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Titanium complexes of π-coordinated thiophene derivatives

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Abstract

π-Coordinated tricarbonylchromium complexes of thiophene and benzothiophene are readily lithiated with butyllithium and reacted with titanocene dichloride to afford the binuclear complexes [Ti{(η^1,η^5-thienyl)Cr(CO)$_3$}Cp$_2$Cl] (**1**) and [Ti{(η^1,η^6-benzothienyl)Cr(CO)$_3$}Cp$_2$Cl] (**5**). These feature an activated chlorine ligand on the titanium moiety, which is easily substituted by a second π-coordinated arene precursor, thiols or water. Several novel bimetallic, trimetallic and tetrametallic complexes were synthesized exploiting this observation and are reported. Dilithiation of [Cr(η^5-thienyl)(CO)$_3$] and subsequent reaction with two equivalents of titanocene dichloride yielded the unstable η^1,η^1,η^6-thienylene-bridged trinuclear complex, [{μ-Cr(η^5-thienyl)(CO)$_3$}{TiCp$_2$Cl}$_2$] (**15**), which was stabilized by replacing the chloro ligands by cyclohexylthiolato ligands. Crystals of the racemic mixture of [{(η^1,η^5-thienyl)Cr(CO)$_3$}$_2$TiCp$_2$] (**4**) was subjected to a single crystal X-ray diffraction study and the presence of both enantiomers causes a thiophene ring to be disordered.
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1. Introduction

The chemistry of thiophene and its derivatives is of interest due to the presence of these compounds in fossil fuels [1] as well as their potential application in material chemistry [2]. The coordination chemistry of these compounds has been studied owing to its relevance in the metal-catalyzed hydrodesulfurization (HDS) of the fossil fuels [3]. Several review articles dealing with model HDS studies have been published [4], reporting a number of other interesting reactions of thiophene discovered during the course of the HDS studies. These reactions opened a new area of thiophene chemistry with application towards organic synthesis [5]. A recent review article by Angelici [6] organized these reactions and a clear idea of the reaction patterns of thiophene in organometallic chemistry is perceived. It is concluded that the specific types of reactivity are dependent on the modes of thiophene coordination to a metal, which in turn are determined by the electronic properties of the metal and its ligands. Although several coordination modes of thiophene (T) are known [7], one of the most common is the η^5 mode, i.e. coordination through the π-system of the heteroaromatic ring usually to a d^6 metal fragment. Benzothiophenes (BT) coordinate to these metal complexes [4c] through the six carbon atoms of the benzene ring, since kinetic studies [8] showed a higher affinity of metals for benzene over thiophene as well as stronger bond formation. It also showed that benzothiophenes bind more strongly to metals than thiophenes.

The wide application of π-arene complexes of chromium in stereoselective [9] and regioselective [10] syntheses motivated the initial interest in synthesizing heterobimetallic compounds by attaching the π-hetero-arene ring to a second metal fragment. The coordination of early, middle and late transition metals with benzene [11–13] or substituted benzene [12,14] as bridging ligand has been investigated. It was found that a carbonyl-inserted bridged benzoyl product was isolated when lithiated [Cr(η^6-benzene)(CO)$_3$] was reacted with

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[Mn(CO)$_5$Br], while the σ,π-phenyl-bridged product could only be isolated when the large, more basic PPh$_3$ ligand was introduced on the manganese [12]. When the lithiated benzene precursor is substituted for lithiated [Cr(η^5-thiophene)(CO)$_3$] [15] or [Cr(η^6-benzothiophene)(CO)$_3$] [16], the reaction with [Mn(CO)$_5$Br] affords both products but with the carbonyl-inserted product in a lesser yield. The resulting [Mn{(η^1,η^5-thienyl)Cr-(CO)$_3$}(CO)$_5$] product was observed to undergo an unusual intramolecular metal exchange reaction [17], in which the two metal centers irreversibly exchanged σ,π-coordination sites. Reactions between lithiated [Cr(η^5-thiophene)(CO)$_3$] or [Cr(η^6-benzothiophene)-(CO)$_3$] with late transition metals [18], in this case [PtL$_2$Cl$_2$], resulted in the substitution of both chlorine ligands by the π-coordinated heteroarene fragment. The intermediate complex, which formed after replacing one chloro with a π-coordinated heteroarene ligand, is highly activated and the remaining chloro ligand becomes the target of a second attack by the lithiated precursor. In the case of the thiophene-bridged product, the loss of one of the Cr(CO)$_3$ moieties occurs spontaneously but in the benzothiophene product both stayed intact. The remaining issue of interest is the reaction of an early transition metal with lithiated [Cr(η^5-thiophene)(CO)$_3$] or [Cr(η^6-benzothiophene)(CO)$_3$]. In this study, the properties and diverse reactivity of the products isolated in these reactions are discussed.

2. Results and discussion

The π-bonded heteroarene complexes, [Cr(η^5-thiophene)(CO)$_3$] and [Cr(η^5-benzothiophene)(CO)$_3$], were prepared in a two-step synthetic process in variable yields. [Cr(CO)$_6$] was converted into [Cr(CO)$_3$(NH$_3$)$_3$] [19,20] and thereafter treated with an excess of thiophene and three equivalents of the Lewis acid BF$_3$ in diethyl ether. The complex [Cr(η^6-benzothiophene)(CO)$_3$] was also prepared by refluxing [Cr(CO)$_6$] and benzothiophene in dibutyl ether for several hours [21], but isolation of the target product proved difficult due to the formation of several by-products. Metallation of these complexes is readily achieved with butyl lithium in THF at −78 °C [22], creating a strong nucleophilic center on the metallated carbon. The lithiated precursors were prepared using this same procedure.

Upon addition of [Cr(η^1,η^5-lithiothienyl)(CO)$_3$] to titanocene dichloride in THF at low temperatures (Scheme 1), the red solution turned green. Chromatographic separation of the mixture yielded four products: the green complexes **1**, **3** and **4** as well as the brown complex **2**. During column chromatography it was observed that the column material turned orange upon elution of the reaction mixture. This orange product could not be eluted from the column, even with polar

solvents such as THF or acetone. Since only a small quantity of the initial portion of **1** in the reaction mixture was eluted from the column, it was suggested that **1** reacts with the hydroxy groups of the silica gel to form an orange-colored complex. Thin layer chromatography of **1** supported this suggestion. The trimetallic complexes **3** and **4** were found to be more stable than **1**, which is contradictory to observation that [TiCp$_2$(R)Cl] is more stable than the corresponding disubstituted compound [TiCp$_2$R$_2$], with R being methyl groups [23] or [(η^6-R′C$_6$H$_4$)Cr(CO)$_3$] [12]. By contrast, the mono-substituted complex could not even be isolated in the case of the reaction between [PtL$_2$Cl$_2$] (L = PMe$_3$, CO or L$_2$ = dppe) and [Cr(η^1,η^5-lithiothienyl)(CO)$_3$] [18]. Both chlorine ligands were immediately substituted by [Cr(η^5-thienyl)(CO)$_3$] fragments. The novel complexes **3** and **4** exist as two diastereomers where **3** is the *meso*, achiral isomer displaying a mirror plane while **4** represents an enantiomeric pair of C2 symmetry. Using benzene as eluent, these two diastereomers were separated on a column. As expected, the *meso* compound **3** was less polar than **4**. The formation of **2** was unexpected and its origin leads to some speculation. It was anticipated that **1** reacted with water on the column to substitute the chlorine group for a hydroxy group, which could have reacted with titanocene dichloride to yield the target product. Another possibility was that the compound [{TiCp$_2$Cl}$_2$(μ-O)] was present as an impurity in titanocene dichloride [24] and, upon reaction with [Cr(η^1,η^5-lithiothienyl)(CO)$_3$], formed **2** (vide infra). Although several test reactions were performed in order to imitate the formation of **2**, it was concluded that this was not trivial to explain.

The reaction of lithiated [Cr(η^6-benzothienyl)(CO)$_3$] with titanocene dichloride (Scheme 2) afforded two products initially, the green bimetallic complex **5** and the trimetallic complex **6**, even though the ratio of reagents was 1:1. This is again an indication of the enhanced reactivity of the chlorine ligand. The green color of the compounds is seldom observed for arene–chromium complexes, although more often for titanocene derivatives. On purification of the green compound **5**, the complex reacted with the hydroxy group of the silica gel, substituting the remaining chloro ligand, forming an orange compound that could not be eluted. In order to record an NMR spectrum of **6**, the complex was dissolved in acetone. The color of the solution was orange and not the expected green. In acetone, one of the Cr(CO)$_3$ moieties was decomplexed and only the benzo[*b*]thiophene ligand remained bonded, affording compound **7**.

Since the bimetallic complexes **1** and **5** are very reactive because of the high lability of the Ti–Cl bond, it was decided to exchange the chlorine ligand for other groups (Scheme 3). The substrates chosen for these substitution reactions were the thiols, cyclohexylthiol
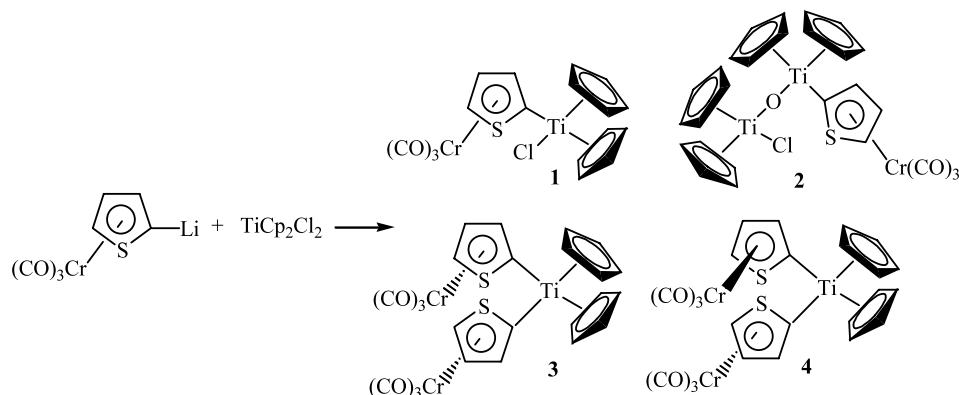
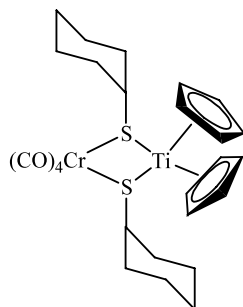Scheme 1. Synthesis of **1**, **2**, **3** and **4**.

and thiophenol. It was anticipated that this substitution would increase the solubility of the complexes in nonpolar solvents. It is also known that the Ti–S bond in complexes of the type [TiCp$_2$(SR)(SR′)] was less reactive [25] than the Ti–O bond in [TiCp$_2$(OR)(OR′)] with regard to thermal conditions. The conversion of **1** with cyclohexylthiol in dichloromethane in the presence of excess TMEDA gave the target complex **8**. When the reaction was repeated with an excess of cyclohexylthiol compared to the rest of the reagents, the Ti–C σ-bond was also broken and the blue complex **9** was formed in a low yield (Fig. 1). Examples of this type of complexes can be found in literature [26] and was synthesized by reacting [TiCp$_2$(SR)$_2$] with [(norbornadien)M(CO)$_4$].

For the analogous reaction with **5** a different sulfur compound was chosen, i.e. thiophenol. The reason for this choice was to assign all the NMR signals in the arene region unambiguously. In the same manner as described for the synthesis of **8**, the orange-red complex **11** was prepared.

The substitution kinetics of the chlorine ligands of titanocene dichloride in aqueous solution was investigated by Toney and Marks [27] in their studies to clarify

the mechanism of [MCp$_2$X$_2$] antitumor activity in aqueous solution. While it was observed that the coordination of a [Cr(η^6-arene)(CO)$_3$] moiety to titanocene dichloride enhanced the reactivity of the remaining chlorine ligand, it was anticipated that this substitution should proceed effortlessly. This was indeed the case, as the red complexes **10** and **12** were formed, respectively, after stirring **1** and **5** in water for some time. Stone and coworkers [28] were the first to synthesize and char-
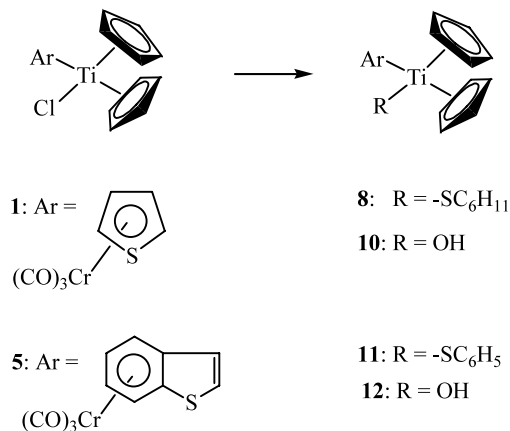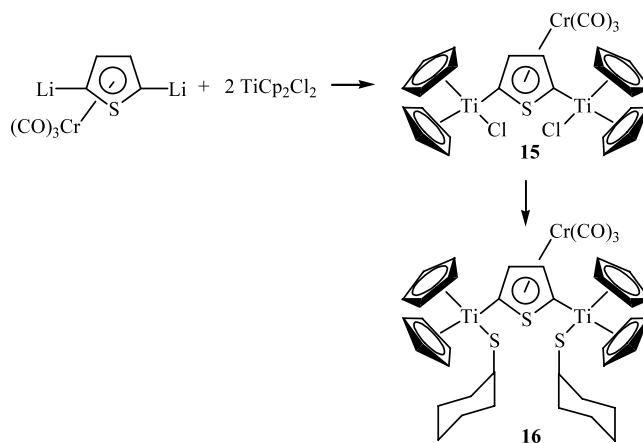

Scheme 3. Synthesis of **8**, **10**, **11** and **12**.
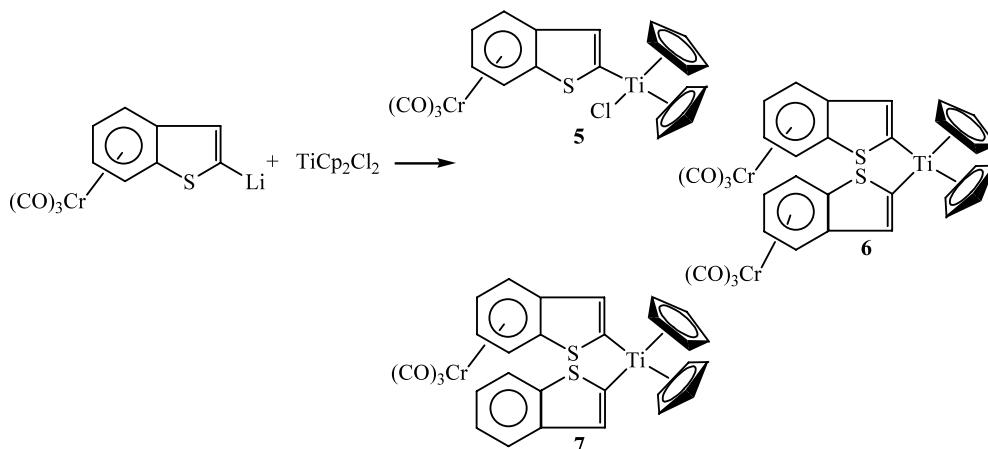
Scheme 2. Synthesis of **5**, **6** and **7**.

Fig. 1. Structure of **9**.

Scheme 5. Synthesis of **15** and **16**.

acterize compounds of the type [TiCp$_2$R(OH)]. This was accomplished by adding a mixture of THF and water to the compound [TiCp$_2$(C$_6$F$_5$)Cl] in the presence of KOH.

When [{TiCp$_2$Cl}$_2$(μ-O)] was reacted with two equivalents of [Cr(η^1,η^5-lithiothienyl)(CO)$_3$], two tetrametallic diastereomers, **13** and **14**, were obtained (Scheme 4). For these two complexes, both chlorine ligands are substituted in each case, as expected, and the monosubstituted complex **2** is not observed. The possibility of [{TiCp$_2$Cl}$_2$(μ-O)] being the precursor to **2** was therefore not supported by these results. In this instance, the diastereomers could not be separated using column chromatography.

Dimetallation of thiophene in [Cr(η^5-thiophene)(CO)$_3$] is readily achieved [22] and reaction with two equivalents of titanocene dichloride affords the green, trimetallic complex **15** (Scheme 5). This complex was found to be more reactive than **1** and all attempts to purify the product with column chromatography were unsuccessful. By converting **15** to **16** with cyclohex-

ylthiol the stability and solubility of the complex were increased and **16** could be purified on a column without conversion.

3. Spectroscopic properties

The replacement of a proton by a titanium moiety in [Cr(π-arene)(CO)$_3$] (arene = thiophene, benzothiophene) complexes has a definite effect on the electronic structure of the complex. This can be deduced from the difference in the wavenumbers (Table 1) of the bands in the IR spectra of the monometallic substrate and the bimetallic products. The decrease in wavenumber with the addition of the titanium fragment, compared to the wavenumbers of the complexes [Cr(π-arene)(CO)$_3$] (are-
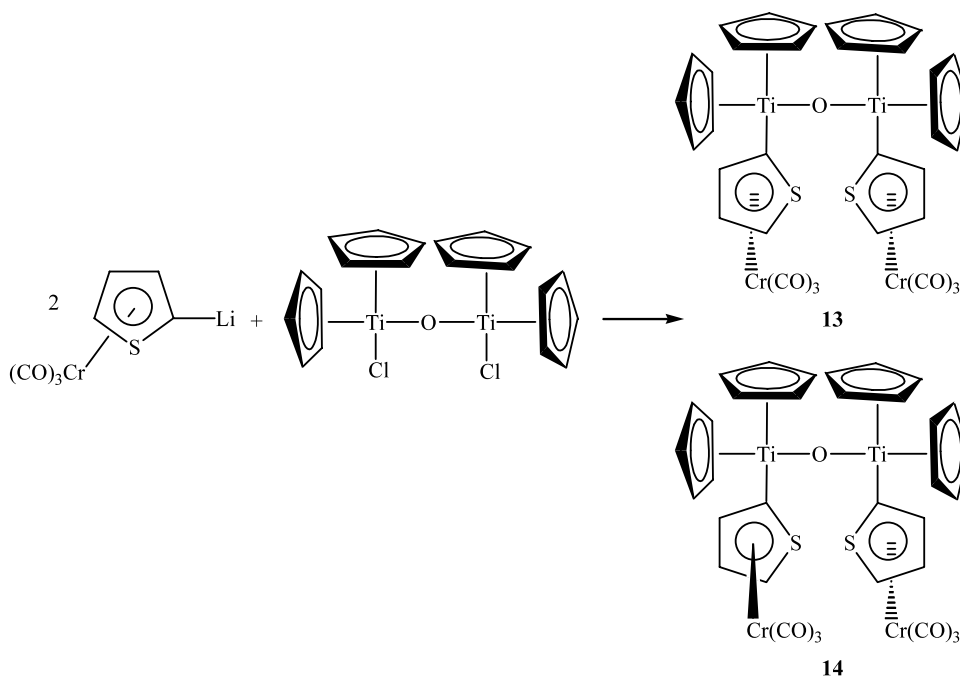

Scheme 4. Synthesis of **13** and **14**.

Table 1
Spectroscopic data of complexes **1-16**

Complex	IR [a] (ν (cm^{-1}) in CH$_2$Cl$_2$)	^{1}H-NMR (δ (ppm) in CDCl$_3$)	^{13}C-NMR (δ (ppm) in CDCl$_3$)
1	1945 (s), 1848, 1866 (vs)	6.73 (s, 5H, Cp), 6.53 (s, 5H, Cp), 6.21 (dd, 1H, H5, $^3J_{HH} = 3.44$, $^4J_{HH} = 0.58$), 5.84 (t, 1H, H4, $^3J_{HH} = 3.23$), 5.58 (dd, 1H, H3, $^3J_{HH} = 3.12$, $^4J_{HH} = 0.57$)	236.0 (CrCO$_3$), 143.2 (C2), 106.1 (C3), 97.4 (C5), 96.1 (C4), 119.9, 119.7 (Cp)
2	1943 (s), 1855 (vs), 720 (Ti–O–Ti)	6.44 (s, 5H, Cp), 6.42 (s, 5H, Cp), 6.21 (s, 10H, Cp), 6.27 (d, 1H, H5, $^3J_{HH} = 3.38$), 6.18 (d, 1H, H3, $^3J_{HH} = 2.97$), 6.07 (t, 1H, H4, $^3J_{HH} = 3.23$)	236.0 (CrCO$_3$), 137.0 (C2), 107.4 (C3), 99.3 (C5), 97.1 (C4), 115.0, 115.6, 117.1 (Cp)
3	1938 (s), 1866 (vs)	6.76 (s, 10H, Cp), 6.21 (dd, 2H, H5 and H5′, $^3J_{HH} = 3.53$), 6.19 (d, 2H, H3 and H3′, $^3J_{HH} = 3.11$), 5.80 (t, 2H, H4 and H4′, $^3J_{HH} = 3.34$)	236.3 (CrCO$_3$), 144.4 (C2), 106.3 (C3), 97.9 (C5), 97.2 (C4), 116.5 (Cp)
4	1938 (s), 1859 (vs)	6.76 (s, 5H, Cp), 6.73 (s, 5H, Cp), 6.23 (d, 2H, H5 and H5′, $^3J_{HH} = 3.44$), 6.13 (d, 2H, H3 and H3′, $^3J_{HH} = 3.13$), 5.83 (t, 2H, H4 and H4′, $^3J_{HH} = 3.40$)	236.3 (CrCO$_3$), 144.4 (C2), 106.3 (C3), 97.9 (C5), 97.2 (C4), 116.1, 117.3 (Cp)
5	1953 (s), 1872 (vs)	6.45 (m, 10H, Cp), 6.40 (d, 1H, H3, $^4J_{HH} = 1.0$), 6.16 (d, 1H, H8, $^3J_{HH} = 6.7$), 6.08 (dd, 1H, H5, $^3J_{HH} = 6.2$, $^4J_{HH} = 1.0$), 5.32 (dd, 1H, H7, $^3J_{HH} = 6.7$, $^3J_{HH} = 6.3$), 5.21 (dd, 1H, H6, $^3J_{HH} = 6.2$, $^3J_{HH} = 6.3$)	234.0 (CrCO$_3$), 123.5 (C3), 90.4 (C7), 89.0 (C6), 86.8 (C5), 85.5 (C8), 116.7, 116.9 (Cp)
6	1954 (s), 1875 (vs)	6.40 (s, 5H, Cp), 6.39 (s, 5H, Cp), 6.33 (s, 2H, H3 and H3′), 6.20 (d, 2H, H8 and H8′, $^3J_{HH} = 6.5$), 5.99 (dd, 2H, H5 and H5′, $^3J_{HH} = 6.1$, $^4J_{HH} = 1.3$), 5.22 (dd, 2H, H7 and H7′, $^3J_{HH} = 5.9$, $^3J_{HH} = 5.9$), 5.21 (dd, 2H, H6 and H6′, $^3J_{HH} = 5.9$, $^3J_{HH} = 5.9$)	234.5 (CrCO$_3$), 150.2 (C2, C2′), 126.6 (C3, C3′), 103.1 (C9, C9′), 98.8 (C4, C4′), 90.3 (C7, C7′), 89.1 (C6, C6′), 87.5 (C5, C5′), 87.3 (C8, C8′), 116.0, 116.3 (Cp)
7	1953 (s), 1873 (vs)	6.60 [b] (s, 5H, Cp), 6.51 (s, 5H, Cp), 7.19 (m, 4H, H5′, H6′, H7′, H8′), 6.65 (d, 1H, H8, $^3J_{HH} = 6.0$), 6.55 (s, 1H, H3′), 6.49 (d, 1H, H3, $^4J_{HH} = 1.68$), 6.33 (d, 1H, H5, $^3J_{HH} = 6.0$), 5.54 (dd, 1H, H7, $^3J_{HH} = 4.3$, $^3J_{HH} = 6.1$), 5.53 (dd, 1H, H6, $^3J_{HH} = 4.3$, $^3J_{HH} = 6.1$)	236.0 [b] (CrCO$_3$), 150.9 (C2), 173.7 (C2′), 138.3 (C3), 168.4 (C3′), 105.3 (C9), 132.5 (C4′), 92.5 (C7), 129.6 (C7′), 90.9 (C6), 128.9 (C6′), 89.7 (C5), 127.6 (C5′), 89.3 (C8), 126.0 (C8′), 119.1, 119.3 (Cp)
8	1939 (s), 1845 (vs)	6.42 (s, 5H, Cp), 6.24 (s, 5H, Cp), 6.03 (d, 1H, H5, $^3J_{HH} = 3.39$), 5.73 (t, 1H, H4, $^3J_{HH} = 3.24$), 5.47 (d, 1H, H3, $^3J_{HH} = 2.89$), 4.17 (m, 1H, H1), 1.1–1.9 (m, 10H, C$_6$H$_{11}$S-group)	237.0 (CrCO$_3$), 140.4 (C2), 107.3 (C3), 98.1 (C5), 97.2 (C4), 113.1, 114.3 (Cp), 57.1, 36.4, 27.0, 25.8 (C$_6$H$_{11}$S-group)
9	2069 (w), 1988 (s), 1941 (m), 1897 (vs)	5.69 (s, 10H, Cp), 2.71 (m, 2H, H1), 1.2–2.0 (m, 20H, C$_6$H$_{11}$S-group)	221 (CrCO$_4$), 108.9 (Cp), 68.7, 38.4, 28.2, 25.8 (C$_6$H$_{11}$S-group)
10	1940 (s), 1847 (vs)	12.44 (s, 1H, O–H), 6.41 (s, 5H, Cp), 6.19 (s, 5H, Cp), 6.14 (d, 1H, H5, $^3J_{HH} = 3.01$), 5.83 (t, 1H, H4, $^3J_{HH} = 3.18$), 5.72 (d, 1H, H3, $^3J_{HH} = 2.94$)	237.2 (CrCO$_3$), 139.3 (C2), 107.1 (C3), 97.5 (C5), 97.1 (C4), 115.7, 115.9 (Cp)
11	1952 (s), 1870 (vs)	7.27–7.30 (m, C$_6$H$_5$S group), 6.09 (s, 5H, Cp), 6.10 (s, 5H, Cp), 6.44 (s, 1H, H3), 6.21 (d, 1H, H8, $^3J_{HH} = 6.0$), 6.00 (d, 1H, H5, $^3J_{HH} = 6.4$), 5.22 (dd, 1H, H6, $^3J_{HH} = 7.7$, $^3J_{HH} = 6.4$), 5.22 (dd, 1H, H7, $^3J_{HH} = 7.6$, $^3J_{HH} = 6.0$)	234.8 (CrCO$_3$), 128.4 (C3), 90.5 (C7), 89.4 (C6), 87.7 (C5), 87.6 (C8), 113.4 (Cp)
12	1952 (s), 1870 (vs)	8.06 (s, 1H, O–H), 6.40 (s, 5H, Cp), 6.39 (s, 5H, Cp), 6.43 (s, 1H, H3), 5.23 (dd, 1H, H7, $^3J_{HH} = 6.2$, $^3J_{HH} = 6.0$), 5.22 (dd, 1H, H6, $^3J_{HH} = 6.3$, $^3J_{HH} = 5.9$)	NR
13 and **14**	1942 (s), 1853 (vs), 723 (Ti–O–Ti)	6.33 (s, 5H, Cp), 6.25 (s, 5H, Cp), 6.23 (s, 5H, Cp), 6.14 (s, 5H, Cp), 6.29 (d), 6.19 (m), 6.11 (t)	236.6, 236.5 (CrCO$_3$), 136.4, 136.0 (C2, C2′), 107.4 (C3, C3′), 99.7, 99.4 (C5, C5′), 97.9, 97.5 (C4, C4′), 115.6, 115.1 (Cp)
15	1925 (s), 1833, 1850 (vs)	6.68 (s, 10H, Cp), 6.56 (s, 10H, Cp), 5.63 (s, 2H, H3 and H4)	108 (C3 and C4), 119.2, 119.1 (Cp)
16	1918 (s), 1821 (vs)	6.39 (s, 10H, Cp), 6.23 (s, 10H, Cp), 5.46 (s, 2H, H3 and H4), 4.10 (m, 2H, H1), 1.0–1.8 (m, 20H, C$_6$H$_{11}$S-group)	239.4 (CrCO$_3$), 148.9 (C2 and C5), 108.8 (C3 and C4), 113.6, 113.4 (Cp), 57.1, 32.2, 27.3, 26.0 (C$_6$H$_{11}$S-group)

NR, not recorded.

[a] Carbonyl region.

[b] Recorded in deuterated acetone.

ne = thiophene 1967(s) cm^{-1}, 1877(vs) cm^{-1}; benzothiophene 1964(s) cm^{-1}, 1885(vs) cm^{-1} [29], suggests that the electron density is higher on the substituted arene ring relative to the [Cr(π-arene)(CO)$_3$] (arene = thiophene, benzothiophene) substrate. It is ascribed to a large polarization effect of the Ti–C(arene) bond, with $\delta+$ at the titanium and $\delta-$ at the ring. This effect is enhanced for complexes **15** and **16**, resulting in even lower wavenumbers, signifying high electron density on the arene ring, two highly polarized Ti–C(arene)

bonds and consequently the instability of **15**. The electronic influence of the different substituents on the titanium moiety is apparently negligible, since the vibrational frequencies for the different types of complexes are approximately the same.

Two singlets were observed for the two Cp-ring protons on the NMR spectra of the compounds belonging to the class Cp_2TiXY (**1**, **2**, **5**, **7**, **8**, **10**, **11** and **12**), which indicate the absence of a mirror plane in the molecule and hence the two Cp-rings are not equivalent but diastereotopic. On the spectrum of **5**, instead of two singlet resonances for the two Cp-rings, a broad, unresolved multiplet was observed. For complexes belonging to the class Cp_2TiX_2 two cases should be considered. In the case where the Cp-rings are equivalent, a mirror plane should be present in the molecule, for example complexes **3** and **9**. On the spectra of these complexes the Cp-rings resonate as a singlet. Complexes **4** and **6** both exist as enantiomeric pairs and thus display two Cp signals each. The same is true for the oxygen-bridged dimers **13** and **14**, which show four different environments for the Cp-rings. The Cp signals of **15** and **16** are similar to those of the Cp_2TiXY class, although a symmetry plane exists in these complexes, resulting in a doubling of the number of protons. The ^{1}H- and ^{13}C-NMR chemical shifts of the Cp-rings were shifted more upfield for **8** and **11** compared to those of **1**, **5**, **10** and **12**. In **8** and **11**, a sulfur atom, a stronger donor ligand compared to Cl^- and OH^-, is bonded to the titanium atom. Thus, electron density is shifted to the titanium and causes greater shielding of the Cp-protons. This may also simply be a result of the difference in electronegativity of the donor atoms. Assignments of chemical shift values for the thienyl protons are based on studies by Gronowitz [30].

4. Crystal structure

Single crystal X-ray diffraction studies confirmed the molecular structure of **4**. The compound crystallized in both enantiomeric forms in such a way that the thiophene ring S2, C15, C16, C17, C18 appears as a disordered ring. S2 and C16 alternatively occupied the same position. The green crystals were afforded from a dichloromethane−hexane (1:1) solution. Selected bond distances and angles are given in Table 2. Fig. 2 represents ball-and-stick plots of the enantiomeric pair, form **A** and form **B**.

The torsion angle S1−C11−C15−S2 for form **A** is 126.1° and for form **B** is −1.0°. Both thiophene units, coordinated to $Cr(CO)_3$ moieties, are planar. The thiophene ring carbons are equidistant from the Cr atoms, signifying η^5-coordination. The Cr−C(ring) distances range from 2.183(16) to 2.281(3) Å and the Cr−S distances are 2.371(1) and 2.425(3) Å, respectively,

Table 2
Selected bond distances (Å) and angles (°) of **4**

Bond distance	
Cr1−C11	2.281(3)
Cr1−C12	2.222(3)
Cr1−C13	2.227(3)
Cr1−C14	2.197(3)
Cr2−C15	2.229(3)
Cr2−C16	2.183(16)
Cr2−C17	2.200(3)
Cr2−C18	2.202(4)
Cr1−S1	2.371(1)
Cr2−S2	2.425(3)
S1−C11	1.768(3)
C11−C12	1.445(5)
C12−C13	1.442(4)
C13−C14	1.385(5)
C14−S1	1.723(4)
S2−C15	1.733(5)
C15−C16	1.469(15)
C16−C17	1.476(16)
C17−C18	1.378(5)
C18−S2	1.660(5)
Bond angle	
C11−S1−C14	95.2(1)
S1−C11−C12	106.2(2)
C11−C12−C13	114.7(3)
C12−C13−C14	112.5(3)
C13−C14−S1	111.1(3)
C15−S2−C18	93.9(2)
S2−C15−C16	106.4(6)
C15−C16−C17	115.0(7)
C16−C17−C18	106.1(5)
C17−C18−S2	118.1(3)
C11−Ti−C15	85.2(1)
Ti−C11−S1	124.2(1)
Ti−C11−C12	128.5(2)
Ti−C15−S2	123.0(1)
Ti−C15−C16	129.4(6)

which correspond well with structural data reported for $[Cr(\eta^5-C_4H_3S)(CO)_3]$ [31], although the Cr−S distances in **4** are slightly longer. The tripod formed by the three carbonyl ligands on the chromium metal is characteristic of arene−chromium complexes [32]. These tripods are arranged with one carbonyl ligand *trans* to the sulfur atom [31]. The Ti−C11 and Ti−C15 distances are equal within experimental error and are 2.204(3) Å on average. This value does not differ significantly from values for Ti−C(arene) bonds of similar titanium complexes reported in literature [12,33−35]. By contrast, Ti−C distances with perceivable π-interaction distributions between titanium and a carbon atom are significantly shorter and ranges from 2.00 to 2.10 Å [36].

On comparing the bond lengths of the thienyl ring in complex **4** with the bond lengths of uncoordinated thiophene [37], all of the bonds are longer in the complex. Usually, the bond lengths of the η^5-coordinated thienyl ring follow the trend of short C11−C12 and C13−C14 bonds and a long C12−C13 bond
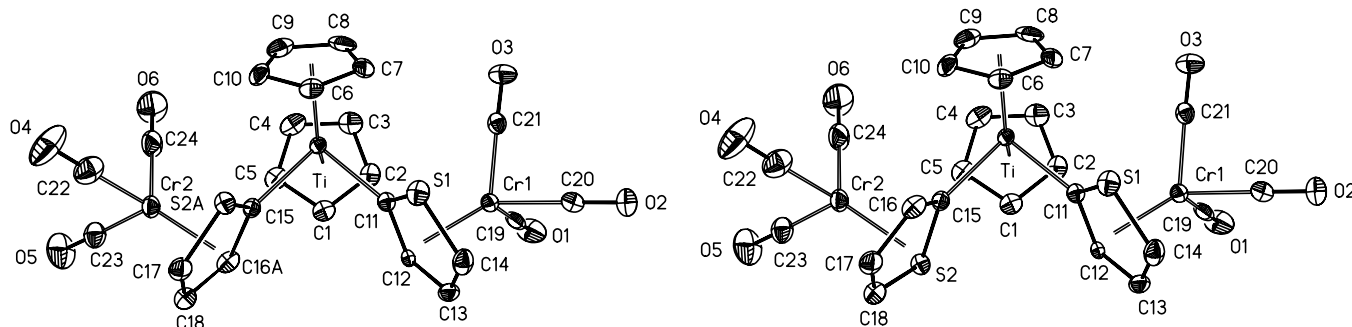
Fig. 2. Molecular structures of the enantiomeric forms of **4**.

[15,17,38]. In this case, however, the C11–C12 (C15–C16) and C12–C13 (C16–C17) bonds are the longer bonds and C13–C14 (C17–C18) is the short bond, displaying allylic character. This sequence is characteristic of thiophene rings bonded in a η^1-fashion to a metal fragment with significant π-delocalization from the ring to the metal [17,38]. The longer bond lengths compare with the characteristic bond distances of a $C(sp^2)$–$C(sp^2)$ single bond (1.46 Å), while the short bond distance resemble a $C(sp^2)$–$C(sp^2)$ double bond (1.32 Å) [39].

5. Experimental

5.1. Materials and method

All reactions and manipulations were performed under an inert atmosphere using standard Schlenk tube techniques [40]. Solvents were dried by the usual procedures [41] and distilled under nitrogen prior to use. The starting materials thiophene, benzo[*b*]thiophene and *n*-BuLi were used as obtained from Aldrich and thiophene was purified as described in literature [42]. The precursors [Cr(NH$_3$)$_3$(CO)$_3$] [43], [Cr(η^5-thiophene)(CO)$_3$] [20] and [{TiCp$_2$Cl}$_2${μ-O}] [44] were synthesized according to known literature methods. Column chromatography was performed on silica gel (0.063–0.200 mm) on columns that were cooled by circulating cold isopropanol (-20 °C) through column jackets. The solvents used for column chromatography were dichloromethane–petroleum ether mixtures in varying ratios, unless stated otherwise. NMR spectra were recorded in CDCl$_3$ as solvent on a Bruker AC-300 spectrometer with reference to the deuterium signal CDCl$_3$. ^{1}H- and ^{13}C-NMR spectra were measured at 300.133 and 75.469 MHz, respectively. Infrared spectra were recorded as CH$_2$Cl$_2$ solutions on a BOMEM Michelson-100 FT spectrophotometer. Mass spectra were recorded on a Perkin–Elmer RMU-6H instrument operating at 70 eV. Melting points were recorded in capillaries on a Gallenkamp hot-stage apparatus and are uncorrected.

5.1.1. Syntheses: general preparation of [Cr(η^5-thiophene)(CO)$_3$] and [Cr(η^6-benzothiophene)(CO)$_3$]

[Cr(NH$_3$)$_3$(CO)$_3$] (2.00 g, 10.7 mmol) was dissolved in diethyl ether (~ 95 cm^3). Freshly distilled Et$_3$OBF$_4$ (3.95 cm^3, 33 mmol) was added to the solution, followed by 21 mmol of thiophene substrate. The reaction mixture was stirred for 12 h. Diethyl ether (100 cm^3) was added and the solution was cooled to 0 °C after which 100 cm^3 of air-free water was added. The mixture was repeatedly extracted with diethyl ether until the extracts were virtually colorless. The ether extracts were combined and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The product was purified with column chromatography that afforded the starting compound and the orange product. The crude product was recrystallized from a dichloromethane–hexane mixture. The orange crystals were washed with cold hexane and dried. Yields were higher than 70% based on the mass of [Cr(NH$_3$)$_3$(CO)$_3$].

5.1.2. [Ti{(η^1,η^5-thienyl)Cr(CO)$_3$}Cp$_2$Cl] (**1**)

1.2 g (5.46 mmol) of [Cr(η^5-thiophene)(CO)$_3$] was dissolved in 30 cm^3 of THF and cooled to -90 °C when 3.6 cm^3 (5.76 mmol) *n*-BuLi (1.6 M solution in hexane) was added. The color of the reaction mixture changed from orange to yellow. The mixture was stirred at -70 °C for 10 min and then cooled to -90 °C again. A solution of 1.36 g (5.46 mmol) of [TiCp$_2$Cl$_2$] in THF was added. The solution was allowed to warm to room temperature (r.t.) while the color changed from red to green. The solvent was removed in vacuo. Column chromatography of the residue yielded three fractions. The first red band isolated was unreacted starting compound, [Cr(η^5-thiophene)(CO)$_3$], while the second green band contained a mixture of products, *meso*-[Ti{(η^1,η^5-thienyl)Cr(CO)$_3$}$_2$Cp$_2$] (**3**) and [Ti{(η^1,η^5-thienyl)Cr(CO)$_3$}$_2$Cp$_2$] (**4**), in a 1:1 ratio. These two compounds were separated on a second column using toluene as eluent. The main product, **1**, was isolated as a green fraction. After isolation of this compound, the polarity of the eluent was increased to dichloromethane–ether (1:1) and a brown product [(TiCp$_2$Cl)-

(Ti{(η^1,η^5-thienyl)Cr(CO)$_3$}Cp$_2$){μ-O}] (**2**) as well as the yellow compound [{TiCp$_2$Cl}$_2${μ-O}] were isolated.

1—Yield: 0.74 g (36%). C$_{17}$H$_{13}$ClO$_3$SCrTi (432.7)—Calc.: C, 47.19; H, 3.03. Found: C, 46.88; H, 2.85%.

2—Yield: 0.12 g (6%). C$_{27}$H$_{23}$ClO$_4$SCrTi$_2$ (626.8)—Calc.: C, 51.74; H, 3.70. Found: C, 51.92; H, 3.93%.

3 and **4**—Yield: 1.03 g (36%). C$_{24}$H$_{16}$O$_6$S$_2$Cr$_2$Ti (616.4)—Calc.: C, 46.77; H, 2.62. Found: C, 46.48; H, 2.34%.

5.1.3. *[Ti{(η^1,η^6-benzothienyl)Cr(CO)$_3$}Cp$_2$Cl] (5)*

[Cr(η^6-benzothienyl)(CO)$_3$] (0.55 g, 2.04 mmol) was dissolved in THF ($\sim$ 15 cm^3). The solution was cooled to $-40\,^\circ$C and 1.4 cm^3 (2.24 mmol) of *n*-BuLi was added to the stirred solution. Stirring was maintained for 1 h at this temperature during which time the color of the solution changed from orange-yellow to dark brown. 0.50 g (2.04 mmol) of [TiCp$_2$Cl$_2$] was gradually added to the cooled reaction mixture, after which stirring was maintained for a further 30 min. The mixture was heated to r.t. and stirred for 30 min. The mixture was filtered through silica gel, using dichloromethane as eluent. The solvent was removed under reduced pressure. Two bands were separated by means of column chromatography (eluent: petroleum ether–dichloromethane (1:2)). The first band removed from the column was characterized as unreacted orange starting compound. The second green band was identified as [Ti{(η^1,η^6-benzothienyl)Cr(CO)$_3$}Cp$_2$Cl] (**5**) while a third green product was characterized as [Ti{(η^1,η^6-benzothienyl)Cr(CO)$_3$}$_2$Cp$_2$] (**6**).

5—Yield: 0.54 g (55%). C$_{21}$H$_{15}$ClO$_3$SCrTi (482)—Calc.: C, 52.25; H, 3.13. Found: C, 52.41; H, 3.25%. MS (EI); *m/z*: 482 [M$^+$], 398 [M$^+$ $-$3CO], 346 [M$^+$ $-$3CO$-$Cr], 213 [TiCp$_2$Cl$^+$], 148 [TiCpCl$^+$].

6—Yield: 0.54 g (37%). C$_{32}$H$_{20}$O$_6$S$_2$Cr$_2$Ti (716.5)—Calc.: C, 53.64; H, 2.81. Found: C, 53.90; H, 2.97%.

7—C$_{29}$H$_{20}$O$_3$S$_2$Cr$_2$Ti (664.5)—Calc.: C, 52.42; H, 3.03. Found: C, 52.66; H, 3.16%.

5.1.4. *Reaction of 1 with [C$_6$H$_{11}$SH]*

a) 100 mg (0.23 mmol) of **1** was dissolved in 5 cm^3 (33.3 mmol) of TMEDA, 4 cm^3 (32.6 mmol) of [C$_6$H$_{11}$SH] and 10 cm^3 dichloromethane. The mixture was stirred for 1 h at r.t. and the color of the solution changed from green to brown-green. The solvent was removed under reduced pressure. Column chromatography yielded the orange compound [Cr(η^5-thiophene)(CO)$_3$] and the complex [Ti{(η^1,η^5-thienyl)Cr(CO)$_3$}(SC$_6$H$_{11}$)Cp$_2$] (**8**).

8—Yield: 98.3 mg (83%). C$_{23}$H$_{24}$O$_3$S$_2$CrTi (512.5)—Calc.: C, 53.91; H, 4.72. Found: C, 53.69; H, 4.94%.

b) 100 mg (0.23 mmol) of **1** was dissolved in 4 cm^3 (26.6 mmol) of TMEDA, 8 cm^3 (65.2 mmol) of [C$_6$H$_{11}$SH] and 10 cm^3 dichloromethane. The mixture was stirred for 1 h at r.t. and the color of the solution changed from green to violet. The solvent was removed under reduced pressure. Column chromatography yielded the blue complex [(TiCp$_2$)(Cr(CO)$_4$){μ-C$_6$H$_{11}$S}] (**9**), the orange compound [Cr(η^5-thiophene)(CO)$_3$] and the violet compound [TiCp$_2$(C$_6$H$_{11}$S)$_2$] (76.4 mg, 81%).

9—Yield: 6.0 mg (6%). C$_{26}$H$_{32}$O$_4$S$_2$CrTi (572.6)—Calc.: C, 54.54; H, 5.63. Found: C, 54.68; H, 5.75%.

5.1.5. *Reaction of 1 with water*

A solution of 114 mg (0.26 mmol) of **1** in 40 cm^3 of distilled water was stirred at r.t. for 20 min. The color of the solution changed from green to red. The solution was concentrated until a red precipitate appeared, while the solution was only lightly colored. Dichloromethane (80 cm^3) was added to this suspension and the red organic layer was separated from the water phase. The organic phase was dried over anhydrous sodium sulfate and the residue was recrystallized from a dichloromethane–petroleum ether (1:1) mixture. Red-brown needle-like crystals of [Ti{(η^1,η^5-thienyl)Cr(CO)$_3$}Cp$_2$(OH)] (**10**) were formed.

10—Yield: 86 mg (79%). C$_{17}$H$_{14}$O$_4$SCrTi (414.3)—Calc.: C, 49.29; H, 3.41. Found: C, 48.82; H, 3.29%.

5.1.6. *Reaction of 5 with thiophenol*

Thiophenol (0.92 cm^3, 7.46 mmol) was added to 0.40 g (0.82 mmol) of **5**. Dichloromethane (10 cm^3) and 0.62 cm^3 (4.10 mmol) of TMEDA were added and the mixture was stirred for 1 h at r.t. The color changed from green to orange-red. The solvent was removed under reduced pressure. Three bands were separated with column chromatography (eluent: petroleum ether–dichloromethane (1:2)). The first yellow band was identified as the starting compound [Cr(η^6-benzothiophene)(CO)$_3$]. The second orange-red band was characterized as [Ti{(η^1,η^6-benzothienyl)Cr(CO)$_3$}Cp$_2$(SC$_6$H$_5$)] (**11**). The third purple band was characterized as TiCp$_2$(SPh)$_2$. Yield: 0.13 g (41%).

11—Yield: 0.11 g (24%). C$_{27}$H$_{20}$O$_3$S$_2$CrTi (556.5)—Calc.: C, 58.28; H, 3.62. Found: C, 58.42; H, 3.73. MS (EI); *m/z*: 500 [M$^+$ $-$2CO], 472 [M$^+$ $-$3CO], 420 [M$^+$ $-$3CO$-$Cr], 287 [TiCp$_2$SPh$^+$], 178 [TiCp$_2^+$].

5.1.7. *Reaction of 5 with water*

5 (0.48 g, 1.00 mmol) was dissolved in dichloromethane ($\sim$ 50 cm^3). Distilled water ($\sim$ 20 cm^3) was added and the mixture was stirred for 12 h, during which time the color of the solution changed from green to orange. The organic and water layers were separated and the organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The orange-brown product [Ti{(η^1,η^6-benzothie-

nyl)Cr(CO)$_3$}Cp$_2$(OH)] (**12**) was washed with hexane and dried in vacuo. Yield: 0.28 g (65%).

12—Yield: 0.28 g (65%). C$_{21}$H$_{16}$CrO$_4$STi (464.3)— Calc.: C, 54.33; H, 3.47. Found: C, 54.52; H, 3.58%.

5.1.8. meso-[Ti{(η^1,η^5-thienyl)Cr(CO)$_3$}Cp$_2$Cl]$_2${μ-O} (13) and [Ti{(η^1,η^5-thienyl)Cr(CO)$_3$}Cp$_2$Cl]$_2${μ-O} (14)

0.6 g (2.71 mmol) of [Cr(η^5-thiophene)(CO)$_3$] was dissolved in 30 cm^3 of THF and cooled to −90 °C when 1.8 cm^3 (2.88 mmol) n-BuLi was added. The color of the reaction mixture changed from orange to yellow. The mixture was stirred at −70 °C for 10 min and then cooled to −90 °C again. A cooled solution of 0.6 g (1.35 mmol) of [{TiCp$_2$Cl}$_2$(μ-O)] in 80 cm^3 of THF was added. The solution was allowed to warm to r.t. while the color changed from yellow-red to dark red. The solvent was removed in vacuo. Column chromatography (dichloromethane–petroleum ether) of the residue yielded the starting material and the red-brown isomers **13** and **14**.

13 and **14**—Yield: 0.85 g (77%). C$_{34}$H$_{26}$O$_7$S$_2$Cr$_2$Ti$_2$ (810.5)—Calc.: C, 50.39; H, 3.23. Found: C, 50.01; H, 3.08%.

5.1.9. [TiCp$_2$Cl]$_2${μ-Cr(η^5-thienyl)(CO)$_3$} (15)

0.6 g (2.73 mmol) of [Cr(η^5-thiophene)(CO)$_3$] was dissolved in 30 cm^3 of THF and cooled to −90 °C. 5.1 cm^3 (8.18 mmol) of n-BuLi was added and the mixture was stirred for 10 min at −50 °C. The color of the reaction mixture changed from orange to yellow. The solution was again cooled to −90 °C and a solution of 1.36 g (5.46 mmol) of [TiCp$_2$Cl$_2$] in 100 cm^3 of THF was added. The temperature of the solution was allowed to warm to −20 °C after which the solvent was evaporated. The green residue was dissolved in 80 cm^3 of dichloromethane and filtered. The green solid **15** was recrystallized from acetone and the crystals washed with an ether–petroleum ether (1:1) mixture and dried.

15—Yield: 0.50 g (34%). C$_{27}$H$_{22}$Cl$_2$O$_3$SCrTi$_2$ (645.2)—Calc.: C, 50.26; H, 3.44. Found: C, 50.45; H, 3.22%.

5.1.10. Reaction of 15 with C$_6$H$_{11}$SH

0.50 g (0.78 mmol) of **15** was reacted with 12 cm^3 (79.9 mmol) of TMEDA, 9 cm^3 (73.4 mmol) of C$_6$H$_6$SH and 20 cm^3 of dichloromethane. The solution was stirred for 1 h at r.t. The color of the solution changed from green to black-green. The solvent was removed in vacuo and column chromatography of the residue yielded an olive-green complex [TiCp$_2$(C$_6$H$_{11}$S)]$_2${μ-Cr(η^5-thienyl)-(CO)$_3$} (**16**).

16—Yield: 0.47 g (76%). C$_{39}$H$_{44}$CrO$_3$S$_3$Ti$_2$ (804.8)— Calc.: C, 58.21; H, 5.51. Found: C, 57.95; H, 5.32%.

5.2. Crystal structure determination

The intensity data for the compound were collected on a Nonius CAD4 diffractometer, using graphite-monochromated Mo–K$_\alpha$ radiation. Data were corrected for Lorentz polarization and absorption effects [45]. The structures were solved by direct methods (SHELXS) [46] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97) [47]. The thienyl ring S2, C15, C16, C17, C18 is disordered in such a way that S2 and C16 alternatively occupied the same positions. This disorder could be solved. The hydrogen atoms of the structure 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 (Table 3).

Table 3
Crystal data and structure refinement of **4**

Empirical formula	C$_{24}$H$_{16}$O$_6$S$_2$Cr$_2$Ti
Formula weight (g mol^{-1})	616.39
Temperature (K)	183(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P$\bar{1}$
Unit cell dimensions	
a (Å)	7.942(1)
b (Å)	10.290(1)
c (Å)	14.679(1)
α (°)	80.84(1)
β (°)	79.71(1)
γ (°)	85.90(1)
Volume (Å^3)	1164.1(2)
Z	2
Density (calculated) (mg m^{-3})	1.758
Absorption coefficient (mm^{-1})	1.471
F(0 0 0)	620
Crystal size (mm^3)	0.40 × 0.38 × 0.36
Theta range for data collection (°)	2.28–27.44
Index ranges	−10 ≤ h ≤ 9, −13 ≤ k ≤ 0, −19 ≤ l ≤ 18
Reflections collected	5549
Independent reflections	5266 [R_{int} = 0.0315]
Absorption correction	PSI-SCAN
Max./min. transmission	0.364/0.325
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3516/0/322
Goodness-of-fit on F^2	0.962
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.041, wR_2 = 0.099
R indices (all data)	R_1 = 0.100, wR_2 = 0.108
Largest difference peak and hole (e Å^{-3})	0.557 and −0.720

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 180975 (FO429). 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).

References

[1] W.L. Orr, C.M. White (Eds.), Geochemistry of Sulfur in Fossil Fuels, American Chemical Society, Washington, DC, 1990.
[2] (a) G.M. Tsivgoulis, J.-M. Lehn, Angew. Chem. Int. Ed. Engl. 34 (1995) 1119;
(b) S. Le Stang, F. Paul, C. Lapinte, Organometallics 19 (2000) 1035;
(c) M. Hmyene, A. Yassar, M. Escorne, A. Percheron-Guegan, F. Garnier, Adv. Mater. 6 (1994) 564.
[3] B.C. Gates, J.R. Katzer, G.C.A. Schuit, Chemistry of Catalytic Processes, McGraw-Hill, New York, 1979.
[4] (a) R.J. Angelici, Acc. Chem. Res. 21 (1988) 387;
(b) R.J. Angelici, Coord. Chem. Rev. 105 (1990) 61;
(c) R.J. Angelici, Bull. Soc. Chim. Belg. 104 (1995) 265;
(d) C. Bianchini, A. Meli, J. Chem. Soc. Dalton Trans. (1996) 801.;
(e) C. Bianchini, A. Meli, Acc. Chem. Res. 31 (1998) 109.
[5] (a) C. Bianchini, A. Meli, Synlett 6 (1997) 643;
(b) W.D. Harman, Chem. Rev. 97 (1997) 1953.
[6] R.J. Angelici, Organometallics 20 (2001) 1259.
[7] (a) T.B. Rauchfuss, Prog. Inorg. Chem. 21 (1991) 259;
(b) J. Chen, R.J. Angelici, Coord. Chem. Rev. 206–207 (2000) 63.
[8] (a) J.W. Hachgenei, R.J. Angelici, Organometallics 8 (1989) 14;
(b) S. Zhang, J.K. Shen, F. Basolo, T.D. Ju, R.F. Lang, G. Kiss, C.D. Hoff, Organometallics 13 (1994) 3692;
(c) J.A.S. Howell, P.C. Yates, N.F. Ashford, D.T. Dixon, R. Warren, J. Chem. Soc. Dalton Trans. (1996) 3959.
[9] (a) J. Besancon, J. Tiroflet, A. Card, Y. Dusausoy, J. Organomet. Chem. 59 (1973) 267;
(b) F. Rose-Munch, O. Bellot, M. Laurent, A. Semra, F. Robert, Y. Jeannin, J. Organomet. Chem. 402 (1991) 1.
[10] (a) M.F. Semmelhack, J. Bisaha, M. Czarney, J. Am. Chem. Soc. 101 (1979) 768;
(b) M. Ghavshou, D.A. Widdowson, J. Chem. Soc. Perkin Trans. 1 (1983) 3065.
[11] S. Lotz, M. Schindehutte, P.H. van Rooyen, Organometallics 11 (1992) 629.
[12] P.H. van Rooyen, M. Schindehutte, S. Lotz, Organometallics 11 (1992) 1104.
[13] (a) J.A. Heppert, M.A. Morgenstern, D.M. Scherubel, F. Takusagawa, M.R. Shaker, Organometallics 7 (1988) 1715;

(b) G. Richter-Addo, A.D. Hunter, N. Wichrowska, Can. J. Chem. 68 (1990) 41.
[14] R. Meyer, P.L. Wessels, P.H. van Rooyen, S. Lotz, Inorg. Chim. Acta 284 (1999) 127.
[15] T.A. Waldbach, P.H. van Rooyen, S. Lotz, Angew. Chem. Int. Ed. Engl. 32 (1993) 710.
[16] M. Landman, T. Isenburg, S. Lotz, Unpublished results.
[17] T.A. Waldbach, R. van Eldik, P.H. van Rooyen, S. Lotz, Organometallics 16 (1997) 4056.
[18] A. du Toit, M. Landman, S. Lotz, J. Chem. Soc. Dalton Trans. (1997) 2955.
[19] M.D. Rausch, G.A. Moser, E.J. Zaiko, A.L. Lipman, Jr., J. Organomet. Chem. 23 (1970) 185.
[20] M. Novi, G. Guanti, C. Dell'Erba, J. Heterocycl. Chem. 12 (1975) 1055.
[21] C.A.L. Mahaffy, P.L. Pauson, Inorg. Synth. 38 (1990) 136.
[22] M.N. Nefedova, V.N. Setikina, D.N. Kursanov, J. Organomet. Chem. 244 (1983) C21.
[23] M. Bottrill, P.D. Gavens, J.W. Kelland, J. McMeeking, Comprehensive Organometallic Chemistry, Part 22, vol. 405, Pergamon Press, Oxford, 1982.
[24] A.N. Nesmeyanov, E.I. Fedin, O.V. Nogina, N.S. Kochetkova, V.A. Dubovitsky, P.V. Petrovsky, Tetrahedron Suppl. 8 (1966) 389.
[25] H. Köpf, B. Block, M. Schmidt, Chem. Ber. 101 (1968) 272.
[26] (a) P.S. Braterman, V.A. Wilson, K.K. Joshi, J. Chem. Soc. A (1971) 191.;
(b) C.J. Ruffing, T.B. Rauchfuss, Organometallics 4 (1985) 524.
[27] J.H. Toney, T.J. Marks, J. Am. Chem. Soc. 107 (1985) 947.
[28] M.A. Chaudhari, P.M. Treichel, F.G.A. Stone, J. Organomet. Chem. 2 (1964) 206.
[29] M.J. Sanger, R.J. Angelici, Organometallics 13 (1994) 1821.
[30] S. Gronowitz, Adv. Heterocycl. Chem. 1 (1963) 1.
[31] M.F. Bailey, L.F. Dahl, Inorg. Chem. 4 (1965) 1306.
[32] E.L. Muetterties, J.R. Bleeke, E.J. Wuckerer, T.A. Albricht, Chem. Rev. 82 (1982) 499.
[33] R. Meyer, M. Schindehutte, P.H. van Rooyen, S. Lotz, Inorg. Chem. 33 (1994) 3605.
[34] J.D. Zeinstra, J.H. Teuben, F. Jellinek, J. Organomet. Chem. 170 (1979) 39.
[35] J.L. Attwood, W.E. Hunter, D.C. Hrncir, E. Samuel, H. Alt, Inorg. Chem. 14 (1975) 1757.
[36] A.K. Rappe, Organometallics 6 (1987) 354.
[37] W.R. Harshbarger, S.H. Bauer, Acta Crystallogr. B 26 (1970) 1010.
[38] (a) T.A. Waldbach, P.H. van Rooyen, S. Lotz, Organometallics 12 (1993) 4250;
(b) S. Lotz, P.H. van Rooyen, R. Meyer, Adv. Organomet. Chem. 37 (1995) 219.
[39] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc. Perkin Trans. II (1987) S1.
[40] D.F. Shriver, M.A. Drezdzon, The Manipulation of Air-sensitive Compounds, 2nd ed., Wiley, New York, 1980.
[41] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, 2nd ed., Pergamon Press, New York, 1980.
[42] G.H. Spies, R.J. Angelici, Organometallics 6 (1987) 1897.
[43] M.D. Rausch, G.A. Moser, E.J. Zaiko, A.L. Lipman, Jr., J. Organomet. Chem. 23 (1970) 185.
[44] D. Nath, R.K. Sharma, A.N. Bhat, Inorg. Chim. Acta 20 (1976) 109.
[45] MOLEN, An Interactive Structure Solution Procedure, Enraf-Nonius, Delft, The Netherlands, 1990.
[46] G.M. Sheldrick, Acta Crystallogr. A 46 (1990) 467.
[47] G.M. Sheldrick, SHELXL-97 (Release 97-2), University of Göttingen, Germany, 1997.