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Synthesis, characterization and decomposition patterns for thienylene bridged dinuclear biscarbene complexes of manganese and chromium in refluxing carbon disulphide and acetone

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Abstract

The dinuclear complexes $[ML_3(CO)_2\{C(OEt)C_4H_2SC(OEt)\}M(CO)_2L_3]$ (M = Cr, L = CO **1**; M = Mn, $L_3 = \eta^5$-C_5H_4R, R = H **2** and Me **3**) were synthesized from dilithiated thiophene according to the Fischer-method. The highly reactive biscarbene complexes are unstable in acetone and react to afford $[ML_3(CO)_2\{C(OEt)C_4H_2SC(O)OEt]$ (M = Cr **4**, M = Mn, R = H **5** and Me **6**). When refluxed in carbon disulphide, **1** affords as the only isolable product **4**, whereas **2** and **3**, in addition to **5** and **6**, reacts with CS_2 to give the thiono ester compounds $[Mn(\eta^5$-$C_5H_4R)(CO)_2\{C(OEt)C_4H_2SC(S)OEt\}]$ with R = H **7** and Me **8**, respectively. Compound **1** crystallizes in the monoclinic space group $C2/c$ with $a = 21.593(12)$, $b = 10.235(3)$, $c = 22.531(12)$ Å, $\beta = 92.06(4)°$ and $Z = 8$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Carbene; Biscarbene complexes; Bimetallic complexes; Thiophene

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1. Introduction

The activation of benzene [1] and thiophene [2] derivatives in complexes with more than one transition metal has been the focus point of current research carried out in our laboratories. Bimetallic complexes with σ,σ-attachments to transition metal fragments and containing a π-conjugated bridge are attractive compounds to study for their physical and chemical properties. Areas with possible application include constructing materials with non-linear optical and liquid crystalline properties, light harvesting devices, as precursors for metallodendrimers and macrocycles, molecular magnets and as molecular wires [3]. These expectations can be rationalized on the basis of metal-to-ligand charge transfer and extended delocalizations of electron density over an unsaturated chain of an unique ligand. Dinuclear biscarbene complexes with conjugated spacers have been known for some time [4]. Recently, dinuclear biscarbene complexes incorporating thienylene moieties have also come to the fore and the symmetrically substituted $(CO)_5W\{C(XR)CHCHC_4H_2$-$SCHCHC(XR)W(CO)_5$ [5] and 2,2′-bithienylene biscarbene complexes $[(CO)_5M\{C(OEt)SC_4H_2SC_4H_2C(OEt)$-$M(CO)_5]$ (M = Cr and/or W) have been synthesized [6].

Whereas mononuclear carbene complexes are being extensively exploited in the synthesis of novel organic compounds [7], systematic comparative studies between the reactivities of mononuclear carbene and dinuclear biscarbene complexes have been neglected. Thermal decomposition of Fischer type carbene complexes can lead to the coupling of two carbene ligands affording alkenes [8]. When applied to dinuclear biscarbene complexes this might well have interesting consequences as a new dinuclear biscarbene complex could form with a longer bridging spacer. Complexes with a thienylene moiety between the two carbene carbons provide the exciting possibility that upon intermolecular carbene–

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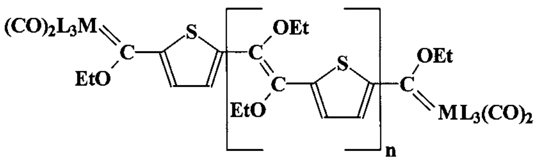
carbene coupling at one carbene site, the spacer may grow and yield interesting σ,σ-bimetallic polythienylene complexes with a conjugated bridge linking the metal centres.



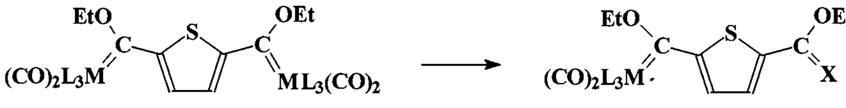
Bimetallic complexes of chromium and manganese with Fischer-type carbene ligands attached on both sides of a thienylene spacer, $[L_3(CO)_2M\{C(OEt)C_4H_2SC(OEt)\}M(CO)_2L_3]$ (M = Cr, L = CO **1**; M = Mn, $L_3 = \eta^5$-C_5H_4R, R = H **2**, Me **3**), were synthesized and fully characterized. A crystal structure determination of **1** confirmed the structure of the dinuclear complexes. The study also describes reactivity patterns of the compounds in refluxing solutions of acetone and carbon disulphide resulting in the formation of mononuclear carbene complexes, $[L_3(CO)_2M\{C(OEt)C_4H_2SC(OEt)X\}]$ (M = Cr, L = CO, X = O **4**; M = Mn, $L_3 = \eta^5$-C_5H_4R, R = H, X = O **5**, S **7**; R = Me, X = O **6**, S **8**). Reactions of monocarbene complexes with elemental sulphur and isothiocynates resulted in the insertion of sulphur into the metal–carbene bond to give thioketone complexes [9]. The oxidation of carbene complexes affording ketones or esters are well documented [10].

2. Results and discussion

Thiophene is readily metallated by butyllithium in THF or ether [11]. The dimetallation, however, is not possible in these solvents, but the monomeric BuLi-TMEDA complex is capable of abstracting protons in both the 2- and 5-positions of thiophene in hexane [12]. The first deprotonation occurs at a relatively low temperature, but the removal of the second proton is sufficiently fast only at elevated temperatures. The addition of two equivalents of chromium hexacarbonyl and cyclopentadienyl or methylcyclopentadienyl manganese tricarbonyl at low temperatures (−40°C) afforded the dilithium bisacylates, which after quenching with two equivalents of triethyloxonium tetrafluoroborate, yielded the neutral dinuclear biscarbene complexes **1–3**, respectively. In addition to the purple biscarbene complex **1**, the well known thienyl monocarbene $[Cr\{C(OEt)C_4H_3S\}(CO)_5]$ [13] and butylcarbene complex $[Cr\{C(OEt)Bu\}(CO)_5]$ [14] were also isolated after purification by column chromatography. For complex **1**, purple crystals were obtained which were fairly stable under inert conditions in the solid state, but slowly decomposed in hexane or dichloromethane solutions. Suitable crystals for X-ray diffraction studies were obtained from dichloromethane/hexane mixtures. Modification of one of the carbene ligands in oxygen-containing solvents is fast, and it is impossible, for example, to obtain a ^{1}H-NMR spectrum in a deuterated acetone solution without excessive decomposition. On the other hand, dinuclear manganese biscarbene complexes **2** and **3** were obtained as the only products and in much higher yields. Of these, **2**, which were isolable as purple crystals and stable under inert conditions in the solid state, slowly decomposed in hexane or dichloromethane solutions. Complex **3** could only be obtained as a far less stable, sticky oil.

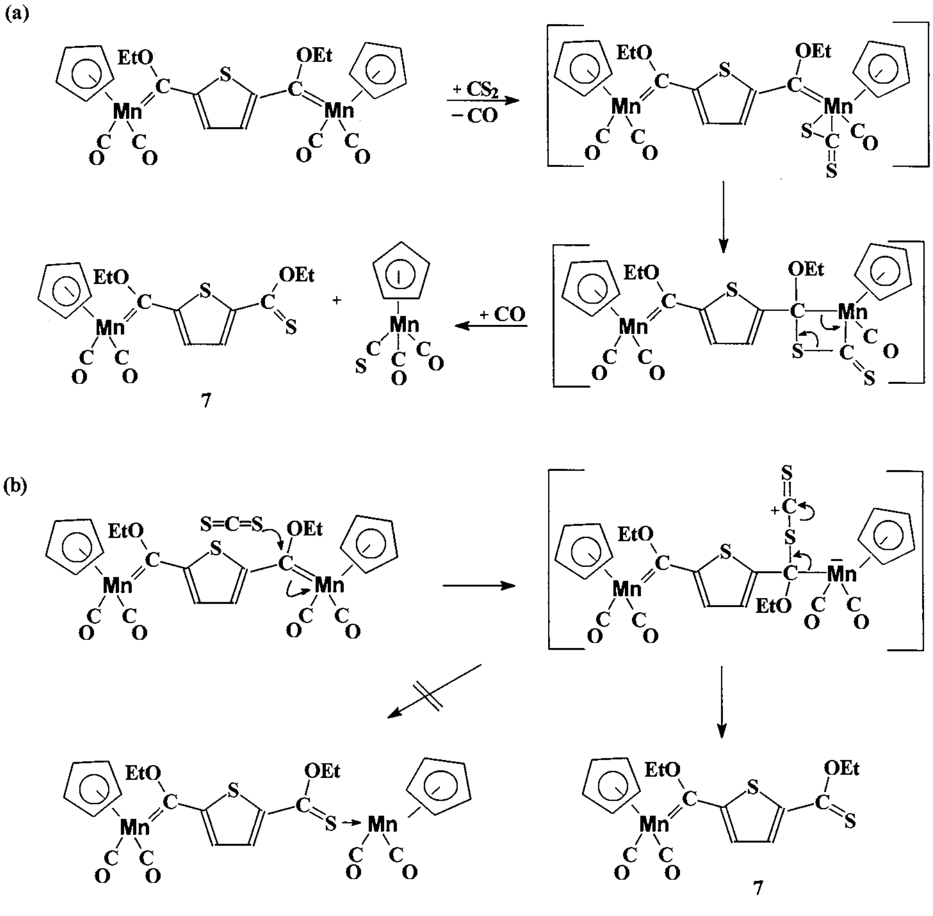
An electrophilic carbene carbon can be protected by the negative charge in metalacylates [15] and we have recently successfully employed this concept in our laboratories to synthesize dinuclear biscarbene complexes with different metal fragments in reasonable yields [16]. The stepwise addition of two different metal carbonyl precursors to dilithiated 2,2′-bithiophene was used previously to prepare $[(CO)_5Cr\{C(OEt)SC_4H_2SC_4H_2C(OEt)W(CO)_5]$ [6]. However, in this case incomplete reactions and the formation of mixtures of mono- and biscarbene complexes of W and Cr complicated procedures and is synthetically unattractive.

The dinuclear biscarbene complexes **1–3** were dissolved in carbon disulphide and refluxed for 3 h, affording as the only isolable product for **1**, and as minor products from the reactions of **2** and **3**, the corresponding *o*-ethyl thienyl carboxylate monocarbene complexes **4–6**. By contrast, the major products from the reac-



M	L3	
Cr	3xCO	1
Mn	Cp	2
	MeCp	3

M	L3	X	
Cr	3xCO	O	4
Mn	Cp	O	5
		S	7
Mn	MeCp	O	6
		S	8



Scheme 1.

tions of **2** and **3** were the *o*-ethyl thienyl thiocarboxylate monocarbene complexes **7** and **8**, respectively. Higher yields of **4–6** were obtained by stirring solutions of **1–3** in acetone for 2 h and almost quantitative yields could be obtained almost instantly when the acetone solutions were subjected to UV-radiation during stirring. However, no evidence indicating oxygen transfer from an acetone molecule could be found during the purification and isolation of products from the reaction mixture. Products where both carbene moieties were oxidized or sulphurized did not form. No evidence of the formation of a dinuclear biscarbene complex with carbene–carbene coupled olefinic units, resulting in an extended spacer between the metals, was observed. Many other minor products formed during the reactions, but in very low yields of 1–2%. These were not isolated as the results were poorly reproducible. The formation of **4–6** represents final products and no proof of their participation in any further reactions or modifications were detected. The much higher reactivity of the dinuclear biscarbene complexes compared to analogous mononuclear carbene complexes towards oxygen is notable.

The formation of **7** or **8** as well as the thiocarbonyl complex, $[Mn(\eta^5\text{-}C_5H_4R)(CO)_2(CS)]$ (R = H or Me) [17] during this reaction suggested that the reaction proceeded according to one of the pathways presented in Scheme 1. The presence of thiocarbonyl complexes in the reaction mixtures was verified spectroscopically after purification. In (a) the coordination of CS_2 in a η^2-fashion in cyclopentadienyl complexes of manganese is well documented [18], and could be important to initialize and facilitate the formation of **7**. The next step probably involves an intermediate displaying a four-membered metallacycle which is comparable to the key intermediate of metathesis reactions of alkenes and carbenes [19]. Opening of the ring in the opposite direction, thereby cleaving the metal–carbon bond of the carbene, leads to the formation of **7** and the resulting thiocarbonyl complex. In an alternative route (b), the carbonyl stays coordinated and a direct attack of the nucleophilic sulphur of CS_2 on the electrophilic Fischer carbene carbon atom initiates the reaction. Hence, the reaction of **2** with CS_2 to give **7** resembles those of heterocumulenes which have been used before to cleave metal–carbene bonds [9,20]. In the reaction of Group VI transition metal carbene complexes with isothiocyanate, the heterocumulene has been found to directly attack the carbene carbon by the sulphur atom. The generation of ylide intermediates from the reaction

Table 1
Spectral data for **1**–**8**

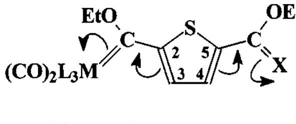
Complex	IR[a] (ν/cm^{-1} in hexane)	^{1}H-NMR[b] (δ/ppm in $CDCl_3$)
1	2054 (m), 1987 (vw), 1964 (m), 1953 (vs)	8.06 (s, 2H, H3 and H4), 5.21 (q, 2H, $^3J_{HH} = 7.2$, CH_2), 1.69 (t, 3H, $^3J_{HH} = 7.1$, CH_3)
2	1948, 1896	7.52 (s, 2H, H3 and H4) 4.97 (q, 2H, $^3J_{HH} = 7.2$, CH_2), 1.57 (t, 3H, $^3J_{HH} = 7.0$, CH_3), 4.61 (s, 5H, Cp)
3	1944, 1893	7.65 (s, 2H, H3 and H4), 4.97 (q, 2H, $^3J_{HH} = 6.8$, CH_2), 1.57 (t, 3H, $^3J_{HH} = 6.8$, CH_3), 4.50 and 4.36 (s, br, 2H, Cp), 1.75 (s, 3H, CH_3)
4	2060 (m), 1980 (vw), 1963 (m), 1951 (vs) 1726 (C(O))	8.09 (d, H, $^3J_{HH} = 4.3$, H3), 7.76 (d, H, $^3J_{HH} = 4.2$, H4) 5.20 (q, 2H, $^3J_{HH} = 7.1$, CH_2), 1.69 (t, 3H, $^3J_{HH} = 7.0$, CH_3), 4.37 (q, 2H, $^3J_{HH} = 7.2$, CH_2), 1.37 (t, 3H, $^3J_{HH} = 7.1$, CH_3)
5	1953, 1898, 1725 (C(O))	7.65 (d, H, $^3J_{HH} = 4.3$, H3), 7.53 (d, H, $^3J_{HH} = 4.2$, H4), 4.96 (q, 2H, $^3J_{HH} = 7.1$, CH_2), 1.58 (t, 3H, $^3J_{HH} = 7.0$, CH_3), 4.34 (q, 2H, $^3J_{HH} = 7.1$, CH_2), 1.47 (t, 3H, $^3J_{HH} = 7.1$, CH_3), 4.61 (s, 5H, Cp)
6	1950, 1893, 1724 (C(O))	7.70 (d, H, $^3J_{HH} = 4.3$, H3), 7.55 (d, H, $^3J_{HH} = 4.2$, H4), 4.97 (q, 2H, $^3J_{HH} = 7.1$, CH_2), 1.57 (t, 3H, $^3J_{HH} = 7.0$, CH_3), 4.49 (q, 2H, $^3J_{HH} = 7.1$, CH_2), 1.36 (t, 3H, $^3J_{HH} = 7.1$, CH_3), 4.34 (s, br, 4H, Cp), 1.86 (s, 3H, CH_3)
7	1940, 1895, 1247 (C(S))	7.69 (d, H, $^3J_{HH} = 4.0$, H3), 7.50 (d, H, $^3J_{HH} = 3.8$, H4), 4.95 (q, 2H, $^3J_{HH} = 7.1$, CH_2), 1.58 (t, 3H, $^3J_{HH} = 7.0$, CH_3), 4.66 (q, 2H, $^3J_{HH} = 7.0$, CH_2), 1.47 (t, 3H, $^3J_{HH} = 7.1$, CH_3), 4.61 (s, 5H, Cp)
8	1937, 1892, 1264 (C(S))	7.70 (d, H, $^3J_{HH} = 4.0$, H3), 7.53 (d, H, $^3J_{HH} = 4.0$, H4), 4.96 (q, 2H, $^3J_{HH} = 6.8$, CH_2), 1.58 (t, 3H, $^3J_{HH} = 6.8$, CH_3), 4.66 (q, 2H, $^3J_{HH} = 7.0$, CH_2), 1.36 (t, 3H, $^3J_{HH} = 7.0$, CH_3), 4.50 and 4.39 (s, br, 4H, Cp), 1.79 (s, 3H, CH_3)

[a] Carbonyl region [b] sequence for rows: thienylene/ethoxy (carbene)/ethoxy/cyclopentadienyl.

of organic compounds containing heteroatoms, including sulphur, with electrophilic carbene carbons, has been documented [21].

Complexes **1**–**8** were characterized spectroscopically (Table 1). A molecular ion peak, M^+, was observed for all the compounds and a general fragmentation pattern emerges for the dinuclear biscarbene complexes **1**–**3**. After the initial fragmentation of the carbonyl ligands, the carbene units are stripped of their ethyl groups and the acyl residues decarbonilated in a stepwise fashion to afford dinuclear thienylene fragment ions. The frequencies observed and the patterns and relative intensities of the bands in the carbonyl region of the IR spectra of **1**–**3**, confirm the respective metal carbonyl fragments. Complex **2** reveal bands of lower frequencies compared to those reported for the phenylene linked dinuclear complex $[(\eta^5\text{-}C_5H_5)(CO)_2MnC(Ph)C_6H_4C(Ph)Mn(\eta^5\text{-}C_5H_5)(CO)_2]$ (1977, 1914 cm^{-1}). This is an indication that more electron density is left on the manganese centres for π-backbonding to the carbonyl ligands in **2** due to differences in the electron distribution within the spacer ligands [22].

The thienylene protons, H3 and H4, in the ^{1}H-NMR spectra of **1**–**3** gave a single chemical shift downfield from the corresponding resonance for free thiophene (δ 6.96 ppm) [23], indicating a withdrawal of electron density from the thienylene ring towards the electrophilic carbene carbons. The ^{13}C-NMR chemical shifts of the carbene carbons in **1**, the mononuclear thienylcarbene complex $[Cr\{C(OEt)C_4H_3S\}(CO)_5]$ (319 ppm) and **4** are almost the same [24]. The carbene carbon resonances of **2** and **3**, which are the same as that recorded for the ethylene linked biscarbene complex $[(\eta^5\text{-}C_5H_4Me)(CO)_2MnC(OEt)CH{=}CHC(OEt)Mn(\eta^5\text{-}C_5H_4Me)(CO)_2]$ (320 ppm) [25], lie upfield from those of the mononuclear complexes $[Mn(\eta^5\text{-}C_5H_4R)(CO)_2\{C(Ph)Ph\}]$ (R = H, Me) (353, 351, respectively) [22] and the 339 ppm recorded for the complex $[(\eta^5\text{-}C_5H_4Me)(CO)_2MnC(OEt)CH_2CH_2C(OEt)Mn(\eta^5\text{-}C_5H_4Me)(CO)_2]$ [25]. The deshielding of the thienylene ring owing to the effect of carbene carbon atoms as substituents in the 2- and 5-positions is also demonstrated by significant downfield shifts for C2 and C5 or C3 and C4 compared to free thiophene (δ 124.9 or 126.7 ppm) [23]. By contrast, the chemical shifts of the carbonyl ligands in all of the above examples are insensitive to different substituents on the carbene ligands and chemical shifts are typical for $M(CO)_5$ and $M(CO)_2$ fragments [26].



The chemical shifts of H3 or H4, which appear as doublets owing to the different substituents in the 2- and 5-positions, are virtually the same in the spectra of compounds **4**–**8**. In the proton NMR spectra of **4**–**8**, the resonances of H3 are observed downfield from those of H4, indicating greater delocalization of elec-

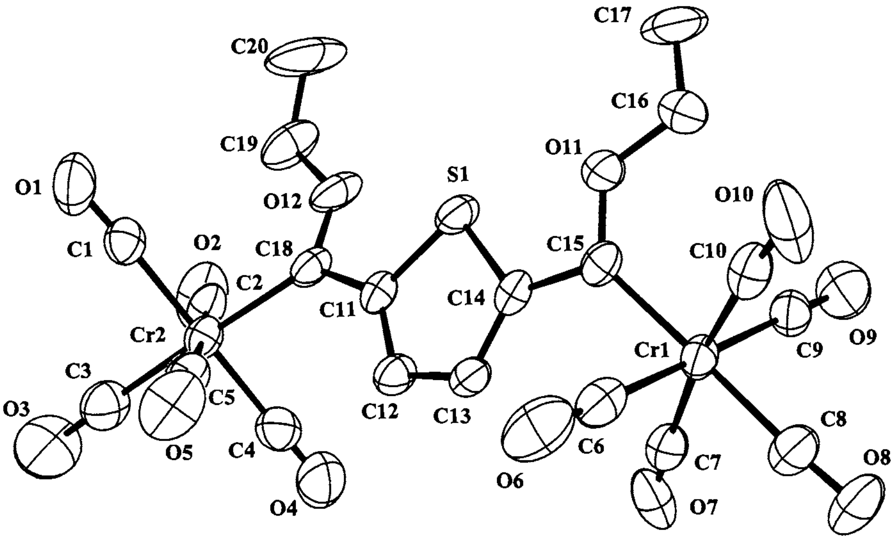


Fig. 1. The molecular structure of [(CO)$_5$Cr{C(OEt)C$_4$H$_2$SC(OEt)}Cr(CO)$_5$] **1** in the solid state showing the atom labelling scheme.

tron density towards the carbene carbon atom compared to the ester group. The chemical shift of H3 or H4 in the spectra of **1–3**, are upfield from H3, but downfield or the same as the resonances of H4 in the corresponding spectra of **4–8**. A substituent in the 2-position of the thienyl SC$_4$H$_3$C(O)OMe afforded resonances in the aromatic region of 7.80 (H3), 7.10 (H4) and 7.55 (H5) ppm [27]. The old analogy to replace a metal fragment by an oxygen atom in Fischer-type carbene complexes to imitate properties, especially reactivity patterns of carbene carbon atoms, are of interest in complexes **4–6** [28]. Both these functionalities are situated directly opposite one another and linked by π-resonance effects via the bridging thienylene unit. The ester group or thiono ester in the 5-position in thienylene competes with the carbene carbon in the 2-position for electron density from the ring. A comparison of the chemical shifts of the thienylene protons reveals an electron withdrawing ability of the carbene moiety greater than that of the substituent in the 5-position. The chemical shifts of the ethoxy substituent of the carbene ligands, a quartet for the methylene and a triplet for the methyl groups, are practically the same for all the compounds and are therefore only affected by the nature of the transition metal in thienylcarbene complexes. Whereas the chemical shifts of **4–6** for the thienylene protons are upfield from those reported for (CO)$_5$W{C(OEt)SC$_4$H$_2$C(O)OEt (H3 8.02 and H4 7.78 ppm, respectively), the ethoxy substituent of both the carbene (5.01 (CH$_2$) and 1.69 (CH$_3$) ppm, respectively) and ester (4.39 (CH$_2$) and 1.39 (CH$_3$) ppm, respectively) units show much smaller deviations [15]. The only significant difference in the chemical shifts of **5** or **6** and **7** or **8** is found in the resonances of the ethoxy group forming part of the ester or thiono ester substituent in the 5-position. Discrimination between –C(O)OEt and –C(S)OEt moieties of the thienylene substituent in the products is made on the basis of the characteristic chemical shifts of the methylene protons of the OEt substituent of the ester units in the monocarbene complexes, which are approximately 0.3 ppm downfield for the thiono ester compared to the ester group.

2.1. Structural studies

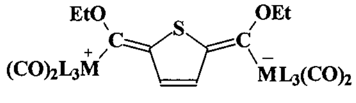
The crystal structure of the dichromium biscarbene complex **1** was confirmed by single crystal X-ray crystallography. The molecular structure and atom-labelling scheme is presented in Fig. 1, whereas selected bond lengths and angles are summarized in Table 2.

Table 2
Selected bond distances (Å) and angles (°) for **1**

Bond distances (Å)			
Cr1–C15	2.040(5)	C18–O12	1.330(6)
Cr2–C18	2.043(5)	C15–O11	1.319(5)
C11–C18	1.456(6)	C16–O11	1.447(6)
C11–C12	1.385(6)	C19–O12	1.443(6)
C11–S1	1.730(5)	Cr1–CO$_{trans}$	1.891(5)
C12–C13	1.388(6)	Cr1–CO$_{cis}$	1.894(6)
S1–C14	1.732(5)	Cr2–CO$_{trans}$	1.896(6)
C13–C14	1.371(6)	Cr2–CO$_{cis}$	1.895(6)
C14–C15	1.496(6)		
Bond angles (°)			
Cr1–C15–C14	124.3(4)	Cr2–C18–C11	125.3(4)
Cr1–C15–O11	130.4(4)	O12–C18–Cr2	129.2(3)
O11–C15–C14	105.2(4)	O12–C18–C11	105.5(4)
S1–C11–C12	109.3(4)	C12–C11–C18	130.4(5)
C11–C12–C13	114.8(5)	C13–C14–C15	129.8(5)
C12–C13–C14	112.6(5)	C18–Cr2–C(O)$_{trans}$	177.4(2)
C13–C14–S1	111.0(4)	C18–Cr2–C(O)$_{cis}$	91.9(2)
C11–S1–C14	92.3(2)	C15–Cr1–C(O)$_{trans}$	179.3(2)
C11–C18–O12	105.5(4)	C15–Cr1–C(O)$_{cis}$	91.9(3)

The thienylene ring, carbene carbons and metals are almost in a plane. The dihedral angles of Cr1–C15–C14–C13 and Cr2–C18–C11–C12 (13.0(8) and 11.7(8)°, respectively) are small which emphasizes the flat nature of the spacer ligand. This differs significantly from $(CO)_5Cr\{C(NMe_2)C_6H_4C(NMe_2)m\}$-$Fe(CO)_4$ where the reported structure displayed metal–carbene bonds perpendicular to the plane of the benzene ring [29]. The planar nature of the link in **1** is ideal for π-conjugation and a redistribution of electron density through the bridging biscarbene ligand. In **1**, the $Cr(CO)_5$ fragments are found on the same side of the thiophene ring, i.e. on the side opposite to the sulphur atom in the ring. By contrast, the $Cr(CO)_5$ fragments in $(CO)_5Cr\{C(OEt)C_6H_4–C_6H_4C(OEt)\}Cr(CO)_5$ are on opposite sides of the axis connecting the two carbene carbons [30].

Complex **1** shows structural features around the carbene carbon that are typical for other carbene complexes of chromium and the carbene substituents are in a staggered position with respect to the *cis*-carbonyls, thereby avoiding unfavourable steric interactions (examples: dihedral angles C6–Cr1–C15–C14, −61.1(5)°; C7–Cr1–C15–C14, 32.4(5)°, C4–Cr2–C18–C11, −57.6(5)°, C5–Cr2–C18–C11, 36.3(5)°) [31]. The Cr–C(carbene) distances of 2.04 Å are well in the range of Cr–C(carbene) distances (2.00–2.10 Å) reported for alkoxycarbene complexes of chromium and is the same as the 2.04(3) Å recorded for $[Cr\{C(OMe)Ph\}(CO)_5]$ [31]. There are no significant differences between the Cr–C(carbonyl) distances of the *cis*-carbonyls and the carbonyls *trans* to the carbene ligand. The carbon–carbon bond lengths in free thiophene are distinctly different and represent bond orders which are double (1.370(2)), single (1.424(2)) and double (1.370(2) Å). The corresponding distances in **1** are the same within experimental error, indicating a degree of delocalization in the thiophene ring in the solid state. The averaged distance of 1.38 Å lies between the characteristic bond distances of a $C(sp^2)–C(sp^2)$ single (1.46) and a $C(sp^2)–C(sp^2)$ double bond (1.32 Å) [32]. However, the C15–C14 and C18–C11 distances are almost typical single bond distances which represents a break in the delocalization of electron density between the thiophene ring and the carbene carbon atoms. Therefore, this data does not support a large contribution of the resonance structure below and conjugation from one metal via the bridging ligand to the second metal.



3. Experimental section

3.1. General details

All reactions were carried out under nitrogen with the use of standard Schlenk techniques [33]. Solvents were dried by usual procedures and distilled under nitrogen prior to use [34]. The starting materials $[Mn(\eta^5\text{-}C_5H_4R)(CO)_3]$ ($R = H$, CH_3), CS_2 and BuLi were purchased from Aldrich and used without further purification or standardization. Thiophene was purified [35] and triethyloxonium tetrafluoroborate prepared [36], as described previously. The method for the double lithiation of thiophene was taken from the literature [12]. Chromatography was performed on silica gel (0.063–0.200 mm) and the columns (1.5 × 40 cm) cooled by recycling cold (−20°C) *iso*-propanol through the column jacket. NMR spectra were recorded at −20°C on a Bruker AC-300 spectrometer with reference to the deuterium signal of the solvent employed. The ^1H and ^{13}C-NMR spectra were measured at 300.15 and 75.469 MHz, respectively. NMR solvents were degassed by several freeze-pump-thaw cycles, and NMR sample tubes were sealed under nitrogen. IR spectra were recorded as liquid solutions on a Bomen Michelson-100 FT spectrophotometer, and frequencies (cm^{-1}) were assigned relative to a polystyrene standard. Irradiation by UV-light was performed in a 200 cm^3 Pyrex flask equipped with a water cooled quartz finger and a Philips G3136E medium pressure mercury lamp as the UV-source. Mass spectra were recorded on a Perkin-Elmer RMU-6H instrument operating at 70 eV. Elemental analyses were carried out by the Analytical Division (PCMT) of the Council for Scientific and Industrial Research, Pretoria, South Africa.

3.2. Synthesis of the biscarbene complexes

3.2.1. Preparation of $[(CO)_5CrC(OEt)C_4H_2SC(OEt)Cr(CO)_5]$ (**1**)

In total 18.6 cm^3 of a 1.6 mol dm^{-3} hexane solution of butyllithium (27.3 mmol) was added to 3.7 cm^3 (24.7 mmol) of tetramethylethylenediamine (TMEDA) and stirred at 0°C for 15 min. To this mixture was added dropwise 0.99 cm^3 (12.4 mmol) of thiophene dissolved in 40 cm^3 of hexane at room temperature (r.t.). A white suspension gradually formed and the conversion was completed by refluxing the mixture for 30 min. The suspension was cooled to below 0°C and 40 cm^3 of THF was added. After further cooling to −40°C, 5.0 g (22.7 mmol) of $[Cr(CO)_6]$ was gradually added to the vigorously stirred mixture. The reaction mixture was allowed to reach r.t. and stirring was maintained for a further 15 min during which time the colour changed to dark brown. After the reaction had been completed, solvents were removed under reduced pressure, the residue was washed with cold hexane and the solid material dissolved in 40 cm^3 of dichloromethane. Triethyloxonium tetrafluoroborate (4.55 g, 24.7 mmol) dissolved in 30 cm^3 of dichloromethane, was carefully added to the stirred mixture at −30°C. The reaction mixture which had changed to a very dark purple colour, was washed through a filter containing anhydrous sodium sulphate and silica gel with dichloromethane. Volatile materials were removed under reduced pressure. The residue was dissolved in 50 cm^3 of dichloromethane, adsorbed onto silica gel in the cold and dried in vacuo. The resulting solid material was placed on a prepacked column. The product was purified by starting with hexane as eluting agent, and gradually increasing the polarity by adding dichloromethane until the product could be isolated using a mixture of hexane and dichloromethane (500 cm^3 hexane and 10 cm^3 dichloromethane). Three bands separated. The first yellow band isolated, yielded 0.77 g (15.3%) of the butyl carbene complex, $[Cr\{C(OEt)Bu\}(CO)_5]$ [14]. The second orange band afforded 1.02 g (20.4%) of the known thienylcarbene complex, $[Cr\{C(OEt)C_4H_3S\}(CO)_5]$ [13]. The third, purple zone was isolated after two minor bands (less 2%) were discarded and afforded 3.04 g (7.5 mmol, 60.7%) of the dinuclear biscarbene complex $[(CO)_5CrC(OEt)C_4H_2SC(OEt)Cr(CO)_5]$ (**1**).

Complex **1**: Anal. Calc. for $C_{20}H_{12}O_{12}SCr_2$: C 41.39; H 2.08%. Found: C 41.51; H 2.17%. MS (EI): *m*/*z* 580 [M^+], stepwise fragmentation of ten carbonyls lead to 300 [M^+−10CO], 271 [M^+−10CO−Et], 242 [M^+−10CO−2Et], 214 [M^+−11CO−2Et], [M^+−12CO−2Et]. ^{13}C-NMR ($CDCl_3$, ppm): δ 321.9 (carbene), 223.7 (*trans* CO), 216.5 (*cis* CO), 157.7 (C2/5), 137.1 (C3/4), 77.4 (CH_2), 15.2 (CH_3).

3.2.2. Preparation of $[(\eta^5\text{-}C_5H_5)(CO)_2MnC(OEt)C_4H_2SC(OEt)Mn(\eta^5\text{-}C_5H_5)(CO)_2]$ (2)

In total 7.5 cm^3 of a 1.6 mol/dm^3 (12 mmol) hexane solution of butyllithium was added to 1.8 cm^3 (12 mmol) of TMEDA and stirred at 0°C for 15 min. This mixture was added dropwise to 0.5 cm^3 (6 mmol) of thiophene dissolved in 40 cm^3 of hexane at r.t. This mixture was treated as above and after cooling to −40°C, 2.04 g (10 mmol) of $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$ was gradually added to the vigorously stirred solution. The temperature was allowed to reach r.t. and stirring was maintained for a further 45 min during which time the colour changed to dark brown. After the reaction had completed all solvents were removed under reduced pressure, the residue was washed with cold hexane and the solid material dissolved in 40 cm^3 of dichloromethane. Triethyloxonium tetrafluoroborate (2.2 g, 12 mmol), dissolved in 15 cm^3 of dichloromethane, was carefully added to the stirred mixture at −30°C. The reaction mixture, which changed colour to a very dark red–purple, was washed with dichloromethane through a filter containing anhydrous sodium sulphate and silica gel. The mixture was treated as above for **1** and subjected to column chromatography. The purple product was isolated after two minor bands (less 3%) were discarded and this afforded 2.2 g (4 mmol, 80%) of the dinuclear biscarbene complex $[(\eta^5\text{-}C_5H_5)(CO)_2MnC(OEt)C_4H_2SC(OEt)Mn(\eta^5\text{-}C_5H_5)(CO)_2]$ (**2**).

Complex **2**: Anal. Calc. for $C_{24}H_{22}O_6SMn_2$: C, 52.56; H, 4.05%. Found: C, 52.87; H 4.30%. MS (EI): *m*/*z* 548 [M^+], 436 [M^+−4CO], 407 [M^+−4CO−Et], 378 [M^+−4CO−2Et], 322 [M^+−6CO−2Et]. ^{13}C-NMR ($CDCl_3$, ppm): δ 319.6 (carbene), 230.5 (CO), 157.2 (C2/5), 132.4 (C3/4), 74.0 (CH_2), 15.3 (CH_3), 84.6 (Cp).

3.2.3. Preparation of $[(\eta^5\text{-}C_5H_4Me)(CO)_2MnC(OEt)C_4H_2SC(OEt)Mn(\eta^5\text{-}C_5H_4Me)(CO)_2]$ (3)

A total of 17.2 cm^3 of a 1.6 mol/dm^3 hexane solution of butyllithium (27.5 mmol) and 4.0 cm^3 (27 mmol) TMEDA was reacted with 1.1 cm^3 (13.5 mmol) thiophene as above. The complex $[Mn(\eta^5\text{-}C_5H_4CH_3)(CO)_3]$ (3.3 cm^3, 23 mmol) was treated with the dilithiated reagent and the reaction, alkylation and purification of the final product proceeded according to the method described for **2**. In total 4.6 g (8 mmol, 70%) of the red–purple product $[(\eta^5\text{-}C_5H_4CH_3)(CO)_2MnC(OEt)C_4H_2SC(OEt)Mn(\eta^5\text{-}C_5H_4CH_3)(CO)_2]$ (**2**) was obtained.

Complex **3**: MS (EI): *m*/*z* 576 [M^+], 464 [M^+−4CO], 435 [M^+−4CO−Et], 406 [M^+−4CO−2Et], 350 [M^+−6CO−2Et]. ^{13}C-NMR ($CDCl_3$, ppm): δ 319.5 (carbene), 230.8 (CO), 157 (C2/5), 132.5 (C3/4), 73.9 (CH_2), 15.3 (CH_3), 84.4 and 83.3 (Cp), 13.5 (CH_3)

3.3. Decomposition studies

3.3.1. Modification of $[(CO)_5CrC(OEt)C_4H_2SC(OEt)Cr(CO)_5]$ in refluxing carbon disulphide

Complex **1** (0.51 g, 0.9 mmol) was dissolved in 300 cm^3 of CS_2. The solution was refluxed for 3 h, after which time the reaction mixture had changed colour from purple to reddish–pink. Thin layer chromatography revealed that the starting dinuclear biscarbene complex had disappeared and that two major products were present in the reaction mixture. The reaction was stopped and the solvent removed under reduced pressure. The two bands were separated with column chromatography using as eluting agent petroleum ether and dichloromethane in a 1:1 mixture. An unstable pink product was isolated, which decomposed during purification and spectroscopy. The second red product was stable and fully characterized as [Cr{C(OEt)C_4H_2S-C(O)OEt}$(CO)_5$] (**4**). Yield 0.15 g (31%).

Complex **4**: Anal. Calc. for $C_{15}H_{12}O_8SCr$: C, 44.59; H, 3.00%. Found: C, 44.71; H 3.11%. MS (EI): *m*/*z* 404 [M^+], 376 [M^+–CO], 348 [M^+–2CO], 292 [M^+–4CO], 264 [M^+–5CO], 235 [M^+–5CO–Et], 206 [M^+–5CO–2Et], 178 [M^+–6CO–2Et]. ^{13}C-NMR ($CDCl_3$, ppm): δ 320.2 (carbene), 233.3 (*trans* CO), 216.6 (*cis* CO), 162.3 (C2), 158.4 (C5), 138.8 (C3), 133.0 (C4), 77.5 (CH_2), 15.9 (CH_3), 61.9 (CH_2), 14.2 (CH_3).

3.3.2. Reaction of (η^5-C_5H_4R)$(CO)_2$MnC(OEt)C_4H_2SC-(OEt)Mn(η^5-C_5H_4R)$(CO)_2$] (R = H or Me) in refluxing CS_2

Complex **2** (0.5 g, 0.9 mmol) was dissolved in 30 cm^3 of CS_2. The solution was refluxed for 3 h, after which thin layer chromatography revealed that three major products were present in the reaction mixture. The reaction was stopped and the solvent removed under reduced pressure. The three bands were separated with column chromatography using as eluting agent petroleum ether and dichloromethane in a 1:1 mixture. The first band afforded the known complex [Mn(η^5-C_5H_5)$(CO)_2$(CS)] (0.09 g, 0.3 mmol, 23%) [17]. The second band afforded 0.12 g (17%, 0.3 mmol) of [Mn(η^5-C_5H_5)$(CO)_2${C(OEt)C_4H_2SC(O)OEt}] (**5**) and the third 0.28 g (38%, 0.7 mmol) of [Mn(η^5-C_5H_5)$(CO)_2${C(OEt)C_4H_2SC(S)OEt}] (**7**). A fourth, pink product, that formed in a very low yield was not isolated. The experiment was repeated, both under nitrogen and in air, but the yields of the pink product were even lower. [Mn(η^5-C_5H_5)$(CO)_2$(CS)]: *m*/*z* 220 [M^+], IR(CS_2, cm^{-1}): ν(CO) 2001, 1949. ν(CS) 1268. ^{1}H-NMR (CS_2, ppm): 4.49 (s, Cp). Complex **5**. Anal. Calc. for $C_{17}H_{17}O_5SMn$: C, 52.62; H, 4.41%. Found: C, 52.91; H 4.70%. MS (EI): *m*/*z* 388 [M^+], 332 [M^+–2CO], 274 [M^+–2CO–2Et], 218 [M^+–4CO–2Et].

Complex **7**: Anal. Calc. for $C_{17}H_{17}O_4S_2Mn$: C, 50.54; H, 4.21%. Found: C, 50.90; H 4.47%. MS (EI): *m*/*z* 404 [M^+], 348 [M^+–2CO], 290 [M^+–2CO–2Et], 246 [M^+–2CO–2Et–CS], 218 [M^+–3CO–2Et–CS]. ^{13}C-NMR ($CDCl_3$, ppm): δ 304.2 (carbene), 230.7 (CO), 182.1 (C(S)), 155.0 (C2), 150.0 (C5), 139.0 (C3), 132.9 (C4), 73.7 (CH_2), 15.2 (CH_3), 53.4 (CH_2), 14.1 (CH_3), 84.2 (Cp).

The same procedure was used for **3**, but in this case 0.58 g (1 mmol) of **3** afforded 0.08 g (0.3 mmol, 17%) of [Mn(η^5-C_5H_4Me)$(CO)_2$(CS)] [17], 0.16 g (20%, 0.4 mmol) of [Mn(η^5-C_5H_4Me)$(CO)_2${C(OEt)C_4H_2SC(O)-OEt}] (**6**) and 0.21 g (25%, 0.5 mmol) of [Mn(η^5-C_5H_4Me)$(CO)_2${C(OEt)C_4H_2SC(S)OEt}] (**8**) and unreacted **3** (0.1 g, 17%, 0.2 mmol). Complex **6** was the major product under these conditions.

Complex **6**: MS (EI): *m*/*z* 402 [M^+], 346 [M^+–2CO], 288 [M^+–2CO–2Et], 232 [M^+–4CO–2Et].

Complex **8**: MS (EI): *m*/*z* 418 [M^+], 362 [M^+–2CO], 304 [M^+–2CO–2Et], 260 [M^+–2CO–2Et–CS], 232 [M^+–3CO–2Et–CS].

3.3.3. Decomposition studies of [$(CO)_5$Cr{C(OEt)C_4H_2SC(OEt)Cr$(CO)_5$] in acetone

Complex **1** (0.5 g, 0.9 mmol) was dissolved in 400 cm^3 acetone and stirred at r.t. The reaction was continuously monitored with thin layer chromatography. After 4 h, three products were visible. The solvent was removed under reduced pressure and the products were purified with column chromatography and, using a 1:1 mixture of dichloromethane and hexane as eluting medium. The first band removed and recovered was unreacted starting compound, yield 0.15 g (30.2%). The second pale yellow band represented a compound in very low yield and was not collected. The third band was collected and characterized as [Cr$(CO)_5${C(OEt)-C_4H_2SC(O)OEt}] **4** in 0.2 g (59%) yield.

3.3.4. Decomposition studies of (η^5-C_5H_4R)$(CO)_2$MnC-(OEt)C_4H_2SC(OEt)Mn(η^5-C_5H_4R)$(CO)_2$] (R = H or Me) in acetone

Complex **2** or **3** (0.5 g, 0.9 mmol) was dissolved in acetone and the mixture exposed to UV rays for 2 h during which time a colour change was detected and thin layer chromatography showed that only one product had formed. The product was filtered through silica gel and the solvent removed under reduced pressure leaving a red–brown residue of [Mn(η^5-C_5H_4R)$(CO)_2${C(OEt)C_4H_2SC(O)OEt] R = H **5** or Me **6**. The yield of **5** was 0.33 g (0.85 mmol, 94% based on a ratio of 1:1 for **2**:**5**).

3.4. Crystal structure determination

Crystal parameters and experimental details for compound **1** are listed in Table 3. The data were collected on an Enraf–Nonius CAD4 diffractometer by using graphite monochromatized Mo–K_α (λ = 0.7107 Å) radiation at r.t. Accurate unit cell parameters were obtained by least-squares methods from the position of 25 centred reflections for **1**. Three standard reflections were monitored after every 200 reflections were measured. Reflections were corrected for Lorentz-polarization and absorption effects. The structures were solved by conventional Patterson and Fourier techniques using SHELX86 [37]. The non-hydrogen atoms were refined anisotropically [38], and the hydrogen atoms were placed in calculated positions with common isotropic thermal parameters which were also refined. Atomic scattering factors were taken from the literature [39]. A perspective view of the molecule was prepared with ORTEP [40].

Table 3
Crystal data, collection and refinement details for **1**

Empirical formula	$Cr_2C_{20}H_{12}O_{12}S$
Molecular weight	580
Crystal size (mm)	$0.17\times0.17\times0.24$
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	21.593(12)
b (Å)	10.235(3)
c (Å)	22.531(12)
α (°)	90
β (°)	92.06(4)
γ (°)	90
Z	8
V (Å^3)	4976(1)
$D_{calc.}$ (g cm^{-3})	1.55
μ (mm^{-1})	9.47
Radiation, λ (Å)	Mo–K$_\alpha$ (0.7107)
Temperature (K)	298
Scan type (ω: 2θ)	1:1 ω-2θ
Scan range, θ (°)	$3\leq\theta\leq30$
hkl ranges	0:30; 0:14; -31:31
Maximum scan speed (deg min^{-1})	5.49
Scan angle ($\omega+0.34\tan\theta$)°	0.45
Reflections collected	7771
Unique reflections ($>3\sigma(I)$)	3267
Parameters	325
$R(F)$, Rw[a]	0.053, 0.035

[a] $R(F)=\Sigma(|F_o|-|F_c|)\Sigma|F_o|$; $Rw=[\Sigma w(|F_o^2|-|F_c^2|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, $w=1/\sigma^2|F_o|$.

4. Supplementary material

Synthesis, characterization and decomposition for thienylene bridged dinuclear biscarbene complexes of manganese and chromium in refluxing carbon disulphide and acetone. Copies of supplementary data are available upon request from the author.

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