Monocyclopentadienyl−Titanium Aryloxide Sulfide Complexes

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In this report we extend titanium−sulfide chemistry, describing the syntheses, structures, and chemistry of monocyclopentadienyl−titanium aryloxide sulfide complexes. Reduction of $Cp'Ti(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)Cl_2$ ($Cp' = Cp$ (**1**), Cp^* (**3**)) with *n*-BuLi affords the Ti(III) compounds $[CpTi(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(\mu\text{-}Cl)]_2$ (**2**) and $[Cp^*Ti(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(\mu\text{-}Cl)]_2$ (**4**). Compound **2** is oxidized by moisture, giving $[CpTi(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)Cl]_2(\mu\text{-}O)$ (**5**). Oxidation of **4** by sulfur led to a mixture of uncharacterized products; however, reaction of **3** with 2 equiv of *n*-BuLi followed by subsequent addition of sulfur afforded a new diamagnetic species, $Cp^*Ti(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)S_5$ (**6**). Oxidation of **2** by S_8 yields $[CpTi(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)]_2(\mu\text{-}S)(\mu\text{-}S_2)$ (**7**). Reaction of the known sulfide-bridged dimer $[CpTi(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(\mu\text{-}S)]_2$ (**8**) with sulfur provides an alternative route to **7**. The conversion of **7** to **8** is reversible as reaction of **7** with PPh_3 yields $SPPh_3$ and **8** quantitatively. Reaction of **1** with Li_2S proceeds cleanly to give **8**. Reduction of $CpTi(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(SPh)Cl$ (**9**) with *n*-BuLi affords the diamagnetic product $[CpTi(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(\mu\text{-}SPh)]_2$ (**10**), which reacts with phenylpyridine to generate the paramagnetic species $CpTi(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(SPh)(NC_5H_4Ph)$ (**11**). Attempts to isolate a monosulfide-bridged complex are described. Isolation of a monosulfide-bridged species, $[CpTi(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_2]_2(\mu\text{-}S)$ (**14**), is achieved via reaction of $[CpTi(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_2]Cl$ (**13**) with Li_2S. Structural data for **2**, **4**−**7**, **10**, and **14** are reported. Comparisons are made with the related titanocene−sulfide systems, and the implications are considered.

Introduction

Much of the study of chemistry of early transition metals with sulfur ligands has been motivated by the relevance to biological systems[1−3] and the utility of such complexes in the synthesis of organosulfur compounds and as precursors for metal sulfide materials in MOCVD processes.[3,4] In the case of titanium, while Ti−S complexes are not relevant to biology, the potential for synthetic and materials applications has drawn studies of a more fundamental nature. A variety of titanium sulfide derivatives are known, and this chemistry has been reviewed.[4] Mono- and dimetallic compounds such as Cp_2TiS_5,[5] $1,5\text{-}(Cp_2Ti)_2S_6$, and $1,4\text{-}(Cp_2Ti)_2S_4$[6] have been shown to be related via desulfurization chemistry. Larger cyclopentadienyl−titanium−sulfur aggregates, such as $[CpTiS]_4$[7] and $Cp_5Ti_5S_6$,[8] were reported some years ago while more recently we have described the Ti−S aggregates $(CpTi)_4(\mu_3\text{-}S)_3(\mu_2\text{-}S)(\mu_2\text{-}SEt)_2$ and $(CpTi)_6(\mu_3\text{-}S)_4(\mu_3\text{-}O)_4$[9] (see Chart 1). The formation of these higher order aggregates is perhaps expected as a result of the steric accessibility of the metal centers in comparison with the

Chart 1. Examples of Ti−S Aggregates
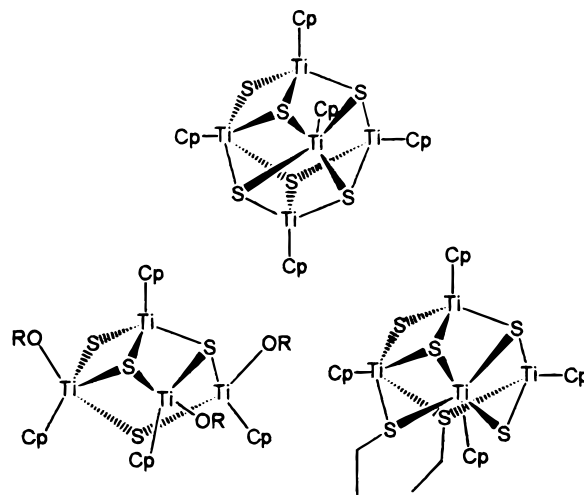
dicyclopentadienyl−titanium derivatives. We have recently shown that incorporation of a bulky ancillary ligand into monocyclopentadienyl−titanium systems significantly alters the chemistry[10−12] in comparison to mono- or dicyclopentadienyl−titanium compounds. In the present report, we examine the titanium−sulfide chemistry of such systems, describing the syntheses, structures, and chemistry of monocyclopentadienyl−titanium aryloxide sulfide complexes. Comparisons with the related titanocene systems offer some insight into both the steric and electronic factors that alter Ti−S chemistry. The implications of these results are considered.

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Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 employing either Schlenk line techniques or a Vacuum Atmospheres inert atmosphere glovebox. Solvents were reagent grade, distilled from the appropriate drying agents under N_2, and degassed by the freeze−thaw method at least three times prior to use. All organic reagents were purified by conventional methods. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker Avance 300 and 500 MHz instruments. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to SiMe$_4$. Low- and high-resolution EI mass spectra were obtained employing a Kratos Profile mass spectrometer outfitted with a N_2 glovebag enclosure for the inlet port. ESR data were recorded employing a Bruker EPS 300e spectrometer equipped with a nuclear magnetometer and an HP frequency counter. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, TN, E+R Microanalytical Laboratory, Corona, NY, or Schwarzkopf Laboratories, Woodside, NY. CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)-Cl$_2$ (**1**), [CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(*μ*-S)]$_2$ (**8**), CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(SPh)-Cl (**9**), CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(SPh)$_2$ (**12**), CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)$_2$Cl (**13**), and Cp*Ti(OC$_6$H$_3$-2,6-*i*-Pr$_2$)Cl$_2$ (**3**) were prepared via known methods.[10,11]

Synthesis of [CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(*μ*-Cl)]$_2$ (2) and [Cp*Ti-(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(*μ*-Cl)]$_2$ (4). These compounds were prepared in a similar fashion, and thus one preparation is detailed. To a suspension of **1** (100 mg, 0.26 mmol) in hexane (5 mL) was added *n*-BuLi (151 *μ*L of a 1.7 M solution, 0.26 mmol) dropwise. The reaction mixture was stirred for 30 min and filtered, and the solvent volume was reduced to 1 mL. Dark red crystals of **2** were obtained in 67% yield. **2**: EPR (C$_6$H$_6$): *g* = 1.9899. Calcd for C$_{34}$H$_{44}$O$_2$Ti$_2$Cl$_2$: (HRMS) 650.1677. Found: 650.1677. Calcd: C: 62.69; H, 6.81. Found: C: 62.48; H, 6.66. **4**: EPR (C$_6$H$_6$): *g* = 1.9889. Anal. Calcd for C$_{44}$H$_{64}$O$_2$Ti$_2$Cl$_2$: (HRMS) 790.3232. Found: 790.3212. Anal. Calcd: C, 66.75; H, 8.15. Found: C, 66.56; H, 8.01.

Synthesis of [CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)Cl]$_2$(*μ*-O) (5). To **2** (100 mg, 0.15 mmol) dissolved in benzene (5 mL) was added H$_2$O dropwise (2.70 *μ*L, 0.15 mmol). The reaction mixture was stirred for 12 h and then filtered, after which the solvent was reduced. Bright yellow crystals of **5** were obtained in 87% yield. ^{1}H NMR (C$_6$H$_6$, 25 °C): *δ* 1.34 (d, 24H, |J_{H-H}| = 7 Hz) 3.54 (sept, 4H, |J_{H-H}| = 7 Hz), 6.28 (s, 10H), 6.96−7.09 (m, 6H). ^{13}C{^{1}H} NMR (C$_6$H$_6$, 25 °C): *δ* 24.0, 26.7, 118.7, 123.6, 137.7, 161.3. Anal. Calcd for C$_{34}$H$_{44}$Ti$_2$OCl$_2$: (HRMS) 666.1616. Found: 666.1610. Anal. Calcd: C, 64.27; H, 6.98. Found: C, 64.16; H, 6.89.

Synthesis of Cp*Ti(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(S$_5$) (6). To **4** (100 mg, 0.22 mmol) dissolved in hexane (5 mL) was added *n*-BuLi dropwise (352 *μ*L of a 1.7 M solution, 0.52 mmol). The reaction mixture was stirred for a few minutes and then filtered, and S$_8$ (35.2 mg, 1.2 mmol) was added. The mixture was stirred for 12 h, after which the solvent volume was reduced to 1 mL. Orange crystals of **6** were obtained in 78% yield. ^{1}H NMR (C$_6$D$_6$, 25 °C): *δ* 1.23 (br, 12H), 1.81 (s, 15H), 3.26 (sept, 2H, |J_{H-H}| = 7 Hz), 6.96−7.19 (m, 6H). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C): *δ* 13.5, 24.6, 25.8, 26.5, 121.6, 124.0, 125.7, 138.6, 160.8. Anal. Calcd for C$_{22}$H$_{32}$TiOS$_5$: (HRMS) 520.0536. Found: 520.0521. Anal. Calcd: C, 50.75; H, 6.19. Found: C, 50.57; H, 6.05.

Synthesis of [CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)]$_2$(*μ*-S)(*μ*-S$_2$) (7). (i) To **8** (100 mg, 0.15 mmol) dissolved in benzene was added S$_8$ (4.6 mg, 0.02 mmol). The reaction mixture was stirred for 12 h at 60 °C, after which the solvent was reduced. Orange crystals of **7** were obtained in 78% yield. (ii) To [CpTi(OR*)(SPh)]$_2$ (25 mg, 0.035 mmol) dissolved in benzene was added S$_8$ (160 mg, 0.5 mmol). The mixture was heated at 60 °C for 12 h and filtered, the solvent was removed, and the products were monitored by NMR spectroscopy. ^{1}H NMR (C$_6$D$_6$, 25 °C): *δ* 1.17 (d,12H, |J_{H-H}| = 7 Hz), 1.25 (d, 12H, |J_{H-H}| = 7 Hz), 3.13 (sept, 4H, |J_{H-H}| = 7 Hz), 6.17 (s, 10H), 6.96 (t, 2H, |J_{H-H}| = 7 Hz), 6.99 (d, 4H, |J_{H-H}| = 7 Hz). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C): *δ* 23.8, 24.1, 27.4, 114.4, 122.2, 123.3, 137.9, 162.2. Anal. Calcd for C$_{34}$H$_{44}$-Ti$_2$O$_2$S$_3$: (HRMS) 676.1462. Found: 676.1470. Anal. Calcd: C, 60.35; H, 6.55. Found: C, 60.16; H, 6.41.

Alternative Syntheses of [CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(*μ*-S)]$_2$ (8). (i) To a solution of **1** (100 mg, 0.26 mmol) in THF (5 mL) was added Li$_2$S (11 mg, 0.26 mmol). The reaction mixture was stirred for 12 h, and the solvent was removed in vacuo. The residue was extracted into benzene, the reaction mixture filtered, and the solvent removed. Solid **8** was obtained in 83% yield. (ii) To **14** (100 mg, 0.10 mmol) in benzene was added (Me$_3$Si)$_2$S (22 mg, 0.15 mmol). The reaction mixture was heated for 12 h. ^{1}H NMR resonance revealed the quantitative formation of **8**. (iii) To **7** (100 mg, 0.15 mmol) in benzene was added PPh$_3$ (36.9 mg, 0.15 mmol). The reaction was allowed to stand for 1 h and then monitored by ^{1}H and ^{31}P NMR spectroscopy, revealing quantitative formation of **8**.

Synthesis of [CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(*μ*-SPh)]$_2$ (10). To **9** (120 mg, 0.26 mmol) dissolved in hexane was added *n*-BuLi dropwise (151 mL of a 1.7 M solution, 0.26 mmol). The reaction mixture was stirred for a few minutes and then filtered, after which the solvent was reduced. Dark red crystals were obtained in 47% yield. ^{1}H NMR (C$_6$D$_6$, 25 °C): *δ* 1.18 (d, 24H, |J_{H-H}| = 7 Hz), 3.76 (sept, 4H, |J_{H-H}| = 7 Hz), 5.81 (s, 10H), 6.96−7.19 (m, 16H), 7.78 (d, 4H, |J_{H-H}| = 7 Hz). Anal. Calcd for C$_{46}$H$_{54}$Ti$_2$O$_2$S$_2$: (HRMS) 798.2524. Found: 798.2520. Anal. Calcd: C, 69.16; H, 6.81. Found: C, 69.03; H, 6.61.

Generation of CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(SPh)(NC$_5$H$_4$Ph) (11). Compound **10** (25 mg, 0.037 mmol) was dissolved in benzene, and *p*-phenylpyridine (31 mg, 0.2 mmol) was added. An immediate color change from bright red to bright blue was observed. EPR (C$_6$H$_6$): *g* = 1.9758.

Synthesis of [CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)$_2$]$_2$(*μ*-S) (14). To **13** (100 mg, 0.20 mmol) dissolved in THF was added Li$_2$S (4.5 mg, 0.10 mmol). The reaction mixture was stirred for 12 h, after which the solvent was removed in vacuo. The mixture was dissolved in benzene, filtered, and stripped again. Orange solid was obtained in 80% yield. ^{1}H NMR (C$_6$D$_6$, 25 °C): *δ* 1.24 (d,12H,|J_{H-H}| = 7 Hz), 1.30 (d, 12H, |J_{H-H}| = 7 Hz), 3.82 (sept, 4H, |J_{H-H}| = 7 Hz), 6.47 (s, 5H), 6.96 (t, 2H, |J_{H-H}| = 7 Hz), 7.06 (d, 4H, |J_{H-H}| = 7 Hz). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C): *δ* 24.0, 24.6, 26.9, 116.6, 122.9, 123.6, 138.0, 163.3. Anal. Calcd for C$_{58}$H$_{68}$Ti$_2$O$_4$S: (HRMS) 956.3797. Found: 956.3789. Anal. Calcd: C, 72.79; H, 7.16. Found: C, 72.59; H, 7.04.

X-ray Data Collection and Reduction. X-ray quality crystals of **2**, **4−7**, **10**, and **14** were obtained directly from the preparations as described above. The crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Rigaku AFC6 diffractometer equipped with graphite-monochromatized Mo Kα radiation or on a Siemens SMART system CCD diffractometer. When the Rigaku diffractometer was used, the initial orientation matrices were obtained from 20 machine-centered reflections selected by an automated peak search routine. These data were used to determine the crystal systems. Automated Laue system check routines around each axis were consistent with the crystal system. Ultimately, 25 reflections (20° < 2θ < 25°) were used to obtain the final lattice parameters and the orientation matrices. Crystal data are summarized in Table 1. The observed extinctions were consistent with the space groups in each case. The data sets were collected in three shells (4.5°< 2θ <45−50.0°), and three standard reflections were recorded every 197 reflections. Fixed scan rates were employed. Up to 4 repetitive scans of each reflection at the respective scan rates were averaged to ensure meaningful statistics. The number of scans of each reflection was determined by the intensity. The intensities of the standards showed no statistically significant change over the duration of the data collections. The data were processed using the TEXSAN crystal solution package operating on a SGI Challenger mainframe with remote X-terminals. The reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinements.

Diffraction experiments performed on a Siemens SMART System CCD diffractometer involved collecting a hemisphere of data in 1329 frames with 10 s exposure times. A measure of decay was obtained by re-collecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and XPREP processing package. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package operating on a SGI computer.

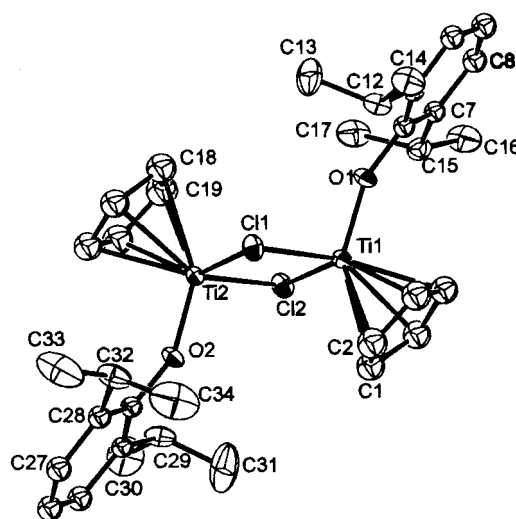**Table 1.** Crystallographic Parameters

	2	4	5	6	7·C₆H₆	10	14·THF
formula	C₃₄H₄₄Ti₂O₂Cl₂	C₄₄H₆₄Cl₂O₂Ti₂	C₃₄H₄₄Cl₂O₃Ti₂	C₃₂H₃₂OS₅Ti	C₄₀H₅₀O₂S₃Ti₂	C₄₆H₅₄O₂S₂Ti₂	C₆₂H₇₄O₅Ti₂S
fw	651.43	791.7	667.42	520.69	754.78	798.82	1027.12
a (Å)	12.513(3)	9.866(1)	9.582(5)	8.933(6)	9.8558(3)	19.32970(10)	15.101(8)
b (Å)	17.003(2)	10.106(1)	15.692(4)	18.07(1)	15.0095(4)	20.7884(3)	17.6141(5)
c (Å)	16.112(3)	12.227(2)	11.796(4)	16.253(4)	15.4839(4)	10.82650(10)	13.044(7)
α (deg)		81.995(2)			111.4410(10)		96.28(4)
β (deg)	90.94(2)	69.531(2)	103.77(3)	90.54(2)	101.2400(10)	92.18(1)	102.53(4)
γ (deg)		71.627(2)			94.5950(10)		114.62(3)
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
V (Å³)	3427.5(9)	1083.3(2)	1722(1)	2622(1)	2062.19(10)	4347.31(8)	2999(2)
D_{calcd} (g cm⁻¹)	1.26	1.21	1.32	1.22	1.22	1.22	1.14
Z	4	1	2	4	2	8	2
abs coeff, μ, cm⁻¹	6.49	5.25	6.49	7.36	5.70	4.98	3.45
R (%)	6.90	6.80	9.30	6.20	9.71	5.06	9.30
R_w (%)	5.40	6.50	7.20	4.50	19.8[a]	15.6[a]	7.80

[a] Weighted R based on all data, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma(|F_o| - |F_c|)^2]/\Sigma|F_o|^2]^{0.5}$.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[13−15] The Ti atom positions were determined using direct methods employing either the SHELXTL or Mithril direct methods routines. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $\omega(|F_o| - |F_c|)^2$ where the weight ω is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, the number of non-hydrogen atoms assigned anisotropic temperature factors was determined so as to maintain a reasonable data:variable ratio. The remaining atoms were assigned isotropic temperature factors. Empirical absorption corrections were applied to the data sets based either on ψ-scan data or on a DIFABS calculation and employing the software resident in the TEXSAN or SHELXTL packages. Hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. The hydrogen atom contributions were calculated, but not refined. The final values of R, R_w, and the goodness of fit in the final cycles of the refinements are given in Table 1. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Tables of crystallographic data have been deposited as Supporting Information.

Results and Discussion

We have previously reported both the C−H and the C−S bond activation chemistry of monocyclopentadienyl titanium aryloxide thiolate complexes.[10] In developing related titanium−sulfur chemistry, we began by employing a typical strategy of oxidation of a Ti(III) precursor. To that end, we treated CpTi-(OC₆H₃-2,6-*i*-Pr₂)Cl₂ (**1**) with *n*-BuLi in a hexane slurry. The reaction mixture quickly became dark brown-black in color. Following workup, the dark product **2** was isolated in 67% yield. This paramagnetic compound exhibits an EPR signal at $g = 1.9899$. Crystallographic data confirmed the formulation of **2** as [CpTi(OC₆H₃-2,6-*i*-Pr₂)(μ-Cl)]₂ (Figure 1). The two titanium centers are bridged by two chloride ligands. The cyclopentadienyl and aryloxide ligands bonded to the respective titanium atoms adopt a *transoid* disposition with respect to the Ti₂Cl₂ core. The Ti−Cl distances are slightly dissymmetric, averaging

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Figure 1. ORTEP drawing of [CpTi(OC₆H₃-2,6-*i*-Pr₂)(μ-Cl)]₂ (**2**); 30% thermal ellipsoids are shown. Distances (Å): Ti(1)−Cl(1) 2.406(4), Ti(1)−Cl(2) 2.397(4), Ti(1)−O(1) 1.808(8), Ti(2)−Cl(1) 2.395(4), Ti(2)−Cl(2) 2.405(4), Ti(2)−O(2) 1.808(8). Angles (deg): Cl(1)−Ti(1)−Cl(2) 96.7(1), Cl(1)− Ti(1)−O(1) 102.7(3), Cl(2)−Ti(1)−O(1) 103.4(3), Cl(1)−Ti(2)−Cl(2) 96.8(1), Cl(1)−Ti(2)−O(2) 103.4(3), Cl(1)−Ti(2)−O(2) 103.4(3), Cl(2)−Ti(2)−O(2) 102.6(3), Ti(1)−Cl(1)−Ti(2) 83.2(1), Ti(1)−Cl(2)−Ti(2) 83.2(1), Ti(1)−O(1)-C(6) 158.0(8), Ti(2)−O(2)-C(23) 155.8(8).

2.406(4) and 2.396(4) Å. These are significantly shorter that the average Ti−Cl distances of 2.537(3) and 2.550(4) Å found in [Cp₂Ti(μ-Cl)]₂ and [(CH₃C₅H₄)₂Ti(μ-Cl)]₂, respectively.[16] The shorter Ti−Cl bonds are consistent with the relative electron deficiency of the Ti center in **2**. The Ti−O distance of 1.808(8) Å is slightly increased and the Ti−O−C angle of 158.4(8)° is slightly decreased from those seen in related Ti(IV) species,[10] inferring a diminished donation of electron density from the aryloxide by the Ti(III) center in **2** relative to related Ti(IV) species. In a similar manner, reactions of Cp*Ti(OC₆H₃-2,6-*i*-Pr₂)Cl₂ (**3**) with *n*-BuLi afford the compound [Cp*Ti(OC₆H₃-2,6-*i*-Pr₂)(μ-Cl)]₂ (**4**). Compound **4**, like **2**, is paramagnetic and was formulated on the basis of crystallographic data (Figure 2). Structurally, **4** is similar to **2** although the Ti−Cl distances are slightly longer, averaging 2.427(3) Å, consistent with greater electron donation from the pentamethylcyclopentadienyl ligand, and thus weaker Ti−Cl interactions.
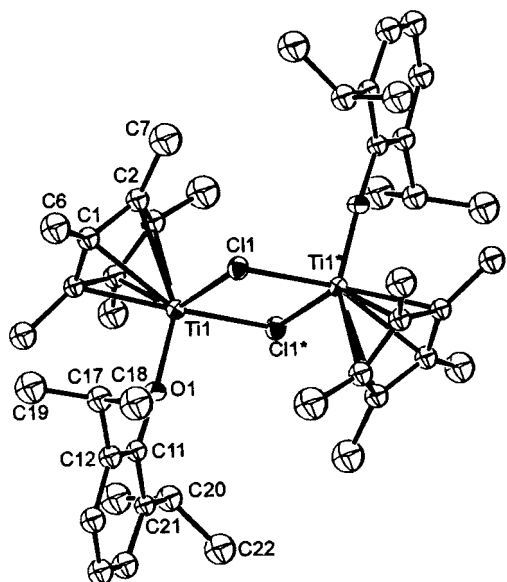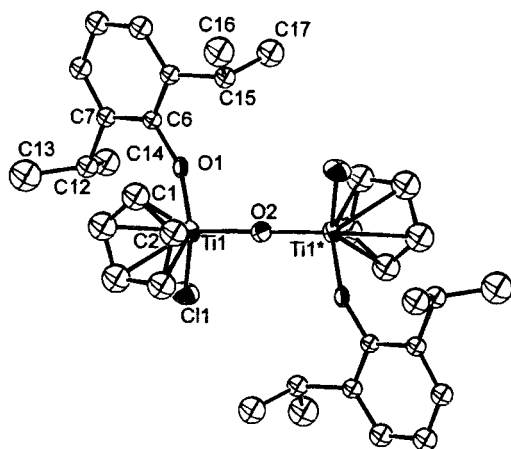
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Figure 2. ORTEP drawing of [Cp*Ti(OC$_6$H$_3$-2,6-i-Pr$_2$)(μ-Cl)]$_2$ (**4**); 30% thermal ellipsoids are shown. Distances (Å): Ti(1)−Cl(1) 2.423(3), Ti(1)−Cl(1) 2.430(3), Ti(1)−O(1) 1.825(6). Angles (deg): Cl(1)−Ti(1)− Cl(1) 92.5(1), Cl(1)−Ti(1)−O(1) 102.0(2), Cl(1)−Ti(1)−O(1) 101.6(2), Ti(1)−Cl(1)−Ti(1)′ 87.5(1).

Figure 3. ORTEP drawing of [CpTi(OC$_6$H$_3$-2,6-i-Pr$_2$)Cl]$_2$(μ-O) (**5**); 30% thermal ellipsoids are shown. Distances (Å): Ti(1)−Cl(1) 2.266(7), Ti(1)−O(1) 1.80(1), Ti(1)−O(2) 1.794(2). Angles (deg): Cl(1)−Ti(1)− O(1) 103.6(4), Cl(1)−Ti(1)−O(2) 103.0(2), Ti(1)−O(2)−Ti(1)′ 180.0°.

Compound **2** is readily oxidized. Reaction of **2** with water proceeds to rapidly form a diamagnetic yellow product **5**. NMR data together with crystallographic data confirmed the formulation of **5** as [CpTi(OC$_6$H$_3$-2,6-i-Pr$_2$)Cl]$_2$(μ-O) (Figure 3). This centrosymmetric bimetallic compound contains a single oxygen atom bridging two titanium centers. The angle at this oxygen atom is crystallographically restricted to 180° while the bridging Ti−O distance is 1.794(2) Å, typical for bridged titanium oxides.[17]

Oxidation of **4** with sulfur led to a mixture of uncharacterized products. However, reaction of **3** with 2 equiv of *n*-BuLi followed by subsequent addition of sulfur afforded a new diamagnetic species, **6** (Scheme 1). While the NMR data confirmed the presence of the pentamethylcyclopentadienyl and aryloxide ligands, it was only by crystallographic study that the identity of **6** could be established as Cp*Ti(OC$_6$H$_3$-2,6-i-Pr$_2$)S$_5$

(17) Bottomley, F.; Drummond, D. F.; Egharevba, G. O.; White, P. S. *Organometallics* **1986**, *5*, 1620.
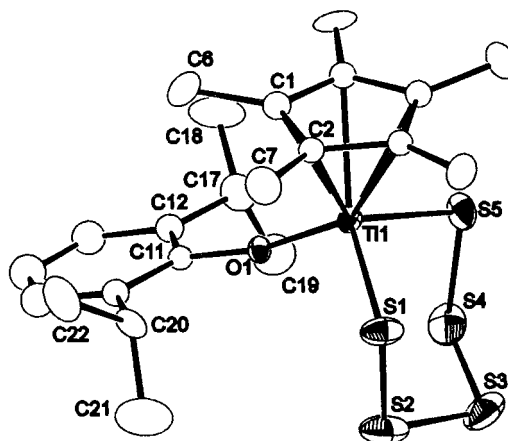
Figure 4. ORTEP drawing of Cp*Ti(OC$_6$H$_4$-i-Pr$_2$)(S$_5$) (**6**); 30% thermal ellipsoids are shown. Distances (Å): Ti(1)−S(1) 2.360(4), Ti(1)−S(5) 2.353(4), Ti(1)−O(1) 1.795(6), S(1)−S(2) 2.057(5), S(2)− S(3) 2.039(6), S(3)−S(4) 2.039(6), S(4)−S(5) 2.057(5). Angles (deg): S(1)−Ti(1)−S(5) 104.8(2), S(1)−Ti(1)−O(1) 107.2(2), S(5)−Ti(1)− O(1) 107.4(2), Ti(1)−S(1)−S(2) 101.6(2), S(1)−S(2)−S(3) 105.9(2), S(2)−S(3)−S(4) 103.8(2), S(3)−S(4)−S(5) 105.8(2), Ti(1)−S(5)−S(4) 98.4(2).

Scheme 1. Formation of **4** and **6**
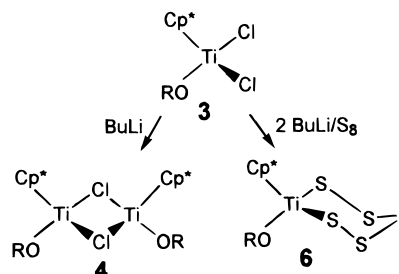
(Figure 4). The six-membered TiS$_5$ ring adopts a pseudochair conformation with the pentamethylcyclopentadienyl ligand occupying an axial position. The Ti−S and S−S distances average 2.357(4) and 2.057(5) Å, respectively. This structure of **6** is analogous to that reported for Cp$_2$TiS$_5$,[5] although the presence of the aryloxide ligand in **6** generates a relatively electron deficient metal center and thus shorter Ti−S distances. It is noteworthy that Cp$_2$TiS$_5$ is prepared via oxidation of the Ti(II) precursor Cp$_2$Ti(CO)$_2$ by S$_8$.[5] Presumably, **6** is formed in a similar manner although the Ti(II) intermediate is yet to be characterized.

Oxidation of **2** by sulfur occurs rapidly to give a mixture of two products. ^{1}H NMR data confirm the identity of one of the products as **1**, while the second product **7** exhibited new resonances attributable to cyclopentadienyl and aryloxide ligands. The ^{1}H NMR spectra are consistent with two inequivalent environments of the isopropyl groups on the aryloxide ligands, suggesting a dissymmetric species, unlike the known sulfide-bridged dimer [CpTi(OC$_6$H$_3$-2,6-i-Pr$_2$)(μ-S)]$_2$ (**8**).[10] Attempts to isolate compound **7** from this mixture were unsuccessful. The identity of **7** was uncovered via the development of an alternative synthesis. Reaction of **8** with sulfur proceeds upon heating with a slight lightening in color of the solution. NMR data confirm that this reaction results in the clean conversion to compound **7** (Scheme 2). Workup affords orange crystals of **7** in 78% yield. The nature of **7** was determined crystallographically (Figure 5), confirming the formulation as [CpTi(OC$_6$H$_3$-2,6-i-Pr$_2$)]$_2$(μ-S)(μ-S$_2$) (**7**). This dimeric species **7** is similar to **8**; however, the two titanium centers in **7** are bridged by both a sulfide and a disulfide unit. While the Ti−S
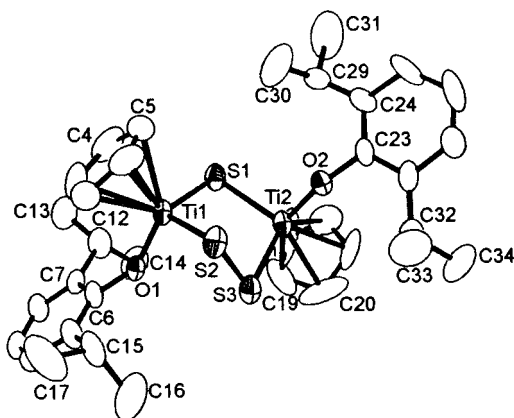
Figure 5. ORTEP drawing of [CpTi(OC$_6$H$_4$-*i*-Pr$_2$)]$_2$(μ-S)(μ-S$_2$) (**7**); 30% thermal ellipsoids are shown. Distances (Å): Ti(1)−O(1) 1.813(7), Ti(1)−S(2) 2.317(3), Ti(1)−S(1) 2.334(3), Ti(1)−Ti(2) 3.317(2), Ti(2)−O(2) 1.816(7), Ti(2)−S(1) 2.306(3), Ti(2)−S(3) 2.320(3), S(2)−S(3) 2.065(4). Angles (deg): O(1)−Ti(1)−S(2) 106.5(2), O(1)−Ti(1)−S(1) 106.3(2), S(2)−Ti(1)−S(1) 108.25(10), O(2)−Ti(2)−S(3) 107.0(2), S(1)−Ti(2)−S(3) 105.25(10), Ti(2)−S(1)−Ti(1) 91.27(10), S(3)−S(2)−Ti(1) 87.59(14), S(2)−S(3)−Ti(2) 95.81(15).

Scheme 2. Ti−S Chemistry of Monocyclopentadienyl−Titanium−Aryloxide Complexes
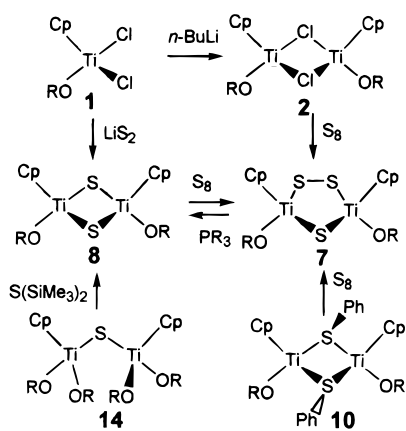
distances of average 2.319(5) Å are comparable to those observed in **8**, the Ti−Ti distance in **7** is significantly greater (3.317(2) Å) than that seen in **8** (3.141(3) Å).[10] The S−S in the disulfide fragment of 2.065(4) Å is typical.[18]

The conversion of **8** to **7** is reversible. Reaction of **7** with PPh$_3$ was monitored by NMR spectroscopy. ^{31}P NMR confirms the consumption of PPh$_3$ and formation of SPPh$_3$ while ^{1}H NMR indicated the quantitative conversion of **7** to **8**.

Stoichiometric reaction of **1** with Li$_2$S proceeds cleanly to give **8**. This compound was previously prepared via thermally induced C−S bond cleavage in the precursor CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(SCH$_2$Ph)$_2$.[12] In contemplating this conversion of **1** to **8**, one might speculate about the intermediacy of a monosulfide-bridged species of the form [CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)Cl]$_2$(μ-S), the sulfur analogue of **5** (Scheme 3). Despite efforts to control the stoichiometry, such an intermediate was not isolable. The reaction of **1** with Li$_2$S also failed to yield a monosulfide-bridged species. However, it was noted that, in a 2:1 ratio of **1**:Li$_2$S, the product mixture was composed of **1** and **8**. This suggests three possibilities: (i) the proposed intermediate is more reactive with Li$_2$S than **1**, (ii) the intermediate undergoes facile ligand redistribution to give **1** and **8**, or (iii) the reaction does not

(18) Steudel, R.; Kustos, M.; Prenzel, A. *Z. Naturforsch.* **199**7, *52b*, 79.
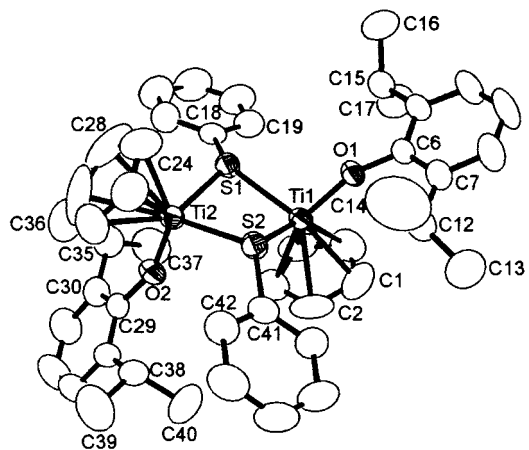
Figure 6. ORTEP drawing of [CpTi(OC$_6$H$_4$-*i*-Pr$_2$)(SPh)]$_2$ (**10**); 30% thermal ellipsoids are shown. Distances (Å): Ti(1)−O(1) 1.828(2), Ti(1)−S(1) 2.3865(9), Ti(1)−S(2) 2.4090(10), Ti(1)−Ti(2) 3.3942(8), Ti(2)−O(2) 1.822(2), Ti(2)−S(1) 2.3871(10), Ti(2)−S(2) 2.4245(9). Angles (deg): O(1)−Ti(1)−S(1) 103.94(7), O(1)−Ti(1)−S(2) 101.89(8), S(1)−Ti(1)−S(2) 85.69(3), O(2)−Ti(2)−S(1) 105.97(8), O(2)−Ti(2)−S(2) 106.69(8), S(1)−Ti(2)−S(2) 85.33(3).

Scheme 3. Possible Intermediate in the Formation of **8**
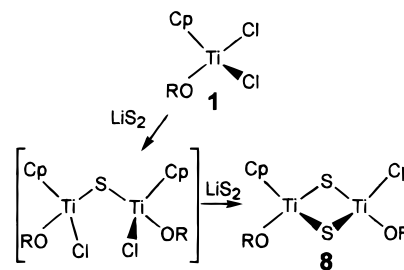
proceed through a sulfide-bridged bimetallic intermediate. To probe this question several synthetic alternatives were undertaken.

Reaction of CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(SPh)Cl^{10} (**9**) with *n*-BuLi affords the diamagnetic product **10**. An indication that **10** is a Ti(III) dimer is that reaction of **10** with phenylpyridine generates a paramagnetic species **11** which exhibits an EPR signal at $g =$ 1.9758. Crystallographic data for compound **10** (Figure 6) establishes that this compound is [CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(μ-SPh)]$_2$, which contains two Ti centers that are bridged by two phenyl thiolate fragments with Ti−S distances in the range 2.3865(9)−2.4090(10) Å. The phenyl rings are oriented in a cisoid fashion with respect to the Ti$_2$S$_2$ core. The Ti−Ti distance of 3.3942(8) Å is slightly longer than that seen in [Cp$_2$Ti(μ-OCH$_3$)]$_2$ (3.35 Å).[19] Compound **10** is diamagnetic at room temperature, in contrast to [Cp$_2$Ti(μ-OCH$_3$)]$_2$. Previous work inferred a role of the bridging ligands[20] in mediating antiferromagnetic coupling in related dimers. In the case of **10**, the vacant yet accessible d orbitals of sulfur presumably participate in mediating electronic communication between the metal centers. The formulation of **10** also infers that reaction with phenylpyridine splits the dimer, generating the paramagnetic monometallic species CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(SPh)-(NC$_5$H$_4$Ph) (**11**).

In an attempt to generate a monosulfide-bridged compound, reaction of **10** with sulfur was undertaken. This reaction leads to a mixture of two products, CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(SPh)$_2$^{10}

(19) Samuel, E.; Harrod, J. F.; Gourier, D.; Dromzee, Y.; Robert, F.; Jeannin, Y. *Inorg. Chem.* **1992**, *31*, 3252.
(20) Dick, D. G.; Stephan, D. W. *Can. J. Chem.* **1991**, *69*, 1146.
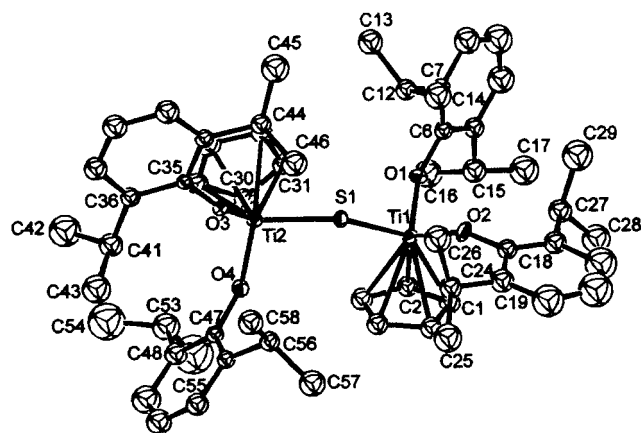
Figure 7. ORTEP drawing of [CpTi(OC$_6$H$_4$-i-Pr$_2$)$_2$]$_2$(μ-S) (**14**); 30% thermal ellipsoids are shown. Distances (Å): Ti(1)–S(1) 2.321(6), Ti(1)–O(1) 1.84(1), Ti(1)–O(2) 1.80(1), Ti(2)–S(1) 2.318(5), Ti(2)–O(3) 1.80(1), Ti(2)–O(4) 1.81(1). Angles (deg): S(1)–Ti(1)–O(1) 105.2(4), S(1)–Ti(1)–O(2) 101.0(4), O(1)–Ti(1)–O(2) 102.0(5), S(1)–Ti(2)–O(3) 100.4(4), S(1)–Ti(2)–O(4) 104.7(4), O(3)–Ti(2)–O(4) 103.2(5), Ti(1)–S(1)–Ti(2) 122.3(2).

(**12**) and **8**. No evidence for a monosulfide-bridged species was seen. Similar reaction of **9** with Li$_2$S led to a mixture of **12** and **8** and no evidence of a monosulfide-bridged intermediate. In retrospect, given the established propensity for ligand redistribution reactions of titanium thiolate complexes, it is perhaps not surprising that a monosulfide-bridged complex could not be isolated via this synthetic approach.

Isolation of a monosulfide-bridged species was achieved via inhibition of ligand redistribution reactions employing aryloxide ligands. Reaction of CpTi(OC$_6$H$_3$-2,6-i-Pr$_2$)$_2$Cl^{12} (**13**) with Li$_2$S proceeds cleanly and smoothly to give the new product **14** in 80% yield. NMR data reflect molecular dissymmetry of the product, and integration data are consistent with a 2:1 ratio of aryloxide:cyclopentadienyl groups. Crystallographic data confirmed the formulation of **14** as [CpTi(OC$_6$H$_3$-2,6-i-Pr$_2$)$_2$]$_2$(μ-S) (Figure 7). The Ti–S distances in this sulfur-bridged dimer average 2.319(6) Å, similar to those seen in **7** and **8**. The Ti–S–Ti angle of 122.3(2)° in **14** appears unrestrained, suggesting little extended π-bonding in constrast to the oxide-bridged complex **5**. Compound **14** is readily converted to **8**. Monitoring of the reaction of **14** with S(SiMe$_3$)$_2$ by NMR reveals the quantitative conversion to **8** and the silyl ether byproduct, Me$_3$SiOC$_6$H$_3$-2,6-i-Pr$_2$.

Summary

We have described synthetic routes to several Ti–S complexes which incorporate monocyclopentadienyl–titanium–aryloxide fragments. The presence of the ancillary aryloxide ligand generates a Ti center which is electron deficient relative to the titanocene fragment. This is reflected in the structural data as well as, in some instances, in the chemistry. The conversions of a monosulfide bimetallic to di- and trisulfide complexes described herein are prompting further study. Of particular interest is the reversible uptake of sulfur by **7** and **8**. Future endeavors will target systems with a view to examining their potential in desulfurization and sulfur atom transfer chemistry.