ELSEVIER

Journal of Organometallic Chemistry 526 (1996) 203–214

Journal of Organometallic Chemistry

Titanocene complexes of ring-opened dibenzothiophene and related dimercaptobiaryl ligands [1]

Philip R. Stafford, Thomas B. Rauchfuss *, Atul K. Verma, Scott R. Wilson

School of Chemical Sciences, Box 21 Noyes Lab, 505 South Mathews Avenue, Urbana, IL 61801, USA

Received 26 February 1996; revised 31 May 1996

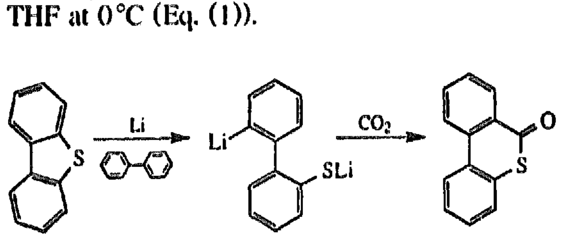
Abstract

This paper describes organotitanium derivatives resulting from the reactions of titanocene dichloride with derivatives of dibenzothiophene (DBT). Lithium cleavage of DBT gives 2,2'-Li(LiS)$C_{12}H_8$ which reacts with $(C_5H_5)_2TiCl_2$ to give the metallacyclic complex $(C_5H_5)_2TiSC_{12}H_8$ (**1**). Two side products were isolated in smaller amounts, the thiolates $(C_5H_5)_2Ti(SC_6H_4\text{-}2\text{-}Ph)_2$ (**2**) and $(C_5H_5)_2Ti(SC_6H_4\text{-}2\text{-}Ph)Cl$. DNMR studies showed that **1** and its MeC_5H_4 analog **3** are stereochemically non-rigid as a result of the folding of the organosulfur chelate. The structure of $(MeC_5H_4)_2TiSC_{12}H_8$ was verified by single crystal X-ray diffraction; the complex consists of the expected $(MeC_5H_4)_2Ti$ moiety coordinated to the carbon and sulfur of the ring-cleaved DBT. An attempt to generate 2,2'-Li(LiS)$C_{12}H_8$ via the double metalation of 2-phenylbenzenethiol with two equivalents of BuLi in the presence of TMEDA, followed by treatment with $(C_5H_5)_2TiCl_2$, gave the deep green complex $(C_5H_5)_2TiS_2C_{24}H_{16}$ (**4**). Single crystal X-ray diffraction indicated that **4** is a complex of the 2,2-dimercapto-3,3'-diphenylbiphenyl ligand (2,2'-$(LiS)_2$-3,3'-$Ph_2C_{12}H_6$), resulting from the coupling of two molecules of 1-Ph-2-LiS-3-LiC_6H_3. DNMR studies showed that this complex is stereochemically rigid. The free dithiol was liberated by treatment of **4** with anhydrous HCl. The complex of the unsubstituted 2,2'-dimercaptobiphenyl was prepared by treatment of 2,2'-Li(LiS)$C_{12}H_8$ with one equivalent of sulfur followed by quenching the reaction with titanocene dichloride to give $(C_5H_5)_2TiS_2C_{12}H_8$ (**6**). Electrochemical studies show that the $Ti^{IV/III}$ couple is reversible for all new compounds; the reduction potentials are lower for the chelating dithiolates and highest for the C–S chelate complexes **1** and **3**.

Keywords: Titanium; Lithium; Sulfur; Metallocene; Chirality; Thiolate

1. Introduction

In 1957 Gilman and Dietrich [1] reported the reduction of dibenzothiophene (DBT) with lithium in refluxing dioxane to generate a ring-cleaved product which was identified by its conversion to coumarin upon treatment with carbon dioxide. An improved procedure was later reported by Eisch [2] utilizing lithium–biphenyl in THF at 0°C (Eq. (1)).



(1)

C–S cleavage reactions involving DBT are relevant to the chemistry of fossil fuel desulfurization since DBTs are major sulfur-containing contaminants in fossil fuels as well as being amongst the most difficult to desulfurize. These heterocycles are hydrogenolyzed in the industrial HDS process by the action of metal catalysts to give hydrocarbons and hydrogen sulfide [3]. We have proposed that the hydrogenolysis involves electron transfer from the metal to the coordinated heterocycle followed by protonation, i.e. a heterolytic pathway [4]. Given this mechanistic proposal, it was of interest to examine the coordinating properties of the reduced thiophenes; the reduction of DBT by lithium to give a ring-cleaved product afforded this opportunity.

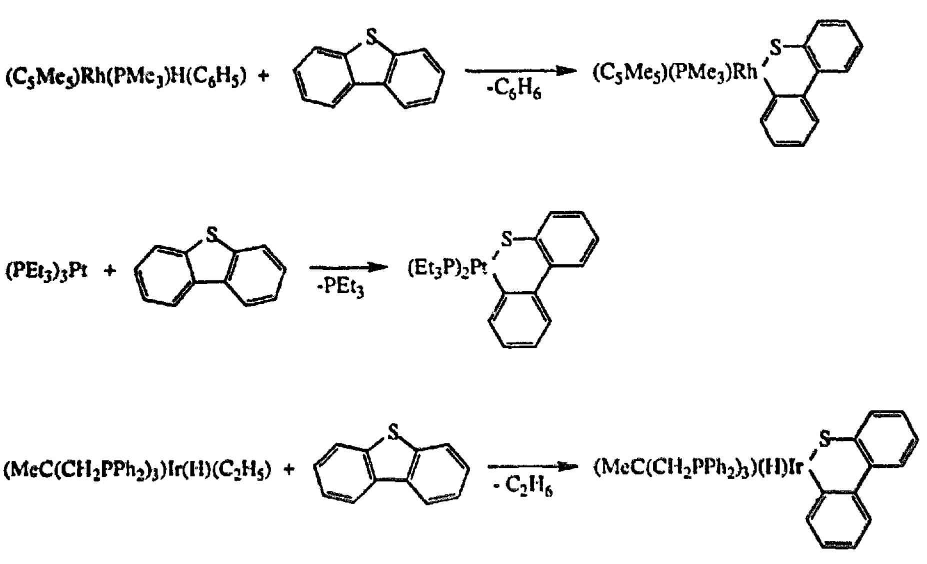
Other groups have recently examined the complexes of ring-opened DBT (Scheme 1). Jones and coworkers [5] have shown that $(C_5Me_5)Rh(PMe_3)$, generated from $(C_5Me_5)Rh(PMe_3)H(Ph)$, cleaves DBT and other thiophenes to give metallacycles. Closely related products

---

* Corresponding author.

[1] Dedicated to Professor Max Herberhold in recognition of his 60th birthday.

PII S0022-328X(96)06581-3



Scheme 1.

were obtained by the thermolysis of $(C_5Me_5)Rh(C_2H_4)_2$ or $(C_5Me_5)Co(C_2H_4)_2$ in the presence of DBT [6]. Maitlis and coworkers [7] reported that $Pt(PEt_3)_3$ adds DBT oxidatively to give a metallacycle which reacts further with triethylsilane to give biphenyl. In related work, Bianchini et al. [8] also observed C–S cleavage using a (triphos)Ir(I) source. Heating this compound to 170°C under 30 atm of hydrogen affords biphenyl.

In the present study we generate metallacycles by metathetical routes starting with Eisch's dilithio compound. The titanocene derivatives have allowed us to probe the conformational properties of the metallacycles, a point that was not explored in previous work. We also examine the utility of the ring-cleaved compounds as precursors to biaryl ligands. 2,2'-Disubstituted biaryl ligands, especially binaphthol (BINOL), have been of wide interest in the area of asymmetric synthesis [9]. Titanium complexes of BINOL have been used in olefin polymerization [10] and carbonyl–ene reactions [11]. The dimercaptobiaryl compounds have not been examined to a great extent [12], although 1,1'-binaphthyl-2,2'-dithiol has been used for [4 + 2] cycloaddition reactions [13] and as a coligand in the asymmetric hydroformylation of styrene by Rh(I) [14].

Previous work on metallocene derivatives of thiophenes involved the metallacyclic complex $(C_5H_5)_2WSC_4H_4$, derived from the photolysis of $(C_5H_5)_2WH_2$ in the presence of thiophene [15]. The complex is unstable with respect to the thienyl hydride $(C_5H_5)_2WH(2\text{-}C_4H_3S)$.

Table 1
Spectroscopic data for compounds 1–6

Compound	^{1}H NMR [a]	^{13}C{^{1}H} NMR [b]
1	7.60 (d, 1H), 7.35 (m, 2H), 7.23 (m, 2H), 6.95 (dd, 1H), 6.80 (dd, 1H), 6.61 (d, 1H), 6.44 (br, 5H), 5.80 (br, 5H)	188.8, 148.2, 145.9, 145.1, 135.2, 131.2, 131.0, 130.1, 126.4, 126.0, 124.6, 123.4, 114.8 (br), 113.4 (br)
2	7.96 (d, 1H), 7.39 (m, 4H), 7.30 (m, 3H), 7.22 (dd, 1H), 5.90 (s, 5H)	147.2, 142.7, 142.4, 134.5, 130.4 (2 C), 130.1, 127.9 (2 C), 127.7, 127.0, 126.2, 112.7
3	7.62 (d, 1H), 7.38 (m, 2H), 7.24 (m, 2H), 7.02 (dd, 1H), 6.88 (dd, 1H), 6.52 (d, 1H), 5.7 (br, 8H), 1.8 (br, 6H)	191.3, 148.4, 145.7, 145.1, 135.3, 130.8 (2 C), 130.1, 126.1, 125.7, 124.4, 123.6, 113.7 (br), 16.0 (br)
4	7.70 (d, 2H), 7.24–7.44 (m, 6H), 7.05 (d, 1H), 5.75 (s, 5H)	151.9, 144.6, 143.9, 142.9, 131.2 (2 C), 129.6, 129.5, 127.9 (2 C), 127.2, 126.2, 114.3
5	7.72 (d, 2H), 7.39 (m, 4H), 7.27 (m, 2H), 7.01 (d, 1H), 5.85 (m, 1H), 5.72 (m, 1H), 5.55 (m, 1H), 5.45 (m, 1H), 1.63 (s, 3H)	151.1, 145.2, 143.9, 143.0, 131.2 (2 C), 129.8, 129.5, 127.8 (2 C), 127.1, 125.9, 117.2, 115.1, 113.7, 112.8, 15.5
6	7.73 (d, 1H), 7.36 (dd, 1H), 7.20 (dd, 1H), 7.02 (d, 1H), 6.17 (s, 5H)	151.9, 142.4, 133.9, 130.1, 127.7, 126.3, 115.1

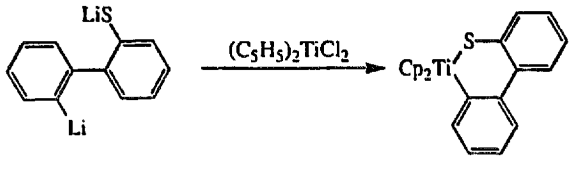
[a] 400 MHz, CD_2Cl_2.
[b] 75.5 MHz, CD_2Cl_2.

2. Results and discussion

2.1. Titanocene derivatives of ring-opened dibenzothiophene

Initial studies focused on optimizing the synthesis of 2,2′-Li(LiS)$C_{12}H_8$ by the lithium reduction of the DBT. The progress of the reaction was monitored by quenching aliquots with acid and analysis of the organic soluble products by gas chromatography. The yield of 2-phenylbenzenethiol maximized at 60% conversion, comparable with Eisch's results.

The reaction of a solution containing 2,2′-Li(LiS)$C_{12}H_8$ generated in situ from DBT and $Li_2C_{12}H_{10}$ with $(C_5H_5)_2TiCl_2$ in THF at −78 °C resulted in a deep red–purple solution (Eq. (2)).



(2)

(1)

The compound $(C_5H_5)_2TiSC_{12}H_8$ (1) was purified by chromatography on silica gel. We were unable to induce a reaction between DBT and $(C_5H_5)_2Ti(CO)_2$ or $(C_5H_5)_2TiCl_2/Mg$. Similarly we observed no reaction between DBT and $(C_5H_5)_2Zr(II)$, generated in situ from $(C_5H_5)_2ZrBu_2$ [16]. The organosulfur ligand in **1** can be removed by treatment with anhydrous HCl to give spectroscopically pure 2-phenylbenzenethiol.

The synthesis of **1** afforded small amounts of side products. Two of these minor products were the thiolates $(C_5H_5)_2Ti(SC_6H_4\text{-}2\text{-}Ph)_2$ (**2**) and $(C_5H_5)_2$-$Ti(SC_6H_4\text{-}2\text{-}Ph)Cl$. These probably arise from the partial hydrolysis of the intermediate 2,2′-Li(LiS)$C_{12}H_8$ prior to its reaction with $(C_5H_5)_2TiCl_2$. The bis(thiolate) **2** was independently prepared from 2-phenylbenzenethiol. Compound **2** is spectroscopically similar to many analogous titanocene and zirconocene dithiolates [17] (Table 1).

In the ^1H NMR spectrum of **1**, six signals are observed for the eight non-equivalent protons on the organosulfur ligand (Fig. 1(a)). Difference nuclear Overhauser enhancement (nOe) measurements and ^1H–^1H COSY experiments established the assignments as shown in Fig. 1. The assignment of H_a was based on the positive nOe observed from the irradiation of the C_5H_5 protons at δ 5.8. This interaction is also supported by the results of X-ray crystallographic study (see below). The $^{13}C\{^1H\}$ NMR spectrum of **1** reveals 12 signals for the $SC_{12}H_8$ ligand with the Ti–*C* resonance at δ 188.8.

DNMR studies showed that **1** is stereochemically non-rigid (Fig. 2). While the multiplicity of the signals for the organosulfur ligand does not change with temperature, two cyclopentadienyl signals are observed at low temperatures and only one at higher temperatures. This observation is in accord with a non-planar structure for the organosulfur ligand. The ligand inverts its conformation reversibly, resulting in the equivalency of the C_5H_5 signals (Eq. (3)). Using the Eyring equation, the free energy of activation ($\Delta G^{\neq}$) of this inversion was determined to be 78 kJ mol^{-1} [18].

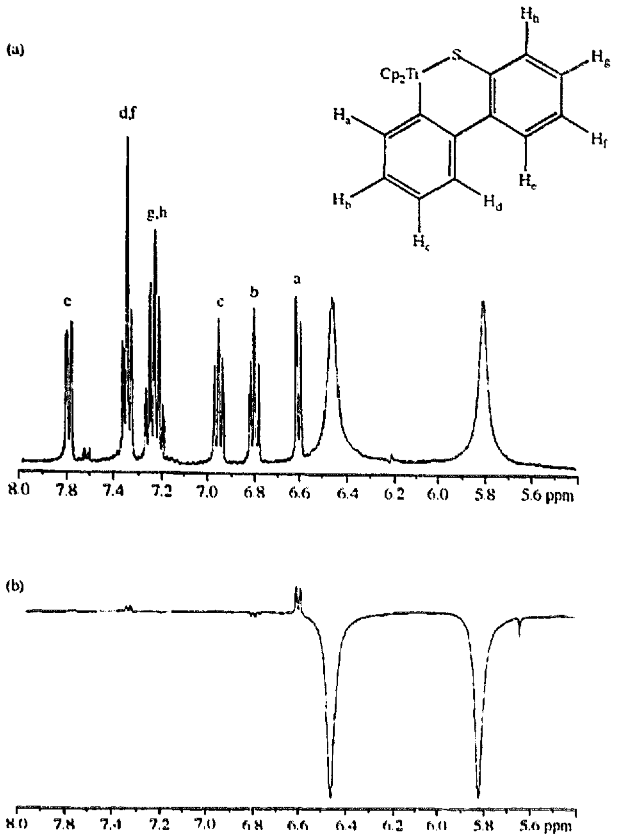
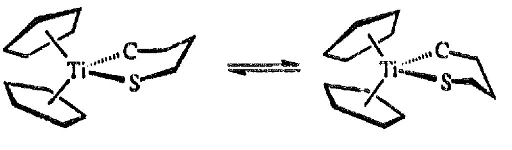


Fig. 1. (a) 400 MHz ^1H NMR of $(C_5H_5)_2TiSC_{12}H_8$ (1) with assignments (acetone-d_6). (b) 400 MHz ^1H NMR difference nOe with decoupler at 5.82 ppm (20 °C, acetone-d_6).



(3)

The synthesis of $(MeC_5H_4)_2TiSC_{12}H_8$ (**3**) was similar to that of **1**. The ^1H NMR spectrum of **3** in the $SC_{12}H_8$ region is very similar to that for **1** (Fig. 3), as is the barrier to inversion of the chelate ring (71 kJ mol^{-1}). One added insight afforded by the MeC_5H_4 derivative is proof that the complex is chiral, as indicated by the splitting of the MeC_5H_4 signals to eight multiplets at low temperatures. At higher temperatures, these signals coalesce into four multiplets (Fig.

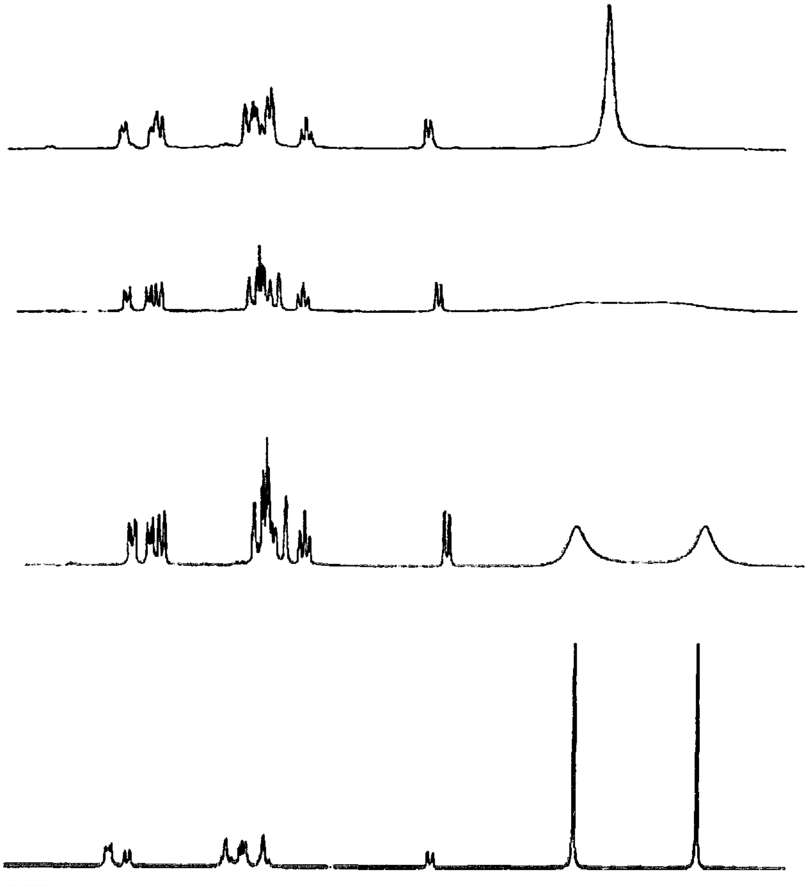
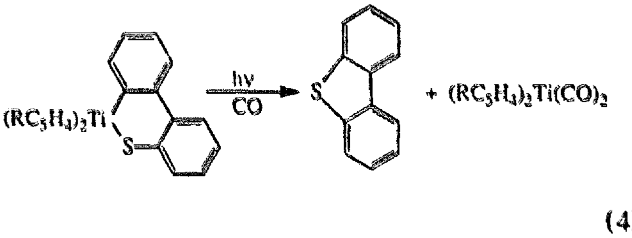


Fig. 2. 400 MHz ^1H NMR spectra of $(C_5H_5)_2TiSC_{12}H_8$ (**1**) at various temperatures (toluene-d_8).

4). The optical spectra for the monothiolates **1** and **3** feature absorptions at 500 nm ($2.3 \times 10^{-3}\ M^{-1}\,cm^{-1}$) and 498 nm ($3.0 \times 10^{-3}\ M^{-1}\,cm^{-1}$) respectively. The bis(thiolate) **2** absorbs at a lower energy, 548 nm ($3.8 \times 10^{-3}\ M^{-1}\,cm^{-1}$) (Table 2).

While thermally stable at 105 °C, complexes **1** and **3** are unstable with respect to light, resulting in the reductive elimination of DBT. The sensitivity is only moderate under normal laboratory light. By performing the photolysis under a CO atmosphere, we were able to recover $(C_5H_5)_2Ti(CO)_2$ in a 77% yield (Eq. (4)). This reaction also produces DBT in good yield, indicating that CO does not insert into the Ti–C bond prior to reductive elimination.



(4)

2.2. *Structure of $(MeC_5H_4)_2TiSC_{12}H_8$ (3)*

The complex consists of the expected $(MeC_5H_4)_2Ti$ moiety coordinated to the carbon and sulfur of the ring-cleaved DBT, thereby forming a six-membered metallacycle. The Ti–S and Ti–C distances are 2.37 and 2.20 Å respectively (Table 3). The shortest contact between the MeC_5H_4 and the $SC_{12}H_8$ ligand is 3.03 Å. We suggest that this is responsible for the nOe discussed above. The two phenyl rings of the organosulfur ligand are twisted with respect to each other. The $TiSC_4$ ring is strongly distorted from planarity, especially about the Ti(1)–S(1)–C(12)–C(7) linkage of 47.6(2)°.

2.3. *2,2'-Dimercaptobiphenyl complexes*

This part of the study began with an attempt to generate $2,2'\text{-}Li(LiS)C_{12}H_8$ more cleanly than by the lithium reduction of DBT. Although benzenethiol undergoes ortho metalation [19], we were interested in the possibility that metalation of 2-phenylbenzenethiol would occur not ortho, but on the adjoining phenyl group. Similar regiochemistry has been observed for the

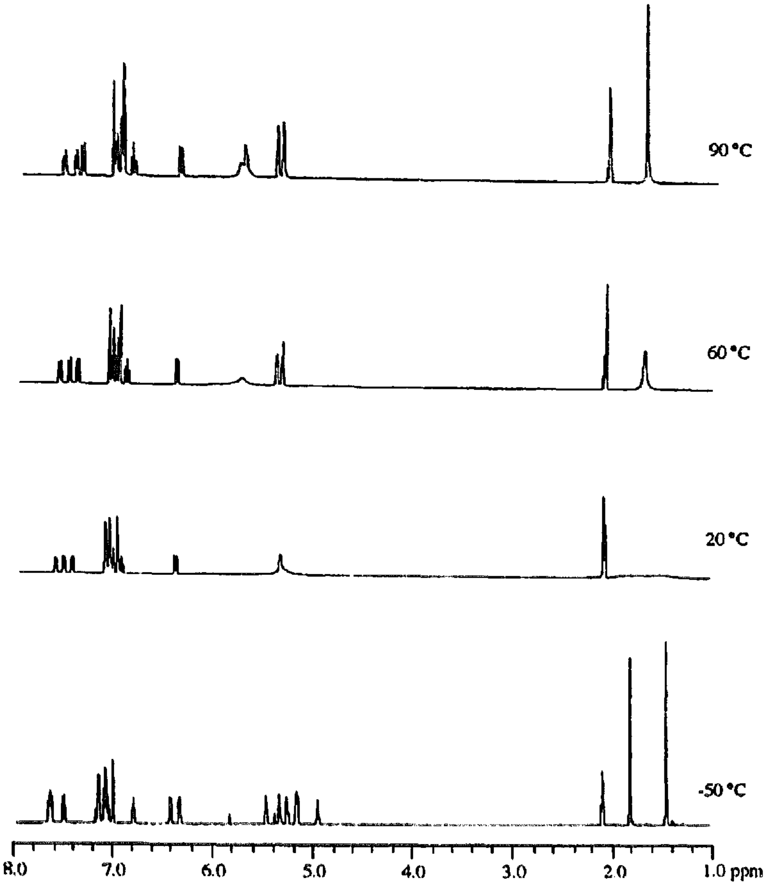
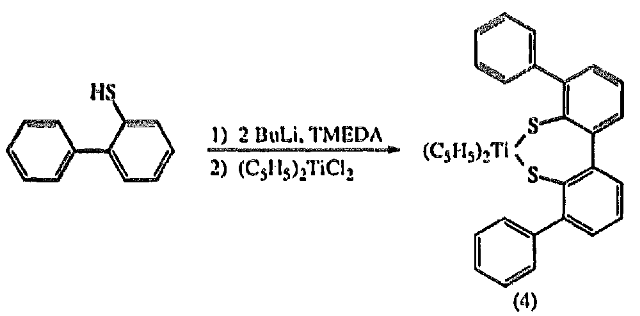


Fig. 3. 400 MHz ^1H NMR spectra of $(MeC_5H_4)_2TiSC_{12}H_8$ (3) at various temperatures (toluene-d_8).

metalation of biphenyl [20]. A solution of 2-phenylbenzenethiol was treated with two equivalents of BuLi in the presence of TMEDA followed by the addition of $(C_5H_5)_2TiCl_2$ (Eq. (5)).



(4)

(5)

Chromatographic work-up gave a new deep green complex whose mass spectrum indicated the formula $(C_5H_5)_2TiS_2C_{24}H_{16}$ (**4**). A modest amount of **2** was also formed. We also prepared the MeC_5H_4 analog, $(MeC_5H_4)_2TiS_2C_{24}H_{16}$ (**5**), by the same route. The optical spectra of **4** and **5** exhibit strong absorptions at 636 nm ($2.4 \times 10^{-3}\ M^{-1}\ cm^{-1}$) and 632 nm ($2.3 \times 10^{-3}\ M^{-1}\ cm^{-1}$) respectively. Notice that the bis(thiolate) **2** absorbs at a higher energy than the chelated dithiolates. The organosulfur ligand in **4** was removed by treatment of the complex with anhydrous HCl to give pure 2,2′-$(HS)_2$-3,3′-$Ph_2C_{12}H_6$. The ^1H NMR spectrum of this species revealed two multiplets for $(HS)_2C_{24}\mathit{H}_{16}$ and a singlet for $(\mathit{HS})_2C_{24}H_{16}$. The $^{13}C\{^1H\}$ NMR spectrum indicates that it consists of two

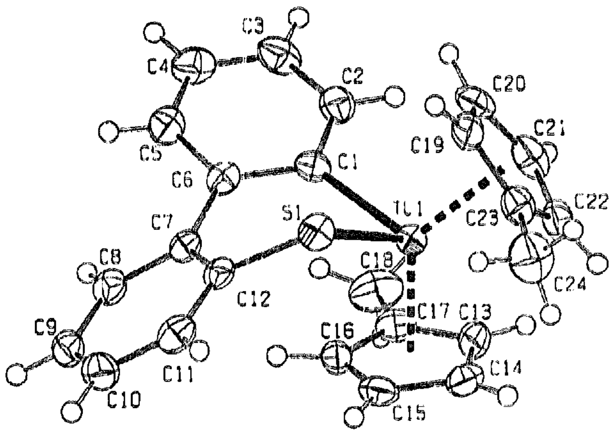


Fig. 4. Structure of $(MeC_5H_4)_2TiSC_{12}H_8$ (3) with thermal ellipsoids drawn at the 50% probability level.

Table 2
Optical and electrochemical data for compounds **1**–**6**

Compound	λ (nm), ε (mM^{-1} cm^{-1})^{a}	$E_{1/2}$ (mV) ^{b}
1	500, 2.3	−1207
2	548, 3.8	−1149 ^{c,d}
3	498, 3.0	−1315
4	636, 2.4	−991
5	632, 2.3	−1188 ^{c}
6	624, 1.6	−969

[a] Toluene.
[b] Potentials vs. Ag/AgCl.
[c] CV recorded in CH_2Cl_2 due to poor solubility in CH_3CN.
[d] Quasi-reversible based on peak current ratio of 0.36.

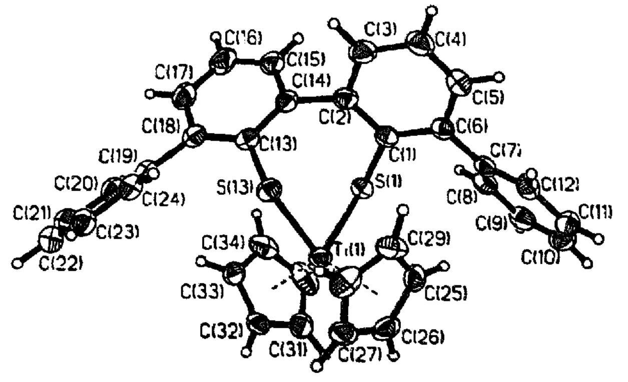


Fig. 5. Structure of $(C_5H_5)_2TiS_2C_{24}H_{16}$ (**4**) with thermal ellipsoids drawn at the 35% probability level.

equivalent $HSC_{12}H_8$ units. In addition to four quaternary carbon signals, six *C*–H resonances were observed with the signals at δ 129.6 and 128.8 appearing at twice the intensity of the remaining *C*–H signals.

The ^{1}H NMR signals corresponding to the $S_2C_{24}H_{16}$ ligand are virtually identical in **4** and **5**. For **4** a single resonance is observed for the two C_5H_5 ligands, while in **5** one *Me*C_5H_4 signal and four MeC_5*H_4* signals are observed. The latter suggest that there is no plane of symmetry bisecting the MeC_5H_4 ligands, but that these MeC_5H_4 groups are related by a C_2 symmetry operation. This conclusion is supported by the observation of four quaternary carbon signals and six *C*–H signals in the ^{13}C{^{1}H} NMR spectra of **4** and **5**, which show that the thioligand is comprised of two equivalent $SC_{12}H_8$ subunits.

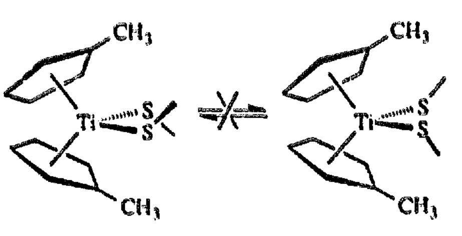
2.4. Structure of $(C_5H_5)_2TiS_2C_{24}H_{16}$ (4)

Complex **4** was shown to contain the 2,2′-dimercapto-3,3′-diphenylbiphenyl ligand by single crystal X-ray diffraction (Fig. 5). The resulting structure shows Ti in the expected tetrahedral environment and a twisted seven-membered TiS_2C_4 metallacycle. The Ti–S distances are 2.40 and 2.41 Å respectively, similar to the Ti–S distance in **3** (Table 3). The Ti–S–C bond angles of **4** are also similar to **3** at 106.94 and 106.73°. The two C_6H_3 rings are twisted with respect to each other. The torsional angle for the biphenyl linkage (C(1)–C(2)–C(14)–C(13)) is 76.46°. In contrast the corresponding torsional angle in **3** (C(1)–C(6)–C(7)–C(12)) is only 35.5°. Space-filling models show that the phenyl substituents do not shield the titanium center.

Table 3
Selected bond lengths (Å) and angles (°) for $(MeC_5H_4)_2TiSC_{12}H_8$ (**2**) and $(C_5H_5)_2TiS_2C_{24}H_{16}$ (**4**)

Compound **2**		Compound **4**	
Ti(1)–C(1)	2.198(3)	Ti(1)–S(1)	2.4023(11)
Ti(1)–S(1)	2.370(1)	Ti(1)–S(13)	2.4055(11)
S(1)–C(12)	1.7593(11)	C(1)–S(1)	1.775(3)
C(6)–C(7)	1.498(4)	C(13)–S(13)	1.780(3)
		C(2)–C(14)	1.497(5)
Ti(1)–S(1)–C(12)	103.80(9)	S(1)–Ti(1)–S(13)	91.67(3)
S(1)–Ti(1)–C(1)	85.29(8)	C(1)–S(1)–Ti(1)	106.94(10)
Ti(1)–C(1)–C(6)	124.0(2)	C(2)–C(1)–S(1)	116.2(2)
S(1)–C(12)–C(7)	122.6(2)		

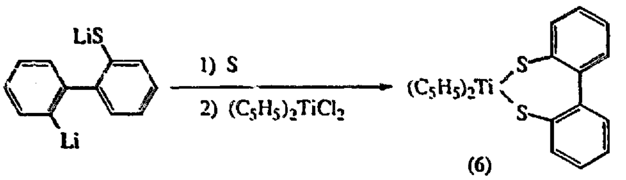
The rigidity of the metallacycle in **5** was investigated by DNMR studies. On the basis of the crystallographic results, the ^{1}H NMR spectrum of **5** should consist of a single resonance for *Me*C_5H_4 and four signals for MeC_5*H_4*. Should the complex undergo the dynamics shown in Eq. (6), then the ^{1}H NMR spectrum should simplify to a 3:2:2 pattern at higher temperatures. NMR measurements from −90 to 100°C failed to indicate any dynamic process, demonstrating that the metallacycle is rigid.



(6)

2.5. $(C_5H_5)_2TiS_2C_{12}H_8$ (6)

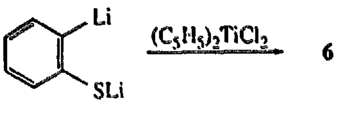
We were interested in simpler analogs of **4** and **5**. Previous work has shown that DBT/Li reaction provides access to the unsubstituted 2,2′-dimercaptobiphenyl via the treatment of 2,2′-Li(LiS)$C_{12}H_8$ with one equivalent of sulfur monochloride followed by $LiAlH_4$ [21]. In a revision of this method, 2,2′-Li(LiS)$C_{12}H_8$ was treated with one equivalent of sulfur followed by quenching the reaction with titanocene dichloride (Eq. (7)). A chromatographic work-up afforded the green complex $(C_5H_5)_2TiS_2C_{12}H_8$ (**6**) in 36% yield.



(7)

The ^1H NMR spectrum of **6** shows an ABCD pattern for the $S_2C_{12}H_8$ ligand and a single C_5H_5 resonance. The $^{13}C\{^1H\}$ NMR spectrum also suggests two equivalent SC_6H_4 units due to the observation of two quaternary carbons and four C–H signals. The optical spectrum of **6** is similar to that of **4** and **5**, with an absorption at 624 nm (1.6×10^{-3} $M^{-1} cm^{-1}$).

We also confirmed that **6** could be prepared from $1,2\text{-}Li_2SC_6H_4$, derived from the ortholithiation of lithium thiophenolate (Eq. (8)).



(8)

Treatment of **6** with etherial HCl afforded 2,2′-dimercaptobiphenyl.

2.6. *Electrochemical properties*

The electrochemical properties of **1**–**6** were examined by cyclic voltammetry on MeCN solutions (Table 2). Complex **1** undergoes reduction at −1.21 V vs. Ag/AgCl, while the reduction of complex **3** occurs approximately 100 mV more negatively at −1.32 V. The shift is due to the inductive effect of the methyl group. The corresponding $E_{1/2}$ values for the dithiolates **4** and **6** reveal reductions at −0.99 and −0.97 V respectively, suggesting that substitution on the organosulfur ligand has little electronic effect on the Ti^{IV}–Ti^{III} couple. The dithiolates are also easier to reduce than the monothiolate **1** by 200 mV. Both the scan dependence of the peak current as well as the $\Delta E_{1/2}$ values indicate that the Ti^{IV}–Ti^{III} couples are reversible.

3. Summary

A series of thiolato titanocene complexes can be prepared using the ring-opened derivative of dibenzothiophene. The direct reaction affords the metallacycles **1** and **3**, formally consisting of the aryl-thiolate $SC_{12}H_8^{2-}$ chelated to Ti^{IV}. DNMR studies on **1** and **3** indicate that the $TiSC_4$ chelate ring is stereochemically non-rigid. While this chelate complex was isolated in pure form and fully characterized, it is not photochemically stable. The metallacyclic complexes decompose via reductive elimination of DBT and formation of a Ti^{II} species which was trapped with CO. Since compound **1** is easily prepared, it is an attractive source of the $(C_5R_5)_2Ti(II)$ moiety.

The double metalation of 2-phenylbenzenethiol followed by treatment with $(C_5H_5)_2TiCl_2$ results in aryl-aryl coupling, affording the 2,2′-dimercapto-3,3′-diphenylbiphenyl chelate in good yield. Precedence suggests that this coupling involves the reduction of Ti^{IV}. Treatment of $(C_5H_5)_2Ti(C_6H_5)_2$ with excess phenyllithium results in the generation of some biphenyl via a postulated Ti^{II} intermediate [22]. The oxidative coupling of ortho metallated benzenethiolates represents an easy way to generate the new class of chelating dithiolato ligands.

Whereas the $TiSC_{12}H_8$ chelate ring easily inverts on the NMR timescale, the corresponding $TiS_2C_{12}H_8$ rings do not. There have been multiple studies on the stereodynamics of five- and six-membered metallacyclic derivatives of titanocene. The dithiolenes $(C_5R_5)_2TiS_2C_2R_2$ and the polysulfides $(C_5R_5)_2TiS_5$ and $(C_5R_5)_2TiS_4CR_2$ undergo ring inversion with barriers in the 55–85 kJ mol^{-1} range [23]. The present dimercaptobiphenyl derivatives are even more rigid. The high ring inversion barriers in the 2,2′-dimercaptobiphenyl complexes are attributed to the strong steric interactions between the 6,6′ protons at the transition state. This suggestion finds support in the fact that the barriers are lower in **1** where these protons are held further apart.

Overall this work demonstrates the utility of titanocene dichloride in the synthesis of thiolate ligands. The thiolato complexes are sufficiently stable to be purified by standard chromatographic procedures, but the organosulfur ligands are easily displaced. The 2,2′-dimercaptobiphenyl ligands merit further study.

4. Experimental details

4.1. *Materials and methods*

All reactions were performed using standard Schlenk techniques unless otherwise indicated. The following speciality reagents were purchased or prepared: $(C_5H_5)_2TiCl_2$ (Boulder Scientific), $(MeC_5H_4)_2TiCl_2$ [24], dibenzothiophene (Aldrich), biphenyl (Aldrich), and 3.2 mm Li wire (Aldrich). THF and TMEDA were distilled from Na/K/benzophenone, reagent grade hexane was distilled from Na/K, and toluene was distilled from Na.

NMR spectra were acquired on Varian U400 or GE 300NB spectrometers. Cyclic voltammograms were collected using a BAS-100 electrochemical analyzer on CH_3CN solutions which were 10^{-3} M in analyte and 0.1 M in $[Bu_4N][PF_6]$. Gas chromatography data were obtained on a Hewlett–Packard 5890A gas chromatograph with a fused methyl silicate capillary column. Photochemical irradiation was performed with a Spectronic black light lamp (λ = 365 nm), Spectroline Model MB-100. The EI mass spectra were recorded on a Finnigan-MAT CH5 instrument with an ionization potential of 70 eV by the School of Chemical Sciences Mass Spectrometry Laboratory. Elemental analyses were performed by the University of Illinois Microanalytical Laboratory.

4.2. Solution of 2,2′-Li(LiS)$C_{12}H_8$

Solutions of 2,2′-Li(LiS)$C_{12}H_8$ were prepared immediately prior to their use. In a typical procedure, a 250 ml Schlenk flask was charged with 2.51 g (16.3 mmol) of biphenyl and 50 ml of THF followed by the addition of 0.26 g (37 mmol) of Li in the form of short pieces of wire. The mixture slowly changed from green to blue as the Li dissolved. The mixture was cooled to 0 °C and treated with a solution of 3.07 g (16.7 mmol) of DBT in 50 ml of THF followed by the slow (30 min) addition of 50 ml of diethyl ether. The solution was allowed to warm to room temperature during which time it changed from blue to red and a red precipitate formed. After 4 h the mixture was used.

4.3. $(C_5H_5)_2TiSC_{12}H_8$ (1)

A solution of 2,2′-Li(LiS)$C_{12}H_8$ was prepared according to the above procedure using 2.51 g (16.3 mmol) of biphenyl, 0.26 g (37 mmol) of Li metal, and 3.07 g (16.7 mmol) of dibenzothiophene. The mixture was cooled to −78 °C and a suspension of 4.15 g (16.7 mmol) of $(C_5H_5)_2TiCl_2$ in 50 ml of THF was added via a polyethylene cannula. The flask was covered to protect against light and the mixture was allowed to warm to room temperature overnight. The solvent evaporated from the red solution and the resulting red paste was extracted into CH_2Cl_2. The extract was filtered through Celite to remove an orange solid and the filtrate was concentrated to yield a red oil. This red oil was chromatographed on silica (8 × 50 cm) using toluene as eluent. The red band was collected and the solvent was removed under vacuum to yield red $(C_5H_5)_2TiSC_{12}H_8$. Yield 2.42 g (37% yield based on dibenzothiophene). The product can be recrystallized using toluene/hexane at −35 °C. Anal. Found: C, 73.02; H, 5.03. $C_{22}H_{18}STi$ Calc.: C, 72.93; H, 5.01%. EI-MS (m/z): 362 (M^+).

4.4. Acid hydrolysis of 1

A 50 ml Schlenk flask was charged sequentially with 0.1621 g (0.4473 mmol) of **1**, 20 ml of THF, and 20 ml of a 1 M solution of HCl in ether. After the red colored mixture was stirred overnight, the solvent was evaporated. After washing with hexane, the red residue was collected by filtration and shown by ^1H NMR spectroscopy to be $(C_5H_5)_2TiCl_2$. Yield 0.0951 g (85%). The hexane extract was evaporated to give a yellow oil which was shown by ^1H NMR spectroscopy to be 2-phenylbenzenethiol [26], yield 0.0844 g (96%).

4.5. Photochemical reaction of 1 with CO

A 50 ml Schlenk flask was charged with 0.1559 g (0.4302 mmol) of **1**, 0.0802 g (0.4311 mmol) of ferrocene (an NMR standard), and 20 ml of toluene. This solution was flushed with CO gas and then irradiated at 365 nm for four days during which time the solution changed color from red to red/brown. The solvent was evaporated and the residue was dissolved in C_6D_6 and analyzed by ^1H NMR spectroscopy. Based on the integrated intensities, the yields of dibenzothiophene and $(C_5H_5)_2Ti(CO)_2$ [25] were 89 and 77% respectively.

4.6. 2-Phenylbenzenethiol [26]

A solution of 2,2′-Li(LiS)$C_{12}H_8$ was prepared as described above using 3.95 g (25 mmol) of biphenyl, 0.39 g (55 mmol) of Li metal, and 4.60 g (25 mmol) of dibenzothiophene. The red solution was treated with 0.6 M HCl until the aqueous layer was acidic. The organic layer was separated from the aqueous layer and evaporated to leave a colorless oil. The oil was dissolved in toluene and mixed with an NaOH solution. The layers were separated and the organic phase was discarded. The aqueous layer was reacidified and the resulting white precipitate was extracted with toluene. The organic layer was separated, dried over Na_2SO_4, and the solvent was removed under vacuum to leave a yellow oil. A toluene solution of the yellow oil was eluted through a plug of silica using toluene. Evaporation of the eluent resulted in a colorless oil which solidified upon cooling to −35 °C. Yield 2.4 g (52% based on dibenzothiophene).

4.7. $(C_5H_5)_2Ti(SC_{12}H_9)_2$ (2)

A 100 ml Schlenk flask was charged with 0.7171 g (3.85 mmol) of 2-phenylbenzenethiol and 25 ml of THF. The colorless solution was treated with 2.4 ml (3.8 mmol) of 1.6 M BuLi in hexanes causing the solution to warm. After stirring for 3 h, the yellow solution was cooled to −78 °C and treated with a solution of 0.4794 g (1.93 mmol) of $(C_5H_5)_2TiCl_2$ in 25 ml of THF. The mixture was warmed to room temperature during which time the solution became purple. The solvent was evaporated and the residue was extracted into toluene and chromatographed on silica gel. A purple band was collected, removal of the solvent yielded the product. Yield 0.9665 g (92% based on $(C_5H_5)_2TiCl_2$). Anal. Found: C, 74.30; H, 5.34. $C_{34}H_{28}S_2Ti$ Calc.: C, 74.44; H, 5.15%. EI-MS (*m/z*): 548 (M^+).

4.8. $(MeC_5H_4)_2TiSC_{12}H_8$ (3)

The synthesis is similar to that of **1**. Starting with 4.62 g (16.7 mmol) of $(MeC_5H_4)_2TiCl_2$, the yield of $(MeC_5H_4)_2TiSC_{12}H_8$ was 2.3 g (35% based on dibenzothiophene). Anal. Found: C, 73.36; H, 5.58. $C_{24}H_{22}STi$ Calc.: C, 73.84; H, 5.68%. EI-MS (*m/z*): 390 (M^+).

4.9. $(C_5H_5)_2TiS_2C_{24}H_{16}$ (4)

A 100 ml Schlenk flask was charged with 1.01 g (5.41 mmol) of 2-phenylbenzenethiol and 50 ml of hexane. This solution was treated with 6.8 ml of 1.6 M BuLi in hexanes (11 mmol) to give a precipitate. After the addition of the BuLi, 1.6 ml of TMEDA was added and the precipitate dissolved, resulting in a yellow solution. The solution was stirred at room temperature overnight, cooled to −78 °C, and treated with a solution of 1.35 g (5.4 mmol) of $(C_5H_5)_2TiCl_2$ in 20 ml of THF. This mixture was stirred at room temperature for 12 h, after which two additional 1.35 g portions of $(C_5H_5)_2TiCl_2$ were added. The solvent was evaporated, the residue extracted into toluene, and the extract was filtered through Celite. The filtrate was chromatographed on silica gel (4.5 × 55 cm^2). A purple band of **2** and a green band of **4** eluted with toluene. The yield of **2** was 0.3503 g (24% based on 2-phenylbenzenethiol) and the yield of **4** was 0.8211 g (56% based on 2-phenylbenzenethiol). Compound **4** can be recrystallized from toluene/pentane. Anal. Found: C, 74.57; H, 5.04. $C_{34}H_{26}S_2Ti$ Calc.: C, 74.71; H, 4.80%. EI-MS (*m/z*): 546 (M^+).

4.10. $(MeC_5H_4)_2TiS_2C_{24}H_{16}$ (5)

The synthesis is similar to that of **4**. Starting from 0.4758 g (2.55 mmol) of 2-phenylbenzenethiol, 3.2 ml (5.1 mmol) of 1.6 M BuLi, 0.8 ml of TMEDA, and three 0.39 g (4.2 mmol) portions of $(MeC_5H_4)_2TiCl_2$, the yield of $(MeC_5H_4)_2TiS_2C_{24}H_{16}$ was 0.29 g (40% based on 2-phenylbenzenethiol). This species is spectroscopically similar to **4**. EI-MS (*m/z*): 574 (M^+).

4.11. $(C_5H_5)_2TiS_2C_{12}H_8$ (6)

4.11.1. Method A from dibenzothiophene

A solution of 2,2′-Li(LiS)$C_{12}H_8$ was prepared as described above using 2.51 g (16.3 mmol) of biphenyl, 0.26 g (37 mmol) of Li metal, and 3.07 g (16.7 mmol) of dibenzothiophene. The solution was then cooled to −78 °C and 0.51 g (16 mmol) of sulfur was added. The mixture was allowed to warm to room temperature over a period of 12 h, during which time the solution became yellow. This solution was again cooled to −78 °C and treated with 4.15 g (16.7 mmol) of $(C_5H_5)_2TiCl_2$. After warming the reaction mixture to room temperature, the solvent was evaporated and the residue was extracted into CH_2Cl_2. The resulting solution was filtered through a plug of silica gel, concentrated, and diluted with pentane. Green crystals of **6** separated upon cooling to −35 °C. The product was filtered off and the solvent was removed from the filtrate to leave a red/purple paste. The resulting residue was taken up in toluene and chromatographed on silica gel (4.5 × 55 cm^2) using toluene as eluent. The first green band was collected and evaporated. Recrystallization of this material using CH_2Cl_2–pentane mixtures gave a second crop of **6**. Yield 2.40 g (36% based on $(C_5H_5)_2TiCl_2$). Anal. Found: C, 67.00; H, 4.60. $C_{22}H_{18}S_2Ti$ Calc.: C, 67.00; H, 4.60%. EI-MS (*m/z*): 394 (M^+).

4.11.2. Method B from thiophenol

Lithium 2-lithiobenzenethiolate · TMEDA was synthesized using the method of Block et al. [19] with 6.9 ml (1 mmol) of 1.6 M ^{n}BuLi, 1.6 ml (11 mmol) of TMEDA, and 20 ml of cyclohexane. The dilithium compound was dissolved in 50 ml of precooled (−78 °C) THF, and this solution was treated with 1.29 g (5.0 mmol) of $(C_5H_5)_2TiCl_2$. The solution color turned from clear pale yellow to dark wine red. The mixture was warmed to room temperature overnight, and became dark brown. Two more additions of $(C_5H_5)TiCl_2$ (5.0 mmol, 1.3 g) were carried out at −78 °C, removing the ice bath and allowing the solution to warm to room temperature between additions. The reaction mixture was worked up as in Method A to yield 0.263 g (27% based on thiophenol) of **6**.

4.12. 2,2′-$(HS)_2$-3,3′-$Ph_2C_{12}H_6$

A solution of 0.3516 g (0.64 mmol) of **4** in 25 ml of THF was treated with 3 ml of 1 M HCl in ether. The solution slowly turned from green to red and after 16 h the solvent was removed under vacuum. The red paste was extracted with CH_2Cl_2 and water, the layers were separated, and the CH_2Cl_2 layer was dried over Na_2SO_4. The solvent was evaporated and the red residue was extracted with a 5:1 mixture of pentane and toluene. The red solid of $(C_5H_5)_2TiCl_2$ was collected by filtration. The pentane/toluene extract was eluted through a plug of silica and evaporation of the solvent gave the colorless product. Yield 0.28 g (85% based on **4**). M.p. 144–145 °C. Anal. Found: C, 77.74; H, 4.68. $C_{24}H_{18}S_2$ calc.: C, 77.80; H, 4.90%. EI-MS (*m/z*): 370 (M^+). ^{1}H

NMR (400 MHz, CD_2Cl_2): 7.5–7.4 (m, 5H), 7.35–7.22 (m, 3H), 3.41 (s, 1H) ppm. $^{13}C\{^1H\}$ (100 MHz, CD_2Cl_2): 141.5, 141.4, 139.8, 132.0, 130.3, 129.6, 129.6, 128.8, 128.1, 125.4 ppm.

4.13. Structure of $(MeC_5H_4)_2TiSC_{12}H_8$

The red translucent data crystal was cut from a larger crystal and was mounted using an epoxy to a thin glass fiber with the (−3 −1 −1) scattering planes roughly normal to the spindle axis. The data crystal was bound by the (0 1 1), (0 −1 −1), (1 0 0), (−1 0 0), (0 −1 1), and (0 1 −1) faces. Distances from the crystal center to these facial boundaries were 0.19, 0.19, 0.20, 0.20, 0.23, and 0.23 nm respectively. Data were measured at 198 K on an Enraf–Nonius CAD4 diffractometer. Crystal refinement data are given in Table 4. Systematic conditions suggested the space group $P2_1/n$; refinement confirmed the presence of a symmetry center. Three standard intensities monitored every 90 min showed no decay; no decay correction was applied. Step-scanned intensity data were reduced by profile analysis [27] and corrected for Lorentz–polarization effects and for absorption [28]. Scattering factors and anomalous dispersion terms were taken from standard tables [29].

The structure was solved by direct methods [30]; correct positions for Ti and S atoms were deduced from an E-map. Subsequent cycles of isotropic least-squares refinement followed by unweighted difference Fourier syntheses revealed positions for all non-H atoms. Methyl H atom positions, $R{-}CH_3$, were optimized by rotation about R–C bonds with idealized C–H, R–H, and H–H distances. Remaining H atoms were included as fixed idealized contributors. H atom U values were assigned as 1.2 times the U_{eq} of adjacent non-H atoms. Non-H atoms were refined with anisotropic thermal coefficients. Successful convergence of the full-matrix least-squares refinement [31] on F^2 was indicated by the maximum shift/error for the last cycle. The highest peak in the final difference Fourier map was in the vicinity of atoms C7 and C12; the final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed a dependence on resolution. The plot in Fig. 4 employed A.L. Spek's PLATON-92 software (Vakgroep kristalen structuurchemie, University of Utrecht, Padualaan 8, 3584 CH Utrecht, Netherlands, 1992).

Table 4
Crystal data and structure refinement details for $(MeC_5H_4)_2TiSC_{12}H_8$ (2)

Empirical formula $C_{24}H_{22}STi$
FW = 390.38
T = 198(2) K
λ = 0.71073 Å
Crystal system: monoclinic
Space group $P2_1/n$
Unit cell dimensions: a = 14.671(3), b = 15.665(3), c = 16.289(3) Å
$\alpha = 90°$, $\beta = 90.48(3)°$, $\gamma = 90°$
V = 3743.4(13) Å^3
Z = 8
d(calc) = 1.385 Mg m^{-3}
Absolute coefficient μ = 0.573 mm^{-1}
Crystal size 0.23 × 0.20 × 0.19 mm^3
Θ Range for data collection 1.86–23.48°
Index ranges: $-16 \le h \le 0$, $-17 \le k \le 0$, $-18 \le l \le 18$
Collection method: $\Omega{-}\Theta$ scan profiles
No. of reflections collected 5755 [$R(I)$ = 0.0261]
No. of independent reflections 5515 [4393 observed, $I > 2\sigma(I)$]
Refinement method: full-matrix least-squares on F^2
Data/restraints/parameters: 5515/0/473
Goodness-of-fit on F^2 1.151
Final R indices (observed data): R_1 = 0.0373 [a], wR_2 = 0.1055 [b]
R indices (all data): R_1 = 0.0574 [a], wR_2 = 0.1162 [b]
Largest difference peak and hole: 0.608 and −0.525 e Å^{-3}

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = \{\sum[(F_o^2 - F_c^2)]^2/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0700P)^2 = 1.0861P]$, where $P = \max\{F_o^2, O + 2(F_c^2)\}$.

4.14. Structure of $(C_5H_5)_2TiS_2C_{24}H_{16}$

The opaque, prismatic data crystal was mounted using oil (Paratone-N, Exxon) to a thin glass fiber with the (−8 1 −6) scattering planes roughly normal to the spindle axis. The data crystal was bound by the (0 1 −1), (0 −1 1), (1 0 0), (−1 0 0), (0 1 1), and (0 −1 −1) faces. Distances from the crystal center to these facial boundaries were 0.07, 0.07, 0.15, 0.15, 0.16, and 0.16 nm respectively. Crystal twinning caused some minor overlap problems. Data were measured at 198 K on an Enraf–Nonius CAD4 diffractometer. Crystal and refinement details are given in Table 5. Systematic conditions suggested the ambiguous space group $P2/c$; refinement confirmed the presence of a symmetry center. Three standard intensities monitored every 90 min showed no decay. A total of five reflections had imbalanced backgrounds, ten reflections were poorly centered, and nine intensities flooded the counter. Step-scanned intensity data were reduced by profile analysis [27] and corrected for Lorentz–polarization effects and for absorption [28]. Scattering factors and anomalous dispersion terms were taken from standard tables [29].

The structure was solved by direct methods [30]; correct positions for all ordered non-H atoms were deduced from an E-map. One cycle of isotropic least-squares refinement followed by an unweighted difference Fourier synthesis revealed positions for disordered solvate atoms. Two-fold symmetry was imposed on one of the host molecules and inversion symmetry was imposed on the disordered toluene solvate molecule. Positional parameters for the solvate molecule were refined as a rigid idealized group. Methyl H atom positions, $C{-}CH_3$, were optimized by rotation about

Table 5
Crystal data and structure refinement details for $(C_5H_5)_2TiS_2C_{24}H_{16}$ (4)

Empirical formula $C_{34}H_{26}S_2Ti$
FW = 1731.84
$T = 198(2)$ K
$\lambda = 0.71073$ Å
Crystal system: monoclinic
Space group $P2/c$
Unit cell dimensions: $a = 24.911(5)$, $b = 10.154(2)$, $c = 16.827(3)$ Å
$\alpha = 90°$, $\beta = 91.64(3)°$, $\gamma = 90°$
$V = 4254.6(13)$ Å^3
$Z = 2$
d(calc) = 1.352 Mg m^{-3}
Absolute coefficient $\mu = 0.474$ mm^{-1}
Crystal size 0.38 × 0.36 × 0.16 mm^3
Θ Range for data collection 1.64–22.97°
Index ranges: $-27 \leq h \leq 27$, $0 \leq k \leq 11$, $-18 \leq l \leq 0$
Collection method: O–Θ scan profiles
No. of reflections collected 6171 [$R(\,f\,) = 0.0371$]
No. of independent reflections 5901 [4571 observed, $I > 2\sigma(I)$]
Absolute correction: integration
Max and min transmission: 0.942 and 0.875
Refinement method: full-matrix least-squares on F^2
Data/restraints/parameters: 5900/15/550
Goodness-of-fit on F^2 1.078
Final R indices (observed data): $R_1 = 0.0358$ [a], $wR_2 = 0.0864$ [b]
R indices (all data): $R_1 = 0.0628$, $wR_2 = 0.1003$
Largest difference peak and hole: 0.352 and −0.264 e Å^{-3}

[a] $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$.
[b] $wR_2 = \{\Sigma[w(F_0^2 - F_c^2)]^2/\Sigma[w(F_0^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_0^2) + (0.0700P)^2 + 1.0861P]$, where $P = \max(F_0^2, O + 2(F_c^2))$.

C–C bonds with idealized C–H, R–H, and H–H distances. Remaining H atoms were included as fixed idealized contributors. H atom U values were assigned as 1.2 times the U_{eq} of adjacent non-H atoms. Non-H atoms were refined with anisotropic thermal coefficients. Successful convergence of the full-matrix least-squares refinement [31] on F^2 was indicated by the maximum shift/error for the last cycle. The highest peak in the final difference Fourier map was in the vicinity of the disordered solvate molecule: the final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed no dependence on amplitude or resolution.

There were two crystal morphologies noted in the sample vial. The predominant acicular form was severely twinned and no reliable cell parameters were obtained. The prismatic form was also twinned, but the unit cell was obvious.

5. Supplementary material available

Tables of atomic coordinates, thermal parameters, and bond angles and distances are available. Ordering information is given on any current masthead page.

Acknowledgements

This research was funded by the US Department of Energy under Contract DEFG02-90ER14146. We thank Sue Beatty for checking the synthesis of **6** from thiophenol.

References

[1] H. Gilman and J.J. Dietrich, *J. Org. Chem.*, *22* (1957) 851.
[2] J.J. Eisch, *J. Org. Chem.*, *28* (1963) 707.
[3] B.C. Gates, *Catalytic Chemistry*, Wiley, New York, 1992; T.B. Rauchfuss, *Progr. Inorg. Chem.*, *31* (1991) 259.
[4] S. Luo, T.B. Rauchfuss and S.R. Wilson, *J. Am. Chem. Soc.*, *114* (1992) 8515; S. Luo, T.B. Rauchfuss and Z. Gan, *J. Am. Chem. Soc.*, *115* (1993) 4943.
[5] W.D. Jones and L. Dong, *J. Am. Chem. Soc.*, *113* (1991) 559; L. Dong, S.B. Duckett, K.F. Ohman and W.D. Jones, *J. Am. Chem. Soc.*, *114* (1992) 151; A.W. Meyers, W.J. Jones and S.M. McClements, *J. Am. Chem. Soc.*, *117* (1995) 11704.
[6] W.D. Jones and R.M. Chin, *J. Am. Chem. Soc.*, *114* (1992) 9851; *J. Organomet. Chem.*, *472* (1994) 311.
[7] J.J. Garcia, B.E. Mann, H. Adams, N.A. Bailey and P.M. Maitlis, *J. Am. Chem. Soc.*, *117* (1995) 2179.
[8] C. Bianchini, M.V. Jiménez, A. Meli, S. Moneti, F. Vizza, V. Herrera and R.A. Sánchez-Delgado, *Organometallics*, *14* (1995) 2342.
[9] R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, Wiley, New York, 1994.
[10] A. van der Linden, C.J. Schaverien, N. Meijboom, C. Ganter and A.G. Orpen, *J. Am. Chem. Soc.*, *117* (1995) 3008.
[11] M. Terada and K. Mikami, *J. Chem. Soc., Chem. Commun.*, (1995) 2391; K. Mikami, T. Yajima, T. Takasaki, S. Matsukawa, M. Terada, T. Uchimaru and M. Maruta, *Tetrahedron*, *52* (1996) 85; D. Kitamoto, H. Imma and T. Nakai, *Tetrahedron Lett.*, *36* (1995) 1861.
[12] U.K. Bandarage, L.R. Hanton and R.A.J. Smith, *Tetrahedron*, *51* (1995) 787; S. Cossu, A. Dore, O. De Lucchi, V. Lucchini and G. Valle, *Tetrahedron*, *49* (1993) 4333; D. Fabbri, G. Delogu and O. De Lucchi, *J. Org. Chem.*, *58* (1993) 1748; R. Kuroda and S.F. Mason, *Tetrahedron*, *37* (1981) 1995; G. Delogu, O. DeLucchi, P. Maglioli and G. Valle, *J. Org. Chem.*, *56* (1991) 4467.
[13] O. DeLucchi, D. Fabbri, S. Cossu and G. Valle, *J. Org. Chem.*, *56* (1991) 1888.
[14] C. Claver, S. Castillon, N. Ruiz, G. Delogu, D. Fabbri and S. Gladiali, *J. Chem. Soc., Chem. Commun.*, (1993) 1833.
[15] A. Samat, J. Sala-Pala, R. Guglielmetti and J. Guerchais, *Nouv. J. Chem.*, *2* (1978) 13; W.D. Jones, R.M. Chin, T.W. Crane and D.M. Baruch, *Organometallics*, *13* (1994) 4449.
[16] T. Takahashi, M. Kotora, R. Fischer, Y. Nishihara and K. Nakajima, *J. Am. Chem. Soc.*, *117* (1995) 11039; E. Negishi and F.E. Cederbaum, *Tetrahedron Lett.*, *27* (1986) 2829.
[17] S.A. Giddings, *Inorg. Chem.*, *6* (1967) 849; P.C. Wailes, R.S. Coutts and H. Weigold, *Organometallic Chemistry of Titanium, Zirconium, and Hafnium*, Academic Press, New York, 1974; D.W. Stephan and T.T. Nadasdi, *Coord. Chem. Rev.*, *147* (1996) 147; W.A. Howard, T.M. Trnka and G. Parkin, *Inorg. Chem.*, *34* (1995) 5900.
[18] H. Freibolin, *Basic One- and Two-Dimensional NMR Spectroscopy*, VCH, New York, 1991, pp. 269–271.
[19] G.D. Figuly, C.K. Loop and J.C. Martin, *J. Am. Chem. Soc.*, *111* (1989) 654; K. Smith, C.M. Lindsay and G.J. Pritchard, *J. Am. Chem. Soc.*, *111* (1989) 665; E. Block, G. Ofori-Okai and J. Zubieta, *J. Am. Chem. Soc.*, *111* (1989) 2327.

[20] L. Brandsma and H.D. Verkruijsse, *Preparative Polar Organometallic Chemistry 1*, Springer, Berlin, 1987; D.A. Shirley, J.R. Johnson and J.P. Hendrix, *J. Organomet. Chem.*, *11* (1968) 209.

[21] S. Cossu, G. Delogu, O. De Lucchi, D. Fabbri and M.P. Fois, *Synth. Commun.*, *19* (1989) 3431.

[22] V.N. Latyaeva, L.I. Vyshinskaya, V.B. Shur, L.A. Fyodorov and M.E. Volpin, *J. Organomet. Chem.*, *16* (1969) 103.

[23] D.M. Giolando and T.B. Rauchfuss, *Organometallics*, *3* (1984) 487.

[24] J. Darkwa, D.M. Giolando, C.M. Murphy and T.B. Rauchfuss, *Inorg. Synth.*, *27* (1990) 51.

[25] P. Biagini, F. Calderazzo and G. Pampaloni, *Organomet. Synth.*, *4* (1988) 12.

[26] L.H. Klemm and J.J. Karchesy, *J. Heterocyclic Chem.*, *15* (1978) 281.

[27] P. Coppens, R.H. Blessing and P. Becker, *J. Appl. Crystallogr.*, *7* (1972) 488.

[28] G.M. Sheldrick, SHELX-76, *Program for Crystal Structure Determination*, University of Cambridge, UK.

[29] A.J.C. Wilson (ed.), *International Tables for X-ray Crystallography*, Vol. C, Kluwer Academic, Dordrecht, Netherlands, 1989; scattering factors, pp. 500–502; anomalous dispersion corrections, pp. 219–222.

[30] G.M. Sheldrick, SHELXS-86, *Acta Crystallogr.*, *A46* (1990) 467.

[31] G.M. Sheldrick, SHELXL-93.