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# Synthesis of tricarbonyl $\eta^6$ - and $\eta^5$ -[(3-thiophenyl)organo]chromium and -manganese complexes

Damien Prim<sup>a</sup>, José Giner Planas<sup>b</sup>, Audrey Auffrant<sup>c</sup>, Françoise Rose-Munch<sup>c,\*</sup>,  
Eric Rose<sup>c</sup>, Jacqueline Vaissermann<sup>d</sup>

<sup>a</sup> Laboratoire SIRCOB, UMR CNRS 8086, Bâtiment Lavoisier, Université Versailles-Saint-Quentin, 45 Avenue des Etats-Unis, 78035 Versailles Cedex, France

<sup>b</sup> ICMAB-CSIC, Campus UAB, 08193 Bellaterra (Barcelona), Spain

<sup>c</sup> Laboratoire de Synthèse Organique et Organométallique, UMR CNRS 7611, case courrier 181, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France

<sup>d</sup> Laboratoire de Chimie Inorganique et Matériaux Moléculaires, UMR CNRS 7071, case courrier 42, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France

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## Abstract

The syntheses of tricarbonyl  $\eta^6$ -[(3-thiophenyl)arene]chromium **1a**, **1b** and  $\eta^5$ -[(3-thiophenyl)cyclohexadienyl]manganese complexes **2** are reported using a Stille cross-coupling methodology. A two-step strategy involving a Stille reaction–*exo*-hydride abstraction sequence allowed selective access to cationic tricarbonyl  $\eta^6$ -[(3-thiophenyl)arene]manganese complex **3**. <sup>1</sup>H-NMR data of these 3-thiophenylchromium and manganese complexes are presented as well as a comparison with the corresponding 2-thiophenyl-substituted derivatives described in the literature. The crystal structure determinations of 3-thiophenyl and 2-thiophenyl- $\eta^6$ -(arene)Cr(CO)<sub>3</sub> complexes showing the conformations of the Cr(CO)<sub>3</sub> tripods are also reported.

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**Keywords:** Stille cross-coupling; Thiophenyl; Chromium

## 1. Introduction

Although  $\eta^6$ -[(thiophenyl)arene]Cr(CO)<sub>3</sub> complexes have been known since the early 1970s [1], such metallocene-type (Fe, Cr, Mn) thiophenic fragments attracted much attention only very recently due to their beneficial contribution as building blocks for mono- and dinuclear organometallic complexes with potential high optical properties [2]. Indeed, promising results obtained by combining thiophene units and metallocene-type complexes are undoubtedly related to the moderate resonance energy of thiophene and to the polarizing

ability of the organometallic entities. In most of these structures, '( $\eta^6$ -arene)M' fragments (M = Cr, Fe) were bonded to one of the  $\alpha$ -carbons of the thiophene ring [3]. In contrast, examples of complexes linked to one of the  $\beta$ -carbons are still scarce [4].

As part of our ongoing interests in palladium-catalyzed reactions of  $\eta^5$ -chlorocyclohexadienylMn(CO)<sub>3</sub> and  $\eta^6$ -(chloro)areneCr(CO)<sub>3</sub> complexes [5,6], we sought to improve our method to introduce organometallic entities at the  $\beta$ -position of thiophenes, keeping  $\alpha$ -positions free for further functionalizations. We report herein the preparation and the study, in solution and in the solid state, of new neutral  $\eta^6$ -[(3-thiophenyl)arene]Cr(CO)<sub>3</sub> and  $\eta^5$ -[(3-thiophenyl)cyclohexadienyl]Mn(CO)<sub>3</sub> complexes as well as the corresponding cationic  $\eta^6$ -areneMn(CO)<sub>3</sub> derivative.

\* Corresponding author. Tel.: +33-1-4427-6235; fax: +33-1-4427-5504.

E-mail address: [rosemun@ccr.jussieu.fr](mailto:rosemun@ccr.jussieu.fr) (F. Rose-Munch).

## 2. Results and discussion

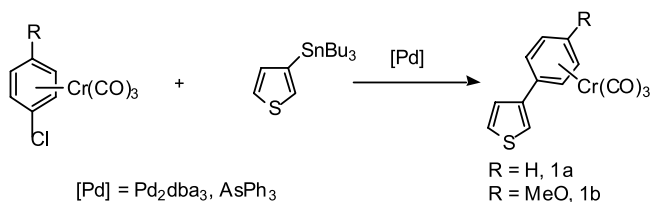
### 2.1. Syntheses of complexes **1a**, **1b**, **2** and **3**

Preparation of  $\eta^6$ -[(thiophenyl)arene]Cr(CO)<sub>3</sub> complexes by thermal complexation of the Cr(CO)<sub>3</sub> moiety to the six-membered ring of the appropriate phenylthiophene compounds was reported 30 years ago [1]. However the low yields of these reactions (7% [7]) prevented the use of these complexes as building blocks for other more elaborate organometallic frameworks. We recently developed a new and convenient methodology which greatly increased the yields of these complexes using Pd-catalyzed Stille cross-coupling reaction and allowed the synthesis of the previously unknown cationic Mn analogs [5,6]. We now extend this methodology to the preparation of the related  $\beta$ -substituted-thiophene complexes  $\eta^6$ -[(3-thiophenyl)arene]Cr(CO)<sub>3</sub> **1a**, **1b** [8], and  $\eta^6$ -[(3-thiophenyl)arene]Mn(CO)<sub>3</sub> **3** via the formation of the  $\eta^5$ -cyclohexadienyl complex **2**.

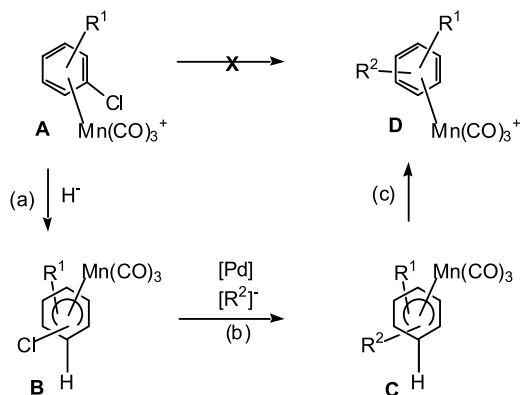
The reaction of  $\eta^6$ -(chlorobenzene)Cr(CO)<sub>3</sub> or  $\eta^6$ -(*p*-chloroanisole)Cr(CO)<sub>3</sub> complex with 3-tributylstannylthiophene under Stille-coupling reaction conditions using the modified catalytic system Pd<sub>2</sub>(dba)<sub>3</sub>, AsPh<sub>3</sub> [6] lead to the formation of complex **1a** or **1b** in 55% and 40% yields, respectively (Scheme 1).

As already evidenced, cationic ( $\eta^6$ -chloroarene)Mn(CO)<sub>3</sub> complexes behave similarly to their chromium neutral analogues towards Pd(0) complexes [9]. Indeed, an oxidative addition adduct could be isolated and characterized. However, this first intermediate of the catalytic cycle has been found to be unreactive under classical coupling conditions, precluding Pd-catalyzed reactions on cationic ( $\eta^6$ -chloroarene)Mn(CO)<sub>3</sub> complexes. An elegant alternative (Scheme 2) consists in the formation of the neutral  $\eta^5$ -(chlorocyclohexadienyl)Mn(CO)<sub>3</sub> complexes **B** by addition of hydride to cationic complex **A** (step a) then, after Pd-catalyzed functionalization (step b) of complexes **B** to form **C**, the *exo*-hydride abstraction (step c) affords the desired substituted cationic ( $\eta^6$ -arene)Mn(CO)<sub>3</sub> complexes **D** [5] (Scheme 2).

One advantage of this methodology is that unlike the cationic ( $\eta^6$ -arene)Mn(CO)<sub>3</sub> complexes, neutral  $\eta^5$ -(chlorocyclohexadienyl)Mn derivatives are soluble in organic solvents and can be easily purified by column chromatography. Thus, this strategy applied to Stille



Scheme 1. Synthesis of Cr complexes **1a** and **1b**.



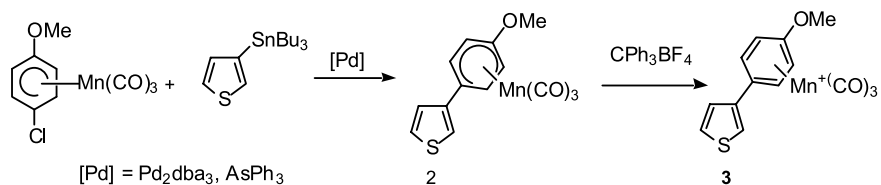
Scheme 2. Pd-catalyzed coupling reactions applied to cationic  $\eta^6$ -

cross-coupling of 3-tributylstannyl-thiophene with  $\eta^5$ -[1-chloro-4-methoxy-cyclohexadienyl]Mn(CO)<sub>3</sub> gave the desired new neutral complex  $\eta^5$ -[(3-thiophenyl)*p*-anisole]Mn(CO)<sub>3</sub> (**2**). In a second step, *exo*-hydride abstraction by Ph<sub>3</sub>C<sup>+</sup>BF<sub>4</sub><sup>-</sup> afforded the new cationic [ $\eta^6$ -[(3-thiophenyl)*p*-anisole]Mn(CO)<sub>3</sub>][BF<sub>4</sub><sup>-</sup>] (**3**) in 67% yield (Scheme 3).

### 2.2. <sup>1</sup>H-NMR study

Having these new complexes in hand, we wanted to know whether there is any influence of the substitution position ( $\alpha$  or  $\beta$ ) of the thienyl group on the chemical shifts of the coordinated arene protons [10]. First of all, the NMR data of monosubstituted complexes **1a** and **4a** (Table 1) present very similar chemical shifts for the protons of the coordinated cycles (5.65, 5.48, 5.28 ppm and 5.68, 5.47, 5.26 ppm for **1a** and **4a**, respectively). Comparison with the chemical shift of the unsubstituted benzene protons in  $\eta^6$ -(benzene)Cr(CO)<sub>3</sub> **10** evidenced that substitution by thiophenyl rings allows H2 and H3 protons to resonate at higher frequencies, with a maximum difference of chemical shift  $\delta$ H- $\delta$ H[C<sub>6</sub>H<sub>6</sub>Cr(CO)<sub>3</sub>] reaching 0.42 ppm for **4a** [11].

Then, we compared the NMR data of the disubstituted complex series: **1b**, **2**, **3** with the analogous complexes **4b** [6a], **5** and **6** [5] which were obtained by coupling reactions between 2-tributylstannyl-thiophene and the same starting Cr and Mn complexes (Table 2). Again, no noticeable change was observed for proton chemical shifts of Cr complexes **1b** and **4b** (5.87, 5.21 ppm and 5.92, 5.20 ppm, respectively, entries 1 and 2) neither for those of  $\eta^6$  Mn complexes **2** and **5** (5.22, 5.80 ppm and 5.27, 5.76 ppm, respectively, entries 3 and 4) nor for those of  $\eta^6$  Mn complexes **3** and **6** (7.65, 6.67 ppm and 7.58, 6.63 ppm respectively, entries 5 and 6). Furthermore, by comparison with the NMR data of monosubstituted arene complexes **7** [12], **8** and **9** [13] (Scheme 4, Table 3), the chemical shifts of Cr complexes **1b** and **4b** resonated at higher frequencies than those of

Scheme 3. Synthesis of Mn complexes **2** and **3**.Table 1  
Selected <sup>1</sup>H-NMR data of complexes **1a** and **4a**

Entry	Complex	H2	H3	H4	$\delta(\text{Hi})-\delta_0(\text{i})^b$
1	<b>1a</b> <sup>a</sup>	5.65	5.48	5.28	0.39 (2) 0.22 (3) 0.02 (4)
2	<b>4a</b> <sup>a</sup>	5.68	5.47	5.26	0.42 (2) 0.19 (3) 0.00 (4)

<sup>a</sup> Solvent: CDCl<sub>3</sub>.<sup>b</sup> C<sub>6</sub>H<sub>6</sub>Cr(CO)<sub>3</sub>: **10**,  $\delta_0 = 5.26$  ppm in CDCl<sub>3</sub>,  $\delta(\text{Hi})-\delta_0$ : deshielding effect if positive.Table 2  
Selected <sup>1</sup>H-NMR data of complexes **1b**, **4b**, **2**, **5**, **3** and **6**

Entry	Complex	H2	H3
1	<b>1b</b> <sup>a</sup>	5.87	5.21
2	<b>4b</b> <sup>a</sup>	5.92	5.20
3	<b>2</b> <sup>a</sup>	5.22	5.80
4	<b>5</b> <sup>a</sup>	5.27	5.76
5	<b>3</b> <sup>b</sup>	7.65	6.67
6	<b>6</b> <sup>b</sup>	7.58	6.63

<sup>a</sup> Solvent: CDCl<sub>3</sub>.<sup>b</sup> Solvent: C<sub>3</sub>D<sub>6</sub>O.

complex **7** with a larger deviation for protons *ortho* to the thiophenyl residue (5.87 and 5.92 ppm for H<sub>2,6</sub> of **1b** and **4b** (Table 2, entries 1 and 2) compared to 5.54 ppm for H<sub>2,6</sub> of **7** (Table 3, entry 1)). The same observation could be made for H<sub>2,6</sub> protons of complexes **3** and **6** (7.65 and 7.58 ppm, Table 2, entries 5 and 6) in comparison with H<sub>2,6</sub> protons of complex **9** (7.14 ppm, Table 3, entry 3) as well as for H<sub>2</sub> protons of Mn complexes **2** and **5** (5.22 and 5.27 ppm, Table 2, entries 3 and 4) and H<sub>2</sub> proton of complex **8** (4.79 ppm, Table 3, entry 2).

All these data stress that the thiophenyl groups have a similar electronic effect on the proton chemical shifts of the six-membered ring of Cr and Mn complexes whichever carbon ( $\alpha$  or  $\beta$ ) is linked to the coordinated arenes.

### 2.3. X-ray structures of complexes **1a** and **4a**

In order to know more about the conformation of the Cr(CO)<sub>3</sub> tripod with respect to the arene ring, we tried

to get crystals of complexes **1a**, **1b**, and **4a** (X-ray structure of **4b** having been already described [6a]).

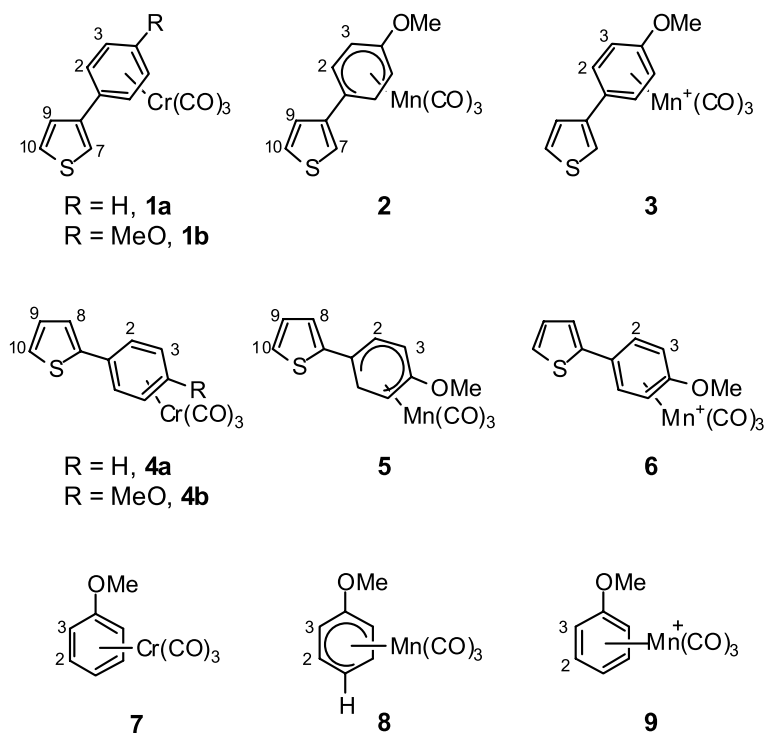
We did not succeed in crystallizing **1b**, but fortunately we obtained monocrystals of **1a** and **4a** whose ORTEP views are shown Figs. 1 and 2. Two main features are worthy of note. First of all, the thiophenyl groups are in the same plane as the six-membered rings for both of them. Furthermore the conformation of Cr(CO)<sub>3</sub> tripods are very similar, almost staggered with respect to the thiophenyl groups. Thus, the values of the torsion angles C(5)–C(100)–Cr–C(11), C(7)–C(100)–Cr–C(13) and C(9)–C(100)–Cr–C(12) for **1a** (C(100) being the center of the six-membered ring) are 26°. The corresponding values C(5)–C(100)–Cr–C(13), C(7)–C(100)–Cr–C(12) and C(9)–C(100)–Cr–C(11) for **4a** are 28, 28 and 27°, respectively. These data clearly show that the solid state conformations of the Cr(CO)<sub>3</sub> entities are almost the same regardless of the carbon ( $\alpha$  or  $\beta$ ) of the thiophenyl group which is linked to the coordinated arene. Furthermore, these angles have slightly larger values than the corresponding ones of complex **4b** [6a]: 23, 22 and 23°, respectively, which is in good agreement with the electron-donor effect of the methoxy group which usually leads to a more eclipsed conformation of Cr(CO)<sub>3</sub> tripod [14].

In conclusion, new (3-thiophenyl)-arene and -cyclohexadienyl chromium and manganese complexes have been prepared by a modified Stille-coupling reaction. The new Cr and Mn  $\eta^6$ -arene complexes exhibit similar NMR data for the arene moiety to that for the (2-thiophenyl)-arene analogs and the Cr  $\eta^6$ -arene complexes show the same Cr(CO)<sub>3</sub> conformation as the (2-thiophenyl)-arene Cr analogs. These complexes, whose  $\alpha$  positions of the thiophenyl groups could be functionalized in view of a more sophisticated framework, could be considered as interesting versatile building blocks for new materials.

## 3. Experimental

### 3.1. Materials and instrumentation

All reactions and manipulations were routinely performed under nitrogen atmosphere and protected from exposure to light. Et<sub>2</sub>O was dried over sodium benzophenone ketyl, but other solvents were used as received.



Scheme 4. Complexes studied in Tables 1–3 and atom numbering.

Table 3  
Selected  $^1\text{H-NMR}$  data for compounds **7**, **8** and **9**

Entry	Complex	H2	H3	H1
1	<b>7</b> <sup>a</sup>	5.54	5.10	4.86
2	<b>8</b> <sup>a</sup>	4.79	5.81	2.29
3	<b>9</b> <sup>b</sup>	7.14	6.44	6.28

<sup>a</sup> Solvent:  $\text{CDCl}_3$ .<sup>b</sup> Solvent:  $\text{C}_3\text{D}_6\text{O}$ .

The starting materials were prepared by the literature methods: tricarbonyl(Cl-benzene)chromium [12], tricarbonyl(4-Cl-anisole) chromium [12]. Other reactants listed in the text were purchased from Strem Chemicals, Inc. and used as received.  $^1\text{H}$ - and  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were obtained on Bruker AC200, AC300 or DRX500 spectrometer. Elemental analyses were performed by Le Service de Microanalyses de l'Université Pierre et Marie Curie.

### 3.2. Preparation of complexes **1a**, **1b**, **2** and **3**

#### 3.2.1. General method for the cross-coupling reactions: tricarbonyl- $\eta^6$ -(3-thiophenyl)benzene-chromium (**1a**)

A typical reaction procedure is as follows:  $\text{Pd}_2(\text{dba})_3$  (107.2 mg, 0.117 mmol) and  $\text{AsPh}_3$  (125.5 mg, 0.410 mmol) were added successively to tricarbonyl(Cl-benzene)chromium complex (575.2 mg, 2.32 mmol) and 10 ml of anhydrous DMF. After 30 min at room temperature (r.t.), 3-tributylstannylthiophene (868.1 mg, 2.33 mmol)

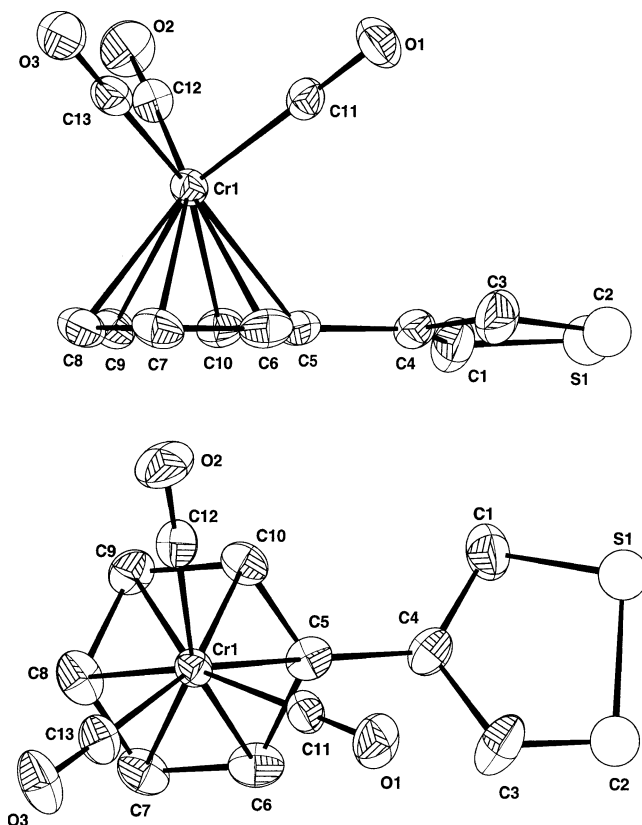


Fig. 1. ORTEP views of complex **1a** (thermal ellipsoids are at 30% probability). Selected bond lengths ( $\text{\AA}$ ) and dihedral angles ( $^\circ$ ): Cr–C(5), 2.230(7); Cr–C(6), 2.221(8); Cr–C(7), 2.215(8); Cr–C(8), 2.209(9); Cr–C(9), 2.212(8); Cr–C(10), 2.215(8); C(4)–C(5), 1.49(1). C(5)–C(100)–Cr(1)–C(11) = C(7)–C(100)–Cr(1)–C(13) = C(9)–C(100)–Cr(1)–C(12) = 26.

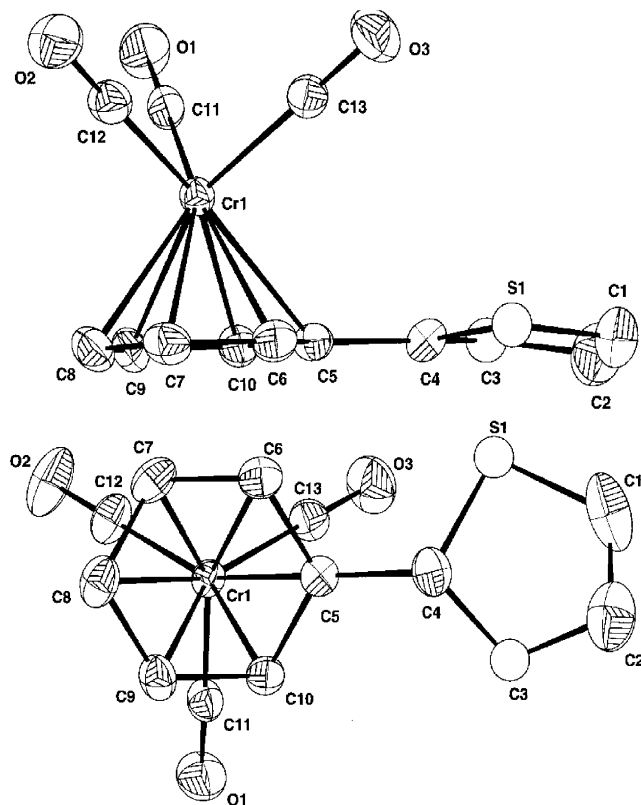


Fig. 2. ORTEP views of complex **4a** (thermal ellipsoids are at 30% probability). Selected bond lengths (Å) and dihedral angles (°): Cr–C(5), 2.244(4); Cr–C(6), 2.220(5); Cr–C(7), 2.211(5); Cr–C(8), 2.222(5); Cr–C(9), 2.204(5); Cr–C(10), 2.216(4); C(4)–C(5), 1.460(7). C(5)C(100)–Cr–C(13) = 28; C(7)–C(100)–Cr–C(12) = 18; C(9)–C(100)–Cr–C(11) = 27.

was added and the reaction mixture was stirred at r.t. for 22 h. The reaction mixture was poured into 100 ml of iced water, and extracted three times with 50 ml of Et<sub>2</sub>O. The combined organic phases were dried over magnesium sulfate, filtered with celite and evaporated under reduced pressure. The residue was then purified by flash chromatography on silica gel (petroleum ether–Et<sub>2</sub>O, 95/5) to afford complex **1a** ( $R_f=0.2$ ) as a yellow crystalline solid (375 mg, 1.25 mmol): yield 55%. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): δ 7.39 (m, 2H, *H7* and *H9*), 7.21 (m, 1H, overlapped with residual CHCl<sub>3</sub>, *H10*), 5.65 (d,  $J=6.5$  Hz, 2H, *H2*), 5.48 (t,  $J=6.0$  Hz, 2H, *H3*), 5.28 (t,  $J=5.8$  Hz, 1H, *H4*). <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>): 77.7 (*C4*), 91.3 (*C3* and *C5*), 93.3 (*C2* and *C6*), 105.6 (*C1*), 122.7 (*C10*), 126.1 (*C7*), 127.4 (*C8*), 130.9 (*C9*), 233.2 (*CO*).

### 3.2.2. Tricarbonyl-η<sup>6</sup>-[1-(3-thiophenyl)-4-anisole]-chromium (**1b**)

Pd<sub>2</sub>(dba)<sub>3</sub> (95.6 mg, 0.104 mmol); AsPh<sub>3</sub> (115.2 mg, 0.376 mmol); tricarbonyl(4-anisole)chromium complex (577.0 mg, 2.07 mmol); DMF (10 ml); 3-tributylstannylthiophene (782.4 mg, 2.10 mmol). Work up as in the previous reaction afforded a residue which was purified

by flash chromatography on silica gel (cyclohexane–diethyl ether 50/50) to afford complex **1b** ( $R_f=0.62$ ) as a yellow crystalline solid (270 mg, 0.83 mmol): yield 40%. Anal. Calc. for C<sub>14</sub>H<sub>10</sub>CrO<sub>4</sub>S: C, 51.53; H, 3.09. Found: C, 51.50; H, 3.10%. IR (C<sub>6</sub>H<sub>6</sub>, cm<sup>-1</sup>): 1956 (CO), 1890 (CO). <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): 7.33 (m, 2H, *H7* and *H9*), 7.17 (m, 1H, overlapped with residual CHCl<sub>3</sub>, *H10*), 5.87 (d,  $J=6.0$  Hz, 2H, *H2*), 5.21 (d,  $J=6.0$  Hz, 2H, *H3*), 3.72 (s, 3H, *OCH*<sub>3</sub>). <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>): 56.8 (*OCH*<sub>3</sub>), 80.4 (*C3* and *C5*), 95.8 (*C2* and *C6*), 99.8 (*C1*), 122.7 (*C10*), 126.9 (*C7*), 128.2 (*C8*), 129.4 (*C9*), 143.7 (*C4*), 233.2 (*CO*).

### 3.2.3. Tricarbonyl-η<sup>5</sup>-[1-(3-thiophenyl)-4-MeO-cyclohexadienyl]-manganese (**2**)

Pd<sub>2</sub>(dba)<sub>3</sub> (42.8 mg, 0.047 mmol); AsPh<sub>3</sub> (51.8 mg, 0.169 mmol); tricarbonyl(η<sup>5</sup>-4-Cl-cyclohexadienyl)-manganese (266.5 mg, 0.919 mmol); anhydrous DMF (6 ml); 3-tributylstannylthiophene (342.7 mg, 0.920 mmol). Work up as in the previous reactions afforded a residue which was purified by flash chromatography on silica gel (petroleum ether–Et<sub>2</sub>O 95/5) to afford complex **2** as a yellow oil (152 mg, 0.460 mmol): yield 50%. Anal. Calc. for MnC<sub>14</sub>H<sub>11</sub>O<sub>4</sub>S: C, 50.92; H, 3.36. Found: C, 50.76; H, 3.73%. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): δ 7.26 (dd,  $J=5.0, 3.0$  Hz, 1H, *H9*), 6.96 (dd,  $J=3.0, 1.5$  Hz, 1H, *H7*), 6.87 (dd,  $J=5.2, 1.5$  Hz, 1H, *H10*), 5.80 (dd,  $J=5.9, 2.5$  Hz, 1H, *H3*), 5.22 (dd,  $J=5.9, 1.0$  Hz, 1H, *H2*), 3.52 (s, 3H, *OCH*<sub>3</sub>), 3.25 (ddd,  $J=12.8, 6.4, 1.5$  Hz, 1H, *H5*), 3.10 (dd,  $J=6.4, 2.5$  Hz, 1H, *endo-H6*), 2.60 (d,  $J=12.3$  Hz, 1H, *exo-H6*). <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>): 30.4 (*C6*), 35.6 (*C5*), 54.7 (*OCH*<sub>3</sub>), 63.8 (*C1*), 65.8 (*C3*), 91.4 (*C2*), 119.3 (*C9*), 124.3 (*C10*), 126.9 (*C7*), 142.3 (*C8*), 143.4 (*C4*), 222.6 (*CO*).

### 3.2.4. Cationic tricarbonyl-η<sup>6</sup>-[1-(3-thiophenyl)-4-anisole]-manganese (**3**)

Complex **2** (85 mg, 0.26 mmol) was suspended in CH<sub>2</sub>Cl<sub>2</sub> (5 ml). This solution was injected using a cannula into a solution of CPh<sub>3</sub>BF<sub>4</sub> (two equivalents) in CH<sub>2</sub>Cl<sub>2</sub> (3 ml). The reaction mixture was stirred at r.t. until the completion of the reaction. The solvent was then partly removed under N<sub>2</sub> and placed in an ice bath. After addition of anhydrous Et<sub>2</sub>O, precipitation of complex **3** occurred. Filtration of the solid followed by washings with anhydrous Et<sub>2</sub>O, afforded pure complex **3** in 67% yield.

Anal. Calc. for C<sub>14</sub>H<sub>10</sub>MnO<sub>4</sub>S: C, 51.53; H, 3.09. Found: C, 51.50; H, 3.10%. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): δ 8.40 (m, 1H, *H9*), 7.78 (m, 2H, *H10* and *H7*), 7.65 (d,  $J=8.0$  Hz, 2H, *H2* and *H6*), 6.67 (d,  $J=8.0$  Hz, 2H, *H3* and *H5*), 4.23 (s, 3H, *OCH*<sub>3</sub>). <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>): 58.1 (*OCH*<sub>3</sub>), 84.6 (*C3* and *C5*), 96.1 (*C2* and *C6*), 101.6 (*C1*), 126.7, 128.6, 130.3 (*C7*, *C9*, *C10*), 129.4 (*C9*), 148.7 (*C4*), 215.8 (*CO*).

### 3.3. X-ray crystallographic studies

Structure solution and refinement for complexes **1a** and **4a**. Intensity data were collected at room temperature on an Enraf–Nonius CAD4 diffractometer using Mo–K $\alpha$  radiation. Accurate cell dimensions and orientation matrices were obtained from least-square refinements of the setting angles of 25 well-defined reflections. No significant decay in the intensity of two standard reflections was observed during the course of the data collections. Crystal data, collection parameters and other significant details are listed in Table 4. The usual corrections for Lorentz and polarization effects were applied. Computations were performed using CRYSTALS [15]. Scattering factors and corrections for anomalous

Table 4  
Crystallographic data, data collection and refinement of **1a** and **4a**

	<b>1a</b>	<b>4a</b>
Formula	C <sub>13</sub> H <sub>8</sub> CrO <sub>3</sub> S	C <sub>13</sub> H <sub>8</sub> CrO <sub>3</sub> S
Formula weight	296.3	296.3
<i>a</i> (Å)	7.302(9)	7.331(2)
<i>b</i> (Å)	17.318(6)	17.622(3)
<i>c</i> (Å)	9.658(5)	19.154(3)
$\alpha$ (°)	90	90
$\beta$ (°)	93.53(8)	94.68(2)
$\gamma$ (°)	90	90
<i>V</i> (Å <sup>3</sup> )	1219(2)	2466.3(9)
<i>Z</i>	4	8
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>a</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
Linear absorption coefficient $\mu$ (cm <sup>-1</sup> )	10.7	10.6
Density $\rho$ (g cm <sup>-3</sup> )	1.61	1.60
Diffractometer	CAD4 Enraf–Nonius	CAD4 Enraf–Nonius
Radiation	Mo–K $\alpha$ ( $\lambda$ = 0.71069 Å)	Mo–K $\alpha$ ( $\lambda$ = 0.71069 Å)
Scan type	$\omega/2\theta$	$\omega/2\theta$
Scan range (°)	0.8+0.345 tg $\theta$	0.8+0.345 tg $\theta$
$\theta$ Limits (°)	1–25	1–30
Temperature of measurement	295 K	295 K
Octants collected	0, 8; 0, 20; –11, 11	0, 10; 0, 24; –26, 26
Decay%	24%	None
Number of data collected	2413	7926
Number of unique data collected	2147 ( $R_{\text{int}} = 0.04$ )	7173 ( $R_{\text{int}} = 0.01$ )
Number of unique data used for refinement	1275 ( $F_o$ ) <sup>2</sup> > 3 $\sigma$ ( $F_o$ ) <sup>2</sup>	4132 ( $F_o$ ) <sup>2</sup> > 3 $\sigma$ ( $F_o$ ) <sup>2</sup>
$R = \Sigma  F_o  -  F_c  /\Sigma F_o $	0.0752	0.0649
$Rw^* = [\Sigma w( F_o  -  F_c )^2]/\Sigma w F_o ^2$	0.0983 <sup>a</sup>	0.0897 <sup>b</sup>
<i>S</i>	0.98	0.82
Extinction parameter	None	205
Number of variables	160	317
$\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	–0.74	–1.11
$\Delta\rho_{\text{max}}$ (e Å <sup>-3</sup> )	0.74	1.74

\*  $w = w'[1 - ((|F_o| - |F_c|)/6 \cdot \sigma(F_o))^2]$  with  $w' = 1/\Sigma r_A r_T(X)$  with three coefficients (a) 13.9, 1.10 and 10.9, (b) 11.7, 4.39 and 8.11 for a Chebyshev series, for which  $X$  is  $F_c/F_o(\text{max})$ .

dispersion were taken from the International Table for X-ray Crystallography [16]. The structures were resolved by direct methods (SHELXS [17]) and refined by least squares with anisotropic thermal parameters for all nonhydrogen atoms except when disordered. Hydrogens were introduced in calculated positions and only one overall isotropic thermal parameter was refined.

For both compounds the thiophen appear to be disordered. The sulfur atom is shared between the two  $\alpha$  positions **4a** or the two  $\beta$  positions **1a**. All atoms involved in these disorders were left isotropic and were allocated an overall  $U_{\text{iso}}$  thermal parameter; furthermore, restraints were applied on the C–S and C–C distances. For **1a** the involved atoms are S(1) and C(2) (or S(2) and C(21)); for **4a** the involved atoms are S(1) and C(3) (or S(2) and C(31)). The final solutions for the treatment of these disorders are not quite satisfactory but are the best we can propose after many attempts.

### 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 196545 (**4a**) and 196546 (**1a**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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