C−H and C−S Bond Cleavage in Cyclopentadienyltitanium Phenoxide Thiolate Complexes

Andrea V. Firth and Douglas W. Stephan*

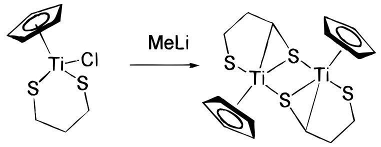
Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4

Received December 26, 1996[⊗]

The thiolate complexes $CpTi(OC_6H_3$-2,6-*i*-$Pr_2)(SR)Cl$ (R = Et, **1**; *t*-Bu, **2**; CH_2Ph, **3**; Ph, **4**) were prepared. Attempts to methylate **1−4** and thus obtain the potentially reactive alkyltitanium thiolate derivatives were unsuccessful. Thiolation of $CpTi(OC_6H_3$-2,6-*i*-$Pr_2)(Me)Cl$ (**5**) with 1,1-dimethylethanethiol in the presence of base afforded the species $CpTi(OC_6H_3$-2,6-*i*-$Pr_2)(Me)(SCMe_3)$ **(6)**. The analogous species $CpTi(OC_6H_3$-2,6-*i*-$Pr_2)(Me)(SCH_2Me)$ **(7)** is unstable, liberating methane and yielding the dimeric product of C−H bond activation, $[CpTi(OC_6H_3$-2,6-*i*-$Pr_2)(\mu$-$SCHMe)]_2$ **(8)**. In a related thermolysis of $CpTi(OC_6H_3$-2,6-*i*-$Pr_2)(SBn)_2$ **(9)**, the dimer species $[CpTi(\mu$-$S)(OC_6H_3$-2,6-*i*-$Pr_2)]_2$ **(10)** and $(PhCH_2)_2S$ are obtained. In contrast, thermolysis of the closely related species $CpTi(OC_6H_3$-2,6-*i*-$Pr_2)((SCH_2)_2C_6H_4)$ **(11)** and $CpTi(OC_6H_3$-2,6-*i*-$Pr_2)(SCH_2Me)_2$ **(12)** resulted in no reaction, suggesting a radical process is operative in the formation of **10**. Reduction of **2** with $LiPCy_2$ gave $(PCy_2)_2$ and the S−C bond cleavage product $[CpTi(OC_6H_3$-2,6-*i*-$Pr_2)(\mu^3$-$S)]_3TiCp$ **(13)**. These pathways of C−H and C−S bond activation are discussed and the implications considered.

Introduction

Early-metal thiolates are a class of compounds that have drawn attention for a number of reasons over the years. This chemistry has been recently reviewed.[1] The long-standing interest of chemists in biological systems containing early metals has prompted and continues to prompt numerous studies.[2] More recently, the utility of such complexes in the synthesis of organosulfur compounds and as precursors for metal sulfide materials in MOCVD processes has resulted in further studies.[3] In the case of titanium thiolates, the bulk of the chemistry known to date centers around titanocene derivatives, while much less is known about homoleptic and monocyclopentadienyl derivatives.[1] We have recently reported several studies addressing various aspects of monocyclopentadienyltitanium thiolate derivatives.[4−6] Synthetic routes to complexes of the form $CpTi(SR)_x(L)_{3-x}$ have been described and the structural implications of the Lewis acidity of the Ti center described.[4] The utility of monocyclopentadienyltitanium thiolate derivatives as metalloligands for early−late heterobimetallics has also been probed.[5] Most recently, we have described C−H bond activation in the species $CpTi(SCH_2CH_2CH_2S)Cl$. The thiametallacycle $[CpTi(SCHCH_2CH_2S)]_2$ provides a metal-mediated synthetic route to a variety of organosulfur compounds.[6] In this report, we describe the synthesis of related thiolate derivatives of monocyclopentadienyltitanium phenoxide complexes. Alkylation, thermolysis, or reduction of these species is shown to induce C−H bond activation or S−C bond cleavage, depending on the nature of the thiolate substituents. These results are presented and the implications considered.



Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 employing either Schlenk line techniques or a Vacuum Atmospheres inert atmosphere glovebox. Solvents were reagent grade, distilled from the appropriate drying agents under N_2, and degassed by the freeze−thaw method at least three times prior to use. All organic reagents were purified by conventional methods. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC-300 operating at 300 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 operating at 81 MHz and are referenced to 85% H_3PO_4. Combustion analyses were performed by Galbraith Laboratories Inc. (Knoxville, TN) or Schwarzkopf Laboratories (Woodside, NY). $CpTiCl_3$, $CpTi(OC_6H_3$-2,6-*i*-$Pr_2)Cl_2$, and $CpTiMeCl_2$ were prepared via literature methods.[7−9]

Synthesis of CpTi$(OC_6H_3$-2,6-*i*-$Pr_2)(SR)Cl$ (R = Et, 1; *t*-Bu, 2; CH_2Ph, 3; Ph, 4)**.** These compounds were prepared in a

---

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1997.

(1) Stephan, D. W.; Nadasdi, T. T. *Coord. Chem. Rev.* **1996**, *147*, 147.

(2) (a) Steifel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1. (b) Robson, R. L.; Eady, E. E.; Richardson, T. H.; Miller, R. W.; Hawkins, M.; Postgate, J. R. *Nature* **1986**, *322*, 388. (c) Hales, B. J.; Case, E. E.; Morningstar, J. E.; Dzeda, M. F.; Mauterer, L. A. *Biochemistry* **1986**, *25*, 7251. (d) Kustin, K.; Macara, I. G. *Comments Inorg. Chem.* **1982**, *2*, 1.

(3) Bochmann, M.; Hawkins, I.; Wilson, L. M. *J. Chem. Soc., Chem. Commun.* **1988**, 344.

(4) Nadasdi, T. T.; Huang, Y.; Stephan, D. W. *Inorg. Chem.* **1993**, *32*, 347.

(5) Nadasdi, T. T.; Stephan, D. W. *Inorg. Chem.* **1994**, *33*, 1532.

(6) (a) Huang, Y.; Nadasdi, T. T.; Stephan, D. W. *J. Am. Chem. Soc.* **1994**, *116*, 5483. (b) Huang, Y.; Etkin, N.; Heyn, R. R.; Nadasdi, T. T.; Stephan, D. W. *Organometallics* **1996**, *15*, 2320.

(7) Erskine, G. J.; Hurst, G. J. B.; Weinberg, E. L.; Hunter, B. K.; McCowan, J. D. *J. Organomet. Chem.* **1984**, *267*, 265.

S0276-7333(96)01093-X CCC: $14.00

similar manner, and thus only one representative preparation is described. To CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)Cl$_2$ (50 mg, 0.13 mmol) dissolved in benzene were added ethanethiol (9.5 μL, 0.13 mmol) and NEt$_3$ (20 μL, 0.14 mmol). The reaction mixture was stirred for 8 h and filtered, and then the solvent was removed. Red/orange crystals of **1** were obtained from a hexane solution in 64% yield.

1: ^{1}H NMR (C$_6$D$_6$, 25 °C) δ 1.17 (d, 6H, $|J_{H-H}| = 7$ Hz), 1.24 (d, 6H, $|J_{H-H}| = 7$ Hz), 1.30 (dd, 3H, $|J_{H-H}| = 7$ Hz), 3.45 (sept, 2H, $|J_{H-H}| = 7$ Hz), 3.94 (dq, 2H, $|J_{H-H}| = 7$ Hz), 6.09 (s, 5H), 7.01 (m, 3H); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C) δ 17.1, 23.6, 23.8, 26.3, 35.5, 116.9, 123.4, 123.5, 138.1, 162.3. Anal. Calcd for C$_{19}$H$_{27}$ClOSTi: C, 58.99; H, 7.04. Found: C, 58.79; H, 6.90.

2: yield 59%; ^{1}H NMR (C$_6$D$_6$, 25 °C) δ 1.20 (d, 3H, $|J_{H-H}| = 7$ Hz), 1.23 (d, 3H, $|J_{H-H}| = 7$ Hz), 1.70 (s, 9H), 3.53 (sept, 2H, $|J_{H-H}| = 7$ Hz), 6.14 (s, 5H), 7.00−7.14 (m, br, 3H); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C) δ 23.8, 24.2, 26.0, 33.9, 52.9, 117.5, 123.5, 123.6, 138.4, 162.3. Anal. Calcd for C$_{21}$H$_{31}$ClOSTi: C, 60.79; H, 7.53. Found: C, 60.59; H, 7.46.

3: yield 83%; ^{1}H NMR (C$_6$D$_6$, 25 °C) δ 1.19 (d, 6H, $|J_{H-H}| = 7$ Hz), 1.26 (d, 6H, $|J_{H-H}| = 7$ Hz), 3.49 (sept, 2H, $|J_{H-H}| = 7$ Hz), 5.12 (d, 1H, $|J_{H-H}| = 13$ Hz), 5.26 (d, 1H, $|J_{H-H}| = 13$ Hz), 6.08 (s, 5H), 7.0−7.30 (m, br, 8H); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C) δ 23.7, 24.0, 26.4, 44.9, 117.1, 123.5, 123.6, 126.8, 128.1, 128.8, 138.2, 141.0, 162.4. Anal. Calcd for C$_{24}$H$_{28}$ClOSTi: C, 64.36; H, 6.30. Found: C, 64.19; H, 6.15.

4: yield 79%; ^{1}H NMR (C$_6$D$_6$, 25 °C) δ 1.09 (d, 6H, $|J_{H-H}| = 7$ Hz), 1.15 (d, 6H, $|J_{H-H}| = 7$ Hz), 3.37 (sept, 2H, $|J_{H-H}| = 7$ Hz), 6.11 (s, 5H), 6.8−7.2 (m, 7H), 7.8 (d, 1H, $|J_{H-H}| = 7$ Hz); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C) δ 23.5, 24.1, 26.3, 117.9, 123.4, 123.5, 126.6, 128.7, 131.8, 138.4, 142.7, 162.7. Anal. Calcd for C$_{23}$H$_{26}$ClOSTi: C, 63.67; H, 6.04. Found: C, 63.39; H, 6.00.

Synthesis of CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(Me)Cl (5). (i) To a solution of CpTiCl$_2$Me (90 mg, 0.45 mmol) in benzene was added Li(OC$_6$H$_3$-2,6-*i*-Pr$_2$) (85 mg, 0.45 mmol). The reaction was stirred for 1 h at 25 °C and then filtered. The benzene was removed, and a yellow solid was crystallized from hexane. (ii) An alternative synthesis of **5** is achieved via the reaction of CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)Cl$_2$ (200 mg, 0.51 mmol) with ZnMe$_2$ (140 mL of a 2 M solution in toluene, 0.70 mmol) in THF (0.5 mL). The mixture was stirred at 25 °C overnight and the solvent removed. The residue was extracted into hexane and filtered, and then the solvent was removed to give 132 mg of the yellow solid **5** (80%): ^{1}H NMR (C$_6$D$_6$, 25 °C) δ 1.17 (d, 6H, $|J_{H-H}| = 7$ Hz), 1.23 (d, 6H, $|J_{H-H}| = 7$ Hz), 1.48 (s, 3H), 3.28 (sept, 2H, $|J_{H-H}| = 7$ Hz), 5.93 (s, 5H), 6.8−6.95 (m, br, 3H); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C) δ 23.4, 23.5, 26.9, 61.6, 116.2, 123.3, 123.4, 137.9, 162.1. Anal. Calcd for C$_{18}$H$_{25}$ClOTi: C, 63.45; H, 7.40. Found: C, 63.25; H, 7.19.

Synthesis of CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(Me)(S-*t*-Bu) (6), To CpTiCl$_2$Me (91 mg, 0.46 mmol) in hexane was added NEt$_3$ (70.4 μL, 0.46 mmol), followed by 57.0 μL (0.46 mmol) of HS-*t*-Bu. After the solution was stirred for a few minutes 92.5 mg, (0.50 mmol) of LiOC$_6$H$_3$-2,6-*i*-Pr$_2$ was added. This mixture was allowed to stir a few minutes and then filtered. A red solid was isolated after a few days in 53% yield: ^{1}H NMR (C$_6$D$_6$, 25 °C) δ 1.07 (s, 3H), 1.20 (d, 6H, $|J_{H-H}| = 7$ Hz), 1.21 (d, 6H, $|J_{H-H}| = 7$ Hz), 1.68 (s, 9H), 3.44 (sept, 2H, $|J_{H-H}| = 7$ Hz), 6.00 (s, 5H), 6.9−7.1 (m, 3H); ^{13}C{^{1}H} NMR (C$_6$D$_8$, 25 °C) δ 23.5, 23.8, 26.6, 35.3, 50.0, 52.3, 114.6, 123.5, 138.1, 161.4. Anal. Calcd for C$_{22}$H$_{34}$OSTi: C, 66.99; H, 8.69. Found: C, 66.59; H, 8.65.

Generation of CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(Me)(SEt) (7). The procedure for the generation of **7** was analogous to that employed for **6**. The instability of **7** precluded isolation and complete characterization: ^{1}H NMR (C$_6$D$_6$, 25 °C) δ 1.04 (s, 3H), 1.22 (d, 6H, $|J_{H-H}| = 7$ Hz), 1.25 (d, 6H, $|J_{H-H}| = 7$ Hz), 1.30 (dd, 3H, $|J_{H-H}| = 7$ Hz), 3.40 (sept, 2H, $|J_{H-H}| = 7$ Hz), 3.70 (dq, 2H, $|J_{H-H}| = 13.0, 7$ Hz), 3.80 (dq, $|J_{H-H}| = 13, 7$ Hz), 5.98 (s, 5H), 6.9−7.1 (m, 3H).

Synthesis of [CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(μ-SCHMe)]$_2$ (8). To CpTiCl$_2$Me (91 mg, 0.46 mmol) suspended in pentane were added ethanethiol (34 μL, 0.46 mmol), NEt$_3$ (66 μL, 0.47 mmol), and Li(OC$_6$H$_3$-2,6-*i*-Pr$_2$) (84 mg, 0.46 mmol). The mixture was stirred for 12 h and then filtered. The solvent was removed and the residue extracted into benzene and heated overnight at 70 °C. During this time, gas evolution was observed, concurrent with the darkening to orange-brown. On cooling, brown crystals of **8** were deposited in 14% yield: ^{1}H NMR (C$_7$D$_8$, 230 K) δ 0.38 (d, 3H, $|J_{H-H}| = 7$ Hz), 0.75 (d, 3H, $|J_{H-H}| = 7$ Hz), 1.23 (d, 3H, $|J_{H-H}| = 7$ Hz), 1.33 (d, 3H, $|J_{H-H}| = 7$ Hz), 2.27 (d, 3H, $|J_{H-H}| = 7$ Hz), 2.67 (sept, 1H, $|J_{H-H}| = 7$ Hz), 3.74 (sept, 1H, $|J_{H-H}| = 7$ Hz), 4.28 (q, 1H, $|J_{H-H}| = 7$ Hz), 5.92 (s, 5H), 6.7−6.9 (m, 3H); ^{13}C{^{1}H} NMR (C$_7$D$_8$, 230 K) δ 20.4, 25.3, 25.5, 26.0, 27.5, 29.0, 99.5, 114.7, 121.9, 122.9, 124.6, 137.2, 137.7, 162.2. Anal. Calcd for C$_{38}$H$_{52}$O$_2$S$_2$Ti$_2$: C, 65.13; H, 7.48. Found: C, 65.00; H, 7.25.

Synthesis of CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(SBn)$_2$ (9), CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)((SCH$_2$)$_2$C$_6$H$_4$) (11), and CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(SEt)$_2$ (12). These compounds were prepared in a similar manner, and thus only one representative preparation is described. To a solution of CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)Cl$_2$ (50 mg, 0.13 mmol) in pentane were added benzyl mercaptan (30.1 μL, 0.26 mmol) and NEt$_3$ (30 mg, 0.30 mmol). The solution was stirred at 25 °C for 30 min and then filtered, and the solvent was removed under vacuum, affording **9** in 54% yield.

9: ^{1}H NMR (C$_6$D$_6$, 25 °C) δ 1.23 (d, 12H, $|J_{H-H}| = 7$ Hz), 3.62 (sept, 2H, $|J_{H-H}| = 7$ Hz), 4.74 (s, 4H), 6.07 (s, 5H), 7.0−7.3 (m, 13H); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C) δ 24.0, 26.4, 43.4, 115.2, 123.4, 123.5, 126.7, 128.4, 128.7, 138.1, 141.9, 161.8. Anal. Calcd for C$_{31}$H$_{36}$OS$_2$Ti: C, 69.38; H, 6.76. Found: C, 69.19; H, 6.65.

11: yield 24%; ^{1}H NMR (C$_6$D$_6$, 25 °C) δ 1.25 (d, 12H, $|J_{H-H}| = 7$ Hz), 3.65 (sept, 2H, $|J_{H-H}| = 7$ Hz), 4.62 (d, 2H, $|J_{H-H}| = 14$ Hz), 4.93 (d, 2H, $|J_{H-H}| = 14$ Hz), 5.93 (s, 5H), 6.9−7.1 (m, br, 7H); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C) δ 23.9, 26.2, 37.7, 114.0, 122.9, 123.4, 128.3, 128.8, 136.2, 138.4, 142.11, 164.4. Anal. Calcd for C$_{25}$H$_{30}$OS$_2$Ti: C, 65.48; H, 6.59. Found: C, 65.29; H, 6.42.

12: yield 58%; ^{1}H NMR (C$_6$D$_6$, 25 °C) δ 1.23 (d, 12H, $|J_{H-H}| = 7$ Hz), 1.32 (t, 6H, $|J_{H-H}| = 7$ Hz), 3.57 (q, 4H, $|J_{H-H}| = 7$ Hz), 3.61 (sept, 2H, $|J_{H-H}| = 7$ Hz), 6.07 (s, 5H), 7.0−7.1 (m, 3H); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C) δ 18.5, 24.0, 26.1, 33.3, 114.9, 123.1, 123.5, 138.2, 161.5. Anal. Calcd for C$_{21}$H$_{32}$OS$_2$Ti: C, 61.14; H, 7.82. Found: C, 60.99; H, 7.75.

Synthesis of [CpTi(μ-S)(OC$_6$H$_3$-2,6-*i*-Pr$_2$)]$_2$ (10). To a suspension of CpTiCl$_2$(OC$_6$H$_3$-2,6-*i*-Pr$_2$) (150 mg, 0.39 mmol) in hexane were added benzyl mercaptan, (95.6 mg, 0.77 mmol) and NEt$_3$ (80 mg, 0.8 mmol). The mixture was stirred overnight at 25 °C and then filtered. The solvent was removed and the solid redissolved in toluene. This mixture was heated at 80 °C overnight. Dark red crystals of **10** were deposited from toluene at −4 °C after 12 h in 49.6% yield: ^{1}H NMR (C$_6$D$_6$, 25 °C) δ 1.39 (d, 12H, $|J_{H-H}| = 7$ Hz), 3.40 (sept, 2H, $|J_{H-H}| = 7$ Hz), 6.3 (s, 5H), 7.0−7.22 (m, 3H); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C) δ 23.8, 27.0, 115.8, 122.1, 123.5, 137.4, 163.8. Anal. Calcd for C$_{34}$H$_{44}$O$_2$S$_2$Ti$_2$: C, 63.35; H, 6.88. Found: C, 63.09; H, 6.65.

Synthesis of [CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(μ^3-S)]$_3$TiCp (13). To a suspension of **2** (150 mg, 0.36 mmol) in benzene (2 mL) was added LiPCy$_2$ (68 mg, 0.36 mmol). The mixture immediately became dark green-black and was stirred overnight at 25 °C and then filtered. Upon standing for 7 days, dark crystals of **13** were deposited in 58% yield. EPR (C$_7$H$_8$) *g* 1.990. Anal. Calcd for C$_{56}$H$_{71}$O$_3$S$_3$Ti$_4$: C, 62.28; H, 6.63. Found: C, 62.09; H, 6.60.

X-ray Data Collection and Reduction. X-ray quality crystals of **4** and **8**−**13** were obtained directly from the preparations as described above. The crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O$_2$-free environment for each crystal. Diffraction

---

(8) Fussing, I. M. M.; Pletcher, D.; Whitby, R. J. *J. Organomet. Chem.* **1994**, *470*, 109.

(9) Erskine, G. J.; Hurst, G. J. B.; Weinberg, E. L.; Hunter, B. K.; McCowan, J. D. *J. Organomet. Chem.* **1984**, *267*, 265.

Table 1. Crystallographic Parameters[a]

	4	**8**	**9**	**10**	**11**	**12**	**13**
formula	$C_{23}H_{27}OTiSCl$	$C_{38}H_{52}O_2S_2Ti_2$	$C_{31}H_{36}OTiS_2$	$C_{34}H_{44}O_2Ti_2S_2$	$C_{25}H_{30}OTiS_2$	$C_{21}H_{32}OS_2Ti$	$C_{56}H_{71}Ti_4S_4O_3$
formula weight	434.88	700.75	536.64	644.64	457.52	412.50	1112.02
a, Å	10.918(7)	11.129(3)	10.945(8)	12.649(6)	10.636(3)	13.064(7)	10.4161(1)
b, Å	12.89(2)	16.560(4)	14.84(1)	16.75(1)	11.814(3)	17.716(6)	14.1133(4)
c, Å	16.46(1)	20.415(3)	9.745(7)	16.076(4)	9.985(3)	10.665(7)	21.8288(6)
α, deg			106.39(8)		96.95(3)	94.70(4)	107.385(1)
β, deg	92.82(8)	99.72(3)	91.46(6)	91.59(4)	97.27(2)	99.60(5)	95.458(1)
γ, deg			75.00(7)		102.50(2)	106.75(3)	91.287(1)
V, Å^3	2314(3)	3708(1)	1464(2)	3403(3)	1200.7(6)	2308(2)	3044.1(1)
space group	$P2_1/n$	$P2_1/n$	P-1	$P2_1/c$	P-1	P-1	P-1
d(calc), g cm^{-1}	1.25	1.25	1.22	1.26	1.26	1.19	1.21
Z	4	4	2	4	2	2	2
μ, cm^{-1}	5.8	5.74	4.55	6.19	5.43	5.58	6.80
scan speed, deg/min	8.0	16.0	32.0	16.0	32.0	32.0	na
no. of data collected	2601	6796	5150	6217	2540	8147	6246
2θ/index ranges, deg	4.5−45	4.5−50	4.5−50	4.5−50	4.5−45	4.5−50	4.5−42.0
no. of data $F_o^2 > 3\sigma(F_o^2)$	594	2047	2585	1986	1478	2506	2776
no. of variables	94	287	316	251	197	281	315
transmission factors	0.81−1.00	0.83−1.00	0.87−1.00	0.87−1.00	0.85−1.00	0.69−1.00	0.99−1.00
R, %[b]	9.3	6.5	5.0	7.4	5.9	9.0	8.0
R_w, %[c]	9.7	5.5	3.8	5.8	5.1	7.1	9.0
goodness of fit	1.93	1.58	1.51	1.95	1.96	2.40	2.22

[a] All data collected at 24 °C with Mo Kα radiation ($\lambda = 0.710\,69$ Å), a scan range of 1.0 above $K\alpha_1$ and 1.0 below $K\alpha_1$, with a background to scan ratio of 0.5. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{0.5}$.

experiments for **4** and **8**−12 were performed on a Rigaku AFC6 diffractometer equipped with graphite-monochromatized Mo Kα radiation. The initial orientation matrix was obtained from 20 machine-centered reflections selected by an automated peak search routine. These data were used to determine the crystal systems. Automated Laue system check routines around each axis were consistent with the crystal system. Ultimately, 25 reflections (20° < 2θ < 25°) were used to obtain the final lattice parameters and the orientation matrices. Crystal data are summarized in Table 1. The observed extinction coefficients were consistent with the space groups in each case. The data sets were collected in three shells (4.5°< 2θ < 45−50.0°), and three standard reflections were recorded every 197 reflections. Fixed scan rates were employed. Up to four repetitive scans of each reflection at the respective scan rates were averaged to ensure meaningful statistics. The number of scans of each reflection was determined by the intensity. The intensities of the standards showed no statistically significant change over the duration of the data collections. The data were processed using the TEXSAN crystal solution package operating on a SGI Challenger mainframe with remote X-terminals. The reflections with $F_o^2 > 3\sigma F_o^2$ were used in the refinements. In the case of **13**, X-ray data were collected on a Siemens SMART system CCD diffractometer and processed employing the SHELXS software package.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[10,11] The Ti atom positions were determined using direct methods employing either the SHELX-86 or Mithril direct methods routines. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $\omega(|F_o| - |F_c|)^2$, where the weight ω is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, the number of non-hydrogen atoms assigned anisotropic temperature factors was determined so as to maintain a reasonable data: variable ratio. The remaining atoms were assigned isotropic temperature factors. Empirical absorption corrections were applied to the data sets based on either ψ-scan data or a DIFABS calculation and employing the software resident in the TEXSAN package. Hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded, assuming a C−H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. The hydrogen atom contributions were calculated but not refined. The final values of R, R_w, and the goodness of fit in the final cycles of the refinements are given in Table 1. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as Supporting Information.

Results and Discussion

The incorporation of titanium−alkyl and titanium−thiolate bonds into a single complex offers one avenue to initiate C−H or S−C bond cleavage reactions. To that end, we have prepared the series of complexes CpTi(OC_6H_3-2,6-i-Pr_2)(SR)Cl (R = Et, **1**; t-Bu, **2**; Bn, **3**; Ph, **4**) via thiolate substitution reactions on CpTi(OC_6H_3-2,6-i-Pr_2)Cl_2. Complexes **1**−**4** were characterized via NMR spectroscopy, and the structure of **4** was confirmed crystallographically (Figure 1). Attempts to replace the remaining chloride ligand with a methyl group, thus generating the desired alkyltitanium thiolate derivatives, were unsuccessful. Reactions of **1**−**4** with MeLi led to a mixture of uncharacterized products. Attempts to alkylate with $AlMe_3$ or $ZnMe_2$ resulted in thiolate and/or alkoxide abstraction, together with a mixture of Ti products including $CpTiCl_2Me$, CpTi(OC_6H_3-2,6-i-Pr_2)Cl_2, and CpTi(OC_6H_3-2,6-i-Pr_2)MeCl.

An alternative synthetic approach involved the initial preparation of the species CpTi(OC_6H_3-2,6-i-Pr_2)(Me)-Cl (**5**) via reaction of CpTi(OC_6H_3-2,6-i-Pr_2)Cl_2 with $ZnMe_2$ or via reaction of $CpTiMeCl_2$ with Li(OC_6H_3-2,6-i-Pr_2). Reaction of **5** with 1,1-dimethylethanethiol in the presence of base afforded the species CpTi(OC_6H_3-2,6-i-Pr_2)(Me)($SCMe_3$) (**6**) in 53% isolated yield. The formulation of this species was confirmed by NMR data. This species was thermally robust, exhibiting no C−H or S−C bond activation upon heating to 80 °C for 12 h. In an analogous preparation, the species CpTi(OC_6H_3-

---

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

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

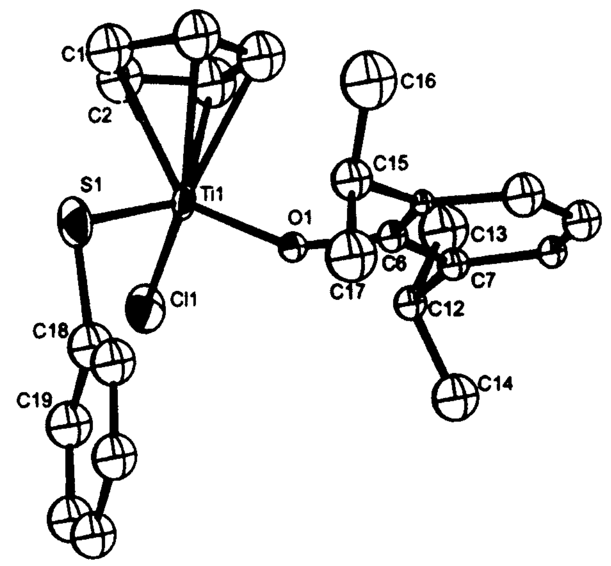
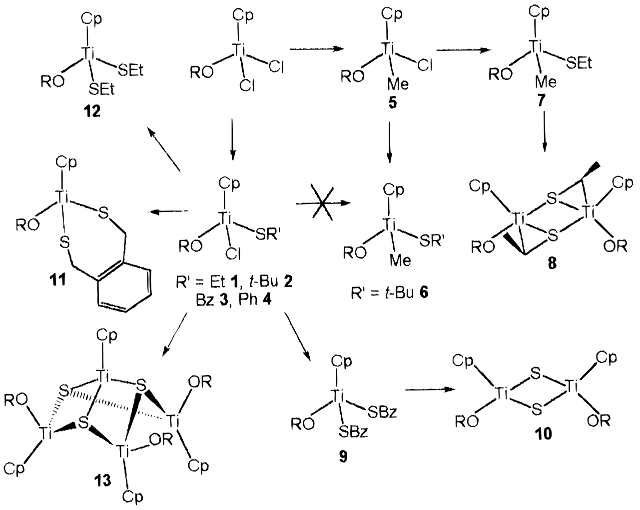
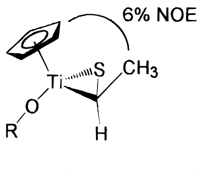


Figure 1. ORTEP drawing of **4**; 30% thermal ellipsoids are shown. Ti(1)−Cl(1) 2.26(1), Å; Ti(1)−S(1), 2.333(8) Å; Ti(1)−O(1), 1.80(2) Å; Cl(1)−Ti(1)−S(1), 106.8(4)°; Cl(1)−Ti(1)−O(1), 102.5(6)°; S(1)−Ti(1)−O(1),108.5(6)°.

Scheme 1



2,6-*i*-Pr$_2$)(Me)(SCH$_2$Me) (**7**) was generated in solution and observed as a transient species by ^{1}H NMR spectroscopy. However, the instability of **7** precluded its isolation. Heating the reaction mixture to 80 °C liberated methane, and the resulting product **8** was crystallized from solution. The NMR data and, in particular, the observation of a methine group as evidenced by the ^{13}C resonance at 99.1 ppm and the ^{1}H signal at 4.28 ppm prompted the empirical formulation of this new species **8** as CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(SCHMe). A 6% nuclear Overhauser effect was observed between the cyclopentadienyl ring protons and the methyl group proton, consistent with a geometry in which both of these groups reside on the same side of the thiametallacyclopropane ring. This, together with the dimeric nature of **8**, was subsequently confirmed crystallographically (Figure 2).



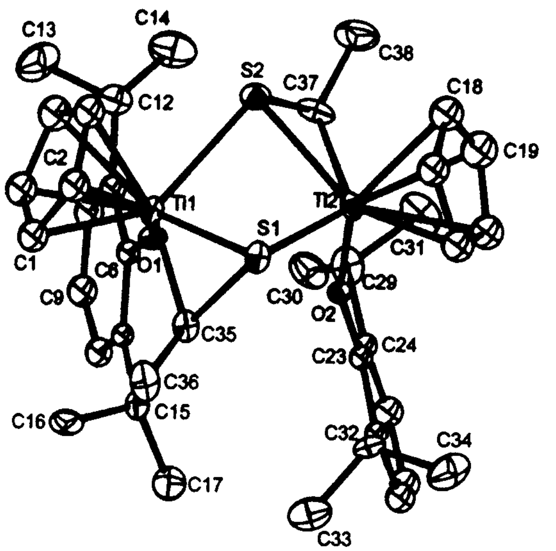


Figure 2. ORTEP drawing of **8**; 30% thermal ellipsoids are shown. Ti(1)−S(1), 2.441(4) Å; Ti(1)−S(2), 2.545(4) Å; Ti(1)−O(1), 1.814(7) Å; Ti(1)−C(35), 2.14(1) Å; Ti(2)−S(1), 2.556(4) Å; Ti(2)−S(2), 2.440(4) Å; Ti(2)−O(2), 1.816(7) Å; Ti(2)−C(37), 2.14(1) Å; S(1)−Ti(1)−S(2), 78.1(1); S(1)−Ti(1)−O(1), 120.5(2)°; S(1)−Ti(1)−C(35), 45.0(3)°; S(2)−Ti(1)−O(1), 94.4(2)°; S(2)−Ti(1)−C(35), 119.9(3)°; O(1)−Ti(1)−C(35), 98.7(4)°; S(1)−Ti(2)−S(2), 77.9(1)°; S(1)−Ti(2)−O(2), 96.8(2)°; S(1)−Ti(2)−C(37), 119.3(4)°; S(2)−Ti(2)−O(2), 121.0(2)°; S(2)−Ti(2)−C(37), 44.6(3)°; O(2)−Ti(2)−C(37), 98.1(4)°; Ti(1)−C(35)−S(1), 76.5(4)°; Ti(2)−C(37)−S(2), 76.8(5)°.

Mechanistically, the formation of **8** is thought to involve intramolecular loss of methane followed by dimerization. This is in contrast to the mechanism proposed for the formation of [CpTi(SCHCH$_2$CH$_2$S)]$_2$, where β-hydrogen abstraction is thought to occur.[6] Nonetheless, this view is consistent with the formation and stability of **6**, where the lack of hydrogen atoms β to the Ti permits isolation. It is also noteworthy that a concerted four-center cyclometalation process is operative in the formation of thioformaldehyde complexes of zirconocene.[12] Attempts to obtain kinetic data for the formation of **8** were unsuccessful, as the initial formation of the intermediate **7** was not clean, the species being apparently subject to both redistribution and metalation reactions.

Attempts to prepare the benzenethiolate analog of **6** were unsuccessful. Reaction of **5** with benzenethiolate results in a complex mixture of products. NMR data suggest that the myriad of products may include the desired substitution products in addition to a variety of Ti complex anions. Reaction of **5** with benzyl mercaptan and base at 25 °C also resulted in formation of a mixture of compounds. However, in this case, the major product was identified as CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(SCH$_2$Ph)$_2$ (**9**). This was confirmed via independent synthesis from CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)Cl$_2$ and 2 equiv of thiol in the presence of base. The formulation of **9** was also confirmed crystallographically (Figure 3).

The inability to obtain CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(Me)(SCH$_2$Ph) may arise because thiol protolysis of the Ti−methyl bond is competitive with deprotonation of the

---

[12] (a) Buchwald, S. L.; Nielsen, R. B.; Dewan, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 1590. (b) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1988**, *110*, 3171. (c) Buchwald, S. L.; Fisher, R. A.; Davis, W. M. *Organometallics* **1989**, *8*, 2082. (d) Fisher, R. A.; Nielsen, R. B.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 165.

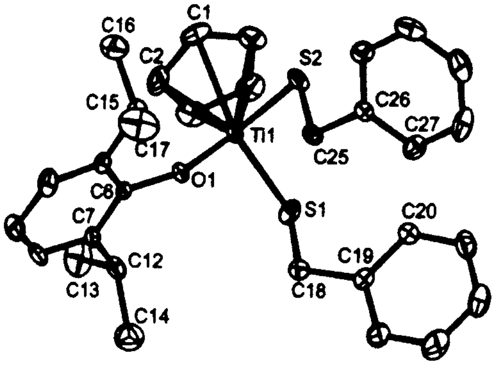


Figure 3. ORTEP drawing of **9**; 30% thermal ellipsoids are shown. Ti(1)–S(1), 2.318(2) Å; Ti(1)–S(2), 2.339(2) Å; Ti(1)–O(1), 1.796(3) Å; S(1)–Ti(1)–S(2), 108.90(7)°; S(1)–Ti(1)–O(1), 105.6(1)°; S(2)–Ti(1)–O(1), 104.2(1)°.

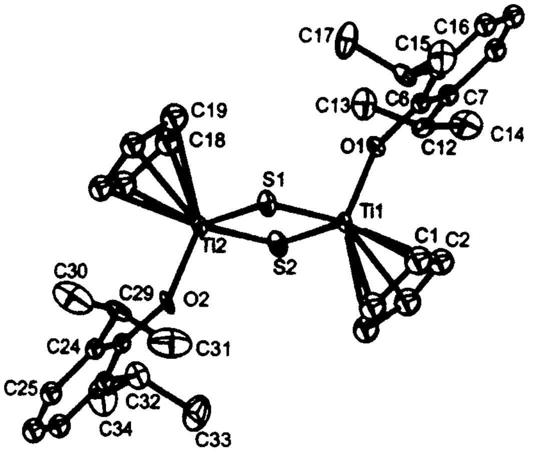


Figure 4. ORTEP drawing of **10**; 30% thermal ellipsoids are shown. Ti(1)–Ti(2), 3.141(3) Å; Ti(1)–S(1), 2.314(4) Å; Ti(1)–S(2), 2.302(4) Å; Ti(1)–O(1), 1.802(8) Å; Ti(2)–S(1), 2.295(4) Å; Ti(2)–S(2, 2.307(4) Å; Ti(2)–O(2), 1.819(8) Å; S(1)–Ti(1)–S(2), 93.9(2)°; S(1)–Ti(1)–O(1), 105.3(3)°; S(2)–Ti(1)–O(1), 105.6(3)°; S(1)–Ti(2)–S(2), 94.3(2)°; S(1)–Ti(2)–O(2), 106.0(3)°; S(2)–Ti(2)–O(2), 104.6(3)°; Ti(1)–S(1)–Ti(2), 85.9(2)°; Ti(1)–S(2)–Ti(2), 85.9(2)°.

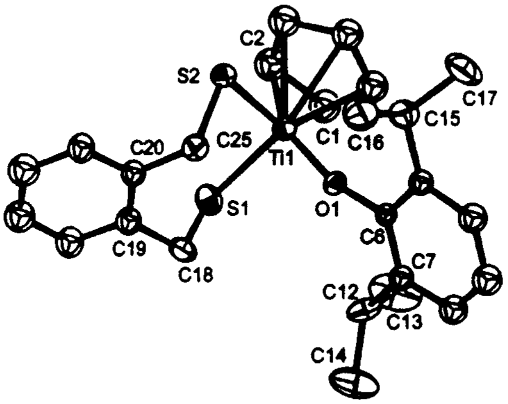


Figure 5. ORTEP drawing of **11**; 30% thermal ellipsoids are shown. Ti(1)–S(1), 2.321(3) Å; Ti(1)–S(2), 2.313(3) Å; Ti(1)–O(1), 1.793(5) Å; S(1)–Ti(1)–S(2), 102.9(1)°; S(1)–Ti(1)–O(1), 103.7(2)°; S(2)–Ti(1)–O(1), 103.6(2)°.

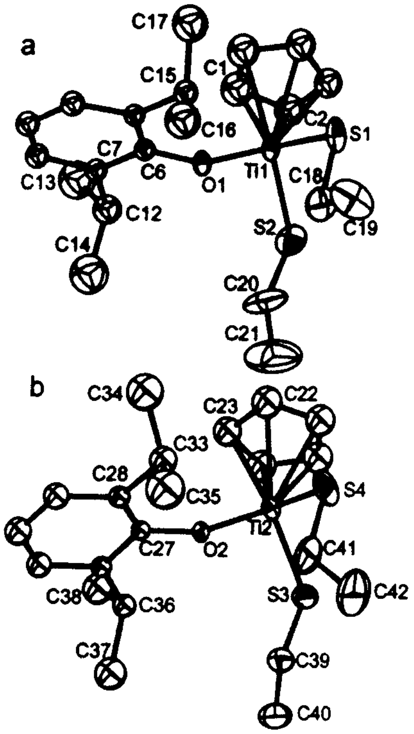


Figure 6. ORTEP drawing of **12**; 30% thermal ellipsoids are shown. Ti(1)–S(1), 2.329(5) Å; Ti(1)–S(2), 2.304(5) Å; Ti(1)–O(1), 1.802(8) Å; Ti(2)–S(3), 2.313(5) Å; Ti(2)–S(4), 2.318(6) Å; Ti(2)–O(2), 1.809(8) Å; S(1)–Ti(1)–S(2), 107.6(2)°; S(1)–Ti(1)–O(1), 104.7(3)°; S(2)–Ti(1)–O(1), 104.1(3)°; S(3)–Ti(2)–S(4), 108.4(2)°; S(3)–Ti(2)–O(2), 104.4(3)°; S(4)–Ti(2)–O(2), 103.9(3)°.

thiol by base. Alternatively, it may be that redistribution of CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(Me)(SCH$_2$Ph) to **9** and other uncharacterized species is facile. Heating the reaction mixture containing **9** resulted in isolation in low yield of a new species, **10**. This species exhibited ^{1}H NMR resonances attributable to the cyclopentadienyl and aryl oxide ligands only. X-ray crystallographic characterization of **10** confirmed the formulation as [CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)S]$_2$ (Figure 4). An alternative and higher yielding synthesis of **10** was subsequently shown from the thermolysis of pure **9**. In this way, **10** is obtained cleanly and quantitatively. The organic byproduct of this S–C bond cleavage reaction was identified as (PhCH$_2$)$_2$S by spectroscopic comparison to an authentic sample.[13]

The closely related species CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)((SCH$_2$)$_2$C$_6$H$_4$) **(11)** and CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(SCH$_2$Me)$_2$ **(12)** were prepared in a manner analogous to that employed for **9**. NMR and crystallographic data (Figures 5 and 6) confirmed the formulations. Thermolysis of **11** or **12** at 80 °C for 12–18 h resulted in no reaction. It is also noteworthy that similar thermolysis of **3** resulted in no reaction, and, as well, no radical coupling products are observed in the formation of **10**, other than the sulfide SBn$_2$. Given that the S–C bond strengths and nucleophilicity of ethanethiolate and benzenethiolate are expected to be similar, the conversion of **9** to **10** suggests a radical process within a solvated cage. While this supposition appears consistent with the data and chemical intuition, further mechanistic studies are required to confirm this postulate.

The implication of a radical process prompts questions of the role of Ti(III) in S–C bond activation. In other work,[14] we have found phosphides to be convenient and

---

[13] A sample of SBn$_2$ was prepared via direct reaction of LiSBn and BnCl: ^{1}H NMR (C$_6$D$_6$, 25 °C) δ 3.33 (s, 4H), 7.13 (m, 10H).

[14] (a) Dick, D. G.; Hou, Z.; Stephan, D. W. *Organometallics* **1992**, *11*, 2378. (b) Dick, D. G.; Stephan, D. W. *Organometallics* **1990**, *9*, 1910. (c) Ho, J.; Stephan, D. W. *Inorg. Chem.* **1994**, *33*, 4595. (d) Dick, D. G.; Stephan, D. W. *Organometallics* **1991**, *10*, 2811. (e) Dick, D. G.; Stephan, D. W. *Can. J. Chem.* **1991**, *69*, 1146.

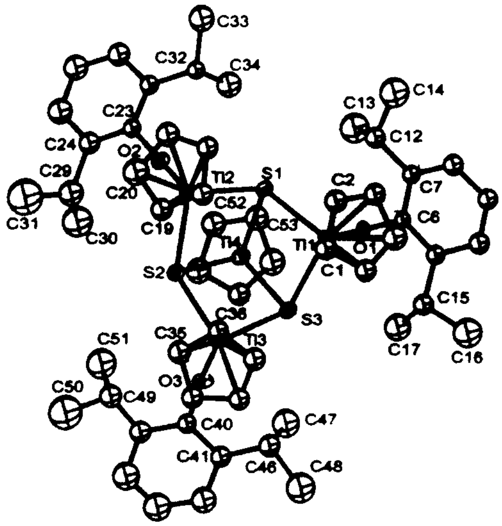


Figure 7. ORTEP drawing of **13**; 30% thermal ellipsoids are shown. Ti(1)–Ti(4), 3.072(5) Å; Ti(1)–S(1), 2.399(6) Å; Ti(1)–S(3), 2.417(5) Å; Ti(1)–O(1), 1.82(1) Å; Ti(2)–Ti(4), 3.067(5) Å; Ti(2)–S(1), 2.396(6) Å; Ti(2)–S(2), 2.407(5) Å; Ti(2)–O(2), 1.81(1) Å; Ti(3)–Ti(4), 3.075(4) Å; Ti(3)–S(2), 2.415(6) Å; Ti(3)–S(3), 2.393(6) Å; Ti(3)–O(3), 1.79(1) Å; Ti(4)–S(1), 2.344(6) Å; Ti(4)–S(2), 2.346(6) Å; Ti(4)–S(3), 2.345(6) Å; S(1)–Ti(1)–S(3), 95.3(2)°; S(1)–Ti(1)–O(1), 102.6(4)°; S(3)–Ti(1)–O(1), 101.6(4)°; S(1)–Ti(2)–S(2), 95.4(2)°; S(1)–Ti(2)–O(2), 100.6(4)°; S(2)–Ti(2)–O(2), 102.7(4)°; S(2)–Ti(3)–S(3), 95.3(2)°; S(2)–Ti(3)–O(3), 103.2(4)°; S(3)–Ti(3)–O(3), 102.8(4)°; S(1)–Ti(4)–S(2), 98.4(2)°; S(1)–Ti(4)–S(3), 98.7(2)°; S(2)–Ti(4)–S(3), 98.5(2)°; Ti(1)–S(1)–Ti(2), 131.3(2)°; Ti(1)–S(1)–Ti(4), 80.7(2)°; Ti(2)–S(1)–Ti(4), 80.6(2)°; Ti(2)–S(2)–Ti(3), 130.7(3)°; Ti(2)–S(2)–Ti(4), 80.4(2)°; Ti(3)–S(2)–Ti(4), 80.4(2)°; Ti(1)–S(3)–Ti(3), 130.4(2)°; Ti(1)–S(3)–Ti(4), 80.3(2)°; Ti(3)–S(3)–Ti(4), 80.9(2)°; Ti(1)–O(1)–C(6), 151(1)°; Ti(2)–O(2)–C(23), 157(1)°; Ti(3)–O(3)–C(40), 152(1)°.

effective reducing agents. Treatment of **2** with LiPCy$_2$ resulted in a dramatic color change from orange to dark green. ^{31}P{^{1}H} NMR spectra of the reaction mixture revealed the formation of (PCy$_2$)$_2$,[14] implying redox chemistry had, indeed, occurred. The paramagnetic Ti-containing product **13** was isolated by fractional crystallization and shown crystallographically to be [(CpTi(OR)(μ^3-S)]$_3$TiCp (Figure 7). Related S–C bond scission/reduction reactions in zirconium 1,1-dimethylethanethiolate complexes have been previously reported to yield the complexes Zr$_3$S$_3$(S-*t*-Bu)$_2$(BH$_4$)$_4$, Zr$_6$S$_6$(S-*t*-Bu)$_2$(BH$_4$)$_8$, and Zr$_3$S(S-*t*-Bu)$_{10}$.[15] It is interesting to contrast the thermal stability of the titanium(IV) 1,1-dimethylethanethiolate complex **6** with the facile S–C bond cleavage upon reduction of the metal center.

Structural Data

The structural studies of **4**, **8**–**13** are similar in that they all contain CpTi(OR) fragments. T–O–C angles in the range of 151(1)–165.0(6)° and the Ti–O distances of 1.793(5)–1.82(1) Å are consistent with Ti–O π-bonding. In the case of compounds **4**, **9**, **11**, and **12** (Figures 1 3, 5, and 6), the geometries of the Ti coordination spheres are best described as distorted "three-legged piano stools", in which the cyclopentadienyl ligand serves as the seat of the stool while the three other ligands are the legs. In these compounds, the Ti–S distances are very similar, all falling in the range of 2.304(5)–2.333(8) Å, as is typical of compounds containing terminal titanium thiolate ligands.[1] In addition, the Ti–S–C angles in **4**, **9**, **11**, and **12** fall within the narrow range of 100.6(3)–106.9(2)°, consistent with minimal π-donation from S to the Ti centers.

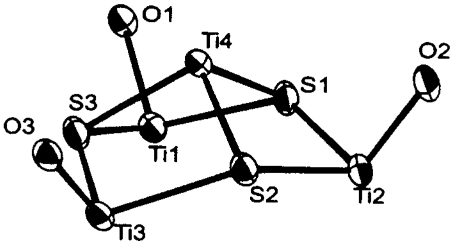


Figure 8. ORTEP drawing of the TiSO core of **13**; 30% thermal ellipsoids are shown.

The structural study of **8** confirms that two CpTi(OR) centers form titanathiacyclopropane rings (Figure 2), in which the Ti–C bond distances are 2.14(1) Å. The sulfur atoms bridge the two metal centers, yielding the dimeric complex. The Ti–S distances within the thiatitanacyclopropane ring are 2.441(4) Å. In contrast to the species [CpTi(SCHCH$_2$CH$_2$S)]$_2$, the S atoms within the metallacycle in **8** bridge to the adjacent Ti with an average Ti–S distance of 2.550(6) Å.[6] The cyclopentadienyl rings are *transoid* with respect to the Ti$_2$S$_2$ core. Ring strain within the thiatitanacyclopropane ring is evidenced by C–Ti–S angles of 45.0(3)° and 44.6(3)° and Ti–C–S angles of 76.5(4)° and 76.8(5)°, respectively. A similar dimeric structure is seen for **10** (Figure 4), in which two sulfur atoms bridge the Ti centers at Ti–S distances of 2.295(4)–2.314(4) Å. In a manner similar to that of **8**, the cyclopentadienyl ligands are *transoid* with respect to the Ti$_2$S$_2$ plane, presumably a consequence of steric preference.

The molecular structure of **13** (Figure 7) is comprised of three CpTi(OR)S fragments forming a cyclic trimeric ring (Figure 8). The three bridging sulfur atoms are capped by a fourth CpTi unit. The three OR ligands are oriented on the same side of the [CpTi(OR)S]$_3$ ring, again presumably an accommodation which minimizes steric congestion. The Ti–S distances about the trimeric ring average 2.405(7) Å, while the Ti–S distances to the central Ti average 2.346(5) Å.

Summary

In conclusion, C–H and S–C bond activation reactions of the titanium thiolate complexes described herein provide access to novel metallacyclic and sulfide bridged products. The potential utility of these compounds in either the functionalization of thiols or desulfurization of organosulfur compounds is the subject of current study.

Acknowledgment. Financial support from the NSERC of Canada is gratefully acknowledged. Dr. Glenn Yap of the Windsor Molecular Structure Centre is thanked for data collection for **13**.

Supporting Information Available: Spectroscopic data and tables of crystallographic parameters, hydrogen atom parameters, and thermal parameters (43 pages). Ordering information is given on any current masthead page.

OM961093P

---

(15) (a) Coucouvanis, D.; Hadjikyriacou, A.; Kanatzdis, M. G. *J. Chem. Soc., Chem. Commun.* **1985**, 1224. (b) Coucouvanis, D.; Lester, R. K.; Kanatzdis, M. G.; Kessissoglou, D. P. *J. Am. Chem. Soc.* **1985**, *107*, 8279.