DALTON
FULL PAPER

Synthesis and characterisation of derivatives of monocyclopentadienylbis(arene-1,2-dithiolato)titanium(IV); crystal structures of M[Ti(η^5-C_5Me_5)(1,2-$S_2C_6H_4$)$_2$] [M = Tl or N(PPh_3)$_2$]

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Thallium(I) derivatives of monocyclopentadienylbis(arene-1,2-dithiolato)titanium, Tl[Ti(η^5-$C_5H_nMe_{5-n}$)($S_2C_6H_3R$)$_2$ (**1**–**6**; $n = 0$, 4 or 5; R = H or Me), have been synthesised and isolated in yields of 31–65% from reactions of the corresponding trichloromonocyclopentadienyltitanium reagents, Ti(η^5-$C_5H_nMe_{5-n}$)Cl_3 and thallium salts of the benzene-1,2-dithiol or toluene-3,4-dithiol in tetrahydrofuran. Reaction between Tl[Ti(η^5-C_5Me_5)(1,2-$S_2C_6H_4$)$_2$] and bis(triphenylphosphine)iminium chloride, [N(PPh_3)$_2$]Cl, has also afforded the derivative [N(PPh_3)$_2$][Ti(η^5-C_5Me_5)(1,2-$S_2C_6H_4$)$_2$] **7**. Products have been characterised by elemental analysis, NMR, IR and mass spectroscopy, and by X-ray diffraction. The structure of **7**, in the crystalline state as a tris(dichloromethane) solvate, comprises an ionic lattice containing discrete [Ti(η^5-C_5Me_5)(1,2-$S_2C_6H_4$)$_2$]$^-$ anions of four-legged piano stool geometry with two chelating benzene-1,2-dithiolate ligands folded along the S···S axis in *exo* and *endo* conformations, respectively, relative to the cyclopentadienyl ring. The crystal structure of Tl[Ti(η^5-C_5Me_5)($S_2C_6H_4$)$_2$] **1** contains two forms of the anion [Ti(η^5-C_5Me_5)($S_2C_6H_4$)$_2$]$^-$ in *endo*/*endo* and *endo*/*exo* conformations, respectively, which are unsymmetrically co-ordinated to the Tl^I cations. A Tl^I ion is connected by two Tl–S bonds to *endo* dithiolate ligands of each anion and there is also one Tl–S interaction between pairs of *endo*/*endo* and *endo*/*exo* forms. Additional weaker Tl···S interactions to the Tl^I ions generate a linked chain of dimeric units. In solution, NMR spectra suggest a more symmetrical structure for all derivatives but shifts in resonances support the retention of co-ordinate links between the cyclopentadienylbis(arene-1,2-dithiolato)titanium anion and Tl^I.

Previous work in this laboratory on Group 6 metals has established various aspects of the chemistry of monocyclopentadienyl-molybdenum- and -tungsten-thiolates and shown that anionic complexes, particularly those containing four fluoroarylthiolate ligands, will co-ordinate to thallium and larger Group 1 metal ions.[1] Complexes such as [MoCp(SC_6F_5)$_4$]$^-$ (Cp = η^5-C_5H_5) have four-legged piano stool geometry and a metal counter ion can be held within the cavity defined by the four sulfur atoms, the transition metal and four *ortho*-fluorine substituents of the aromatic rings.[2] Monocyclopentadienylthiolato derivatives of earlier Group 4 and 5 transition metals have received little attention until relatively recently.[3] The preparation of simple thiolate derivatives of monocyclopentadienyltitanium(IV) was reported in 1968,[4] but subsequent studies by Köpf and co-workers were not published until the late 1980s.[5] Stephan and co-workers have since published a series of papers on propane-1,3 and ethane-1,2-dithiolate derivatives of cyclopentadienyltitanium,[3,6–8] including several compounds structurally characterised by X-ray diffraction.

Unsaturated ene- or arene-1,2-dithiolates (dithiolenes) are generally more versatile sulfur ligands[9] and complexes of monocyclopentadienyltitanium [TiCp(S–S)$_2$]$^-$, with S–S = maleonitriledithiolate (mnt),[10a,b] 3,4,5,6-tetrachlorobenzene-1,2-dithiolate,[10c] toluene-3,4-dithiolate[11] (tdt) and benzene-1,2-dithiolate,[12] (bdt), are known. These anionic complexes have only been characterised with non-co-ordinating counter cations, [NEt_4]$^+$ or [PPh_4]$^+$, and the crystal structure of ionic [PPh_4][TiCp(1,2-$S_2C_6H_4$)$_2$] has been determined.[12] Herein we report arene-1,2-dithiolates of monocyclopentadienyltitanium containing cyclopentadienyl rings with differing degrees of alkyl substitution (η^5-$C_5H_nMe_{5-n}$, $n = 0$, 4 or 5) and the influence of Tl^+ as an interacting counter ion.

Results and Discussion

Syntheses and general characterisations

Reactions of the thallium salts of benzene-1,2-dithiol and toluene-3,4-dithiol with trichloro(η^5-pentamethylcyclopentadienyl)titanium, TiCp*Cl_3 (Cp* = η^5-C_5Me_5) in 2:1 molar ratios in tetrahydrofuran (thf) afforded the bimetallic dithiolate derivatives TlTiCp*(bdt)$_2$ **1** and TlTiCp*(tdt)$_2$ **2**, [H_2bdt = 1,2-(HS)$_2C_6H_4$; H_2tdt = 3,4-(HS)$_2C_6H_3CH_3$], as crystalline, dark red-purple solids in yields of 65 and 32%, respectively. When equimolar amounts of Tl_2tdt and TiCp*Cl_3 were reacted under similar conditions the only isolable product was also TlTiCp*(tdt)$_2$, albeit in rather low yield (17%). Similar reactions between thallium salts of benzene-1,2-dithiolate or toluene-3,4-dithiolate with TiCp′Cl_3 (Cp′ = η^5-C_5H_4Me) or TiCpCl_3 gave the corresponding products TlTiCp′(bdt)$_2$ **3**, TlTiCp′(tdt)$_2$ **4**, TlTiCp(bdt)$_2$ **5** and TlTiCp(tdt)$_2$ **6** in isolable yields of 31–41%. The identities of the new products have been established by elemental analysis, ^{1}H NMR spectra and, in some cases, FAB mass spectrometry. All complexes are thermally stable as solids or in solution, but are susceptible to hydrolysis. Complexes **1** and **2** dissolve in toluene, thf and chlorinated organic solvents but with decreasing methyl substitution of the cyclopentadienyl ring the compounds become progressively less soluble and compound **5** is sparingly soluble in toluene, chloroform and dichloromethane, in contrast to the reported solubility[12] of the related ionic species, [PPh_4][TiCp(bdt)$_2$].

In the ^{1}H NMR spectra of **1** and **2** the hydrogens of the Cp* ligands give rise to one sharp singlet resonance. At ambient temperature, the aromatic hydrogen resonances of the benzene rings of **1** occur as well defined AA′ and BB′ multiplets of two equivalent AA′BB′ systems, of correct relative intensity and with J_{AB} 7.7, $J_{AB'}$ 1.5, $J_{AA'} \approx 0.1$ and $J_{BB'} \approx 7.1$ Hz, obtained by simulation. For compound **2**, the methyl hydrogens of the toluene ligands give rise to only one singlet resonance and

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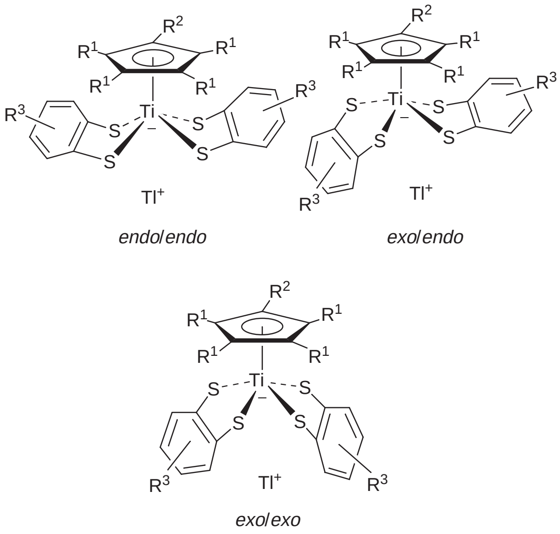


1 R^1 = R^2 = Me, R^3 = H **2** R^1 = R^2 = Me, R^3 = 1-Me
3 R^1 = H, R^2 = Me, R^3 = H **4** R^1 = H, R^2 = Me, R^3 = 1-Me
5 R^1 = R^2 = H, R^3 = H **6** R^1 = R^2 = H, R^3 = 1-Me

Scheme 1

the aromatic resonances occur as multiplets assignable to three inequivalent hydrogens of two equivalent rings. Therefore, there is no evidence from the NMR spectrum for the existence of isomers which could result from *syn* and *anti* placements of the two methyl substituents and this may indicate the preferential formation of one isomeric form. Proton NMR spectra of the other thallium compounds **3**–**6** show similar resonances for hydrogen nuclei of two equivalent benzene or toluene dithiolate ligands and resonances typical of Cp′ or Cp rings, as appropriate, with correct relative intensities (see Experimental section). Possible conformations of the dithiolate ligands are illustrated in Scheme 1.

The FAB mass spectrum of **1** shows a strong parent ion, [TlTiCp*(bdt)$_2$]$^+$, with a pattern of *m*/*z* values corresponding to isotopic distributions, and other bands include fragmentation ions formed by loss of Cp* and Tl, as well as peaks for $^{203/205}$Tl$^+$. A weak signal around *m*/*z* = 879 can be assigned to the dithallium ion [Tl$_2$TiCp*(bdt)$_2$]$^+$. Other dithiolate derivatives did not give clear molecular ions but showed fragmentation ions in FAB mass spectra. The IR spectra of the new compounds include bands typical of cyclopentadienyl and arenedithiolate ligands.

A metathetical reaction of TlTiCp*(bdt)$_2$ **1** with 1 equivalent of bis(triphenylphosphine)iminium chloride, [N(PPh$_3$)$_2$]Cl, in dichloromethane produced the derivative [N(PPh$_3$)$_2$][TiCp*(bdt)$_2$] **7**. This product initially crystallised from dichloromethane–light petroleum as a solvate with CH$_2$Cl$_2$, and crystals suitable for study by X-ray diffraction had the stoichiometry [N(PPh$_3$)$_2$][TiCp*(bdt)$_2$]·3CH$_2$Cl$_2$. However, dichloromethane is readily lost from the isolated solid at room temperature, so that the crystals for structural analysis had to be handled expeditiously and kept at low temperature (see below). Thorough drying under vacuum removed dichloromethane to give unsolvated **7**, as shown by elemental analysis and the ^{1}H NMR spectrum, which included distinguishable aromatic resonances assignable to two equivalent benzenedithiolate ligands and a [N(PPh$_3$)]$^+$ cation. The complex [PPh$_4$][TiCp*(bdt)$_2$] was similarly prepared from **1** and [PPh$_4$]Br, and characterised by its ^{1}H NMR spectrum.

Table 1 Selected interatomic distances (Å) and angles (°) for compound **7**

Ti–S(1)	2.432(2)	Ti–C(10)	2.390(6)
Ti–S(2)	2.419(2)	Ti–C(11)	2.404(6)
Ti–S(3)	2.414(2)	Ti–C(12)	2.399(6)
Ti–S(4)	2.446(2)	Ti–C(13)	2.390(6)
N(1)–P(1)	1.588(5)	Ti–C(14)	2.381(6)
N(1)–P(2)	1.575(5)		
S(2)–Ti–S(1)	82.33(6)	C(20)–S(1)–Ti	98.3(2)
S(3)–Ti–S(2)	79.33(6)	C(25)–S(2)–Ti	98.2(2)
S(3)–Ti–S(4)	80.41(6)	C(30)–S(3)–Ti	105.5(2)
S(1)–Ti–S(4)	81.84(6)	C(35)–S(4)–Ti	104.5(2)
S(3)–Ti–S(1)	130.86(7)	C(25)–C(20)–S(1)	120.7(4)
S(2)–Ti–S(4)	135.62(7)	C(20)–C(25)–S(2)	120.3(5)
C(35)–C(30)–S(3)	120.3(4)	C(30)–C(35)–S(4)	118.6(4)
P(2)–N(1)–P(1)	140.4(3)	N(1)–P(1)–C(60)	108.8(3)
N(1)–P(1)–C(40)	113.3(3)	N(1)–P(2)–C(80)	110.1(3)
N(1)–P(1)–C(50)	111.8(3)	N(1)–P(2)–C(70)	115.3(2)
N(1)–P(2)–C(90)	109.8(3)		

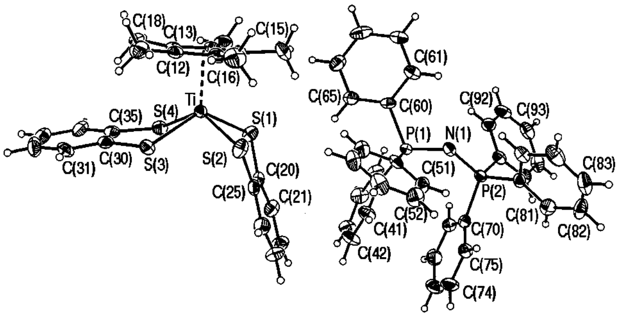


Fig. 1 Perspective view of ion pairs of [N(PPh$_3$)$_2$][TiCp*(bdt)$_2$]·3CH$_2$Cl$_2$, **7**·3CH$_2$Cl$_2$ (50% probability displacement ellipsoids)

Solid-state structure of compound 7

Large needle-like crystals of solvated **7**, [N(PPh$_3$)$_2$][TiCp*(bdt)$_2$]·3CH$_2$Cl$_2$, were cut and rapidly cooled to 160 K for structural analysis by X-ray diffraction, minimising loss of dichloromethane and disintegration of the crystal. Fig. 1 shows a perspective view of the structure of an anion/cation pair, with relevant atom labelling and Table 1 lists selected geometrical parameters. The compound is clearly ionic with [TiCp*(bdt)$_2$]$^-$ and [N(PPh$_3$)$_2$]$^+$ existing as discrete units. The solvent molecules do not appear to interact strongly with the ions, with the shortest contacts between CH$_2$Cl$_2$ and [TiCp*(bdt)$_2$]$^-$ being H···S(3) at 2.884(8) Å and C···S(3) at 3.750(8) Å. The geometry of the [N(PPh$_3$)$_2$]$^+$ cation is as expected.

The titanium atom in the complex anion has a four-legged piano stool arrangement of ligating atoms. The four sulfur atoms lie on an approximate plane (root mean square, r.m.s. deviation 0.045 Å) opposite the plane of Cp* ring at an interplanar angle of 2.1(3)°. The Ti–S distances are in the range 2.414(2)–2.446(2) Å; on average these are slightly longer than Ti–S bonds in [PPh$_4$][TiCp(bdt)$_2$],[12] or in terminal thiolates of neutral monocyclopentadienyltitanium(IV) species,[6–8] but the longer distances are comparable to Ti–S bond lengths in [TiCp{S$_2$(CH$_2$)$_n$}$_2$]$^-$ (n = 2 or 3).[7,8] The Ti–Cp* (centroid) distance of 2.066 Å is close to that found in [PPh$_4$][TiCp(bdt)$_2$] (2.060 Å),[12] and S–Ti–Cp* (centroid) angles are in the range 111.1–116.1°.

The two benzenedithiolate ligands are folded along the S···S axis relative to the adjacent TiS$_2$ plane but have different conformations. One benzenedithiolate is *endo* with respect to the Cp* ring, with a dihedral angle Ti–S(3)–S(4)/S(3)–S(4)–C$_6$H$_4$ of 27.3(1)°, and the other is *exo*, with an angle Ti–S(1)–S(2)/S(1)–S(2)–C$_6$H$_4$ of 40.3(1)°. An *endo*/*exo* conformation was proposed for the neutral compound [TaCp*(SCH=CHS)$_2$],[13] and was also observed in the solid-state structure of the anion in [PPh$_4$][TiCp(bdt)$_2$],[12] but the dihedral angles in the latter species, 36.3° (*endo*) and 23.3° (*exo*) differ significantly from

Table 2 Selected interatomic distances (Å) and angles (°) for compound **1**

Ti(1)–S(1)	2.418(3)	Ti(2)–S(5)	2.421(3)
Ti(1)–S(2)	2.436(3)	Ti(2)–S(6)	2.423(3)
Ti(1)–S(3)	2.438(3)	Ti(2)–S(7)	2.410(3)
Ti(1)–S(4)	2.427(3)	Ti(2)–S(8)	2.480(3)
Tl(1)–S(1)	3.436(3)	Tl(2)–S(5)	3.412(3)
Tl(1)–S(2)	3.518(4)	Tl(2)–S(7)	3.167(3)
Tl(1)–S(3)	3.296(3)	Tl(2)–S(8)	3.148(3)
Tl(1)–S(4)	3.157(3)	Tl(2)–S(3)	3.173(2)
Tl(1)–S(7)	3.472(3)	Tl(2)–S(8B)	3.338(2)
Tl(1)–S(2A)	3.430(3)	Ti(2)–C(22)	2.353(9)
Ti(1)–C(14)	2.356(10)	Ti(2)–C(24)	2.371(9)
Ti(1)–C(10)	2.366(10)	Ti(2)–C(23)	2.377(9)
Ti(1)–C(11)	2.393(9)	Ti(2)–C(21)	2.399(10)
Ti(1)–C(12)	2.419(10)	Ti(2)–C(20)	2.400(10)
Ti(1)–C(13)	2.422(9)		
S(1)–Ti(1)–S(2)	80.58(11)	S(5)–Ti(2)–S(6)	81.99(11)
S(4)–Ti(1)–S(3)	80.94(10)	S(7)–Ti(2)–S(6)	79.32(11)
S(4)–Ti(1)–S(2)	78.19(11)	S(7)–Ti(2)–S(8)	79.96(10)
S(1)–Ti(1)–S(3)	78.96(11)	S(5)–Ti(2)–S(8)	80.88(11)
S(2)–Ti(1)–S(3)	132.44(12)	S(7)–Ti(2)–S(5)	125.34(12)
S(1)–Ti(1)–S(4)	127.19(11)	S(6)–Ti(2)–S(8)	137.99(11)
C(51)–C(50)–S(1)	119.9(8)	C(30)–C(35)–S(5)	119.4(8)
C(50)–C(51)–S(2)	119.4(9)	C(35)–C(30)–S(6)	121.9(8)
C(60)–C(65)–S(3)	118.7(8)	C(41)–C(40)–S(7)	119.4(8)
C(40)–C(41)–S(8)	119.9(8)	C(65)–C(60)–S(4)	121.0(8)

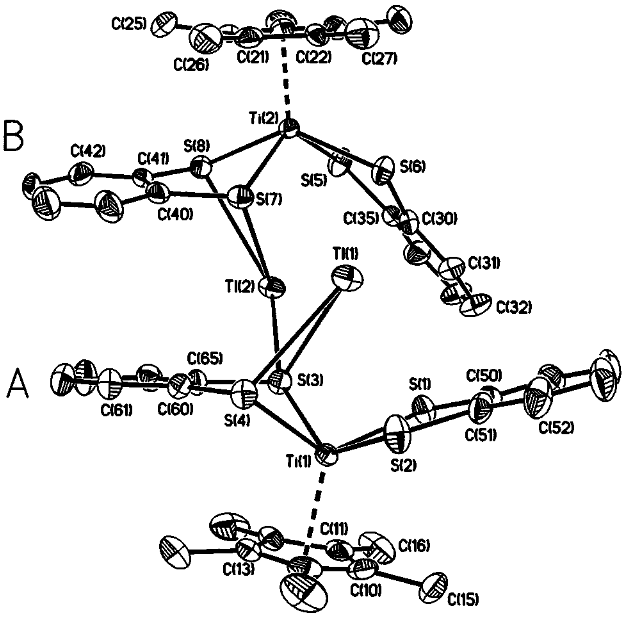


Fig. 2 Perspective view of the two structurally different units of TlTiCp*(bdt)$_2$ **1** (30% probability displacement ellipsoids)

those of **7**. These differences in dihedral angles may be attributed to the presence of the five methyl substituents on the cyclopentadienyl ring of **7**.

Solid-state structure of compound 1

The structure of a single crystal of **1** was determined by X-ray diffraction at ambient temperature, and selected geometrical parameters are listed in Table 2. There are two crystallographically independent TlTiCp*(bdt)$_2$ units which are linked *via* S(3), and these are depicted as A and B in Fig. 2, with relevant atom labelling. In both forms, the titanium has the four-legged piano stool arrangement of ligating atoms, with the least-squares plane of the four sulfur atoms (r.m.s. deviations: A, 0.047; B, 0.115 Å) being close to parallel with the plane of the Cp* ring [interplanar angles: A, 1.3(6); B 1.4(6)°]. The Ti–S bond lengths are similar to those in **7**, with all but one Ti–S distance lying in the range 2.418(3)–2.438(3) Å; Ti(2)–S(8) [2.480(3) Å] is slightly longer, although distances of this magnitude are found in titanium(IV) compounds with thiolates coordinated to a second titanium centre or to Cu^{I} or Rh^{I}.[6–8] The Ti–Cp* (centroid) distances are 2.074 and 2.055 Å, and S–Ti–Cp* (centroid) angles are in the ranges 112.7–116.4 and 110.8–118.0° for A and B, respectively.

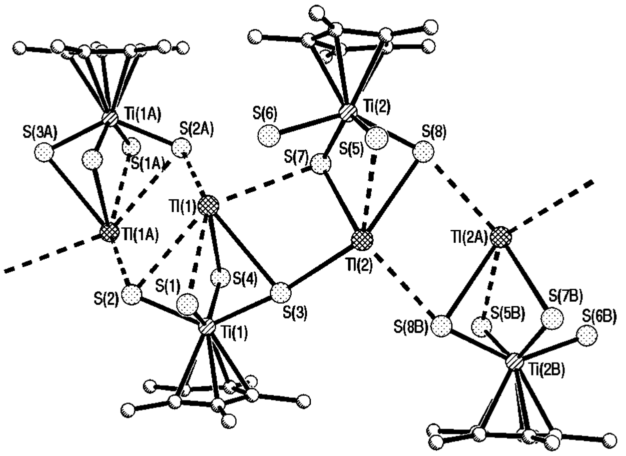


Fig. 3 Structure of TlTiCp*(bdt)$_2$ showing weak Tl···S interactions and a fragment of the chain structure (*ortho*-phenylene groups of benzenedithiolate ligands omitted for clarity)

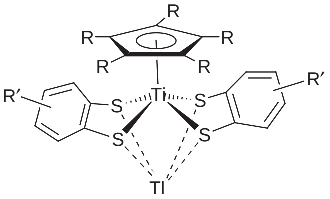
The conformations of the aromatic dithiolate ligands differ from that in compound **7**, In A, the ligands adopt an *endo*/*endo* conformation, with dihedral angles between TiS$_2$ and S$_2$C$_6$H$_4$ planes of 43.4(2) and 7.5(3)°. In B the conformation is *endo*/*exo*, as in **7**, but the respective dihedral angles are 35.2(2) and 23.0(2)°. In both forms, one thallium ion is more closely associated with one organotitanium anion and lies *trans* to the Cp* ligand, with an angle 174.8° for Tl(1)–Ti(1)–Cp* (centroid) in A and 169.8° for Tl(2)–Ti(2)–Cp* (centroid) in B, and interacts unsymmetrically with the sulfur atoms of the dithiolate ligands. In A, there are two shorter Tl–S distances of 3.157(3) and 3.296(3) Å to the more folded dithiolate ligand, S(3)C$_6$H$_4$S(4). The bending of the dithiolate ligands permits greater interaction of sulfur electron pairs with thallium and these Tl^{I}–S bond lengths are comparable with those in [TlMoCp(SC$_6$F$_5$)$_4$][1] and in crown thioether complexes [Tl([9]aneS$_3$)]$^+$ and [Tl([18]aneS$_3$)]$^+$,[14a] and are within the range of the four Tl^{I}–S interactions on the dimeric anion [Tl$_2$(bdt)$_2$]$^{2-}$.[15] There are also two longer Tl···S distances of 3.436(3) and 3.518(4) Å, to the less folded dithiolate ligand, and two Tl···S distances to neighbouring anions of 3.430(3) and 3.472(3) Å (see Fig. 3); these lengths are comparable to others in systems where weak Tl···S interactions have been claimed but are larger than the sum of the formal ionic radii of Tl^{I} and S (3.34 Å).[14]

There are two short Tl–S bonds in B between the associated Tl(2) and the *endo*-dithiolate ligand with lengths of 3.167(3) and 3.148(3) Å, and the shortest distance involves S(8) which has the longest Ti–S bond. The Tl–S distances to the *exo*-dithiolate of B are 3.412(3) and 3.910(3) Å [to S(6)], indicative of weakly and non-interacting atoms, respectively, and are consistent with the unfavourable orientation of electron pairs on these sulfurs; there is also a distance, Tl(2)–S(8B), of 3.338(2) Å to the neighbouring species related by a centre of inversion. More significant, however, is the short Tl(2)–S(3) contact of 3.173(2) Å linking Tl(2) to the dithiolate ligand of the adjacent anion of molecule A (see Fig. 3). This bridging interaction involving Tl(2) creates dimers from pairs of A and B units. If the longer, weak Tl···S interactions are also considered, the overall crystal structure comprises chains of these dimeric entities (Fig. 3). The long Tl···Ti distances of 3.557(2) Å in A and 3.581(2) Å in B and the minimum Tl···Tl separation of 4.174(2) Å preclude any significant metal–metal interactions.

NMR studies in solution

Low-temperature ^{1}H NMR spectra of **1**, down to −90 °C (in CD_2Cl_2) or to −119 °C (in CF_3Cl–CD_2Cl_2), merely show a slight broadening of all resonances, with the loss of structure of the AA′BB′ multiplet of the aromatic hydrogens at temperatures < −70 °C. Although this broadening could be related to a slowing of intramolecular conformational interchanges of benzenedithiolate ligands, it is also consistent with an increase in solvent viscosity at the low temperature, and since no new resonances were observed the spectra provide no clear evidence for inequivalence of the benzenedithiolate rings of **1** in solution, contrary to the different conformations of these ligands found in the crystal. Moreover, no inequivalences of arenedithiolate (or of cyclopentadienyl groups) were observed for the other products and this has also been observed by Köpf and co-workers for other monocyclopentadienyltitaniumdithiolates.[11,12] This may be due to rapid, time-averaged interchange of *endo* and *exo* ligands, although barriers for such inversions in arenedichalcogenates of dicyclopentadienylmetal systems have been monitored by variable-temperature NMR and are >40 kJ mol^{-1}.[16] Alternatively, in solution the dithiolate anions may adopt a more symmetrical form with equivalent ligands.

The ^{1}H NMR data for the thallium complex **1** and related $[N(PPh_3)_2]^+$ derivative **7** show significant differences between the chemical shifts of AA′ and BB′ components of the benzenedithiolate ligands and a smaller variation in the chemical shift of the Cp* rings. Thus, in $CDCl_3$ under similar conditions, the AA′ and BB′ multiplets occur at δ 7.39 and 6.97 in **1** and at δ 7.15 and 6.50 in **7**, respectively, with the latter shifts being unchanged on replacing the $[N(PPh_3)_2]^+$ cation with $[PPh_4]^+$. Differences in chemical shifts are also noted for the ^{1}H NMR resonances of aromatic and cyclopentadienyl hydrogens (see Experimental section) of $TlTiCp(bdt)_2$ **5** (in CD_2Cl_2) and $TlTiCp(tdt)_2$ **6** (in $CDCl_3$) compared to those reported for the respective ionic derivatives $[PPh_4][TiCp(bdt)_2]$[12] and $[NEt_4]$-$[TiCp(tdt)_2]$[11] in the same solvents. These shifts support differing interactions between $[Ti(\eta^5\text{-}C_5H_nMe_{5-n})(S_2C_6H_3R)_2]^-$ and Tl^+ or the large organo-phosphorus or nitrogen cations in solution, and are consistent with Tl^I being co-ordinated to the S-donor sites of the dithiolate ligands in contrast to non-co-ordinating $[N(PPh_3)_2]^+$, $[PPh_4]^+$ or $[NEt_4]^+$ ions, as found in the solid state. The NMR observations may indicate a structure shown below in solution.



Conclusion

Thallium derivatives of monocyclopentadienylbis(arene-1,2-dithiolato)titanium(IV) anions containing pentamethyl-, monomethyl- and non-substituted -cyclopentadienyl ligands can be prepared, and methylation of the rings does not markedly influence the stability of these compounds. The free anion $[TiCp^*(bdt)_2]^-$, with $[N(PPh_3)_2]^+$ as counter cation, in complex **7** adopts a structure in the crystalline state with an *endo*/*exo* conformation of the two benzene-1,2-dithiolate ligands.

In the solid state, the related heterometallic derivative $TlTiCp^*(bdt)_2$ **1** contains thallium(I) ions unsymmetrically co-ordinated to sulfur atoms of anions $[TiCp^*(bdt)_2]^-$. There are two different forms of the anion with *endo*/*endo* or *endo*/*exo* conformation, respectively, and in both forms one Tl^I ion interacts with two sulfur atoms of an *endo* dithiolate ligand. The Tl^I associated closely with the *endo*/*endo* ligand (A) also shows evidence for weaker interactions with sulfur atoms of the less folded *endo* ligand and with sulfur atoms of two neighbouring $TlTiCp^*(bdt)_2$ units. The Tl^I closely associated with the *endo*/*exo* complex (B) interacts weakly with one sulfur atom of the *exo* ligand and with a sulfur atom of a neighbouring B unit but is also more strongly associated with a sulfur atom of an adjacent complex A. The overall crystalline structure can be considered to comprise dimeric $[TlTiCp^*(bdt)_2]_2$ units weakly linked in chains. In solution, ^{1}H NMR spectra of the thallium derivatives support the presence of co-ordinative interactions between organometallic dithiolate anions and Tl^I.

Experimental

All reactions and operations were conducted under an atmosphere of dry, oxygen-free nitrogen gas, using Schlenk techniques. All 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 $TiCp^*Cl_3$,[17] $TiCp'Cl_3$[18] and $TiCpCl_3$[19] were prepared by literature methods. Benzene-1,2-dithiol, toluene-3,4-dithiol, $[N(PPh_3)_2]Cl$ and thallium(I) acetate were obtained commercially (Lancaster, Fluka or Aldrich Chemical Companies) and used as supplied. Thallium arene-1,2-dithiolates were made by reaction of thallium(I) acetate and arenedithiol in methanol. The IR spectra were measured on a Nicolet Impact 400 FT spectrometer, and FAB mass spectra on an upgraded VG MS9 using a nitrobenzyl alcohol matrix. The ^{1}H 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.

Preparations

$Tl[Ti(\eta^5\text{-}C_5Me_5)(1,2\text{-}S_2C_6H_4)_2]$ 1. The compound $TiCp^*Cl_3$ (0.10 g, 3.5 × 10^{-4} mol) was dissolved in thf (4 cm^3) 1.2-$(TlS)_2C_6H_4$ (0.39 g, 7.1 × 10^{-4} mol) was suspended in thf (5 cm^3). The solution of $TiCp^*Cl_3$ was added to the Tl_2bdt suspension and the reaction mixture stirred overnight. Filtration through Celite, followed by the removal of solvent *in vacuo* afforded a dark purple solid. Crystallisation from CH_2Cl_2–light petroleum yielded pure **1** (0.15 g, 65%). Further recrystallisation from the same solvents afforded X-ray diffraction quality crystals (Found: C, 39.4; H, 3.4. $C_{22}H_{23}S_4TiTl$ requires C, 39.5; H, 3.4%). ^{1}H NMR ($CDCl_3$, 20 °C): δ 2.08 (s, 15 H, C_5Me_5), 6.97 (BB′ part of AA′BB′, $J_{BA} + J_{BA'} = 9.2$, 4 H, $H^{4,5}$ of C_6H_4), 7.39 (AA′ part of AA′BB′, $J_{AB} + J_{AB'} = 9.2$ Hz, 4 H, $H^{3,6}$ of C_6H_4); (CD_2Cl_2, 20 °C): δ 1.99 (s, 15 H, C_5Me_5), 6.91 (BB′ part of AA′BB′, 4 H, $H^{4,5}$ of C_6H_4); 7.30 (AA′ part of AA′BB′, 4 H, $H^{3,6}$ of C_6H_4); (CF_3Cl–CD_2Cl_2, −119 °C): δ 6.90 (br, 4 H), 7.25 (br, 4 H). IR (KBr) cm^{-1}: 3036w (CH str), 2901m (CH_3 str), 1431s (C–C str), 1373s (CH_3 def), 1020m, 736vs (CH def). FAB MS, *m*/*z* (^{205}Tl) significant ions: 879 (2, $[M + Tl]^+$), 668 (16, M^+), 667 (24), 533 (4, $[M - Cp^*]^+$), 532 (5), 464 (2) 463 (1, $[M - Tl]^+$), 205 (60, Tl^+).

$Tl[Ti(\eta^5\text{-}C_5Me_5)(3,4\text{-}S_2C_6H_3CH_3\text{-}1)_2]$ 2. The compound $TiCp^*Cl_3$ (0.090 g, 3.1 × 10^{-4} mol) was dissolved in thf (5 cm^3) and transferred *via* cannula to a suspension of Tl_2tdt (0.37 g, 6.5 × 10^{-4} mol) in thf (5 cm^3). The reaction mixture became dark red in colour rapidly after mixing and was left stirring at ambient temperature for 18 h. The reaction mixture was filtered through Celite, removing precipitated TlCl and unreacted Tl_2tdt. The dark red solution was reduced to dryness *in vacuo*, yielding a dark purple solid. The crude product was purified by crystallisation from CH_2Cl_2–light petroleum, yielding pure **2**

(0.070 g, 32%) (Found: C, 41.3; H, 3.8. $C_{24}H_{27}S_4TiTl$ requires C, 41.4; H, 3.8%). ^1H NMR ($CDCl_3$, 20 °C): δ 2.08 (s, 15 H, C_5Me_5), 2.22 (s, 6 H, CH_3), 6.85 (m, 2 H, H^5 of C_6H_3), 7.23 (m, 2 H, H^2 of C_6H_3), 7.27 (d, *J* 7 Hz, 2 H, H^6 of C_6H_3).

Tl[Ti(η^5-C_5H_4Me)(1,2-$S_2C_6H_4$)$_2$] 3. By a similar procedure to that described above, $TiCp'Cl_3$ (0.10 g, 4.3 × 10^{-4} mol) and Tl_2bdt (0.47 g, 8.6 × 10^{-4} mol) gave, after purification from thf–light petroleum, **3** (0.08 g, 31%) (Found: C, 35.0; H, 2.3. $C_{18}H_{15}S_4TiTl$ requires C, 35.3; H, 2.4%). ^1H NMR [$(CD_3)_2SO$, 20 °C]: δ 2.10 (s, 3 H, C_5H_4Me), 5.74 [AA′ part of AA′BB′ (≈t, *J* ≈ 5), 2 H, C_5H_4Me], 5.92 [BB′ part of AA′BB′ (≈t, *J* ≈ 5), 2 H, C_5H_4Me], 6.82 (BB′ part of AA′BB′, $J_{BA} + J_{BA'} = 9.1$ Hz, 4 H, $H^{4,5}$ of C_6H_4), 7.22 (AA′ part of AA′BB′, 4 H, $H^{3,6}$ of C_6H_4).

Tl[Ti(η^5-C_5H_4Me)(3,4-$S_2C_6H_3CH_3$-1)$_2$] 4. Similarly, $TiCp'Cl_3$ (0.10 g, 4.3 × 10^{-4} mol) and Tl_2tdt (0.50 g, 8.8 × 10^{-4} mol) were reacted in thf (5 cm^3) at room temperature for 16 h. After purification from CH_2Cl_2–thf–light petroleum **4** was obtained as a dark purple solid (0.1 g, 40%) (Found: C, 37.8; H, 3.1. $C_{20}H_{19}S_4TiTl$ requires C, 37.6; H, 3.0%). ^1H NMR ($CDCl_3$, 20 °C): δ 2.26 (s, 6 H, CH_3), 2.29 (s, 3 H, C_5H_4Me), 6.32 [AA′ part of AA′BB′ (≈t, *J* ≈ 5), 2 H, C_5H_4Me], 6.47 [BB′ part of AA′BB′ (≈t, *J* ≈ 5), 2 H, C_5H_4Me], 6.84 (m, 2 H, H^5 of C_6H_3), 7.27 (m, 2 H, H^2 of C_6H_3), 7.31 (d, *J* 8 Hz, 2 H, H^6 of C_6H_3).

Tl[Ti(η^5-C_5H_5)(1,2-$S_2C_6H_4$)$_2$] 5. Similarly, $TiCpCl_3$ (0.10 g, 4.5 × 10^{-4} mol) and Tl_2bdt (0.50 g, 9.1 × 10^{-4} mol) gave, after purification from thf–light petroleum, **5** (0.10 g, 41%) as a dark coloured solid (Found: C, 33.9; H, 2.0. $C_{17}H_{13}S_4TiTl$ requires C, 34.1; H, 2.2%). ^1H NMR [$(CD_3)_2SO$, 20 °C]: δ 5.96 (s, 5 H, C_5H_5), 6.82 (BB′ part of AA′BB′, $J_{BA} + J_{BA'} = 9.2$ Hz, 4 H, $H^{4,5}$ of C_6H_4), 7.22 (AA′ part of AA′BB′, 4 H, $H^{3,6}$ of C_6H_4); (CD_2Cl_2, 20 °C): δ 6.49 (s, 5 H, C_5H_5), 7.07 (BB′ part of AA′BB′, 4 H, $H^{4,5}$ of C_6H_4), 7.45 (AA′ part of AA′BB′, 4 H, $H^{3,6}$ of C_6H_4).

Tl[Ti(η^5-C_5H_5)(3,4-$S_2C_6H_3CH_3$-1)$_2$] 6. Similarly, $TiCpCl_3$ (0.10 g, 4.5 × 10^{-4} mol) and Tl_2tdt (0.55 g, 9.8 × 10^{-4} mol) gave, after purification from CH_2Cl_2–light petroleum, **6** (0.10 g, 36%) as a dark coloured solid (Found: C, 36.0; H, 2.6. $C_{19}H_{17}S_4TiTl$ requires C, 36.5; H, 2.7%). ^1H NMR ($CDCl_3$, 20 °C): δ 2.27 (s, 6 H, CH_3), 6.50 (s, 5 H, C_5H_5), 6.85 (m, 2 H, H^5 of C_6H_3), 7.27 (m, 2 H, H^2 of C_6H_3), 7.32 (d, *J* 8 Hz, 2 H, H^6 of C_6H_3).

[N(PPh_3)$_2$][Ti(η^5-C_5Me_5)(1,2-$S_2C_6H_4$)$_2$] 7. Compound **1** (0.10 g, 1.5 × 10^{-4} mol) was dissolved in CH_2Cl_2 (10 cm^3), [N(PPh_3)$_2$]Cl (0.085 g, 1.5 × 10^{-4} mol) was dissolved in CH_2Cl_2 (2 cm^3). The two solutions were combined and stirred at room temperature for 16 h. The reaction mixture was filtered through Celite and the solvent removed *in vacuo*, yielding a dark red oily material. Trituration with light petroleum, followed by crystallisation from CH_2Cl_2–light petroleum gave dark red crystals, containing solvated dichloromethane. Extensive drying under vacuum gave pure, unsolvated **7** (0.11 g, 73%) (Found: C, 69.2; H, 5.7; N, 1.3. $C_{58}H_{53}NP_2S_4Ti$ requires C, 69.5; H, 5.3; N, 1.4%). ^1H NMR ($CDCl_3$, 20 °C): δ 1.90 (s, 15 H, C_5Me_5), 6.50 (BB′ part of AA′BB′, $J_{BA+BA'} = 9.1$ Hz, 4 H, $H^{4,5}$ of C_6H_4), 7.15 (AA′ part of AA′BB′, 4 H, $H^{3,6}$ of C_6H_4), 7.2–7.5 [complex, 30 H, P(C_6H_5)$_3$].

X-Ray data collections and crystal structure determinations

Single crystals of **1** and **7**, the latter as the tris(dichloromethane)-solvate, were grown by slow diffusion of dichloromethane solutions with light petroleum at −15 °C. A single crystal of **1** was mounted in epoxy resin glue in a sealed, thin-walled glass capillary under dry nitrogen. Crystals of **7** were found to be very sensitive to solvent loss and a crystal was cut, mounted in Nujol and vacuum grease on a glass fibre and placed quickly into a cold stream of nitrogen gas on a Siemens P4 diffractometer at 160 K.[20] Details of the crystal structure determinations of **1** and **7** are given in Table 3.

Table 3 Crystallographic data for complexes **1** and **7**·3CH_2Cl_2

	1	**7**·3CH_2Cl_2
Formula	$C_{22}H_{23}S_4TiTl$	$C_{58}H_{53}NP_2S_4Ti\cdot 3CH_2Cl_2$
M	667.91	1256.87
System	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Temperature/K	293	160
a/Å	12.2824(9)	11.473(3)
b/Å	13.9012(10)	15.545(4)
c/Å	15.6661(12)	16.778(6)
α/°	70.396(5)	89.08(2)
β/°	68.067(8)	88.04(2)
γ/°	84.155(6)	89.859(14)
U/Å^3	2336.6(3)	2990.2(15)
Z	4	2
D_c/g cm^{-3}	1.899	1.396
μ(Mo-Kα)/mm^{-1}	7.594	0.644
Data measured	9248	10 398
Unique data	8014	10 377
R_{int}	0.044	0.068
Observed data [$I > 2\sigma(I)$]	5095	6296
R, *wR*2 (observed data)	0.0470, 0.0839	0.0646, 0.1451

CCDC reference number 186/943.

See http://www.rsc.org/suppdata/dt/1998/1581/ for crystallographic files in .cif format.

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