Synthesis, Structure, and Reactivity of Lewis Acidic Cyclopentadienyltitanium Dithiolate Complexes

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The reaction of $CpTiCl_3$ with 1,3-propanedithiol yields the mononuclear Ti(IV) species $CpTi(SCH_2CH_2CH_2S)Cl$ (**1**). This diamagnetic chelate complex crystallizes in the space group $P\bar{1}$ with a = 8.729 (4) Å, b = 10.114 (2) Å, c = 6.620 (4) Å, α = 90.70 (4)°, β = 109.35 (4)°, γ = 97.02 (4)°, V = 546 (1) Å³, and Z = 2. Subsequent reaction of **1** with 1 equiv of sodium benzenethiolate yields the species $CpTi(SCH_2CH_2CH_2S)(SC_6H_5)$ (**2**). This compounds crystallizes in the space group $P2_1$ with a = 7.506 (2) Å, b = 19.761 (5) Å, c = 10.487 (3) Å, β = 102.02 (3)°, V = 1521.5 (7) Å³, and Z = 4. The Lewis acidity of these Ti(IV) species is demonstrated by their reactivity. For example, reaction of **1** with 2 equiv of sodium benzenethiolate generates the anionic Ti species $[CpTi(SCH_2CH_2CH_2S)(SC_6H_5)_2]^-$ (**3**). In a similar vein, reaction of **1** with $Me_2PCH_2CH_2PMe_2$ yields several products which were identified spectroscopically. These include two isomers formulated as $CpTi(SCH_2CH_2CH_2S)Cl(Me_2PCH_2CH_2PMe_2)$ in which the bidentate phosphine is either dangling or chelated. In addition the compound $(CpTi(SCH_2CH_2CH_2S)Cl)_2(\mu-Me_2PCH_2CH_2PMe_2)$ (**4**) is isolated in low yield from this reaction. This species **4** crystallizes in the space group $P2_1/n$ with a = 9.058 (5) Å, b = 12.941 (8) Å, c = 13.340 (6) Å, β = 107.11 (4)°, V = 1494 (3) Å³, and Z = 4. Alternatively, a donor atom can be incorporated in the dithiolate backbone; thus, reaction of $CpTiCl_3$ with $S(CH_2CH_2SSiMe_3)_2$ affords the compound $CpTi(SCH_2CH_2SCH_2CH_2S)Cl$ (**5**). Compound **5** crystallizes in the space group $P2_1/n$ with a = 9.146 (7) Å, b = 10.894 (7) Å, c = 13.082 (4) Å, β = 106.12 (4)°, V = 1252 (1) Å³, and Z = 4. The reaction of **1** with 1 equiv of $NaSCH_2CH_2CH_2SNa$ affords the complex $[CpTi(SCH_2CH_2CH_2S)_2]Na$ (**6**). This compound crystallizes in two forms. **6(i)**, which is formulated as **6**·THF·benzene, crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 14.760 (2) Å, b = 17.574 (7) Å, c = 9.546 (2) Å, Z = 4, and V = 2476 (2) Å³. **6(ii)**, formulated as **6**·2THF, crystallizes in the orthorhombic space group $Pna2_1$ with a = 32.908 (11) Å, b = 10.009 (4) Å, c = 14.877 (3) Å, Z = 4, and V = 4900 (7) Å³. Compound **6** adopts two polymeric forms in the solid state. The geometry at Ti is essentially constant with variations occurring in the coordination sphere of the bridging sodium atoms. The reaction of **1** with base and 1 equiv of H_2O affords the oxo-bridged bimetallic species $[CpTi(SCH_2CH_2CH_2S)]_2O$ (**7**). This species also crystallizes in two forms crystallizing in either the space group $C2$ with a = 32.373 (8) Å, b = 7.941 (3) Å, c = 18.015 (5) Å, β = 120.24 (2)°, Z = 8, and V = 4001 (4) Å³ or in the space group $P2_1/c$ with a = 14.528 (4) Å, b = 7.840 (4) Å, c = 18.238 (4) Å, β = 104.71 (2)°, Z = 4, and V = 2009 (1) Å³. The Lewis acidity of the Ti centers is satisfied by Ti–O π-bonding, which is reflected in the Ti–O–Ti' bond angles which range from 158 to 170°. Fenske–Hall MO calculations support the notion that the Lewis acidity of the Ti centers in **1** is attributable to three vacant low-lying orbitals of a_1 and e symmetry. The Lewis acidity is dominated by the 1e orbitals which are largely Ti d_{xy} and $d_{x^2-y^2}$ in character. This affords either a π-interaction or formal Lewis base donation in the plane parallel to the cyclopentadienyl ring. This proposition is consistent with the molecular structures **1**, **2**, **4**, **6**, and **7**. Further interaction with the a_1 orbital, which is largely Ti d_{z^2} in character, is sterically blocked, but interaction with this vacant orbital can be induced by a constrained ligand geometry. Compound **5** is a rare example of a $CpML_4$ complex which adopts a pseudo-trigonal bipyramidal geometry in which a donor atom occupies the "axial" site trans to the cyclopentadienyl ring thus forcing an interaction with the a_1 orbital.

Introduction

The chemistry of early metal thiolates has drawn attention for several reasons. While several groups continue to explore the pertinence of such complexes to bioinorganic systems,[1] others including ourselves have had interest in early metal thiolate derivatives motivated by their ability to act as metalloligands and thus as synthons for heterobimetallic complexes.[2-11] In these efforts we have developed systems based on metallocene derivatives

incorporating simple thiolates[3-5] or thiolato ligands with pendant donor groups.[6-8] In addition we have recently described bimetallic, macrocyclic systems in which dithiolate moieties link metallocene fragments.[9-11] The redox properties and the nature of bonding as well as the conformational aspects of simple thiolate derivatives of early metal metallocenes have also been studied by several groups.[12,13] In contrast to these systems, the related monocyclopentadienyl analogues have been studied to a much less extent. The tantalum compounds $Cp*Ta(SCH=CHS)_2$[14] and $CpTa(SPh)_4$[15] have been recently studied by the research groups of

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Nakamura and Curtis, while Davidson et al.[16] have described the bimetallic systems [CpM(SC$_6$F$_5$)$_4$Tl (M = Mo, W). In the case of titanium, early reports of compounds formulated as CpTi-(SMe)$_3$, CpTi(SMe)$_2$Cl, and CpTi(SC$_{10}$H$_7$)Cl$_2$ were included in a 1961 patent,[17] but such species have drawn little attention since.[18-20] This has been attributed to both the malodorous nature and sensitivity of such species to hydrolysis.[21] In this report, we described the high–yield syntheses of several CpTi thiolate derivatives. X-ray structural characterizations are also presented. The Lewis acidity of these species is examined via structural, spectroscopic, and theoretical studies. These results are described, and their implications are considered.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O$_2$-free N$_2$ employing 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. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AC-300 spectrometer operating at 300 and 75 MHz, respectively. Trace amounts of protonated solvents were used as references, and the chemical shifts are reported relative to SiMe$_4$. ^{31}P-{^{1}H} NMR spectra were recorded on a Bruker AC-200 spectrometer operating at 81 MHz and employing 85% H$_3$PO$_4$ as the external reference. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, TN, and Schwarzkopf Laboratories, Woodside, NY. 2-Mercaptoethyl sulfide, 1,3-propanedithiol, and benzenethiol were purchased from the Aldrich Chemical Co. Bis(dimethylphosphino)ethane (dmpe) was purchased from the Pressure Chemical Co. Me$_3$SiSCH$_2$CH$_2$SCH$_2$-CH$_2$SSiMe$_3$ was prepared by methods analogous to those used to prepare Me$_3$SiSCH$_2$CH$_2$SSiMe$_3$.[11]

Synthesis of CpTi(SCH$_2$CH$_2$CH$_2$S)Cl (1). CpTiCl$_3$ (1.00 g, 4.60 mmol) and imidazole (0.685 g, 10.06 mmol) were combined in benzene (15 mL), and a dark brown solid appeared immediately. Propanedithiol (0.493 g, 4.60 mmol) was added dropwise to the stirred suspension. After 12 h a white precipitate was removed and a bright orange solution remained. Upon slow evaporation of the solvent bright orange crystals of **1** were obtained, yield 90%. ^{1}H NMR (δ, 298 K, C$_6$D$_6$): Cp, 6.05 (s, 5H); CH$_2$, 3.88 (m, 1H), 3.84 (m, 1H), 3.72 (m, 1H), 3.68 (m, 1H), 2.56 (m, 1H), 2.50 (m, 1H). ^{13}C{^{1}H} NMR (δ, 298 K, C$_6$D$_6$): Cp, 115.0; CH$_2$, 40.7, 32.6. Anal. Calcd for C$_8$H$_{11}$ClS$_2$Ti: C, 37.73; H, 4.35. Found: C, 37.53; H, 4.40.

Synthesis of CpTi(SCH$_2$CH$_2$CH$_2$S)SPh (2). A flask was charged with **1** (0.050 g, 0.20 mmol), NaSPh (0.026 g, 0.20 mmol), and THF (3 mL). The solution was stirred for 12 h over which time the solution became red. The solvent was removed, and the residue was taken up into benzene (3 mL). A white precipitate was filtered out from the solution. Orange crystals of **2** were obtained from a liquid/vapor diffusion of the benzene solution and hexane after 48 h, yield 95%. ^{1}H NMR (δ, 298 K, C$_6$D$_6$): Ph, 7.34 (d, 2H), 6.99 (t, 2H), 6.86 (t, 1H); Cp, 5.99 (s, 5H); CH$_2$, 3.94 (m, 1H), 3.91 (m, 1H), 3.84 (m, 1H), 3.79 (m, 1H), 2.62 (m, 1H), 2.59 (m, 1H). ^{13}C{^{1}H} NMR (δ 298 K, C$_6$D$_6$): Ph, 132.9, 128.9, 125.7; Cp, 114.4; CH$_2$, 41.5, 34.0. Anal. Calcd for C$_{14}$H$_{16}$S$_3$Ti: C, 51.21; H, 4.91. Found: C, 51.00; H, 5.01.

Synthesis of [CpTi(SPh)$_2$(SCH$_2$CH$_2$CH$_2$S)]Na (3). **1** (0.050 g, 0.20 mmol) and NaSPh (0.052 g, 0.40 mmol) were placed in a flask with THF (3 mL). The solution immediately became black in color. The solution was filtered, and the solvent was removed in vacuo. The black-red residue was taken up into THF-d_8. Yield: >80% (by NMR). ^{1}H NMR (δ, 298 K, C$_4$D$_8$O): Ph, 7.38 (br, 4H), 7.04 (br, 4H), 6.91 (br, 2H); Cp, 6.17 (s, 5H); CH$_2$, 3.48 (br m, 2H), 3.08 (br m, 2H), 2.82 (br m, 1H), 1.91 (br m, 1H). ^{13}C{^{1}H} NMR (δ, 298 K, C$_4$D$_8$O): Ph, 132.4, 128.3, 123.7; Cp, 114.7; CH$_2$, 36.6, 28.4.

Synthesis of [CpTi(SCH$_2$CH$_2$CH$_2$S)Cl]$_2$(μ-Me$_2$PCH$_2$CH$_2$PMe$_2$) (4). Bis(dimethylphosphino)ethane (dmpe) (0.030 g, 0.20 mmol) was added dropwise to a stirred solution of **1** (0.050 g, 0.20 mmol) in THF (3 mL).

The solution immediately turned from orange to dark brown. Hexane (0.5 mL) was layered on the solution, and it was allowed to stand at 238 K for 48 h at which time orange crystals of **4** were deposited, yield 5%. Alternatively, dmpe (0.025 g, 0.10 mmol) was added dropwise to a stirred THF solution of **1** (0.007 g, 0.05 mmol) and allowed to stir for 10 min. Yield by NMR: **4**, 60%; **4b**, 30%; **4c**, 10%. ^{1}H NMR (δ, 180 K, C$_4$D$_8$O) (**4, 4b, 4c**): Cp, 6.65 (**4b**), 6.55 (**4**), 6.34 (**4c**); CH$_2$, 3.97 (br m), 3.86 (br m), 3.34 (br m), 3.26 (br m), 2.62 (br m), 2.04 (br m); CH$_3$, 1.48 (br s). ^{31}P{^{1}H} NMR (δ, 180 K, THF): **4**, 2.69 (br, s); **4b**, 27.65 (d), 25.35 (d), $|J_{P-P}|$ = 44.0 Hz; **4c**, 3.10 (d), –47.42 (d), $|J_{P-P}|$ = 19.5 Hz. Anal. Calcd for C$_{22}$H$_{38}$Cl$_2$P$_2$S$_4$Ti$_2$: C, 40.07; H, 5.81. Found: C, 39.88; H, 5.90.

Synthesis of CpTi(SCH$_2$CH$_2$SCH$_2$CH$_2$S)Cl (5). CpTiCl$_3$ (0.100 g, 0.45 mmol) was dissolved in 5 mL of THF. This solution was added to a stirred solution of Me$_3$SiSCH$_2$CH$_2$SCH$_2$CH$_2$SSiMe$_3$ (0.250 g, 0.83 mmol). The mixture was stirred overnight and then refluxed for a further 2 h. The solvent was then removed in vacuo, and the resulting orange solid was washed three times with 2-mL portions of hexane. Upon recrystallization in THF at 278 K orange crystals of **5** were obtained, yield 46%. ^{1}H NMR (δ, 298 K, CDCl$_3$): Cp, 6.69 (s, 5H); CH$_2$, 3.87 (m, 4H), 3.50 (m, 2H), 3.42 (m, 2H). ^{13}C{^{1}H} NMR (δ, 298 K, CDCl$_3$): Cp, 118.46; CH$_2$, 40.2, 38.2. Anal. Calcd for C$_9$H$_{13}$ClS$_3$Ti: C, 48.32; H, 3.52. Found: C, 48.50; H, 3.49.

Synthesis of [CpTi(SCH$_2$CH$_2$CH$_2$S)$_2$Na(THF)$_x$]$_n$ (x = 1, 6(i); x = 2, 6(ii)). Compound **1** (0.050 g, 0.20 mmol) and NaSCH$_2$CH$_2$CH$_2$SNa (0.030 g, 0.20 mmol) were placed in THF (5 mL) and stirred for 0.5 h. The solution changed color from bright orange to dark red with the precipitation of NaCl. Following filtration and solvent removal, the residue was extracted into THF and benzene was added slowly by vapor diffusion. This afforded dark red crystals of **6(i)**·benzene upon standing for 4 days. Yield: 45%. If crystallization was induced by diffusion of hexane into the THF solution, crystals of **6(ii)** formed after 2 days. Yield: 50%. ^{1}H NMR (δ, 298 K, C$_4$D$_8$O): Cp, 6.13 (s, 5H); CH$_2$, 3.48 (m, 4H), 3.02 (m, 4H), 2.54 (m, 2H), 1.79 (m, 2H). ^{13}C{^{1}H} NMR (δ, 298 K, C$_4$D$_8$O): Cp, 113.3; CH$_2$, 36.7, 28.4. Anal. Calcd for C$_{11}$H$_{17}$NaS$_4$Ti (powdered sample, solvent removed in vacuo): C, 37.92; H, 4.92. Found: C, 38.01; H, 4.95.

Synthesis of [CpTi(SCH$_2$CH$_2$CH$_2$S)]$_2$O (7). Method i. Imidazole (0.009 g, 0.132 mmol) was added to a stirred solution of **1** (0.015 g, 0.059 mmol) in THF (2 mL). After 10 min, H$_2$O (0.54 μL, 0.030 mmol) was added to the mixture and the color turned immediately from brown to orange. A white precipitate was filtered off. Removal of the solvent afforded compound **7**, yield >90% (by NMR).

Method ii. Propanedithiol (222 mg, 2.06 mmol) and imidazole (300 mg, 4.42 mmol) were dissolved in 5 mL of wet THF. This solution was added dropwise to a stirred solution of CpTiCl$_3$ (300 mg, 1.38 mmol) in 2 mL of THF. The solution immediately became bright orange. The solution was stirred for 10 min, and a white precipitate (imidazole·HCl) was filtered off. Upon standing for 2–3 weeks, bright orange crystals of **7** were deposited (crystal form **7(i)**). Yield: 10%.

Method iii. Alternatively the reaction was performed as in (ii), but following filtration the solvent was removed and replace with 2 mL of wet benzene. This bright orange solution also gave bright orange crystals of **7**, upon standing for 2–3 weeks (crystal form **7(ii)**). Yield: 10%. ^{1}H NMR (δ, 298 K, C$_6$D$_6$): Cp, 6.13 (s, 10H); CH$_2$, 3.78 (m, 2H), 3.74 (m, 2H), 3.41 (d, 2H), 3.37 (d, 2H), 2.53 (m, 2H), 2.48 (m, 2H). ^{13}C{^{1}H} NMR (δ, 298 K, C$_6$D$_6$): Cp, 114.0; CH$_2$, 37.7, 33.0. Anal. Calcd for C$_{16}$H$_{22}$OS$_4$Ti$_2$: C, 42.29; H, 4.88. Found: C, 42.00; H, 5.00.

Molecular Orbital Calculations. Fenske–Hall molecular orbital (FHMO) calculations were performed on compounds derived from the crystallographic data for **1, 4,** and **5**. In the case of **4** the substituents on phosphorus were modeled by hydrogen atoms employing a P–H distance of 1.45 Å yielding the model compound **4′**. Calculations were also performed on the model compounds CpTiCl$_3$ and CpTi(SH)$_3$. In these cases an idealized pseudo-3-fold symmetry was employed, using C–Ti, Ti–S, Ti–Cl, and S–H distances of 2.30, 2.25, 2.25, and 1.13 Å, respectively. A detailed description of the Fenske–Hall nonemperical MO method can be found elsewhere.[22] Calculations were performed on a VAX 3520 workstation operating under the VMS operating system.

X-ray Data Collection and Reduction. X-ray-quality crystals of **1, 2, 4, 5, 6** (two crystal forms), and **7** (two crystal forms) were obtained 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

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Table I. Crystallographic Parameters

	1	2	4	5	6(i)	6(ii)	7(i)	7(ii)
formula	$C_8H_{11}ClS_2Ti$	$C_{28}H_{32}S_3Ti$	$C_{11}H_{19}ClPS_2Ti$	$C_9H_{13}ClS_3Ti$	$C_{21}H_{31}NaOS_4Ti$	$C_{38}H_{66}Na_2O_4S_8Ti_2$	$C_{13}H_{22}Ti_2S_4O$	$C_{13}H_{22}Ti_2S_4O$
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_12_12_1$ (No. 19)	$Pna2_1$ (No. 33)	$C2$ (No. 5)	$P2_1/c$ (No. 14)
a (Å)	8.729 (4)	7.506 (2)	9.058 (5)	9.146 (7)	14.760 (2)	32.908 (11)	32.373 (8)	14.528 (4)
b (Å)	10.114 (2)	19.761 (5)	12.941 (8)	10.894 (7)	17.574 (7)	10.009 (4)	7.941 (3)	7.840 (4)
c (Å)	6.620 (4)	10.487 (3)	13.340 (6)	13.082 (4)	9.546 (2)	14.877 (3)	18.015 (5)	18.238 (4)
α (deg)	90.70 (4)							
β (deg)	109.35 (4)	102.02 (2)	107.11 (4)	106.12 (4)			120.24 (2)	104.71 (2)
γ (deg)	97.02 (4)							
V (Å³)	546 (1)	1521.5 (7)	1494 (3)	1252 (1)	2476 (2)	4900 (7)	4001 (4)	2009 (1)
Z	2	4	4	4	4	4	8	4
abs coeff, μ (cm^{-1})	13.364	9.321	10.955	13.338	6.922	7.012	11.922	11.870
temp (°C)	24	24	24	24	24	24	24	24
R (%)^a	6.91	5.59	8.69	4.02	8.79	7.90	7.81	6.51
R_w (%)^a	7.70	5.49	8.82	4.21	8.13	7.59	8.31	6.71

^{a} $R = \sum\|F_o| - |F_c\|/\sum|F_o|$. $R_w = |\sum w(|F_o| - |F_c|)^2/\sum w/|F_o|^2|^{1/2}$.

on a Rigaku AFC6-S four-circle diffractometer with graphite-monochromatized Mo Kα radiation. The initial orientation matrices were obtained from 20 reflections located by an autosearch routine. These data were used to determine the crystal system. An automated check of the Laue symmetry confirmed the crystal systems. Ultimately, 25 reflections ($15° < 2\theta < 35°$) were used to obtain the final lattice parameters and the orientation matrices. Machine parameters, crystal data, and data collection parameters are summarized in Table I. The observed extinctions and subsequent refinements confirmed the respective space groups. The data sets were collected in four shells ($4.5° < 2\theta < 50.0°$), and three standard reflections were recorded every 150 reflections. The intensities of the standards showed no statistically significant change over the duration of the data collections. The data were processed using the TEXSAN software program package on a VAX 3520 workstation located in the Department of Chemistry and Biochemistry at the University of Windsor. The reflections with $F_o^2 > 3\sigma F_o^2$ were used in each of the refinements.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[23] The heavy-atom positions for each structure were determined using direct methods employing the Mithril option of the TEXSAN package. 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 $w(|F_o| - |F_c|)^2$, where the weight, w, is defined as $1/\sigma^2(F_o)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the cases where it is necessary to confirm the correct enantiomorph, this was done by data inversion and rerefinement. In the final cycles of refinement all the non-hydrogen atoms were refined as individual anisotropic atoms for 1, 5, and 7(ii). In the case of 2, 4, 6(ii), and 7(i) the heavy atoms and some of the carbons were refined anisotropically. This was done to maintain a reasonable data:variable ratio. The remaining non-hydrogen atoms were refined isotropically. In the case of 6(i), a fully isotropic refinement was required as the diffraction data was weak. Repeated attempts to grow and collect data on better quality crystals of 6(i) were unsuccessful. In all cases, hydrogen atom positions were calculated 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. In all cases the hydrogen atom contributions were calculated but not refined. Empirical absorption corrections were applied to each data based on ψ-scan data. The final refinement data are given in Table I. The largest peaks in the final difference Fourier map calculations showed residual electron densities of no chemical significance. The following data are tabulated: positional parameters (Table II) and selected bond distances and angles (Table III). Thermal parameters (Tables S1) and hydrogen atom parameters (Tables S2) have been deposited as supplementary material.

Results

The synthetic routes to cyclopentadienyltitanium derivatives are illustrated in Figure 1. The results of the crystallographic

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studies discussed herein as illustrated in Figures 3–9, and the numerical and metric data are tabulated in Tables I–III. FHMO calculations were performed, and the pertinent orbitals and energy diagrams are presented in Figures 12 and 13. Spectral, structural, and theoretical data are presented in the Experimental Section, and the tables and figures indicated above will be introduced and discussed at the appropriate places in the discussion.

Discussion

Syntheses. We have previously reported the facile formation of Ti–S bonds via the reaction of Cp$_2$TiCl$_2$ with dithiols in the presence of imidazole.[11] In the present system we have employed the identical procedure employing CpTiCl$_3$ as the Ti reagent. In this case, the reactions proceed rapidly to afford a bright orange solution and a white precipitate. The precipitate has been confirmed to be the hydrochloride salt of imidazole. The weight of recovered salt is consistent with a 1:1 reaction of CpTiCl$_3$ and propanedithiol. The initial orange product 1 was formulated as CpTi(SCH$_2$CH$_2$CH$_2$S)Cl on the basis of the ^{1}H NMR data. The formulation of 1 was confirmed crystallographically (vide infra). This species was extremely air and moisture sensitive, and thus manipulations of this material were performed only in the drybox.

Substitution reactions in which the chloride in compound 1 is replaced were studied. Reaction of 1 with 1 equiv of benzenethiolate in THF gave orange crystals of 2 (Figure 1). The ^{1}H NMR spectrum shows the resonances expected on the basis of the formulation of 2 as CpTi(SCH$_2$CH$_2$CH$_2$S)(SC$_6$H$_5$). This formulation was confirmed by an X-ray structural study (vide infra). Reaction of 2 with a second equivalent of benzenethiolate proceeds with a dramatic color change from orange to red-black. ^{1}H NMR characterization of the reaction product 3 showed resonances attributable to cyclopentadienyl, methylene, and aromatic protons. The integration of the spectra suggest a formulation of [CpTi(SCH$_2$CH$_2$CH$_2$S)(SC$_6$H$_5$)$_2$]$^-$. All attempts to isolate 3 either as the Na salt or as a tetraalkylammonium derivative failed to yield crystalline material of this extremely air-sensitive material; instead 2 was recovered. However, it is reasonable to suggest a four-legged "piano-stool" type structure similar to that recently reported for CpTa(SPh)$_4$[15] and [CpM-(SC$_6$F$_5$)$_4$]Tl (M = Mo, W).[16]

In addition to substitution reactions, compound 1 also reacts with phosphorus donors to form adducts. In the case of dmpe, the reaction mixture was monitored by ^{31}P{^{1}H} NMR. At 293 K, a broad singlet at −37.6 ppm as well as a pair of low-intensity doublets at 25.8 and 21.4 ppm is observed in THF. On cooling to 180 K, the averaging process is slowed but not completely stopped; however, attempts to record the spectrum at lower temperature were precluded by the solvent. At 180 K, three species are observed in solution (Figure 2). The least abundant species, about 10% of the total, gives rise to a pair of doublets

Table II. Positional Parameters

atom	x	y	z	atom	x	y	z
			Molecule 1				
Ti(1)	0.6211 (3)	0.2771 (2)	0.3766 (4)	C(3)	0.417 (2)	0.174 (2)	0.070 (3)
Cl	0.7667 (4)	0.4680 (3)	0.3314 (6)	C(4)	0.391 (2)	0.121 (1)	0.244 (4)
S(1)	0.7734 (4)	0.1164 (3)	0.3466 (7)	C(5)	0.351 (2)	0.216 (3)	0.360 (3)
S(2)	0.6630 (4)	0.2835 (4)	0.7335 (6)	C(6)	0.965 (2)	0.182 (1)	0.555 (3)
C(1)	0.358 (2)	0.331 (2)	0.254 (5)	C(7)	0.963 (2)	0.185 (2)	0.785 (3)
C(2)	0.396 (2)	0.302 (2)	0.076 (3)	C(8)	0.890 (2)	0.300 (2)	0.845 (2)
			Molecule 2				
Ti(1)	0.5102 (3)	0.3378	0.3246 (2)	C(11)	0.559 (2)	0.464 (1)	0.750 (2)
Ti(2)	0.9220 (3)	0.1349	0.9030 (2)	C(12)	0.411 (2)	0.469 (1)	0.805 (2)
S(1)	0.4850 (5)	0.2348 (2)	0.2251 (4)	C(13)	0.272 (2)	0.427 (1)	0.767 (2)
S(2)	0.8152 (5)	0.3586 (2)	0.3618 (4)	C(14)	0.280 (2)	0.3742 (9)	0.685 (2)
S(3)	0.4423 (5)	0.3004 (2)	0.5209 (4)	C(15)	1.198 (2)	0.0751 (9)	0.951 (2)
S(4)	0.6525 (5)	0.1495 (3)	0.9639 (4)	C(16)	1.162 (2)	0.100 (1)	1.068 (2)
S(5)	1.0521 (5)	0.2393 (2)	0.9391 (4)	C(17)	1.006 (2)	0.0673 (9)	1.091 (2)
S(6)	0.8049 (5)	0.1251 (3)	0.6791 (4)	C(18)	0.943 (2)	0.0248 (8)	0.988 (1)
C(1)	0.483 (2)	0.4238 (9)	0.169 (2)	C(19)	1.063 (2)	0.028 (1)	0.904 (2)
C(2)	0.438 (3)	0.452 (1)	0.285 (2)	C(20)	0.862 (2)	0.2929 (9)	0.860 (2)
C(3)	0.281 (2)	0.4187 (9)	0.300 (2)	C(21)	0.696 (2)	0.290 (1)	0.925 (2)
C(4)	0.229 (2)	0.3746 (9)	0.203 (2)	C(22)	0.573 (2)	0.2307 (9)	0.885 (1)
C(5)	0.355 (2)	0.3781 (8)	0.120 (2)	C(23)	0.990 (2)	0.1055 (7)	0.603 (1)
C(6)	0.678 (2)	0.1863 (9)	0.321 (1)	C(24)	0.969 (2)	0.0524 (9)	0.513 (2)
C(7)	0.860 (2)	0.2163 (8)	0.331 (1)	C(25)	1.114 (2)	0.0390 (9)	0.452 (2)
C(8)	0.910 (2)	0.2763 (9)	0.423 (2)	C(26)	1.268 (2)	0.074 (1)	0.479 (2)
C(9)	0.433 (2)	0.3703 (7)	0.629 (1)	C(27)	1.291 (2)	0.127 (1)	0.565 (2)
C(10)	0.574 (2)	0.4138 (9)	0.660 (2)	C(28)	1.151 (2)	0.1426 (9)	0.630 (1)
			Molecule 4				
Ti(1)	0.5593 (8)	0.1620 (6)	0.2977 (5)	C(4)	0.426 (4)	0.008 (3)	0.293 (3)
Cl	0.685 (1)	0.2693 (7)	0.2083 (7)	C(5)	0.555 (5)	−0.010 (3)	0.247 (3)
S(1)	0.363 (1)	0.283 (1)	0.2918 (9)	C(6)	0.456 (5)	0.369 (3)	0.401 (3)
S(2)	0.621 (1)	0.1716 (9)	0.4828 (8)	C(7)	0.429 (4)	0.331 (3)	0.493 (3)
P(1)	0.858 (1)	0.1099 (8)	0.3748 (7)	C(8)	0.460 (5)	0.214 (4)	0.517 (3)
C(1)	0.538 (5)	0.047 (3)	0.154 (3)	C(9)	0.937 (4)	0.058 (3)	0.272 (3)
C(2)	0.397 (5)	0.091 (3)	0.142 (3)	C(10)	0.914 (4)	0.014 (3)	0.481 (3)
C(3)	0.337 (5)	0.070 (3)	0.220 (3)	C(11)	0.983 (4)	0.220 (3)	0.429 (3)
			Molecule 5				
Ti(1)	0.2237 (1)	0.7503 (1)	0.48135 (8)	C(3)	−0.046 (1)	0.8365 (7)	0.6134 (7)
Cl(1)	0.3533 (2)	0.9167 (2)	0.5819 (1)	C(4)	−0.1416 (8)	0.7949 (7)	0.5058 (7)
S(1)	0.2906 (2)	0.5538 (2)	0.5561 (2)	C(11)	0.184 (1)	0.703 (2)	0.2993 (7)
S(2)	0.1319 (2)	0.7536 (2)	0.6524 (1)	C(12)	0.227 (2)	0.827 (1)	0.312 (1)
S(3)	−0.0349 (2)	0.7949 (2)	0.4083 (1)	C(13)	0.376 (2)	0.823 (1)	0.374 (1)
C(1)	0.2134 (9)	0.5216 (6)	0.6678 (5)	C(14)	0.413 (1)	0.703 (2)	0.3959 (8)
C(2)	0.0758 (8)	0.5971 (7)	0.6618 (5)	C(15)	0.297 (2)	0.635 (1)	0.350 (1)
			Molecule 6(i)				
Ti(1)	0.0291 (4)	0.7288 (4)	0.0633 (6)	C(8)	−0.116 (2)	0.676 (2)	−0.176 (3)
S(1)	0.0861 (6)	0.7127 (6)	−0.170 (1)	C(9)	−0.063 (2)	0.909 (2)	0.130 (4)
S(2)	−0.0924 (6)	0.6436 (5)	−0.009 (1)	C(10)	−0.019 (3)	0.947 (2)	0.016 (4)
S(3)	−0.0984 (6)	0.8129 (5)	0.085 (1)	C(11)	0.054 (2)	0.904 (2)	−0.068 (4)
S(4)	0.1176 (6)	0.8453 (5)	0.043 (1)	C(12)	−0.308 (3)	0.653 (3)	0.446 (6)
Na(1)	−0.2429 (9)	0.7142 (8)	0.141 (1)	C(13)	−0.328 (2)	0.584 (2)	0.516 (4)
O(1)	−0.247 (2)	0.636 (2)	0.333 (3)	C(14)	−0.270 (3)	0.528 (3)	0.470 (6)
C(1)	0.066 (2)	0.727 (2)	0.304 (4)	C(15)	−0.218 (2)	0.560 (2)	0.339 (5)
C(2)	0.015 (3)	0.661 (2)	0.279 (4)	C(16)	0.720 (4)	0.131 (4)	0.931 (5)
C(3)	0.060 (3)	0.614 (2)	0.193 (4)	C(17)	0.738 (4)	0.065 (4)	0.997 (7)
C(4)	0.143 (3)	0.649 (3)	0.158 (4)	C(18)	0.691 (5)	0.034 (3)	1.097 (7)
C(5)	0.144 (3)	0.710 (3)	0.235 (5)	C(19)	0.615 (6)	0.076 (5)	1.119 (8)
C(6)	0.043 (2)	0.631 (2)	−0.246 (4)	C(20)	0.610 (5)	0.136 (4)	1.070 (8)
C(7)	−0.059 (2)	0.637 (2)	−0.293 (3)	C(21)	0.660 (5)	0.172 (3)	0.989 (8)
			Molecule 6(ii)				
Ti(1)	0.8620 (1)	0.2661 (5)	1.1373	C(1)	0.813 (1)	0.444 (3)	1.120 (2)
Ti(2)	0.8518 (1)	0.2096 (5)	0.5969 (4)	C(2)	0.846 (1)	0.496 (2)	1.165 (2)
S(1)	0.8513 (3)	0.0768 (8)	1.2394 (6)	C(3)	0.851 (1)	0.431 (3)	1.251 (2)
S(2)	0.8368 (2)	0.1209 (8)	1.0243 (7)	C(4)	0.816 (1)	0.346 (3)	1.253 (2)
S(3)	0.8922 (2)	0.3656 (8)	1.0056 (6)	C(5)	0.796 (1)	0.360 (4)	1.173 (3)
S(4)	0.9294 (2)	0.2255 (9)	1.1875 (6)	C(6)	0.867 (1)	−0.067 (3)	1.178 (2)
S(5)	0.8485 (3)	0.0793 (9)	0.7327 (7)	C(7)	0.8356 (9)	−0.122 (3)	1.116 (2)
S(6)	0.9016 (3)	0.052 (1)	0.5471 (7)	C(8)	0.806 (1)	−0.018 (3)	1.074 (2)
S(7)	0.8732 (2)	0.3704 (8)	0.7065 (7)	C(9)	0.934 (1)	0.260 (3)	0.981 (3)
S(8)	0.8894 (4)	0.3423 (9)	0.4897 (7)	C(10)	0.972 (1)	0.291 (3)	1.028 (2)
Na(1)	0.8279 (3)	0.300 (1)	0.8666 (9)	C(11)	0.967 (1)	0.336 (3)	1.122 (2)
Na(2)	0.9250 (3)	0.116 (1)	0.366 (1)	C(12)	0.783 (1)	0.596 (3)	0.790 (2)
O(1)	0.8054 (6)	0.539 (2)	0.868 (2)	C(13)	0.798 (1)	0.739 (4)	0.782 (3)
O(2)	0.7563 (7)	0.247 (2)	0.854 (2)	C(14)	0.824 (1)	0.759 (5)	0.868 (4)
O(3)	0.9479 (7)	−0.108 (2)	0.334 (1)	C(15)	0.827 (1)	0.642 (4)	0.912 (3)
O(4)	0.9932 (7)	0.182 (2)	0.399 (1)	C(16)	0.737 (1)	0.121 (4)	0.874 (3)

Table II (Continued)

atom	x	y	z	atom	x	y	z
			Molecule 6(ii)				
C(17)	0.706 (2)	0.169 (6)	0.945 (4)	C(29)	0.887 (1)	0.528 (3)	0.655 (2)
C(18)	0.686 (2)	0.246 (8)	0.896 (6)	C(30)	0.929 (1)	0.516 (3)	0.604 (2)
C(19)	0.726 (2)	0.329 (4)	0.886 (3)	C(31)	0.932 (1)	0.405 (4)	0.548 (2)
C(21)	0.781 (1)	0.193 (4)	0.621 (2)	C(32)	0.933 (1)	-0.230 (5)	0.374 (4)
C(22)	0.792 (1)	0.086 (3)	0.569 (2)	C(33)	0.956 (1)	-0.331 (4)	0.306 (3)
C(23)	0.804 (1)	0.141 (3)	0.491 (2)	C(34)	0.980 (2)	-0.269 (5)	0.252 (4)
C(24)	0.800 (1)	0.271 (4)	0.497 (3)	C(35)	0.978 (1)	-0.128 (4)	0.272 (3)
C(25)	0.790 (1)	0.310 (4)	0.583 (3)	C(36)	1.013 (1)	0.296 (4)	0.367 (3)
C(26)	0.898 (1)	0.044 (3)	0.750 (3)	C(37)	1.053 (2)	0.308 (5)	0.425 (4)
C(27)	0.914 (1)	-0.080 (3)	0.706 (2)	C(38)	1.050 (2)	0.204 (6)	0.486 (4)
C(28)	0.900 (1)	-0.097 (3)	0.606 (2)	C(39)	1.016 (1)	0.116 (4)	0.466 (3)
			Molecule 7(i)				
Ti(1)	0.6076 (1)	0.2289	0.2880 (2)	C(10)	0.7226 (9)	0.273 (3)	0.571 (2)
Ti(2)	0.6415 (1)	0.3331 (7)	0.5027 (2)	C(11)	0.7974 (8)	0.102 (3)	0.125 (2)
Ti(3)	0.9019 (1)	0.2377 (7)	0.0586 (2)	C(12)	0.8165 (8)	0.094 (3)	0.210 (1)
Ti(4)	0.8441 (1)	0.3383 (7)	0.1791 (2)	C(13)	0.7989 (8)	0.218 (3)	0.235 (1)
S(1)	0.6792 (2)	0.125 (1)	0.3110 (4)	C(14)	0.7657 (8)	0.319 (4)	0.164 (2)
S(2)	0.5960 (2)	0.452 (1)	0.2006 (4)	C(15)	0.7664 (8)	0.236 (4)	0.094 (1)
S(3)	0.6478 (2)	0.617 (1)	0.5305 (4)	C(16)	0.9368 (8)	-0.036 (3)	0.090 (1)
S(4)	0.5727 (2)	0.268 (1)	0.5062 (4)	C(17)	0.9536 (8)	0.057 (3)	0.167 (1)
S(5)	0.8393 (2)	0.116 (1)	-0.0591 (3)	C(18)	0.9814 (7)	0.184 (3)	0.164 (1)
S(6)	0.9123 (2)	0.481 (1)	0.0010 (4)	C(19)	0.9797 (7)	0.183 (3)	0.086 (1)
S(7)	0.9045 (2)	0.351 (1)	0.3203 (3)	C(20)	0.9540 (7)	0.049 (3)	0.039 (1)
S(8)	0.8241 (2)	0.6178 (9)	0.1534 (4)	C(21)	0.7148 (6)	0.315 (3)	0.343 (1)
O(1)	0.6213 (4)	0.322 (2)	0.3894 (7)	C(22)	0.6982 (7)	0.455 (3)	0.276 (1)
O(2)	0.8755 (5)	0.306 (2)	0.1214 (8)	C(23)	0.6548 (8)	0.562 (3)	0.266 (1)
C(1)	0.5831 (7)	-0.050 (3)	0.282 (1)	C(24)	0.5884 (8)	0.680 (3)	0.451 (2)
C(2)	0.5531 (7)	0.048 (3)	0.293 (1)	C(25)	0.551 (1)	0.609 (4)	0.461 (2)
C(3)	0.5258 (8)	0.159 (3)	0.223 (1)	C(26)	0.5347 (7)	0.431 (3)	0.433 (1)
C(4)	0.5415 (8)	0.113 (3)	0.165 (1)	C(27)	0.7976 (7)	0.294 (3)	-0.096 (1)
C(5)	0.5747 (8)	-0.013 (4)	0.198 (2)	C(28)	0.8133 (8)	0.456 (3)	-0.128 (1)
C(6)	0.6985 (8)	0.131 (4)	0.539 (2)	C(29)	0.8506 (8)	0.556 (3)	-0.060 (1)
C(7)	0.676 (1)	0.093 (4)	0.582 (2)	C(30)	0.9429 (6)	0.512 (3)	0.309 (1)
C(8)	0.6876 (8)	0.204 (3)	0.644 (1)	C(31)	0.920 (1)	0.679 (3)	0.277 (2)
C(9)	0.7159 (8)	0.325 (3)	0.632 (1)				
			Molecule 7(ii)				
Ti(1)	0.3065 (2)	0.0267 (3)	0.1357 (1)	C(6)	0.050 (1)	-0.121 (2)	0.237 (1)
Ti(2)	0.2080 (2)	-0.0631 (3)	0.2927 (2)	C(7)	0.060 (2)	-0.140 (3)	0.313 (2)
S(3)	0.3383 (3)	-0.1702 (6)	0.3785 (3)	C(8)	0.119 (2)	-0.275 (3)	0.337 (1)
S(1)	0.3325 (4)	0.3152 (6)	0.1298 (3)	C(9)	0.148 (1)	-0.338 (2)	0.277 (1)
S(2)	0.1788 (3)	-0.0056 (7)	0.0335 (3)	C(10)	0.101 (2)	-0.247 (3)	0.214 (1)
S(4)	0.1815 (3)	0.1839 (6)	0.3509 (3)	C(26)	0.302 (1)	0.268 (2)	0.373 (1)
O(1)	0.2569 (7)	0.009 (1)	0.2167 (5)	C(25)	0.379 (1)	0.175 (2)	0.423 (1)
C(1)	0.368 (1)	-0.213 (3)	0.088 (1)	C(24)	0.413 (1)	0.018 (3)	0.3900 (9)
C(2)	0.404 (2)	-0.212 (3)	0.164 (1)	C(23)	0.099 (1)	0.159 (3)	0.055 (1)
C(3)	0.461 (1)	-0.073 (3)	0.187 (1)	C(22)	0.137 (2)	0.335 (3)	0.058 (1)
C(4)	0.462 (1)	0.016 (2)	0.120 (2)	C(21)	0.213 (2)	0.387 (2)	0.128 (1)
C(5)	0.407 (1)	-0.074 (3)	0.061 (1)				

centered at 27.65 and 25.35 ppm with $|J_{P-P}|$ = 44.0 Hz. These resonances are attributed to CpTi(SCH$_2$CH$_2$CH$_2$S)Cl(dmpe) in which the diphosphine chelates to the Ti (Figure 2 (**4b**)). A second species (30%) results in a pair of doublets centered at 3.10 and −47.42 ppm with $|J_{P-P}|$ = 19.5 Hz. The inequivalence of the phosphorus atoms and the similarity of one chemical shift to that of the free phosphine are consistent with the formulation of CpTi-(SCH$_2$CH$_2$CH$_2$S)Cl(dmpe) in which the diphosphine is dangling (Figure 2 (**4c**)). The most abundant species, 60% of the products, in solution exhibits a broad resonance at 2.69 ppm. This resonance is attributed to the species [CpTi(SCH$_2$CH$_2$CH$_2$S)Cl]$_2$(μ-dmpe) (**4**) in which the dmpe bridges two Ti centers (Figure 2). This proposition is supported by the isolation, albeit in low yield, and subsequent structural characterization of **4** from this reaction mixture. It is perhaps a bit surprising that chelation of dmpe is not favored in this reaction. An examination of molecular models is instructive. If the chair conformation of the propanedithiolate ring on Ti is retained, then coordination of the second phosphorus to Ti in what can be described as the "axial" position would present significant steric interactions between the propyl chain and the methyl substituents on phosphorus. Such interactions can only be overcome by a change in ring conformation; thus, formation of the chelated complex is inhibited.

In a similar sense an additional donor atom may coordinate to the Ti center by incorporation of such a donor in the dithiolate ligand. Reaction of S(CH$_2$CH$_2$SSiMe$_3$)$_2$ with CpTiCl$_3$ affords orange crystals of **5**. The ^{1}H NMR data suggest a formulation similar to **1**. The X-ray crystallographic study of **5** (vide infra) confirms this formulation and shows also that the central thioether sulfur is also bonded to Ti.

Reaction of **1** with the disodium salt of 1,3-propanedithiol affords the dark red product **6** and the precipitation of NaCl. On the basis of the integration of the ^{1}H NMR data, this material was formulated as [CpTi(SCH$_2$CH$_2$CH$_2$S)$_2$]Na. This formulation of this extremely sensitive product was confirmed crystallographically (vide infra).

Controlled hydrolysis of compound **1** was performed by employing base and 1 equiv of water. This reaction affords the oxo-bridged complex [CpTi(SCH$_2$CH$_2$CH$_2$S)]$_2$O (**7**). The structure of **7** was confirmed by X-ray methods (vide infra). The ^{1}H NMR spectrum of **7** shows six sets of methylene resonances in the ^{1}H NMR at 3.79, 3.74, 3.41, 3.37, 2.53, and 2.48 ppm as well as a resonance attributable to cyclopentadienyl protons. The two upfield methylene resonances are attributable to the pairs of protons on the central carbons of the chelates. Attempts were made to complete an assignment of the resonances via a seris of

Table III. Selected Interatomic Distances (Å) and Angles (deg)

Molecule 1

Distances

Ti(1)–Cl	2.258 (4)	Ti(1)–S(1)	2.268 (4)	Ti(1)–C(4)	2.31 (1)	C(6)–C(7)	1.53 (2)
Ti(1)–S(2)	2.267 (5)	Ti(1)–C(1)	2.30 (1)	Ti(1)–C(5)	2.33 (1)	C(7)–C(8)	1.50 (2)
Ti(1)–C(2)	2.33 (2)	Ti(1)–C(3)	2.34 (2)	S(1)–C(6)	1.82 (2)	S(2)–C(8)	1.86 (1)

Angles

Cl–Ti(1)–S(1)	104.0 (2)	Cl–Ti(1)–S(2)	103.9 (2)	Ti(1)–S(2)–C(8)	101.0 (5)	S(1)–Ti(1)–S(2)	101.2 (2)
Ti(1)–S(1)–C(6)	98.7 (5)	Cl–Ti(1)–C(4)	148.4 (5)				

Molecule 2

Distances

Ti(1)–S(1)	2.278 (5)	Ti(1)–S(2)	2.278 (5)	Ti(2)–C(16)	2.33 (2)	Ti(2)–C(17)	2.36 (2)
Ti(1)–S(3)	2.340 (5)	Ti(1)–C(1)	2.34 (2)	Ti(2)–C(18)	2.35 (2)	Ti(2)–C(19)	2.36 (2)
Ti(1)–C(2)	2.34 (2)	Ti(1)–C(3)	2.32 (2)	S(1)–C(6)	1.85 (2)	S(2)–C(8)	1.84 (2)
Ti(1)–C(4)	2.34 (2)	Ti(1)–C(5)	2.36 (2)	S(3)–C(9)	1.80 (1)	S(4)–C(22)	1.85 (2)
Ti(2)–S(4)	2.263 (4)	Ti(2)–S(5)	2.280 (5)	S(5)–C(20)	1.83 (2)	S(6)–C(23)	1.78 (1)
Ti(2)–S(6)	2.337 (4)	Ti(2)–C(15)	2.35 (2)				

Angles

S(1)–Ti(1)–S(2)	102.9 (2)	S(1)–Ti(1)–S(3)	96.2 (2)	Ti(1)–S(1)–C(6)	103.4 (5)	Ti(1)–S(2)–C(8)	101.8 (5)
S(2)–Ti(1)–S(3)	107.6 (2)	S(4)–Ti(2)–S(5)	102.4 (2)	Ti(1)–S(3)–C(9)	110.8 (5)	Ti(2)–S(4)–C(22)	102.1 (5)
S(4)–Ti(2)–S(6)	97.1 (2)	S(5)–Ti(2)–S(6)	107.5 (2)	Ti(2)–S(5)–C(20)	100.5 (5)	Ti(2)–S(6)–C(23)	107.5 (5)

Molecule 5

Distances

Ti(1)–Cl(1)	2.357 (2)	Ti(1)–S(1)	2.363 (2)	Ti(1)–C(15)	2.371 (9)	S(1)–C(1)	1.825 (7)
Ti(1)–S(2)	2.600 (2)	Ti(1)–S(3)	2.342 (3)	S(2)–C(2)	1.795 (7)	S(2)–C(3)	1.803 (8)
Ti(1)–C(11)	2.365 (9)	Ti(1)–C(12)	2.378 (8)	S(3)–C(4)	1.809 (8)		

Angles

Cl(1)–Ti(1)–S(1)	115.68 (8)	Cl(1)–Ti(1)–S(2)	75.02 (8)	Ti(1)–S(1)–C(1)	113.1 (2)	Ti(1)–S(2)–C(2)	102.3 (3)
Cl(1)–Ti(1)–S(3)	111.25 (9)	S(1)–Ti(1)–S(2)	76.39 (8)	Ti(1)–S(2)–C(3)	104.1 (3)	C(2)–S(2)–C(3)	104.1 (4)
S(1)–Ti(1)–S(3)	118.23 (8)	S(2)–Ti(1)–S(3)	79.48 (8)	Ti(1)–S(3)–C(4)	113.2 (2)		

Molecule 7(i)

Distances

Ti(1)–S(1)	2.295 (8)	Ti(4)–O(2)	1.80 (2)	Ti(2)–O(1)	1.80 (1)	S(5)–C(27)	1.84 (2)
Ti(1)–S(2)	2.272 (8)	Ti(4)–C(11)	2.30 (3)	Ti(2)–C(6)	2.28 (3)	S(6)–C(29)	1.83 (2)
Ti(1)–O(1)	1.81 (1)	Ti(4)–C(12)	2.32 (3)	Ti(2)–C(7)	2.31 (3)	S(7)–C(30)	1.86 (3)
Ti(1)–C(1)	2.34 (2)	Ti(4)–C(13)	2.36 (3)	Ti(2)–C(8)	2.44 (2)	S(8)–C(32)	1.81 (3)
Ti(1)–C(2)	2.31 (2)	Ti(4)–C(14)	2.42 (3)	Ti(2)–C(9)	2.36 (2)	Ti(2)–C(10)	2.32 (3)
Ti(1)–C(3)	2.36 (2)	Ti(4)–C(15)	2.34 (2)	Ti(3)–S(5)	2.283 (6)	Ti(3)–S(6)	2.300 (9)
Ti(1)–C(4)	2.35 (2)	S(1)–C(21)	1.81 (2)	Ti(3)–O(2)	1.81 (2)	Ti(3)–C(16)	2.38 (3)
Ti(1)–C(5)	2.39 (3)	S(2)–C(23)	1.88 (2)	Ti(3)–C(17)	2.32 (2)	Ti(3)–C(18)	2.35 (2)
Ti(2)–S(3)	2.29 (1)	S(3)–C(24)	1.79 (2)	Ti(3)–C(19)	2.36 (2)	Ti(3)–C(20)	2.41 (3)
Ti(2)–S(4)	2.319 (9)	S(4)–C(26)	1.81 (2)	Ti(4)–S(7)	2.301 (5)	Ti(4)–S(8)	2.293 (9)

Angles

S(1)–Ti(1)–S(2)	101.7 (3)	S(1)–Ti(1)–O(1)	104.7 (5)	Ti(1)–S(1)–C(21)	100.5 (8)	Ti(1)–S(2)–C(23)	99.6 (7)
S(3)–Ti(2)–S(4)	101.1 (3)	S(3)–Ti(2)–O(1)	103.6 (6)	Ti(2)–S(3)–C(24)	99.2 (8)	Ti(2)–S(4)–C(26)	97.5 (9)
S(2)–Ti(1)–O(1)	104.6 (5)	S(4)–Ti(2)–O(1)	102.4 (5)	Ti(3)–S(5)–C(27)	98.9 (7)	Ti(3)–S(6)–C(29)	100.3 (9)
S(5)–Ti(3)–S(6)	101.6 (3)	S(5)–Ti(3)–O(2)	103.3 (4)	Ti(4)–S(7)–C(30)	98.7 (6)	Ti(4)–S(8)–C(32)	98.1 (9)
S(7)–Ti(4)–S(8)	100.3 (3)	S(7)–Ti(4)–O(2)	103.4 (4)	Ti(1)–O(1)–Ti(2)	157.9 (9)	Ti(3)–O(2)–Ti(4)	170.0 (9)
S(6)–Ti(3)–O(2)	104.7 (6)	S(8)–Ti(4)–O(2)	102.0 (5)				

Molecule 7(ii)

Distances

Ti(1)–S(1)	2.301 (5)	S(1)–C(21)	1.82 (2)	Ti(1)–C(5)	2.38 (2)	Ti(2)–S(3)	2.288 (5)
Ti(1)–S(2)	2.286 (5)	S(2)–C(23)	1.84 (2)	Ti(2)–S(4)	2.287 (6)	Ti(2)–O(1)	1.80 (1)
Ti(1)–O(1)	1.81 (1)	S(4)–C(26)	1.82 (2)	Ti(2)–C(6)	2.31 (2)	Ti(2)–C(7)	2.34 (3)
Ti(1)–C(1)	2.34 (2)	Ti(1)–C(2)	2.33 (2)	Ti(2)–C(8)	2.36 (3)	Ti(2)–C(9)	2.31 (2)
Ti(1)–C(3)	2.33 (2)	Ti(1)–C(4)	2.35 (2)	Ti(2)–C(10)	2.33 (2)	S(3)–C(24)	1.82 (2)

Angles

S(1)–Ti(1)–S(2)	100.3 (2)	S(1)–Ti(1)–O(1)	102.6 (4)	Ti(2)–S(3)–C(24)	98.6 (5)	Ti(1)–S(1)–C(21)	97.8 (6)
S(3)–Ti(2)–S(4)	101.6 (2)	S(3)–Ti(2)–O(1)	102.8 (3)	Ti(1)–S(2)–C(23)	100.1 (6)	Ti(2)–S(4)–C(26)	98.3 (6)
S(2)–Ti(1)–O(1)	104.4 (3)	S(4)–Ti(2)–O(1)	103.6 (4)	Ti(1)–O(1)–Ti(2)	166.0 (7)		

selective decoupling experiments; however, this was unsuccessful due to the lack of spectral dispersion.

Structural Studies. ORTEP drawings of **1**, **2**, and **4–7** are shown in Figures 3–8 and 10. The coordination sphere of Ti in compound **1** is comprised of an η^5-cyclopentadienyl ring and two sulfur and one chlorine atoms which adopt a pseudo-tetrahedral arrangement around Ti (Figure 3). The six membered ring formed by the chelation of 1,3-propanedithiolate to Ti adopts a typical chair conformation. The orientation of the ring is such that the

carbons α to S are down, away from the cyclopentadienyl ring thereby minimizing steric interactions.

The geometry of the Ti coordination sphere of compound **2** is similar to **1** with the replacement of the chlorine by the sulfur of benzenethiolate (Figure 4). Also similar is the chair conformation of the propanedithiolate chelate ring. The Ti–S distances in **1** average 2.267 (5) Å, while the Ti–S distances within the chelate of **2** average 2.275 (5) Å. The S–Ti–S angle of 101.2 (2)° in **1** is significantly larger than the corresponding angle of
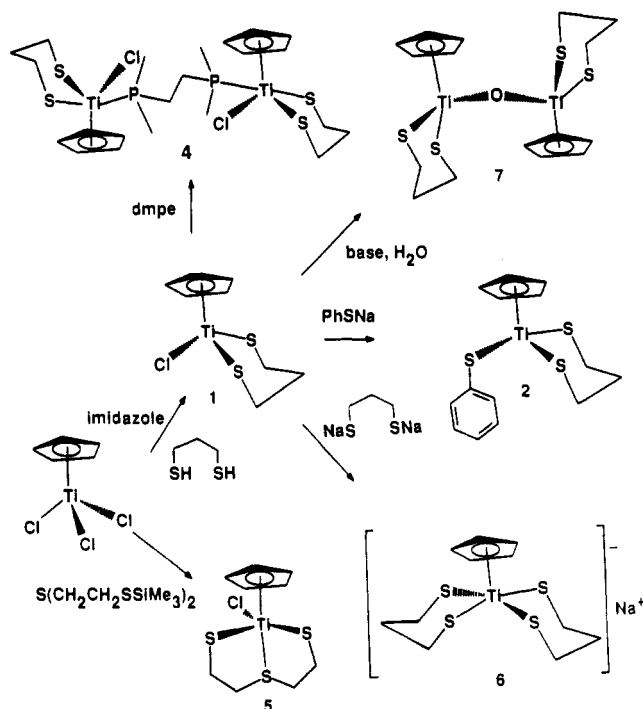
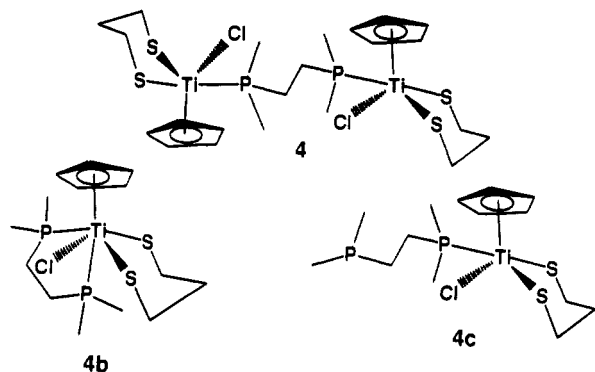**Figure 1.** Synthetic routes to cyclopentadienyltitanium dithiolate derivatives.

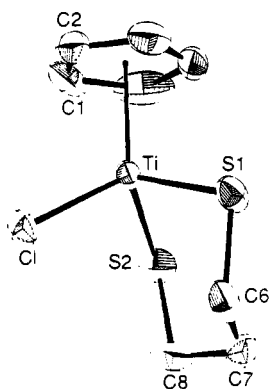**Figure 2.** Products observed in the reaction of **1** with dmpe.

Figure 3. ORTEP drawing of molecule **1**, with 30% thermal ellipsoids shown. Hydrogen atoms, which are numbered according to the number of the carbon to which they are bonded, are omitted for clarity.

86.91 (4)° found in $Cp_2V(SCH_2CH_2CH_2S)$.[24] The larger angle accommodates the pseudo-tetrahedral geometry about the Ti center without introducing severe strain into the six-membered ring. The benzenethiolate Ti–S distances (2.340 (5) and 2.337 (4) Å) in **2** are significantly longer than the corresponding Ti–S alkanethiolate distances, consistent with the lower basicity of the
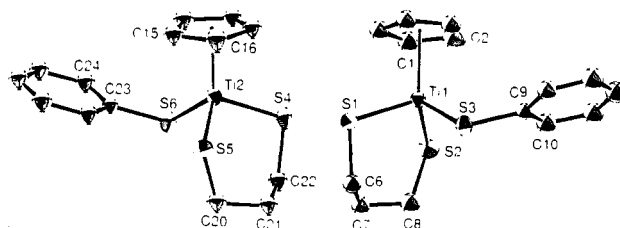
Figure 4. ORTEP drawing of the two independent molecules of **2** in the asymmetric unit, with 30% thermal ellipsoids are shown. Hydrogen atoms, which are numbered according to the number of the carbon to which they are bonded, are omitted for clarity.
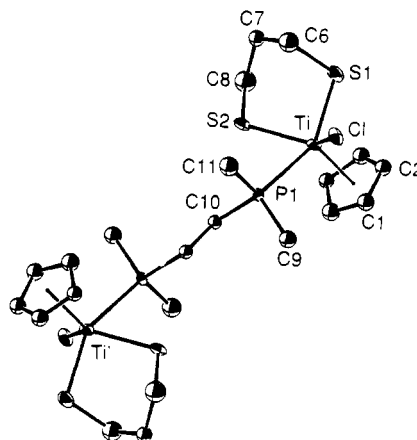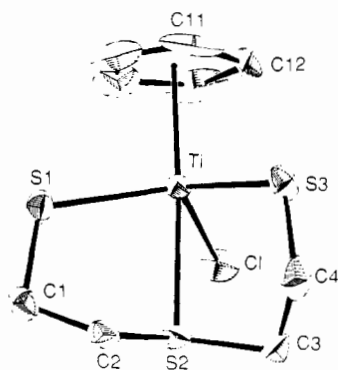

Figure 5. ORTEP drawing of molecule **4**, with 30% thermal ellipsoids shown. Hydrogen atoms, which are numbered according to the number of the carbon to which they are bonded, are omitted for clarity.

arenethiolate. In a similar fashion to **1**, the S–Ti–S angle in **2** is 102.9 (2)°. The orientation of the phenyl substituent on S(3) and S(6) in **2** is such that the cyclopentadienyl ring and the phenyl ring are approximately parallel. This orientation clearly is the preferred geometry as it minimizes steric interaction between the aryl ring and the propanedithiolate ring. It may also be that electronically this orientation offers the best overlap of the lone pairs on sulfur with the vacant orbitals on Ti. This view is supported by FHMO calculations (vide infra).

The structure of compound **4** (Figure 5) is best described as two molecules of **1** linked by the dmpe ligand. The geometry at Ti is perturbed such that it adopts what is approximately a four-legged "piano-stool" type of geometry. Although Ti(III)–phosphine complexes are known,[25-28] **4** is a rare example of a Ti(IV) complex with a phosphine ligand.

The molecular structure of **5** is depicted in Figure 6. This compound adopts a significantly different geometry compared to those described above. The coordination which is comprised of the cyclopentadienyl group, the two thiolate sulfurs, the thioether sulfur, and the chloride ligand can be described as pseudo-trigonal bipyramidal. The cyclopentadienyl ring and the thioether sulfur are approximately trans to each other. The Cl–Ti–S and the S–Ti–S angles in the trigonal plane are 115.68 (8), 111.25 (9), and 118.23 (8)°, respectively. The angles of the pseudo-trigonal plane to the pseudo-axial thioether sulfur are 75.02 (8), 79.48 (8), and 76.39 (8)°, indicating that the plane is pushed down slightly away from the cyclopentadienyl ring. This distorted geometry achieves a minimization of steric interactions of the trigonal plane constituents with the cyclopentadienyl ring and as

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Figure 6. ORTEP drawing of molecule **5**, with 30% thermal ellipsoids shown. Hydrogen atoms, which are numbered according to the number of the carbon to which they are bonded, are omitted for clarity.
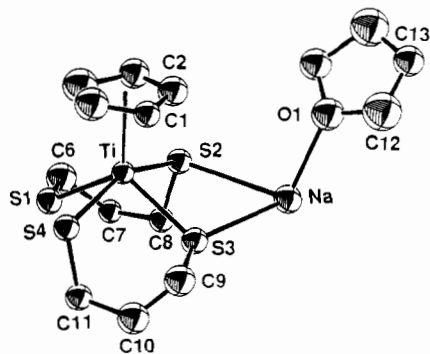
Figure 7. ORTEP drawing of the asymmetric unit of molecule **6(i)**, with 30% thermal ellipsoids shown. Hydrogen atoms, which are numbered according to the number of the carbon to which they are bonded, are omitted for clarity.

Figure 8. ORTEP drawing of the asymmetric unit of molecule **6(ii)**, with 30% thermal ellipsoids shown. Hydrogen atoms, which are numbered according to the number of the carbon to which they are bonded, are omitted for clarity.

Figure 9. PLUTO drawing showing the polymeric nature of (a) **6(i)** and (b) **6(ii)**. The shaded atoms are Ti, while the hatched atoms are Na.

well accommodates the constraints imposed by the formation of five-membered rings. The Ti–S distances involving the thiolate ligands average 2.353 (3) Å, which is also significantly longer than that of the corresponding Ti–S distances found in **1** and **2**. This is again consistent with the presence of the additional donor atom, in this case the thioether sulfur. The Ti–S distance for this sulfur atom is 2.600 (2) Å reflecting the comparatively poor basicity of the thioether.

Compound **6** crystallized in two forms depending on the solvent used for crystallization. In the crystal form **6(i)** (Figure 7), which is derived from THF/benzene solution, the Ti adopts a four-legged piano-stool geometry with four sulfur atoms acting as the legs of the cyclopentadienyl stool. The sulfur atoms bridge to a pseudo-square pyramidal sodium ion whose coordination sphere is comprised of four sulfur atoms and an axial THF moiety. In the solid state, this asymmetric unit is repeated to afford a TiS$_2$-Na polymeric chain. A slightly different geometry is seen in the crystal form **6(ii)** derived from a THF/hexane mixture (Figure 8). In this case the asymmetry unit is comprised of two Ti and two Na fragments. The coordination sphere of the Ti is similar to that seen in **6(i)**, but the Na atom is coordinated to two THF molecules and two bridging sulfur atoms with two longer contacts (3.0 Å) to two more sulfur atoms. Again, this arrangement results in a polymeric array in the solid state. The two polymeric forms are shown in Figure 9. In spite of the polymeric nature of **6** in the solid state, it is not surprising that the NMR data for this product show no evidence of ion pairing or oligomerization in solution.

Compound **7** (Figure 10) was found to crystallize in two different space groups depending on the conditions under which the crystals were grown. A π-bonded cyclopentadienyl ring and a propanedithiolate chelate are bonded to each of the two Ti atoms which are linked by a single oxygen atom. The Ti–S distances average 2.295 (9) and 2.290 (6) Å in forms **7(i)** and **7(ii)**, respectively. These are slightly longer than the corre-
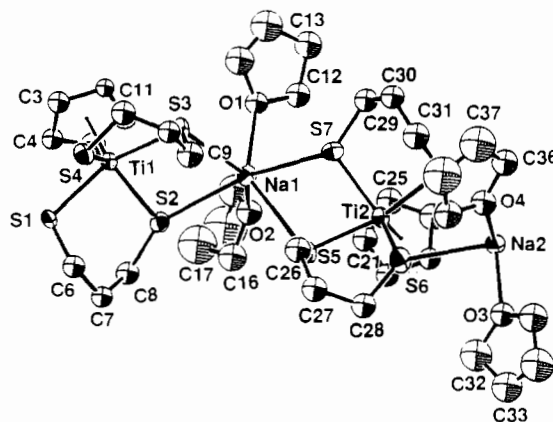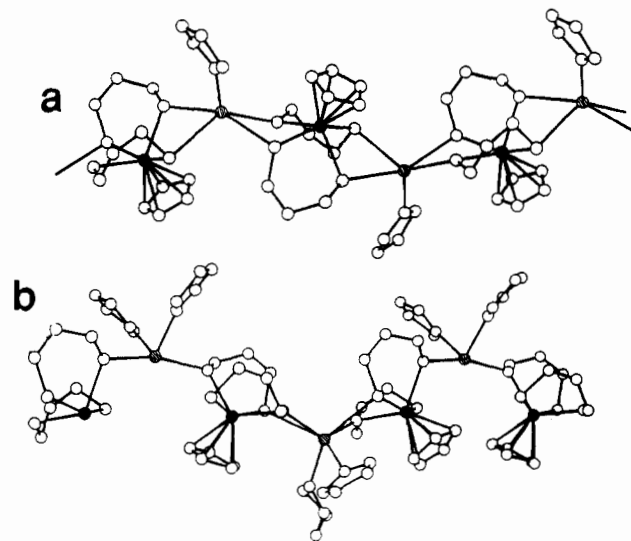
sponding distances in **1** and **2**. This may arise as a result of the significant π-donation to the Ti center from the bridging oxygen atom. The Ti–S distances are also significantly shorter than those seen in Cp$_2$Ti(SMe)$_2$ (2.400 (1) Å)[4] or Cp$_2$Ti(SPCy$_2$)$_2$ (2.423 (3), 2.427 (3) Å).[29] Presumably the presence of only one cyclopentadienyl ligand on Ti results in an enhanced Lewis acidity of the Ti center and thus accounts for the relatively short Ti–S bonds. The S–Ti–S′ angles average 101.2 (5) and 100.9 (3)° in forms **7(i)** and **7(ii)**, respectively. This is significantly larger than the S–V–S′ angle of 86.91 (4)° seen in Cp$_2$V(SCH$_2$CH$_2$-CH$_2$S)[24] and S–Ti–S′ angle of 93.7 (1)° seen in Cp$_2$Ti(SMe)$_2$.[4] Again it appears that the comparatively small steric demands about the Ti center in **1** permit the opening of the S–Ti–S′ angle. The mean Ti–O bond distances were found to be 1.81 (2) and 1.805 (9) Å in the two crystal forms. These are similar in length to the Ti–O bond distances found in (Cp$_2$TiCl)$_2$(μ-O) (1.777 (1) Å)[30] and [(C$_5$H$_4$Me)TiCl(μ-O)]$_4$ (1.797 (1), 1.801 (3), 1.800 (1), 1.792 (3) Å)[31] and significantly shorter than those found in (Cp*Ti)$_4$O$_6$ (1.978 (4) Å).[32] The Ti–O–Ti′ angles were found to be 157.9 (9) and 170.0 (8)° in form **7(i)** and 166.0 (7)° in form **6(ii)**. These compare with the linear Ti–O–Ti′ moieties found in (Cp$_2$TiCl)$_2$(μ-O).[30] The relatively short Ti–O distances and

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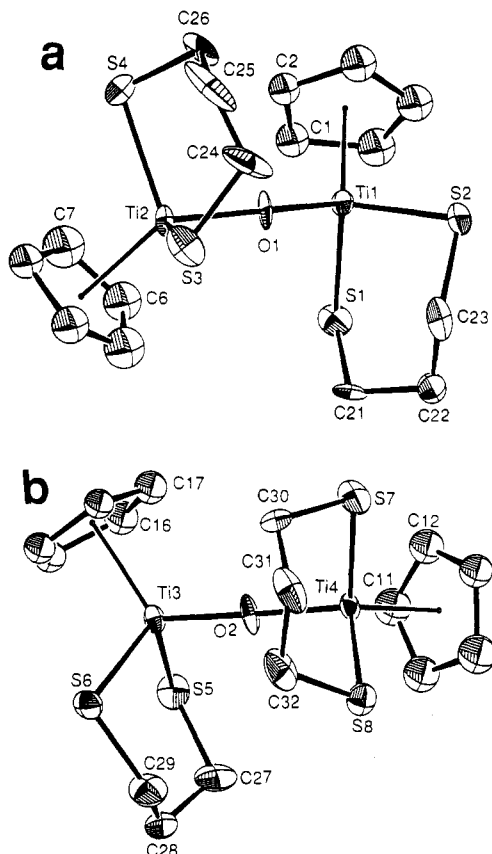(32) Babcock, L. M.; Day, V. W.; Klemperer, W. G. *J. Chem. Soc., Chem. Commun.* **1987**, 858, 29.

Figure 10. ORTEP drawing of the two crystallographically independent molecules of 7(i), with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Note that the atom-numbering scheme for 7(ii) is indentical to that used for 7(i), molecule 1 (part a).
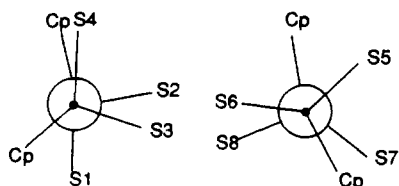

Figure 11. Idealized Newman projections down the Ti–O–Ti' vector of 7(i).

the large Ti–O–Ti' angles are consistent with π-bonding between the Ti and O. The variations in the Ti–O–Ti' angles and their deviations from linearity observed in **7** may be associated with the steric demands of the dithiolate chelate rings on the adjacent Ti atoms and are also structural evidence for variations in the degree of Ti–O π-bonding. Similar π interactions have been substantiated in related Zr–alkoxide complexes, by both structural and theoretical evidence.[9]

The features of the two crystalline forms of **7** are similar. The two crystalline forms differ only in the sense of the rotation about the Ti–O–Ti' vector. In the crystalline form **7(i)**, the two independent molecules differ in the sense of the rotation about the Ti–O–Ti' vector. If one idealizes a linear geometry at oxygen, then two Newman projections down the Ti–O–Ti' vectors are presented by the two independent molecules in form **7(i)** (Figure 11). These projections reveal that the two independent molecules are almost enantiomeric, mismatched only by a slight rotation down the Ti–O–Ti' vector. In contrast, the symmetry of the crystalline form **7(ii)** requires the presence of exact mirror images in the unit cell. In **7(ii)**, S(1) and S(4) are "eclipsed", while S(2) and S(3) are eclipsed by the respective cyclopentadienyl groups. In either case, it is clear that all of the methylene groups of the dithiolate ligands are in distinct environments. This is consistent with the observation of six sets of resonances in the ^{1}H NMR.
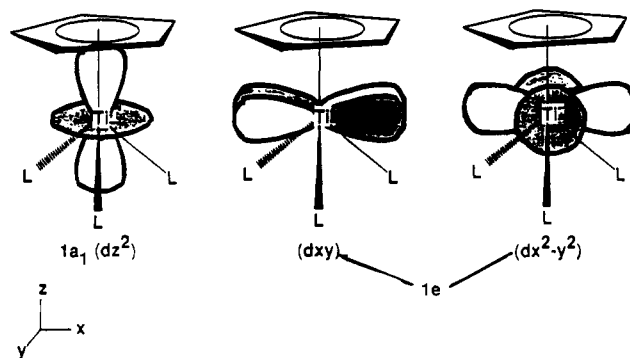

Figure 12. Low-lying vacant orbitals on CpTiCl₃.

Molecular Orbital Calculations. A series of Fenske–Hall molecular orbital (FHMO) calculations were performed in order to address the nature of the Lewis acidity of the Ti centers. The bonding scheme in the simplest model system, i.e. CpTiCl₃, is identical in symmetry to that previously described for CpMn(CO)₃.[33] As a result the bonding will not be discussed in detail; rather attention will be focused on the low-lying vacant or frontier orbitals which give rise to the Lewis acidity. The previously described Mn species is an 18-electron complex, while CpTiCl₃ has 12 valence electrons. The result is that the 1a₁ and 1e orbitals are vacant in the Ti case. These orbitals are largely metal-based comprised primarily of metal d_{z^2}, d_{xy}, and $d_{x^2-y^2}$ character (Figure 12). FHMO calculations show only a small energy gap (0.45 eV) between the e set and the 1a₁ orbital. Interestingly, FHMO calculations for the model CpTi(SH)₃ show a reversal in order of these vacant orbitals with respect to energy (Figure 13a). This is attributable to the orientation of the sulfur lone pairs toward the e set thus establishing a weak π-interaction between the sulfur and the Lewis acidic Ti center. Removal of the 3-fold symmetry at Ti, as in the case of **1**, results in a splitting of the degeneracy of the pair of e orbitals. Calculations employing the crystallographically determined geometry for **1** reveal that the character of these vacant orbitals mix to give three hybrids. The LUMO is comprised of a mix of the Ti $d_{x^2-y^2}$ and a slightly smaller contribution from the Ti d_{z^2} orbital (Figure 13a). One example of a Lewis base interacting with this LUMO is found in molecule **7**. The orientation of the substituents about the Ti–O–Ti' vector in molecule **7** is such that the cyclopentadienyl rings are approximately orthogonal. This orientation allows the interaction of the LUMO on each Ti atom with one of the two pairs of electrons on the bridging oxygen atom, affording significant Ti–O π-bonding. This avenue for π-interaction is reminiscent of that describe by Kubacek et al. for CpML₄ complexes.[34]

Direct reaction of **1** with a Lewis base is exemplified by the formation of the four-legged piano stool, **4**. The geometry of **4** is consistent with the significant contribution of the $d_{x^2-y^2}$ orbital to the LUMO of **1**. A similar situation arises in **6** where a propanedithiolate replaces the chloride in **1** affording the piano-stool geometry at Ti. Calculations for the model compound CpTiCl(SCH₂CH₂CH₂S)(PH₃) (**4'**) show that the LUMO for this species is primarily Ti d_{xy} and $d_{x^2-y^2}$ in character (Figure 13a). This is consistent with data described for related four-legged piano stools.[15,33] The nature of this LUMO hinders chelation of dmpe to **1** although FHMO calculations reveal an energy gap of only 1.1 eV to the next vacant orbital which is largely d_{z^2} in character. It is interaction with this orbital that is required for chelation of dmpe to **1** to occur.

Previous extended Huckel calculations have predicted and rationalized the preference of CpML₄ complexes for a piano-stool geometry over a pseudo-trigonal bipyramidal geometry.[34]

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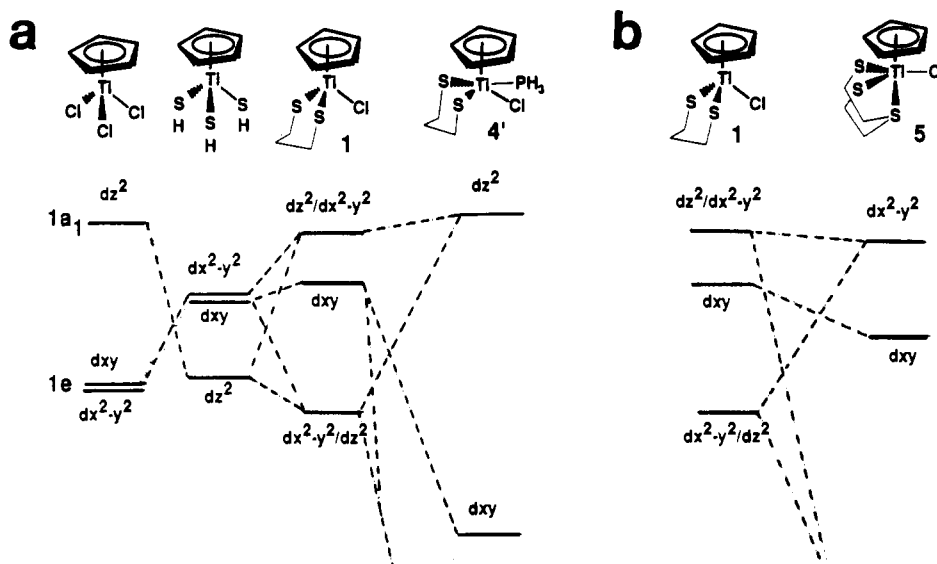(34) Kubacek, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180.

Figure 13. Energy level diagrams for the low-lying vacant orbitals for (a) $CpTiCl_3$, $CpTi(SH)_3$, **1**, and **4'** and (b) **1** and **5**. The major contributions derived from the Ti-based atomic orbitals are indicated.

Compound **5** is a rare example of a $CpML_4$ species which adopts a so-called "3:3:1"[34] or pseudo-trigonal bipyramidal geometry. This may be attributed to the ligand modification which constrains the thioether sulfur to interact with the vacant Ti d_{z^2} orbital. As expected, this leaves the reminents of the e set vacant, and thus the LUMO for the complex $CpTi(SCH_2CH_2SCH_2CH_2S)Cl$ is largely Ti d_{xy} in character, while the next vacant orbital which is Ti $d_{x^2-y^2}$ in character and is only 0.4 eV higher in energy (Figure 10b).

Summary. Synthetic routes to cyclopentadienyltitanium dithiolate derivatives have been developed, and the structural features of these compounds have been characterized. The reactivity of these compounds is dominated by their Lewis acidity. This is attributable to three low-lying vacant orbitals. In general satisfaction of the Lewis acidity is primarily directed in the xy plane, that is the plane parallel to the cyclopentadienyl ring. Donation to the electron-deficient metal center may take the form of π-interactions with donor atoms or direct acceptance of electron density from a Lewis base affording four-legged piano-stool type derivatives. A donor interaction with the vacant orbital orthogonal to the xy plane, that is along the axis trans to the cyclopentadienyl ring, can be imposed by a constrained ligand system. This affords a rare example of a $CpML_4$ complex which adopts a 3:3:1 or pseudo-trigonal bipyramidal geometry. Further studies of the reactivity of related systems which incorporate such electron-deficient, Lewis acidic metal centers are ongoing.