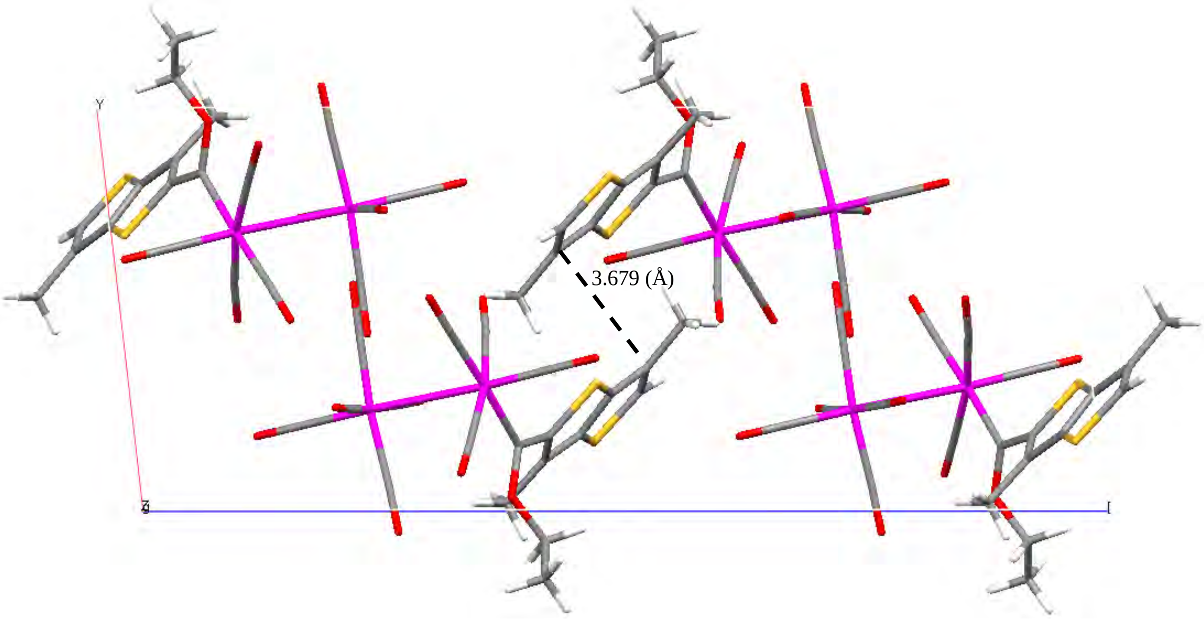
Complexes	**1**	**3**
Bonds distances (Å)		
C2–C3	1.400 (8)	1.379 (8)
C3–C4	1.403 (8)	1.396 (8)
C4–C5	1.326 (11)	1.378 (8)
C2–S	1.723 (5)	1.739 (6)
C5–S	1.695 (8)	1.721 (5)
Ring internal angles (angles centered on named atoms) (°)		
C2	110.2 (4)	112.7 (4)
C3	111.9 (6)	110.1 (5)
C4	113.0 (6)	115.8 (5)
C5	113.6 (5)	110.1 (4)
S	91.3 (3)	91.2 (3)

A comparison of the internal angles of the thiophene substituent of complex **1** show that the angles centered on C2 and C5 do have a significant difference from the values determined for thiophene by microwave spectroscopy. Even though they are in most cases not significantly different, taken into account the experimental errors of the measurements, the ring C–C bonds in **3** are marginally shorter than the corresponding distances in **1**. There are also small differences in corresponding angles between the two thiophene rings of the substituents of complex **3** and the differences are assumed to have little significance.

An examination of the packing of these two complexes (Figure 4.6) does not indicate that hydrogen–bonding plays a role in determining the packing. With complex **1**, the thiophene substituents are placed far apart. The positioning of the individual molecules in **3** suggests possible *π*–interaction, with a distance of 3.7 Å between closest ring carbon atoms of two 3,6–dimethylthieno[3,2–*b*]thiophene substituents.



Complex **1**



Complex **3**

Figure 4.6: Crystal packing for **1** and **3**

4.3 Tetrarhenium biscarbene complexes

4.3.1 Complex 7

The molecule consists of two Fischer carbene ligands attached at both ends of a linking thiophene bridge. The carbene ligands then both have {OCH_2CH_3} and {$Re_2(CO)_9$} fragments bonded to them. The complex structure is shown in Figure 4.7.

The metal fragments are directed away from the sulfur atom of the thiophene ring and the ethoxy carbene substituents are on the same side of the sulfur atom of the aromatic ring. The equatorial carbonyls of the two metal fragments are again staggered and both carbene ligands are found in equatorial positions. Selected bond distance and bond angle data are given in Table 4.4a and 4.4b.

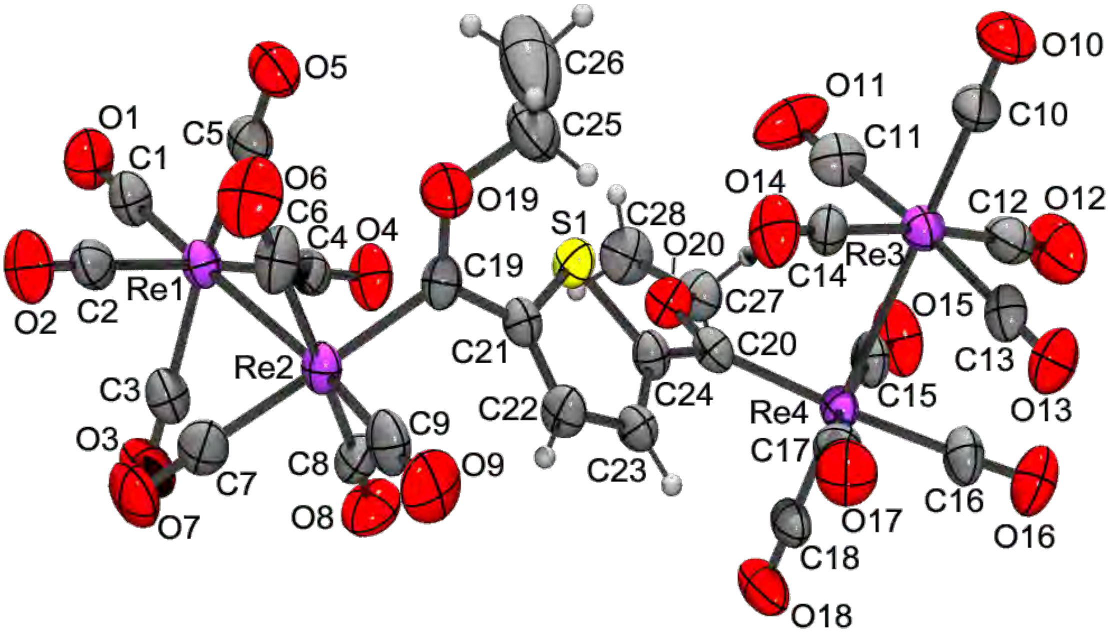


Figure 4.7: Molecular structure of **7**

The first impression when looking at the image of the molecule is that the carbene substituents of this complex are sterically constrained. In the planar thiophene biscarbene arrangement the ethoxy groups in the complex can interfere with each other across the ring, and as a result the one lies above and one below the plane of the thiophene ring (Figure 4.8).

The molecule seems to be twisted “out of shape”. The two sides are non–equivalent in terms of angles and bond distances. The Re–Re bonds of the two fragments are not the same length, evidence of the inner strain present in the molecule. The shorter one is comparable to the Re–Re bond of **3**.

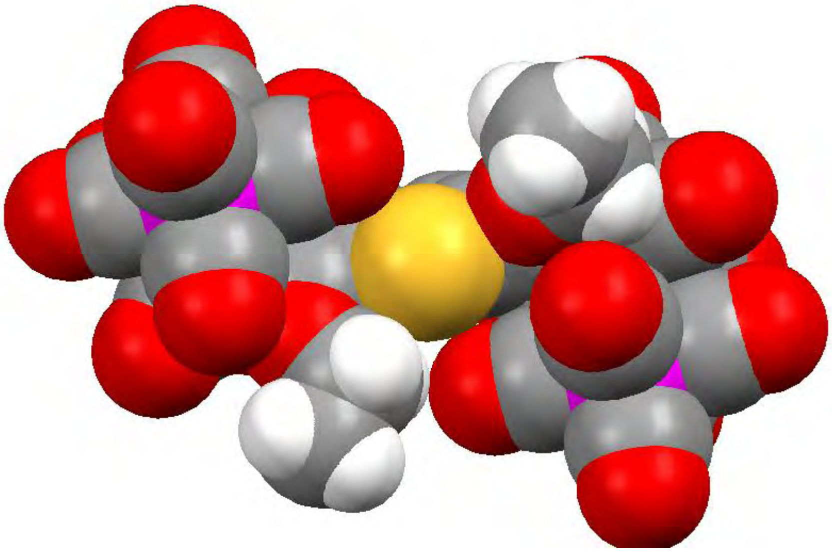


Figure 4.8: Ethoxy groups are orientated to the opposite sides of the thiophene ring (central)

If one were to draw lines along the Re–Re bonds, the two lines would, by rough estimation, be perpendicular to each other, which are shown in Figure 4.9. In fact – the torsional angle between them is 95°. The image also shows that the CO ligands of the two metals are in the staggered conformation, when viewed along the metal–metal bonds. The second carbene ethoxy substituent is almost co–planar to the Re–Re bond of the first carbene ligand and *vice versa*. The dihedral angle between the two ethoxy groups is 78° (O–C1–C1′–O).

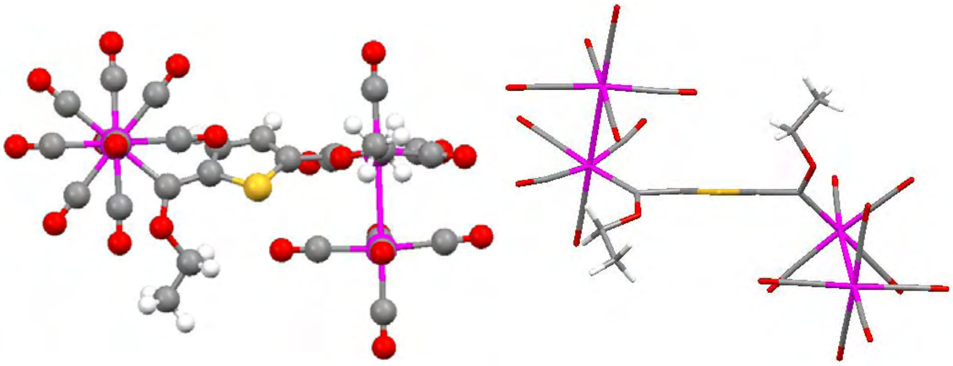


Figure 4.9: Lines along Re–Re bonds are perpendicular

Table 4.4a: Selected bond lengths of **7** (Å)

Carbene bond lengths			
C19–Re2	2.093 (10)	C20–Re4	2.076 (10)
C19–O19	1.303 (13)	C20–O20	1.338 (12)
C19–C21	1.476 (14)	C20–C24	1.480 (12)
Thienyl bond lengths			
C21–C22	1.363 (14)	C23–C24	1.347 (13)
C22–C23	1.421 (14)		
Ethoxy bond lengths			
O19–C25	1.465 (15)	O20–C27	1.438 (13)
C25–C26	1.39 (2)	C27–C28	1.511 (17)
Re–Re bond lengths			
Re1–Re2	3.0434 (6)	Re3–Re4	3.0569 (7)
Re–CO bond lengths (Re1, Re2)			
Re–CO$_{avg}$ of *eq*–Re(CO)$_5$	1.989 (12)	Re–CO$_{avg}$ (Re(CO)$_4$ *trans*–CO carbonyls)	1.994 (12)
ax–CO of Re(CO)$_5$	1.934 (11)	*ax*–CO of Re(CO)$_4$	1.907 (13)
Re(CO) *trans* carbene	1.984 (12)		
Re–CO bond lengths (Re3, Re4)			
Re–CO$_{avg}$ of *eq*–Re(CO)$_5$	1.988 (14)	Re–CO$_{avg}$ (Re(CO)$_4$ *trans*–CO carbonyls)	1.983 (12)
ax–CO of Re(CO)$_5$	1.952 (11)	*ax*–CO of Re(CO)$_4$	1.942 (11)
Re(CO) *trans* to carbene	1.993 (12)		

Table 4.4b: Bond and torsion angles for complex **7** (°)

Carbene ligand angle to *cis* carbonyl ligands			
C19–Re2–C6	88.5 (4)	C20–Re4–C17	92.9 (4)
C19–Re2–C8	90.2 (4)	C20–Re4–C15	97.2 (4)
Deviation relative to equatorial CO ligands because of carbene ligand			
O19–C19–Re2–C6	9.7 (8)	O20–C20–Re4–C15	5.1 (9)
O19–C19–Re2–C8	17.7 (8)	O20–C20–Re4–C17	5.2 (9)
C21–C19–Re2–C6	13.6 (8)	C24–C20–Re4–C15	4.6 (8)
C21–C19–Re2–C8	21.6 (8)	C24–C20–Re4–C17	5.7 (8)
Thienyl twist out of the carbene plane			
S1–C21–C19–Re2	46.3 (7)	S1–C24–C20–Re4	30.2 (5)
S1–C21–C19–O19	50.2 (13)	S1–C24–C20–O20	30.7 (10)
C22–C21–C19–Re2	44.2 (14)	C23–C24–C20–Re4	36.7 (14)
C22–C21–C19–O19	48.0 (11)	C23–C24–C20–O20	37.1 (11)
Ethoxy substituent twist out of the carbene plane			
C19–O19–C25–C26	33.1 (17)	C20–O20–C27–C28	10.4 (9)

The carbene ligand with its substituents causes a large deviation of the two *cis* equatorial carbonyl ligands from linearity. This applies to both of the carbenes. The two *cis* carbonyl ligands are again bent away from the carbene ligand (except for C6–O6, which is slightly bent towards the carbene ligand), as was the case for **1** and **3**. This deviation is given in Table 4.4b.

The ethoxy groups of the carbene ligands are oppositely orientated relative to their metals. Notably the oxygen–lone pairs of one are towards the ring and of the other towards the metals. Sierra[3] reported a favoured positioning of the oxygen lone pairs away from the metal carbonyl fragment in monocarbene complexes to minimize interaction of the lone pairs with the “carbonyl wall”. The ethoxy group C19–O19–C25–C26 has the lone–pair towards the metal substituent and is bent by 33° out of the carbene plane, while the other one (C20–O20–C27–C28) has the lone–pairs away from the metal and is only bent by 10 degrees out of the carbene plane.

If one assumes the alkylation is a stepwise process, one could start by alkylating the first oxygen according to the Sierra favoured position with the lone–pairs in a position away from the metal. The presence of a second metal with carbonyls, in close proximity, could change the alkylation site of the second alkylation. This seems to be the case as the other ethyl group is orientated with the lone–pairs towards the second metal fragment. Arguably the intermediate pre–alkylation complex (Figure 4.10) was more planar than the final complex. This argument relies on the assumption that the largest steric hindrance in the molecule comes from the two ethoxy carbene substituents that can interfere with each other across the thiophene ring. The first alkylation then proceeded in such a way that the Et^+ attached from the thiophene side so that it points 'towards' the metals (the oxygen lone pairs are over the ring), as is observed in the conformation of the monocarbene complex **1**. This is then ethoxy group C20–O20–C27–C28, which also happens to be more planar than ethoxy group C19–O19–C25–C26, which is perceived to have been alkylated afterwards.

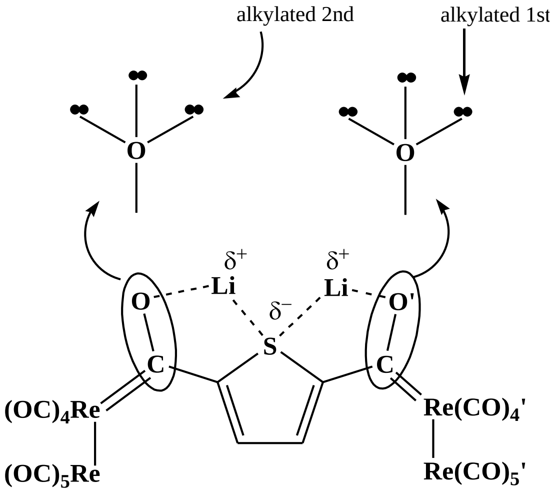


Figure 4.10: Visualization of intermediate state of **7**

A comparison of the bond lengths and internal angles of the thienyl ring of **7** with those of complex **1** provides insight (Table 4.5). Unfortunately the larger experimental error of structure **7** limits the potential for meaningful comparison. Based on the values, with experimental error taken into account, one cannot say that the two thiophene rings of the two complexes are different in terms of bond lengths. The differences in inner bond angles between the rings of the two complexes are also small. It is interesting to note that the thiophene ring with two carbenes attached (**7**) is more symmetrical than the thiophene ring of **1**. The carbene carbon atoms of complex **7** are linked by a π–conjugated link through the thiophene ring. As a result of this they compete for electron density equally well from the ring and the ring displays localized single and double bonds. The more distorted thiophene ring of complex **1** also differs more from the mean values of thiophene in terms of bond length.

Table 4.5: Comparison of bond distances (Å) and angles (°) of thienyl rings of **1** and **7**

	1	**7**
Bonds distances (Å)		
C2–C3	1.400 (8)	1.363 (14)
C3–C4	1.403 (8)	1.421 (14)
C4–C5	1.326 (11)	1.347 (13)
C2–S	1.723 (5)	1.736 (10)
C5–S	1.695 (8)	1.744 (10)
Ring internal angles, centered on named atoms (°)		
C2	110.2 (4)	110.1 (7)
C3	111.9 (6)	113.7 (9)
C4	113.0 (6)	113.3 (9)
C5	113.6 (5)	110.8 (7)
S	91.3 (3)	92.0 (5)

Finally, the complex is enantiomeric. In Figure 4.11 the complex and its mirror image is shown. The two are non–super–imposable.

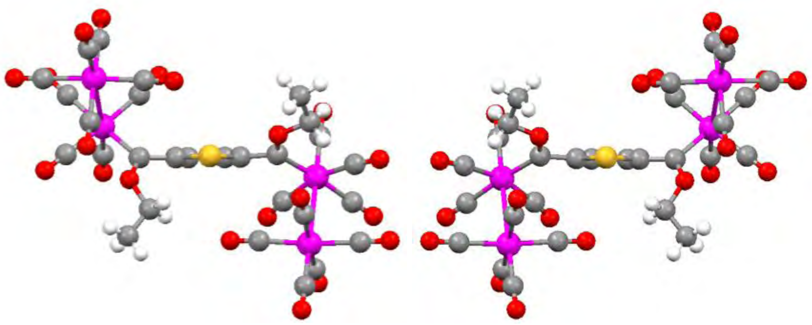


Figure 4.11: Stereo–isomers of **7**

The packing observed for this complex has the aromatic thiophene bridges of the biscarbene complexes far apart and π–stacking does not play a role.

4.3.2 Complex 8

Complex **8** displays two carbene carbon atoms attached to the two sides of a bithiophene bridge. The composition of the complex is similar to **7**, but with a bithiophene, rather than a thiophene, bridge there is far more free space between the {$Re_2(CO)_9$} and ethoxy fragments. The molecule has a centre of symmetry and the two sides are identical. The carbene ligands are equatorial ligands and the ethoxy groups are orientated on the same side as the sulfur atoms of the rings. They also have the electron–pairs of the oxygen atoms directed towards the rings.

A view of the complex is given below in Figure 4.12. In this view one observes the bithiophene side–on. With the space afforded by the bithiophene, one could also have expected a complex where the two {$Re_2(CO)_9$} fragments are on the same side of the bithiophene plane. A rotation around the carbene–ring carbon bond would place them on the same side, but then the ethoxy substituent would not be on the sulfur side of the ring any more.

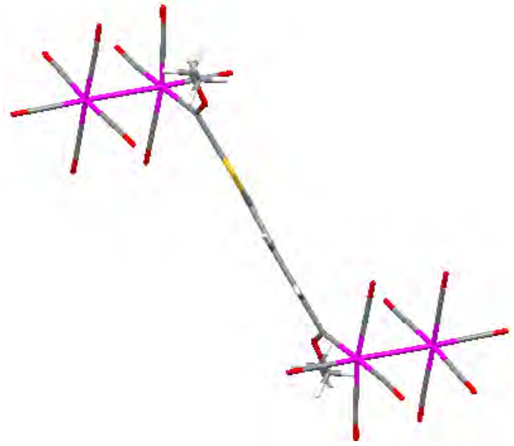


Figure 4.12: Complex view: end–on view of bithiophene carbene substituent

The structure of **8** is shown in Figure 4.13 and crystal data for this complex is given in Table 4.6a and 4.6b.

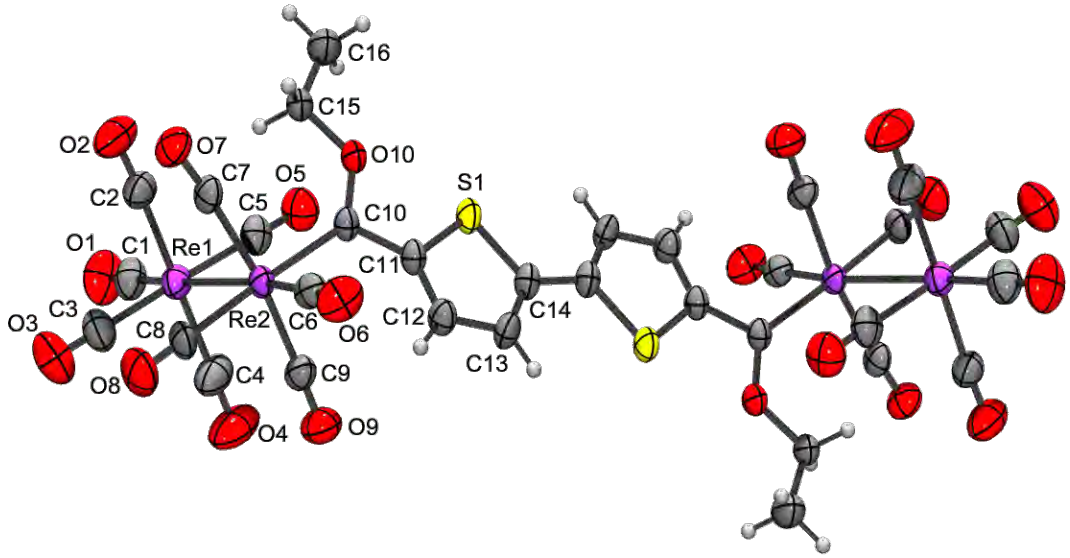


Figure 4.13: Molecular structure of **8**

Table 4.6a: Complex **8** bond lengths (Å)

Carbene distances			
C10–Re2	2.121 (5)	C10–C11	1.470 (6)
C10–O10	1.319 (6)		
Thienyl bond distances			
C11–C12	1.359 (7)	C13–C14	1.360 (7)
C12–C13	1.398 (7)	C14–C14′	1.452 (9)
Other bonds			
O10–C15	1.440 (5)	Re1–Re2	3.1422 (4)
C15–C16	1.491 (7)		
Re–CO bond lengths			
Re–CO$_{avg}$ of *eq*–Re(CO)$_5$	1.990 (7)	Re–CO$_{avg}$ (Re(CO)$_4$ *trans*–CO carbonyls)	1.989 (6)
ax–CO of Re(CO)$_5$	1.938 (6)	*ax*–CO of Re(CO)$_4$	1.908 (5)
Re(CO) *trans* carbene	1.991 (5)		

The structure of bithiophene was determined[10] and the values are shown below. It has a predominantly transoid structure and the long C1–C2 bond is an artifact of disorder. The two rings are planar.

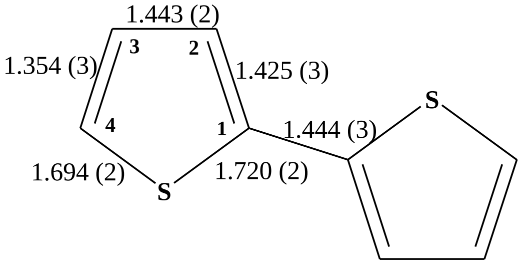


Figure 4.14: Bond distances of 2,2'–bithiophene (Å)

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[10] P. A. Chaloner, S. R. Gunatunga, P. B. Hitchcock; *Acta Cryst.*, **1994**, *C50*, 1941–1942

The bithiophene substituent in this complex has a C12–C13 bond that is significantly shorter than the equivalent bond in bithiophene, which indicates that there is more electron density in the bond.

The internal ring bond angles centered on the atoms are: S (92.20 (9)°), C1 (112.3 (1)°), C2 (108.3 (2)°), C3 (114.8 (2)°) and C4 (112.4 (1)°) and for the ring with the carbene the equivalent internal angles in complex **8** are 91.5 (2)°, 111.1 (3)°, 113.1 (5)°, 114.0 (4)°, 110.2 (3)°, respectively. It can be seen that some of the angles are significantly distorted.

Table 4.6b: Torsional angles of **8** (°)

Carbene plane twist relative to equatorial CO ligands			
O10–C10–Re2–C7	20.0 (5)	C11–C10–Re2–C7	22.4 (4)
O10–C10–Re2–C9	26.4 (5)	C11–C10–Re2–C9	28.8 (4)
Thienyl rings deviation out of the carbene plane			
S1–C11–C10–Re2	18.6 (2)	C12–C11–C10–Re2	19.9 (7)
S1–C11–C10–O10	20.4 (5)	C12–C11–C10–O10	21.7 (5)
Ethoxy twist out of the carbene plane			
C15–O10–C10–Re2	4.6 (7)	C15–O10–C10–C11	2.5 (4)
Ethoxy with respect to thienyl substituent			
O10–C10–C11–S1	20.4 (5)	O10–C10–C11–C12	21.7 (5)

The complex differs from **7** in a few aspects. Primarily, the two sides of the complex are identical. If lines were drawn along the Re–Re bonds, they would be parallel. The image in Figure 4.15 illustrates the orientation of the $\{Re_2(CO)_9\}$ fragments. The equatorial carbonyl ligands of the dirhenium parts eclipse each other (as viewed along the metal–metal bonds). It is rare for $\{Re_2(CO)_9\}$ complexes and is a higher–energy conformation for carbonyl ligands to adopt. As a consequence a Re–Re bond lengthening was observed. From the structure it is clear that this unfavourable conformation results from the ethyl groups that wedge into the open space between the equatorial carbonyls of two rhenium atoms. This can be seen more clearly from the space–filled representation of the structure shown in Figure 4.15. Other conformational features associated with the ethoxy substituents place them in ideal positions.

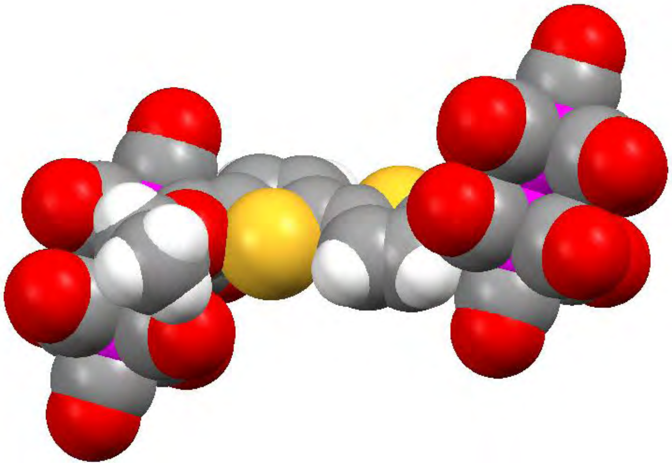


Figure 4.15: View of **8** showing carbonyl orientations

The extra thiophene ring places the metal–carbonyl fragments farther apart and creates more space for the carbene substituents. One can see in this complex (**8**) that the two ethoxy carbene substituents are more coplanar with the bithiophene than the ethoxy groups of **7** are in the plane of the thiophene.

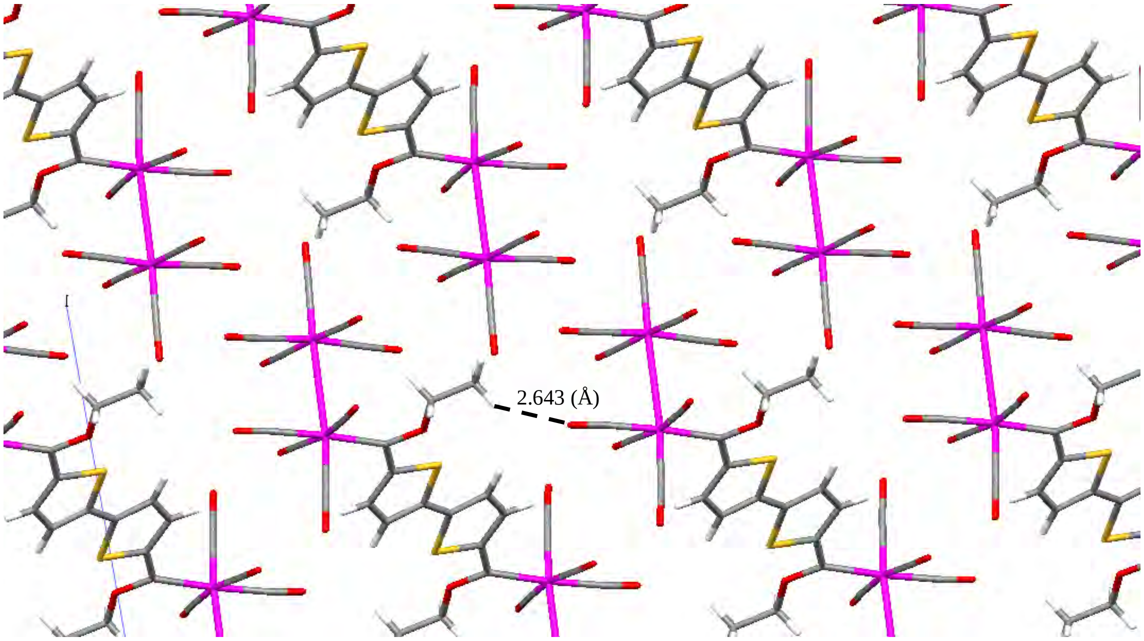
Torsional angle data show that the carbene with its substituents is twisted with respect to the equatorial carbonyl ligands that are *cis* to it by an angle of 20 to 29°. The thienyl substituent is twisted with respect to the carbene plane by an angle of about 20° and the ethoxy substituent is more in the plane of the carbene ligand. It is internally twisted by 17°.

The complex has the longest Re–Re bond length of **1**, **3**, **7** and **8** and therefore the equatorial carbonyl ligands on the two rhenium atoms are farther apart from each other, in this complex than in the other complexes. This would reduce their steric conflict of being in the eclipsed conformation.

The Re–C bond lengths of the equatorial carbonyl ligands of the complex are all the same length, within experimental error. The axial CO ligands have shorter Re–C bond lengths and the shortest of all is the Re–CO_{ax} bond of the fragment bearing the carbene ligand.

The closest atoms of the bithiophene bridges are separated from each other in the crystal by about 4 Å (C2–S) and π–stacking is not a determining factor in the packing of the complex molecules. This complex is unique in that the carbonyl ligands on the rhenium atoms are eclipsed. The positioning of the ethoxy group may also be supported by hydrogen–bonding interaction with a neighbouring complex molecule in the crystal structure. One of the ethoxy CH_3 hydrogen atoms is 2.64 Å from the carbonyl ligand oxygen atom on a neighbouring molecule (the carbonyl that is *trans* to the carbene carbon atom). The crystal packing, as viewed along the three axes, is shown below:

(a)



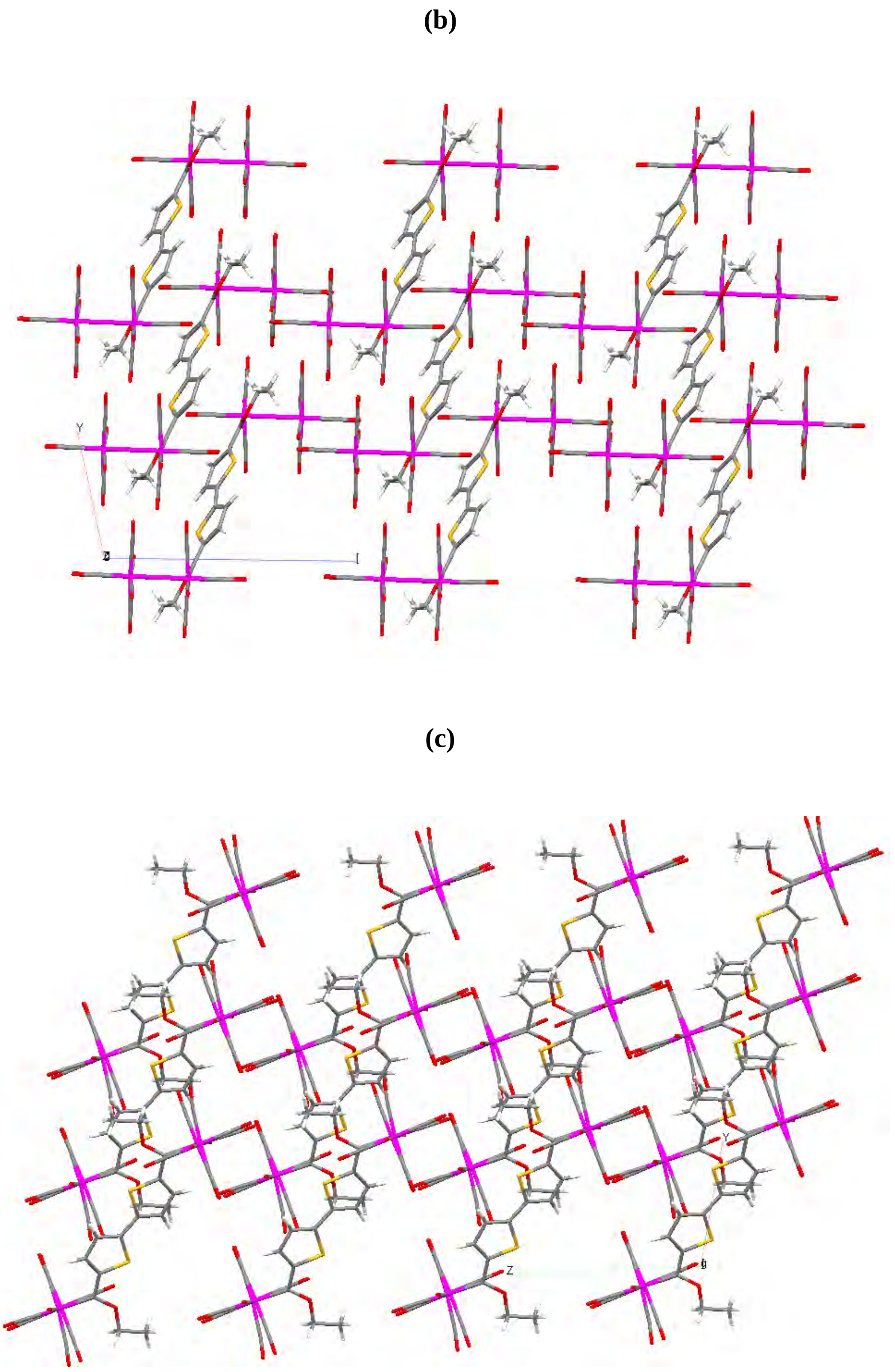


Figure 4.16: Packing of **8** observed along a, b and c axes

4.4 Monorhenium monocarbene complexes

4.4.1 Complex 5

The structure features a carbene carbon with three attached groups – a {Re(CO)$_4$Br} metal fragment, an ethoxy substituent and a bithienyl aromatic substituent. The ethoxy substituent is orientated to the sulfur side of the ring and it is situated with the oxygen lone pairs directed towards the ring.

An interesting feature of the complex is the thienyl rings of the bithiophene substituent which are orientated with the sulfur atoms on the same side. However, there is uncertainty about the positioning of the second ring. The second ("S2") ring is disordered. Its site occupation factors are 78.0(6) % and 22.0(6) %. The minor orientation of the ring represents a rotation of approximately 180° around the external C–C bond. The crystal structure of the complex is shown in Figure 4.17 and some of the bond distances and angles for the complex are given in Tables 4.7a and 4.7b.

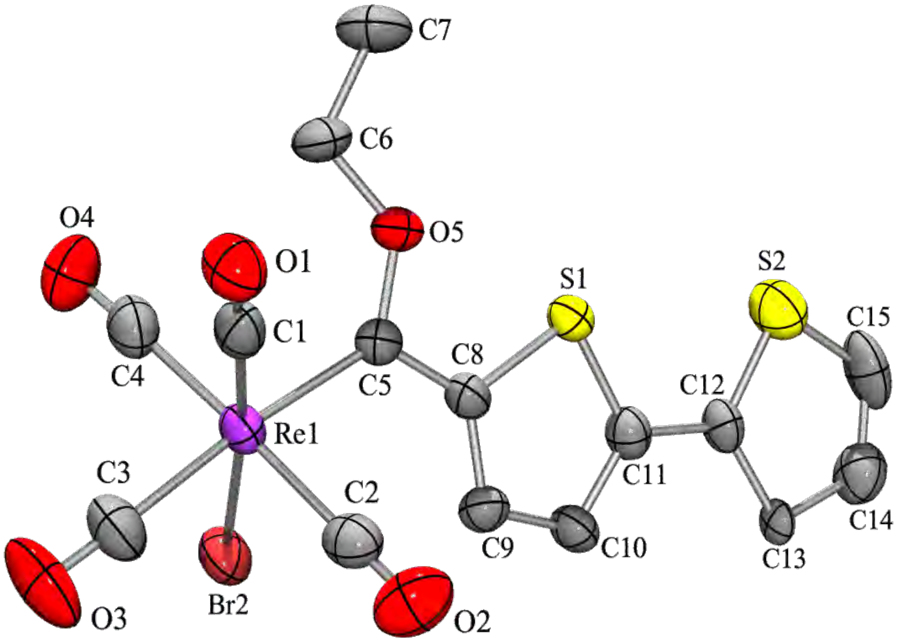


Figure 4.17: Molecular structure of **5**

The C–C bond lengths of the thienyl ring with the carbene attached are the same lengths, within experimental error. This bond–equalization is due to delocalization of electron density. For the second thienyl ring it is only the C14–C15 bond that displays a significantly longer value, but this distance is the same as the corresponding distance C10–C11 in the first ring. The C8–C9 and C10–C11 distance is between the corresponding values for 2,2′–bithiophene and 5–formyl–2,2′–bithiophene.

Table 4.7a: Complex **5** bond lengths (Å)

Carbene bond distances			
C5–Re1	2.164 (4)	C5–C8	1.434 (6)
C5–O5	1.328 (4)		
Thienyl bond distances			
C8–S1	1.745 (4)	C12–S2	1.7466
C8–C9	1.383 (5)	C12–C13	1.3774
C9–C10	1.380 (5)	C13–C14	1.3770
C10–C11	1.392 (5)	C14–C15	1.3970
C11–S1	1.709 (4)	C15–S2	1.7038
C11–C12	1.444 (6)		
Other bond distances			
O5–C6	1.435 (5)	Re1–Br2	2.6365 (5)
Re–CO bond lengths			
Re–CO$_{avg}$ (*trans* to CO)	2.005 (5)	Re–CO$_{\textit{trans}\text{–Br}}$	1.924 (5)
Re–CO$_{\textit{trans}\text{–carbene}}$	2.000 (5)		

The carbonyl ligands are all equally far from the metal, except for the carbonyl ligand that is *trans* to the bromide ligand, which has a shorter Re–C bond distance than the others in **5**. Its value is closer to the mean value for a terminal CO ligand (1.936 Å).

There is a possibility of hydrogen bonding to the bromo ligand from the hydrogen atom at position 3 of the bithiophene ring. The non–bonding H3–Br distance is 2.77 Å, a value that falls in the range of a hydrogen bond.

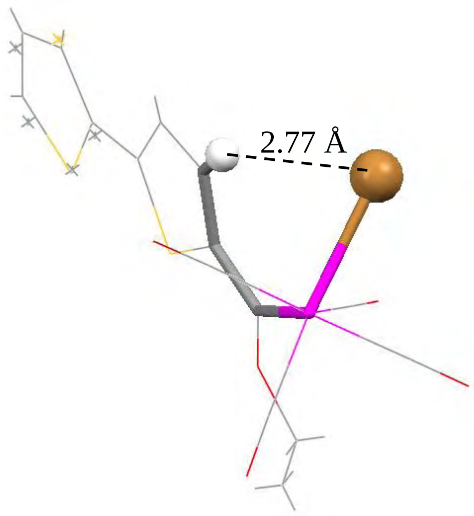


Figure 4.18: Hydrogen bonding between H3 and bromo ligand

The Re–Br distance of 2.6365 (5) Å is longer than the mean value of 2.573 Å[7] and also longer than the Re–Br bond (2.606 (2) Å) of an equivalent cyclic dioxycarbene complex prepared by Angelici[11].

Unfortunately, suitable crystals could not be obtained for a structure determination of uncleaved complex **2**. One could speculate about the structure of complex **2** – and assume that the two complexes look very similar except that **2** has a {Re(CO)$_5$} ligand, where **5** has a bromo ligand. It is likely that the bithiophene substituent lies at the same place than it does in this complex, but that it is more twisted out of the carbene plane (see next structure discussion for details). The loss of a bulky Re(CO)$_5$ group allows for better positioning of the hetero–aromatic ring, in a way that promotes conjugation. Therefore the substituent can contribute more to carbene stabilization and therefore a more shielded

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[11] G. L. Miessler, S. Kim, R. A. Jacobson, R. J. Angelici; *Inorg. Chem.*, **1987**, *26*, 1690–1695

carbene carbon atom and a shift to higher field strength in the ^{1}H NMR spectrum is observed (Tables 3.1 and 3.3).

Table 4.7b: Torsional angles of **5** (°)

Carbene plane deviation relative to equatorial CO ligands			
O5–C5–Re1–C2	45.5 (3)	C8–C5–Re1–C2	43.0 (3)
O5–C5–Re1–C4	46.4 (3)	C8–C5–Re1–C4	43.9 (3)
Thienyl twist out of the carbene plane			
S1–C8–C5–Re1	5.0 (19)	C9–C8–C5–Re1	8.3 (6)
S1–C8–C5–O5	2.9 (4)	C9–C8–C5–O5	6.2 (4)
Ethoxy twist out of the carbene plane			
C6–O5–C5–Re1	4.0 (5)	C6–O5–C5–C8	1.8 (4)
Ethoxy with respect to thienyl substituent			
S1–C8–C5–O5	2.9 (4)	C9–C8–C5–O5	6.2 (4)
Ethoxy twist			
C5–O5–C6–C7	0.9 (4)		
Planarity of the thiophene rings			
S1–C11–C12–S2	3.3 (8)	S2–C12–C11–C10	2.9 (4)
S1–C11–C12–C13	1.5 (3)	C10–C11–C12–C13	1.1 (8)

As was the case for most of the other structures, the orientation of the ethoxy group is such that the two lone pairs of the oxygen are orientated away from the metal towards the thienyl group. The ethoxy carbene substituent is almost completely flat, being internally bent by an angle of less than 1°. This contrasts with what was seen with the other complexes' (that have been discussed) ethoxy substituents and suggests a sterically less hindered situation.

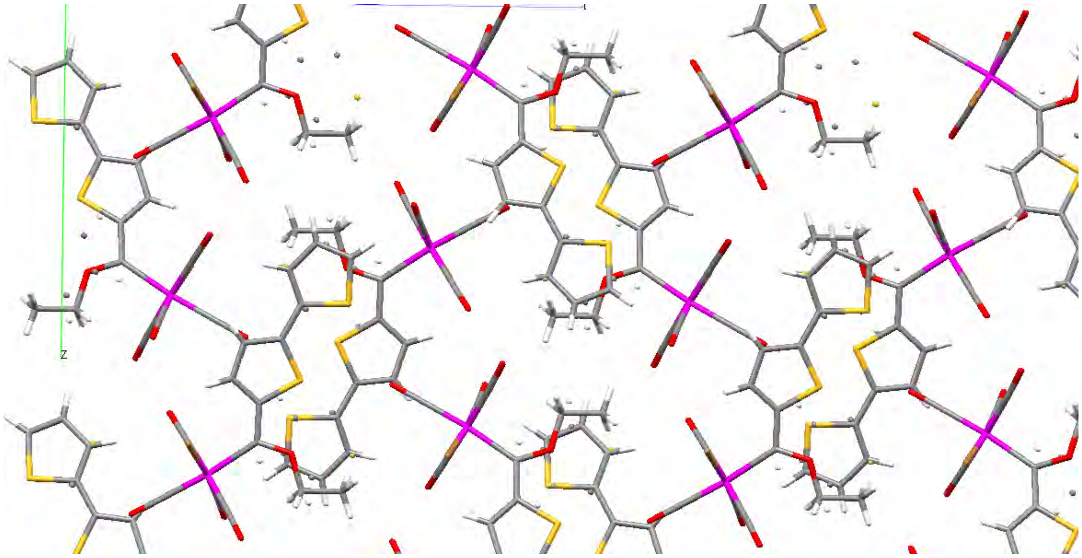
The orientation of the carbene ligand is shown below. In the Angelici cyclic dioxycarbene complex the carbene ligand is twisted with respect to the plane defined by the carbonyl ligands *cis* to the bromo ligand by an angle of 51.8 °. The two rings of the bithienyl substituent are coplanar.

Figure 4.19: Carbene orientation with respect to the carbonyl ligands

Internal angles of the thiophene ring with the carbene attached are 91.99 (18)° (S1), 109.6 (3)° (C8), 114.4 (3)° (C9), 112.5 (4)° (C10) and 111.5 (3)° (C11). There is a slight distortion within the ring.

In the following figure the views of the molecular packing in the crystal is provided.

(a)



(b)

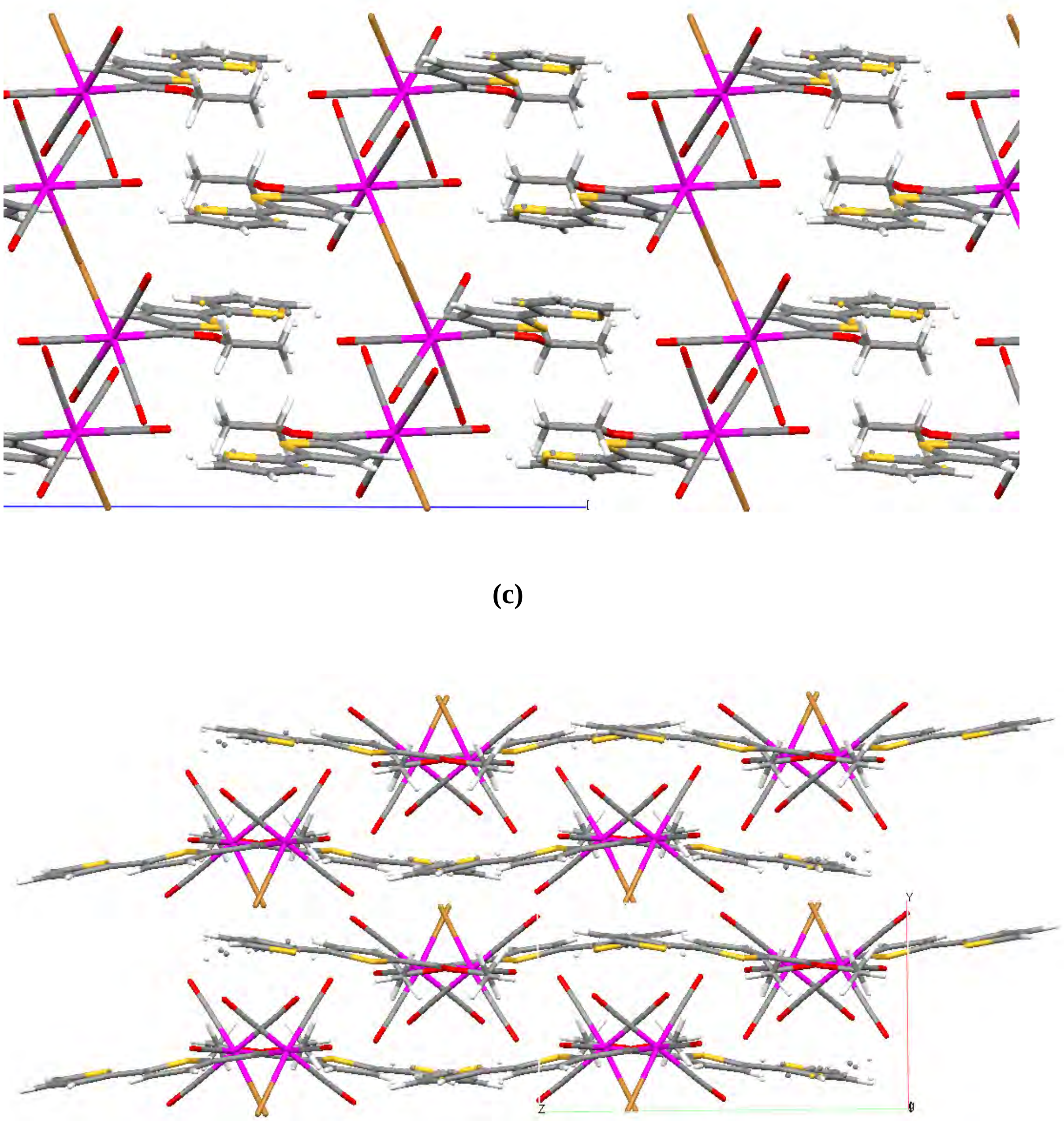


Figure 4.20: Packing of **5** observed along a, b and c axes

Distances between ring atoms of the thienyl substituents of complexes that lie next to each other in the crystal are quite large and indicate that π–stacking is not important in determining the packing of the molecules.

4.4.2 Complex 6

The complex consists of a carbene carbon with these three groups attached: {ReBr(CO)$_4$}, 3,6–dimethylthieno[3,2–*b*]thiophene and {OCH$_2$CH$_3$}. The bromo ligand is *cis* to the carbene ligand with little distortion of the octahedral arrangement of ligands.

Interestingly, the ethoxy substituent in this complex is situated on the opposite side of the ring, away from the sulfur atom of the ring and one can ascribe this to less steric hindrance between the substituent and the ring methyl (C12) than there would be between the metal fragment and the ring methyl. This complex is similar to a chromium complex prepared by Landman et al[12]. In this complex of 3,6–dimethylthieno[3,2–*b*]thiophene, the ethoxy substituent assumes a similar position (on the side of the methyl of the ring) and the ethyl part is also positioned away from the methyl, as in this complex. The structure of the complex is shown in Figure 4.21 and some bond distances and angles are given in Tables 4.8a and 4.8b.

The carbene–O bond is significantly shorter than the ethoxy O–CH$_2$ bond (1.456 (6) Å), once again pointing to a degree of double bonding between the carbene and the oxygen atom. The bond between the carbene and the carbon of the thienyl substituent (C5–C6) is slightly shorter than the bonds between the ring methyls and the carbon atoms (C7–C12, C10–C13) to which they are attached. This seems to suggest that the bond between the carbene and the aromatic substituent displays some double bond character but is mostly a single bond, based on bond length. The CH$_2$–CH$_3$ bond length of the ethoxy substituent is 1.502 (8) Å, making the three C–C single bonds of the complex (the other two are the ring–methyl bonds) all the same length, within experimental error.

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[12] M. Landman, H. Görls, S. Lotz; *Eur. J. Inorg. Chem.*, **2001**, 233–238

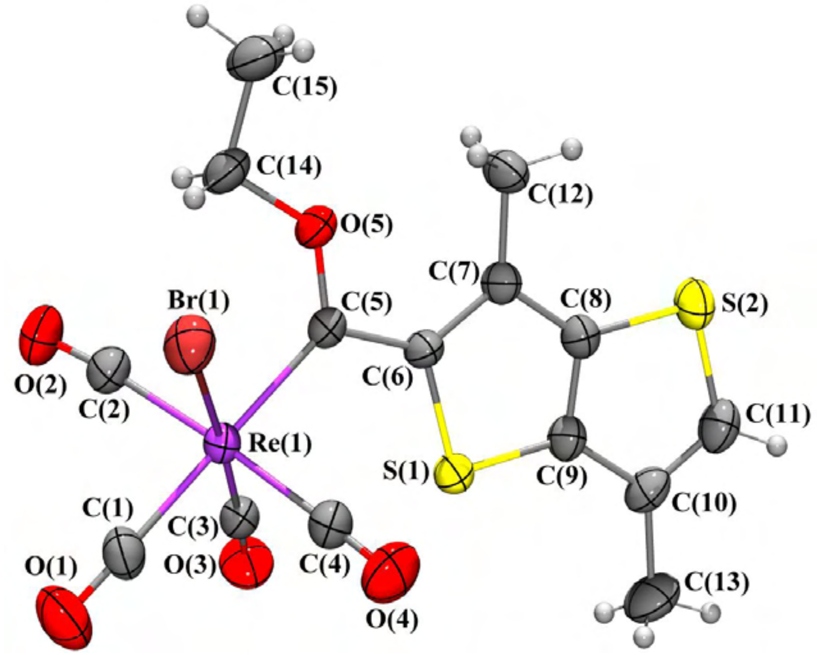


Figure 4.21: Molecular structure of **6**

All the C–C bonds of the aromatic rings are shorter than the C5–C6 bond, and the shortest of them is C10–C11, which is the double bond farthest away from the carbene. The longest distance in the thienyl rings is between C9 and C10. The second thienyl ring is more typical – with a shorter and a longer bond. It is interesting to see that not all of the ring carbon–sulfur bonds are the same length. The inner C–S bonds C4–S2 and C5–S1 are the shortest and the longest is C2–S1. It is assumed that the carbene takes electron density out of the C2–S1 bond, causing it to be lengthened. The bond lengths of the thienyl substituents of complex **3** and **6** are very similar.

The Re–Br bond of 2.6383 (5) Å is slightly longer than the Re–Br bond of complex **5**. The Re–C bond distance *trans* to the bromide ligand, is significantly shorter (1.914 (5) Å) than the corresponding distance (2.000 (5) Å; average) of rhenium carbonyl ligands *trans* to carbonyls. It shows that the metal back–donates more electron density into the π* orbital of this ligand (the bromide ligand is not a π–acceptor and does not compete with the CO ligand for electron density). The Re–C bond distance of the carbonyl ligand that is *trans* to the carbene ligand is slightly shorter (1.980 (6) Å) than the Re–C distance of carbonyl ligands *trans* to a carbonyl ligand.

Table 4.8a: Complex **6** bond lengths (Å)

Carbene bond distances			
C5–Re1	2.166 (5)	C5–C6	1.447 (6)
C5–O5	1.319 (6)		
Thienyl bond distances			
C6–S1	1.757 (4)	C8–S2	1.725 (5)
C6–C7	1.403 (6)	C9–C10	1.423 (6)
C7–C8	1.402 (6)	C10–C11	1.348 (8)
C7–C12	1.490 (6)	C10–C13	1.498 (8)
C8–C9	1.385 (7)	C11–S2	1.731 (6)
C9–S1	1.716 (5)		
Metal–ligand bond distances			
Re–Br	2.6383 (5)		
Re–CO bond lengths			
Re–CO$_{avg}$ (*trans* to CO)	2.000 (5)	Re–CO$_{\textit{trans}\text{–Br}}$	1.914 (5)
Re–CO$_{\textit{trans}\text{–carbene}}$	1.980 (6)		

There is a possibility of hydrogen bonding between the bromo ligand and a hydrogen atom of the ethoxy substituent. The distance between them is only 2.67 Å and is shown in Figure 4.22. This hydrogen bonding would also contribute to the positioning taken by the ethoxy substituent.

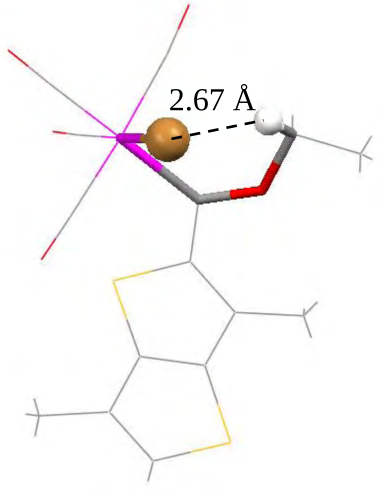


Figure 4.22: Hydrogen bonding between H14 and bromo ligand

Table 4.8b: Torsion angles of **6** (°)

Carbene plane deviation relative to cis equatorial CO ligands			
O5–C5–Re1–C2	36.5 (5)	C6–C5–Re1–C2	34.1 (4)
O5–C5–Re1–C4	41.4 (4)	C6–C5–Re1–C4	39.0 (4)
Thienyl twist out of the carbene plane			
S1–C6–C5–Re1	16.5 (6)	C7–C6–C5–Re1	19.3 (4)
S1–C6–C5–O5	14.5 (3)	C7–C6–C5–O5	17.3 (7)
Ethoxy twist out of the carbene plane			
C14–O5–C5–Re1	2.2 (7)	C14–O5–C5–C6	0.1 (4)
Ethoxy substituent with respect to thienyl substituent			
O5–C5–C6–S1	14.5 (3)	O5–C5–C6–C7	17.3 (7)
Ethoxy substituent twist			
C5–O5–C14–C15	20.2 (5)		

In Figure 4.23, the deviations of the thienyl plane out of the carbene plane (defined by the oxygen of the ethoxy substituent and the metal) can clearly be seen. The oxygen lies above and the rhenium below this plane, with the aromatic substituent in front, as viewed. The aromatic ring substituent deviates more out of the carbene plane in the case of uncleaved complex **3** than in the case of **6**. For bithiophene complex **5** the correspondence is even closer, as is shown below – Figure 4.24.

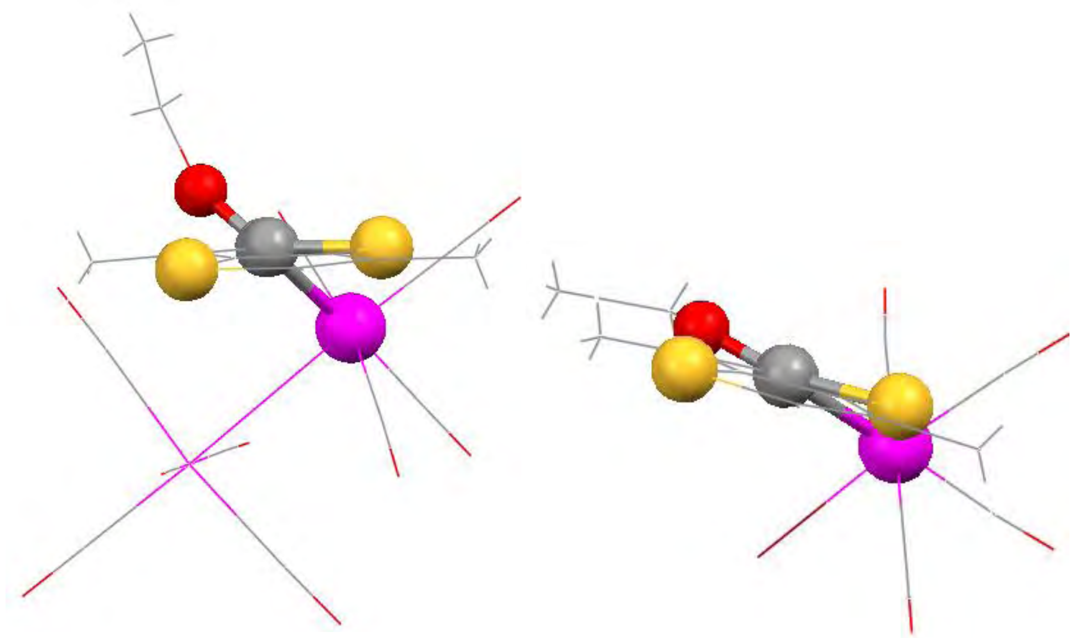


Figure 4.23: Showing twist angle of aromatic substituent in **3** and **6**

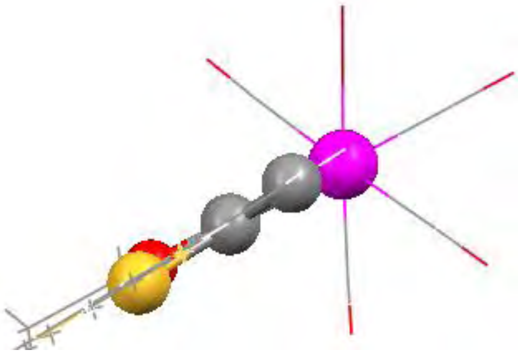
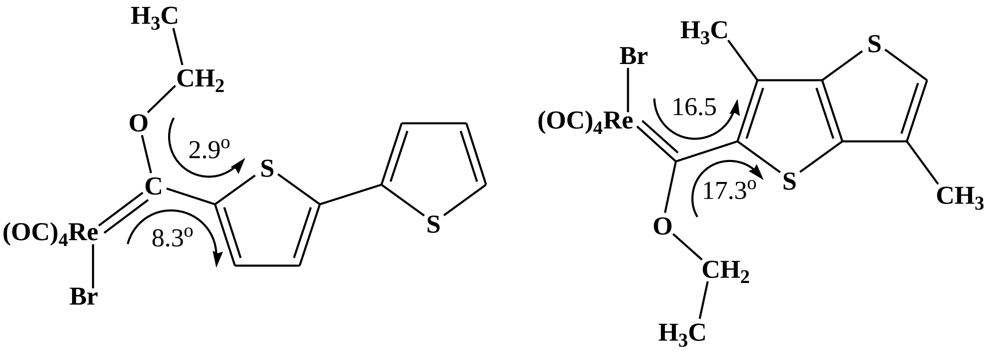


Figure 4.24: Showing twist angle of aromatic substituent in complex **5**

The difference in the relative twist can also be seen from the dihedral angles of **5** and **6**, shown in Figure 4.25.



5 **6**

Figure 4.25: The carbene substituents in **5** are closer to coplanarity than those of **6**

The packing of the molecules in the crystal of **6** are different from the packing of **3**. With the molecules of this complex – in the crystal – the thienyl substituents are too far apart to consider π–stacking as a determining factor in how the complex molecules have assembled. No atoms that could hydrogen–bond to each other are close enough for such bonding.

4.5 Dirhenium monocarbene aldehyde complex

4.5.1 Complex 13

The complex displays a carbene carbon atom with dirhenium nonacarbonyl, an ethoxy and the 9–formyl–bithiophene substituent attached to it. The carbonyl ligands in the equatorial planes of the two rhenium atoms are in the favoured staggered conformation. The ethoxy substituent is on the side of the sulfur atom of the thienyl ring as is found for most complexes of this kind[13]. The metals have an octahedral arrangement of ligands with the greatest deviation from linearity by the two carbonyls *cis* to the carbene ligand (C6–Re2–C7 = 92.6 (2)°; C6–Re2–C9 = 93.6 (2)°).

The structure is shown in Figure 4.26 and the data given in Tables 4.9a and 4.9b.

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[13] S. Lotz, C. Crause, A. J. Olivier, D. C. Liles, H. Görls, M. Landman, D. I. Bezuidenhout; *Dalton Trans.*, **2009**, 697–710

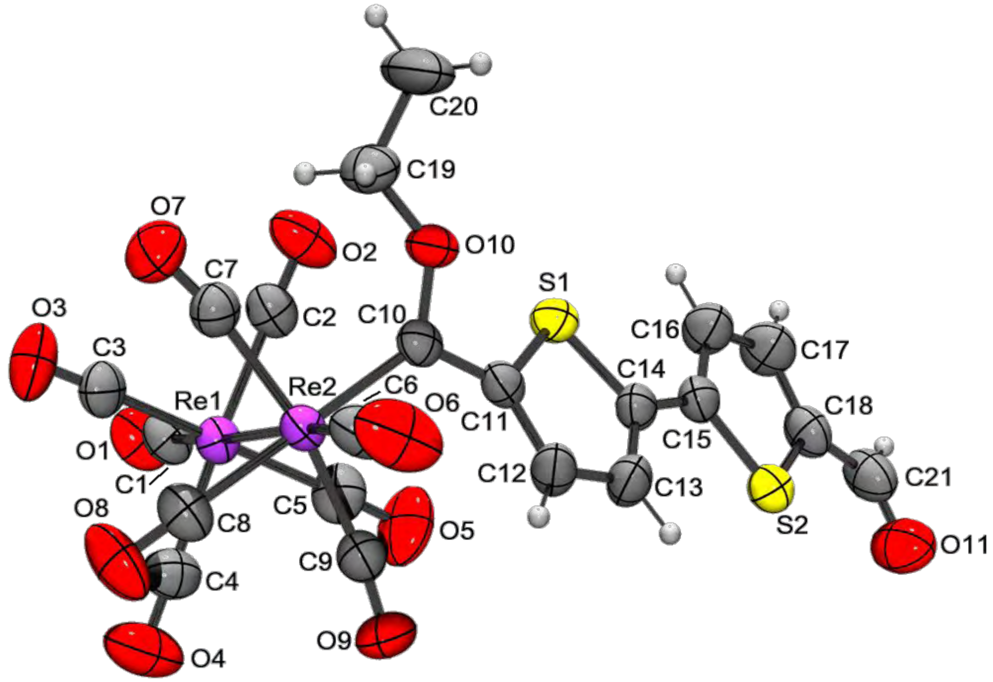

Figure 4.26: Crystal structure of **13**

The carbon–carbon bonds of the first ring are not all the same length – C11–C12 and C13–C14 are shorter than C12–C13. The carbon–carbon bonds are for the second ring, however, all the same length, within experimental error. The carbon–sulfur bonds of the rings are the same length within experimental error, except for C11–S1, which is longer than the other C–S bonds.

The rhenium–rhenium bond is shorter than the Re–Re bond of complex **8** (from which this complex derives) and about the same as the rhenium–rhenium bond of the other complexes. All the equatorial carbonyl ligand metal–carbon bonds are the same length. The axial carbonyl ligands’ Re–C bonds are shorter, with the axial carbonyl of the metal fragment that also bears the carbene ligand, having the shortest bond.

Table 4.9a: Complex **13** bond lengths (Å)

Carbene bond distances			
C10–Re2	2.117 (4)	C10–C11	1.460 (6)
C10–O10	1.323 (5)		
Aldehyde functionality bond distances			
C21–O11	1.186(7)	C18–C21	1.456 (7)
Aromatic substituent C–C bond distances			
C11–C12	1.373 (6)	C15–C16	1.370 (6)
C12–C13	1.400 (7)	C16–C17	1.387 (7)
C13–C14	1.360 (6)	C17–C18	1.374 (8)
C14–C15	1.453 (6)		
Carbon–sulfur bond distances			
C11–S1	1.737 (4)	C15–S2	1.712 (5)
C14–S1	1.716 (4)	C18–S2	1.715 (5)
Ethoxy substituent bonds			
O10–C19	1.445 (6)	C19–C20	1.513 (7)
Metal–metal bond			
Re1–Re2	3.0770 (3)		
Re–CO bond distances			
Re–CO$_{avg}$ of eq–Re(CO)$_5$		Re–CO$_{avg}$ (Re(CO)$_4$ *trans*–CO carbonyls)	1.983 (5)
ax–CO of Re(CO)$_5$	1.934 (5)	ax–CO of Re(CO)$_4$	1.917 (5)
Re–CO$_{\textit{trans}\text{–carbene}}$	1.978 (5)		

The structure of 5–formyl–2,2′–bithiophene was determined[14] and the bond distances are shown below. The molecule has a predominantly *cisoid* structure and the two rings and aldehyde are almost coplanar. In complex **13**, the bond lengths of the ring with the

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[14] S. P. Armes, P. A. Chaloner, P. B. Hitchcock, M. R. Simmons; *Acta Cryst.*, **1994**, *C50*, 1945–1947

aldehyde are not meaningfully different from the analogous bonds of the thiophene ring with the aldehyde of 5–formyl–2,2′–bithiophene. The aldehyde functionality of 5–formyl–2,2′–bithiophene also causes a distortion of the ring bond lengths of the ring to which it is attached (compared to bithiophene). The same was seen in the case of bithiophene monocarbene complex **5**, which is also predominantly cisoid.

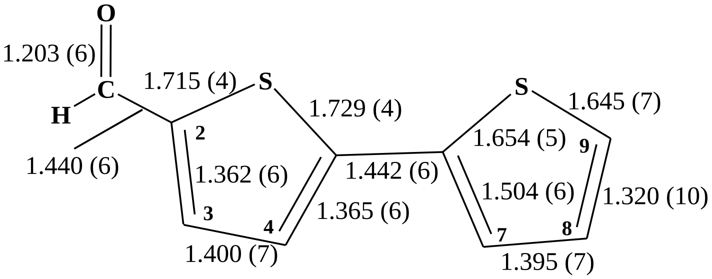


Figure 4.27: Bond distances of 5–formyl–2,2'–bithiophene (Å)

Three connecting carbon–carbon bonds can be seen in **13**, they are the bonds between the two rings and between the pendant carbene and aldehyde functions on the rings. These bonds are remarkably similar in bond length. Furthermore, the carbon–carbon bond lengths of the ring with the aldehyde attached are the same as the equivalent bonds of the ring with the carbene attached.

The double bonding between the carbene carbon atom and the oxygen and the aldehyde carbon atom and oxygen atom is clearly seen upon comparing C10–O10 (1.323 (5) Å) and C21–O11 (1.186 (7) Å) – the latter bond is shorter. This bond length does not differ significantly from the aldehyde C–O bond length of 5–formyl–2,2′–bithiophene or from the mean value for this type of bond: 1.192 Å[5]. Looking at the two bonds of the ethoxy oxygen atom, one sees that the carbene–O bond is definitely shorter than the O–CH_2CH_3 bond (1.445 (6) Å). It was also observed for the other complexes.

Table 4.9b: Selected bond torsion angles of **13** (°)

Carbene plane twist relative to cis equatorial CO ligands			
O10–C10–Re2–C7	2.8 (4)	C11–C10–Re2–C7	6.7 (4)
O10–C10–Re2–C9	4.0 (4)	C11–C10–Re2–C9	0.1 (4)
Thienyl twist out of the carbene plane			
S1–C11–C10–Re2	30.8 (2)	C12–C11–C10–Re2	35.1 (6)
S1–C11–C10–O10	27.8 (4)	C12–C11–C10–O10	32.1 (5)
Ethoxy twist out of the carbene plane			
C19–O10–C10–Re2	7.3 (7)	C19–O10–C10–C11	3.9 (4)
Ethoxy with respect to thienyl			
O10–C10–C11–S1	27.8 (4)	O10–C10–C11–C12	32.1 (5)
Aldehyde twist with respect to thienyl substituent			
O11–C21–C18–S2	5.0 (8)	O11–C21–C18–C17	3.4 (6)
Ethoxy internal twist			
C10–O10–C19–C20	3.4 (5)		

The carbene plane is close to being coplanar with the plane of the other equatorial ligands of the rhenium (the one of which the carbene is a ligand – see Figure 4.28).

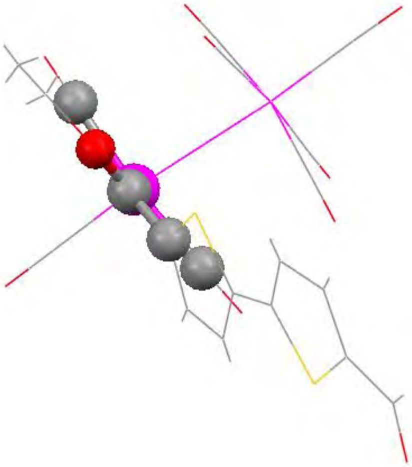


Figure 4.28: Coplanarity of carbene plane with equatorial ligands’ plane

The two aromatic rings (they are coplanar) are twisted around the bond to the carbene and the angle between their plane and that of the carbene is roughly 30°. The ethoxy group is close to being coplanar with the carbene plane and is only slightly twisted out of the carbene plane.

The carbonyl ligand that is next to the ethoxycarbene substituent is pushed away by ~10°. The other one has more space (bithiophene rings are twisted out of the carbene plane) and is twisted away by only ~7.5°. The axial carbonyl ligand is almost straight. Besides steric crowding, there is also an electronic reason for these two carbonyl ligands to be bent – the carbene ligand π–interacts with one of the two d–orbitals that π–interacts with the two *cis* carbonyl ligands causing an imbalance in charge distribution.

There is an indication that π–stacking played a determining factor in how the complex **13** molecules packed in the crystal structure. As the following image shows, the thiophene rings of the thienyl substituent lie approximately over each other and distances of about 3.5–3.7 Å are measured between closest ring carbon atoms. Hydrogen–bonding is not believed to have played a significant role in the crystal packing.

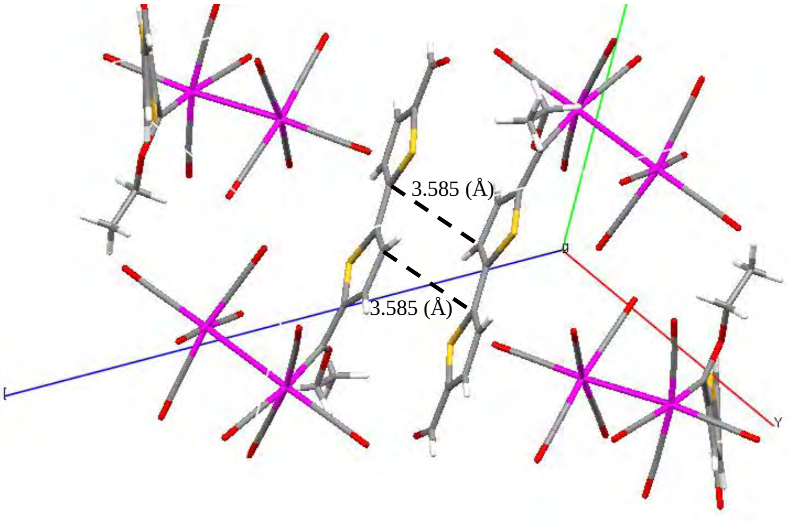


Figure 4.29: Crystal packing in **13**

4.6 Dirhenium bis–carbene/acyl complex

4.6.1 Complex 15

In this complex there are two rhenium atoms, each with one carbene/acyl–intermediate ligand. The rhenium atoms have only four other carbonyl ligands. The carbene/acyl ligands lie next to each other. The two fragments of the molecule are held together by bonds to two hydrogen atoms. One is located between the oxygen atoms of the carbene/acyl ligands. The other is located between the two rhenium atoms. An eight–membered ring, dirhenium metalla–cycle, is formed by the two metal atoms, the carbene acyl moieties/ligands and the bridging hydrogen atoms. The bridging hydrogen atoms place the acyl and carbene ligands in the same plane (C9–Re1–Re2–C10). The sulfur atoms of the thienyl rings are on the same side as the oxygen atoms of the acyl and hydroxycarbene ligands. The structure is shown in Figure 4.30 and the data of the complex is in Tables 4.10a and 4.10b.

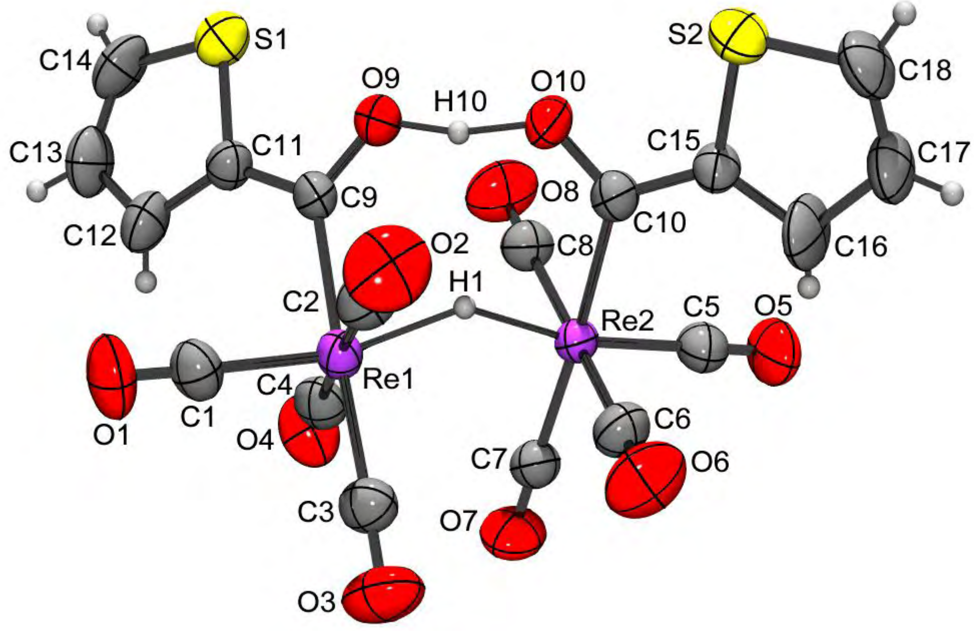


Figure 4.30: Crystal structure of complex **15**

Table 4.10a: Selected bond lengths of **15** (Å)

Carbene/acyl ligand bond distances			
C9–Re1	2.159 (4)	C10–Re2	2.173 (4)
C9–O9	1.271 (4)	C10–O10	1.283 (4)
C9–C11	1.456 (5)	C10–C15	1.444 (6)
Thienyl bond lengths			
C11–C12	1.429 (11)	C15–C16	1.414 (13)
C12–C13	1.392 (10)	C16–C17	1.440 (13)
C13–C14	1.322 (8)	C17–C18	1.310 (8)
C11–S1	1.739 (4)	C15–S2	1.722 (4)
C14–S1	1.671 (7)	C18–S2	1.687 (7)
O–H bond lengths			
O9–H10	1.19 (7)	O10–H10	1.26 (7)
Re–ligand bond lengths			
Re1–Re2	3.3622 (2)	Re2–H1	1.79 (4)
Re1–H1	1.77 (4)		
Re–CO bond distances			
Re–CO$_{avg}$ (*trans* CO)	1.989 (5)	Re2–CO$_{avg}$ (*trans* CO)	1.992 (4)
Re1–CO$_{\textit{trans}\text{–carbene}}$	1.977 (4)	Re2–CO$_{\textit{trans}\text{–carbene}}$	1.971 (4)
Re1–CO$_{\textit{trans}\text{–hydride}}$	1.926 (4)	Re2–CO$_{\textit{trans}\text{–hydride}}$	1.937 (4)

Both of the thiophene rings are disordered, but the “S1” ring is disordered only to a very small extent (major orientation: 94.3 (6) %). For the “S2” ring it is 88.3 (6) % (major orientation) and 11.7 (6) % (minor orientation).

The two Re–C (carbene, acyl) bonds are the same length, within experimental error. The same applies to the carbene (acyl) – oxygen bonds and also to the bonds to the bridging hydrogen atoms (the hydrogen atoms could be located). This shows that, even though the two components are regarded as an 18–electron hydroxycarbene hydride complex and a

16–electron acyl carbonyl complex, in this complex there are two resonance structures of equal importance.

The carbene–rhenium bond length of **1** is 2.125 (5) Å, a shorter bond than the rhenium–carbon (carbene, acyl) bonds of 2.159 (4) Å and 2.173 Å for **15**. On the other hand, the carbene/acyl–oxygen bonds of this complex are much shorter than the carbene–oxygen bond of complex **1**. The bonds to the thienyl ring are the same for the two complexes **1** and **15**.

The distance between the two rhenium atoms is longer than the Re–Re bond distance of complex **1** (3.0899 (3) Å) by about 0.27 Å. Formally there is no bond between the two metals. The 16–electron [Re$(CO)_4${C(O)T}] fragment receives electron density from the other rhenium and the hydrogen (hydride). This represents a three–center, two–electron bond. The other Re fragment is an 18–electron species: [Re$(CO)_4$H{C(OH)T}] and do not require a bond to another Re atom.

Even though the determination of the bond lengths to the bridging hydrogen atoms H1 and H10 is not precise, one can still see that the distances between the oxygen atoms and H10 is shorter than the distances between the rhenium atoms and bridging hydride H1. This is due to rhenium being bigger than oxygen. Due to experimental error one cannot say conclusively that the Re–H bonds are shorter than the mean value of 1.832 Å[7].

Of all the carbonyl ligands of Re1, the one that is *trans* to the hydride ligand is significantly closer to the rhenium atom than the other carbonyl ligands. With Re2 the situation is the same, but the other carbonyl ligands are not equally close to the metal. Re2–C7O7 (*trans* to carbene) is shorter than Re2–C6O6 (*trans* to carbonyl).

The thiophene rings are close to being coplanar with the carbene planes, thus maximizing delocalization potential. Ring S2–C15–C16–C17–C18 is twisted slightly more out of the carbene plane than ring S1–C11–C12–C13–C14.

Table 4.10b: Selected torsion angles of **15** (°)

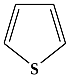
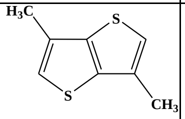
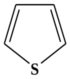
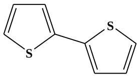
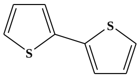
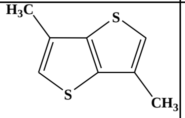
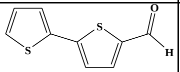
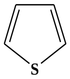
Carbene plane deviation relative to equatorial CO ligands			
O9–C9–Re1–C1	35.9 (3)	O10–C10–Re2–C5	34.5 (3)
C11–C9–Re1–C1	38.7 (3)	C15–C10–Re2–C5	32.3 (4)
Thienyl twist out of the carbene plane			
S1–C11–C9–Re1	0.3 (2)	S2–C15–C10–Re2	8.2 (2)
C12–C11–C9–Re1	0.6 (8)	C16–C15–C10–Re2	7.2 (11)
S1–C11–C9–O9	2.7 (5)	S2–C15–C10–O10	6.2 (5)
C12–C11–C9–O9	1.8 (7)	C16–C15–C10–O10	5.2 (9)
Hydroxy twist out of the carbene plane			
H10–O9–C9–Re1	3.1 (5)	H10–O10–C10–Re2	0.3 (9)
H10–O9–C9–C11	5.5 (7)	H10–O10–C10–C15	1.6 (11)

4.7 Summary of bond parameters around the carbene carbon atoms for the complexes

This section provides an overview of the structural features of the complexes.

In Table 4.11 the carbene–substituent bond lengths are given for the complexes. The first seven complexes that were discussed are all ethoxy carbene complexes and the carbene–OCH_2CH_3 bonds are all the same length, within experimental error. Complex **15** has the shortest carbene–oxygen bonds, as expected as it represents the average of a C–O double bond (acyl) and a C–O (carbene) bond. These ligands of complex **15** have a dual nature, i.e. that of an acyl and a hydroxycarbene ligand. The carbene–C (thienyl) bonds of the eight complexes are also all the same length.

Table 4.11: Carbene–substituent bonds lengths (Å) and angles (°)

	R–group	Re=[C]* (Å) *Re–[C]–O (°)*	O–[C] (Å) *O–[C]–R (°)*	R–[C] (Å) *R–[C]–Re (°)*	Re–Re / Re–Br
1		2.125 *129.9 (4)*	1.335 *105.2 (4)*	1.461 *124.9 (4)*	3.0899 (3)
3		2.098 *117.4 (4)*	1.326 *116.4 (5)*	1.466 *126.1 (4)*	3.0468 (4)
7		2.093 *119.1 (7)*	1.303 *118.2 (9)*	1.476 *122.7 (7)*	3.0434 (6)
		2.076 *131.5 (6)*	1.338 *104.5 (8)*	1.480 *124.1 (7)*	3.0569 (7)
8		2.121 *131.8 (3)*	1.319 *105.6 (4)*	1.470 *122.6 (3)*	3.1422 (4)
5		2.164 *128.4 (3)*	1.328 *106.8 (3)*	1.434 *124.8 (2)*	2.6365 (5)
6		2.166 *128.0 (3)*	1.319 *106.5 (4)*	1.447 *125.4 (3)*	2.6383 (5)
13		2.117 *130.9 (3)*	1.323 *104.1 (3)*	1.460 *125.0 (3)*	3.0770 (3)
15		2.173 *122.1 (3)*	1.283 *113.1 (3)*	1.444 *124.8 (3)*	3.3622 (2)
		2.159 *123.6 (3)*	1.271 *111.9 (3)*	1.456 *124.4 (3)*	

* [C] represents the carbene carbon atom

The metal–carbene bond lengths of the complexes are not all the same length. The Re–C (carbene) distances all fall in the range 2.076–2.166 Å. Some are shorter and some are longer than the mean value for an alkoxycarbene complex of rhenium – 2.098 Å. The rhenium–carbene bond lengths of the [Re]Br complexes, and of the dirhenium hydride–bridged complex, are longer than that of the other carbene complexes. A possible explanation for this, in the case of the rhenium–bromo carbene complexes, may be that the other two carbene substituents are more involved in carbene stabilization and the metal is less involved (smaller π–back bonding makes for a longer Re–C bond). As representative examples, consider complexes **3** and **6**. In **15** we find longer Re–C (carbene) and shorter C (carbene)–O lengths, due to the ligand being intermediate between an acyl and a carbene ligand.

In a Re(V) dioxo complex with four equivalent N–heterocyclic carbene ligands, which is representative of a long Re–carbene distance, the lengths of the bonds between the carbon atoms and the metal are 2.22–2.23 Å[15]. σ–Bonding dominates the bonding between the metal and the carbene ligands since the metal doesn't have any electrons to π–donate. The bonds of the complexes discussed here are all significantly shorter than that, evidence for the existence of π–bonding.

There is a fine balance of energetically most favoured conformation between ring planarity, carbene planarity and orientation of carbonyl ligands and electronic factors are readily influenced by steric constraints in the molecule.

If one considers the angles around the carbene carbon atom, you see that the angle made by the R substituent, the carbene and the metal are for all the complexes roughly the same, falling in the range of 122–127°. The ethoxy group is more variable in its position, as can be seen by looking at the values for the R–C–O and M–C–O bond angles. Because of the sp^3–carbons it is more flexible. The complexes that show the largest strain are again **3** and **7** (only one of the two ethoxy substituents is very twisted). Complexes with flat ethoxy groups are **5**, **13** and **1**.

Of the eight complexes, complexes **3** and **7** show the largest torsional twist between the thienyl substituent and the carbene plane. The thienyl substituent of complex **3** is 3,6–

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[15] H. Braband, T. I. Zahn, U. Abram; *Inorg. Chem.* **2003**, *42*, 6160–6162

dimethylthieno[3,2–*b*]thiophene. Steric hindrance between the pendant methyl at ring position 3 and carbonyl ligands may be responsible for the large twisting. The ethoxy groups of **7** interfere with each other across the thiophene bridge. Complexes **5** and **15**, on the other hand have thienyl substituents that are almost coplanar with the carbene plane.