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Heterobimetallic Derivatives of Cyclopentadienyltitanium Bis(dithiolate) Anions: $[CpTi(S(CH_2)_nS)_2M]_x$ and $CpTi(S(CH_2)_nS)_2ML$ ($M = Cu, Rh; n = 2, 3$)

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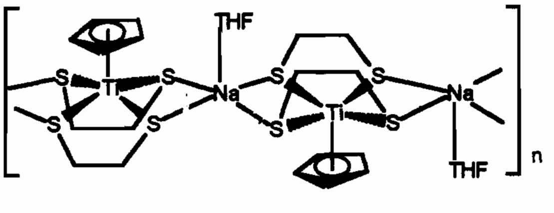
The compounds $[CpTi(SCH_2CH_2S)_2Na]_n$ and $[CpTi(SCH_2CH_2CH_2S)_2Na]_n$ have been used as precursors to heterometallic compounds. Reaction with $[Cu(NCMe)_4]BF_4$ gives insoluble compounds formulated as $[CpTi(SCH_2CH_2S)_2Cu]_n$ (**1**) and $[CpTi(SCH_2CH_2CH_2S)_2)Cu]_n$ (**2**), respectively. Compound **1** is also formed in the reaction of $[CpTi(SCH_2CH_2S)Cl]_2$ with $[Cu(NCMe)_4]BF_4$. The Rh(I) derivative $[CpTi(SCH_2CH_2CH_2S)_2Rh]_n$ (**3**) has been synthesized from the reaction of $[CpTi(SCH_2CH_2CH_2S)_2Na]_n$ and $[(C_2H_4)_2RhCl]_2$. Compounds **1** and **2** react with PMe_3 to give $CpTi(SCH_2CH_2S)_2CuPMe_3$ (**4**) and $CpTi(SCH_2CH_2CH_2S)_2CuPMe_3$ (**5**), respectively. In compound **4** the Ti coordination sphere is best described as a pseudo-four-legged piano stool while three sulfur atoms bridge to the $CuPMe_3$ fragment completing the pseudotetrahedral coordination sphere of Cu. Reaction of **1** with bis(dimethylphosphino)ethane (DMPE) leads to the formation of the salt $[CpTi(SCH_2CH_2S)_2][Cu(DMPE)_2]$ (**6**), in which the cation and anion have no close contacts. Addition of 1 equiv of NBD to a suspension of **4** generates $[CpTi(SCH_2CH_2CH_2S)_2]Rh(NBD)$ (**7**). Compound **7** is also prepared by reaction of $CpTi(SCH_2CH_2CH_2S)Cl$ with $[(NBD)RhCl]_2$ or $[(NBD)_2Rh]BF_4$. In a manner similar to observations in **3**, three of the sulfur atoms bound to Ti bridge to the pseudotrigonal bipyramidal Rh center in **7**. This compound is not stable in solution, decomposing to the Ti(III) product $[CpTi(SCH_2CH_2CH_2S)_2][Rh(NBD)]_2$ (**8**). In this case, the Rh centers adopt pseudo square planar geometries with two bridging sulfur atoms with the NBD fragment completing the coordination sphere. These results are presented, and the implications regarding the nature of these heterobimetallic complexes is considered. Structural data are presented for the compounds **4**, **6**, **7**, and **8**. Complex **4** crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.458(1)$ Å, $b = 11.297(2)$ Å, $c = 9.244(1)$ Å, $\alpha = 93.96(1)°$, $\beta = 103.63(1)°$, $\gamma = 106.41(1)°$, $V = 911.0(3)$ Å^3, and $Z = 2$. Compound **6** crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.453(9)$ Å, $b = 19.002(8)$ Å, $c = 14.231(5)$ Å, $\beta = 105.71(3)°$, $V = 3245(2)$ Å^3, and $Z = 4$. Compound **7** crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.182(7)$ Å, $b = 12.222(3)$ Å, $c = 17.557(4)$ Å, $\beta = 91.83(4)°$, $V = 1958(1)$ Å^3, and $Z = 4$. Compound **8** crystallizes in the tetragonal space group $P4_12_12$ with $a = 11.346(5)$ Å, $c = 23.531(8)$ Å, $V = 3029(1)$ Å^3, and $Z = 4$.

Introduction

A variety of heterobimetallic systems which incorporate group IV metallocene fragments have been synthesized and characterized.[1] Such systems exhibit interesting features such as dative interactions between the disparate metal centers attributable to the Lewis acidity of the early metal center and the presence of electron rich late metal transition atoms. Such compounds typically incorporate bridging ligands such as thiolates or phosphides derived from metallocene metalloligand precursors.[1] Related group IV monocyclopentadienyl–early transition metal systems that might act as synthons for heterobimetallics have received much less attention.[2] In the case of CpTi–thiolate complexes, this is attributable to higher oxophilicity of the metal center which makes synthesis and manipulation of such compounds more difficult than the related metallocene systems. In recent work, we have examined synthetic routes to such reactive Lewis acidic Ti compounds.[3] The Lewis acidity of the simple pseudotetrahedral complexes of the form $CpTi(SR)_2Cl$, is exemplified by the formation of the anion $[CpTi(S(CH_2)_nS)_2]^-$ in which the Ti adopts a four-legged piano stool type geometry. Sodium salts of these anions form polymeric structures in the solid state via sulfur bridges between the Ti and Na atoms.[3] In this paper, we employ these salts as synthons for related heterobimetallic derivatives in which the sodium ions are replaced with Cu(I) and Rh(I). As well, other synthetic routes to these Ti/Cu and Ti/Rh species are described. Structural data imply the presence of dative interactions between the electron rich late transition metal and the Lewis acidic Ti center when sulfur atoms bridge the two metal centers. The nature and implications of such metal–metal interactions are considered.



Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 employing either a Vacuum Atmospheres inert atmosphere glovebox or standard Schlenk-line techniques. 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. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer operating at 300 MHz and 75 MHz respectively. Trace amounts of protonated solvents were used as references and chemical shifts are reported relative to $SiMe_4$. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC-200 spectrometer operating at 81 MHz and employing 85% H_3PO_4 as the external reference. All NMR chemical shifts are reported in ppm. FAB and EI mass spectra were recorded at Wayne State University, Detroit, MI. X-Band EPR spectra were recorded using a Bruker EPS-300e EPR spectrometer, employing DPPH as the external reference. Combustion analyses were performed by Galbraith Laboratories Inc. Knoxville, TN. $[(NBD)RhCl]_2$ (NBD = norbornadiene) and $[Cu(NCMe)_4]PF_6$ were purchased from the Aldrich Chemical Co. Bis(dimethylphosphino)ethane (DMPE) and PMe_3 were purchased from the Pressure Chemical Co.

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$[(NBD)_2Rh]BF_4$,[4] $[(C_2H_4)_2RhCl]_2$,[5] $[Cu(NCMe)_4]BF_4$,[6] and $[CpTi(SCH_2CH_2S)Cl]_2$[7] were prepared by the literature methods.

Synthesis of $[CpTi(SCH_2CH_2S)_2Cu]_n$ (1). (i) $[CpTi(SCH_2CH_2S)_2Na]_n$ (0.050 g, 0.16 mmol) and $[Cu(NCMe)_4]BF_4$ (0.049 g, 0.16 mmol) were added to THF (3 mL). The suspension was stirred for 1 h after which time an insoluble purple solid was filtered off. Yield: >95%. **(ii)** $[CpTi(SCH_2CH_2S)Cl]_2$ (0.050 g, 0.10 mmol) and $[Cu(NCMe)_4]BF_4$ (0.031 g, 0.10 mmol) were placed in a flask containing 3 mL of THF. The red-brown solution turned orange-brown with a purple precipitate over a 12-h period. The dark purple precipitate was filtered off leaving an orange-yellow filtrate. Yield: 48%. Anal. Calcd for $C_{11}H_{13}S_4TiCu$: C, 29.95; H, 3.63. Found: C, 30.04; H, 3.68.

Synthesis of $[CpTi(SCH_2CH_2CH_2S)_2Cu]_n$ (2). $CpTi(SCH_2CH_2CH_2S)Cl$ (0.050 g, 0.14 mmol) was placed in 3 mL of THF. $[Cu(NCMe)_4]BF_4$ (0.045 g, 0.14 mmol) was added to the stirred solution. Over a period of 2 h the solution turned orange-yellow with a purple precipitate. The precipitate was filtered off and washed with C_6H_6. Yield: >95%. Anal. Calcd for $C_{11}H_{17}S_4TiCu{\cdot}NaBF_4$: C, 26.48; H, 3.43. Found: C, 26.27; H, 3.51.

Synthesis of $[CpTi(SCH_2CH_2CH_2S)_2Rh]_n$ (3). $[CpTi(SCH_2CH_2CH_2S)_2Na]_n$ (0.057 g, 0.16 mmol) was dissolved in 3 mL of THF. $[(C_2H_4)_2RhCl]_2$ (0.032 g, 0.08 mmol) was added to the stirred solution. The mixture turned brown over the course of 0.5 h. The reaction mixture was stirred for 6 h after which time a brown precipitate was filtered off. Yield: 57%. Anal. Calcd for $C_{11}H_{17}S_4TiRh{\cdot}NaCl$: C, 27.14; H, 3.52. Found: C, 27.01; H, 3.57.

Synthesis of $[CpTi(SCH_2CH_2S)_2CuPMe_3]$ (4). Compound **1** (0.030 g, 0.08 mmol) was suspended in 3 mL of THF. PMe_3 (0.006 g, 0.08 mmol) was added dropwise to the stirred suspension. The solid dissolved, and the mixture became homogeneous and turned dark brown in color. The solvent was removed *in vacuo* and the residue taken up in C_6H_6. Slow evaporation of the solvent afforded dark brown crystals after 14 days. Yield: 88%, ^1H NMR (δ, 263 K, CD_2Cl_2): Cp, 6.49 (s, 5H); CH_2, 3.65 (m, 1H), 3.40 (m, 2H), 3.15 (m, 1H), 3.04 (m, 1H), 2.96 (m, 2H), 2.96 (m, 1H); CH_3, 1.72 (d, 9H, $|J_{P-H}| = 13.4$ Hz). $^{31}P\{^1H\}$ NMR (δ, 298 K, CD_2Cl_2): –42.1 (br s). Anal. Calcd for $C_{12}H_{22}S_4PTiCu$: C, 32.99; H, 5.07. Found: C, 33.12; H, 4.93.

Synthesis of $[CpTi(SCH_2CH_2CH_2S)_2CuPMe_3]$ (5). Compound **2** (0.050 g, 0.13 mmol) was suspended in 3 mL of THF. PMe_3 (0.010 g, 0.13 mmol) was added dropwise to the stirred suspension. The solid dissolved; the mixture became homogeneous and turned dark brown in color. The reaction mixture was filtered and the solvent was removed leaving a dark brown residue. Yield: 92%. ^1H NMR (δ, 263 K, CD_2Cl_2): Cp, 6.45 (s, 5H); CH_2, 3.65 (m, 2H), 3.39 (m, 1H), 3.22 (m, 2H), 2.71 (m, 3H), 2.64 (m, 2H), 1.83 (m, 2H); CH_3, 1.71 (d, 9H, $|J_{P-H}| = 13.4$ Hz). $^{31}P\{^1H\}$ NMR (δ, 298 K, CD_2Cl_2): –47.2 (br s). Anal. Calcd for $C_{14}H_{26}S_4PTiCu$: C, 36.16; H, 5.64. Found: C, 36.31; H, 5.45.

Synthesis of $[CpTi(SCH_2CH_2S)_2][Cu(Me_2PCH_2CH_2PMe_2)_2]$ (6). Compound **1** (0.050 g, 0.14 mmol) was suspended in 3 mL of THF. DMPE (0.021 g, 0.14 mmol) was added dropwise to the stirred suspension. The solid dissolved to some extent and immediately turned red-black in color. The reaction mixture was filtered, and crystals of **6** were deposited directly from this solution after 5 days. Yield: 45%. ^1H NMR (δ, 298 K, CD_2Cl_2): Cp, 6.52 (s, 5H); CH_2, 3.62 (m, 4H), 3.51 (br s, 8H), 3.34 (m, 4H), 2.74 (m, 2H) 2.13 (m, 2H); CH_3, 1.35 (br m, 24H). $^{31}P\{^1H\}$ NMR (δ, 185 K, CD_2Cl_2): DMPE, –16.1 ($|J_{Cu-P}| = 779.7$ Hz). Anal. Calcd for $C_{21}H_{45}S_4P_4TiCu$: C, 38.15; H, 6.86. Found: C, 37.98; H, 6.92.

Synthesis of $[CpTi(SCH_2CH_2CH_2S)_2Rh(NBD)]$ (7). (i) $CpTi(SCH_2CH_2CH_2S)Cl$ (0.062 g, 0.18 mmol) was dissolved in 3 mL of THF. $[(NBD)RhCl]_2$ (0.041 g, 0.09 mmol) was added to the stirred solution. The mixture turned brown over the course of 1 h. The reaction mixture was stirred for 5 h after which time a white precipitate was filtered off and the solvent removed. Yield: 54%. **(ii)** $CpTi(SCH_2CH_2CH_2S)Cl$ (0.041 g, 0.12 mmol) was dissolved in 3 mL of THF. $[(NBD)_2Rh]BF_4$ (0.044 g, 0.12 mmol) was added to the stirred solution. The solution immediately turned brown. The reaction mixture was stirred for 15 min after which time a white precipitate was filtered off. X-ray quality crystals of **7** were obtained after 24 h from a THF/pentane liquid/vapor diffusion of the filtrate. Yield: 65%. **(iii)** NBD (2.5 μL, 0.02 mmol) was added to a suspension of **3** (0.010 g, 0.02 mmol) in 1 mL of $CDCl_3$. The mixture became a brown solution over a 5-min period. ^1H NMR (δ, 298 K, $CDCl_3$): Cp, 6.53 (s, 5H); CH_2, 3.51 (br m, 2H), 3.33 (br m, 2H), 3.12 (br m, 2H), 2.63 (br m, 2H), 2.44 (br m, 2H), 1.98 (br m, 2H); NBD, 3.52 (s, 4H), 3.38 (s, 2H), 1.23 (s, 2H). $^{13}C\{^1H\}$ NMR (δ, 298 K, $CDCl_3$): Cp, 114.13; CH_2, 35.71 (br s), 32.84 (br s), 29.87 (br s), 28.57 (br s), 23.52 (br s), 18.47 (br s); NBD, 97.42, 51.87, 42.44. Anal. Calcd for $C_{18}H_{25}S_4TiRh$: C, 41.54; H, 4.84. Found: C, 41.36; H, 4.72.

Synthesis of $CpTi(SCH_2CH_2CH_2S)_2[Rh(NBD)]_2$ (8). Procedure ii for the preparation of **7** was repeated, and the filtrate was allowed to stand for 3 weeks after which time X-ray quality dark-brown crystals of **8** were obtained. Yield: 20%. EPR (298 K, THF): $g = 1.9836$; $\langle a_{Ti}\rangle = 11.0$ G. Anal. Calcd for $C_{18}H_{25}S_4TiRh$: C, 41.97; H, 4.65. Found: C, 42.12; H, 4.55.

X-Ray Structure Determinations. X-ray quality crystals of **4**, **6**, **7**, and **8** 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-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 systems. Ultimately, 25 reflections ($15° < 2\theta < 35°$) were used to obtain the final lattice parameters and the orientation matrices. The data sets were collected in 4 shells ($4.5° < 2\theta < 50.0°$), and three standard reflections were recorded every 150 reflections. The intensity measurements were collected employing a fixed scan rate/multiple scan method. The number of scans per reflection was dependent on the peak intensity; thus weaker reflections were scanned up to four times and the counts averaged. 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 or using the TEXSAN crystal solution package operating on a SGI workstation with remote X-terminals. 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.[8–10] The heavy atom positions for each structure were determined using direct methods employing either the SHELX-86 or MITHRIL direct methods routines 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. The observed extinctions and subsequent refinements confirmed the respective space groups. In the final cycles of refinement all of the non-hydrogen atoms were refined as individual anisotropic atoms for **4** and **7**. In the case of **8**, the imposition of crystallographic symmetry results in disordering of the cyclopentadienyl ring on Ti. In modeling this disorder a rigid C_5H_5 group was employed with 50% site occupancy and a group thermal parameter. Furthermore, for **4** and **8**, the heavy atoms and only some of the carbons were refined anisotropically. This was done to maintain reasonable data:variable ratios. The remaining non-hydrogen atoms were refined isotropically. 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 factors of the carbon atoms to which they are bonded. In all cases the hydrogen atom contributions were calculated, but not refined. Empirical absorption corrections were applied to all data, based on ψ-scan data employing the correction software resident in the TEXSAN package. In the case of **8**, the correct enantiomorph was determined by comparison of the refinement with that derived from model inversion. This led to reductions in the values of R and R_w from 0.0682 and 0.0625 to 0.0670 and 0.0620 respectively. Complete machine parameters, crystal data, and data collection parameters, selected bond distances and angles, positional parameters, hydrogen atom parameters, thermal parameters have been deposited in the supplementary material. Selected crystallographic parameters are given in Tables 1–3.

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Table 1. Crystallographic Parameters

	4	6	7	8
formula	$C_{12}H_{22}S_4PTiCu$	$C_{21}H_{45}S_4P_4TiCu$	$C_{18}H_{25}S_4TiRh$	$C_{29}H_{41}S_4OTiRh_2$
fw	436.97	697.20	520.44	789.61
a, Å	9.458(1)	12.453(9)	9.182(7)	11.346(5)
b, Å	11.297(2)	19.002(8)	12.222(3)	
c, Å	9.244(1)	14.231(5)	17.557(4)	23.531(8)
α, deg	93.96(1)			
β, deg	103.63(1)	105.71(3)	91.83(4)	
γ, deg	106.41(1)			
vol, Å^3	911.0(3)	3245(2)	1958(1)	3029(1)
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P4_12_12$ (No. 92)
Z	2	4	4	4
μ (cm^{-1})	21.36	13.70	16.74	16.03
d(calc), g/cm^3	1.59	1.43	1.77	1.73
temp °C	24	24	24	24
λ, Å (Mo Kα)	0.710 69	0.710 69	0.710 69	0.710 69
R,[a] %	3.20	6.30	5.73	6.70
R_w,[a] %	2.70	6.40	5.00	6.20

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{0.5}$.

Results

The reaction of $[CpTi(SCH_2CH_2S)_2Na]_n$ with $[Cu(NCMe)_4]BF_4$ proceeds with a color change indicative of metal ion exchange to give an insoluble dark purple powder, **1**. FAB and EI mass spectrometry were consistent with the presence of the ions containing the fragments $[CpTi(SCH_2CH_2S)_2]$ and Cu. Although the nature of this species has not been unambiguously determined, the extreme insolubility of the compound as well as derivatization experiments (*vide infra*) suggest a solid-state mixed-metal bimetallic oligomer or polymer of the form $[CpTi(SCH_2CH_2)_2Cu]_n$.

The product **1** is isolated in lower yield but in a form free of $NaBF_4$ by employing the reaction of the macrocyclic compound $[CpTi(SCH_2CH_2S)Cl]_2$ with $[Cu(NCMe)_4]BF_4$. This reaction is thought to proceed via disproportionation of $[CpTi(SCH_2CH_2S)Cl]_2$ to form $[CpTi(SCH_2CH_2S)_2]^-$ and $[CpTiCl_2]^+$. Reaction of the anion with the Cu(I) ions yields **1** while the cation reacts with BF_4^- to give $CpTiCl_2F$. This view is supported by the observation of ^1H NMR resonances attributable to $CpTiCl_2F$. In a similar reaction employing $[Cu(NCMe)_4]PF_6$ formation of poly(tetramethylene oxide) is seen indicative of the presence of PF_5.[11]

The reaction of $[CpTi(SCH_2CH_2CH_2S)_2Na]_n$ with $[Cu(NCMe)_4]BF_4$ proceeds in an analogous manner to that seen for **1** to give a dark purple compound, formulated as $[CpTi(SCH_2CH_2CH_2S)_2Cu]_n$ (**2**), in apparent high yield. Also in a manner similar to the preparation of **1**, the insoluble purple product was not readily separated from the reaction byproduct $NaBF_4$.

In a similar reaction, the compound $[CpTi(SCH_2CH_2CH_2S)_2Rh]_n$ (**3**) was prepared from the reaction of $[CpTi(SCH_2CH_2CH_2S)_2Na]_n$ and $[(C_2H_4)_2RhCl]_2$, which resulted in a color change and the precipitation of a brown-black product suggesting metal ion exchange although again separation of a Ti/Rh product from the NaCl byproduct proved difficult. As is the case for each of the insoluble products **1**–**3**, analytical data and the analogy to known structures of the sodium salts suggest formulations as heterobimetallic polymer materials. However, these formulations have not been unambiguously confirmed, prompting derivatization experiments.

Derivatization

The reaction of **1** with 1 equiv of PMe_3 proceeds with the immediate dissolution of the insoluble solid and a color change from deep purple to dark brown. Slow evaporation of the solvent led to dark brown crystals of **4**. ^1H NMR data for **4** were consistent with the presence of Cp, methylene and methyl protons suggesting the formulation $[CpTi(SCH_2CH_2S)_2CuPMe_3]$ (Scheme 1.) A crystallographic structure determination (*vide infra*) verified the formulation of **4**. In a similar manner, reaction of PMe_3 with **2** led to a dissolution of the purple solid and a color change from purple to a dark brown product formulated as $[CpTi(SCH_2CH_2CH_2S)_2CuPMe_3]$ **5** on the basis of similar spectroscopic data. The reaction of **1** and DMPE was performed in an analogous manner. ^1H NMR and ^{31}P data are consistent with the formulation of **6** as the salt $[CpTi(SCH_2CH_2S)_2][Cu(DMPE)_2]$ (Scheme 1). This was confirmed crystallographically (*vide infra*).

The ^{31}P NMR spectrum of **4** exhibits one broad peak at 298 K suggesting an exchange process. At low temperature (185 K) the ^{31}P NMR resonance sharpens to a four-line signal, attributable to Cu ($I = {}^3/_2$) bound PMe_3. ^{63}Cu NMR at 185 K confirms the presence of $[Cu(PMe_3)_4]^+$ in solution. This implies that dissociation of Cu from **4** generating $[CpTi(SCH_2CH_2S)_2]^-$ anion.

The insoluble Ti/Rh product **3** reacts rapidly with NBD to give a soluble dark brown species. The new product **7** was subsequently isolated. ^1H NMR data revealed resonances attributable to cyclopentadienyl protons, six broad sets of methylene resonances as well as three peaks attributable to a coordinated NBD moiety suggesting the formulation of **7** as $[CpTi(SCH_2CH_2CH_2S)_2Rh(NBD)]$ (Figure 3). This formulation was confirmed crystallographically. The product **7** was also derived from the reactions of $[CpTi(SCH_2CH_2CH_2)_2Na]_n$ and $[(NBD)RhCl]_2$ or $[(NBD)_2Rh]BF_4$ (Scheme 2).

Although **7** can be isolated in moderate to good yields, the solutions containing this compound are unstable and yield crystals of a new species **8** after several weeks of standing. The product **8**, which is isolated in 20% yield, is paramagnetic exhibiting a strong EPR signal at $g = 1.9836$ with an $\langle a_{Ti} \rangle$ of 11.0 G. An X-ray structure determination (*vide infra*) of the dark-brown crystals revealed **8** to be the Ti(III) complex $CpTi(SCH_2CH_2CH_2S)_2[Rh(NBD)]_2$ (Scheme 2). ^1H NMR data for the mother liquor reveal the presence of the bis(disulfide) $(SCH_2CH_2CH_2S)_2$[12] as well as other unidentified Ti species (Scheme 2). While it is clear that **7** is unstable with respect to a degradative redox process affording **8** and other products, the mechanism of electron transfer is not understood.

Structural Studies

An ORTEP drawing of **4** is shown in Figure 1. The geometry about the Ti center is best described as "piano stool" geometry comprised of an (η^5-cyclopentadienyl)titanium moiety with two

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Table 2. Positional Parameters

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Compound **4**							
Cu(1)	0.5094(8)	0.2885(6)	0.2212(7)	C(4)	0.8913(7)	0.1182(5)	0.5407(7)
Ti(1)	0.7536(1)	0.2341(8)	0.3910(1)	C(5)	0.8358(6)	0.1847(6)	0.6373(6)
S(1)	0.7540(2)	0.3600(1)	0.1858(1)	C(6)	0.7564(7)	0.2627(5)	0.0231(6)
S(2)	0.7504(2)	0.0806(1)	0.2009(2)	C(7)	0.661(7)	0.1270(5)	0.0248(6)
S(3)	0.4907(1)	0.1180(1)	0.3625(1)	C(8)	0.4228(6)	0.1950(5)	0.5016(6)
S(4)	0.6447(2)	0.4066(1)	0.4627(1)	C(9)	0.5349(6)	0.3200(5)	0.5811(6)
P(1)	0.2980(2)	0.2900(1)	0.0610(1)	C(10)	0.3108(7)	0.3036(6)	−0.1300(6)
C(1)	0.9050(7)	0.3097(5)	0.6430(6)	C(11)	0.2211(7)	0.4141(5)	0.1057(6)
C(2)	1.0051(6)	0.3268(6)	0.5514(7)	C(12)	0.1351(6)	0.1524(5)	0.0323(7)
C(3)	0.9981(6)	0.2074(6)	0.4877(6)				
Compound **6**							
Cu(1)	0.2161(2)	0.5460(1)	0.8179(2)	C(7)	−0.136(2)	0.195(1)	0.830(2)
Ti(1)	−0.2363(3)	0.3378(2)	0.6766(3)	C(8)	−0.040(2)	0.347(1)	0.545(1)
S(1)	−0.1396(5)	0.3386(4)	0.8501(4)	C(9)	−0.112(2)	0.286(1)	0.510(2)
S(2)	−0.227(6)	0.2121(3)	0.7009(5)	C(10)	0.301(2)	0.403(1)	0.735(1)
S(3)	−0.0551(5)	0.3763(3)	0.6626(4)	C(11)	0.359(2)	0.399(1)	0.847(2)
S(4)	−0.2594(5)	0.3051(3)	0.5065(4)	C(12)	0.192(2)	0.481(1)	0.567(2)
P(1)	0.2746(5)	0.4960(3)	0.6942(4)	C(13)	0.410(2)	0.526(1)	0.683(2)
P(2)	0.2730(5)	0.4492(3)	0.9129(4)	C(14)	0.162(2)	0.387(1)	0.917(1)
P(3)	0.0354(5)	0.5813(3)	0.7987(4)	C(15)	0.366(2)	0.447(1)	1.039(2)
P(4)	0.2775(5)	0.6574(3)	0.8594(4)	C(16)	0.052(2)	0.666(1)	0.853(2)
C(1)	−0.440(2)	0.356(1)	0.623(2)	C(17)	0.141(2)	0.709(1)	0.834(2)
C(2)	−0.392(2)	0.413(1)	0.584(2)	C(18)	−0.053(2)	0.543(1)	0.867(2)
C(3)	−0.330(2)	0.452(1)	0.661(2)	C(19)	−0.055(2)	0.593(1)	0.681(2)
C(4)	−0.341(2)	0.422(1)	0.747(2)	C(20)	0.361(2)	0.706(1)	0.791(2)
C(5)	−0.405(2)	0.363(1)	0.723(2)	C(21)	0.353(2)	0.683(1)	0.985(2)
C(6)	−0.061(2)	0.258(1)	0.865(2)				
Compound **7**							
Rh(1)	0.0695(8)	0.0895(6)	0.1991(4)	C(7)	0.277(1)	0.030(1)	0.3857(6)
Ti(1)	−0.1175(2)	0.1539(1)	0.3229(9)	C(8)	0.249(1)	0.153(1)	0.3776(5)
S(1)	−0.0015(3)	−0.0216(2)	0.3161(1)	C(9)	−0.294(1)	0.161(1)	0.1385(5)
S(2)	0.0750(3)	0.2001(2)	0.4118(1)	C(10)	−0.191(1)	0.242(1)	0.1018(6)
S(3)	−0.2008(3)	0.0595(2)	0.2001(1)	C(11)	−0.116(1)	0.3226(9)	0.1554(6)
S(4)	0.0024(3)	0.2700(2)	0.2334(1)	C(12)	0.180(1)	0.1490(8)	0.1077(5)
C(1)	−0.248(1)	0.2914(9)	0.3894(6)	C(13)	0.283(1)	0.1275(8)	0.1682(5)
C(2)	−0.234(1)	0.2024(9)	0.4365(5)	C(14)	0.347(1)	0.0144(9)	0.1543(5)
C(3)	−0.312(1)	0.1170(8)	0.4039(6)	C(15)	0.212(1)	−0.0517(8)	0.1712(5)
C(4)	−0.375(1)	0.151(1)	0.3348(6)	C(16)	0.110(1)	−0.0352(8)	0.1133(5)
C(5)	−0.335(1)	0.262(1)	0.3261(6)	C(17)	0.182(1)	0.0434(9)	0.0580(5)
C(6)	0.141(1)	−0.0421(9)	0.3901(5)	C(18)	0.345(1)	0.0094(9)	0.0673(5)
Compound **8**·THF							
Rh(1)	0.3597(2)	0.1155(2)	0.04160(8)	Ti(1)	0.0726(4)	0.07	
S(1)	0.0817(6)	0.1840(6)	−0.0898(3)	S(2)	0.2700(6)	−0.0139(5)	−0.0209(3)
O(1)	0.912(2)	0.0880	1/4	C(1)	−0.049(5)	−0.059(4)	−0.049(1)
C(2)	−0.127(4)	0.019(4)	−0.023(2)	C(3)	−0.116(4)	0.006(4)	0.036(2)
C(4)	−0.031(4)	−0.081(4)	0.046(1)	C(5)	0.011(3)	−0.121(3)	−0.006(2)
C(6)	0.195(3)	0.152(3)	−0.143(1)	C(7)	0.309(3)	0.107(3)	−0.126(1)
C(8)	0.327(2)	−0.004(2)	−0.094(1)	C(9)	0.501(2)	0.189(2)	−0.007(1)
C(10)	0.541(2)	0.090(2)	0.022(1)	C(11)	0.586(2)	0.135(2)	0.082(1)
C(12)	0.471(2)	0.171(2)	0.110(1)	C(13)	0.432(2)	0.261(2)	0.085(1)
C(14)	0.523(2)	0.298(2)	0.041(1)	C(15)	0.637(2)	0.258(2)	0.064(1)

chelating ethanedithiolate ligands. The geometry about Ti is similar to that previously described for $[CpTi(SCH_2CH_2CH_2S)_2Na(THF)_x]_n$.[3] Three of the four sulfur atoms bridge to the Cu center at distances of 2.334(2), 2.3901(1), and 2.383(1) Å. These Cu–S distances are significantly longer than those seen in $[Cp_2Ti(SEt)_2CuL]^+$ (2.269(2), 2.261(2), 2.238(5), 2.240(4) Å) reflecting the Lewis acidity of the Ti center in **4**.[14,17] The fourth sulfur is 3.73 Å from the Cu, and thus the Cu atom is not directly "trans" to the cyclopentadienyl ring. Rather, it is slightly askew to accommodate the pseudotetrahedral coordination sphere of Cu, which is completed by the terminal PMe_3 ligand. One of the three bridging-sulfur Ti–S distances (2.563(2) Å) is considerably longer than the other two (2.448(1) and 2.403(2) Å). The observed variation in the Ti–S bond lengths may reflect steric conflicts between the phosphine on Cu and the methylene groups of the dithiolate ligands. Each of the bridging Ti–S distances are longer than the single terminal Ti–S bond (2.372(2) Å), which is typical. Ti–C and Cu–P distances are typical and require no further comment.

Metal–metal distances as well as angles at bridging atoms have been used in the past to infer the presence of direct metal–metal interactions.[1] The Cu···Ti approach in **4** (2.720(1) Å) is significantly shorter than those seen in the related species $[Cp_2Ti(SEt)_2CuL]^+$ (2.803(3)–2.847(2) Å) and $[Cp_2Ti(SCH_2CH_2PPh_2)_2Cu]^+$ (3.024(1) Å)[13–15], while the Cu–S–Ti angles in **4** are 69.29(4), 69.15(4), and 66.60(4)°. These structural data support the notion of a dative $d^{10} \rightarrow d^0$ interaction in **4** similar to that described for a series of related thiolate-bridged heterobimetallics.[1,13–17]

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Table 3. Selected Bond Distances and Angles

Compound **4**

Bond Distances (Å)

Cu(1)–Ti(1)	2.720(1)	Ti(1)–S(3)	2.403(2)	S(1)–C(6)	1.809(5)
Cu(1)–S(1)	2.334(2)	Ti(1)–S(4)	2.563(2)	S(2)–C(7)	1.818(5)
Cu(1)–S(3)	2.390(1)	Ti(1)–C(1)	2.381(5)	S(3)–C(8)	1.836(5)
Cu(1)–S(4)	2.383(1)	Ti(1)–C(2)	2.381(5)	S(4)–C(9)	1.828(5)
Cu(1)–P(1)	2.196(1)	Ti(1)–C(3)	2.387(5)	P(1)–C(10)	1.812(6)
Ti(1)–S(1)	2.448(1)	Ti(1)–C(4)	2.387(5)	P(1)–C(11)	1.817(5)
Ti(1)–S(2)	2.372(2)	Ti(1)–C(5)	2.385(5)	P(1)–C(12)	1.805(6)

Bond Angles (deg)

S(1)–Cu(1)–S(3)	110.31(5)	S(3)–Cu(1)–S(4)	82.35(5)	Cu(1)–S(3)–C(8)	92.0(2)
S(1)–Cu(1)–S(4)	80.37(5)	S(3)–Cu(1)–P(1)	116.55(5)	Cu(1)–S(4)–Ti(1)	66.60(4)
S(1)–Cu(1)–P(1)	125.08(5)	S(3)–Ti(1)–S(4)	78.42(5)	Cu(1)–S(4)–C(9)	100.8(2)
S(1)–Ti(1)–S(2)	81.94(5)	S(4)–Cu(1)–P(1)	131.46(6)	Ti(1)–S(1)–C(6)	107.0(2)
S(1)–Ti(1)–S(3)	106.12(5)	Cu(1)–S(1)–Ti(1)	69.29(4)	Ti(1)–S(2)–C(7)	105.0(2)
S(1)–Ti(1)–S(4)	74.77(5)	Cu(1)–S(1)–C(6)	107.2(2)	Ti(1)–S(3)–C(8)	107.6(2)
S(2)–Ti(1)–S(3)	86.38(6)	Cu(1)–S(3)–Ti(1)	69.15(4)	Ti(1)–Cu(1)–P(1)	167.48(5)
S(2)–Ti(1)–S(4)	147.18(6)				

Compound **6**

Bond Distances (Å)

Cu(1)–P(1)	2.286(6)	Ti(1)–S(3)	2.432(7)	Ti(1)–C(5)	2.42(2)
Cu(1)–P(2)	2.280(7)	Ti(1)–S(4)	2.439(7)	S(1)–C(6)	1.80(2)
Cu(1)–P(3)	2.293(7)	Ti(1)–C(1)	2.47(2)	S(2)–C(7)	1.89(20
Cu(1)–P(4)	2.277(7)	Ti(1)–C(2)	2.47(2)	S(3)–C(8)	1.82(2)
Ti(1)–S(1)	2.437(7)	Ti(1)–C(3)	2.44(3)	S(4)–C(9)	1.86(2)
Ti(1)–S(2)	2.414(7)	Ti(1)–C(4)	2.45(2)		

Bond Angles (deg)

P(1)–Cu(1)–P(2)	90.5(2)	S(1)–Ti(1)–S(2)	82.2(3)	S(3)–Ti(1)–S(4)	81.9(2)
P(1)–Cu(1)–P(3)	122.5(2)	S(1)–Ti(1)–S(3)	82.3(2)	Ti(1)–S(2)–C(7)	107.8(8)
P(1)–Cu(1)–P(4)	115.6(2)	S(1)–ti(1)–S(4)	154.2(3)	Ti(1)–S(2)–C(7)	107.8(8)
P(2)–Cu(1)–P(3)	116.4(2)	S(2)–Ti(1)–S(3)	106.2(3)	Ti(1)–S(3)–C(8)	108.1(7)
P(2)–Cu(1)–P(4)	124.7(3)	S(2)–Ti(1)–S(4)	82.8(3)	Ti(1)–S(4)–C(9)	100.1(7)
P(3)–Cu(1)–P(4)	90.5(2)				

Compound **7**

Bond Distances (Å)

Rh(1)–Ti(1)	2.915(2)	Rh(1)–C(16)	2.183(9)	Ti(1)–C(3)	2.351(9)
Rh(1)–S(1)	2.563(3)	Ti(1)–S(1)	2.397(3)	Ti(1)–C(4)	2.37(1)
Rh(1)–S(3)	2.496(3)	Ti(1)–S(2)	2.380(3)	Ti(1)–C(5)	2.39(1)
Rh(1)–S(4)	2.372(3)	Ti(1)–S(3)	2.541(3)	S(1)–C(6)	1.82(1)
Rh(1)–C(12)	2.054(9)	Ti(1)–S(4)	2.406(3)	S(2)–C(8)	1.81(1)
Rh(1)–C(13)	2.095(9)	Ti(1)–C(1)	2.38(1)	S(3)–C(9)	1.83(1)
Rh(1)–C(15)	2.226(9)	Ti(1)–C(2)	2.367(9)	S(4)–C(11)	1.836(9)

Bond Angles (deg)

S(1)–Rh(1)–S(3)	68.94(8)	S(3)–Rh(1)–C(13)	164.6(3)	Rh(1)–S(4)–Ti(1)	75.21(9)
S(1)–Rh(1)–S(4)	102.41(9)	S(3)–Rh(1)–C(15)	118.2(3)	Rh(1)–S(4)–C(11)	106.7(4)
S(1)–Rh(1)–C(12)	163.1(3)	S(3)–Rh(1)–C(16)	95.2(2)	Ti(1)–S(1)–C(6)	113.1(3)
S(1)–Rh(1)–C(13)	125.9(3)	S(3)–Ti(1)–S(4)	80.99(9)	Ti(1)–S(2)–C(8)	110.1(3)
S(1)–Rh(1)–C(15)	86.0(2)	S(4)–Rh(1)–C(12)	90.4(3)	Ti(1)–S(3)–C(9)	108.4(4)
S(1)–Rh(1)–C(16)	103.6(3)	S(4)–Rh(1)–C(13)	96.3(3)	Ti(1)–S(4)–C(11)	115.0(3)
S(1)–Ti(1)–S(2)	85.8(1)	S(4)–Rh(1)–C(15)	159.2(3)	C(12)–Rh(1)–C(13)	40.2(3)
S(1)–Ti(1)–S(3)	70.8(1)	S(4)–Rh(1)–C(16)	151.1(3)	C(12)–Rh(1)–C(15)	78.4(4)
S(1)–Ti(1)–S(4)	106.5(1)	Rh(1)–S(1)–Ti(1)	71.91(8)	C(12)–Rh(1)–C(16)	67.0(4)
S(2)–Ti(1)–S(3)	149.1(1)	Rh(1)–S(1)–C(6)	116.8(4)	C(13)–Rh(1)–C(16)	63.8(4)
S(2)–Ti(1)–S(4)	86.9(1)	Rh(1)–S(3)–Ti(1)	70.73(7)	C(13)–Rh(1)–C(16)	78.3(3)
S(3)–Rh(1)–S(4)	82.62(9)	Rh(1)–S(3)–C(9)	109.8(3)	C(15)–Rh(1)–C(16)	36.2(3)
S(3)–Rh(1)–C(12)	124.5(3)				

Compound **8**·THF

Bond Distances (Å)

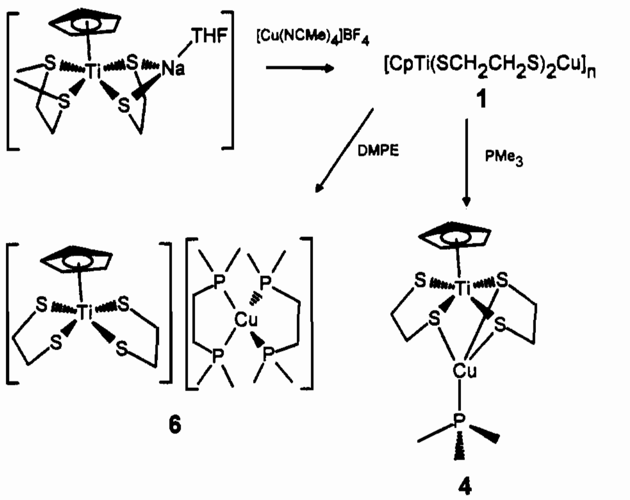
Rh(1)–Ti(1)	3.436(4)	Rh(1)–C(13)	2.10(2)	Ti(1)–C(2)	2.33(3)
Rh(1)–S(1)	2.324(6)	S(1)–C(6)	1.85(3)	Ti(1)–C(3)	2.38(4)
Rh(1)–S(2)	2.319(6)	Ti(1)–S(1)	2.466(6)	Ti(1)–C(4)	2.43(4)
Rh(1)–C(9)	2.17(2)	Ti(1)–S(2)	2.496(7)	Ti(1)–C(5)	2.41(4)
Rh(1)–C(10)	2.11(2)	Ti(1)–C(1)	2.35(4)	S(2)–C(8)	1.86(2)
Rh(1)–C(12)	2.12(2)				

Bond Angles (deg)

S(1)–Ti(1)–S(2)*	74.0(2)	S(1)–Ti(1)–S(1)*	134.1(3)	C(12)–Rh(1)–C(13)	37.6(9)
S(1)*–Ti(1)–S(2)*	74.0(2)	S(1)*–Ti(1)–S(2)*	89.9(2)	Rh(1)–Ti(1)–Rh(1)	79.20(8)
S(1)–Ti(1)–S(2)	89.9(2)	S(1)–Rh(1)–S(2)	80.1(2)	Rh(1)–S(1)–Ti(1)	91.6(2)
S(2)–Ti(1)–S(2)*	138.3(3)	C(9)–Rh(1)–C(10)	38.3(8)	Rh(1)–S(2)–Ti(1)	91.0(2)

In contrast, the crystallographic data for **6** reveals that this species is a pair of discrete ions. The Ti-based anion is shown in Figure 2. The cation $[\mathrm{Cu(DMPE)_2}]^+$ is a typical pseudotetrahedral Cu(I) complex while the anion is a four-legged Ti piano stool similar in geometry to the Ti center in $[\mathrm{CpTi(SCH_2CH_2CH_2S)_2Na(THF)}_x]_n$[3] as exemplified by the Ti–S distances,

Scheme 1



which average 2.431(3) Å in **6**. It is noteworthy that the terminal Ti–S bond in **4** is shorter than those observed in **6** consistent with the diminished electron density at Ti as a result of donation of electron density from S to Cu.

An ORTEP drawing of the Ti/Rh bimetallic complex **7** is shown in Figure 3. The gross structural features of this compound are very similar to those described for **4**. Three of the four sulfur atoms which comprise the legs of the Ti-based piano stool bridge to the Rh center. The bridging sulfur atoms give rise to Ti–S distances of 2.397(3), 2.541(3), and 2.406(3) Å. The terminal Ti–S distance is 2.380(3) Å, much shorter than the bridging Ti–S distances. The Rh–S distances are 2.373(3), 2.496(3), and 2.563(3) Å. This variation, like that observed in **4**, may reflect steric conflicts between the NBD ligand, which completes the Rh coordination sphere, and the methylene chains of the dithiolates. The known preference of Rh for square planar coordination geometry as well as these steric factors may contribute to the observed distortion in the pseudo trigonal bipyramidal Rh coordination sphere. The Rh–S distances compare with those found in $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Rh]^+$ (2.349(3), 2.380(3) Å) and reflect the greater Lewis acidity of the Ti center in **6**.[16] Similar to observations in **4**, the vector formed by the centroid of the cyclopentadienyl ring, Ti, and Rh is not linear. The bridging S–Rh distances average 2.477(6) Å, while the terminal Ti-bound sulfur atom is 3.97 Å from Rh. The Rh–Ti distance in **7** is 2.915(2) Å, and the Rh–S–Ti angles are 71.91(8), 70.73(7), and 75.21(9)°. These structural features are consistent with dative donation from the electron rich Rh center to the electron deficient Ti. It is noteworthy that the Ti–Rh distance is significantly shorter than that observed in $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2Rh]^+$ (3.127(2) Å).[16]

The compound **8** contains a similar piano stool type Ti fragment. The ORTEP drawing of this molecule is shown in Figure 4. The sulfur atoms bridge in a pairwise fashion to two pseudo square planar Rh atoms, forming a S–Rh–S angle of 80.1(2)°. It is also noteworthy that chelation to Rh occurs via sulfur atoms that are not in the same dithiolate fragment. This presumably precludes additional steric interaction between the methylene chains and the diene which completes the Rh coordination sphere. The geometry of the Rh–NBD fragments are typical. The Ti–S distances of 2.466(6) and 2.496(7) Å do not show any significant lengthening compared to those observed in the related Ti(IV) species **7** in spite of the fact that the Ti center in **8** is formally Ti(III). The absence of direct Ti–Rh interactions in **8** is indicated by the Ti–S–Rh angles, which are 91.6(2) and 91.0(2)°, and the Ti–Rh distance of 3.437(5) Å. These contrast dramatically with the analogous parameters in **7**.

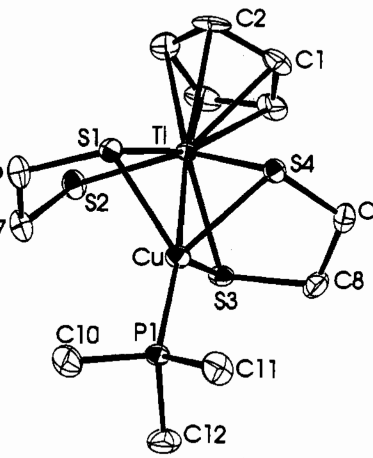


Figure 1. ORTEP drawing of molecule **4**. The 30% thermal ellipsoids are shown; hydrogen atoms are omitted for clarity.

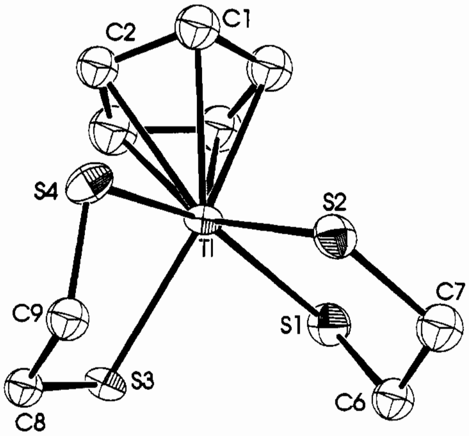


Figure 2. ORTEP drawing of the anion in molecule **6**. The 30% thermal ellipsoids are shown; hydrogen atoms are omitted for clarity.

Discussion

The structure of the oligomeric or polymeric materials **1**–**3** is the subject of speculation. One might consider the metal ion replacing the $Na(THF)_x$ unit in the precursors, thus providing a polymeric chain similar to that previously established for $[CpTi(SCH_2CH_2CH_2S)_2Na(THF)_x]_n$.[3] However, the structures of **4** suggest an alternative in which the ancillary ligands (PMe_3) are replaced by a "fourth" sulfur of an adjacent molecule. Such a structure would require a minimum of molecular reorganization for degradation of the polymer to heterobimetallic species by ancillary ligand addition. While this postulate is favored on intuitive grounds, it is yet to be confirmed as X-ray data for the insoluble materials **1**–**3** are not available.

Structural and theoretical data[13] support the notion of metal–metal bonding in the heterobimetallic complexes which incorporate metallocene–dithiolate metalloligands. In these cases, Ti–M distances as low as 2.765 Å have been observed and the interaction is explained in terms of dative donation from the late metal center to vacant molecular orbitals on Ti derived from the $1a_1$ Frontier orbital for the Cp_2Ti fragment.[18] The structural data for **4** and **7** reveal Ti...M distances of 2.720(1) and 2.915(2) Å, respectively, suggesting the presence of significant metal–metal interactions.[17] In the case of **4**, the distance is significantly shorter than the Ti...Cu distances seen in related thiolato-bridged Ti/Cu compounds (e.g. $[Cp_2Ti(SCH_2CH_2PPh_2)_2Cu]^+$, 3.0241(1) Å;[14] $[Cp_2Ti(SEt)_2Cu(NCMe)_2]^+$, 2.847(2) Å;[15] $[Cp_2Ti(SEt)_2CuPPh_3]^+$ 2.803(3) Å[6]). Similarly, the distance in **7** is much shorter than that seen in $[Cp_2Ti(SCH_2CH_2CH_2PPh_2)_2$-

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[18] Hoffmann, R.; Lauher, J. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

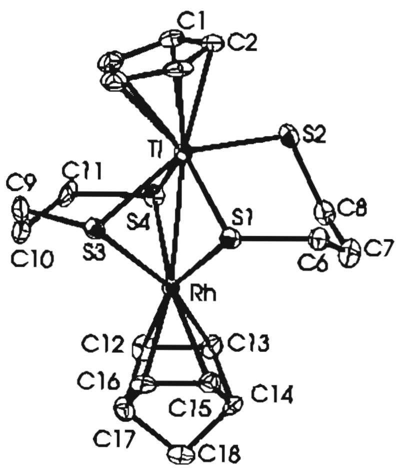


Figure 3. ORTEP drawing of molecule **7**. The 30% thermal ellipsoids are shown; hydrogen atoms are omitted for clarity.

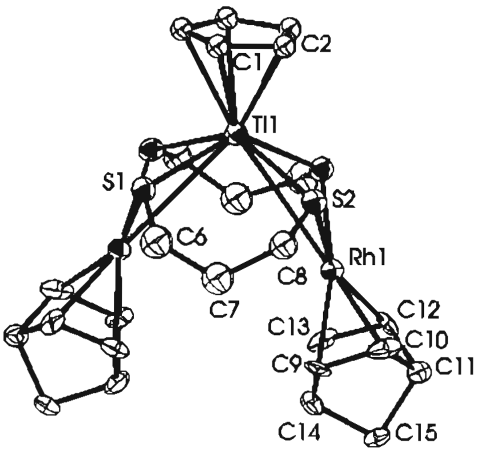
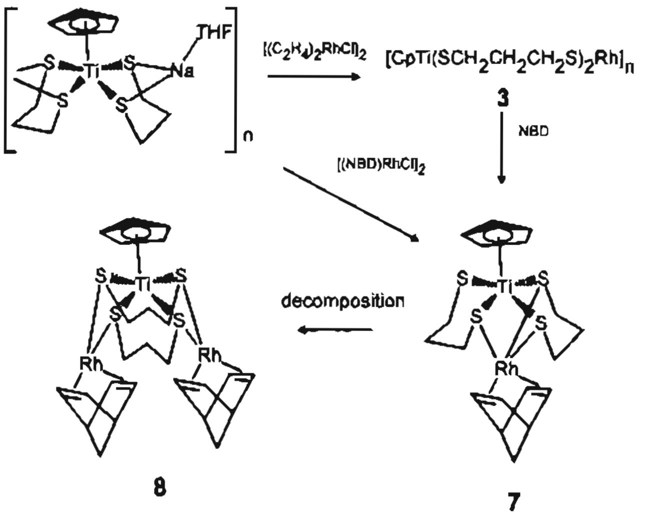


Figure 4. ORTEP drawing of molecule **8**. The 30% thermal ellipsoids are shown; hydrogen atoms are omitted for clarity. Only one orientation of the disordered cyclopentadienyl ring is shown.

Scheme 2



Rh]$^+$ (3.127(2) Å).[16] Previously published molecular orbital calculations have shown that the LUMO for four-legged piano stool complexes is derived from the d_{z^2} orbital on the metal center.[3,19,20] In the present heterobimetallic compounds such a vacant orbital on the Ti fragment is in the direction of the late metal center:

This suggests a venue for dative donation from the d^{10} Cu or d^8 Rh centers to the Lewis acidic Ti. In the formally reduced Ti(III) species **8**, the orbital that is largely d_{z^2} in character becomes the SOMO. The occupation of this orbital by a single electron diminishes the ability of the Ti to accept electron density from the Rh center, resulting in the altered coordination mode to Rh. The absence of a metal–metal interaction in **8** presumably leads to the absence of hyperfine coupling to Rh in the EPR spectrum. In contrast, it should be noted that where such metal–metal interactions are imposed by ligand restraints such as [Cp$_2$Ti(SCH$_2$CH$_2$CH$_2$PPh$_2$)$_2$Rh]^0, hyperfine coupling between the lone electron on Ti and Rh is observed.[16]

Summary

Little is known regarding the precise structures of the insoluble Cu(I) and Rh(I) derivatives of the anions [CpTi(S(CH$_2$)$_n$S)$_2$]$^-$ (**1**–**3**). Nonetheless, the structural data obtained for the heterobimetallics **4** and **7** suggest that **1**–**3** are oligomers of formulae [CpTi(S(CH$_2$)$_n$S)$_2$M]$_n$. Further, it has been demonstrated that the salts [CpTi(S(CH$_2$)$_y$S)$_2$Na(THF)$_x$]$_n$ are useful synthons for heterobimetallic compounds, allowing the facile incorporation of Ti centers with increased Lewis acidity relative to those seen in heterobimetallic derivatives of titanocene–dithiolates. Aspects of the chemistry of such heterobimetallics arising from this increased Lewis acidity are the subject of current study.

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Supplementary Material Available: Tables of crystallographic, hydrogen atom, and the thermal parameters and bond distances and angles for **4**, **6**, **7**, and **8** and on ORTEP diagrams of the structure of the cation of **6** (29 pages). Ordering information is given on any current masthead page.

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(19) Curnow, O. J.; Curtis, M. D.; Rheingold, A.; Haggerty, B. S. *Inorg. Chem.* **1991**, *30*, 4043.

(20) Kubacek, D. L.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180.