Inorg. Chem. **1993**, *32*, 5933-5938 **5933**

Radical Routes to Titanium(IV) Thiolate Complexes: Structure and Reactivity of (η^5-C_5H_5)Ti^{III} and -Ti^{IV} Donor and Thiolate Derivatives

T. Timothy Nadasdi and Douglas W. Stephan*

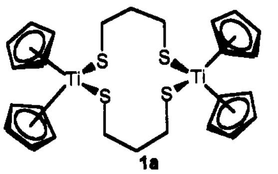
Department of Chemistry and Biochemistry, University of Windsor, Windsor, ON, Canada N9B 3P4

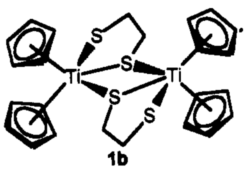
Received June 3, 1993[⊗]

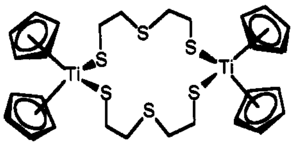
Reaction of Cp_2TiCl_2 with donor ligands such as imidazole or PMe_3 proceeds to a relatively small extent to induce reduction of Ti(IV) yielding the Ti(III) species $Cp_2TiCl(L)$ (**3**) with concurrent loss of a chlorine radical. Subsequent reaction of **3** with 1 equiv of 1,3-propanedithiol gives $[Cp_2TiCl]_2(SCH_2CH_2CH_2S)$ (**4**). In the presence of excess dithiol the known species $[Cp_2Ti(SCH_2CH_2CH_2S)]_2$ (**1a**) is formed. Related reactions of $CpTiCl_3$ have been studied. Reaction of $CpTiCl_3$ with PMe_3 or $PHEt_2$ yields the Ti(IV) adducts $CpTiCl_3(L)$ (L = PMe_3 (**5a**), $PHEt_2$ (**5b**)). The complex **5a** crystallizes in the space group $P2_1/n$ with $a = 8.777(9)$ Å, $b = 13.033(3)$ Å, $c = 11.350(4)$ Å, $\beta = 98.14(7)°$, $V = 1285(3)$ Å^3, and $Z = 4$. The complex **5b** crystallizes in the space group $P2_1/n$ with $a = 7.502(3)$ Å, $b = 16.723(6)$ Å, $c = 10.961(2)$ Å, $\beta = 92.55(2)°$, $V = 1374(1)$ Å^3, and $Z = 4$. Also generated in these reactions are small quantities of the reduced species $CpTiCl_2(L)_2$ (L = PMe_3 (**7a**), $PHEt_2$ (**7b**)), which were characterized by EPR spectroscopy. In similar reactions the reduced species $CpTiCl_2(L)_2$ (L = imidazole (**7c**), methylimidazole (**7d**) are isolated. The compound **7d** crystallizes in the space group $C2_1/c$ with $a = 12.715(5)$ Å, $b = 9.594(2)$ Å, $c = 14.428(4)$ Å, $\beta = 115.00(2)°$, $V = 1595(2)$ Å^3, and $Z = 4$. Reaction of **7d** with 1,2-ethanedithiol give the species $[CpTiCl(SCH_2CH_2S)]_2$ (**8**), which crystallizes in the space group $P2_1/a$ with $a = 12.991(7)$ Å, $b = 8.582(3)$ Å, $c = 17.681(7)$ Å, $\beta = 105.75(4)°$, $V = 1898(3)$ Å^3, and $Z = 4$. Similarly, reaction of **7d** with 1,3-propanedithiol gives the known species $CpTiCl(SCH_2CH_2CH_2S)$ (**9**). Reaction of **8** with a donor (imidazole or PMe_3) and $(PhS)_2$ gives the product $[CpTi(SCH_2CH_2S)(SPh)]_2$ (**10**). This complex crystallizes in the space group $P\bar{1}$ with $a = 9.459(4)$ Å, $b = 10.931(3)$ Å, $c = 9.258(3)$ Å, $\alpha = 106.12(2)°$, $\beta = 114.50(3)°$, $\gamma = 95.01(3)°$, $V = 814.1(5)$ Å^3, and $Z = 1$. In a similar reaction, **9** reacts with PMe_3 to generate the Ti(III) species $CpTi(SCH_2CH_2CH_2S)(PMe_3)_2$ (**11**), which undergoes subsequent reaction with $(PhS)_2$ to give the known product $CpTi(SCH_2CH_2CH_2S)(SPh)$ (**12**). The reactivity, structural, and electrochemical data presented herein suggest that a radical mechanism is operative in the formation of **1**, **4**, **8–10**, and **12**. Such a mechanistic proposal does offer an explanation for the previously observed "base dependence" of thiolate substitution reactions at Ti(IV).

Introduction

We have had a continuing interest in the chemistry of early-metal thiolate derivatives primarily focusing on their ability to act as synthons for early–late heterobimetallic complexes.[1-12] These efforts resulted recently in the syntheses of a series of macrocyclic compounds of the form $[Cp_2Ti(S(CH_2)_nS)]_2$ (n = 3 (**1a**),2 (**1b**))[2] and $[Cp_2Ti(S(CH_2)_nS(CH_2)_nS)]_2$ (n = 3 (**2a**), 2 (**2b**)).[1] These species are capable of late-metal complexation as well as thiolate-transfer reactions. A further interesting feature of these macrocycles concerns the mechanism of their formation. Previous attempts to prepare dithiolate derivatives of titanocene via the reaction of Cp_2TiCl_2 and dithiol in the presence of NEt_3 led only to insoluble, poorly characterized but apparently polymeric products.[13] Similar results are derived by the use of sodium or lihtium dithiolate salts.[14] In contrast, our successful preparations of the above macrocyclic compounds were achieved via reaction of Cp_2TiCl_2 and dithiol in the presence of imidazole.[1,2] This curious base dependence has spawned the present report. We have examined spectroscopically the reactions of Cp_2TiCl_2 with imidazole and other donors. Further, we have studied the related formations of thiolate derivatives of $CpTiCl_3$. These spectroscopic studies, together with the isolation and structural characterization of intermediates, suggest a radical reaction mechanism may be operative in these substitution reactions.


1a


1b


2b

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 by employing either Schlenk line techniques or a Vacuum Atmospheres inert-atmosphere glovebox. Solvents were reagent grade, distilled from the appropriate drying agents under N_2 and degassed by the freeze–thaw method at least three times prior to use. $^{31}P\{^1H\}$, ^{31}P, ^1H, and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AC-300 and AC-200 spectrometers. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to $SiMe_4$ for ^1H and $^{13}C\{^1H\}$ NMR spectra, while 85% H_3PO_4 is the external reference for ^{31}P NMR data. X-band EPR spectra were recorded on a Bruker EPS-300e EPR spectrometer. Quantitation of the EPR signal intensities were performed by employing $Cp_2TiCl(PMe_3)$[15] as the external reference. Integrations of the digitized spectra were performed using the Bruker

---

[⊗] Abstract published in *Advance ACS Abstracts*, November 15, 1993.

(1) Huang, Y.; Drake, R. J.; Stephan, D. W. *Inorg. Chem.* **1993**, *32*, 3022.
(2) Nadasdi, T. T.; Stephan, D. W. *Organometallics* **1992**, *11*, 116.
(3) Stephan, D. W. *J. Chem. Soc., Chem. Commun.* **1991**, 121.
(4) Stephan, D. W. *Organometallics* **1991**, *10*, 2037.
(5) Rousseau, R.; Stephan, D. W. *Organometallics* **1991**, *10*, 3399.
(6) Wark, T. A.; Stephan, D. W. *Inorg. Chem.* **1990**, *29*, 1731.
(7) Wark, T. A.; Stephan, D. W. *Organometallics* **1989**, *8*, 2836.
(8) Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 42.
(9) White, G. S.; Stephan, D. W. *Organometallics* **1988**, *7*, 903.
(10) White, G. S.; Stephan, D. W. *Organometallics* **1987**, *6*, 2169.
(11) Wark, T. A.; Stephan, D. W. *Inorg. Chem.* **1987**, *26*, 363.
(12) White, G. S.; Stephan, D. W. *Inorg. Chem.* **1985**, *24*, 1499.
(13) Kopf, H.; Schmidt, M. *J. Organomet. Chem.* **1965**, *4*, 426.
(14) Stone, F. G. A.; Chaudhary, M. A. *J. Chem. Soc. A* **1966**, 838.

0020-1669/93/1332-5933$04.00/0

software package WIN-EPR. Cyclic voltammetry experiments were performed using a BAS CV-27 potentiometer employing NBu_4BPh_4 as the supporting electrolyte, a Pt disk as the working electrode, and Ag/AgCl electrode as the reference. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, TN, and Schwarzkopf Laboratories, Woodside, NY. Cp_2TiCl_2, imidazole (imid), methylimidazole (Meimid), 1,2-ethanedithiol, 1,3-propanedithiol, diphenyl disulfide, and benzenethiol were purchased from the Aldrich Chemical Co. PMe_3, $PHEt_2$, and bis(dimethylphosphino)ethane (dmpe) were purchased from Strem Chemical Co. $CpTiCl_3$(dmpe)[16] and authentic samples of $CpTi(SCH_2CH_2CH_2S)Cl$ (**9**) and $CpTi(SCH_2CH_2CH_2S)(SPh)$ (**10**)[1] were prepared by literature methods.

Reactions of Cp_2TiCl_2 and Donors. Generation of $Cp_2TiCl(L)$ (L = PMe_3 (3a), $PHEt_2$ (3b), imid (3c), Meimid (3d)). Cp_2TiCl_2 (100 mg, 0.38 mmol) was dissolved in 2 mL of THF, and stoichiometric equivalents or excesses of the appropriate ligand were added. The solutions were monitored by ^{31}P NMR and by EPR. EPR (THF, 25 °C, g): **3a**, 1.987 (d), $\langle a_P \rangle = 20.4$ G, $\langle a_{Ti} \rangle = 10.6$ G; **3b**, 1.987 (d), $\langle a_P \rangle = 19.6$ G, $\langle a_{Ti} \rangle = 11.4$ G; **3c**, 1.977 (br s), $\langle a_{Ti} \rangle = 12.5$ G; **3d**, 1.975 (br s), $\langle a_{Ti} \rangle = 12.0$ G.

Synthesis of $[Cp_2TiCl]_2(SCH_2CH_2CH_2S)$ (4). Method i. To a stirring mixture of Cp_2TiCl_2 (100 mg, 0.40 mmol) and imidazole (164 mg, 2.40 mmol) in THF was added 1,3-propanedithiol (22 mg, 0.20 mmol). The solution was stirred for 10 min, the solvent removed, and the residue extracted into C_6D_6 and monitored by ^1H NMR. Concentration of the solvent afforded **4** in 70% yield.

Method ii. $[Cp_2TiCl]_2$ (50 mg, 0.12 mmol) was dissolved in C_6H_6, and 1,3-propanedithiol (13 mg, 0.12 mmol) was added. After the solution was stirred for 10 min, the solvent was removed and the residue dissolved in C_6D_6 and monitored by ^1H NMR. Concentration of the solvent afforded **4** in 90% yield. ^1H NMR (C_6D_6, 25 °C, δ): 5.87 (s, 20H, Cp); 3.81 (t, 4H, CH_2, $|J_{H-H}| = 6.70$ Hz); 2.20 (q, 2H, CH_2, $|J_{H-H}| = 6.70$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C, δ): 114.96 (s, Cp); 44.05 (s, CH_2); 35.71 (s, CH_2). Anal. Calcd for $C_{23}H_{26}Cl_2S_2Ti_2$: C: 51.80; H: 4.91; Found: C: 52.10; H: 4.98.

Synthesis of $CpTiCl_3(L)$ (L = PMe_3 (5a), $PHEt_2$ (5b)) and Generation of $CpTiCl_2(L)_2$ (L = PMe_3 (7a), $PHEt_2$ (7b)). These compounds were prepared in similar fashions with the appropriate ligand substitution. Thus only one preparation is described. To a THF (2 mL) solution of $CpTiCl_3$ (50 mg, 0.23 mmol) was added PMe_3 (52 mg, 0.69 mmol). The solution became bright orange. Crystals of **5a** were obtained in 90% yield upon standing of the solution. **5a**: Orange crystals, yield 90%. $^{31}P\{^1H\}$ NMR (THF, 25 °C, δ, ppm): 12.3. $^{13}C\{^1H\}$ NMR (THF, 25 °C, δ, ppm): 121.7 (s, Cp), 15.5 (d, CH_3, $|J_{P-C}| = 22.0$ Hz). ^1H NMR (C_6D_6, 25 °C, δ, ppm): 6.07 (s, Cp, 5H), 0.83 (d, CH_3, 9H, $|J_{P-H}| = 8.8$ Hz). Anal. Calcd for $C_8H_{14}Cl_3PTi$: C, 32.52; H, 4.78. Found: C, 33.10; H, 4.67. **5b**: Bright orange crystals, yield 85%, ^{31}P NMR (C_6H_5-CH_3, −83 °C, δ, ppm): 18.8 (d, $|J_{P-H}| = 328.4$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −83 °C, δ, ppm): 122.6 (s, Cp), 42.2 (br, CH_2), 25.1 (s, CH_3). ^1H NMR (CD_2Cl_2, −83 °C, δ, ppm): 6.57 (s, Cp, 5H), 4.51 (d, PH, 1H, $|J_{P-H}| = 328.4$ Hz), 3.35 (q, CH_2, 4H), 1.08 (t, CH_3, 9H, $|J_{H-H}| = 6.9$ Hz). Anal. Calcd for $C_9H_{16}Cl_3PTi$: C, 34.93; H, 5.21. Found: C, 35.15; H, 5.24. EPR (THF, 25 °C, g): **7a**, 1.982, $\langle a_P \rangle = 25.0$ G, $\langle a_{Ti} \rangle = 12.1$ G; **7b**, 1.983, $\langle a_P \rangle = 18.7$ G; $\langle a_{Ti} \rangle = 10.0$ G.

Synthesis of $CpTiCl_2(L)_2$ (L = imid (7c), Meimid (7d)). These compounds were prepared in similar fashions, thus, only one preparation is described. To a THF (2 mL) solution of $CpTiCl_3$ (50 mg, 0.23 mmol) was added imidazole (48 mg, 0.69 mmol). The solution developed a slight brown tinge and gave a brown precipitate. This precipitate is insoluble and diamagnetic; however, crystals of **7d** were obtained in 10% yield upon standing of the mothor liquor. **7c**: Yield 2%. EPR (THF, 25 °C, g): 1.977, $\langle a_{Ti} \rangle = 12.0$ G. **7d**: Yield 10%. EPR (THF, 25 °C, g): 1.977 (br s), $\langle a_{Ti} \rangle = 13.8$ G. Anal. Calcd for $C_{13}H_{17}Cl_2N_4Ti$: C, 44.85; H, 4.92. Found: C, 44.80; H, 4.88.

Synthesis of $[CpTiCl(SCH_2CH_2S)]_2$ (8). Method i. To a 5-mL CH_2Cl_2 solution of $CpTiCl_3$ (100 mg, 0.46 mmol) was added imidazole (94 mg, 1.38 mmol). This resulted in a dark red-black insoluble precipitate. 1,2-Ethanedithiol (43 mg, 0.43 mmol) was added and the resulting mixture stirred for 12 h. The dark precipitate slowly dissolved and was replaced with a white precipitate, which was filtered off. Diethyl ether was added to the filtrate, and red-black block-like crystals were obtained upon standing for 3 days. Yield: 77%.

Method ii. To a THF solution of **7d** (4 mg, 0.01 mmol) was added 1,2-ethanedithiol (0.96 μL, 0.01 mmol) in benzene. The solution changes from brown to red immediately. The solution is stirred for 15 min. Yield: 100% (by NMR). ^1H NMR (CD_2Cl_2, 25 °C, δ): 6.60 (s, 10H, Cp); 4.86 (br s, 4H, CH_2); 4.02 (br s, 4H, CH_2). $^{13}C\{^1H\}$ NMR (CH_2Cl_2, 25 °C, δ): 117.77 (s, Cp); 47.62 (br s, CH_2). Anal. Calcd for $C_{14}H_{18}Cl_2S_4Ti_2$: C, 34.94; H, 3.77. Found: C, 35.05; H, 3.76.

Synthesis of $CpTi(SCH_2CH_2CH_2S)Cl$ (9). To a solution of **7d** (4 mg, 0.01 mmol) in C_6D_6 (2 mL) was added 1,3-propanedithiol (1.15 μL, 0.01 mmol). Monitoring the reaction after 15 min by ^1H NMR revealed quantitative formation of **9**.[1]

Synthesis of $[CpTi(SPh)(SCH_2CH_2S)]_2$ (10). Method i. The compound **8** (100 mg, 0.21 mmol) and NaSPh (56 mg, 0.42 mmol) were combined in THF (5 mL). The solution changed color from red-black to black immediately. The solution was stirred for 1 h, the solvent removed, and the residue extracted into benzene. NaCl was filtered off, and black needles of **10** were obtained upon standing of the filtrate for 1 week. Yield: 100%.

Method ii. PMe_3 (22.8 mg, 0.30 mmol) was added to a THF (5 mL) solution of compound **8** (25 mg, 0.05 mmol). PhSSPh (11 mg, 0.05 mmol) was added. The solution change color from red-black to black immediately. The solution was stirred for 15 min and filtered, the solvent was removed, and the residue was extracted into CD_2Cl_2. Yield: 75% (by NMR). ^1H NMR (CD_2Cl_2, 25 °C, δ): 7.30 (d, 4H, Ph, $|J_{H-H}| = 7.39$ Hz); 6.96 (d of d, 4H, Ph, $|J_{H-H}| = 7.86$ Hz); 6.49, (t, 2H, Ph, $|J_{H-H}| = 6.93$ Hz); 6.42 (s, 10H, Cp); 3.90 (br s, 4H, CH_2); 3.50 (br s, 4H, CH_2). Anal. Calcd for $C_{26}H_{28}S_6Ti_2$: C, 49.67; H, 4.49. Found: C, 49.80; H, 4.52.

Generation of $CpTi(SCH_2CH_2CH_2S)(PMe_3)_2$ (11). To a solution of **9** (20 mg, 0.08 mmol) in THF (2 mL) was added PMe_3 (18 mg, 0.24 mmol). EPR (THF, 25 °C, g): 1.982, $\langle a_P \rangle = 24.9$ G; $\langle a_{Ti} \rangle = 12.3$ G.

Synthesis of $CpTi(SCH_2CH_2CH_2S)(SPh)$ (12). To the above solution of **11** was added $(PhS)_2$ (4.4 mg, 0.04 mmol). The solution became dark brown and subsequently orange. The solvent was removed after 30 min, the residue was dissolved in C_6D_6, and the reaction was monitored by ^1H NMR. This revealed formation of **11** in 70% yield.

X-ray Data Collection and Reduction. X-ray-quality crystals of **5a,b**, **7d**, **8**, and **10** were obtained 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. Diffraciton experiments were performed on a Rigaku AFC6 diffractometer equipped with graphite-monochromatized Mo Kα radiation. The initial orientation matrices were obtained from 20 machine-centered reflections elected by an automated peak search routine. These data were used to determine the crystal systems. Automated Laue system check routines around each axis were consistent with the crystal systems reported in Table I. Ultimately, 25 reflections ($20° < 2\theta < 25°$) 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 were consistent with the space groups given in Table I. The data sets were collected in three shells ($4.5° < 2\theta < 50.0°$), and three standard reflections were recorded every 197 reflections. The intensity measurement 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 changes over the duration of the data collections. The data were processed 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 the refinements.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[17,18] The Ti atom positions were determined using direct methods employing either the SHELX-86 or MITHRIL direct-methods routines. In each case, 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 $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of refinement all heavy atoms were assigned anisotropic temperature factors. The number of carbon atoms assigned anisotropic thermal parameters varied among the five structures and was set so as to maintain

---

(15) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Wolf, B.; Thewalt, U. *J. Organomet. Chem.* **1985**, *297*, 159.

(16) Hughes, D. L.; Leigh, G. J.; Walker, D. G. *J. Organomet. Chem.* **1988**, *355*, 113.

(17) (a) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Theor. Gen. Crystallogr.* **1968**, *A24*, 324. (b) *Ibid.* **1968**, *A24*, 390.

(18) Cromer, D. T.; Waber, J. T. *International Tables for X-ray* Crystallography; Knoch Press: Birmingham, England, 1974.

Table I. Crystallographic Parameters

	5a	**5b**	**7d**	**8**	**10**
formula	$C_8H_{14}Cl_3PTi$	$C_9H_{16}Cl_3PTi$	$C_{13}H_{17}Cl_2N_2Ti$	$C_{14}H_{18}Cl_2S_4Ti_2$	$C_{26}H_{28}S_6Ti_2$
cryst system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$P2_1/a$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	8.777(9)	7.502(3)	12.715(5)	12.991(7)	9.459(4)
b (Å)	13.033(3)	16.723(6)	9.594(2)	8.582(3)	10.931(3)
c (Å)	11.350(4)	10.961(2)	14.428(4)	17.681(7)	9.258(3)
α (deg)					106.12(2)
β (deg)	98.14(7)	92.55(2)	115.00(2)	105.75(4)	114.50(3)
γ (deg)					95.01(3)
V (Å^3)	1285(3)	1374(1)	1595(2)	1898(3)	814.1(5)
Z	4	4	4	4	1
μ (cm^{-1})	13.70	12.86	8.632	15.342	8.97
temp (°C)	24	24	24	24	24
R (%)[a]	4.51	4.22	4.76	6.99	7.13
R_w (%)[a]	3.67	3.52	3.33	5.95	4.66

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

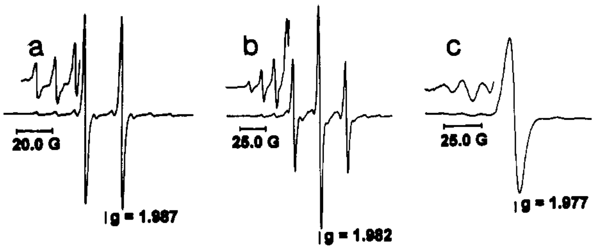
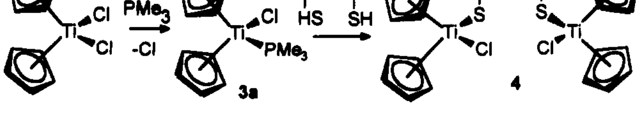


Figure 1. EPR spectra of (a) $Cp_2TiCl(PMe_3)$ (**3a**), (b) $CpTiCl_2(PMe_3)_2$ (**7a**), and (c) $CpTiCl_2(imid)_2$ (**7c**).

a reasonable data:variable ratio in each case. Hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C–H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. In all cases the hydrogen atom contributions were calculated but not refined. The final values of R and R_w are given in Table I. The maximum Δ/σ on any of the parameters in the final cycles of the refinement and the location of the largest peaks in the final difference Fourier map calculation are also given in Table I. The residual electron densities were of no chemical significance. The following data are tabulated: positional parameters (Table II) and selected bond distances and angles (Table III). Crystallographic parameters, thermal parameters, and hydrogen atom parameters have been deposited as supplementary material.

Results

Cp_2TiCl_2/Donor Reactions. In order to examine the course of these reactions leading to the synthesis of **1** and **2**, mixtures of Cp_2TiCl_2 and excess imidazole were monitored by ^1H NMR and EPR spectroscopy. NMR suggested only the presence of the starting materials, however, EPR spectra revealed the presence of a Ti(III) species which exhibited a resonance at $g = 1.977$. Analogus reactions employing phosphines provide some additional structural information as the EPR signals observed in these cases are doublets showing hyperfine coupling to a single phosphorus atom (Figure 1a), suggesting the formulation of these Ti(III) species as $Cp_2TiCl(L)$ (L = PMe_3 (**3a**), $PHEt_2$ (**3b**), imid (**3c**), Meimid (**3d**)). In the case of PMe_3, comparison of the EPR spectra to that of an authentic sample of **3a** confirmed the formulation. Attempts to isolate these reduced products from these reaction mixtures were unsuccessful. This is not surprising as quantitative measurements of the amount of Ti(III) generated in these reactions showed that approximately 2% of the Ti was reduced. It is noteworthy that no reduced species were observed for mixtures of Cp_2TiCl_2 with excess NEt_3 or PPh_3.



3a **4**

While it has been previously shown that addition of 1 equiv of 1,3-propanedithiol to Cp_2TiCl_2/imidazole reaction mixtures afforded the species **1**, addition of a half-equiv of 1,3-propanedithiol to Cp_2TiCl_2/imidazole reaction mixtures afforded the linked bimetallic species $[Cp_2TiCl]_2(SCH_2CH_2CH_2S)$ (**4**).

$CpTiCl_3$/Donor Reactions. The reactions of $CpTiCl_3$ with PMe_3 and $PHEt_2$ in carefully dried THF were monitored by ^{31}P NMR and EPR spectroscopy. NMR spectra showed resonances at 12.3 and 18.8 ppm for the PMe_3 and $PHEt_2$ reactions, respectively, indicative of coordination of phosphine to Ti(IV). Subsequent isolation of the species giving rise to the resonance at 12.3 ppm was confirmed to be $CpTiCl_3(PMe_3)$ (**5a**) crystallographically (*vide infra*). In a similar manner the species $CpTiCl_3(PHEt_2)$ (**5b**) was isolated and structurally characterized (*vide infra*). However, these Ti(IV) adducts were not the only products observed spectroscopically in these reaction mixtures. EPR spectra showed triplet resonances at $g = 1.982$ and 1.983 with $\langle a_P \rangle$ values of 25.0 and 18.7 G, respectively, for the PMe_3 and $PHEt_2$ cases (Figure 1b). These species are formulated as $CpTiCl_2L_2$ (L = PMe_3 (**7a**), $PHEt_2$ (**7b**)). Quantitative determination of the concentration of the paramagnetic Ti(III) phosphine adducts by integration of the EPR signals employing a standard Ti(III) species as a reference was consistent with the reduction of approximately 2% of the total Ti. In the case of the imidazole and methylimidazole reactions, EPR resonances are singlets at $g = 1.977$ and 1.975 with $\langle a_{Ti} \rangle$ values of 12.5 and 12.0 G, respectively (Figure 1c). These signals were attributed to the Ti(III) species $CpTiCl_2L_2$ (L = imid (**7c**), Meimid (**7d**)). In the case of **7d** the product was isolated and the formulation confirmed crystallographically (*vide infra*).

Direct or in situ reactions of **7** with 1,2-ethanedithiol affords the Ti(IV) dithiolate derivative $[CpTiCl(SCH_2CH_2S)]_2$ (**8**). The dimeric nature of **8** is suggested by its ^1H NMR spectrum and has been confirmed crystallographically (*vide infra*). Similar reaction of **7** with 1,3-propanedithiol affords the known compound $CpTi(SCH_2CH_2CH_2S)Cl$ (**9**).[1] Compound **8** reacts with $(PhS)_2$ in the presence of PMe_3 or imidazole to effect substiutiton of Cl by benzenethiolate affording $[CpTi(SCH_2CH_2S)(SPh)]_2$ (**10**). Again the dimeric formulation is consistent with the NMR data and confirmed by crystallography. The corresponding reaction of **9** with PMe_3 affords a Ti(III) species **11** which exhibits a triplet EPR spectrum at $g = 1.982$ with an $\langle a_P \rangle = 24.9$ G and is thus formulated as $CpTi(SCH_2CH_2CH_2S)(PMe_3)_2$ (**11**). Subsequent addition of $(PhS)_2$ to **11** gives the known species $CpTi(SCH_2CH_2CH_2S)(SPh)$ (**12**)[1] (Scheme I). It is noteworthy that **10** and **12** do not form in the absence of PMe_3 when $(PhS)_2$ is present.

Structural Studies. The molecular structures of **5a** (Figure 2) and **5b** (Figure 3) are similar. Each of these molecules are best described as "four-legged piano stool" type complexes with the cyclopentadienyl ligand acting as the seat and the other ligands as the legs of the stool. In the case of the Ti(IV) complexes

Table II. Positional Parameters

atom	*x*	*y*	*z*
	Compound **5a**		
Ti(1)	0.0901(1)	0.1452(1)	0.7589(1)
Cl(1)	0.3332(2)	0.0997(2)	0.8550(2)
Cl(2)	0.0458(2)	–0.0288(1)	0.7243(2)
Cl(3)	0.0578(2)	0.2447(2)	0.9238(2)
P(1)	–0.2020(2)	0.1237(1)	0.7721(2)
C(1)	0.042(2)	0.1617(9)	0.5518(7)
C(2)	–0.030(1)	0.242(1)	0.595(1)
C(3)	0.086(2)	0.3014(6)	0.6569(9)
C(4)	0.223(1)	0.255(1)	0.649(1)
C(5)	0.196(2)	0.172(1)	0.588(1)
C(6)	–0.3230(8)	0.0532(6)	0.6556(7)
C(7)	–0.2234(7)	0.0540(6)	0.9048(6)
C(8)	–0.3167(8)	0.2392(6)	0.7816(7)
	Compound **7d**		
Ti(1)	$^{1}/_{2}$	0.2305(2)	$^{1}/_{4}$
Cl	0.6775(1)	0.3575(2)	0.3406(1)
N(1)	0.4686(4)	0.2897(5)	0.3861(3)
N(2)	0.5018(4)	0.3270(5)	0.5471(4)
C(1)	0.403(1)	0.015(2)	0.233(3)
C(2)	0.403(2)	0.016(2)	0.176(2)
C(3)	0.450(3)	0.017(2)	0.161(1)
C(4)	0.509(4)	0.015(2)	0.168(2)
C(5)	0.571(2)	0.017(1)	0.217(3)
C(6)	0.5483(5)	0.3033(6)	0.4810(5)
C(7)	0.3835(5)	0.3285(7)	0.4917(5)
C(8)	0.3646(5)	0.3050(7)	0.3942(5)
C(9)	0.5645(6)	0.3476(7)	0.6566(5)
	Compound **8**		
Ti(1)	0.3763(2)	–0.1196(3)	0.3468(1)
Ti(2)	0.2683(2)	0.0695(3)	0.1385(1)
Cl(1)	0.5290(3)	0.0517(4)	0.3498(2)
Cl(2)	0.3273(3)	0.3050(4)	0.1938(2)
S(1)	0.3184(3)	0.0345(4)	0.4360(2)
S(2)	0.2108(3)	–0.0090(4)	0.2613(2)
S(3)	0.4002(3)	0.0364(4)	0.0724(2)
S(4)	0.3504(3)	–0.1729(4)	0.1996(2)
C(1)	0.425(2)	–0.273(2)	0.462(1)
C(2)	0.321(1)	–0.313(2)	0.421(1)
C(3)	0.323(2)	–0.380(2)	0.351(1)
C(4)	0.428(2)	–0.383(2)	0.349(1)
C(5)	0.494(1)	–0.318(2)	0.418(1)
C(6)	0.266(1)	0.203(1)	0.3787(8)
C(7)	0.170(1)	0.155(2)	0.3094(8)
C(8)	0.084(1)	0.087(2)	0.0954(8)
C(9)	0.120(1)	0.209(2)	0.0584(8)
C(10)	0.174(1)	0.142(2)	0.0075(7)
C(11)	0.164(1)	–0.019(2)	0.0112(8)
C(12)	0.112(1)	–0.055(2)	0.0667(8)
C(13)	0.511(1)	–0.045(2)	0.1485(7)
C(14)	0.477(1)	–0.194(2)	0.1768(7)
	Compound **10**		
Ti(1)	0.6936(3)	0.4703(2)	1.6848(3)
S(1)	0.5740(4)	0.4832(3)	1.3979(4)
S(2)	0.2724(5)	0.3791(5)	1.0559(4)
S(3)	0.9463(4)	0.5673(3)	1.7240(4)
C(1)	0.747(2)	0.265(1)	1.581(2)
C(2)	0.589(2)	0.241(1)	1.548(2)
C(3)	0.577(2)	0.278(1)	1.695(2)
C(4)	0.735(2)	0.321(1)	1.829(2)
C(5)	0.836(2)	0.312(1)	1.756(2)
C(6)	0.583(1)	0.366(1)	1.222(2)
C(7)	0.442(2)	0.344(2)	1.076(2)
C(8)	0.916(1)	0.712(1)	1.675(1)
C(9)	0.903(1)	0.713(1)	1.521(2)
C(10)	0.881(2)	0.823(1)	1.473(2)
C(11)	0.867(2)	0.930(1)	1.578(2)
C(12)	0.881(2)	0.930(1)	1.728(2)
C(13)	0.904(2)	0.822(1)	1.785(2)
C(14)	0.620(2)	0.045(1)	0.974(2)
C(15)	0.658(2)	0.025(1)	1.125(2)
C(16)	0.532(2)	–0.020(1)	1.149(2)

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

	Compound **5a**		
	Distances		
Ti(1)–Cl(1)	2.331(3)	Ti(1)–Cl(2)	2.326(2)
Ti(1)–Cl(3)	2.327(2)	Ti(1)–P(1)	2.604(3)
Ti(1)–C(1)	2.339(8)	Ti(1)–C(2)	2.365(8)
Ti(1)–C(3)	2.340(8)	Ti(1)–C(4)	2.319(9)
Ti(1)–C(5)	2.299(8)		
	Angles		
Cl(1)–Ti(1)–Cl(2)	87.18(9)	Cl(1)–Ti(1)–Cl(3)	88.45(8)
Cl(1)–Ti(1)–P(1)	142.08(9)	Cl(2)–Ti(1)–Cl(3)	130.0(1)
Cl(2)–Ti(1)–P(1)	76.24(7)	Cl(3)–Ti(1)–P(1)	77.35(7)
	Compound **5b**		
	Distances		
Ti(1)–Cl(2)	2.331(2)	Ti(1)–Cl(3)	2.342(2)
Ti(1)–P(1)	2.579(2)		
	Angles		
Cl(1)–Ti(1)–Cl(2)	130.04(8)	Cl(1)–Ti(1)–Cl(3)	88.78(7)
Cl(1)–Ti(1)–P(1)	79.44(7)	Cl(2)–Ti(1)–Cl(3)	87.16(7)
Cl(2)–Ti(1)–P(1)	76.21(7)	Cl(3)–Ti(1)–P(1)	145.12(8)
	Compound **7d**		
	Distances		
Ti(1)–Cl	2.407(2)	Ti(1)–N(1)	2.237(4)
Ti(1)–C(1)	2.36(1)	Ti(1)–C(2)	2.41(1)
Ti(1)–C(2)	2.41(1)	Ti(1)–C(3)	2.36(2)
Ti(1)–C(4)	2.41(2)	Ti(1)–C(5)	2.37(1)
	Angles		
Cl–Ti(1)–Cl	119.2(1)	Cl–Ti(1)–N(1)	82.5(1)
Cl–Ti(1)–N(1)	82.8(1)	N(1)–Ti(1)–N(1)	150.6(2)
	Compound **8**		
	Distances		
Ti(1)–Cl(1)	2.287(4)	Ti(1)–S(1)	2.334(4)
Ti(1)–S(2)	2.459(4)	Ti(1)–S(4)	2.574(4)
Ti(1)–C(1)	2.36(1)	Ti(1)–C(2)	2.34(1)
Ti(1)–C(3)	2.35(1)	Ti(1)–C(4)	2.36(1)
Ti(1)–C(5)	2.40(2)	Ti(2)–Cl(2)	2.285(4)
Ti(2)–S(2)	2.571(4)	Ti(2)–S(3)	2.339(4)
Ti(2)–S(4)	2.450(4)	Ti(2)–C(8)	2.32(1)
Ti(2)–C(9)	2.38(1)	Ti(2)–C(10)	2.39(1)
Ti(2)–C(11)	2.41(1)	Ti(2)–C(12)	2.34(1)
S(1)–C(6)	1.79(1)	S(2)–C(7)	1.79(1)
S(3)–C(13)	1.82(1)	S(4)–C(14)	1.81(1)
	Angles		
Cl(1)–Ti(1)–S(1)	97.7(2)	Cl(1)–Ti(1)–S(2)	115.2(2)
Cl(1)–Ti(1)–S(4)	89.3(1)	S(1)–Ti(1)–S(2)	78.9(1)
S(1)–Ti(1)–S(4)	143.8(2)	S(2)–Ti(1)–S(4)	66.1(1)
Cl(2)–Ti(2)–S(2)	90.6(1)	Cl(2)–Ti(2)–S(3)	96.6(2)
Cl(2)–Ti(2)–S(4)	120.5(2)	S(2)–Ti(2)–S(3)	144.2(1)
S(2)–Ti(2)–S(4)	66.2(1)	S(3)–Ti(2)–S(4)	80.0(1)
Ti(1)–S(1)–C(6)	102.6(4)	Ti(1)–S(2)–Ti(2)	102.4(1)
Ti(1)–S(2)–C(7)	109.4(5)	Ti(2)–S(2)–C(7)	112.6(5)
Ti(2)–S(3)–C(13)	102.4(4)	Ti(1)–S(4)–Ti(2)	102.5(1)
Ti(1)–S(4)–C(14)	111.4(4)	Ti(2)–S(4)–C(14)	107.5(5)
	Compound **10**		
	Distances		
Ti(1)–S(2)	2.470(4)	Ti(1)–S(2)	2.467(4)
Ti(1)–S(1)	2.377(4)	Ti(1)–S(3)	2.365(4)
Ti(1)–C(1)	2.37(1)	Ti(1)–C(2)	2.37(1)
Ti(1)–C(3)	2.33(1)	Ti(1)–C(4)	2.34(1)
Ti(1)–C(5)	2.36(1)	S(2)–C(6)	1.80(1)
S(1)–C(7)	1.62(2)	S(3)–C(8)	1.78(1)
	Angles		
S(2)–Ti(1)–S(2)	67.8(1)	S(2)–Ti(1)–S(1)	129.7(2)
S(2)–Ti(1)–S(3)	88.7(1)	S(2)–Ti(1)–S(1)	78.5(1)
S(2)–Ti(1)–S(3)	138.2(1)	S(1)–Ti(1)–S(3)	92.9(2)
Ti(1)–S(2)–Ti(1)	112.3(1)	Ti(1)–S(2)–C(6)	122.1(5)
Ti(1)–S(2)–C(6)	111.4(4)	Ti(1)–S(1)–C(7)	110.2(5)
Ti(1)–S(3)–C(8)	103.7(4)		

(**5a,b**) the Ti–Cl distances are typical, averaging 2.328(4) Å. The Cl atom *trans* to P exhibit a slightly longer bond length consistent with strong σ-donation from the phoshine. These compare with the Ti–Cl distances of 2.27(1) and 2.40(1) Å found in $CpTiCl_3$[19] and $CpTiCl_3(dmpe)$,[19] respectively. The lengthening of the Ti–Cl bonds with coordination of the phosphine ligands is consistent with an increase in electron density at the metal center. The

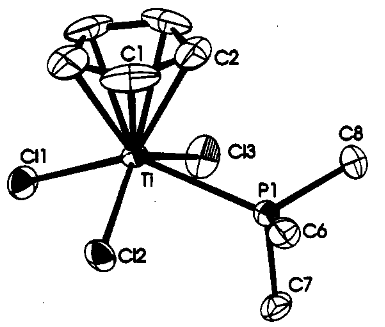


Figure 2. ORTEP drawing of compound $CpTiCl_3(PMe_3)$ (**5a**). Hydrogen atoms are omitted for clarity (with the exception of the P-H hydrogen atom); 30% thermal ellipsoids are shown.

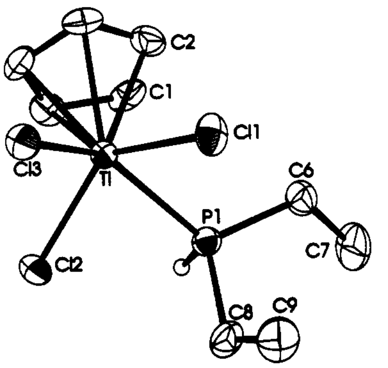
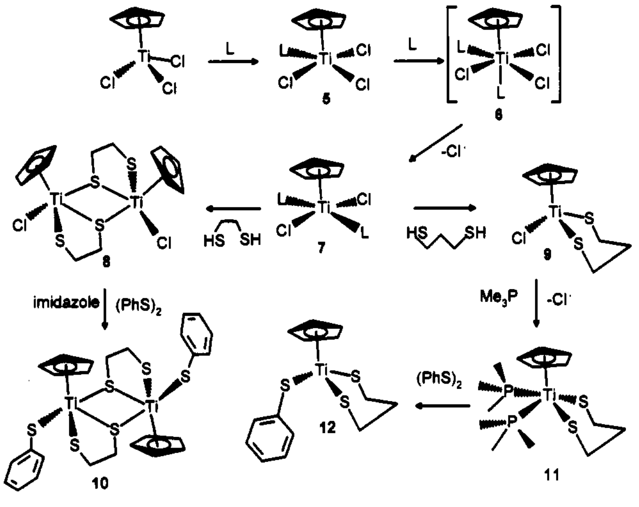


Figure 3. ORTEP drawing of compound $CpTiCl_3(PHEt_2)$ (**5b**). Hydrogen atoms are omitted for clarity (with the exception of the P-H hydrogen atom); 30% thermal ellipsoids are shown.

Scheme I



Ti-P bond distances are 2.604(3) and 2.579(2) Å in **5a,b**, respectively. These too are slightly shorter than those seen in $CpTiCl_3(dmpe)$ consistent with the lesser electron density at the metal centers of **5a,b**.

The structure of **7d** is also best described as a four-legged piano stool (Figure 4). In this case crystallographically imposed symmetry places the Ti on a 2-fold axis. As a result the cyclopentadienyl ligand is disordered. The Ti(III)-Cl distance is 2.407(2) Å, while the Ti-N distance in **7d** is 2.237(4) Å. The increase of the Ti-Cl distance is consistent with the presence of the additional electron on the reduced metal center. The Ti-N distance is 2.237(4) Å, which is shorter than the Ti-N distance of 2.39(1) Å seen in $CpTi(CH_2C_6H_4\text{-}o\text{-}NMe_2)_2$.[20] This is consistent with some degree of π-bonding character in the Ti-N bond of **7d**.

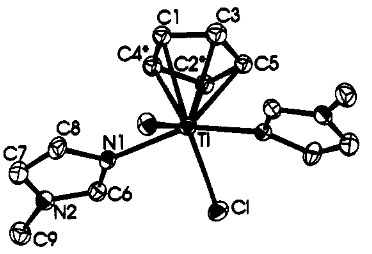


Figure 4. ORTEP drawing of compound $CpTiCl_2$(Meimid) (**7d**). Hydrogen atoms are omitted for clarity; 30% thermal ellipsoids are shown. Atoms shown with asterisks are symmetry related to those given in the tables.

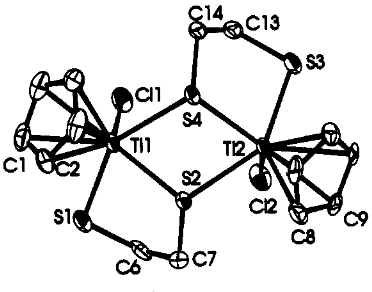


Figure 5. ORTEP drawing of compound $[CpTiCl(SCH_2CH_2S)]_2$ (**8**). Hydrogen atoms are omitted for clarity; 30% thermal ellipsoids are shown.

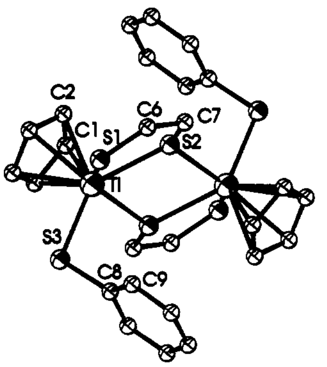


Figure 6. ORTEP drawing of compound $[CpTi(SPh)(SCH_2CH_2S)]_2$ (**10**). Hydrogen atoms are omitted for clarity; 30% thermal ellipsoids are shown.

Compound **8** is confirmed crystallographically to be a dimer (Figure 5). Cyclopentadienyl, chloride, and terminal thiolate ligands are bound to each Ti atom, which is bridged by two thiolate-sulfur atoms. This "twisted dimer" conformation of the Ti_2S_4 core is similar to that seen in **1b** and in contrast to that seen in **9**.[1] This may be due to the tighter chelate bite of the ethanedithiolate ligand. The mutually *cis* disposition of the cyclopentadienyl ligands with respect to the Ti_2S_2 core results in a similarly *cis* disposition of the chloride ligands. The bridging Ti-S bonds average 2.514(6) Å, slightly longer than the terminal Ti-S bond distances which average 2.337(2) Å, as expected.

The compound **10** is also a "twisted dimer" similar to **8** with the replacement of chloride by benzenethiolate (Figure 6). However, the cyclopentadienyl ligands adopt a *trans* disposition as do the benzenethiolate moieties. Presumably, steric demands of the thiolate substituents preclude a cis orientation. The bridging Ti-S bonds average 2.468(4) Å, while the terminal Ti-S bond of the 1,2-ethanedithiolate and bnezenethiolate moieites are 2.377(4) and 2.365(4) Å, respectively.

Electrochemistry. Cyclic voltammetric experiments on $CpTiCl_3$, **5a**, and $CpTiCl_3(dmpe)$ were performed in THF by employing NBu_4BPh_4 as the supporting electrolyte with a scan rate of 200 mV/s. Each of these species exhibit quasi-reversible one-electron redox couples. These waves were found at -0.33, -0.39, and 0.69 V, respectively, relative to a Ag/AgCl reference electrode (Figure 7). These redox potentials increase with increasing electron density at the metal as expected for an external

---

(19) Ganis, P.; Allegra, G. *Atti. Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* **1962**, *33* (8), 303.

(20) Manzer, L. E.; Gearhart, R. C.; Guggenberger, L. J.; Whittney, J. F. *J. Chem. Soc., Chem. Commun.* **1976**, 942.

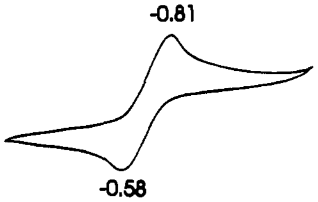


Figure 7. Cyclic voltammetry of $CpTiCl_3(PMe_3)$ (**5a**) in the presence of excess PMe_3: supporting electrolyte, NBu_4BPh_4; working electrode, Pt disk; reference electrode; Ag/AgCl; scan rate, 200 mV/s.

electron-transfer process. The peak-to-peak separations of 530, 350, and 230 mV for $CpTiCl_3$, **5a**, and $CpTiCl_3$(dmpe), respectively, suggest that the addition of phosphine ligands aids in the stabilization of the Ti(III) reduction product.

Similar electrochemical studies of **8** and **10** show irreversible reduction waves at -0.88 and -0.91 V vs Ag/AgCl, respectively.

Discussion

The reactions of Ti(IV) halides with strong σ-donors ligands yield reduced products, whereas reactions with weaker donors do not afford Ti(III) species. Neither the mechanism of these reductions nor the subsequent reactivity arising from the presence of such Ti(III) species have been previously investigated. The present results offer insight into these concerns.

Mechanism. In the reactions of Cp_2TiCl_2 with donors generation of Ti(III) presumably proceeds through radical loss of Cl, while the donor traps the Ti(III) species as **3**. Subsequent reaction of these mixtures to give Ti(IV) thiolates is evidenced by the formation of **1**, **2**, **4**, **8**, and **9**. However, these dithiolate derivatives are formed in extremely low yields under conditions known to lead to nucleophilic substitution of thiolate for halide, such as reactions of NEt_3, Ti(IV) halide, and thiol or of dithiolate salts and Ti(IV) halides. It is suggested that a radical mechanism involving the intermediacy of the Ti(III) species **3** is involved (Scheme I). The direct synthesis of **4** from $[Cp_2TiCl]_2$ supports this view.

It is most important to note that the formation of **3** and **7** occurs simply by the addition of the respective strong σ-donor type Lewis bases and in the *total absence* of reducing agent. In the presence of weak donors like NEt_3 or PPh_3 no reduced species are detected. These observations imply a σ-donor-ligand induced free radical reduction mechanism. In the case of the reactions of Cp_2TiCl_2 we suggest that the coordination of a donor ligand to the Ti center induces a radical reductive loss of $Cl^\bullet$ resulting in the formation of **3**. In the related $CpTiCl_3$ systems, the initial interaction of the donor with the Ti(IV) center is confirmed by the isolation of **5a,b**. Coordination of a second equivalent of ligand to Ti(IV) giving $CpTiCl_3L_2$ (**6**), while not confirmed in the present systems, is suggested by the isolation of the compound $CpTiCl_3(Me_2PCH_2CH_2PMe_2)$.[16] Reductive loss of $Cl^\bullet$ radical from analogues of **6** accounts for the formation of **7** (Scheme I). Subsequent addition of thiol to solutions containing the Ti(II) species affords formation of Ti-thiolate derivatives **1**, **2**, **8**, and **9**. The fate of the $Cl^\bullet$ radical is thought to be combination with $H^\bullet$ derived from thiol or solvent giving the hydrochloride salt of the base.

Generation of **7** in the presence of trityl radical affords trityl chloride, thus supporting the notion of $Cl^\bullet$ radical formation; however, trityl radical reacts directly with Ti(IV) halides to give Ti(III) and trityl chloride. Thus, these trapping experiments do not provide conclusive proof of the formation of $Cl^\bullet$ radical as a result of ligand coordination to Ti(IV). However, reactions of **8** and **9** to give **10** and **12**, respectively, proceed by the addition of donor and $(PhS)_2$. No reaction occurs in the absence of the donor ligand or in the presence of weaker σ-donor ligands. The observation of **11** enroute to **12** leaves little doubt that **11** is the Ti(III) intermediate in a radical mechanism in which donor ligands induced radical reduction of Ti(IV).

Summary

The proposition of a radical mechanism involving Ti(III) in the formation of Ti-S bonds is supported by the electrochemical, structural, and spectroscpic data as well as the reactivity described herein. These data suggest a weakening of the Ti-Cl bond on coordination of donor ligands and provide evidence of the formation and subsequent reaction of these Ti(III) species. The evidence presented here is strongly suggestive of a radical mechanism in reactions involving Ti(IV)/donor and thiol. Such a mechanistic proposal does offer an explanation for the previously observed "base dependence" of thiolate substitution reactions at Ti(IV). While it is possible that nucleophilic substitution may be a competitive mechanism for the formation of Ti-S bonds in the reactions involving thiols, the data here suggest that a radical mechanism is operative at least to some extent. Further, such a radical mechanism in the reactions employing Ti(IV)/donor and disulfides is difficult to dispute.

Acknowledgment. Support from the Petroleum Research Fund, administered by the American Chemical Society, and the NSERC of Canada is acknowledged. The award of an Ontario Graduate Scholarship to T.T.N. as well as summer support from the Electrochemical Society (U.S.-DOE) is also gratefully acknowledged.

Supplementary Material Available: Tables of crystallographic, hydrogen atom, and thermal parameters for **5a,b**, **7**, **8**, and **10** (12 pages). Ordering information is given on any current masthead page.