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Monocyclopentadienyltitanium complexes with thiolate ligands; crystal structure of Ti(η^5-C_5H_5)(SC_6H_5)$_3$

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Abstract

Thallium(I) derivatives of monocyclopentadienylbis(ethane-1,2-dithiolato)titanium, TlTi(η^5-$C_5H_nMe_{5-n}$)(edt)$_2$ {**1**, $n = 0$; **2**, $n = 4$; edt = 1,2-$S_2C_2H_4$}, have been synthesised and isolated in yields of 81 and 45%, respectively, from reactions of the corresponding reagents, Ti(η^5-$C_5H_nMe_{5-n}$)Cl_3 and thallium salts of the ethane-1,2-dithiol. Conformational changes of the chelating dithiolate ligands in compound **1** have been monitored by variable temperature ^{1}H-NMR spectroscopy. The preparation of compounds of the type TiCp(SAr)$_3$ (Cp = η^5-C_5H_5) has been investigated and the crystal structure of TiCp(SC_6H_5)$_3$, **3**, determined by X-ray diffraction; the compound adopts a three-legged piano stool coordination geometry with two parallel phenyl rings (interplanar angle 2.0(2)°) directed away from the cyclopentadienyltitanium unit with inter-ring C–C contacts in the range 3.52–3.62 Å; the third phenyl ring is approximately orthogonal to the other two and lies over a cyclopentadienyl ring of a neighbouring molecule with an intermolecular C–C contact of 3.373(16) Å. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Titanium; Cyclopentadienyl; Thiolate

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1. Introduction

The chemistry of monocyclopentadienyl thiolate complexes of early transition metals has received attention in recent years [1], including previous work from our laboratory on derivatives of metals from Groups 4–6 [2–4]. Our studies have shown that anionic complexes with four-legged piano stool geometry of the type [MoCp(SC_6F_5)$_4$]$^-$ (Cp = η^5-C_5H_5) will coordinate to thallium and larger Group 1 metal ions with the metal counter ion held within the cavity defined by the four sulfur atoms, the transition metal and four *ortho*-fluorine substituents of the aromatic rings [2,3]. Interactions between thallium ions and cyclopentadienyltitanium complexes of arenedithiolate ligands have been also established [4a].

Simple thiolate complexes of cyclopentadienyltitanium were reported by Köpf and coworkers in 1968 [5]; their subsequent studies were not published until the later 1980s and included the tristhiolato derivatives, TiCp(SR)$_3$ (R = Ph [6] and Me [7]) and complexes with arenedithiolate ligands [8]. Stephan et al. have since published a series of papers on propane-1,3- and ethane-1,2-dithiolate derivatives of cyclopentadienyltitanium [9–11], including heterometallic compounds with copper and rhodium; a number of these compounds have been structurally characterised by X-ray diffraction. A related dithiolate compound of tantalum is the ethane-1,2-dithiolate derivative, TaCp*(edt)$_2$ (Cp* = η^5-C_5Me_5) [12]. Herein we report ethane-1,2-dithiolates of monocyclopentadienyltitanium containing methylated cyclopentadienyl rings (η^5-$C_5H_nMe_{5-n}$: $n = 0$, 4) and studies on cyclopentadienyltris(arenethiolato)titanium derivatives.

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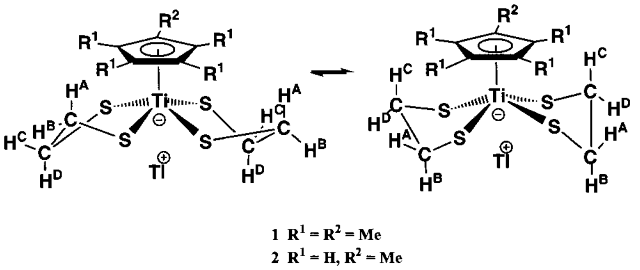
2. Results and discussion

2.1. Complexes with ethane-1,2-dithiolate

Reaction between the thallium salt of ethane-1,2-dithiol and trichloro(η^5-pentamethylcyclopentadienyl)titanium, $TiCp^*Cl_3$, in a 2:1 molar ratio in tetrahydrofuran (thf), afforded the bimetallic dithiolate derivative $TlTiCp^*(edt)_2$ **1** ($H_2edt = HSCH_2CH_2SH$) as a green crystalline solid in a yield of 81%. A similar reaction with the monomethylcyclopentadienyl reagent, $TiCp'Cl_3$ ($Cp' = \eta^5$-C_5H_4Me), gave the related green product, $TlTiCp'(edt)_2$ 2 but in lower yield (45%). The identities of the new products have been established by elemental analysis and ^{1}H-NMR spectroscopy, with typical resonances for hydrogens of cyclopentadienyl and ethanedithiolate ligands of correct relative integrals. All complexes are thermally stable as solids or in solution, but are readily susceptible to hydrolysis.

Bisalkanedithiolate complexes of the non-methylated cyclopentadienyl species $[TiCp\{S(CH_2)_nS\}_2]^-$ ($n = 2$ and 3) have been reported as the free anion, in $[Cu(Me_2PCH_2CH_2PMe_2)_2][TiCp(edt)_2]$ [10], or in coordination to a second metal, as in $TiCp(edt)_2Cu(PMe)_3$ [10] or in polymeric systems such as $[MTiCp(SCH_2CH_2CH_2S)_2]_n$ (M = Cu [10], Rh [10], Na [9a]). Structural characterisations of several of these derivatives have shown that the anion adopts a four-legged piano stool geometry and that three or four sulfur atoms of the bidentate dithiolate ligands may also coordinate to other metal centres.We were unable to produce suitable crystals of compounds **1** or **2** for analysis by X-ray diffraction but it can be assumed that Ti(IV) in these complexes also possesses the basic four-legged piano stool coordination geometry; also, at least in the solid state, there are likely to be interactions between Tl^+ and the sulfur atoms bound to titanium, as found in crystalline $TlTiCp^*(1,2\text{-}S_2C_6H_4)_2$ [4a]. Moreover, chelating ethane-1,2-dithiolate ligands adopt a puckered conformation with axial and equatorial hydrogen sites [13] but inversion may occur to cause interchange of nonequivalent atoms. Probable structures of **1** and **2** are illustrated in Scheme 1, but at ambient temperature the ^{1}H resonances of the ethanedithiolate ligands occur as symmetrical AA′BB′ multiplets so that inversion must be rapid on the NMR time-scale, causing H^A/H^C and H^B/H^D to become chemically equivalent pairs: simulation of the AA′BB′ resonance of compound **1** in d_8-toluene gives the following coupling constants (error $\pm < 0.5$ Hz): $^2J_{AB} = 13.0$, $^3J_{AA'(cis)} = 7.0$, $^3J_{AB'(trans)} = 7.5$ Hz. The difference in chemical shifts between H^A/H^C and H^B/H^D resonances is greater for the pentamethylcyclopentadienyl derivative, **1** (ca. 0.35 ppm), than for the monomethylcyclopentadienyl species, **2** (ca. 0.03 ppm), and ^{1}H-NMR spectra of the former in the temperature range -95 to $+25$°C (Fig. 1) clearly show that less symmetrical chelate rings are present at low temperatures. The observed temperature dependent NMR spectra must arise from the nonequivalence of H^A, H^C, H^B and H^D at slow rates of ring inversion, and this inequivalence could also be partly enhanced by coordination of Tl^+ to sulfur centres since ionic dissociation is likely to be less labile at lower temperatures, as found for $TlMoCp(SC_6F_5)_4$ [3]. Such conformational changes in solution have not been observed for ethane-1,2-dithiolate derivatives of titanium containing the unsubstituted cyclopentadienyl ligand. It is also of note that the ^{1}H-NMR spectrum of the neutral pentamethylcyclopentadienyl species, $TaCp^*(edt)_2$, is reported to show only a symmetrical (A_2B_2) resonance for the ethane-1,2-dithiolate chelate rings over the temperature range -70 to $+70$°C [12].



1 $R^1 = R^2 = Me$
2 $R^1 = H, R^2 = Me$

Scheme 1.

2.2. Complexes with arene thiolates

Köpf and coworkers have previously synthesised complexes of the type $TiCp(SR)_nCl_{3-n}$ ($n = 1$–3) [5–7]. In the earliest paper [5] an orange–red product with $n = 3$, R = Ph was reported, but in 1987 this derivative was described as a violet solid and characterised by elemental analysis and spectroscopic methods [6]. Although the methyl species $TiCp(SMe)_3$ and selenium analogues have since been prepared [7], no other arene monothiolate derivatives, $TiCp(SAr)_3$, have been reported and no simple cyclopentadienyltitanium tristhiolates have been characterised structurally by X-ray diffraction.

In order to fully characterise $TiCp(SPh_3)$, **3**, we repeated the preparation from $TiCpCl_3$ using TlSPh as reactant and obtained a dark red–purple product with resonances in the ^{1}H-NMR spectrum of chemical shifts and relative intensities consistent with the tris(benzenethiolate) compound. Crystallisation of this product from dichloromethane at low temperature gave dark red blocks suitable for study by X-ray diffraction, although decomposition of several crystals occurred in the X-ray beam before a specimen survived long enough to give a suitable set of diffraction data. Fig. 2 shows a perspective view of the structure with relevant

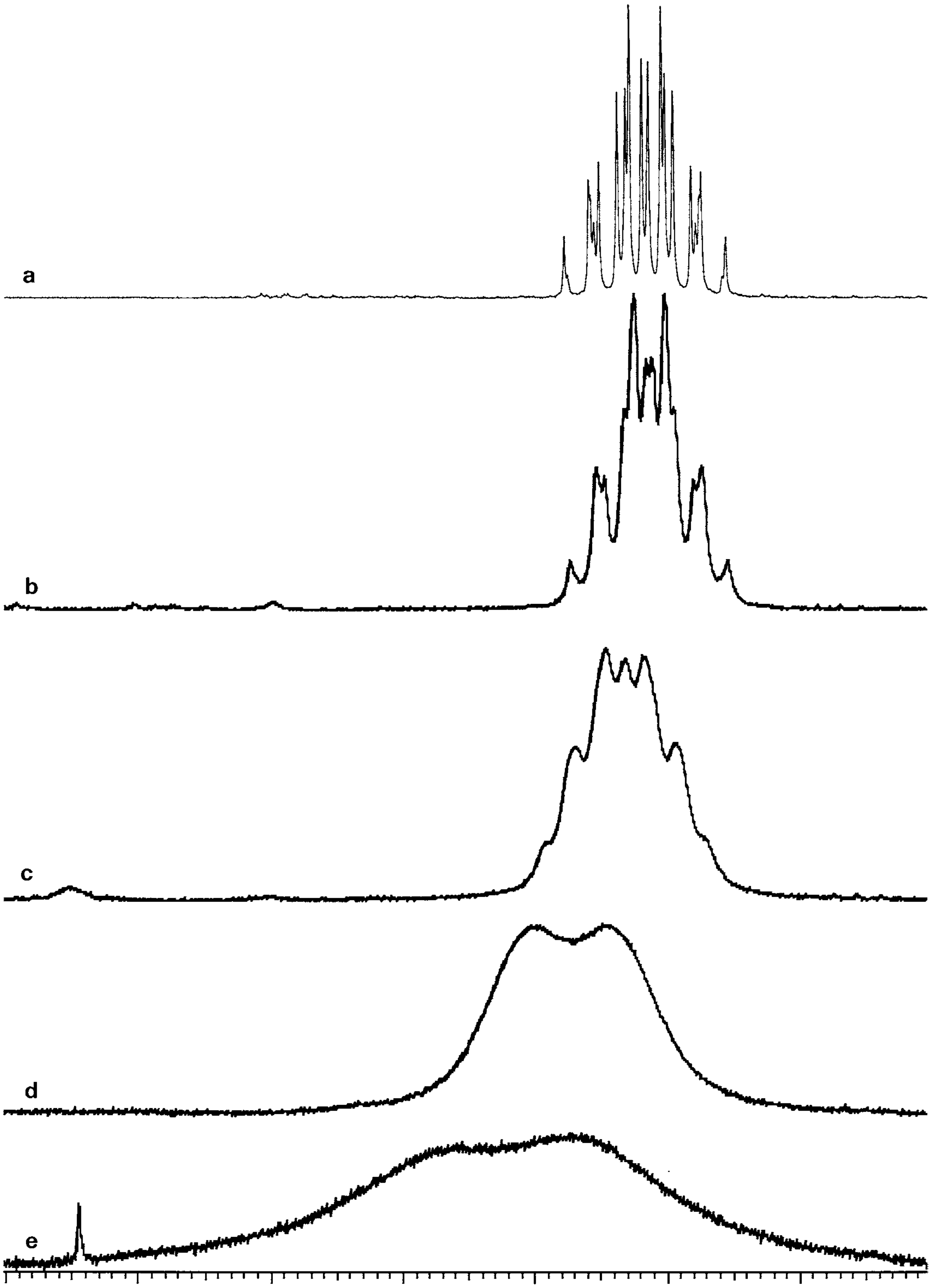


Fig. 1. ^{1}H-NMR resonance of the hydrogens of the ethane-1,2-dithiolate ligands in compound **1** at various temperatures in d_8-toluene at 400 MHz: (a) 20°C; (b) −40°C; (c) −60°C; (d) −80°C; (e) −95°C.

atom labelling and selected geometrical parameters are given in Table 1.

The crystalline **3** forms discrete monomeric units with the expected three-legged piano stool coordination geometry and with typical bond lengths and angles. The propane-1,3-dithiolato derivative $TiCp(SCH_2CH_2CH_2S)(SPh)$ has a similar structure [9a] with a Ti–S(Ph) bond length of 2.34 Å and with the phenyl ring

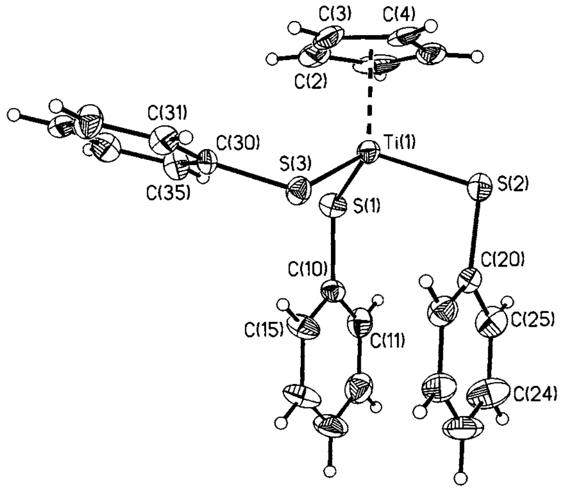


Fig. 2. Perspective view of $TiCp(SPh)_3$, **3** (30% probability displacement ellipsoids).

adopting a similar orientation to ring C(30)–C(35) of **3**. Also, the recently reported 2,3,4,5-tetramethylpyrrolyl derivative, $Ti(\eta^5\text{-}NC_4Me_4)(SPh)_3$, has a closely related structure, with Ti–S bond lengths 2.301 Å (average) and with the three phenyl rings in analogous positions to those of **3** [14]. In contrast, pentamethylcyclopentadienyl-tris(alkanethiolato)zirconium compounds exist as dimers with two bridging thiolate ligands, $[ZrCp^*(SR)_2(\mu\text{-}SR)]_2$ (R = Et, Bnz) [15], and this may be related in part to the larger size of the metal centre.

The orientations of the phenyl rings in **3** are of interest. Two overlapping rings attached to S(1) and S(2) are directed away from the cyclopentadienyltitanium unit and are almost parallel, with a divergence angle of 2.0(2)° and C–C contacts in the range 3.52–3.62 Å. The half thickness of a benzene ring is 1.85 Å [16] so that there may be some π-interaction between these two rings, although less than in graphite with interlayer spacings of 3.354 Å. The angle S(1)–Ti–S(2) of 112.38(8)° is larger than the other angles S–Ti–S and this could be a consequence of the inter-ring interaction. The third phenyl ring, S(3)–Ph, is orthogonal to the other rings and is roughly parallel to the cyclopentadienyl rings in the lattice, with interplanar angles of 12.8(2)°; also, the Cp(centroid)–Ti–S angle for S(3) of 117.1° is distorted more from the tetrahedral geometry than the corresponding angles to S(1) and S(2) of 108.4 and 109.0°, respectively. In addition S(3) lies in an eclipsed conformation with respect to C(3) of the Cp ring [C(3)–Cp(centroid)–Ti–S(3) = −4.4°], whilst the other S atoms lie in intermediate orientations [C(5)–Cp(centroid)–Ti–S(2) = 26.7; C(1)–Cp(centroid)–Ti–S(1) = −23.9°]. In the related molecule $Ti(\eta^5\text{-}NC_4Me_4)(SPh)_3$ a similar orientation of one phenyl ring was rationalised by short end-on intermolecular contacts to the same ring in another molecule related by a centre of inversion [14]. Such an explanation is not valid for **3** in which the crystal packing is different and these intermolecular C–C distances are > 3.8 Å; however, this ring lies almost parallel [12.8(2)°] and face-on to a cyclopentadienyl ring of a neighbouring molecule with C(33)–C(4A) = 3.373(16) Å, (where the suffix A denotes a molecule related by a centre of inversion), see Fig. 3. This arrangement allows effective packing with possible π-interactions between the phenyl and cyclopentadienyl rings.

Table 1
Selected bond lengths (Å) and angles (°) for compound **3**

Bond lengths (Å)			
Ti(1)–S(1)	2.334(2)	S(1)–C(10)	1.768(6)
Ti(1)–S(2)	2.304(2)	S(2)–C(20)	1.777(6)
Ti(1)–S(3)	2.3306(18)	S(3)–C(30)	1.783(3)
Cp[a]–Ti(1)	2.015		
Bond angles (°)			
S(1)–Ti(1)–S(2)	112.38(8)	C(11)–C(10)–S(1)	117.2(3)
S(1)–Ti(1)–S(3)	109.57(8)	C(15)–C(10)–S(1)	122.7(3)
S(2)–Ti(1)–S(3)	100.35(8)	C(21)–C(20)–S(2)	120.5(4)
C(10)–S(1)–Ti(1)	111.4(2)	C(25)–C(20)–S(2)	119.3(4)
C(20)–S(2)–Ti(1)	103.5(2)	C(31)–C(30)–S(3)	117.5(2)
C(30)–S(3)–Ti(1)	111.5(2)	C(35)–C(30)–S(3)	122.3(2)
Cp–Ti(1)–S(1)	108.4	Cp–Ti(1)–S(3)	117.1
Cp–Ti(1)–S(2)	109.0		

[a] Cp, centroid of $\eta^5\text{-}C_5H_5$ ring.

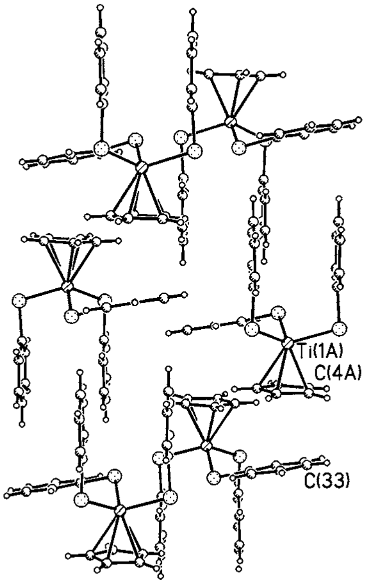


Fig. 3. Molecular packing of compound **3** in the solid state.

Reactions of $TiCpCl_3$ with thallium or sodium derivatives of *p*-thiocresol, under conditions similar to those employed in the formation of **3**, initially produced a deep red oil with ^1H-NMR resonances consistent with the formation mainly of $TiCp(SC_6H_4Me\text{-}4)_3$ (δ ppm ($CDCl_3$): 2.4 (CH_3); 6.15 (C_5H_5); 7.0–7.5 (C_6H_4)). However, attempts to purify this hydrocarbon-soluble product were unsuccessful, with free thiol being liberated and cyclopentadienyltitanium oxy-derivatives being formed in the process. Attempts to prepare pure products of the type $TiCp(SAr)_3$ (Ar = C_6F_5, C_6F_4H-4, $C_6H_4(OMe)$-2) were similarly thwarted. Also, reactions of compound **3** with $[Cu(NCMe)_4]PF_6$ and $Au(SMe_2)Cl$ gave analytical and spectroscopic evidence for the formation of bimetallic species but, as yet, these products have not been isolated in a pure state.

3. Conclusions

Thallium derivatives of monocyclopentadienylbis(ethane-1,2-dithiolato)titanium(IV) anions containing pentamethyl- and monomethylcyclopentadienyl ligands can be prepared and the thiolate rings are fluxional in solution. Cyclopentadienyltris(benzenethiolato)titanium, $TiCp(SPh)_3$, adopts a three-legged piano stool structure in the crystalline state with two parallel phenyl rings and the other phenyl ring interacting with an almost parallel cyclopentadienyl ligand of a neighbouring molecule. Other more soluble compounds of the type $TiCp(SAr)_3$ are very unstable to hydrolytic decomposition and have not been obtained in pure form.

4. Experimental

All reactions and operations were conducted under an atmosphere of dry, oxygen-free nitrogen gas, using Schlenk techniques. Solvents were thoroughly dried, using sodium (toluene), sodium-benzophenone (diethyl ether, tetrahydrofuran, light petroleum) or calcium hydride (dichloromethane), and freshly distilled before use; light petroleum had a boiling range of 60–80°C. Starting materials $Ti(\eta^5\text{-}C_5Me_5)Cl_3$ [17], $Ti(\eta^5\text{-}C_5H_4Me)Cl_3$ [18] and $Ti(\eta^5\text{-}C_5H_5)Cl_3$ [19] were prepared by literature methods. Ethane-1,2-dithiol, thiophenol, *p*-thiocresol and thallium(I) acetate were obtained commercially (Lancaster, Fluka or Aldrich Chemical) and used as supplied. Thallium derivatives of the thiols or dithiol were made by reaction of thallium(I) acetate with the free thiol (or dithiol) in methanol. IR spectra were measured on a Nicolet Impact 400 FT spectrometer. ^1H-NMR spectra were recorded at ambient temperature using a Bruker AC 200 spectrometer, operating at 200.13 MHz, and at variable temperatures on a Bruker DPX 400 instrument at 400.13 MHz, using $SiMe_4$ as internal reference. Elemental analyses were carried out at Heriot-Watt University.

4.1. Preparation of $TlTiCp^*(S_2C_2H_4)_2$ *1*

A solution of $TiCp^*Cl_3$ (0.10 g, 3.5×10^{-4} mol) in thf (10 cm^3) was added to a stirred suspension of 1,2-$(TlS)_2C_2H_4$ (0.37 g, 7.4×10^{-4} mol) in THF (10 cm^3). On mixing a dark brown colouration was observed, and the reaction was left to stir for 18 h at ambient temperature. Filtration through celite, followed by removal of solvent in vacuo afforded a green solid. The crude product was dissolved in toluene and a small amount of insoluble solid removed by filtration. Addition of light petroleum, followed by cooling to − 15°C yielded green needles of $TlTiCp^*(edt)_2$ (0.16 g, 81%). Found: C, 29.2; H, 4.1%; $C_{14}H_{23}S_4TiTl$ requires: C, 29.4; H, 4.0%. ^1H-NMR ($CDCl_3$, 20°C); δ 2.10 (s, 15H, C_5Me_5); 3.61 (AA′BB′ m, 8H, $S_2C_2H_4$); (d_8-toluene, − 95°C); δ 2.12 (br s, 15H, C_5Me_5); 3.42 (br, 8H, $S_2C_2H_4$, see Fig. 1).

4.2. Preparation of $TlTiCp'(S_2C_2H_4)_2$ **2**

$TiCp'Cl_3$ (0.10 g, 4.3×10^{-4} mol), dissolved in toluene (10 cm^3), was added to a suspension of 1,2-$(TlS)_2C_2H_4$ (0.58 g, 1.2×10^{-3} mol) in toluene (10 cm^3). On mixing a dark red coloration was observed, and the reaction was stirred for 18 h at room temperature. Filtration through celite and removal of solvent in vacuo yielded a dark red/brown solid. Purification from THF/light petroleum yielded green solid $TlTiCp'(edt)_2$ (0.10 g, 45%). Found: C, 23.3; H, 2.8%; $C_{10}H_{15}S_4TiTl$ requires C, 23.3; H, 2.9%. ^1H-NMR ($CDCl_3$, 20°C); δ ppm: 2.31 (s, 3H, $C_5H_4CH_3$) 3.67 [m (AA′BB′), 8H, $S_2C_2H_4$]; 6.57 [m (AA′ part of AA′BB′), 2H, $C_5H_4CH_3$], 6.63 [m (BB′ part of AA′BB′), 2H, $C_5H_4CH_3$].

4.3. Preparation of $TiCp(SC_6H_5)_3$ **3**

Freshly sublimed $TiCpCl_3$ (0.20 g, 9.1×10^{-3}) was dissolved in THF (10 cm^3) and $TlSC_6H_5$ (0.85 g, 2.7×10^{-3} mol) was added to the solution. The solution immediately changed from yellow to deep purple in colour and the reaction mixture was stirred for 2 days. The mixture was filtered and the filtrate reduced to dryness to yield a violet oil. The crude product was dissolved in dichloromethane; this solution was concentrated by reduction in volume and cooled at − 15°C to produce dark purple crystals of $TiCp(SPh)_3$ (0.050 g, 12%). ^1H-NMR ($CDCl_3$, 20°C); δ 6.15 (s, 5H, C_5H_5); 7.0–7.5 (complex, 15H, C_6H_5).

4.4. X-ray data collection and crystal structure determination

Single crystals of **3** were grown by slow diffusion of dichloromethane solutions with petroleum ether at − 15°C and were mounted in epoxy resin glue in a sealed, thin-walled glass capillary under dry nitrogen and data were collected at room temperature (293 K) on a Siemens P4 Diffractometer with the program XSCANS [20] using ω scans.

Table 2
Crystallographic data for compound **3**

Formula	$C_{23}H_{20}TiS_3$
M	440.47
Temperature (K)	293(2)
System	Monoclinic
Space group	$C2/c$
a (Å)	14.869(2)
b (Å)	13.606(2)
c (Å)	21.335(3)
β (°)	102.685(13)
U (Å^3), Z	4210.8(10), 8
$D_{calc.}$ (g cm^{-3})	1.390
μ(Mo–K$_\alpha$) (mm^{-1})	0.709
Crystal size (mm)	$0.9\times0.6\times0.3$
Data measured	3348
Unique data	2721 ($R_{int}=0.0525$)
Observed data	1555
R, wR_2 [$I>2\sigma(I)$ data]	0.0573, 0.1225
R, wR_2(all data)	0.1215, 0.1535

Standard reflections were re-measured every 100 data, severe crystal decay (80%) was found and corrected for. All structures were solved by direct and difference Fourier methods and refined by full-matrix least squares against F^2. All non-hydrogen atoms were refined anisotropically. All H atom positions were calculated and treated as riding models with U_{iso} 1.2 times the bound carbon atom U_{eq}, respectively. Phenyl and cyclopentadienyl groups were constrained to be rigid groups, regular hexagons and pentagons, respectively. Crystallographic computing was performed using the SHELXTL [21] system version on a Pentium 90 MHz PC. Further details are given in Table 2. Full details of the crystallographic structure determination have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

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