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Synthesis and crystal structures of carbene complexes with conjugated thiophene units

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Abstract

Binuclear carbene complexes of chromium and tungsten containing a conjugated thiophene spacer, dithieno[3,2-*b*:2′,3′-*d*]thienylene (TTT), were synthesized according to the Fischer method for the synthesis of carbene complexes. Biscarbene complexes of the type $[(CO)_5M\{C(OEt)TTTC(OEt)\}M(CO)_5]$ (M = Cr, **2**; W, **5**) were afforded together with the corresponding monocarbene complexes $[M\{C(OEt)TTTH\}(CO)_5]$ (M = Cr, **1**; W, **4**) and decomposition products $[M\{C(OEt)TTTC(O)OEt\}(CO)_5]$ (M = Cr, **3**; W, **6**), formed in the reaction of the biscarbene complexes with trace amounts of oxygen. X-ray crystallographic determinations were performed on compounds **1**, **2** and **6** to assess the influence of the different substituents in the C9 position of the TTT carbene complexes on the structural features of the condensed rings. The crystallographic data of these three complexes are reported in this paper. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Biscarbene complexes; Thiophene derivatives; Crystal structure; Chromium; Tungsten

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1. Introduction

The past few decades have witnessed intense research world-wide in the field of conductive organometallic polymers, a class of conjugated organic materials that combine the mechanical qualities of polymers with the electrical conductivity of metals [1]. In this context, polythiophenes and their derivatives have occupied an important position, firstly because of their environmental stability and superior charge distribution facilities and secondly because of the versatility of the thiophene moiety in lending itself to synthetic modification. Polythiophenes have been identified as molecules with potential electro-optical properties and some of the most stable molecular switching devices discovered to date include thiophene derivatives [2]. Thiophenes also feature as building units in spacer ligands of binuclear complexes focusing on molecular wires [3] and in polynuclear conducting polymers [4]. In the past few years, research in our laboratories has comprised of the study of binuclear complexes containing thienyl spacer units. This included σ,π-complexes where the σ-attached metal is either directly bonded to the thienyl ring [5] or a carbene moiety [6]. Dinuclear biscarbene complexes with conjugated spacers have been documented for some time [7] and recently complexes containing thienylene [8,9] and 2,2′-bithienylene [10] moieties have also been synthesized. Complexes containing thiophene spacer units constituting one (a), two (b) or three (c) condensed thiophene rings are currently under investigation in our laboratories (Fig. 1).

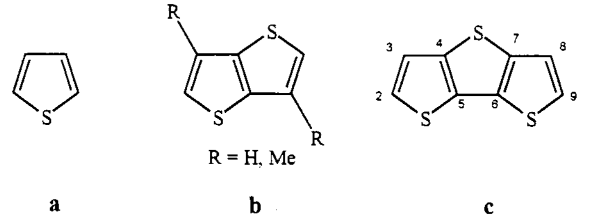

Fig. 1. Series of condensed thiophene compounds.

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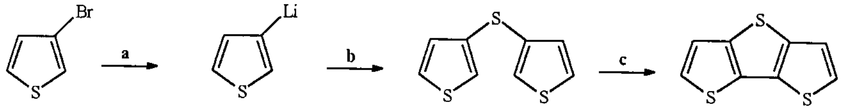


Scheme 1. Synthesis of dithieno[3,2-*b*:2′,3′-*d*] thiophene. Reagents: **a** n-BuLi, **b** SCl_2, **c** (i) 2n-BuLi (ii) $CuCl_2$.

In the case of dinuclear biscarbene complexes containing a thiophene spacer (a), complexes containing chromium and manganese carbene moieties have been reported and investigated extensively regarding their stability, decomposition patterns and structural features [8]. Although research in the area of thieno[3,2-*b*]thiophene (b) with regard to coordination chemistry has been neglected in the past, presumably due to the lack of a convenient synthetic procedure for the preparation of these and related compounds, a one-pot synthesis of the 3,6-dimethyl derivative was recently described in literature [11]. This allowed for the synthesis of several biscarbene complexes of chromium, tungsten [12], molybdenum and manganese [13] incorporating 3,6-dimethylthieno[3,2-*b*]thiophene as a spacer unit. Using a tedious synthetic procedure [14], unsubstituted thieno[3,2-*b*]thiophene could also be isolated in a low yield. In this paper the synthesis and structural features of dinuclear biscarbene complexes of dithieno[3,2-*b*:3′2′-*d*]thiophene (c) are reported.

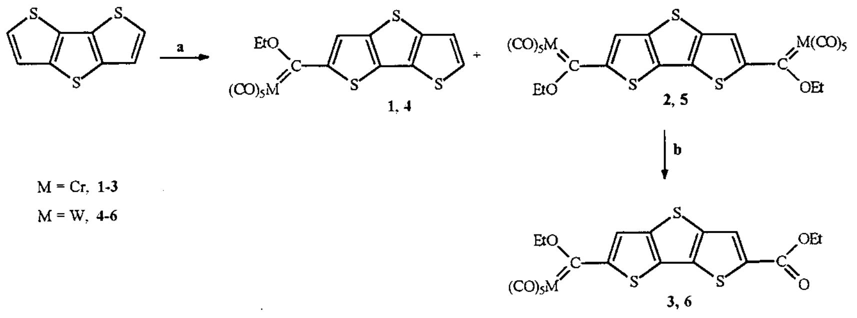
2. Results and discussion

The synthesis of the dithieno[3,2-*b*:2′,3′-*d*]thiophene ligand was based on work done by De Jong and Janssen [15], where 3-bromothiophene is used as starting material. The reported yields of the products, however, could not be met and the oxidative ring closure step especially proved to be challenging. Since this synthesis was time-consuming and the reaction yields were unsatisfactory, several new synthetic routes were considered and performed. These included a procedure where 2,2′-bithiophene was used as starting material. The idea for this synthesis originated from work done by Ohshita et al. [16] in the preparation of dithienosiloles and the prospect of utilising this method to synthesize dithieno[3,2-*b*:2′,3′-*d*]thiophene was attractive. In the first step, 2,2′-bithiophene was treated with excess bromine to afford 3,3′,5,5′-tetrabromo-2,2′-bithiophene [17]. Reaction of the tetrabromo substrate with zinc dust at elevated temperatures resulted in selective α-debromination to yield 3,3′-dibromo-2,2′-bithiophene. Lithiation of 3,3′-dibromo-2,2′-bithiophene with *n*-butyl lithium, followed by the reaction with sulphur dichloride [18], afforded the target product, but unfortunately the desired product was dissolved in a viscous oil which formed as by-product. Attempts to separate the two products failed and this method was abandoned. In another attempt to synthesize dithieno[3,2-*b*:2′,3′-*d*]thiophene, a combination of the methods described by De Jong et al. and Brandsma [18] was employed. In this approach 3-bromothiophene was lithiated and the 3-lithiothiophene species reacted with sulphur dichloride to yield di(3-thienyl)sulphide. Ring closure of this compound, using *n*-butyl lithium followed by the addition of $CuCl_2$, gave dithieno[3,2-*b*:2′,3′-*d*]thiophene in low yields (Scheme 1).

Comparison of the σ^+-values of the different carbon positions of dithieno[3,2-*b*:2′,3′-*d*]thiophene rings reveal the 2- and 9-positions to be the most reactive. This was confirmed by electrophilic substitution studies done on the different dithienothiophene isomers by Archer and Taylor [19]. Dimetallation of dithieno[3,2-*b*:2′,3′-*d*]thiophene was effected according to the method employed by Brandsma et al. [20] for the dimetallation of thiophene. This metallation involved the use of *n*-butyl lithium and TMEDA in hexane at elevated temperatures. Deprotonation of dithieno[3,2-*b*:2′,3′-*d*]thiophene, using two equivalents of *n*-butyl lithium to one equivalent of substrate, occurred at carbon positions 2 and 9. Upon reaction of $[Cr(CO)_6]$ with the dimetallated species and subsequent quenching with the alkylating agent $[Et_3O]BF_4$, three products were afforded i.e. the orange monocarbene complex **1**, the purple biscarbene complex **2** as well as the pink–orange decomposition product, complex **3**. Three analogous compounds were obtained upon repetition of this reaction with tungsten hexacarbonyl. Complexes **4**, **5** and **6** were isolated using column chromatography. The general synthetic procedure for the formation of these complexes is outlined in Scheme 2. The butyl carbene complexes $[M\{C(OEt)Bu\}(CO)_5]$ (M = Cr, W) [21] were formed in low yields as by-products in both reactions. Oxidation of one carbene unit by oxygen in **2** or **5** afforded the monocarbene–ester complexes **3** and **6**, respectively. Solvents such as acetone or THF enhance the oxidation process.

Complexes **1**–**6** were characterized spectroscopically using infrared and NMR spectroscopy as well as mass spectrometry. Suitable crystals for X-ray diffraction studies were obtained from dichloromethane–hexane solutions for **1** and **2**, while **6** crystallised as dark–orange needles from a chloroform–hexane solution. Complex **1** crystallised as orange–red needles while **2** afforded small dark-purple needle-like crystals.

It is evident from the ^{1}H-NMR data in Table 1 that the coordination of metal moieties to the substrate has a significant influence on the electronic distribution in the thiophene rings of the complex. The chemical shift values, recorded in deuterated chloroform, for uncoordinated dithieno[3,2-*b*:2′,3′-*d*]thiophene are 7.34 (H2, H9) and 7.27 ppm (H3, H8). The H3 resonances on the spectra of all the complexes are the most affected by coordination to a carbene moiety and appear in the downfield order of biscarbene complex **2**, **5** < decomposition product **3**, **6** < monocarbene complex **1**, **4**. H8 is almost as much affected by the electron withdrawing nature of the ester group as by that of a carbene moiety, but the combined electron withdrawing effect of two carbene substituents is stronger than that of one carbene moiety and one ester substituent. The substantial chemical shift differences for protons H3 and H8 on the spectra of the biscarbene complexes and the decomposition complexes compared to that of HTTTH indicate that the electrophilic carbene-metal moiety withdraws electron density from the ring. This is also true for the ester substituent in **3** and **6**. On the spectra of the monocarbene complexes a similar trend is observed and it is interesting to note that the protons furthest away from the metal fragment, H8 and H9, are also affected due to conjugation in the ring system. Resonances for the protons of the tungsten complexes are observed upfield compared to those of chromium [22]. Chemical shift values for the ethoxy protons of the chromium and tungsten carbene complexes are little affected by the nature of the spacer unit, the number of condensed thiophene units [8,12,23] as well as the number of carbene ligands. The ^{13}C-NMR spectrum of complex **5** was of an unsatisfactory quality since the poor solubility of the product in $CDCl_3$ prevented the acquisition of a useful data set. The position of the methylene carbon resonances of the ethoxy group were found to have characteristic values and were consistent for all complexes irrespective of the number of conjugated thiophene moieties and, to a large extent, independent of the metal fragment [8,12,24].



Scheme 2. Synthesis of complexes **1**–**6**. Reagents: **a** (i) 2 eq. n-BuLi (ii) $ML_3(CO)_3$ (iii) $Et_3O{\cdot}BF_4$, **b** Oxidation, O_2.

Table 1
Spectroscopic data for **1**–**6**

Complex	IR [a] (ν/cm^{-1} in CH_2Cl_2)	^1H-NMR (δ/ppm in $CDCl_3$)	^{13}C-NMR (δ/ppm in $CDCl^3$)
1	2056 (m), 1982 (vw), 1941 (vs)	8.42 (s, 1H, H3), 7.57 (d, 1H, H9, $^3J_{HH} = 5.2$), 7.32 (d, 1H, H8, $^3J_{HH} = 5.2$), 5.17 (q, 2H, CH_2, $^3J_{HH} = 7.0$), 1.68 (t, 3H, CH_3, $^3J_{HH} = 7.0$)	312.0 (carbene), 217.1, 223.2 ($M(CO)_5$), 154.4 (C2), 135.0 (C3), 142.8, 146.8 (C4, C5, C6, C7), 121.1 (C8), 130.7 (C9), 75.8 (CH_2), 15.2 (CH_3)
2	2054 (m), 1979 (vw), 1944 (vs)	8.38 (s, 2H, H3 and H3′), 5.20 (q, 2H, $^3J_{HH} = 7.0$, CH_2), 1.69 (t, 3H, $^3J_{HH} = 7.0$, CH_3)	314.8 (carbene), 216.8, 223.2 ($M(CO)_5$), 157.5 (C2), 133.4 (C3), 137.0, 146.1 (C4, C5), 76.2 (CH_2), 15.1 (CH_3)
3	2056 (m), 1978 (vw), 1942 (vs)	8.41 (s, 1H, H3), 8.00 (s, 1H, H8), 5.19 (q, 2H, $^3J_{HH} = 7.0$, CH_2), 4.40 (q, 2H, $^3J_{HH} = 7.0$, CH_2), 1.69 (t, 3H, $^3J_{HH} = 7.0$, CH_3), 1.40 (t, 3H, $^3J_{HH} = 7.0$, CH_3)	314.4 (carbene), 216.9, 223.2 ($M(CO)_5$), 161.9 (C2), 134.1 (C3), 137.7, 140.9, 144.6, 145.1 (C4, C5, C6, C7), 126.6 (C8), 156.2 (C9), 76.1, 61.8 (CH_2), 15.2, 14.3 (CH_3)
4	2064 (m), 1976 (vw), 1937 (vs)	8.35 (s, 1H, H3), 7.59 (d, 1H, H9, $^3J_{HH} = 5.2$), 7.31 (d, 1H, H8, $^3J_{HH} = 5.2$), 4.99 (q, 2H, CH_2, $^3J_{HH} = 7.0$), 1.66 (t, 3H, CH_3, $^3J_{HH} = 7.0$)	286.7 (carbene), 197.6, 202.3 ($M(CO)_5$), 158.0 (C2), 135.6 (C3), 142.6, 146.0 (C4, C5, C6, C7), 121.2 (C8), 130.9 (C9), 78.2 (CH_2), 15.0 (CH_3)
5	2064 (m), 1979 (vw), 1937 (vs)	8.29 (s, 2H, H3 and H3′), 5.00 (q, 2H, $^3J_{HH} = 7.0$, CH_2), 1.68 (t, 3H, $^3J_{HH} = 7.0$, CH_3)	197.6, 202.3 ($M(CO)_5$), 133.8 (C3), 78.6 (CH_2), 14.9 (CH_3)
6	2066 (m), 1979 (vw), 1939 (vs)	8.32 (s, 1H, H3), 8.00 (s, 1H, H8), 5.00 (q, 2H, $^3J_{HH} = 7.0$, CH_2), 4.40 (q, 2H, $^3J_{HH} = 7.0$, CH_2), 1.67 (t, 3H, $^3J_{HH} = 7.0$, CH_3), 1.40 (t, 3H, $^3J_{HH} = 7.0$, CH_3)	288.6 (carbene), 197.4, 202.3 ($M(CO)_5$), 161.9 (C2), 134.7 (C3), 132.4, 137.8, 138.3, 145.3 (C4, C5, C6, C7), 126.7 (C8), 159.6 (C9), 78.5, 61.9 (CH_2), 14.9, 14.3 (CH_3)

[a] Carbonyl region

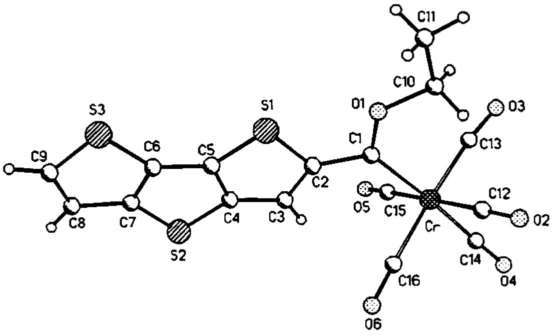


Fig. 2. Molecular structure of **1**.

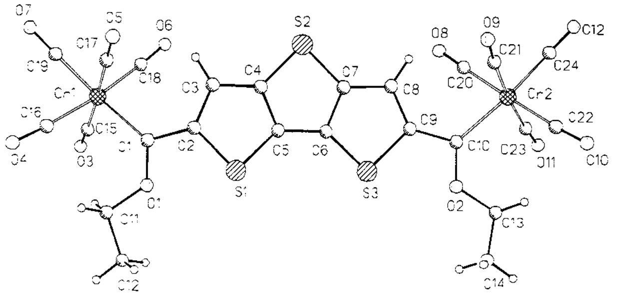


Fig. 3. Molecular structure of **2**.

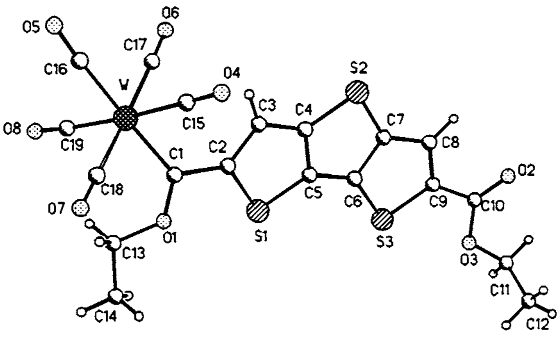


Fig. 4. Molecular structure of **6**.

The mass spectral data seem to indicate that the monocarbene complexes, biscarbene complexes and decomposition complexes have different fragmentation patterns, respectively. The monocarbene complexes show initial fragmentation of five carbonyl groups followed by the loss of the ethyl group and eventually the elimination of the carbene carbonyl group. On the spectra of the biscarbene complexes the molecular ion peaks were not observed. Instead, on both spectra the $M^+ - 4CO$ fragmentation peak was the peak observed at highest m/z-value. A definite fragmentation pattern for the biscarbene complexes could not be distinguished. However, certain discernible fragments could be identified which were present on both spectra. The first meaningful, unrelated peak which could be identified, was the fragment ion corresponding to the M^+ ion of the decomposition product i.e. one metal carbonyl fragment was replaced by an ester group. After this the consecutive loss of five carbonyl groups is observed and the peaks associated with these fragments could be assigned. Interestingly, the principal ion on both the spectra of **2** and **5** is found at an m/z value of 340, which corresponds to a fragment ion where ester groups replace both carbene fragments. The fragmentation patterns of the decomposition products are very similar to that of the monocarbene complexes. The molecular ion peak was observed in both cases and the fragmentation started with the stepwise loss of three carbonyl groups. In the spectrum of **3** the consequent loss of carbonyl groups ensued, while the elimination of the ethyl group preceded the further loss of the carbonyl groups in the spectrum of **6**.

2.1. Structural studies

Single X-ray determinations confirmed the structures of complexes **1**, **2** and **6**. The molecular structures of the respective complexes are represented in Figs. 2–4. Selected bond lengths and angles are given in Table 2. The crystal structure of uncoordinated dithieno[3,2-

Table 2
Selected bond lengths and angles of complexes **1**, **2** and **6**

	1	**2**	**6**
Bond lengths (Å)			
M1–C1	2.091(7)	2.051(9)	2.194(9)
M2–C10		2.077(9)	
S1–C2	1.765(7)	1.760(8)	1.765(8)
S1–C5	1.722(7)	1.727(8)	1.729(7)
S2–C4	1.765(7)	1.744(8)	1.739(7)
S2–C7	1.742(8)	1.740(8)	1.747(8)
S3–C6	1.729(7)	1.713(9)	1.718(8)
S3–C9	1.727(8)	1.776(8)	1.746(8)
C1–C2	1.448(9)	1.454(11)	1.488(10)
C9–C10		1.460(12)	1.477(11)
C2–C3	1.401(9)	1.369(11)	1.400(11)
C3–C4	1.403(10)	1.415(11)	1.405(10)
C4–C5	1.380(10)	1.384(11)	1.406(11)
C5–C6	1.427(10)	1.426(12)	1.416(10)
C6–C7	1.383(10)	1.405(11)	1.401(11)
C7–C8	1.444(10)	1.407(12)	1.426(11)
C8–C9	1.353(12)	1.393(12)	1.349(12)
M–CO *cis*	1.905(7)	1.913(11)	2.038(9)
M–Co *trans*	1.890(8)	1.886(11)	2.015(10)
Bond angles (°)			
M1–C1–C2	125.5(5)	125.7(6)	124.6(6)
M1–C1–O1	129.3(5)	130.1(6)	130.2(5)
O1–C1–C2	105.2(6)	104.2(7)	105.2(7)
C1–M1–Co *cis*	92.3(3)	92.1(4)	91.5(3)
C1–M1–Co *trans*	175.7(3)	176.2(4)	177.7(3)
M2–C10–C9		124.0(6)	
M2–C10–O2		130.1(6)	
O2–C10–C9		105.9(7)	
C10–M2–CO *cis*		91.2(4)	
C10–M2–CO *trans*		174.1(5)	

Table 3
Comparison of selected bond distances (Å) of biscarbene complexes of chromium

Compound	C1–C2	C2–C3	C3–C4	C4–C5	C2–S1	C5–S1	M–C1	Ref.
HTH		1.370(4)	1.442(2)	1.370(4)	1.718(4)	1.718(4)		[30]
[M]T[M]	1.456(6)	1.385(6)	1.388(6)	1.371(6)	1.730(5)	1.732(5)	2.040(5)	[8]
HT′T′H [a]		1.36	1.41	1.36	1.72	1.74		[37]
[M]T′T′[M]	1.473(4)	1.393(4)	1.415(4)	1.378(5)	1.745(3)	1.721(2)	2.068(3)	[12]
HTTTH		1.345	1.409	1.379	1.720	1.710		
[M]TTT[M]	1.454(11)	1.369(11)	1.415(11)	1.384(11)	1.760(8)	1.727(8)	2.051(9)	

[a] T′ = 3-MeT unit.

b:2′,3′-d]thiophene (HTTTH) was determined by Bertinelli et al. [25].

The bond lengths of the ring system in **1**, **2** and **6** are all longer or similar to the bond lengths determined for the same bonds in the structure of HTTTH. It is therefore assumed that the effect of delocalization is present in these molecules. For **1** and **6** this delocalization diminishes on proceeding to the next ring fragment, moving further away from the metal–carbene moiety. From this result it is thus concluded that the ester functionality in **6** plays an inferior role in the delocalization of electron density in the ring system in the solid state, as opposed to a carbene moiety.

In general the bond distances of the C(2)–S(1) and C(9)–S(3) bonds are conspicuously longer than the rest of the C–S bonds of the ring system. This suggests that these two bonds are the most affected by the coordination of TTT to the metal–carbene moieties and that the delocalization of the electron density in the ring excludes the sulphur atoms of the ring. This effect is supported by the longer metal–carbene carbon bonds [26] and shorter C(1)–C(2) bonds, since a normal C–C (single bond) is 1.51 Å [27]. In literature [28] the value obtained for a C(sp^2)–C(aryl) bond for a conjugated arene was 1.47 and for an unconjugated arene 1.49 Å. Bond angles of dithienothiophene in the complexes differ slightly from the literature values, indicating distortion of the rings on coordination to the carbene moiety. A plane of symmetry is found in the structure of **2** and is perpendicular to the bridging ligand, intersecting S(2) and bisecting the C(8)–C(9) bond of the ring.

The bond angles around the carbene carbon atoms are very similar for all the complexes and typical for Fischer carbene complexes [29]. In the structure of **6** the ethoxy group of the ester functionality is orientated towards the sulphur atom of the ligand, similar to the position inhabited by the ethoxy group on the carbene carbon. The bond angles surrounding C10 were determined as O(2)–C(10)–C(9) 123.5(8), O(3)–C(10)–C(9) 111.6(7) and O(2)–C(10)–O(3) 124.9(8)° which differ markedly from the corresponding angles around the carbene carbon atom.

On scrutinising the structural geometries of the complexes of thiophene [8], thienothiophene [12,13] and dithienothiophene, it seems as if the conformation where the metal fragment is positioned on the opposite side of the sulphur atom in the ring is preferred. A crab-like structure is thus observed for the biscarbene complexes. This geometry was encountered in the structures of the chromium [8] and tungsten [30] biscarbene complexes with thienylene spacers as well as for **1**, **2** and **6**. The opposite conformation, where the metal fragment is directed towards the sulphur atom in the ring, was only encountered for complexes containing a 3,6-dimethyl[3,2-*b*]thiophene ligand [12,13]. It was suggested that steric influences of the methyl substituents on the ring prevented the positioning of the metal moiety on that side of the ligand. The importance of hydrogen bonding between the H3 and the oxygen of a carbonyl ligand is a possibility that is currently under investigation.

On comparing the crystal data of all the different structures, it is evident that the heteroaromatic ligand is planar for all the complexes and it is thus possible to facilitate the delocalization of electron density through the π-system of the ligand. Torsion angles confirm the planarity of the ring system, with small distortions observed for some of the complexes. These distortions are mostly observed in the structures of the biscarbene complexes and the decomposition products. For most of the monocarbene complexes the metal atom, carbene carbon and arene rings are all exactly coplanar. In the case of the biscarbene complexes, distortion of the metal atom out of the carbene-arene plane ranges from 10–25°, with the greatest deviations observed for complexes containing 3,6-dimethylthieno[3,2-*b*]thiophene.

In Table 3 the structural data of chromium biscarbene complexes comprising one, two and three condensed thiophene units are compared mutually as well as with the uncoordinated substrates. In the case of the biscarbene complex with thiophene as bridging spacer, the similar bond lengths of the spacer unit especially signify the delocalization of electrons through the ring. The metal–carbene distances are comparable to those of analogous biscarbene complexes reported in literature [26,29] although the value observed for the biscarbene complex with T′T′ as spacer, is slightly longer than the average value of 2.05 Å. The lengthening of both C–S bonds compared to those of the uncoordinated substrates is significant. The involvement of the sulphur atom in the aromaticity of the substrates is thus much more significant. The C(2)–S(1) bond in the complexes is the most affected because of the coordination of the carbene moiety at C(2).

On going from one (thiophene) to two (thienothiophene) to three (dithienothiophene) condensed thiophene rings, it is interesting to note that the ring directly attached to the carbene carbon is the most affected by the delocalization effect while the second and third thiophene fragments are less affected. Bond lengths for these rings indicate more localized bonding and are comparable to those of free thiophene [31].

3. Conclusion

Applications of carbene complexes in organic synthesis and catalysis have escalated extensively over the last few years. Examples of dinuclear biscarbene complexes have been known for some time, but they have not yet been exploited to influence synthetic chemistry. In this study we have synthesized biscarbene complexes with thiophene spacer units with the following future objectives in mind: to include several other heteroaromatic spacer units, find new reaction routes to mixed metal biscarbene complexes, study the resulting activation of the carbene ligand, investigate the potential of two metal carbene moieties in unraveling reaction mechanisms and to use this information to prepare useful products.

4. Experimental

4.1. General details

All NMR spectra were recorded in deuterated chloroform, unless stated otherwise, using TMS as internal standard on a Bruker ARX-300 spectrometer. Infrared spectra were recorded on a BOMEM FT-IR spectrophotometer using dichloromethane as solvent unless otherwise specified. Mass spectra were recorded at ca. 70 eV on a Finnigan Mat 8200 instrument using the electron impact method.

All reactions were performed in an inert atmosphere of either nitrogen or argon by using standard Schlenk techniques and vacuum-line methods. Solvents were dried and distilled under nitrogen prior to use. Column chromatography was carried out under nitrogen using either silica gel (particle size 0.063–0.200 nm) or neutral aluminium oxide as resin. Most chemicals were used directly without prior purification. The following compounds were prepared using known literature methods: 3-bromothiophene [32], triethyl oxonium tetrafluoroborate [33], 3,3′-dithienyl sulfide [18].

4.2. Synthesis of the biscarbene complexes

*4.2.1. Synthesis of [(CO)$_5$Cr{C(OEt)TTTC(OEt)}Cr(CO)$_5$] (**2**)*

HTTTH (0.19 g, 1.0 mmol) was dissolved in hexane (30 ml) and *n*-butyl lithium (1.4 ml, 2.2 mmol) and TMEDA (0.3 ml (2.0 mmol) added to this solution at room temperature. This mixture was refluxed for 45 min and then cooled to 0°C. Lithium chloride precipitated from the yellow solution as a white solid. THF (30 ml) was added and the suspension was cooled even further to −40°C. Cr(CO)$_6$ (0.44 g, 2.0 mmol) was added and the colour of the mixture turned to red–brown. The temperature of the reaction was allowed to rise to room temperature while the mixture was stirred vigorously. After an hour the solvent was removed in vacuo and a solution of triethyl oxonium tetrafluoroborate (0.4 g, 2.0 mmol) in dichloromethane (50 ml) was added to the cooled residue (−20°C), and dissolved in dichloromethane (30 ml). After the addition of the alkylating agent, due to the fact that room temperature had been reached, the colour changed to dark purple. The mixture was filtered, and the solvent removed. Three products were isolated using column chromatography. The products were purified using hexane as eluting agent. The polarity gradient was gradually increased using dichloromethane to a final mixture of 1:1 dichloromethane–hexane for the isolation of the third product. The first orange product was characterized as the monocarbene complex [Cr{C(OEt)TTTH}(CO)$_5$] (**1**) while the second blue-purple product was identified as the biscarbene complex [(CO)$_5$Cr{C(OEt)TTTC(OEt)}Cr(CO)$_5$] (**2**). The third product had a red-purple colour and was characterized as the decomposition product [Cr{C(OEt)TTTC(O)OEt}(CO)$_5$] (**3**).

1: Anal. Calc. for $C_{16}H_8O_6S_3Cr$: C, 43.24; H, 1.81. Found: C, 43.42; H, 1.86%. Yield: 0.14 g (32%), m.p. 181.5–183.7°C; MS (EI): *m*/*z* 444.1 [M$^+$]; 416.2 [M$^+$ − CO]; 388.1 [M$^+$ − 2CO]; 360.1 [M$^+$ − 3CO]; 332.2 [M$^+$ − 4CO]; 304.1 [M$^+$ − 5CO]; 275.0 [M$^+$ − 5CO–Et]; 247.0 [M$^+$ − 6CO–Et]

2: Anal. Calc. for $C_{24}H_{12}O_{12}S_3Cr_2$: C, 41.62; H, 1.75. Found: C, 41.86; H, 1.81%. Yield: 0.27 g (39%); MS (EI): *m*/*z* 580.1 [M$^+$ − 4CO]; 516.2 [**3**$^+$]; 488.3 [**3**$^+$ − CO]; 460.2 [**3**$^+$ − 2CO]; 432.2 [**3**$^+$ − 3CO]; 404.2 [**3**$^+$ − 4CO]; 376.2 [**3**$^+$ − 5CO]

3: Anal. Calc. for $C_{19}H_{12}O_8S_3Cr$: C, 44.18; H, 2.34. Found: C, 44.24; H, 2.41%. Yield: 0.11 g (22%); MS (EI): *m*/*z* 516.2 [M$^+$]; 488.2 [M$^+$ − CO]; 460.1 [M$^+$ − 2CO]; 432.2 [M$^+$ − 3CO]; 404.2 [M$^+$ − 4CO]; 376.1 [M$^+$ − 5CO]; 347.2 [M$^+$ − 5CO–Et]; 319.1 [M$^+$ − 6CO–Et]

Table 4
Crystal data, collection and refinement details for **1**, **2** and **6**

	1	**2**	**6**
Empirical formula	$CrC_{16}H_8O_6S_3$	$Cr_2C_{24}H_{12}O_{12}S_3$	$WC_{19}H_{12}O_8S_3$
Formula weight	444.43	692.54	648.33
Temperature (K)	183(2)	183(2)	183(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\overline{1}$	$P\overline{1}$	$P2_1/c$
Unit cell dimensions			
a (Å)	7.4841(7)	8.3086(9)	11.9206(5)
b (Å)	10.166(1)	14.745(3)	22.4240(1)
c (Å)	14.241(2)	15.453(3)	8.9004(4)
α (°)	92.657(6)	113.12(1)	90
β (°)	102.348(7)	100.68(1)	111.469(3)
γ (°)	110.264(7)	95.89(1)	90
V (Å^3)	984.3(2)	1678.4(5)	2214.1(2)
Z	2	2	4
D_{calc} (g m^{-3})	1.560	1.424	1.945
Absorption coefficient (mm^{-1})	0.933	0.891	5.543
F(000)	468	726	1248
Crystal size (mm^3)	$0.29 \times 0.20 \times 0.10$	$0.28 \times 0.22 \times 0.18$	$0.20 \times 0.20 \times 0.02$
Theta range for data collection (°)	3.65–27.47	2.54–27.58	1.82–27.48
Index ranges	$-9 \leq h \leq 9$, $-13 \leq k \leq 13$, $-18 \leq l \leq 17$	$-10 \leq h = 9$, $-19 \leq k \leq 18$, $-19 \leq l \leq 19$	$-15 \leq h \leq 14$, $-24 \leq k \leq 29$, $-10 \leq l \leq 11$
Reflections collected	7005	11 158	17 609
Independent reflections	4466 [$R_{int} = 0.0763$]	7033 [$R_{int} = 0.0890$]	5041[$R_{int} = 0.1270$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4466/0/244	7033/0/397	5041/0/280
Goodness-of-fit on F^2	1.012	1.090	0.990
Final R indices [$I>2$ sigma(I)]	$R_1 = 0.0860$, $wR_2 = 0.2281$	$R_1 = 0.1208$, $wR_2 = 0.2369$	$R_1 = 0.0550$, $wR_2 = 0.0918$
R indices (all data)	$R_1 = 0.1597$, $wR_2 = 0.2709$	$R1 = 0.2167$, $wR_2 = 0.2786$	$R_1 = 0.1105$, $wR_2 = 0.1060$
Largest difference peak and hole (e Å^{-3})	1.797 and −0.499	1.083 and −0.435	0.855 and –1.761

4.2.2. Synthesis of [(CO)$_5$W{C(OEt)TTTC(OEt)}W(CO)$_5$] (5)

n-Butyl lithium (1.4 ml, 2.2 mmol) and TMEDA (0.3 ml, 2.0 mmol) were added to a solution of HTTTH (0.19 g, 1.0 mmol) in hexane (30 ml). The reaction was effected in the same manner as described for the chromium analogue in 4.2.1 with the addition of tungsten hexacarbonyl (0.70 g, 2 mmol) and subsequent alkylation with triethyl oxonium tetrafluoroborate (0.4 g, 2.0 mmol). Three products were isolated with column chromatography. Hexane was used as starting eluent and the polarity gradient was gradually increased by adding dichloromethane until the last product was isolated using a 1:1 mixture. The first orange product was identified as the monocarbene complex [W{C(OEt)-TTTH}(CO)$_5$] (**4**). The second purple was the biscarbene complex [(CO)$_5$W{C(OEt)TTTC(OEt)}W(CO)$_5$] (**5**). The third product had a brown–orange colour and was characterized as the decomposition product [W{C(OEt)TTTC(O)OEt}(CO)$_5$] (**6**).

4: Anal. Calc. for $C_{16}H_8O_6S_3W$: C, 33.17; H, 1.40. Found: C, 33.22; H, 1.45%. Yield: 0.24 g (42%); MS (EI): m/z 576.2 [M$^+$]; 548.2 [M$^+$ − CO]; 520.0 [M$^+$ − 2CO]; 491.2 [M$^+$ − 3CO]; 463.1 [M$^+$ − 4CO]; 435.1 [M$^+$ − 5CO]; 407.1 [M$^+$ − 5CO–Et]; 379.1 [M$^+$ − 6CO–Et]

5: Anal. Calc. for $C_{24}H_{12}O_{12}S_3W_2$: C, 30.14; H, 1.27. Found: C, 30.34; H, 1.38%. Yield: 0.25 g (26%); MS (EI): m/z (^{183}W) 844.2 [M$^+$ − 4CO]; 648.1 [**6**]; 620.2 [**6** − CO]; 592.0 [**6** − 2CO]; 564.0 [**6** − 3CO]; 536.1 [**6** − 4CO]; 508.2 [**6** − 5CO]

6: Anal. Calc. for $C_{19}H_{12}O_8S_3W$: C, 35.20; H, 1.87. Found: C, 35.28; H, 1.93%. Yield: 0.19 g (30%); MS (EI): m/z 648.5 [M$^+$]; 620.4 [M$^+$ − CO]; 592.4 [M$^+$ − 2CO]; 563.4 [M$^+$ − 2CO–Et]; 535.4 [M$^+$ − 3CO–Et]; 507.4 [M$^+$ − 4CO–Et]; 479.4 [M$^+$ − 5CO–Et]; 451.3 [M$^+$ − 6CO–Et]

4.3. Crystal structure determination

The intensity data for the compounds were collected at −90°C on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo–K$_\alpha$ radiation. Data were corrected for Lorentz and polarization effects, but not for absorption [34,35]. The structures were solved by direct methods (SHELXS) [36] and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97) [37]. The hydrogen atoms of the structures were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. Experimental details are given in Table 4.

5. Supplementary material

Crystallographic data(excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 145129 (**1**), 145128 (**2**) and 145131 (**6**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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