

Synthesis, Characterization, and Reduction Chemistry of Mixed-Cyclopentadienyl/Arylsulfide Titanium Dichlorides

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A series of titanium derivatives [CpTi(SAr)Cl₂] containing both cyclopentadienyl and various substituted arylsulfide ligands (SAr = SC₆H₄Me-4 (**1**), SC₆H₂Me₃-2,4,6 (**2**), SC₆H₂-Prⁱ₃-2,4,6 (**3**), SC₆H₂Ph₃-2,4,6 (**4**)) has been synthesized from the reaction of [CpTiCl₃] with 1 equiv of the lithium salt of the corresponding arylsulfides in benzene. X-ray diffraction studies show that each metal center possesses a pseudo-tetrahedral geometry. The compounds undergo one-electron reduction to produce sulfur-bridged dimers of the type [CpTiCl(μ-SAr)]₂ (SAr = SC₆H₂Me₃-2,4,6 (**5**), SC₆H₂Prⁱ₃-2,4,6 (**6**)). The solid-state structures of these dimers show that the cyclopentadienyl rings are arranged in a transoid fashion about the [Ti(μ-SAr)₂Ti] core. The Ti–Ti distances, 3.242(1) and 3.225(1) Å, respectively, are similar to those found in previously reported Cp/aryloxo dimers with terminal aryloxides and bridging chlorides.

Introduction

Group 4 organometallic chemistry has been dominated by cyclopentadienyl (Cp) ligation.¹ Titanocene dichloride was first synthesized and reported by Wilkinson et al. in 1953² and has been shown to be a versatile stoichiometric reagent and catalyst precursor. The efficacy of [Cp₂TiCl₂] has led to the development of a number of related titanocenes containing a range of alkyl-, aryl-, and heteroatom-substituted Cp rings attached to the metal center. Other developments have included the synthesis of *ansa*-titanocenes that have the two Cp rings connected by a hydrocarbon, heteroatom, or mixed-hydrocarbon/heteroatom bridge group, as well as the synthesis of chiral titanocenes for use in asymmetric synthesis and catalysis.³ Alteration of the Cp ligands has resulted in variations in the physical and chemical properties of titanocenes. The innovation of modified titanocenes has also motivated research into the development of mono-Cp derivatives that contain a different ligand [CpTi(X)Cl₂], including the “constrained geometry” systems where the Cp and non-Cp ligands are linked by a bridging group.⁴

Research in the Rothwell group has focused on the utility of bis(aryloxo) compounds of the type [(ArO)₂TiCl₂], in which the aryloxo ligand can be isolobal with that of cyclopentadienyl, bonding in a σ²π⁴

fashion.⁵ These compounds have several advantages over their Cp counterparts, including tuning of the steric and electronic properties by changing the substituents on the aryl moiety. This has provided both novel and complementary chemistry to the well-studied metallocenes. The advent of these compounds has been followed by the development of mixed-cyclopentadienyl/aryloxo [CpTi(OAr)Cl₂] systems, which have been structurally compared to the related metallocene [Cp₂TiCl₂] and bis(aryloxo) [(ArO)₂TiCl₂] systems.^{6,7} As an extension of our studies, we have begun an investigation into related arylsulfide chemistry.

Many substituted arenethiols are known and can function as ligands that meet a variety of steric and electronic requirements. Simple benzenethiol, 4-methylbenzenethiol, and 2,6-dichlorobenzenethiol are commercially available, while 2,6-diphenylbenzenethiol can be prepared via a Newman–Kwart rearrangement of 2,6-diphenylphenol.⁸ Trisubstituted 2,4,6-trimethylbenzenethiol and 2,4,6-triisopropylbenzenethiol are synthesized by the reduction of the corresponding arene-sulfonyl chloride with lithium aluminum hydride,⁹ while 2,4,6-triphenylbenzenethiol can be prepared by the bromination of 1,3,5-triphenylbenzene, followed by lithiation, addition of elemental sulfur, and workup.¹⁰ More

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complicated literature procedures also exist for the synthesis of other arenethiols, including 2,6-diisopropylbenzenethiol,¹¹ 2,6-dimesitylbenzenethiol,¹² and 2,4,6-tri-*tert*-butylbenzenethiol.¹³

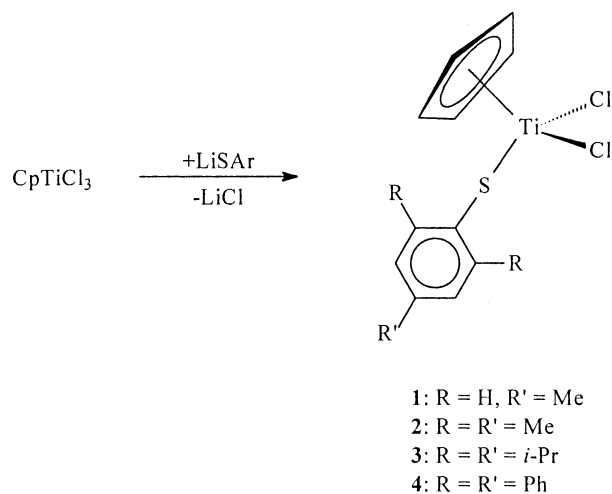
There are numerous studies involving titanium compounds that contain from one to six arylsulfide ligands, and several crystal structures have been reported.¹⁴ However, compounds of the type [CpTi(SAr)Cl₂] have received limited attention. Their utility as cancer inhibitors was reported in 1984,¹⁵ and in 1996 a process for manufacturing ethylene α -olefin copolymers in the presence of cyclopentadienyltitanium catalyst components was patented.¹⁶ These studies focused on very few arenethiols, and there are no data reported in the Cambridge Structural Database for any of these species. One example of a structurally characterized Ti(III) dimer with two bridging arylsulfides exists,¹⁷ but dimeric species of the type [CpTiCl(μ -SAr)]₂ are unknown.

Reported here are the synthesis and characterization of several compounds of the type [CpTi(SAr)Cl₂] and dimeric species of the type [CpTiCl(μ -SAr)]₂ formed via one-electron reductions of the [CpTi(SAr)Cl₂] complexes. The solid-state structures of these compounds are compared to those of the analogous aryloxide systems. Although the dichlorides may have biological applications,¹⁸ we are interested in their potential synthetic applications, particularly as titanacycle precursors.

Results and Discussion

Synthesis and Characterization of Monocyclopentadienyltitanium Arylsulfide Complexes. Synthesis of the mixed-cyclopentadienyl/arylsulfide compounds was attempted using two methods employed successfully for the aryloxide analogues. In the first

Scheme 1



method, the phenol was added to [CpTiCl₃] in the presence of pyridine, resulting in the desired product and pyridinium hydrochloride. This method proved unsuccessful for the synthesis of the arylsulfide systems, resulting instead in a large amount of the previously reported [pyH][CpTiCl₄],⁶ as confirmed by X-ray crystallography. In the second method, lithiation of the benzenethiol using *n*-butyllithium and subsequent addition of the lithio salt to [CpTiCl₃] resulted in a good yield of the desired product (Scheme 1). The NMR spectra of **1–4** were as expected, with one Cp resonance and a single set of arylsulfide signals in each case. In the ¹H NMR spectrum of **1–3**, the Cp protons were observed at δ 6.13, 6.12, and 6.15 ppm, respectively, which are shifted downfield from the δ 5.3–6.0 ppm range typical for [CpTi(OAr)Cl₂] compounds. The Cp resonance for **4** appears further upfield at δ 5.78 ppm as a result of the diamagnetic shielding by the ortho phenyl rings.

Compounds **1–4** have been analyzed by X-ray crystallography (Table 1), and ORTEP drawings for **2** and **4** are represented in Figures 1 and 2, respectively. The titanium dichlorides exhibit a pseudo-tetrahedral geometry about the metal center. Selected structural parameters, along with those for related [(X)Ti(Y)Cl₂] derivatives (X, Y = Cp, OAr),^{6,19} are collected in Table 2. The Ti–Cl bond distance decreases as Cp is replaced by OAr and, to a lesser extent, upon replacement by SAr, reflecting the relative electrophilicity at the metal center. The Cp–Ti–S bond angles are substantially contracted compared to those of the analogous X–Ti–Y angles in the bis(Cp), bis(aryloxide), or mixed-Cp/aryloxide compounds. In addition, the Ti–S–C bond angle is significantly smaller than the Ti–O–C bond angles in the analogous systems. The largest Ti–S–C bond angle observed in these systems is 107°, while the smallest reported Ti–O–C angle is 150°.

Known Ti–S–C bond angles for terminal arylsulfides on titanium metal centers range from 87 to 123°, on the basis of a survey of all reported examples.¹⁴ A plot of Ti–S distances versus the Ti–S–Ar angles indicates that Ti–S bonds are typically between 2.27 and 2.45 Å

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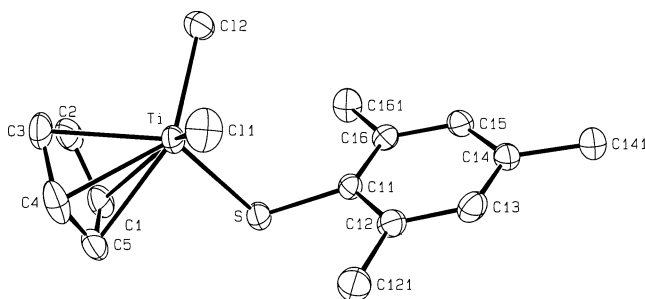
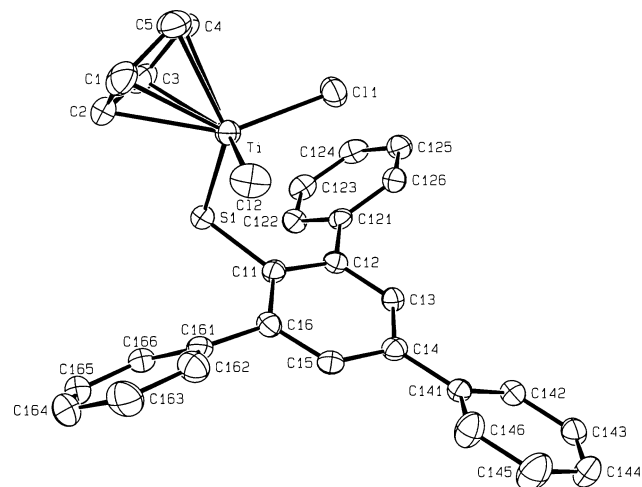
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Table 1. Crystal Data and Data Collection Parameters

	1	2	3	4	5	6
formula	C ₁₂ H ₁₂ Cl ₂ STi	C ₁₄ H ₁₆ Cl ₂ STi	C ₂₀ H ₂₈ Cl ₂ STi	C ₂₉ H ₂₂ Cl ₂ STi	C ₂₈ H ₃₂ Cl ₂ S ₂ Ti ₂ ·0.5C ₆ H ₆	C ₄₀ H ₅₆ Cl ₂ S ₂ Ti ₂
fw	307.10	335.15	419.32	521.37	638.46	767.73
space group	<i>P2₁/n</i> (No. 14)	<i>P1</i> (No. 2)	<i>P1</i> (No. 2)	<i>P2₁/n</i> (No. 14)	<i>P1</i> (No. 2)	<i>Pna2₁</i> (No. 33)
<i>a</i> , Å	7.6209(2)	6.7592(2)	6.1625(2)	11.0173(2)	8.6789(4)	18.7973(6)
<i>b</i> , Å	12.8769(3)	6.9746(2)	11.1142(4)	18.7419(5)	10.7494(6)	13.8957(4)
<i>c</i> , Å	13.9754(3)	16.9957(6)	15.2861(5)	12.9144(3)	16.961(1)	15.6199(4)
α, deg	90	90.454(2)	87.012(2)	90	90.039(3)	90
β, deg	101.139(2)	97.183(2)	89.194(2)	113.717(1)	96.658(3)	90
γ, deg	90	108.217(1)	89.751(2)	90	92.549(2)	90
<i>V</i> , Å ³	1345.6(1)	754.15(8)	1045.4(1)	2441.4(2)	1570.1(3)	4079.9(2)
<i>Z</i>	4	2	2	4	2	4
ρ _{calcd} , g cm ⁻³	1.516	1.476	1.332	1.418	1.350	1.250
temp, K	150	170	150	150	193	150
radiation (wavelength, Å)				Mo Kα (0.710 73)		
<i>R</i>	0.031	0.039	0.071	0.037	0.075	0.049
<i>R_w</i>	0.078	0.095	0.167	0.096	0.135	0.110

Figure 1. ORTEP (50% thermal ellipsoids) view of [CpTi(SC₆H₂Me₃-2,4,6)Cl₂] (**2**).Figure 2. ORTEP (50% thermal ellipsoids) view of [CpTi(SC₆H₂Ph₃-2,4,6)Cl₂] (**4**).

in length, and most Ti–S–Ar angles lie within a small range (Figure 3). These observations differ dramatically from those of titanium aryloxides, where a survey of Ti–O distances versus Ti–O–Ar angles on four-coordinate titanium displays Ti–O–Ar angles covering a much wider range (approximately 110–180°).²⁰

Dimerization via One-Electron Reduction. The one-electron reduction of **2** and **3** was first attempted using a sodium/mercury amalgam (Scheme 2), the method typically used for the analogous aryloxides. Treatment of a benzene solution of **2** with sodium

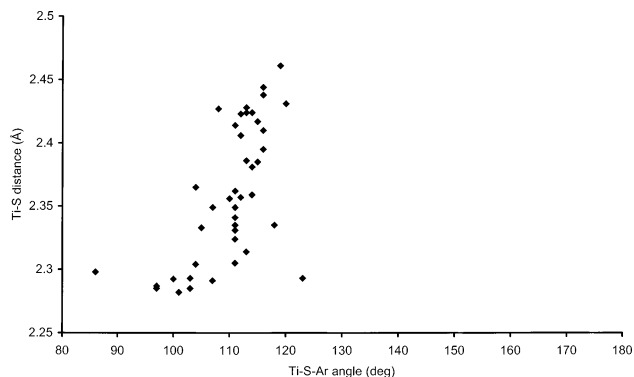


Figure 3. Variation of Ti–S distance with Ti–S–Ar angle for terminal arylsulfides on titanium metal centers.

amalgam (1 equiv of Na/Ti) leads to the formation of **5**, which can be isolated in good yield as a burgundy solid upon precipitation from benzene with pentane. Reaction of **3** with 1 equiv of trimethylaluminum (TMA) affords a dark burgundy solution from which **6** was isolated. The ¹H NMR spectrum of **6** indicates the presence of diastereotopic methyl groups on the *o*-isopropyl substituents. Compounds **5** and **6** have been analyzed by X-ray diffraction (Table 1). Selected bond distances and angles are listed in Tables 3 and 4, respectively, and an ORTEP drawing of **6** is shown in Figure 4. The solid-state structures show dinuclear compounds with a [Ti(μ-SAr)₂Ti] core and terminal chloride and Cp groups. The Cp ligands are arranged in a transoid fashion about the core, and the molecule contains a C₂ axis that runs through the two sulfur atoms.

The analogous aryloxy system is also dimeric, but it contains bridging chlorides and terminal aryloxides. The cyclopentadienyl compound characterized by Stucky et al. exhibits an average Ti–Ti bond length of 3.96 Å, which is too long for any metal–metal interaction.²¹ In the diamagnetic bis(2,6-diphenylphenoxide) species, a much shorter distance of 2.9827(7) Å is observed,²² and the bond lengths in the mixed Cp/OAr species range from 3.19 to 3.336(1) Å. The Ti–Ti distances in **5** and **6** are 3.242(1) and 3.225(1) Å, respectively, which are similar to those found for Cp/OAr compounds containing

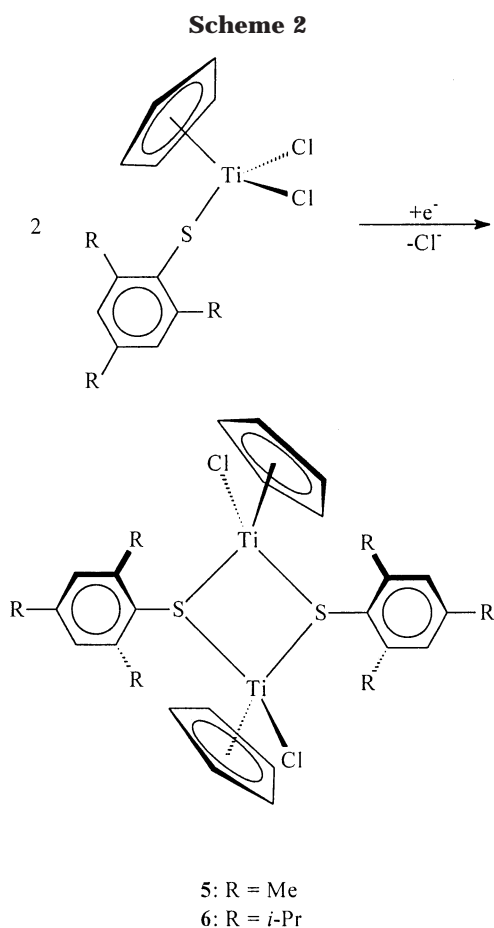
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Table 2. Structural Parameters for [(X)Ti(Y)Cl₂] (X, Y = Cp, OAr, SAR)

compd	Ti–Cl, Å	Ti–Cp, Å	Ti–O/S, Å [Ti–O/S–C, deg]	X–Ti–Y, deg	Cl–Ti–Cl, deg	O/S–Ti–Cl, deg	Cp–Ti–Cl, deg
[Cp ₂ TiCl ₂] ^{19a}	2.367(2) 2.361(1)	2.058 (av)		131	94		106 (av)
[CpTi(OC ₆ HPh ₄ -2,3,5,6)Cl ₂] ⁶	2.255(1) 2.2396(9)	2.016(6)	1.796(2) [150]	115	102	106 104	115 114
[CpTi(OC ₆ HNP ₂ -2,6-Me ₂ -3,5)Cl ₂] ⁶	2.256(2) 2.232(2)	2.010(8)	1.780(4) [153]	116	102	105 103	114 114
[CpTi(OC ₆ HNP ₂ -2,6-Bu ^t -3,5)Cl ₂] ⁶	2.230(2) 2.244(2)	2.04(1)	1.774(3) [164]	119	102	106 102	112 114
[CpTi(OC ₆ H ₂ Ph-2-Bu ^t -4,6)Cl ₂] ⁶	2.2597(8) 2.2690(8)	2.022(4)	1.785(2) [160]	118	99	104 105	114 113
[CpTi(OC ₆ H ₂ Np-2-Bu ^t -4,6)Cl ₂] ⁶	2.334(2) 2.321(2)	2.028(2)	1.786(1) [159]	118	101	106 103	113 113
[CpTi(OC ₆ H ₃ {C ₃ H ₅ }-2-Me-6)Cl ₂] ⁶	2.2666(8) 2.2609(7)		1.780(2) [155]		102	102 104	
[Ti(OC ₆ H ₃ Ph ₂ -2,6) ₂ Cl ₂] ^{19b}	2.206(1)		1.726(2) [169]	109	113	111	
[Ti(OC ₆ H ₃ Me ₂ -2,6) ₂ Cl ₂] ^{19c}	2.192(4) 2.211(4)		1.734(7) [167]	109	111	109, 109 108, 110	
			1.736(8) [169]				
1^a	2.2371(5) 2.2528(5)	2.014	2.2924(5) [100]	107	103	107 106	116 117
2^a	2.2522(8) 2.2557(7)	2.017	2.2912(7) [107]	105	102	107 108	118 117
3^a	2.240(1) 2.251(1)	2.026(5)	2.287(1) [97]	107	103	106 107	116 117
4^a	2.2430(8) 2.2513(8)	2.019(4)	2.2851(8) [97]	105	103	106 109	116 117

^a This work.**Table 3. Selected Bond Distances (Å) and Angles (deg) for 5**

Ti(1)–Ti(2)	3.242(1)	Ti(2)–S(2)	2.306(2)
Ti(1)–Cl(1)	2.278(2)	Ti(1)–Cp	2.020
Ti(2)–Cl(2)	2.280(2)	Ti(2)–Cp	2.026
Ti(1)–S(1)	2.326(2)	S(1)–C(111)	1.783(5)
Ti(1)–S(2)	2.322(2)	S(2)–C(211)	1.787(5)
Ti(2)–S(1)	2.303(2)		
Ti(1)–S(1)–C(111)	137.1(2)	S(1)–Ti(1)–S(2)	90.38(5)
Ti(1)–S(2)–C(211)	137.6(2)	S(1)–Ti(2)–S(2)	91.36(5)
Ti(2)–S(1)–C(111)	134.0(2)	Ti(1)–S(1)–Ti(2)	88.90(5)
Ti(2)–S(2)–C(211)	133.5(2)	Ti(1)–S(2)–Ti(2)	88.93(5)
Cl(1)–Ti(1)–S(1)	105.81(7)	Cp–Ti(1)–Cl(1)	117.0
Cl(1)–Ti(1)–S(2)	104.31(7)	Cp–Ti(1)–S(1)	117.4
Cl(2)–Ti(2)–S(1)	105.47(7)	Cp–Ti(1)–S(2)	118.0
Cl(2)–Ti(2)–S(2)	103.04(7)		

Table 4. Selected Bond Distances (Å) and Angles (deg) for 6

Ti(1)–Ti(2)	3.225(1)	Ti(2)–S(3)	2.309(1)
Ti(1)–Cl(1)	2.282(1)	Ti(2)–S(4)	2.314(1)
Ti(2)–Cl(2)	2.293(2)	Ti(1)–Cp	2.018(6)
Ti(1)–S(3)	2.319(1)	S(3)–C(31)	1.795(4)
Ti(1)–S(4)	2.320(1)	S(4)–C(41)	1.799(4)
Ti(1)–S(3)–C(31)	137.2(2)	S(3)–Ti(1)–S(4)	91.41(5)
Ti(1)–S(4)–C(41)	133.0(2)	S(3)–Ti(2)–S(4)	91.79(4)
Ti(2)–S(3)–C(31)	134.5(2)	Ti(1)–S(3)–Ti(2)	88.37(4)
Ti(2)–S(4)–C(41)	138.7(2)	Ti(1)–S(4)–Ti(2)	88.22(4)
Cl(1)–Ti(1)–S(3)	105.15(5)	Cp–Ti(1)–Cl(1)	117.7(2)
Cl(1)–Ti(1)–S(4)	105.84(5)	Cp–Ti(1)–S(3)	117.3(2)
Cl(2)–Ti(2)–S(3)	104.63(5)	Cp–Ti(1)–S(4)	115.9(2)
Cl(2)–Ti(2)–S(4)	104.22(5)		

from **5** and **6**. They contain bridging alkanedithiolate or benzylthiolate moieties, and the Ti centers are formally d⁰, precluding any metal–metal bonding. The Ti–Ti distances obtained from the Cambridge Struc-

bridging chlorides. The nature of this d¹–d¹ interaction has been discussed by Rothwell et al.⁶

A few Ti–Ti dimers with bridging thiolates have been reported,²³ and most exhibit two distinct differences

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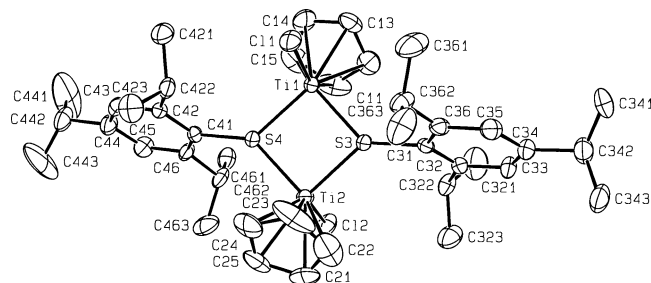


Figure 4. ORTEP (50% thermal ellipsoids) view of $[\text{Cp-TiCl}(\mu\text{-SC}_6\text{H}_2\text{Pr}^i\text{-2,4,6})]_2$ (**6**).

Table 5. Ti–Ti Bond Lengths in Dimers

compd	Ti–Ti, Å
$[\text{Cp}_2\text{Ti}(\mu\text{-Cl})_2]^{21}$	3.96 (av)
$[(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2\text{Ti}(\mu\text{-Cl})_2]^{24}$	2.9827(7)
$[\text{CpTi}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-2,6})(\mu\text{-Cl})_2]^{17}$	3.19 ^b
$[\text{CpTi}(\text{OC}_6\text{H}_2\text{Np-2-Bu}^t\text{-4,6})(\mu\text{-Cl})_2]^{6b}$	3.336(1)
$[\text{CpTi}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-2,6})(\mu\text{-SPh})_2]^{17}$	3.3942(8)
5^a	3.242(1)
6^a	3.225(1)

^a This work. ^b Obtained from Cambridge Structural Database.

tural Database range from 3.418 to 4.117 Å in these compounds. The only reported structure closely related to **5** and **6** is the compound $[\text{CpTi}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-2,6})(\mu\text{-SPh})_2]$, which is a dimer containing two bridging benzenethiolates and terminal Cp and aryloxy ligands.¹⁷ This diamagnetic species has a Ti–Ti distance of 3.3942–(8) Å, slightly longer than those of **5** and **6**. The *S*-phenyl ring of this species approaches coplanarity with the slightly puckered Ti_2S_2 plane, which differs from **5** and **6**, where the *S*-aryl ring is nearly perpendicular to the Ti_2S_2 plane. Table 5 lists Ti–Ti bond lengths for **5** and **6** along with selected related dimeric species.^{6,17,21,24}

Summary and Conclusions

Several mixed-cyclopentadienyl/arylsulfide titanium dichlorides have been prepared and structurally characterized. This represents the first structurally characterized compound of the type $[\text{CpTi}(\text{SAr})\text{Cl}_2]$, and their parameters have been compared to those of various analogous aryloxy species.

The one-electron reduction of these compounds produces a dimer containing bridging arylsulfides and terminal cyclopentadienyl and chloride ligands. The Ti–Ti bond lengths are 3.242(1) and 3.225(1) Å for $[\text{CpTiCl}(\mu\text{-SC}_6\text{H}_2\text{Me}_3\text{-2,4,6})]_2$ and $[\text{CpTiCl}(\mu\text{-SC}_6\text{H}_2\text{Pr}^i\text{-2,4,6})]_2$, which are similar to those of the mixed-cyclopentadienyl/aryloxy species with bridging chlorides.

Experimental Section

General Details. All manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Hydrocarbon solvents were distilled from sodium/benzophenone and stored over sodium ribbon under nitrogen prior to use. The synthesis of $[\text{CpTiCl}_3]$ was carried out according to a literature procedure.²⁵ Pyridine was stored over KOH and 4 Å molecular sieves prior to use. The reagents 2,4,6-trimethylbenzenethiol,⁹ 2,4,6-triisopropylbenzenethiol,⁹ and 2,4,6-

triphenylbenzenethiol¹⁰ were prepared according to literature procedures or slight variations thereof. All other reagents were purchased from Aldrich Chemical Co., Inc., and used as received. The ¹H NMR spectra were recorded on a Varian Inova-300 spectrometer and were referenced to residual protio solvent. The ¹³C NMR spectra were recorded at 75.4 MHz on a Varian Inova-300 spectrometer and were internally referenced to the solvent signal. Elemental analyses and X-ray diffraction studies were performed in-house at Purdue University. Elemental analyses for **4** and **6** were omitted due to the low percentage of carbon found. This is caused by the formation of carbide species, which is typical for early-transition-metal organometallic compounds.

[CpTi(SC₆H₄Me-4)Cl₂] (1). To a solution of 4-methylbenzenethiol (0.57 g, 4.6 mmol) in benzene (50 mL) was slowly added a solution of *n*-BuLi (1.84 mL, 2.5 M in hexanes) via syringe. There was a noticeable increase in temperature, and the solution became opaque as the lithio salt of the arylsulfide formed. The resulting suspension was stirred for several hours and then was added to a solution of $[\text{CpTiCl}_3]$ (1.00 g, 4.6 mmol) in benzene (100 mL), resulting in a color change from green to deep red. The mixture was stirred overnight under nitrogen and then was filtered through a frit using a plug of Celite. The clear, red filtrate was dried in vacuo, yielding a bright orange solid (0.78 g, 55%). The crude product was redissolved in benzene and layered with pentane to obtain X-ray-quality crystals. Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{Cl}_2\text{STi}$: C, 46.94; H, 3.94; Cl, 23.09; S, 10.44. Found: C, 46.55; H, 4.07; Cl, 22.74; S, 10.12. ¹H NMR (C_6D_6 , 25 °C): δ 7.67 (d, *m*-H); 7.01 (d, *o*-H); 6.13 (s, Cp); 2.00 (s, *p*-Me). ¹³C NMR (C_6D_6 , 25 °C): δ 139.8, 138.5, 132.8, 130.5 (aromatics); 119.7 (Cp); 21.0 (*p*-Me).

[CpTi(SC₆H₂Me₃-2,4,6)Cl₂] (2). To a solution of 2,4,6-trimethylbenzenethiol (1.39 g, 9.1 mmol) in benzene (100 mL) was slowly added a solution of *n*-BuLi (3.64 mL, 2.5 M in hexanes) via syringe. The resulting suspension was stirred for 2 h and then was added to a solution of $[\text{CpTiCl}_3]$ (2.00 g, 9.1 mmol) in benzene (150 mL). The mixture was stirred overnight under nitrogen and then was filtered through a frit with a plug of Celite. The clear, red filtrate was concentrated in vacuo and layered with pentane, yielding bright red-orange crystals (2.28 g, 75%). Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{Cl}_2\text{STi}$: C, 50.18; H, 4.81; Cl, 21.16; S, 9.57. Found: C, 49.98; H, 4.79; Cl, 20.99; S, 9.56. ¹H NMR (C_6D_6 , 25 °C): δ 6.91 (s, *m*-H); 6.12 (s, Cp); 2.44 (s, *o*-Me); 2.09 (s, *p*-Me). ¹³C NMR (C_6D_6 , 25 °C): δ 140.1, 138.9, 129.7, 129.1 (aromatics); 119.6 (Cp); 22.3, 20.9 (methyls).

[CpTi(SC₆H₂Prⁱ-2,4,6)Cl₂] (3). To a solution of 2,4,6-triisopropylbenzenethiol (2.00 g, 8.5 mmol) in benzene (60 mL) was slowly added a solution of *n*-BuLi (3.4 mL, 2.5 M in hexanes) via syringe. The resulting suspension was stirred for 2 h and then was added to a solution of $[\text{CpTiCl}_3]$ (1.85 g, 8.5 mmol) in benzene (60 mL). The mixture was stirred overnight under nitrogen and then was filtered through a frit using a plug of Celite, and the clear, red filtrate was dried in vacuo. The crude product was washed several times with pentane, yielding a bright orange solid (2.86 g, 81%). A small amount of product was redissolved in benzene and layered with pentane to obtain X-ray-quality crystals. Anal. Calcd for $\text{C}_{20}\text{H}_{28}\text{Cl}_2\text{STi}$: C, 57.29; H, 6.73; Cl, 16.91; S, 7.65. Found: C, 57.64; H, 6.77; Cl, 16.53; S, 7.94. ¹H NMR (C_6D_6 , 25 °C): δ 7.33 (s, *m*-H); 6.15 (s, Cp); 3.56 (septet, *o*-CHMe₂), ³J(¹H–¹H) = 6.8 Hz; 2.83 (septet, *p*-CHMe₂), ³J(¹H–¹H) = 6.8 Hz; 1.38 (d, *o*-CHMe₂), ³J(¹H–¹H) = 6.8 Hz; 1.22 (d, *p*-CHMe₂), ³J(¹H–¹H) = 6.8 Hz. ¹³C NMR (C_6D_6 , 25 °C): δ 151.8, 148.43, 138.5, 122.3 (aromatics); 119.7 (Cp); 34.6, 33.1 (CHMe₂); 24.1, 23.9 (methyls).

[CpTi(SC₆H₂Ph₃-2,4,6)Cl₂] (4). To a solution of 2,4,6-triphenylbenzenethiol (1.70 g, 5.0 mmol) in benzene (50 mL) was slowly added a solution of *n*-BuLi (2.0 mL, 2.5 M in hexanes) via syringe. The resulting suspension was stirred for 2 h and then was added to a solution of $[\text{CpTiCl}_3]$ (1.00 g, 4.6 mmol) in benzene (100 mL). The mixture was stirred overnight

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under nitrogen and then was filtered through a frit using a plug of Celite, and the filtrate was dried in vacuo, yielding a red oil. The crude product was redissolved in a minimum of benzene and layered with hexane, yielding dark red crystals (0.70 g, 30%). $^1\text{H NMR}$ (C_6D_6 , 25 °C): δ 7.75–7.10 (aromatics); 5.78 (s, C_5H_5). $^{13}\text{C NMR}$ (C_6D_6 , 25 °C): δ 130.4–127.4 (aromatics); 119.4 (Cp).

[CpTiCl(μ -SC₆H₂Me₃-2,4,6)]₂ (5). A solution of **2** (0.50 g, 1.5 mmol) in benzene (40 mL) was added to a benzene solution containing sodium (0.04 g, 1.7 mmol) as a mercury amalgam. The mixture was stirred overnight. The dark red mixture was decanted from the amalgam and filtered through a plug of Celite over fritted glass to remove Na and Hg salts. The solution was dried under vacuum, and the dark solid was redissolved in benzene and layered with pentane to yield large quantities of burgundy crystals (0.30 g, 63%). Anal. Calcd for $\text{C}_{28}\text{H}_{32}\text{Cl}_2\text{S}_2\text{Ti}_2 \cdot 0.5\text{C}_6\text{H}_6$: C, 58.32; H, 5.53; Cl, 11.11; S, 10.04. Found: C, 57.92; H, 5.54; Cl, 11.01; S, 9.74. $^1\text{H NMR}$ (C_6D_6 , 25 °C): δ 6.75 (s, *m*-H); 6.20 (s, Cp); 2.29 (s, *o*-Me); 2.07 (s, *p*-Me). $^{13}\text{C NMR}$ (C_6D_6 , 25 °C): δ 142.2, 130.0, 128.4, 127.1 (aromatics); 113.4 (Cp); 22.4, 20.8, (methyls).

[CpTiCl(μ -SC₆H₂Pr¹₃-2,4,6)]₂ (6). To a solution of **3** (1.75 g, 4.2 mmol) in toluene (50 mL) was added trimethylaluminum (4.2 mL, 2.0 M in toluene) via syringe. The mixture was stirred for 3 h. The dark red mixture was filtered through fritted glass to remove Al salts. The solution was dried under vacuum and rinsed several times with pentane, yielding a burgundy solid (0.92 g, 57%). A small amount of the product was dissolved in pentane and recrystallized by slow evaporation, affording X-ray-quality crystals. $^1\text{H NMR}$ (C_6D_6 , 25 °C): δ 7.21 (s, *m*-H); 6.27 (s, Cp); 3.62 (septet, *o*-CHMe₂), $^3J(^1\text{H}-^1\text{H}) = 6.7$ Hz; 2.76 (septet, *p*-CHMe₂), $^3J(^1\text{H}-^1\text{H}) = 6.8$ Hz; 1.32 (d, *p*-CHMe₂), $^3J(^1\text{H}-^1\text{H}) = 6.6$ Hz; 1.21 (d, *o*-CHMeMe'), $^3J(^1\text{H}-^1\text{H}) = 6.7$ Hz; 1.20 (d, *o*-CHMeMe'), $^3J(^1\text{H}-^1\text{H}) = 6.8$ Hz. $^{13}\text{C NMR}$ (C_6D_6 , 25 °C): δ 153.2, 150.9, 128.5, 123.4 (aromatics); 113.4 (Cp); 34.5, 31.3 (CHMe₂); 25.7, 24.2, 24.0, 24.0 (methyls).

X-ray Data Collection and Reduction. Crystal data and data collection parameters are contained in Table 1. A suitable crystal was mounted on a glass fiber in a random orientation

under a cold stream of dry nitrogen. Preliminary examination and final data collection were performed with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) on a Nonius KappaCCD instrument. Lorentz and polarization corrections were applied to the data.²⁶ An empirical absorption correction using SCALEPACK was applied.²⁷ Intensities of equivalent reflections were averaged. The structure was solved using the structure solution program PATTY in DIRDIF92.²⁸ The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least squares, where the function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$ and the weight w is defined as $w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 1.4064P]$ ($P = (F_o^2 + 2F_c^2)/3$). Scattering factors were taken from ref 29. Refinement was performed on an AlphaServer 2100 using SHELX-97.³⁰ Crystallographic drawings were done using the programs ORTEP.³¹

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Supporting Information Available: Tables giving X-ray crystallographic data for **1–6** and ORTEP drawings for **1**, **3**, and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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