

Bis(Cyclopentadienyl)Titanium Complexes of Naphthalene–1,8-Dithiolates, Biphenyl 2,2'-Dithiolates, and Related Ligands

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Received October 29, 2004

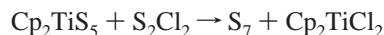
Titanocene 1,8-dithiolato–naphthalene and titanocene 2,2'-dithiolato biphenyl are produced by the reaction of naphtho[1,8-*cd*]-1,2-dithiole [or the biphenyl] with titanocene dicarbonyl (Ti(II)) in toluene at room temperature. The pro-ligands 2,7-di(*tert*-butyl)naphtho[1,8-*cd*]-1,2-dithiole, 5,6-dihydroacenaphtho[5,6-*cd*]-1,2-dithiole, 4,5-dithioace-phenanthrylene, and 13,14-dithiapicene have been used in similar reactions with titanocene dicarbonyl to investigate the effect of steric bulk and of varying the naphthalene backbone on the final complex. The resulting $\text{Cp}_2\text{TiS}_2\text{Ar}$ complexes (Ar = naphthalene) have been shown by temperature-dependent ^1H NMR spectroscopy to exist in solution in an envelope conformation with the six-membered TiS_2C_3 rings undergoing inversion on the NMR time scale while the similar $\text{Cp}_2\text{TiS}_2\text{Ar}$ complexes (Ar = biphenyl, binaphthalene) interconvert more rapidly. Titanocene 2,2'-disulfinato biphenyl has been synthesized by the salt elimination reaction of titanocene dichloride (Ti(IV)) and the disodium salt of biphenyl 2,2'-disulfonic acid. Finally, the effect of using pro-ligands where the sulfur atoms have been mono- or di-oxidized has been studied, and an interesting oxygen elimination reaction is observed for the $\text{S}=\text{O}$ fragments but not for the SO_2 groups. All complexes have been characterized spectroscopically and seven X-ray structures are reported.

Introduction

Thiolato complexes containing the Cp_2Ti group ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) have been known since 1962.¹ These complexes can take a number of different forms where the two sulfur bearing groups can be unconnected ($\text{Cp}_2\text{Ti}(\text{SR})_2$), attached by an organic group ($\text{Cp}_2\text{TiS}_2\text{X}$, X = bridging group) or by a chain of sulfur atoms (Cp_2TiS_5).

There are a number of different ways in which these complexes can be prepared. For example, substitution reaction of a thiolate anion with titanocene dichloride ($\text{Cp}_2\text{-TiCl}_2$) in which the chloride ligands are removed by nucleophilic displacement, thus reaction of titanocene dichloride with two molar equivalents of NaSMe yields $\text{Cp}_2\text{Ti}(\text{SMe})_2$ in excellent yield.² Reactions such as these are of particular interest as the product can be used in further reaction with other complexes of metals such as nickel to

yield heterobimetallic complexes. Furthermore, products formed in this way can be used as ligand transfer reagents with other compounds containing $\text{S}-\text{Cl}$ bonds to reform $\text{Cp}_2\text{-TiCl}_2$ and produce novel sulfur rich compounds. For example, a novel allotrope of sulfur, cycloheptasulfur, was developed by reaction of Cp_2TiS_5 with disulfur dichloride.³



Alternatively, the complex titanocene dicarbonyl ($\text{Cp}_2\text{Ti}(\text{CO})_2$) can be used in an oxidative addition reaction with a disulfide. In this instance, the sulfur sulfur bond of RSSR is cleaved and the Cp_2Ti unit is inserted between the two sulfur atoms to yield a new complex, $\text{Cp}_2\text{Ti}(\text{SR})_2$, with the evolution of carbon monoxide.⁴ There are scattered results in this area^{5–8} and we have studied some examples.⁹ An interesting

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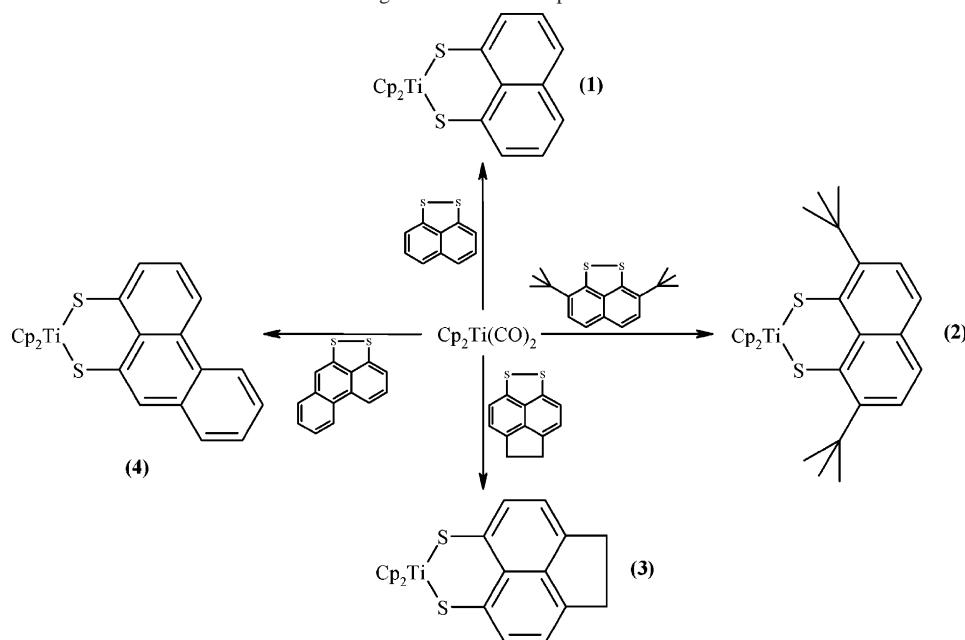
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Scheme 1. Oxidative Addition Reactions of Disulfide Pro-Ligands to Titanium Species

bridging group which we have used in a few cases is naphthalene ($\text{XS}_2 = \text{naphtho}[1,8\text{-}cd]\text{-}1,2\text{-dithiole}$) where the steric strain imposed by the 1,8 substitution is relieved upon coordination. Teo et al. studied the oxidative addition of tetrathionaphthalene (TTT), tetrachlorotetrathionaphthalene (TCTTN), and tetrathiotetracene (TTT) to a number of different low-valent metal substrates.¹⁰ A less constrained bridging group would be biphenyl ($\text{XS}_2 = \text{dibenzo}[ce]\text{-}1,2\text{-dithiine}$) and titanocene 2,2'-dithiolato biphenyl has been previously produced by reaction of 2,2'-Li(LiS) C_{12}H_8 with titanocene dichloride and sulfur¹¹ but this type of complex has never been synthesized by oxidative addition reaction between titanocene dicarbonyl and a disulfur bridged biphenyl compound. Similar biphenyl based thiolato complexes of palladium are also known¹² but these have not been produced from the more readily available sulfur–sulfur bond containing pro-ligand.

Here, we report an investigation into the effect of the backbone on Cp_2TiL complexes. We describe the synthesis of a new titanocene thiolato complex where the two sulfur atoms are connected through a naphthalene backbone. We have also investigated the effect of introducing steric bulk into the backbone, namely by the addition of tertiary butyl groups on the naphthalene ring. An attempt has been made

to investigate the effect of varying the naphthalene backbone slightly while maintaining the rigidity that naphthalene provides. These four complexes have been shown by temperature-dependent ^1H NMR spectroscopy to exist in solution in an envelope conformation with the six-membered TiS_2C_3 chelate rings undergoing rapid inversion.

We also report a new synthesis of the titanocene thiolato complex titanocene 2,2'-dithiolato biphenyl. We have investigated the effect of increasing the steric bulk around the biphenyl backbone by using the pro-ligand 13,14-dithiapi-cene.

The effect of using derivatives of naphtho[1,8-*cd*]-1,2-dithiole and dibenzo[*ce*]-1,2-dithiine whose sulfur atoms have been mono- and di-oxidized as pro-ligands in similar reactions with titanocene dicarbonyl has also been comprehensively examined. This has resulted in us producing two thiolato sulfinato O-bound complexes and also the first example of a disulfinato di-O bound complex with a nine-membered ring. In each case the products have been characterized spectroscopically and complexes **1**, **3**, **5**, **6**, **7** and **8** have been characterized by X-ray crystallography.

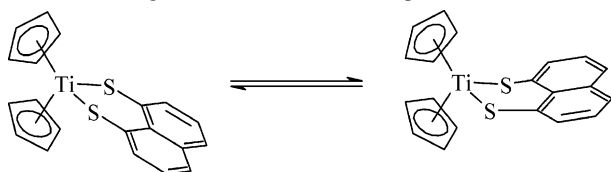
Results and Discussion

The titanocene complexes **1**, **2**, **3**, and **4** were prepared by the reaction of titanocene dicarbonyl with one molar equivalent of the corresponding disulfide pro-ligand in toluene at room temperature.

In each case two equivalents of carbon monoxide were evolved resulting in the oxidative addition of the Cp_2Ti unit into the sulfur–sulfur bond to give a new complex with a greater ring size. They are formed in varying yield (19–80%) and are found to be air stable both in the solid state and in solution.

The ^1H NMR spectrum of complex **1** showed a multiplet in the aromatic region and a broad singlet at 6.31 ppm in the intensity ratio 6:10. These represent the 6 aromatic

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Scheme 2. Ring Inversion of Titanium Complex **1****Table 1.** Activation Parameters of the Chelate Ring Inversions of Complexes **1–4** (all NMR spectra were recorded at 270 MHz in CD₂Cl₂)

complex	δ (cp) (ppm)	T_{cal} (K)	Δ_{v} (Hz)	ΔG_{c}^* (kJ mol ⁻¹)
1	6.31	285	144.2	56.0
2	6.28	<183		
3	5.90	303	60.9	61.9
4	6.31	268	148.9	52.5

naphthalene protons and the 10 cyclopentadienyl protons, respectively. The ¹³C NMR spectrum was as expected with the three nonquaternary aromatic carbons of the naphthalene group being obvious along with two of the three quaternary carbons. Further, the cyclopentadienyl peak came at 114.9 ppm.

Similar titanocene dithiolate complexes^{13,14} where the two sulfur atoms are connected have previously been shown to exhibit interesting temperature-dependent ¹H NMR spectra; typically it was shown that inversion of the chelate ring along the S–S axis occurs.

In the dynamic ¹H NMR spectrum of **1**, the singlet due to the 10 equivalent cyclopentadienyl protons at room temperature was subject to a coalescence phenomenon at a lower temperature and was split into two sharp singlets of equal intensity at temperatures below 0 °C which is compatible with ring inversion (Scheme 2).

The activation parameters of the chelate ring inversions of **1**, **2**, **3**, and **4** are given in Table 1. The singlet representing the cyclopentadienyl protons in the ¹H NMR of complex **2** broadened at 183 K but never split into two equivalent singlets although we believe this would have occurred had we been able to reduce the temperature further.

Previous work carried out on similar titanocene dithiolate complexes^{13,14} has yielded results similar to ours. While we cannot be sure of the exact ΔG_{c}^* of complex **2**, the other values fall in the range 51–62 kJ mol⁻¹. There is no obvious trend such as the activation energy being proportional to the size of the group which is bridging the two sulfur atoms, suggesting that the activation energy is therefore probably influenced more by electronic effects than by steric effects.

The titanocene complexes **5** and **6** were prepared by the reaction of titanocene dicarbonyl with one molar equivalent of the corresponding disulfide pro-ligand in toluene at room temperature.

The ¹H NMR spectrum of complex **5** showed four sets of peaks in the aromatic region, each of equal intensity, corresponding to the four different aromatic environments of the biphenyl ligand. A singlet at 6.17 ppm represents the 10 cyclopentadienyl protons. The ¹³C NMR spectrum was

as expected with two quaternary and four nonquaternary environments being identified and the cyclopentadienyl peak coming at 114.8 ppm, which is close to the analogous fluxional complex titanocene 1,8-dithiolato–naphthalene, **1**. However, in the ¹H NMR spectrum of **5** the cyclopentadienyl peak was found not to split, even at temperatures as low as 183 K. Complex **6** also showed appropriate proton and carbon NMR spectra and mass spectrum, and, like complex **5**, the single peak corresponding to the 10 cyclopentadienyl protons did not split at lower temperatures.

Complex **1** was also produced in the analogous reaction between titanocene dicarbonyl and naphtho-[1,8-*cd*]-1,2-dithiole-1-oxide (Scheme 4).

There was no sign of any complex containing the original pro-ligand in its complete form. This result was unexpected as previous work in our group using this ligand with platinum has resulted in the formation of a di-sulfur bound complex where the oxygen atom is retained.⁹ The loss of oxygen can most likely be attributed to the strong reducing power of Ti(II) in titanocene dicarbonyl. The oxygen which was lost appeared to stimulate the oligomerization of the air-sensitive titanocene dicarbonyl as increased levels of orange insoluble solids were removed from the reaction mixture. This orange compound was characterized by X-ray crystallography and was shown to be a cubic structure with titanium at the 8 corners and the 12 edges of the cube being bridged by oxygen atoms, **10** (Scheme 5). This compound has previously been seen as an acetonitrile solvated complex.¹⁵

Complex **7** was produced in the reaction of titanocene dicarbonyl and naphtho[1,8-*cd*]-1,2-dithiole-1,1-dioxide (Scheme 6). The ligand in this case was found to be bound to the titanium center by one sulfur atom and one oxygen atom. This result is in contrast to previous work carried out by our group where this ligand is found to be bound to a platinum center by both sulfur atoms.⁹ However, this result is explained by the fact that hard titanium prefers to complex to hard oxygen rather than soft sulfur. The ¹H NMR of this complex displayed the expected peaks in the aromatic region and also a pair of singlets of equal intensity which represented the two chemically inequivalent cyclopentadienyl groups. These two singlets did not merge at temperatures as high as 363 K.

7 was also obtained by reaction of titanocene dicarbonyl and naphtho[1,8-*cd*]-1,2-dithiole-1,1,2-trioxide.

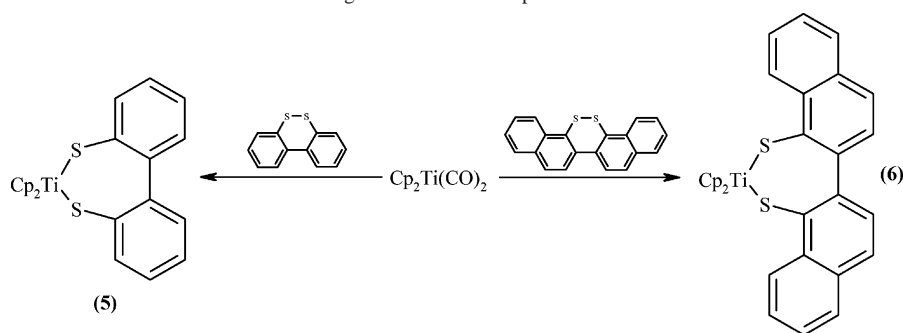
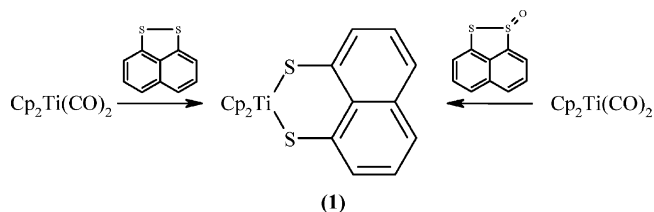
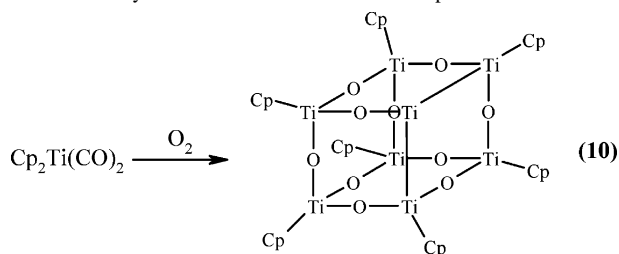
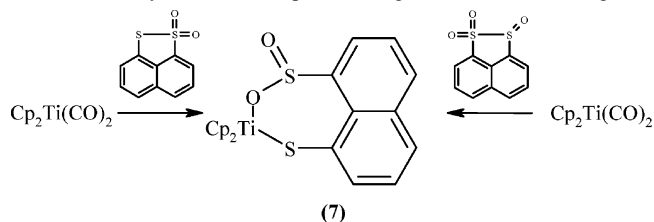
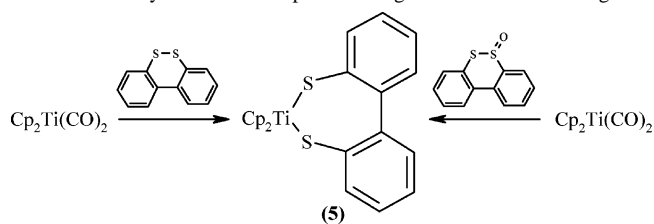
There was no evidence that any complex had been formed which was bound by two oxygen atoms. It appears that the mono-oxidized sulfur of the pro-ligand always loses the oxygen and binds through an oxygen and a sulfur atom. Again, there appeared to be more orange insoluble solid which was filtered out and we believe that this is compound **10**, again produced by the oxygen which was lost from the pro-ligand on complexation.

In the same way that complex **1** was formed by reaction of titanocene dicarbonyl with the pro-ligand naphtho[1,8-*cd*]-1,2-dithiole-1-oxide, so too was complex **5** obtained from

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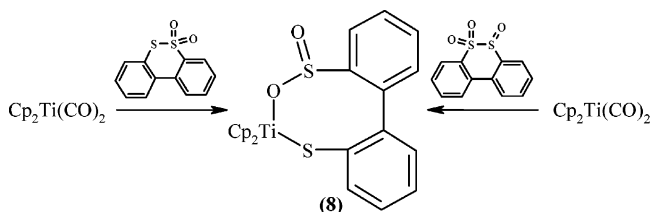
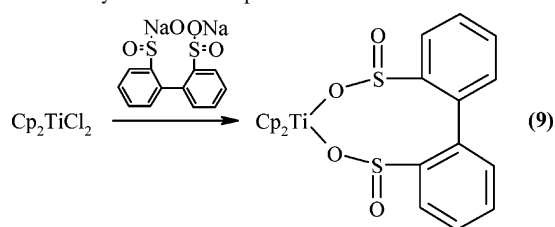
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Scheme 3. Oxidative Addition Reactions of Disulfide Pro-Ligands to Titanium Species**Scheme 4.** Synthesis of Complex **1** Using Two Different Pro-Ligands**Scheme 5.** Synthesis of Cubic Titanocene Compound **10****Scheme 6.** Synthesis of Complex **7** Using Two Different Pro-Ligands**Scheme 7.** Synthesis of Complex **5** Using Two Different Pro-Ligands

the reaction between titanocene dicarbonyl and dibenzo[ce]-1,2-dithiine-5-oxide.

Again, there was no evidence of any complex containing the original pro-ligand in its complete form. This result suggests a general principle for these systems. This emerging trend was observed further when complex **8** was obtained by the reaction of titanocene dicarbonyl with either of the pro-ligands dibenzo[ce]-1,2-dithiine-5,5-dioxide or dibenzo[ce]-1,2-dithiine-5,5,6-trioxide.

The ligand in this case is bound to the titanium center by one sulfur atom and one oxygen atom, just as complex **7** is.

Scheme 8. Synthesis of Complex **8** Using Two Different Pro-Ligands**Scheme 9.** Synthesis of Complex **9**

The ^1H NMR of this complex displayed the expected peaks in the aromatic region and also a pair of singlets of equal intensity which represented the two inequivalent cyclopentadienyl groups.

Finally, complex **9** was formed by salt elimination reaction of titanocene dichloride with the disodium salt of biphenyl 2,2'-disulfonic acid.

The ^1H and ^{13}C NMR spectra of complex **9** were similar to those of **5**. While we were unable to obtain the X-ray crystal structure of **9** we believe that, following previous trends, the ligand is bound to the metal center by two oxygen atoms.

X-ray Crystallography. The crystal structures of complexes **1**, **3**, **5**, **6**, **7**, **8**, and **10** are shown in Figures 1–7, respectively, and selected bond lengths and angles are given in Tables 2–4. The data for **1** and **3** are similar. The Ti–S bond distances (2.3875(9) and 2.4026(11) Å, respectively) closely resemble those of other closely related complexes.^{2,16} The S(1)–C(1) bond lengths are similar to that of the pro-ligand¹⁷ while the main difference between the pro-ligand and these complexes is the splay angle (the deviation from the two S–C bonds being parallel). The pro-ligand has a negative splay angle (-11.21°) due to the sulfur–sulfur bond pulling the two atoms together. The two complexes, however,

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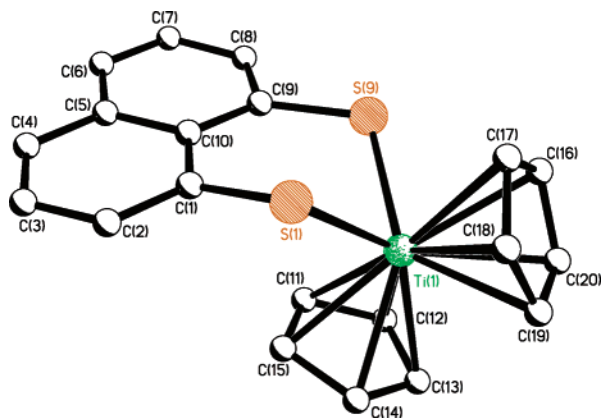


Figure 1. Crystal structure of $\text{Cp}_2\text{Ti}(\text{S}_2\text{C}_{10}\text{H}_6)$ **1**.

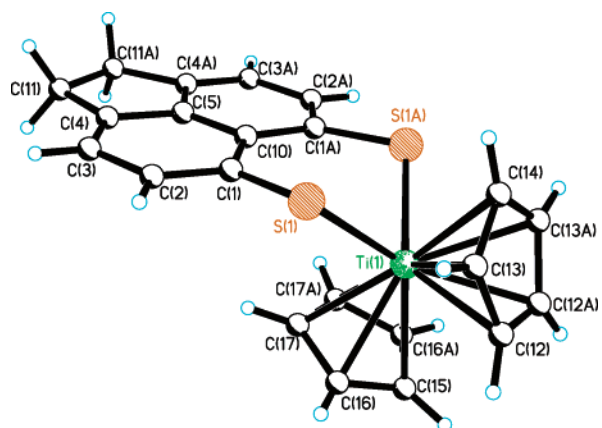


Figure 2. Crystal structure of $\text{Cp}_2\text{Ti}(\text{S}_2\text{C}_{12}\text{H}_8)$ **3**.

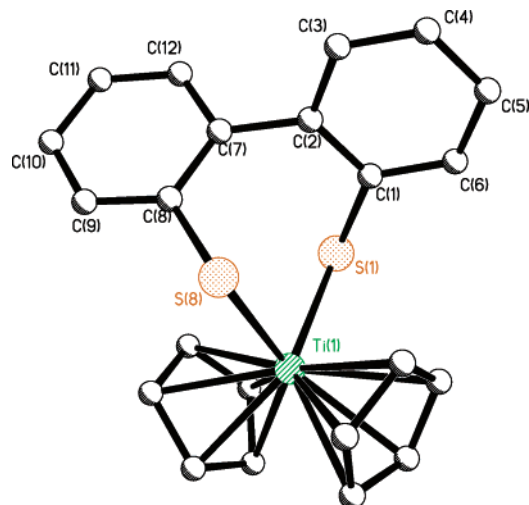


Figure 3. Crystal structure of $\text{Cp}_2\text{TiC}_{12}\text{H}_8\text{S}_2$ **5**.

have positive splay angles (18.9° and 20.0° , respectively) and this can be attributed to the absence of the sulfur–sulfur bond which allows the two atoms to move further apart into a more comfortable position as this alleviates any strain which would have previously been present in the five-membered ring.

The crystal structures of **5** and **6** show the Ti–S bond distances ($2.427(5) - 2.442(5)$ Å) are very close to the Ti–S bond distances in complexes **1** and **3**. The S–C bond lengths are also very similar to those of the corresponding pro-ligands

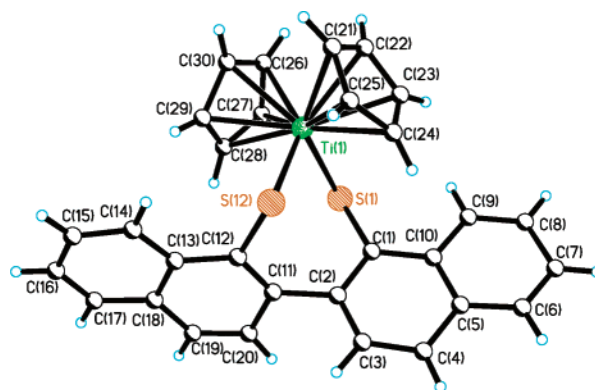


Figure 4. Crystal structure of $\text{Cp}_2\text{TiC}_{20}\text{H}_{12}\text{S}_2$ **6**.

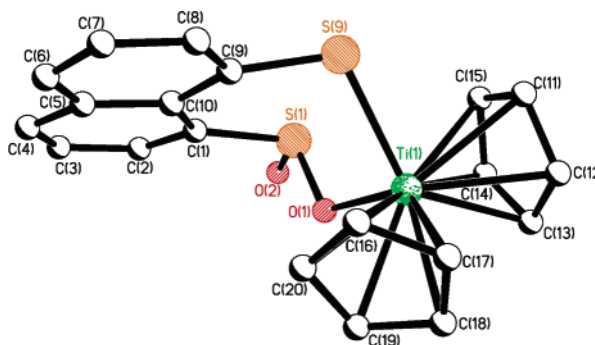


Figure 5. Crystal structure of $\text{Cp}_2\text{Ti}(\text{S}_2\text{O}_2\text{C}_{10}\text{H}_6)$ **7**.

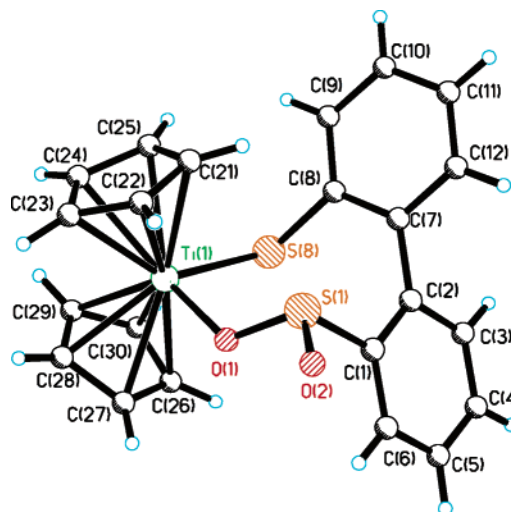


Figure 6. Crystal structure of $\text{Cp}_2\text{TiC}_{12}\text{H}_8\text{S}_2\text{O}_2$ **8**.

dibenzo[*ce*]-1,2-dithiine,¹⁸ and 13,14-dithia-picene¹⁹ and of other complexes **1** and **3**.

The S–Ti–S bond angles of complexes **5** and **6** ($91.79(6)$ and $91.55(17)^\circ$, respectively) are greater than those in titanocene 1,8-dithiolato–naphthalene and titanocene 1,8-dithiolato-5,6-dihydroacenaphthalene but this is to be expected as they are part of a seven-membered ring instead of a six-membered ring in the case of the naphthalene complexes. The S–C–C angles are very similar to the S–C–C angles of the pro-ligands. This is unusual as the free ligands

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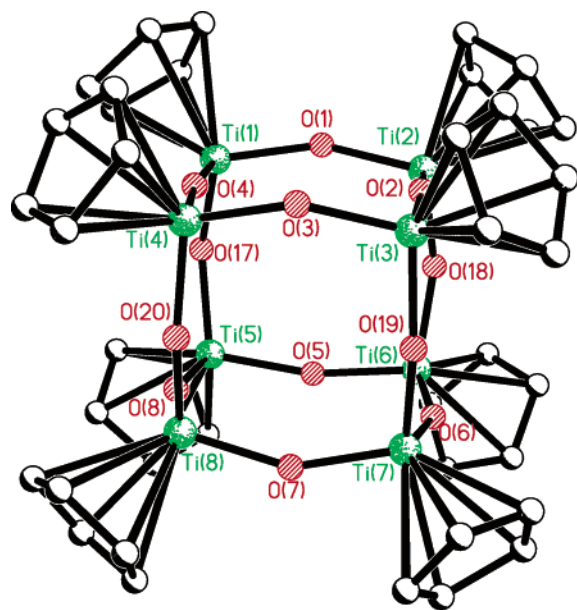


Figure 7. Crystal structure of $\text{Cp}_8\text{Ti}_8\text{O}_{12}$, **10**.

contain a six-membered ring and the insertion of the titanium atom between the two sulfur atoms should theoretically open up the S–C–C bond angles.

Complex **7** has a S(9)–C(9) bond distance (1.771(3) Å) similar to complexes **1** and **3** but the S(1)–C(1) bond is lengthened considerably (1.836(3) Å) compared to the same bond in the pro-ligand (1.768 Å). This is probably due to the removal of the electron density away from the sulfur toward the titanium bound oxygen atom. The splay angle is also positive (15.8°) but not as large as those in complexes **1** and **3** as this angle is part of a seven-membered (Ti–O–S₂–C₃) ring in **7** compared with a six-membered (Ti–S₂–C₃) ring in **1** and **3**. The S=O bond distance in **7** (1.480(2)

Å) is only slightly longer than that of the pro-ligand (1.436 Å) but the S–O bond distance is significantly longer (1.582(2) Å) which is to be expected. The C(1)–S(1)–O(1) and C(1)–S(1)–O(2) bond angles of **7** (97.10(13)° and 103.19(15)°, respectively) are considerably less than the C–S–O angle of the pro-ligand (108.9° which is very close to the idealized 109.5° tetrahedral geometry).

The di-oxo complex **8** has similar S(8)–C(8) and Ti–S(8) bond lengths to **5** and **6** whereas the S(1)–C(1) bond has been lengthened in this complex in comparison with that of the pro-ligand.¹⁸ The S–C–C bond angles are similar to those of complexes **5** and **6** and of the pro-ligand, but the Ti–S–C angle is greater than complexes **5** and **6** since this angle is part of an eight-membered ring in **8** compared with seven-membered rings in **5** and **6**.

The S=O bond length in **8** (1.475(4) Å) is only slightly longer than that of the pro-ligand (1.438(2) Å) but the coordinated S–O bond length is, as is the case with **7**, significantly longer (1.575(4) Å). The C(1)–S(1)–O(1) and C(1)–S(1)–O(2) bond angles in **8** (97.5(2) and 104.0(2)°, respectively) are considerably less than the C–S–O bond angles of the pro-ligand but are very similar to the same angles in complex **7**.

Experimental Section

General. Unless otherwise stated, operations were carried out under an oxygen free nitrogen atmosphere using predried solvents and standard Schlenk techniques. Solvents were dried, purified, and stored according to common procedures.²⁰ The pro-ligands naphtho[1,8-*cd*]-1,2-dithiole,^{21,22} naphtho[1,8-*cd*]-1,2-dithiole-1-oxide,²³ naphtho[1,8-*cd*]-1,2-dithiole-1,1-dioxide,^{22,24} naphtho[1,8-*cd*]-1,2-dithiole-1,1,2-trioxide,²⁵ 2,7-di(*tert*-butyl)naphtho[1,8-*cd*]-1,2-dithiole,²⁶ 5,6-dihydroacenaphtho[1,8-*cd*]-1,2-dithiole,²⁷ 4,5-dithioacephenanthrylene,²⁸ dibenzo[*ce*]-1,2-dithiine,²⁹ dibenzo[*ce*]-1,2-dithiine-5-

Table 2. Bond Lengths [Å] and Angles [deg] for Naphthalene Backboned Complexes **1**, **3**, and **7**

	1	3	7
Ti(1)–S(1)	2.3875(9)	2.4026(11)	
Ti(1)–S(9)	2.3874(10)		2.3920(10)
Ti(1)–Cp(1)	2.371(3)–2.402(3)	2.359(3)–2.376(3)	2.345(3)–2.402(4)
Ti(1)–Cp(2)	2.356(3)–2.395(3)	2.345(4)–2.386(4)	2.370(3)–2.402(4)
Ti(1)–O(1)			1.973(2)
O(1)–S(1)			1.582(2)
S(1)–O(2)			1.480(2)
S(1)–C(1)	1.774(3)	1.772(3)	1.836(3)
S(9)–C(9)	1.761(3)		1.771(3)
C(1)–C(10)	1.457(4)	1.442(3)	1.442(4)
C(9)–C(10)	1.437(4)		1.436(4)
S(1)–Ti(1)–S(9)	84.29(3)	84.80(5)	
Ti(1)–S(1)–C(1)	105.68(10)	107.64(7)	
Ti(1)–S(9)–C(9)	111.25(11)		108.49(11)
S(1)–C(1)–C(10)	125.3(2)	125.2(2)	126.2(2)
C(1)–C(10)–C(9)	126.7(3)	129.6(4)	125.9(3)
S(9)–C(9)–C(10)	126.9(2)		123.7(2)
splay angle ^a	18.9	20	15.8
O(1)–Ti(1)–S(9)			89.36(7)
Ti(1)–O(1)–S(1)			119.09(12)
O(1)–S(1)–O(2)			106.76(13)
O(1)–S(1)–C(1)			97.10(13)
O(2)–S(1)–C(1)			103.19(15)
C(4)–C(5)–C(10)–C(1)	–5.4(4)	–0.1(6)	–3.3(4)
C(4)–C(5)–C(10)–C(9)	175.0(3)	178.4(3)	175.6(3)

^a Splay angle = sum of the four internal ring S–C–C and C–C–C angles – 360.

Table 3. Bond Lengths [Å] and Angles [deg] for Biphenyl Backboned Complexes **5**, **6**, and **8**

	5	6	8
Ti(1)–S(1)	2.428(3)	2.442(5)	
Ti(1)–S(8)	2.429(3)		2.4240(17)
Ti(1)–S(12)		2.427(5)	
Ti(1)–Cp(1)	2.357(6) – 2.412(6)	2.360(19) – 2.416(18)	2.362(6) – 2.392(6)
Ti(1)–Cp(2)	2.352(6) – 2.411(6)	2.372(18) – 2.405(19)	2.352(6) – 2.386(5)
Ti(1)–O(1)			1.976(4)
O(1)–S(1)			1.575(4)
S(1)–O(2)			1.475(4)
S(1)–C(1)	1.782(6)	1.744(17)	1.815(6)
S(8)–C(8)	1.779(6)		1.783(5)
S(12)–C(12)		1.776(17)	
C(1)–C(2)	1.423(8)	1.42(2)	1.382(8)
C(2)–C(7)	1.488(9)		1.481(8)
C(7)–C(8)	1.433(8)		1.404(7)
C(2)–C(11)		1.52(2)	
C(11)–C(12)		1.35(2)	
S(1)–Ti(1)–S(8)	91.79(6)		
S(1)–Ti(1)–S(12)		91.55(17)	
S(8)–Ti(1)–O(1)			93.47(12)
Ti(1)–S(1)–C(1)	105.9(2)	106.7(6)	
Ti(1)–S(8)–C(8)	105.02(19)		112.44(17)
Ti(1)–S(12)–C(12)		106.0(6)	
S(1)–C(1)–C(2)	119.0(4)	119.9(12)	119.8(4)
S(8)–C(8)–C(7)	118.6(4)		119.8(4)
S(12)–C(12)–S(11)		117.8(12)	
C(1)–C(2)–C(7)	122.0(5)		125.4(5)
C(2)–C(7)–C(8)	122.2(5)		121.7(5)
C(1)–C(2)–C(11)		120.0(15)	
C(2)–C(11)–C(12)		123.9(14)	
Ti(1)–O(1)–S(1)			126.6(2)
O(1)–S(1)–O(2)			107.3(2)
O(1)–S(1)–C(1)			97.5(2)
O(2)–S(1)–C(1)			104.0(2)

Table 4. Bond Lengths [Å] and Angles [deg] for Titanocene Cube **10**

	10
Ti–O	1.794(6) – 1.829(6)
Ti–C	2.359(12) – 2.431(11)
O–Ti–O	102.2(3) – 106.1(3)
Ti–O–Ti	143.2(4) – 173.3(4)

oxide,³⁰ dibenzo[*ce*]-1,2-dithiine-5,5-dioxide,²⁵ dibenzo[*ce*]-1,2-dithiine-5,5,6-trioxide,²⁵ disodium biphenyl-2,2'-disulfinate,²⁵ and 13,14-dithiapicene³¹ were prepared according to literature procedures as was the complex titanocene dicarbonyl.³²

¹³C and ¹H NMR spectra were recorded on a JEOL GSX 270 MHz spectrometer with δ referenced to external SiMe₄. ¹³C NMR were all proton decoupled. Infrared spectra were recorded as KBr pellets in the range 4000–400 cm^{−1} on a Perkin-Elmer 2000 FTIR/Raman spectrometer. Microanalysis was performed by the University of St. Andrews microanalysis service. Mass spectrometry was

performed by the EPSRC National Mass Spectrometry Service Centre, Swansea and the University of St. Andrews Mass Spectrometry Service.

Synthesis. Titanocene 1,8-dithiolato–Naphthalene (1). A mixture of titanocene dicarbonyl (323 mg, 1.38 mmol) and naphtho-[1,8-*cd*]-1,2-dithiole (264 mg, 1.38 mmol) in toluene was stirred for 1 h. The resulting red solution was filtered through a small Celite pad to remove any unreacted starting material and any insoluble impurities. The filtrate was concentrated under vacuum to ca. 3 cm³ and hexane (20 cm³) was added to precipitate the product as a red solid (0.277 g, 55%). Found (calcd for (TiS₂C₂₀H₁₆)₄·C₇H₈): C 66.10 (66.74), H 4.41 (4.63), S 16.85 (16.39)%. ¹H NMR (CD₂Cl₂) δ : 7.45–7.18 (m, 6H, aromatics), 6.31 (broad s, 10H, cp groups). ¹³C NMR (CD₂Cl₂) δ : 147.9 (quaternary aromatic), 137.2 (quaternary aromatic), 132.0 (aromatic C–H), 126.8 (aromatic C–H), 124.4 (aromatic C–H), 114.9 (cp groups). Selected IR data (KBr) ν /cm^{−1}: 3077 (m), 1193 (m), 1012 (m), 814 (s), 761 (s). Mass Spec (FAB): (M)⁺ 368.

Method B. A mixture of titanocene dicarbonyl (227 mg, 0.97 mmol) and naphtho-[1,8-*cd*]-1,2-dithiole-1-oxide (200 mg, 0.97 mmol) in toluene was stirred for 1 h. The resulting red solution was filtered through a small Celite pad to remove any unreacted starting material and any insoluble impurities. The filtrate was concentrated under vacuum to ca. 3 cm³ and hexane (20 cm³) was added to precipitate the product as a red solid (0.026 g, 7%). ¹H NMR (CD₂Cl₂) δ : 7.47–7.18 (m, 6H, aromatics), 6.30 (broad s, 10H, cp groups). Mass Spec (FAB): (M)⁺ 368.

Titanocene 1,8-dithiolato-2,7-di(*tert*-butyl)naphthalene (2). A mixture of titanocene dicarbonyl (200 mg, 0.86 mmol) and 2,7-di(*tert*-butyl)naphtho-[1,8-*cd*]-1,2-dithiole (258 mg, 0.86 mmol) in toluene was stirred for 1 h. The resulting dark red solution was filtered through a shallow Celite pad to remove any unreacted

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starting material and any insoluble impurities. The filtrate was concentrated under vacuum to ca. 3 cm³ and hexane (20 cm³) was added to precipitate the product as a purple solid (0.154 g, 38%). Microanalysis: Found (calcd for TiC₂₈H₃₂S₂) C 70.21 (69.98), H 6.68 (6.71)%. ¹H NMR (CDCl₃) δ: 7.54–7.51 (d, 2H, aromatics), 7.41–7.38 (d, 2H, aromatics), 6.28, (s, 10H, cp groups), 1.50 (s, 18H, *t*-Bu groups). ¹³C NMR (CDCl₃) δ: 139.6 (quaternary aromatic), 139.1 (quaternary aromatic), 132.8 (quaternary aromatic), 125.8 (aromatic C–H), 121.9 (aromatic C–H), 120.2 (cp groups), 35.6 (quaternary *t*-Bu), 28.2 (Me groups). Selected IR data (KBr) ν/cm⁻¹: 1354 (m), 1242 (m), 1014 (s) and 819 (s). FAB⁺ MS: *m/z* 480 [M]⁺.

Titanocene 1,8-dithiolato-5,6-dihydroacenaphthalene (3). A mixture of titanocene dicarbonyl (200 mg, 0.86 mmol) and 5,6-dihydroacenaphtho[5,6-*c,d*]-1,2-dithiole (185 mg, 0.86 mmol) in toluene was stirred for 1 h. The resulting red solution was filtered through a small Celite pad to remove any unreacted starting material and any insoluble impurities. The filtrate was concentrated under vacuum to ca. 3 cm³ and the product started to precipitate as a red solid (0.270 g, 80%). Microanalysis: Found (calcd for TiC₂₂H₁₈S₂) C 68.34 (67.0), H 5.19 (4.6)%. ¹H NMR (CD₂Cl₂) δ: 7.20 (m, 4H, aromatics), 6.8–6.0 (broad d, 10H, cp groups), 3.31 (s, 4H, CH₂ × 2). ¹³C NMR (CD₂Cl₂) δ: 144.0 (quaternary aromatic), 143.4 (quaternary aromatic), 140.8 (quaternary aromatic), 132.7 (cp groups), 118.8 (aromatic C–H), 114.7 (aromatic C–H), 30.0 (CH₂). Selected IR data (KBr) ν/cm⁻¹: 1398 (m), 1231 (m), 1016 (s) and 825 (s). EI⁺ MS: *m/z* 394 [M]⁺.

Titanocene 1,8-dithiolato-acephenanthrylene (4). A mixture of titanocene dicarbonyl (200 mg, 0.86 mmol) and 4,5-dithioacephenanthrylene (205 mg, 0.86 mmol) in toluene was allowed to stir for 1 h. The resulting dark solution was filtered through a small Celite pad to remove any unreacted starting material and any insoluble impurities. The filtrate was dried under vacuum, dissolved in a minimum volume of dichloromethane, and hexane (20 cm³) was added to precipitate the product as a brown solid (0.066 g, 19%). Microanalysis: Found (calcd for TiC₂₄H₁₈S₂) C 69.14 (68.9), H 4.09 (4.3)%. ¹H NMR (CD₂Cl₂) δ: 8.48 (m, 2H, aromatics), 7.71–7.35 (m, 6H, aromatics), 6.31 (s, 10H, cp groups). ¹³C NMR (CD₂Cl₂) δ: 114.9 (cp groups), 133.4, 131.3, 127.2, 127.1, 126.0, 124.8, 123.1, 120.8 (all aromatic C–H), 128.5, 125.5, 122.9, 118.5, 118.2, 112.6 (all quaternary aromatics). Selected IR data (KBr) ν/cm⁻¹: 1437 (m), 1201 (m), 1016 (s) and 819 (s). FAB⁺ MS: *m/z* 418 [M]⁺.

Titanocene 2,2'-dithiolato biphenyl (5). A mixture of titanocene dicarbonyl (216 mg, 0.93 mmol) and dibenzo[*ce*]-1,2-dithiine (200 mg, 0.93 mmol) in toluene was stirred for 1 h. The resulting green solution was filtered through a small Celite pad to remove any unreacted starting material and any insoluble impurities. The filtrate was concentrated under vacuum to ca. 3 cm³ and hexane (20 cm³) was added to precipitate the product as a green solid. Yield 0.302 g (83%). Microanalysis: Found (calcd for TiC₂₂H₁₈S₂) C 66.70 (67.0), H 4.80 (4.6)%. ¹H NMR (CDCl₃) δ: 7.74–7.71 (dd, 2H, aromatics), 7.39–7.32 (td, 2H, aromatics), 7.25–7.17 (td, 2H, aromatics), 7.09–7.06 (dd, 2H, aromatics), 6.17 (s, 10H, cp groups). ¹³C NMR (CDCl₃) δ: 151.1, 142.0 (both 2C, quaternary aromatics), 133.4, 130.0, 127.5, 126.3 (all 2C, aromatic C–H), 114.8 (10C, Cp groups). FAB⁺ MS: *m/z* 394 [M]⁺.

Method B. A mixture of titanocene dicarbonyl (200 mg, 0.86 mmol) and dibenzo[*ce*]-1,2-dithiine-5-oxide (198 mg, 0.86 mmol) in toluene was stirred overnight. The resulting green solution was filtered through a small Celite pad to remove any unreacted starting material and any insoluble impurities. The filtrate was concentrated under vacuum to ca. 3 cm³ and hexane (20 cm³) was added to

precipitate the product as a green solid. Yield 0.069 g (21%). ¹H NMR (CD₂Cl₂) δ: 7.71–7.68 (dd, 2H, aromatics), 7.38–7.31 (td, 2H, aromatics), 7.25–7.16 (td, 2H, aromatics), 7.02–6.98 (dd, 2H, aromatics), 6.17 (s, 10H, cp groups). ¹³C NMR (CD₂Cl₂) δ: 151.8, 142.3 (both 2C, quaternary aromatics), 133.5, 129.8, (both 2C, aromatic C–H), 128.8, 128.2 (both 2C, quaternary aromatics), 127.3, 125.9 (both 2C, aromatic C–H), 114.7 (10C, Cp groups). FAB⁺ MS: *m/z* 394 [M]⁺.

Titanocene 1,1'-dithiolato[2,2']binaphthalene (6). A mixture of titanocene dicarbonyl (200 mg, 0.86 mmol) and 13,14-dithiapicene (270 mg, 0.86 mmol) in toluene was stirred for 1 h. The resulting green solution was filtered through a small Celite pad to remove any unreacted starting material and any insoluble impurities. The filtrate was removed under vacuum and the remaining solid was purified by chromatography through silica, using dichloromethane as an elutant. The green layer was collected, dried, and recrystallized from toluene to give dark crystals. Yield 0.091 g (21.5%). ¹H NMR (CD₂Cl₂) δ: 8.66 (d, 2H, aromatics), 7.92 (d, 2H, aromatics), 7.72 (d, 2H, aromatics), 7.68–7.58 (m, 4H, aromatics), 7.14 (d, 2H, aromatics), 6.14 (s, 10H, cp groups). ¹³C NMR (CD₂Cl₂) δ: 140.6, 134.3, 133.2 (all 1C, quaternary aromatics), 128.6, 128.0, 127.3, 125.9, 125.8, 125.7 (all 1C, aromatic C–H), 114.4 (10C, cp groups).

Titanocene 1-sulfinato-8-thiolato-naphthalene (7). A mixture of titanocene dicarbonyl (211 mg, 0.90 mmol) and naphtho-[1,8-*cd*]-1,2-dithiole-1,1-dioxide (200 mg, 0.90 mmol) in toluene was stirred for 1 h. The resulting dark red solution was filtered through a small Celite pad to remove any unreacted starting material and any insoluble impurities. The filtrate was concentrated under vacuum to ca. 3 cm³ and hexane (30 cm³) was added to precipitate the product as a dark red-purple solid (0.161 g, 45%). Found (calcd for (TiC₂₀H₁₆S₂O₂)₂·C₇H₈) C 62.92 (63.22), H 4.51 (4.52)%. ¹H NMR (CD₂Cl₂) δ: 8.42 (dd, 1H, aromatic), 8.01 (dd, 1H, aromatic), 7.87 (dd, 1H, aromatic), 7.74 (dd, 1H, aromatic), 7.57 (dt, 2H, aromatics), 6.52 (s, 5H, cp group) and 5.75 (s, 5H, cp group). ¹³C NMR (CD₂Cl₂) δ: 148.1, 143.0, 135.5, 133.4, 133.0, 131.7, 129.2, 125.7, 125.6, 123.4 (all aromatics) and 117.0 (cp groups). Selected IR data (KBr) ν/cm⁻¹: 3057 (m), 1445 (m), 1334 (m), 1092 (s), 1072 (s), 1054 (s) and 761 (s). Mass Spec (FAB): (M + H)⁺ 401.

Method B. A mixture of titanocene dicarbonyl (284 mg, 1.21 mmol) and naphtho-[1,8-*cd*]-1,2-dithiole-1,1,2-trioxide (290 mg, 1.21 mmol) in toluene was stirred for 1 h. The resulting dark red solution was filtered through a small Celite pad to remove any unreacted starting material and any insoluble impurities. The filtrate was concentrated under vacuum to ca. 3 cm³ and hexane (20 cm³) was added to precipitate the product as a dark red-purple solid (0.197 g, 40%). Selected IR data (KBr) ν/cm⁻¹: 3065 (m), 1445 (m), 1330 (m), 1092 (s) and 759 (s). Mass Spec (FAB): (M + H)⁺ 401.

Titanocene 2-sulfinato 2'-thiolato biphenyl (8). A mixture of titanocene dicarbonyl (189 mg, 0.81 mmol) and dibenzo[*ce*]-1,2-dithiine-5,5-dioxide (200 mg, 0.81 mmol) in toluene was stirred for 1 h. The resulting brown solution was filtered through a small Celite pad to remove any unreacted starting material and any insoluble impurities. The solvent was removed under reduced pressure and the brown solid was purified by chromatography through silica. Dichloromethane was used to elute a green layer which was characterized as complex **1** and then acetone was used to elute an orange layer. The orange layer was recrystallized from toluene. Yield 0.068 g (20%). Microanalysis: Found (calcd for (TiC₂₂H₁₈S₂O₂)₃·C₇H₈) C 63.33 (63.93), H 4.68 (4.56)%. ¹H NMR (CD₂Cl₂) δ: 7.83–7.16 (m, 8H, aromatics), 6.25 (s, 5H, cp group), 6.08 (s, 5H, cp group). ¹³C NMR δ: 133.4, 130.7, 130.2, 129.1,

Table 5. Crystallographic Data for Complexes **1**, **3**, **5**, **6**, **7**, and **8** and Titanocene Cube **10**

Complexes 1 , 3 , and 7 and Titanocene Cube 10				
	1	3	7	10
empirical formula	C _{21.75} H ₁₈ S ₂ Ti	C _{25.50} H ₂₂ S ₂ Ti	C _{23.50} H ₂₀ S ₂ O ₂ Ti	C ₄₆ H ₅₂ Cl ₁₂ O ₁₂ Ti ₈
<i>M</i>	391.38	440.45	446.42	1605.48
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>C2/c</i>	<i>C2/m</i>	<i>C2/c</i>	<i>P2₁/c</i>
<i>a</i> /Å	30.827(5)	21.939(7)	22.998(5)	20.265(4)
<i>b</i> /Å	15.229(3)	12.009(4)	12.703(3)	16.343(3)
<i>c</i> /Å	15.027(3)	7.764(3)	14.269(3)	38.350(8)
α /deg	90	90	90	90
β /deg	94.288(3)	91.461(5)	105.689(7)	103.036(4)
γ /deg	90	90	90	90
<i>V</i> /Å ³	7035(2)	2044.7(12)	4013.3(14)	12373(4)
ρ_{calcd} g/cm ^{−3}	1.478	1.431	1.478	1.724
μ /mm ^{−1}	0.724	0.632	0.652	1.550
reflections measured	17446	6153	7516	73549
independent reflections	5033	1928	3105	22644
final <i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0362, 0.0820	0.0418, 0.0851	0.0425, 0.0807	0.1110, 0.1702
Complexes 5 , 6 , and 8				
	5	6	8	
empirical formula	C ₂₂ H ₁₈ S ₂ Ti	C ₃₀ H ₂₂ S ₂ Ti	C _{22.50} H ₁₉ C _{10.50} O ₂ S ₂ Ti	
<i>M</i>	394.38	494.50	451.12	
crystal system	monoclinic	orthorhombic	monoclinic	
space group	<i>P2₁/c</i>	<i>Pbca</i>	<i>P2₁/c</i>	
<i>a</i> /Å	7.850(7)	10.8920(13)	7.7413(11)	
<i>b</i> /Å	16.344(14)	10.8871(12)	11.5820(17)	
<i>c</i> /Å	14.429(13)	38.317(5)	23.933(4)	
α /deg	90	90	90	
β /deg	92.167(17)	90	98.693(3)	
γ /deg	90	90	90	
<i>V</i> /Å ³	1850(3)	4543.7(9)	2121.1(5)	
ρ_{calcd} g/cm ^{−3}	1.416	1.466	1.413	
μ /mm ^{−1}	0.689	0.578	0.679	
reflections measured	7761	25174	10558	
independent reflections	2597	3953	3793	
final <i>R</i> 1, ω <i>R</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0650, 0.1551	0.2185, 0.4432	0.0711, 0.1603	

128.7, 128.3, 126.6, 120.4 (all 1C, aromatic C–H), 117.0 (5C, cp group), 115.1 (5C, cp group). FAB⁺ MS: *m/z* 449 [M + Na]⁺.

Method B. A mixture of titanocene dicarbonyl (133 mg, 0.57 mmol) and dibenzo[1,2]dithiine-5,5,6-trioxide (150 mg, 0.57 mmol) in toluene was stirred for 1 h. The resulting brown solution was filtered through a small Celite pad to remove any unreacted starting material and any insoluble impurities. The solvent was removed under reduced pressure and the brown solid was purified by chromatography through silica. Dichloromethane was used to elute a green layer which was characterized as complex **1** and then acetone was used to elute an orange layer. The orange layer was recrystallized from toluene. Yield 0.106 g (44%). ¹H NMR (CD₂-Cl₂) δ : 8.01–6.79 (m, 8H, aromatics), 6.18 (s, 5H, cp group), 6.01 (s, 5H, cp group). FAB⁺ MS: *m/z* 449 [M + Na]⁺.

Titanocene 2,2′-disulfonato-biphenyl (9). A mixture of titanocene dichloride (285 mg, 1.15 mmol) and the disodium salt of biphenyl-2,2′-disulfonic acid (373 mg, 1.15 mmol) in tetrahydrofuran was stirred for 24 h. The resulting orange solution was dried under vacuum and the product was extracted into dichloromethane. This was filtered through a shallow Celite pad to remove insoluble impurities and dried under vacuum. The remaining solid was dissolved in a minimum volume of hot dichloromethane (3 cm³), and hexane (20 cm³) was added to precipitate the product as an orange solid (0.280 g, 54%). Found (calcd for (TiS₂O₄C₂₂H₁₈) C 57.59 (57.64), H 3.61 (3.96)%. ¹H NMR (CD₂Cl₂) δ : 8.08 (dd, 2H, aromatic), 7.58 (dt, 2H, aromatics), 7.45 (dt, 2H, aromatic), 7.25 (dd, 2H, aromatic) 6.23 (s, 10H, cp groups). ¹³C NMR δ : 131.4, 130.8, 129.5, 123.4 (all 2C, aromatic C–H), 121.2, 120.4 (both 2C, quaternary aromatic), 119.4 (10C, cp groups). Selected

IR data (KBr) ν /cm^{−1}: 3086 (m), 1108 (s), 1076 (m), 1031 (m), 1013 (w), 824 (s), 807 (s), 758 (s). Mass Spec (ES⁺): (M + Na)⁺ 481.

Crystal Structure Analysis. Single crystals suitable for X-ray diffraction studies of complexes **1**, **3**, **5**, **6**, **7**, **8**, and **10** were obtained by layering a solution of each compound in dichloromethane with hexane. Details of the X-ray characterization experiments are given in Table 5. Data for **1**, **3**, **5**, **8**, and **10** were collected at 125 K on a SMART diffractometer using Mo K α radiation, while data were collected for **6** on a Rigaku MM007/Saturn diffractometer and for **7** at 298 K on a Rigaku Mercury diffractometer. Complex **6** was refined isotropically while in **5** C(1) and C(8) were refined isotropically; in all the other structures all non-H atoms were refined anisotropically. The large residual electron densities in **10** are located about the titanium atoms. All refinements were performed by using SHELXTL (Version 6.12, Bruker AXS). CCDC files 243365 **1**, 243363 **3**, 243650 **5**, 243651 **6**, 243364 **7**, 243646 **8**, and 243362 **10** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+ 44) 1223–336–033; e-mail: deposit@ccdc.cam.ac.uk.

Supporting Information Available: Crystallographic information files for the subject compounds (cif). This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC048483L