Synthesis and Structural and Reactivity Studies of Thiatitanacyclopropane Complexes $[Cp^{\dagger}Ti(SCHCH_2CH_2S)]_2$ ($Cp^{\dagger}$ = Cp, MeCp)

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The complexes $[Cp^{\dagger}Ti(SCHCH_2CH_2S)]_2$ ($Cp^{\dagger}$ = Cp (**3**), MeCp (**4**)) are readily prepared from reaction of $Cp^{\dagger}Ti(SCH_2CH_2CH_2S)Cl$ ($Cp^{\dagger}$ = Cp (**1**), MeCp (**2**)) with MeLi, $AlMe_3$, or *t*-BuLi. Both compounds are centrosymmetric dimers in the solid state containing strained thiatitanacyclopropane rings. PMe_3 cleaves these dimers, establishing equilibria between **3** and **4** and $Cp^{\dagger}Ti(SCHCH_2CH_2S)(PMe_3)$ ($Cp^{\dagger}$ = Cp (**5**), MeCp (**6**)), while compound **3** undergoes facile acidolysis with HCl, acetic acid, PhSH, and propanedithiol affording $CpTiCl_3$, $CpTi(O_2CMe)_3$ (**7**), $CpTi(SCH_2CH_2CH_2S)(SPh)$, and $H^+[CpTi(SCH_2CH_2CH_2S)_2]^-\cdot THF$ (**8**), respectively. The thiametallacycles react with benzophenone to give $Cp^{\dagger}Ti(SCH(CPh_2O)CH_2CH_2S)$ ($Cp^{\dagger}$ = Cp (**9**); MeCp (**10**)) while reaction with cyclohexanone gives the dimeric species $[Cp^{\dagger}Ti(SCH(C_6H_{10}O)CH_2CH_2S)]_2$ ($Cp^{\dagger}$ = Cp (**11**); MeCp (**12**)). Analogous reactions with 2-methylcyclohexanone, menthone, and nopinone give related addition products with varying degrees of diastereoselectivity. The complex **3** also reacts with a series of imines to give complexes of the form $CpTi(SCH(CHRNR)CH_2CH_2S)$, where the diastereoselectivity observed is a function of the steric demands of the substrate substituents. Reaction of **3** with nitriles, methyl isocyanate, dicyclohexylcarbodiimide, and phenyl thioisocyanate results in insertion of the substrate and subsequent enolization to give species of the form $CpTi(SC{=}(C(R)NH)CH_2CH_2S)$. The analogous reaction with phenyl isocyanate yields the bimetallic complex $CpTi(SC(PhNCO)CH_2CH_2S)TiCp(SCH_2CH_2CH_2S)$ (**27**). Crystallographic characterization of a number of these reaction products is reported. Kinetic studies of the formation of **10** and **12** are consistent with initial formation of ketone complex adducts and subsequent intra- and intermolecular C−C bond formation reactions. The nature of the products, reaction mechanisms, and reactivity of strained thiatitanacyclopropane rings are discussed in the light of EHMO calculations.

Introduction

Early transition metal mediated syntheses of organic compounds is an area of chemistry that is developing rapidly. Of particular interest is the potential for the synthesis of organics containing heteroatoms. To this end, reactive early metal reagents have been sought.[1] Most recently interest has focused on the metal−heteroatom double bonds as vehicles to organic derivatives. Ti-, Zr-, and Ta-based systems containing metal−oxo (M═O), metal−sulfido (M═S), metal−imido (M═NR), and metal−phosphidene (M═PR) fragments have been shown to have rich reactivity.[2] While such double-bonded moieties continue to be of interest, heteroatom derivatives of metallacycles present an alternative class of potential reagents. In this regard, Buchwald et al. have applied the reactivity of Zr−imine complexes $Cp_2Zr(RNCHR')(L)$ to prepare allylic amines.[3] Transient azatitanetines have been employed in the catalytic synthesis of dihydropyrrole and tetrahydropyridine derivatives by Livinghouse and co-workers.[4] In this case the diminished steric constraints about the metal center of monocyclopentadienyltitanium systems have been employed. Related sulfur metallacycles have drawn less attention. Zirconocene thioaldehyde deriva-

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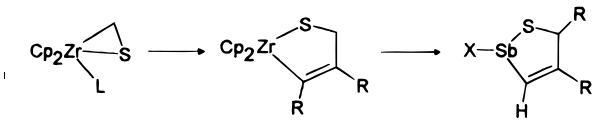
tives[5,6] have been shown to undego alkyne insertion and subsequent transmetalation with antimony halides to yield stibathiolanes;[7]



however, analogous titanium species were found them to be much less useful from a synthetic perspective, as attempted insertion reactions were generally not clean.[8] In contrast, we have recently shown that thiatitanacyclopropanes derived from monocyclopentadienyltitanium species[9] provide effective routes to amino- and alkoxy-substituted dithiols and disulfides.[10] In this paper, we describe the first broad study of reactivity of such thiametallacycles with a variety of unsaturated organic reagents. The nature of the resulting titanium complexes is established and mechanistic aspects are considered with particular reference to issues of regio- and stereochemistry.

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 equipped with a catalyst column and an atmosphere circulation system. Solvents were reagent grade, distilled from the appropriate drying agents under N_2, and degassed by the freeze−thaw method at least three times prior to use. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker AC-300 spectrometer 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 and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker AC-200 operating at 81 MHz, and chemical shifts are reported relative to 85% H_3PO_4. Assignments of the ^{1}H and ^{13}C NMR resonances and determination of coupling constant values were based on a series of homonuclear decoupling and NOE experiments. Combustion analyses were performed by Guelph Analytical Laboratories Inc., Guelph, ON, Canada, and Schwarzkopf Laboratories, Woodside, NY. PMe_3, 1,3-propanedithiol, benzophenone, cyclohexanone, methylcyclohexanone, (−)-menthone, (1*R*)-(+))-nopinone, methyl phenyl ketone, 2-hexanone, benzonitrile, valeronitrile, methyl thiocyanate, dicyclohexylcarbodiimide, phenyl isocyanate, and phenyl isothiocyanate were purchased from the Aldrich Chemical Co. $CpTiCl_3$, $(MeCp)TiCl_3$, and the imines, PhN=CHPh, *rac*-(Naphth)CH(CH$_3$)N=CHPh, PrN=CHPh, PhN=CH(C_6H_4OMe), (C_6H_4OMe)N=CHPh, and (C_6H_4OMe)N=CH(C_6H_4OMe) were prepared by standard methods.[11,12] Compound **1** was prepared as previously described.[9]

Synthesis of (MeCp)Ti(SCH$_2$CH$_2$CH$_2$S)Cl (2). The compound (MeCp)Ti(SCH$_2$CH$_2$CH$_2$S)Cl was prepared in 95% yield by a method analogous to that reported for **1**. ^{1}H NMR (C_6D_6, 25 °C): δ 1.18 (d, t, t, 1H, $|J_{H-H}|$ = 15.3, 13.2, 2.6 Hz), 1.96 (s, 3H), 2.55 (d, t, t, "d septet", 1H, $|J_{H-H}|$ = 15.2, 2.0, 2.0 Hz), 3.71 (d, d, d, 2H, $|J_{H-H}|$ = 13.5, 13.5, 1.1 Hz), 3.86 (d, d, d, 2H, $|J_{H-H}|$ = 14.0, 3.3, 3.3 Hz), 6.01 (d, d, 2H, $|J_{H-H}|$ = 2.5, 2.5 Hz), 6.06 (d, d, 2H, $|J_{H-H}|$ = 2.5, 2.5 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 16.51, 32.83, 40.27, 114.87, 115.93, 131.72. Anal. Calcd for $C_9H_{13}ClS_2Ti$: C, 40.24; H, 4.88. Found: C, 40.14; H, 4.78.

Synthesis of [CpTi(SCHCH$_2$CH$_2$S)]$_2$ (3) and [(MeCp)Ti(SCHCH$_2$CH$_2$S)]$_2$ (4). These two complexes were prepared in similar manners, and thus only one preparation is described. (i) A 1.4 M solution of MeLi in diethyl ether (0.33 mL, 0.47 mmol) was added dropwise to a stirred solution of CpTi(SCH$_2$CH$_2$CH$_2$S)Cl (0.100 g, 0.39 mmol) in THF (3 mL) at −78 °C. The mixture turned from orange to brown immediately and became darker over a 2 h period as it was warmed to room temperature. The solvent was removed in vacuo, and the residue was taken up into benzene. A black-gray precipitate was filtered from the solution, and dark brown crystals of **3** were deposited upon standing of the solution for 24 h, yield 10%. A further 65% yield was contained in the black-gray precipitate. (ii) To a THF (20 mL) solution of CpTi(SCH$_2$CH$_2$CH$_2$S)Cl (2.000 g, 8.0 mmol) was added $AlMe_3$ (8.00 mL of 2.0 M in toluene). The solution was allowed to stand for 2 days. The solution was filtered, and the solid was washed with 2 × 5 mL portions of hexane affording black crystalline **3** in 81% yield. For **4**, the solvent was removed under vacuum, the residue was washed with hexane and dissolved in benzene, and the solution filtered through Celite. Addition of hexane afforded **4**. Data for **3** are as follows. ^{1}H NMR (C_4D_8O, 25 °C): δ 2.15 (d, d, d, d, 1H, $|J_{H-H}|$ = 14.3, 13.6, 4.4, 4.2 Hz), 3.39 (d, d, br, 1H, $|J_{H-H}|$ = 14.3, 4.7 Hz), 3.50 (d, d, br, 1H, $|J_{H-H}|$ = 12.0, 4.2 Hz), 5.13, (d, br, 1H, $|J_{H-H}|$ = 4.4 Hz), 5.60 (m, 1H, $|J_{H-H}|$ = 13.6, 12.0, 4.7 Hz), 6.40 (s, 5H). ^{13}C{^{1}H} NMR (C_4D_8O, 25 °C): δ 47.38, 48.93, 115.44, 115.67. Anal. Calcd for $C_8H_{10}S_2Ti$: C, 44.04; H, 4.62. Found: C, 44.21; H, 4.54. Data for **4** are as follows. Yield: 82%. ^{1}H NMR (C_6D_6, 25 °C): δ 1.87 (s, 3H), 2.14 (t, t, 1H, $|J_{H-H}|$ = 14.1, 4.5 Hz), 3.50 (m, 2 H), 5.12 (d, t, 1H, $|J_{H-H}|$ = 4.4, 1.3 Hz), 5.67 (m, 2H), 5.86 (d, d, d, 1H, $|J_{H-H}|$ = 15.5, 11.5, 4.0 Hz), 6.02 (m, 1H), 6.11 (m, 1H). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 16.33, 47.25, 48.44, 113.09, 114.21, 115.61, 115.73, 115.86, 128.90. Anal. Calcd for $C_9H_{12}S_2Ti$: C, 46.56; H, 5.21. Found: C, 46.34; H, 5.11.

Synthesis of CpTi(SCHCH$_2$CH$_2$S)(PMe$_3$) (5) and (MeCp)Ti(SCHCH$_2$CH$_2$S)(PMe$_3$) (6). These two complexes were generated in similar manners, and thus only one preparation is described. To a suspension of **3** (85 mg, 0.195 mmol) in THF or benzene (1 mL) was added PMe_3 (150 mg, 1.29 mmol). The reaction was stirred at 25 °C for 2 h and the product characterized by NMR. Attempts to isolate the product **5** resulted in loss of PMe_3 and re-formation of **3**. Data for **5** are as follows. ^{1}H NMR (C_6D_6, 25 °C): δ 0.85 (d, 9H, $|J_{H-H}|$ = 7.2 Hz), 2.70 (t, t, 1H, $|J_{H-H}|$ = 11.5, 3.6 Hz), 3.00 (d, d, br, 1H, $|J_{H-H}|$ = 11.5, 4.8 Hz), 3.62 (d, br, 1H, $|J_{H-H}|$ = 11.5, 3.0 Hz), 4.29 (t, d, 1H, $|J_{H-H}|$ = 11.5, 3.0 Hz), 4.56 (d, d, 1H, $|J_{H-H}|$ = 3.6, 1.0 Hz), 5.95 (br s, 5H, Cp). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 14.05 (d, $|J_{P-C}|$ = 18.0 Hz), 37.49, 50.80, 92.24, 110.03 (d, $|J_{P-C}|$ = 7.5 Hz). ^{31}P NMR (C_6D_6, 25 °C): δ −5.69. Data for **6** are as follows. ^{1}H NMR (C_6D_6, 25 °C): δ 0.87 (br, 9H), 2.03 (s, 3H), 2.77 (d, d, t, 1H, $|J_{H-H}|$ = 13.7, 5.3, 4.3 Hz), 3.00 (d, d, d, d, 1H, $|J_{H-H}|$ = 11.0, 5.4, 1.2, 1.2 Hz), 3.57 (d, d, d, d, 1H, $|J_{H-H}|$ = 13.7, 4.0, 1.4, 1.4 Hz), 4.31 (d, d, d, 1H, $|J_{H-H}|$ = 13.8, 11.1, 4.0 Hz), 4.51 (br,d, 1H, $|J_{H-H}|$ = 3.9 Hz), 5.83 (d, d, 1H, $|J_{H-H}|$ = 4.6, 2.2 Hz), 5.87 (d, d, 1H, $|J_{H-H}|$ = 5.4, 2.9 Hz),

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6.35 (d, d, 1H, $|J_{H-H}| = 4.8, 2.2$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 16.26 (br), 16.36, 37.60, 51.14, 93.73, 108.49, 109.17, 111.57, 112.76, 126.45. ^{31}P NMR (C_6D_6, 25 °C): δ −6.25.

Synthesis of $CpTi(O_2CMe)_3$ (7). To a suspension of **3** (85 mg, 0.195 mmol) in THF (3 mL) was added excess acetic acid. The reaction was stirred for 5 h at 25 °C. The solution became yellow. The solvent was removed and the residue extracted into THF and pentane was added to give yellow crystals of **7**. Yield: 86%. ^1H NMR ($CDCl_3$, 25 °C): δ 1.93 (s, 9H), 6.45 (s, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 59.54, 122.87, 189.20. Anal. Calcd for $C_{11}H_{14}O_6Ti$: C, 45.54; H, 4.86. Found: C, 45.33; H, 4.76.

Synthesis of $[CpTi(SCH_2CH_2CH_2S)_2][THFH]$ (8). 1,3-Propanedithiol (0.016 g, 0.15 mmol) was added to a stirred suspension of **3** (0.131 g, 0.30 mmol) in THF (3 mL). The brown-black suspension immediately turned deep red; however, some dark precipitate remained. The solution was filtered, and the remaining red solution was concentrated to 1 mL. Orange-red crystals of **8** were formed from a THF/pentane liquid/vapor diffusion after standing for 4 days. Yield: 45% (by NMR). Yield of crystalline product: 15%. ^1H NMR (C_4D_8O, 25 °C): δ 6.13 (s, 5H), 3.48 (m, 4H), 3.02 (m, 4H), 2.54 (m, 2H), 1.79 (m, 2H). $^{13}C\{^1H\}$ NMR (C_4D_8O, 25 °C): δ 28.41, 36.72, 113.32.

Synthesis of $CpTi(SCH(CPh_2O)CH_2CH_2S)$ (9), $(MeCp)Ti(SCH(CPh_2O)CH_2CH_2S)$ (10), $[CpTi(SCH(C_6H_{10}O)CH_2CH_2S)]_2$ (11), $[(MeCp)Ti(SCH(C_6H_{10}O)CH_2CH_2S)]_2$ (12), $[CpTi(SCH(C_7H_{12}O)CH_2CH_2S)]_2$ (13), $[CpTi(SCH(C_{10}H_{18}O)CH_2CH_2S)]_2$ (14), $[CpTi(SCH(C_9H_{14}O)CH_2CH_2S)]_2$ (15), and $[CpTi(SCH(C_4H_9)C(CH_3)O)CH_2CH_2S)]_2$ (16). These compounds were prepared in similar fashion; thus, one sample preparation is described in detail and the major differences in time, temperature, and solvent are reported. (i) To a suspension of **3** (85 mg, 0.195 mmol) in THF (3 mL) was added Ph_2CO (70 mg, 0.38 mmol). The reaction was stirred for 5 h at 25 °C. The reaction was filtered, the solvent removed, and the residue washed with pentane and extracted into CH_2Cl_2. Crystallization was induced by addition of benzene yielding purple-black product **9** in 92% yield. (ii) An alternative synthesis of **9** and **11** is described as follows: To a THF solution (1 mL) of **5** (58 mg, 0.100 mmol) was added Ph_2CO (18 mg, 0.100 mmol). The solution was stirred for 5 min and the solvent removed. The residue was washed with pentane and dried in vacuo, and the compound **9** isolated in 90% yield. Data for **9** are as follows. ^1H NMR (C_6D_6, 25 °C): δ 2.20 (d, d, t, br, 1H, $|J_{H-H}| = 15.0, 13.5, 4.8$ Hz), 3.40 (d, d, d, 1H, $|J_{H-H}| = 15.0, 3.0, 1.8$ Hz), 3.59 (d, d, d, 1H, $|J_{H-H}| = 13.5, 4.8, 3.0$ Hz), 3.84 (t, d, 1H, $|J_{H-H}| = 13.5, 3.0$ Hz), 5.95 (d, d, 1H, $|J_{H-H}| = 4.8, 1.8$ Hz), 6.57, (s, 5H), 7.14, (m, 2H), 7.24 (t, d, 2H, $|J_{H-H}| = 7.4$ Hz), 7.25 (t, 2H, $|J_{H-H}| = 7.5$ Hz), 7.41 (d, br, 2H, $|J_{H-H}| = 7.5$ Hz), 7.43 (d, br, 2H, $|J_{H-H}| = 7.5$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 34.03, 34.72, 67.15, 98.88, 114.87, 124.70, 124.79, 126.42, 126.55, 128.17, 128.31,146.13, 146.31. Anal. Calcd for $C_{21}H_{20}OS_2Ti$: C, 63.00; H, 5.03. Found: C, 62.80; H, 4.95. Data for **10** are as follows. Method i: reaction time, 24 h; reaction temp, 25 °C. Yield: 80%. ^1H NMR (C_6D_6, 25 °C): δ 1.92 (s, 3H), 2.25 (d, t, br, 1H, $|J_{H-H}| = 13.5, 5$ Hz), 3.16 (m, 1H, $|J_{H-H}| = 13.5$ Hz), 3.60 (m, 1H, $|J_{H-H}| = 14$ Hz), 4.12 (d, t, 1H, $|J_{H-H}| = 13.5, 3$ Hz), 5.67 (m, 1H), 5.90 (m, 1H), 6.05 (m, 1H), 6.85−7.55 (m, 10H). $^{13}C\{^1H\}$ NMR (C_6H_6, 25 °C): δ 15.49, 34.84, 65.79, 98.59, 114.09, 114.31, 114.48, 114.87, 125.01, 125.64, 126.35, 126.51, 128.31, 128.39, 129.97, 147.41, 149.88. Data for **11** are as follows. Method i: reaction time, 5 h; reaction temp, 25 °C. Yield: 95%. Method ii: reaction time, 5 min; reaction temp, 25 °C; recrystallized from CH_2Cl_2/C_6H_6. Yield: 70%. ^1H NMR ($CDCl_3$, 25 °C): δ 1.0−2.0 (m, 20H), 1.95 (d, br, 2H), 2.14 (d, d, br, 2H, $|J_{H-H}| = 13.2, 5.2$ Hz), 3.50 (d, d, d, 2H, $|J_{H-H}| = 13.0, 5.2, 4.0$ Hz), 3.70 (d, d, br, 4H, $|J_{H-H}| = 13.0, 7.2, 3.3$ Hz), 4.50 (d, d, 2H, $|J_{H-H}| = 11.4, 1.0$ Hz), 6.39 (s, 10H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 21.34, 22.50, 25.70, 31.39, 38.36, 40.38, 40.43, 73.17, 95.29, 114.71. Anal. Calcd for $C_{14}H_{20}OS_2Ti$: C, 53.16; H, 6.37. Found: C, 52.88; H, 6.17. Data for **12** are as follows. Method i: reaction time, 16 h; reaction temp, 25 °C. Yield: 89%. ^1H NMR ($CDCl_3$, 25 °C): δ 1.0−1.8 (m, 20H), 1.97 (d, br, 2H, $|J_{H-H}| = 14$ Hz), 2.08 (m, 2H), 2.33 (s, 3H), 3.54 (d, t, 4H, $|J_{H-H}| = 7, 4.5$ Hz), 4.39 (d, d, 2H, $|J_{H-H}| = 11.5, 2.5$ Hz), 6.00 (m, 2H), 6.17 (m, 2H), 6.31 (m, 2H), 6.38 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 16.77, 21.55, 22.60, 25.85, 31.32, 32.19, 37.80, 38.62, 72.18, 94.20, 113.10, 114.25, 114.6, 114.92, 116.69. Data for **13** are as follows. Reaction time, 24 h; recrystallized from CH_2Cl_2/pentane. Yield: 93% (25 °C, **13a**:**13b** = 80:20; −78 °C, **13a**:**13b** = 92:8; from ^1H NMR). **13a**: ^1H NMR ($CDCl_3$, 25 °C): δ 1.06 (d, 6H, $|J_{H-H}| = 6.3$ Hz), 1.0−1.9 (m 18H), 1.95, d, d, br, 2H, $|J_{H-H}| = 12.6, 5.4, 2.0$ Hz), 2.20 (d, br, 2H, $|J_{H-H}| = 13.0$ Hz), 3.40 (d, d, d, 2H, $|J_{H-H}| = 12.9, 5.4, 4.5$ Hz), 3.97 (d, d, d, 2H, $|J_{H-H}| = 12.9, 8.7, 2.0$ Hz), 4.66 (d, d, 2H, $|J_{H-H}| = 11.7, 1.0$ Hz), 6.39 (s, 10H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 16.37, 21.93, 26.38, 31.31, 31.57, 32.50, 38.31, 39.24, 68.05, 97.41, 114.86. **13b**: ^1H NMR ($CDCl_3$, 25 °C): δ 1.01 (d, 6H, $|J_{H-H}| = 6.3$ Hz), 4.50 (d, d, 2H, $|J_{H-H}| = 11.7, 1.0$ Hz), 6.38 (s, 10H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 18.50, 22.89, 26.10, 29.37, 32.50, 33.60, 36.64, 38.76, 71.32, 95.60, 114.90. Anal. Calcd for $C_{15}H_{22}OS_2Ti$: C, 54.54; H, 6.71. Found: C, 54.27; H, 6.66. Data for **14** are as follows. Reaction time, 24 h; reaction temp, −78 °C; recrystallized from CH_2Cl_2/pentane. Yield: 83%. ^1H NMR ($CDCl_3$, 25 °C): δ 0.90 (d, 6H, $|J_{H-H}| = 6.6$ Hz), 0.92 (d, 6H, $|J_{H-H}| = 6.6$ Hz), 0.99 (d, 6H, $|J_{H-H}| = 6.2$ Hz), 1.53, (d, d, d, br, 2H, $|J_{H-H}| = 13.5, 11.4, 5.0$ Hz), 1.1−1.7 (m, 14H), 1.95 (d, d, 2H, $|J_{H-H}| = 13.5, 3.0$ Hz), 2.23 (d, br, 2H, $|J_{H-H}| = 13.0$ Hz), 2.27 (m, 2H), 3.35 (m, 2H) 3.40 (m, 2H), 4.74 (d, br, 2H, $|J_{H-H}| = 11.4$ Hz), 6.34 (s, 10H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 19.89, 21.65, 22.31, 22.73, 23.83, 28.24, 32.17, 34.93, 38.75, 42.40, 49.29, 73.07, 98.85, 114.92. Anal. Calcd for $C_{18}H_{28}OS_2Ti$: C, 58.05; H, 7.58. Found: C, 57.98; H, 7.49. Data for **15** are as follows. Reaction time, 24 h; reaction temp, −78 °C. The reaction residue was washed with pentane (2 × 2 mL), and the residual solvent was removed in vacuo to give **15** as an oil. Yield: 80% (−78 °C, **15a**:**15b**:**15c** = 70:30:trace; 5 °C, **15a**:**15b**:**15c** = 57:36:3; 30 °C, **15a**:**15b**:**15c** = 55:5:20; ratios from ^1H NMR). **15a**: ^1H NMR ($CDCl_3$, 25 °C): δ 0.78 (s, 3H), 1.16 (s, 3H), 1.70−2.30 (m, 8H), 2.95 (t, 1H, $|J_{H-H}| = 7.2$ Hz), 3.50 (d, d, d, 1H, $|J_{H-H}| = 13.5, 5.4, 3.3$ Hz), 3.85 (d, d, d, d, br, 1H, $|J_{H-H}| = 13.5, 5.4, 3.3$ Hz), 4.10 (t, d, 1H, $|J_{H-H}| = 13.5, 3.1$ Hz), 4.70 (d, d, 1H, $|J_{H-H}| = 5.4, 1.8$ Hz), 6.48 (s, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 22.74, 23.70, 26.77, 27.98, 29.31, 34.01, 39.70, 40.69, 52.69, 69.85, 72.19, 101.98, 113.93. **15b**: ^1H NMR ($CDCl_3$, 25 °C): δ 0.79 (s, 3H), 1.15 (s, 3H), 1.7−2.30 (m, 7H), 2.50 (t, 1H, $|J_{H-H}| = 7.2$ Hz), 2.80 (t, d, 1H, $|J_{H-H}| = 12.0, 6.0$ Hz), 3.20 (d, d, d, br, 1H, $|J_{H-H}| = 13.5, 5.4, 3.3$ Hz), 3.80 (d, d, d, br, 1H, $|J_{H-H}| = 13.5, 5.4, 3.3$ Hz), 4.19 (t, d, 1H, $|J_{H-H}| = 13.5, 3.1$ Hz), 4.91 (d, d, 1H, $|J_{H-H}| = 5.4, 1.8$ Hz), 6.52 (s, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 23.05, 24.42, 26.07, 27.98, 29.75, 35.28, 39.89, 40.90, 51.05, 68.01, 74.02, 102.02,114.05. **15c**: ^1H NMR ($CDCl_3$, 25 °C): δ 0.96 (s, 6H), 1.23 (s, 6H), 1.0−2.3 (m, 16H), 2.5 (m, 4H), 3.5 (m, 2H), 3.7 (m, 2H), 4.38 (d, d, 2H, $|J_{H-H}| = 10.8, 1.0$ Hz) 6.28 (s, 10H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 24.23, 24.21, 28.64, 28.67, 29.32, 35.35, 39.55, 47.35, 54.30, 60.05, 74.15, 100.76, 114.74. Anal. Calcd for $C_{17}H_{24}OS_2Ti$: C, 57.30; H, 6.79. Found: C, 57.10; H, 6.54. Data for **16** are as follows. Reaction time, 12 h; reaction temp, −78 °C; recrystallized from CH_2Cl_2/pentane. Yield: 82% (**16a**:**16b** = 66:33, by ^1H NMR). **16a**: ^1H NMR ($CDCl_3$, 25 °C): δ 0.85 (t, 6H, $|J_{H-H}| = 7.2$ Hz), 1.0 (s, 6H), 1.1−1.4 (m, 12H), 1.52 (m, 2H), 2.10 (d, br, 2H, $|J_{H-H}| = 12.5$ Hz), 3.50 (d, br, 2H, $|J_{H-H}| = 13.0$ Hz), 3.74 (d, br, 2H, $|J_{H-H}| = 13.0$ Hz), 4.56 (d, br, 2H, $|J_{H-H}| = 11.1$ Hz), 6.24 (s, 10H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 14.22, 22.19, 23.51, 26.06, 32.68, 39.79, 41.37, 70.48, 95.68, 114.37. **16b**:[11] ^1H NMR ($CDCl_3$, 25 °C): δ 1.10 (s, 3H), 4.60 (d, br, 2H, $|J_{H-H}| = 10.0$ Hz), 6.33 (s, 10H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 14.22, 22.19, 25.53, 26.26, 32.28, 40.24, 41.37, 71.23, 96.00, 114.90. Anal. Calcd for $C_{14}H_{22}OS_2Ti$: C, 52.82; H, 6.97. Found: C, 52.66; H, 6.77.

Synthesis of CpTi(SCH(PhCHNPh)CH_2CH_2S) (17), CpTi(SCH(PhCHNC_6H_4OMe)CH_2CH_2S) (18), CpTi(SCH-((C_6H_4OMe)CHNPh)CH_2CH_2S) (19), CpTi(SCH((C_6H_4OMe)-CHNC_6H_4OMe)CH_2CH_2S) (20), CpTi(SCH(PhCHNPr)-CH_2CH_2S) (21), and CpTi(SCH(PhCHN(CMe(Napth))-CH_2CH_2S) (22). These compounds were prepared in similar fashion; thus, one sample preparation is described in detail and the major differences in time and solvent are reported. To a suspension of **3** (85 mg, 0.195 mmol) in THF (3 mL) was added PhCH=NPr (56 mg, 0.38 mmol). The reaction was stirred for 3 days at 25 °C and then filtered. The solvent was removed and the residue washed with 2 × 1 mL portions of pentane. Recrystallization of the residue from benzene/pentane yielded black crystals of **21** in 87% yield. Data for **17** are as follows. Yield: 78% (**17a**:**17b** = 81:19, by ^{1}H NMR). **17a**: ^{1}H NMR (C_6D_6, 25 °C): δ 2.02 (t, d, d, 1H, $|J_{H-H}|$ = 13.8, 5.4, 3.0 Hz), 2.43 (d, d, br, 1H, $|J_{H-H}|$ = 13.8, 5.4 Hz), 3.66 (d, d, br, 1H, $|J_{H-H}|$ = 13.8, 5.4 Hz), 4.25 (t, d, 1H, $|J_{H-H}|$ = 13.8, 5.4 Hz), 4.79 (t, br, 1H, $|J_{H-H}|$ = 5.4 Hz), 6.04 (s, 5H), 5.78 (d, 1H, $|J_{H-H}|$ = 5.4 Hz) 6.4−7.3 (m, 10H). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 32.67, 36.81, 48.35, 75.15, 114.03, 122.31, 126.91, 127.04, 127.80, 128.91, 129.29, 144.38, 151.94. **17b:** ^{1}H NMR (C_6D_6, 25 °C): δ 2.20 (t, d, br, 1H, $|J_{H-H}|$ = 13.8, 15.4 Hz), 2.60 (d, d, br, 1H, $|J_{H-H}|$ = 13.8, 5.4 Hz), 3.50 (d, br, 1H, $|J_{H-H}|$ = 13.8 Hz), 3.85 (t, br, 1H, $|J_{H-H}|$ = 13.8 Hz), 4.48 (d, br, 1H, $|J_{H-H}|$ = 5.4 Hz), 4.87 (m, br, 1H), 6.26 (s, 5H), 6.4−7.3 (m, 10H). ^{13}C{^{1}H} NMR (C_6D_6, 25 C): δ 31.69, 37.52, 51.60, 76.75, 113.97, 122.18, 126.49, 127.60, 127.97, 128.11, 128.67, 142.95, 152.36. Anal. Calcd for $C_{21}H_{21}NS_2Ti$: C, 63.15; H, 5.30. Found: C, 63.07; H, 5.19. Data for **18** are as follows. Yield: 86% (**18a**:**18b** = 65:35, by ^{1}H NMR). **18a**: ^{1}H NMR ($CDCl_3$, 25 °C): δ 2.01 (t, d, 1H, $|J_{H-H}|$ = 13.8, 3.6 Hz), 2.60 (d, t, br, 1H, $|J_{H-H}|$ = 13.8, 5.4 Hz), 3.40 (d, br, 1H, $|J_{H-H}|$ = 13.8 Hz), 3.68 (s, 3H), 3.80 (m, 1H), 4.90 (t, br, 1H, $|J_{H-H}|$ = 5.4 Hz), 6.09 (d, 1H, $|J_{H-H}|$ = 5.4 Hz), 6.32 (s, 5H), 6.41 (d, 2H, $|J_{H-H}|$ = 8.6 Hz), 6.63 (d, 2H, $|J_{H-H}|$ = 8.6 Hz), 7.1−7.5 (m, 5H). ^{13}C-{^{1}H} NMR ($CDCl_3$, 25 °C): δ 32.60, 36.52, 48.27, 55.05, 75.53, 113.47, 114.17, 126.86, 127.35, 127.88, 128.43, 142.16, 145.37, 155.53. **18b**: ^{1}H NMR ($CDCl_3$, 25 °C): δ 2.32 (t, d, 1H, $|J_{H-H}|$ = 13.8 Hz, $|J_{H-H}|$ = 3.9 Hz), 3.15 (d, br, 1H, $|J_{H-H}|$ = 13.8 Hz), 3.61 (m, 1H), 3.67 (s, 3H), 3.8 (m, 1H), 4.69 (d, br, 1H, $|J_{H-H}|$ = 5.4 Hz), 5.69 (br, 1H), 6.58 (s, 5H), 6.40 (d, 2H, $|J_{H-H}|$ = 8.6 Hz), 6.63 (d, 2H, $|J_{H-H}|$ = 8.6 Hz), 7.1−7.5 (m, 5H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 35.42, 38.55, 51.17, 55.05, 71.30, 113.99, 114.32, 126.73, 127.58, 127.80, 128.11, 143.98, 145.24, 155.53. Anal. Calcd for $C_{22}H_{23}NOS_2Ti$: C, 61.53; H, 5.40; N, 3.26. Found: C, 61.21; H, 5.26; N, 3.12. Data for **19** are as follows. Yield: 80% (**19a**:**19b** = 77:23, by ^{1}H NMR). **19a**: ^{1}H NMR ($CDCl_3$, 25 °C): δ 2.02 (t, d, 1H, $|J_{H-H}|$ = 13.8, 3.6 Hz), 2.65 (d, t, br, 1H, $|J_{H-H}|$ = 13.8, 5.4 Hz), 3.40 (m, 1H), 3.71 (s, 3H), 4.15 (t, d, 1H, $|J_{H-H}|$ = 13.8, 3.6 Hz), 4.89 (t, br, 1H, $|J_{H-H}|$ = 5.4 Hz), 6.07 (d, 1H, $|J_{H-H}|$ = 5.4 Hz), 6.30 (s, 5H), 6.70 (d, 2H, $|J_{H-H}|$ = 8.6 Hz), 7.01 (d, 2H, $|J_{H-H}|$ = 8.6 Hz), 6.8−7.1 (m, 5H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 32.53, 36.67, 48.51, 55.20, 74.08, 113.51, 114.89, 127.77, 127.97, 128.65, 128.81, 134.09, 151.32, 158.11. **19b**: ^{1}H NMR ($CDCl_3$, 25 °C): δ 2.30 (t, br, 1H, $|J_{H-H}|$ = 13.8 Hz), 3.2 (m, 1H), 3.7 (m, 1H), 3.72 (s, 3H), 3.85 (m, 1H), 4.69 (d, br, 1H, $|J_{H-H}|$ = 5.4 Hz), 5.08 (br, 1H), 6.60 (s, 5H), 6.89 (d, 2H, $|J_{H-H}|$ = 8.6 Hz), 7.12 (d, 2H, $|J_{H-H}|$ = 8.6 Hz), 6.8−7.1 (m, 5H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 35.85, 38.26, 51.86, 55.20, 76.14, 113.92, 114.45, 122.47, 127.90, 128.00, 128.77, 135.76, 151.52, 158.59. Anal. Calcd for $C_{22}H_{23}NOS_2Ti$: C, 61.53; H, 5.40; N, 3.26. Found: C, 61.16; H, 5.34; N, 3.22. Data for **20** are as follows. Yield: 83% (**20a**:**20b** = 65:35, by ^{1}H NMR). **20a**: ^{1}H NMR ($CDCl_3$, 25 °C): δ 2.02 (t, d, 1H, $|J_{H-H}|$ = 13.8, 3.6 Hz), 2.63 (d, t, br, 1H, $|J_{H-H}|$ = 13.8, 5.4 Hz), 3.7 (m, 1H), 3.68 (s, 3H), 3.71 (s, 3H), 4.08 (t, br, 1H, $|J_{H-H}|$ = 13.8, 3.6 Hz), 4.87 (t, br, 1H, $|J_{H-H}|$ = 5.4 Hz), 6.04 (d, 1H, $|J_{H-H}|$ = 5.4 Hz), 6.31, (s, 5H), 6.41, (d, 2H, $|J_{H-H}|$ = 8.7 Hz), 6.64 (d, 2H, $|J_{H-H}|$ = 8.7 Hz), 6.70 (d, 2H, $|J_{H-H}|$ = 8.7 Hz), 6.89 (d, 2H, $|J_{H-H}|$ = 8.7 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 32.64, 37.55, 48.29, 55.17, 55.50, 75.01, 113.47, 114.73, 124.15, 127.87, 128.98, 134.20, 145.31, 155.50, 158.05. **20b**: ^{1}H NMR ($CDCl_3$, 25 °C): δ 2.31 (t, d, 1H, $|J_{H-H}|$ = 13.8 Hz, $|J_{H-H}|$ = 3.6 Hz), 3.2 (d, br, 1H, $|J_{H-H}|$ = 13.8 Hz), 3.7 (m, 1H), 3.65 (s, 3H), 3.67 (s, 3H), 3.76 (m, 1H), 4.65 (d, br, 1H, $|J_{H-H}|$ = 5.4 Hz), 5.03 (br, 1H), 6.56 (s, 5H), 6.42, (d, 2H, $|J_{H-H}|$ = 8.7 Hz), 6.64 (d, 2H, $|J_{H-H}|$ = 8.7 Hz), 6.89 (d, 2H, $|J_{H-H}|$ = 8.7 Hz), 7.15 (d, 2H, $|J_{H-H}|$ = 8.7 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 34.75, 40.90, 51.37, 55.20, 55.41, 76.14, 113.99, 114.34, 124.30, 128.42, 129.02, 135.01, 145.42, 155.30, 158.08. Anal. Calcd for $C_{23}H_{25}NO_2S_2Ti$: C, 60.13; H, 5.48; N, 3.05. Found: C, 59.86; H, 5.23; N, 2.86. **21a**: 3 days, yield 87%. Crystals of **21b** were isolated from recrystallizations of **21a**. **21a**: ^{1}H NMR (C_6D_6, 25 °C): δ 0.60 (t, 3H, $|J_{H-H}|$ = 7.2 Hz), 1.2 (m, 2H), 2.37 (t, d, br, 1H, $|J_{H-H}|$ = 13.5, 3.6 Hz), 2.42 (q, 1H, $|J_{H-H}|$ = 7.5 Hz), 2.90 (d, d, d, br, 1H, $|J_{H-H}|$ = 13.5, 7.2, 5.7 Hz), 2.94 (q, 1H, $|J_{H-H}|$ = 7.5 Hz), 3.76 (d, d, d, 1H, $|J_{H-H}|$ = 13.5, 7.2, 3.6 Hz), 3.91 (t, d, 1H, $|J_{H-H}|$ = 13.5, 3.3 Hz), 4.42 (d, 1H, $|J_{H-H}|$ = 5.7 Hz), 4.77 (br, 1H), 6.11 (s, 5H), 7.64 (br, 2H), 7.41 (br, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 11.90, 24.36, 32.77, 39.56, 49.36, 59.80, 74.46, 113.06, 127.12, 127.80, 128.10, 143.44. Anal. Calcd for $C_{18}H_{23}NS_2Ti$: C, 59.17; H, 6.34; N, 3.83. Found: C, 58.90; H, 6.20; N, 3.75. **21b**: ^{1}H NMR (C_6D_6, 25 °C): δ 0.51 (t, 6H, $|J_{H-H}|$ = 6.2 Hz), 1.0−1.4 (m, 4H), 1.55 (m, 2H), 2.39 (m, 2H), 3.0 (t, d, 2H, $|J_{H-H}|$ = 13.0, 3.6 Hz), 3.40 (m, 4H), 3.60 (d, br, 2H, $|J_{H-H}|$ = 13.0 Hz), 4.47 (d, 2H, $|J_{H-H}|$ = 11.4 Hz), 4.70 (d, d, d, 2H, $|J_{H-H}|$ = 13.0, 11.4, 3.6 Hz), 6.18 (s, 10H), 7.2 (m, 10H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 11.92, 21.69, 33.89, 37.39, 58.65, 59.04, 81.64, 113.50, 127.70, 128.42, 129.55, 143.44. Data for **27** are as follows. Reaction time: 6 days. The reaction residue was washed with pentane (2 × 2 mL), and the residual solvent was removed in vacuo. Yield: 83% (**22a**:**22b** = 50:50, by ^{1}H NMR). **22a**: ^{1}H NMR (C_6D_6, 25 °C): δ 1.11 (d, 6H, $|J_{H-H}|$ = 6.6 Hz), 1.85 (d, d, d, br, 2H, $|J_{H-H}|$ = 14.7, 13.0, 4.8 Hz), 2.34 (d, d, d, br, 2H, $|J_{H-H}|$ = 14.7, 5.4, 4.8 Hz), 3.40 (d, d, 2H, $|J_{H-H}|$ = 13.0, 4.8 Hz), 3.60 (t, d, br, 2H, $|J_{H-H}|$ = 13.0, 4.8 Hz), 4.26 (d, br, 2H, $|J_{H-H}|$ = 5.4 Hz), 4.65 (q, 2H, $|J_{H-H}|$ = 6.6 Hz), 4.71 (m, br, 2H), 6.32 (s, 10H), 7.0−8.1(m, br, 24H). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 24.87, 31.28, 37.89, 49.82, 57.25, 73.37, 112.80, 124.03, 125.77, 125.65, 125.89, 128.83, 131.03, 133.99, 141.11, 145.02. **22b**: ^{1}H NMR (C_6D_6, 25 °C): δ 1.35 (d, 6H, $|J_{H-H}|$ = 6.6 Hz), 2.07 (d, d, d, br, 2H, $|J_{H-H}|$ = 14.7, 13.0, 4.8 Hz), 2.95 (d, d, d, d, 2H, $|J_{H-H}|$ = 14.7, 5.4, 4.8, 3.0 Hz), 3.98 (d, d, d, 2H, $|J_{H-H}|$ = 13.0, 4.8, 3.0 Hz), 4.34 (t, d, 2H, $|J_{H-H}|$ = 13.0, 3.0 Hz), 4.43 (d, br, 2H, $|J_{H-H}|$ = 5.4 Hz), 4.85 (q, 2H, $|J_{H-H}|$ = 6.6 Hz), 5.16 (m, br, 2H), 5.48 (s, 10H), 7.0−8.1 (m, br, 24H). ^{13}C{H} NMR (C_6D_6, 25 °C): δ 24.87, 34.89, 38.54, 50.50, 59.68, 74.41, 112.74, 123.80, 125.48, 125.65, 126.42, 128.41, 131.55, 134.10, 140.40, 143.17 (other peaks between 127 and 128 ppm). Anal. Calcd for $C_{27}H_{27}NS_2Ti$: C, 67.91; H, 5.70; N, 2.93. Found: C, 67.69; H, 5.55; N, 2.70.

Synthesis of CpTi(SC(PhCNH)CH_2CH_2S) (23), CpTi-(SC(C_4H_9CNH)CH_2CH_2S) (24), CpTi(SC(MeSCNH)-CH_2CH_2S) (25), CpTi(SC(CyNHCNCy)CH_2CH_2S) (26), CpTi(SC(PhNCO)CH_2CH_2S)TiCp(S$CH_2CH_2CH_2$S) (27), and CpTi(SC(PhNHCS)CH_2CH_2S) (28). These compounds were prepared in similar fashion; thus, one sample preparation is described in detail and the major differences in time and solvent are reported. To a suspension of **1** (85 mg, 0.195 mmol) in THF (1 mL) was added PhCN (39 mg, 0.38 mmol). The reaction was stirred overnight at 25 °C and then filtered. The solvent was removed and the residue extracted into CH_2Cl_2. Crystallization of the residue was induced by addition of benzene yielding purple-black crystals of **23** in 89% yield. Data for **23** are as follows. ^{1}H NMR (C_6D_6, 25 °C): δ 2.26 (t, br, 1H, $|J_{H-H}|$ = 12.6 Hz), 2.40 (m, 1H), 2.57 (m, 1H), 3.60 (d, d, br, 1H, $|J_{H-H}|$ = 12.6, 6.0 Hz), 6.17 (s, 5H), 7.15 (m, 3H), 7.32 (d, d, 2H, $|J_{H-H}|$ = 6.3, 1.5 Hz), 7.8 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 34.96, 40.91, 98.02, 110.63, 127.07, 128.30, 129.32, 136.61, 150.90. Anal. Calcd for $C_{15}H_{15}NS_2Ti$: C, 56.08; H, 4.71; N, 4.36. Found: C, 55.91; H, 4.60; N, 4.16. Data for **24** are as follows. Reaction time: 2 days. Yield: 57%.

^{1}H NMR (C_6D_6, 25 °C): δ 0.86 (t, 3H, $|J_{H-H}| = 6.9$ Hz), 1.2−1.4 (m, 4H), 1.5 (m, 2H), 2.30 (t, d, 1H, $|J_{H-H}| = 12.6, 4.0$ Hz), 2.65 (t, d, 1H, $|J_{H-H}| = 12.6, 6.0$ Hz), 2.93 (d, d, br, 1H, $|J_{H-H}| = 12.9, 6.0$ Hz), 3.42 (d, d, br, 1H, $|J_{H-H}| = 12.6, 4.0$ Hz), 4.0 (m, 1H), 6.15 (s, 5H) . ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 14.07, 23.31, 25.05, 31.65, 37.51, 41.02, 108.02, 111.18,159.80. Anal. Calcd for $C_{13}H_{19}NS_2Ti$: C, 51.82; H, 6.36; N, 4.65. Found: C, 51.65; H, 6.20; N, 4.55. Data for **25** are as follows. Reaction time: 12 h; recrystallized from CH_2Cl_2/pentane. Yield: 85%. ^{1}H NMR (C_6D_6, 25 °C): δ 2.29 (d, 3H, $|J_{H-H}| = 5.4$), 2.54 (t, d, 1H, $|J_{H-H}| = 13.5, 7.5$ Hz), 2.95 (t, d, 1H, $|J_{H-H}| = 13.5, 5.8$ Hz), 3.08 (d, d, br, 1H, $|J_{H-H}| = 13.5, 5.8$ Hz), 3.28 (d, d, 1H, $|J_{H-H}| = 14.4, 5.8$ Hz), 4.3 (m, br, 1H), 6.19 (s, 5H). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 29.94, 32.24, 42.18, 105.60, 109.82, 167.04. Anal. Calcd for $C_{10}H_{13}NS_3Ti$: C, 41.24; H, 4.50; N, 4.81. Found: C, 41.09; H, 4.39; N, 4.78. Data for **26** are as follows. Reaction time: 12 h; recrystallized from THF/pentane. Yield: 93%. ^{1}H NMR (C_6D_6, 25 °C): δ 0.9−2.20 (m, 20H), 2.52 (t, d, 1H, $|J_{H-H}| = 13.0, 6.0$ Hz), 3.08 (m, br, 1H), 3.15 (m, 1H), 3.33 (t, d, 1H, $|J_{H-H}| = 13.0, 5.7$ Hz), 3.40 (d, d, d, 1H, $|J_{H-H}| = 13.0, 6.0, 3.0$ Hz), 3.45 (m, 1H), 3.65 (d, d, d, 1H, $|J_{H-H}| = 14.0, 5.7, 3.0$ Hz), 6.43 (s, 5H). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 24.92, 25.43, 25.71, 26.10, 33.80, 35.16, 35.50, 42.81, 54.28, 62.07, 92.64, 109.30, 154.01. Anal. Calcd for $C_{21}H_{32}N_2S_2Ti$: C, 59.42; H, 7.60; N, 6.60. Found: C, 59.35; H, 7.55; N, 6.45. Data for **27** are as follows. Reaction time: 12 h. Reaction temp: 25 °C. The reaction residue was washed with pentane (2 × 2 mL), and the residual solvent was removed in vacuo to solid **27**, which was recrystallized from benzene/pentane. Yield: 75%. ^{1}H NMR (C_6D_6, 25 °C): δ 2.50 (m, 2H), 3.0 (m, 2H), 3.22 (d, d, br, 1H, $|J_{H-H}| = 14.1, 12.6$ Hz), 3.44 (d, d, br, 1H, $|J_{H-H}| = 14.1, 12.6$ Hz), 3.69 (d, d, br, 1H, $|J_{H-H}| = 14.1, 5.0$ Hz), 3.72 (d, d, br, 1H, $|J_{H-H}| = 14.1, 4.2, 2.0$ Hz), 3.93 (m, 2H), 5.96 (s, 5H), 6.26 (s, 5H), 6.70 (d, br, 1H, $|J_{H-H}| = 7.2$ Hz), 6.76 (t, 2H, $|J_{H-H}| = 7.2$ Hz), 6.90 (t, 2H, $|J_{H-H}| = 7.2$ Hz). ^{13}C{H} NMR (C_6D_6, 25 °C): δ 31.90, 34.77 , 37.51, 38.27, 39.58, 102.41, 110.57, 113.86, 123.84, 124.43,128.96, 147.10, 152.40. Anal. Calcd for $C_{23}H_{26}ONS_4Ti_2$: C, 49.64; H, 4.71; N, 2.52. Found: C, 49.51; H, 4.61; N, 2.43. Data for **28** are as follows. Reaction time: 18 h. Yield: 86%. ^{1}H NMR (C_6D_6, 25 °C): δ 2.26 (t, d, 1H, $|J_{H-H}| = 13.0, 7.2$ Hz), 3.0 (d, d, br, 1H, $|J_{H-H}| = 13.0, 7.2$ Hz), 3.27 (t, d, 1H, $|J_{H-H}| = 13.0, 5.4$ Hz), 3.50 (d, d, br, 1H, $|J_{H-H}| = 13.0, 5.4$ Hz), 6.17 (s, 5H), 6.63 (d, br, 1H, $|J_{H-H}| = 7.5$ Hz), 6.69 (br, 1H), 6.92 (t, 2H, $|J_{H-H}| = 7.5$ Hz), 7.03 (d, 2H, br, $|J_{H-H}| = 7.5$ Hz). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 31.83, 43.76, 110.28, 111.70, 122.62, 124.26, 129.01, 140.42, 160.09. Anal. Calcd for $C_{15}H_{15}NS_3Ti$: C, 50.84; H, 4.55; N, 3.95. Found: C, 50.75; H, 4.43; N, 3.78.

X-ray Data Collection and Reduction. X-ray-quality crystals were obtained directly from the preparations as described above. The crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Rigaku AFC6 diffractometer equipped with graphite-monochromatized Mo Kα radiation. The initial orientation matrices were obtained from 20 machine-centered reflections selected by an automated peak search routine. These data were used to determine the crystal systems. Automated Laue system check routines around each axis were consistent with the crystal systems reported in Table 1. 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 1. The observed extinctions were consistent with the space group given in Table 1. The data sets were collected in one shell ($4.5° < 2\theta < 50.0°$), and three standard reflections were recorded every 197 reflections. The intensities of the standards showed no statistically significant change over the duration of the data collection. The data were processed using the TEXSAN crystal solution package operating on a VAX workstation 3520 or employing the TEXSAN package operating on an SGI mainframe computer with remote X-terminals. The reflections with $F_o^2 > 3\sigma F_o^2$ were used in the refinement. Empirical absorption corrections were applied to the data sets in one of two ways; either a correction was applied on the basis of ψ-scan data or the program DIFABS was employed at the point of a completely isotropic refinement.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[13,14] The Ti atom positions were determined using direct methods by 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 structures and was set so as to maintain a reasonable data:variable ratio in each case. In the cases of **8**, **9**, **11**, **19**, **21**, and **27** solvent molecules were also located and refined. In some cases cyclopentadienyl and phenyl rings were modeled as rigid groups with a C−C bond length of 1.40 Å. This was done in cases where it was necessary to maintain an appropriate data:variable ratio. 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 1. In all cases, the residual electron densities were of no chemical significance. The following data have been deposited as Supporting Information: positional parameters, thermal parameters, hydrogen atom parameters, and selected bond distances and angles.

Kinetic Studies. The reactions of thiatitanacyclopropane **4** with benzophenone and cyclohexanone were monitored by ^{1}H NMR spectroscopy at several initial concentrations of **4** using excess ketone in all cases. Concentrations were determined via integration versus an internal standard. Plots of concentrations versus time were analyzed and the rate constants and order determined in the standard fashion.

Molecular Orbital Calculations.[15] Extended Huckel calculations were performed and visualized by employing the Cache Software system operating on a Power Mac 7100 computer. Initial coordinates and geometric parameters were taken from X-ray data.

Results and Discussion

The reaction of **1** with MeLi proceeds smoothly at −78 °C to give on subsequent workup the microcrystalline product $[CpTi(SCHCH_2CH_2S)]_2$ (**3**) as confirmed by NMR and X-ray diffraction studies. The compound **3** and its analog $[(MeCp)Ti(SCHCH_2CH_2S)]_2$ (**4**) are also prepared from the reaction of **1** with either $AlMe_3$ or *t*-BuLi. Both compounds are centrosymmetric dimers in the solid state (Figure 1) in which the two Ti centers are bridged by two thiolato-sulfur atoms. A second sulfur atom and the carbon *alpha* to it and a cyclopentadienyl ring complete the coordination spheres of the

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

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

(15) CaChe Worksystem software is an integrated modeling, molecular mechanics, and molecular orbital computational software package and is a product of CaChe Scientific Inc.

Table 1. Crystallographic Parameters[a,b]

	3	**4**	**7**	**8**	**9**	**11**	**14**	**19**	**21**	**24**	**26**	**27**
formula	$C_8H_{14}S_2Ti$	$C_9H_{16}S_2Ti$	$C_{11}H_{14}O_6Ti$	$C_{15}H_{26}OS_4Ti$	$C_{21}H_{20}OS_2Ti\cdot 0.5C_6H_6$	$C_{28}H_{40}S_4O_2Ti_2\cdot 2CH_2Cl_2$	$C_{36}H_{56}O_2S_4Ti_2$	$C_{22}H_{23}NOS_2Ti\cdot CH_2Cl_2\cdot H_sO$	$C_{36}H_{46}N_2S_4Ti_2\cdot H_2O$	$C_{15}H_{15}NS_2Ti$	$C_{21}H_{32}N_2S_2Ti$	$C_{23}H_{26}NOS_4Ti_2\cdot C_6H_6$
cryst color, form	black blocks	black blocks	yellow blocks	orange-red blocks	red blocks	red blocks	red blocks	black blocks	black blocks	purple-black blocks	purple-black blocks	purple blocks
a (Å)	8.233(4)	7.073(1)	14.040(2)	17.835(4)	10.817(2)	8.941(2)	12.706(2)	11.759(4)	25.684(6)	17.614(3)	9.766(4)	10.077(2)
b (Å)	8.889(1)	13.550(2)	15.294(14)	13.369(3)	11.042(2)	11.387(3)	9.398(2)	12.900(3)	48.102(13)	13.798(2)	11.031(2)	22.847(4)
c (Å)	12.686(3)	10.529(2)	11.960(4)	17.770(5)	8.909(2)	35.888(11)	16.056(2)	8.786(2)	11.818(2)	11.926(2)	20.711(3)	12.849(2)
α (deg)					94.21(1)			91.51(2)				
β (deg)	103.61(3)	98.58(2)		109.92(2)	111.35(1)	90.10(3)	102.14(1)	111.92(2)			93.97(2)	102.17(1)
γ (deg)					80.15(1)			85.66(2)				
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic	triclinic	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$Pbca$	$C2/c$	$P\bar{1}$	$P2_1/n$	$P2_1$	$P\bar{1}$	$Fdd2$	$Pbca$	$P2_1/n$	$P2_1/a$
V (Å^3)	902.3(5)	997.7(3)	2568(2)	3985(2)	1056.0(3)	3654(2)	1874.4(5)	1232.4(6)	14600(6)	2898(1)	2226(1)	2891.6(9)
D_{calcd} (g cm^{-3})	1.72	1.54	1.50	1.33	1.38	1.46	1.32	1.46	1.36	1.47	1.27	1.28
Z	4	4	8	8	2	4	4	2	16	8	4	8
μ, cm^{-1}	13.20	12.17	6.82	8.45	6.15	9.85	6.79	7.55	6.97	8.64	5.80	8.55
scan speed, deg/min	32.0 ($\theta/2\theta$) (1−3 scans)	32.0 ($\theta/2\theta$) (1−3 scans)	8.0 ($\theta/2\theta$) (1−3 scans)	16.0 ($\theta/2\theta$) (1−3 scans)	16.0 ($\theta/2\theta$) (1−3 scans)	8.0 ($\theta/2\theta$) (1−3 scans)	8.0 ($\theta/2\theta$) (1−3 scans)	8.0 ($\theta/2\theta$) (1−3 scans)	8.0 ($\theta/2\theta$) (1−3 scans)	8.0 ($\theta/2\theta$) (1−3 scans)	16.0 ($\theta/2\theta$) (1−4 scans)	8.0 ($\theta/2\theta$) (1−3 scans)
data collcd	1834	1844	2586	2882	3924	6651	3520	4339	3520	2904	4153	5233
index range	$h,k,\pm l$	$h,k,\pm l$	h,k,l	$h,k,\pm l$	$\pm h,\pm k,l$	$h,k,\pm l$	$h,k,\pm l$	$\pm h,\pm k,l$	h,k,l	h,k,l	$\pm h,k,l$	$h,k,\pm l$
data $F_o^2 > 3\sigma(F_o^2)$	1046	961	1077	1154	2509	1342	2547	1316	1115	1302	1329	2090
variables	100	109	138	140	253	219	286	155	149	172	150	225
R (%)	3.75	6.91	7.47	8.03	4.81	8.27	6.10	6.98	9.81	3.82	6.61	6.40
R_w (%)	2.80	6.23	6.17	5.7	4.30	8.55	5.61	5.82	8.95	2.67	4.75	4.30
largest Δ/σ	0.0001	0.0001	0.003	0.04	0.001	0.004	0.001	0.001	0.08	0.003	0.004	0.001
goodness of fit	1.66	2.71	2.67	2.33	2.19	2.33	2.08	2.31	2.89	1.67	2.13	2.42

[a] In all cases, structure determinations were done using Mo Kα Radiation, $\lambda = 0.710\ 69$ Å at 24 °C, scan ranges of 1.0 below $K\alpha_1$ and 1.0 above $K\alpha_2$, 2θ ranges of 4.5−50° and background/scan ratios of 0.5. [b] Crystal of **4** grown from hexane crystallized in $P2_1/n$ with $a = 7.151(2)$ Å, $b = 18.403(3)$ Å, $c = 7.927(1)$ Å, $b = 105.00(2)°$, and $V = 1007.7(3)$ Å^3.

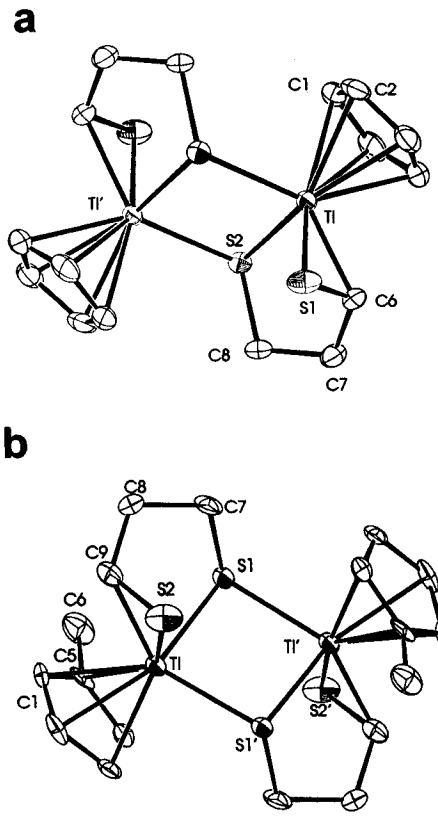


Figure 1. ORTEP drawings of (a) **3** and (b) **4**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. **3**: Ti−S(1) 2.442(2) Å, Ti−S(1′ 2.504(2) Å, Ti−S(2) 2.289(2) Å, Ti−C(8) 2.149(5) Å, S(1)−Ti−S(1′ 92.58(5)°, S(1)−Ti−S(2) 98.77(5)°, S(1)−Ti−S(2′ 86.12(6)°, S(2)−Ti−C(8) 46.1(1)°, Ti−S(1)−Ti′ 87.42(5)°. **4**: Ti−S(1) 2.467(3) Å, Ti−S(1′ 2.493(3) Å, Ti−S(2) 2.284(4) Å, Ti−C(9) 2.16-(1) Å, S(1)−Ti−S(1′ 91.4(1)°, S(1)−Ti−S(2) 98.6(1)°, S(1)−Ti−S(2′ 85.1(1)°, S(2)−Ti−C(9) 47.7(3)°, Ti−S(1)−Ti′ 88.6-(1)°.

Ti centers. The crystallographically imposed center of symmetry dictates a *transoid* disposition of the cyclopentadienyl rings relative to the Ti_2S_2 core. The bridging Ti−S distances in **3** range from 2.442(2) to 2.504(2) Å, which is comparable to those seen in the Ti thiolate dimer $[CpTiCl(SCH_2CH_2S)]_2$[9] and the heterometallic complexes $[(Cp_2Ti(SCH_2CH_2CH_2S)_2Ag]^+$ and $[Cp_2Ti-((SCH_2CH_2SCH_2)_2CH_2)Cu]^+$.[16,17] The Lewis acidity of the Ti centers in both **3** and **4** results in comparatively short terminal Ti−S (**3**, 2.289(2) Å; **4**, 2.284(4) Å) and Ti−αC (**3**, 2.149(5) Å; **4**, 2.16(1) Å) distances while the ring strain in the thiatitanacyclopropane is evidenced by the S−Ti−C angles (**3**, 46.1(1)°; **4**, 47.7(3)°).

The mechanism of formation of **3** and **4** could, in principle, be either via β-hydrogen elimination or β-hydrogen abstraction. Attempts to slow the reaction at low temperature in order to observe alkylated intermediates were unsuccessful. It is noteworthy that Buchwald et al. confirmed a concerted four-center cyclometalation process is operative in the formation of thioformaldehyde derivatives of zirconocene.[6]

Compounds **3** and **4** are readily cleaved in solution in the presence of PMe_3 affording $Cp^{\dagger}Ti(SCHCH_2CH_2S)-(PMe_3)$ ($Cp^{\dagger}$ = Cp (**5**), MeCp (**6**)). However, **3** and **4** are

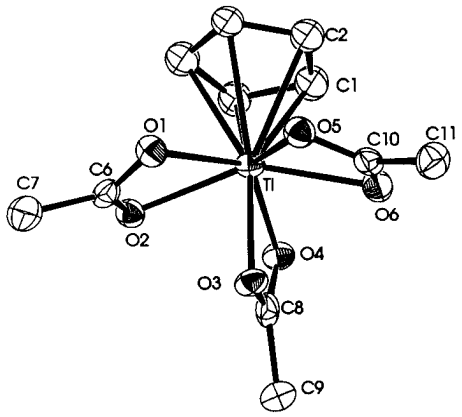
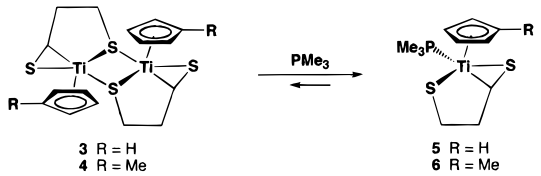
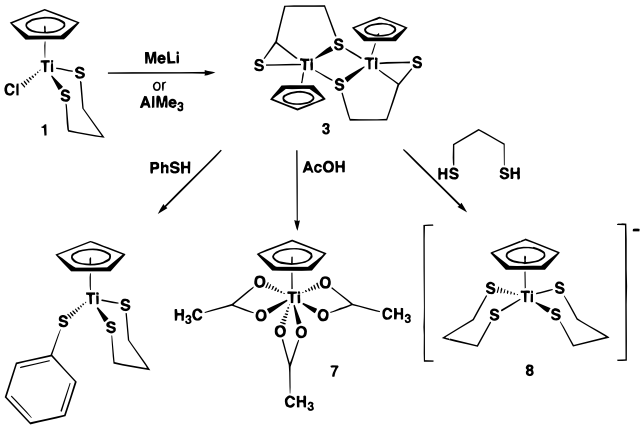


Figure 2. ORTEP drawing of **7**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Distances and angles: Ti−O(1) 2.107(7) Å, Ti−O(2) 2.247-(7) Å, Ti−O(3) 2.153(6) Å, Ti−O(4) 2.094(6) Å, Ti−O(5) 2.115(7) Å, Ti−O(6) 2.205(7) Å, O(1)−Ti−O(2) 59.6(3)°, O(3)−Ti−O(4) 61.4(2)°, O(5)−Ti−O(6) 60.2(2)°.

Scheme 1



Scheme 2



recovered upon attempts to isolate these adducts. This indicates equilibria govern the formation of these monometallic species from the corresponding dimers (Scheme 1).

Acidolysis. Compound **3** reacts rapidly with protic reagents. Reaction with HCl cannot be easily controlled, and thus hydrolysis of the Ti−C and Ti−S bonds occurs rapidly, yielding $CpTiCl_3$. Similarly, addition of acetic acid to **3** yields the triacetate derivative $CpTi-(O_2CMe)_3$ (**7**) as confirmed by crystallography (Figure 2). Controlled acidolysis in which the Ti−S bonds were not severed was achieved in the reactions of **3** with thiols (Scheme 2). Reaction of **3** with 1 equiv of benzenethiol gave the known Ti species $CpTi(SCH_2CH_2-CH_2S)(SPh)$ in quantitative yield (^{1}H NMR),[9] while the similar reaction with propanedithiol gave the salt $H^+[CpTi(SCH_2CH_2CH_2S)_2]^-\cdot$THF (**8**). The nature of **8** was also confirmed crystallographically (Figure 3). We have previously described polymeric sodium salts containing the anion of **8**.[18] The formation of these

(16) Huang, Y.; Nadasdi, T. T.; Drake, R. J.; Stephan, D. W. *Inorg. Chem.* **1993**, *32*, 3022.
(17) Nadasdi, T. T.; Stephan, D. W. *Organometallics* **1992**, *11*, 116.

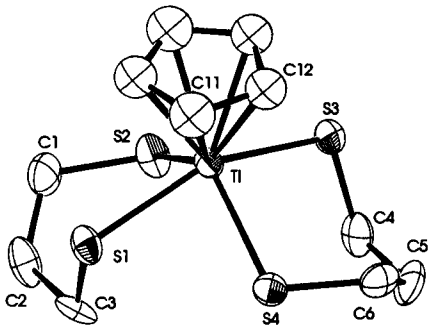
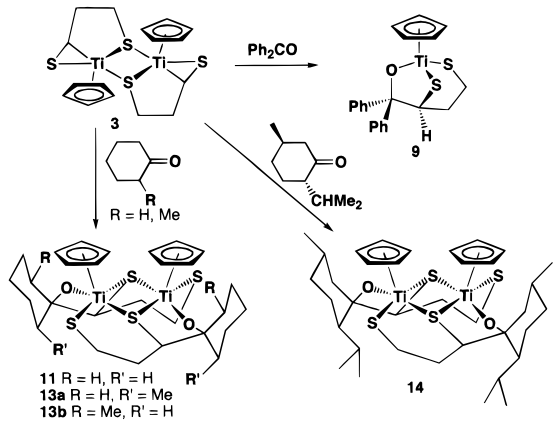


Figure 3. ORTEP drawing of anion of **8**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Distances and angles: Ti−S(1) 2.469(5) Å, Ti−S(2) 2.378(5) Å, Ti−S(3) 2.448(5) Å, Ti−S(4) 2.383(5) Å, S(1)−Ti−S(2) 84.1(2)°, S(3)−Ti−S(4) 86.4(2)°, S(1)−Ti−S(4) 79.8(2)°, S(2)−Ti−S(3) 86.4(2)°.

Scheme 3



products of acidolysis suggests considerable nucleophilic character must be attributed to the C atom of the thiatitanacyclopropane fragment while the facile electrophilic attack at sulfur is similar to that described for Zr−thioaldehyde derivatives.[6,7]

Reactions with Ketones. The reactions of **3** with a variety of ketones are summarized in Scheme 3. The reactions of **3** and **4** with benzophenone proceed smoothly and quantitatively to give the products $Cp^{\dagger}Ti(SCH(CPh_2O)CH_2CH_2S)$ ($Cp^{\dagger}$ = Cp (**9**); MeCp (**10**)) in 90% and 80% isolated yields, respectively. Coupling of the methine protons to the adjacent methylene protons is consistent with an equatorial positioning of the methine protons in six-membered rings of pseudo-chair conformation and, thus, mononuclear complexes. A crystallographic study of **9** (Figure 4) confirmed the pseudo-three-legged piano stool geometry in which the alkoxy-carbon atom (C9) adopts an axial position relative to the six-membered ring formed by chelation of the dithiolate to Ti.

In the analogous reactions of **3** and **4** with cyclohexanone, products **11** and **12** are also are derived from insertion of ketone into the Ti−C bond. However, ^{1}H NMR data revealed couplings of the methine proton to the adjacent methylene protons of 11.4 and 1.0 Hz, respectively (Figure 5a). These data are consistent with an axial disposition of the methine proton relative to the six-membered chelate ring formed by the dithiolate moiety. This orientation is not geometrically compatible

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

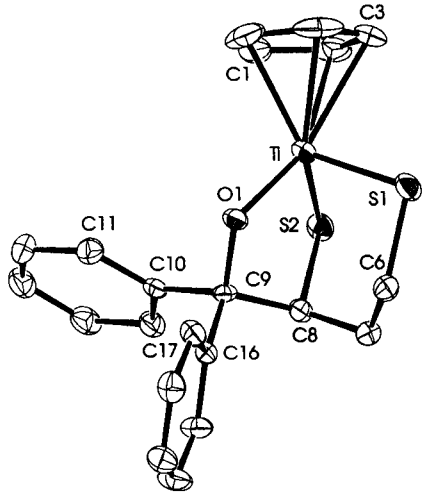


Figure 4. ORTEP drawing of **9**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Distances and angles: Ti−S(1) 2.301(1) Å, Ti−S(2) 2.299(1) Å, Ti−O(1) 1.820(3) Å, S(1)−Ti−S(2) 99.91(5)°, S(1)−Ti−O(1) 99.5(1)°, S(2)−Ti−O(1) 87.73(9)°.

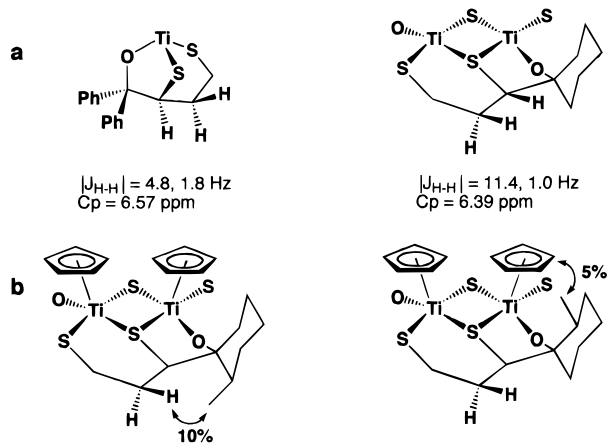


Figure 5. (a) NMR data used to distinguish monomeric from dimeric complexes. (b) NOE observed for **13**. Note: partial structures are shown.

with mononuclear species, which suggests a dimeric formulation, i.e. $[Cp^{\dagger}Ti(SCH(C_6H_{10}O)CH_2CH_2S)]_2$ ($Cp^{\dagger}$ = Cp (**11**); MeCp (**12**)). In the case of **11** this was subsequently confirmed crystallographically (Figure 6). Two thiolate sulfur atoms bridge the Ti centers; thus, two tridentate S_2O ligands span the two metals. The cyclopentadienyl rings adopt a *cisoid* disposition relative to the Ti_2S_2 core in contrast to **3**. The geometries about the Ti atoms are best described as "four-legged piano stools" in which two of the legs are shared.

Reactions of **3** with unsymmetrical ketones result in diastereomeric products; for example, 2-methylcyclohexanone and menthone yield the dimeric products $[CpTi(SCH(C_7H_{12}O)CH_2CH_2S)]_2$ (**13**) and $[CpTi(SCH(C_{10}H_{18}O)CH_2CH_2S)]_2$ (**14**), respectively. In the former case, two isomers, **13a**,**b**, are formed in 80:20 and 92:8 ratios when the reaction is performed at 25 and −78 °C, respectively. NOE experiments indicate that the major isomer (**13a**) has the single methyl substituent oriented away from the cyclopentadienyl ring while the orientation is reversed in the minor isomer (**13b**) (Figure 5b). NMR and X-ray data (Figure 7) confirm the formation of **14** proceeds with complete diastereoselectivity. The general structural features of **14** are similar

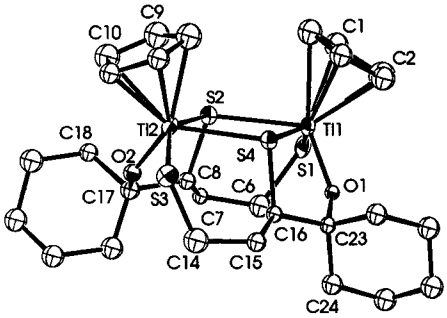


Figure 6. ORTEP drawing of **11**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Distances and angles: Ti(1)−S(1) 2.401(9) Å, Ti(1)−S(2) 2.513(9) Å, Ti(1)−S(4) 2.564(8) Å, Ti(1)−O(1) 1.84(2) Å, Ti(2)−S(2) 2.590(9) Å, Ti(2)−S(3) 2.393(9) Å, Ti(2)−S(4) 2.516(9) Å, Ti(2)−O(2) 1.81(2) Å, S(1)−Ti(1)−S(2) 82.0(3)°, O(1)−Ti(1)−S(4) 76.7(5)°, S(3)−Ti(2)−S(4) 82.2(3)°, O(2)−Ti(2)−S(2) 76.2(6)°, Ti(1)−S(2)−Ti(2) 104.5(3)°, Ti(1)−S(4)−Ti(2) 105.2(3)°.

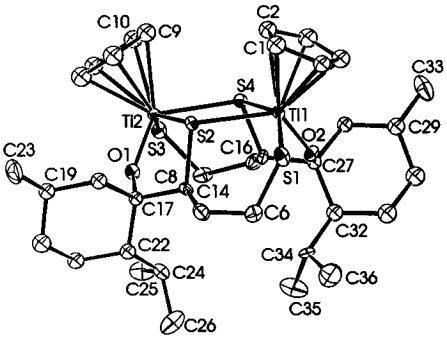


Figure 7. ORTEP drawing of **14**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Distances and angles: Ti(1)−S(1) 2.390(3) Å, Ti(1)−S(2) 2.534(3) Å, Ti(1)−S(4) 2.569(3) Å, Ti(1)−O(2) 1.826(7) Å, Ti(2)−S(2) 2.588(3) Å, Ti(2)−S(3) 2.402(4) Å, Ti(2)−S(4) 2.519(3) Å, Ti(2)−O(1) 1.827(6) Å, S(1)−Ti(1)−S(2) 81.5(1)°, O(2)−Ti(1)−S(4) 77.9(2)°, S(3)−Ti(2)−S(4) 81.3(1)°, O(1)−Ti(2)−S(2) 77.3(2)°, Ti(1)−S(2)−Ti(2) 105.2(1)°, Ti(1)−S(4)−Ti(2) 106.3(1)°.

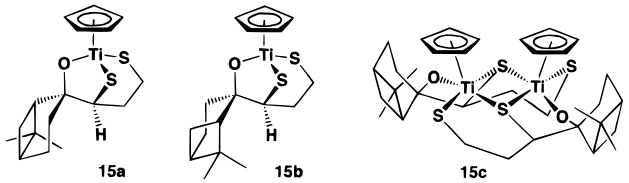


Figure 8. Isomers of **15**.

to those described for **11**, with the isopropyl groups oriented away from the cyclopentadienyl ring on the proximal Ti center. In both **13** and **14**, the preferred geometry is consistent with the minimization of steric congestion about the metal center.

The reaction of nopinone with **3** affords two monomeric diastereomers $CpTi(SCH(C_9H_{15}O)(CH_2CH_2S)$ (**15a**,**b**) as the major products and a dimeric product **15c** in varying amounts. NOE experiments for **15c** are consistent with a dimeric formulation in which the *gem*-dimethyl groups are oriented away from the cyclopentadienyl ring on the proximal Ti center (Figure 8). When the reaction is performed at −78 °C, the ratio **15a**:**15b** is 80:20 with a trace of the dimer **15c**, while, at higher temperatures, the amount of dimeric product is increased. The dependence of the product distribution on the temperature at which the reaction was performed

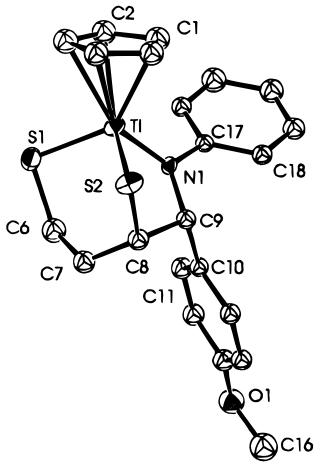
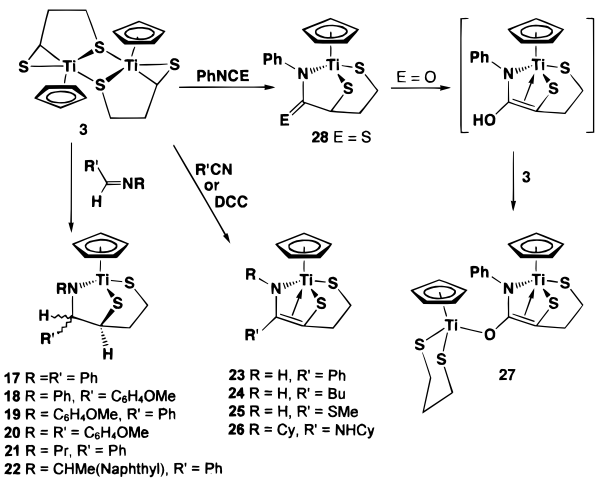


Figure 9. ORTEP drawing of **19**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Distances and angles: Ti−S(1) 2.306(4) Å, Ti−S(2) 2.280(4) Å, Ti−N(1) 1.939(9) Å, S(1)−Ti−S(2) 102.3(2)°, S(1)−Ti−N(1) 101.8(3)°, S(2)−Ti−N(1) 91.9(3)°.

Scheme 4



indicates that the monomeric and dimeric products are not interconvertible.

Reaction of 2-hexanone with **3** results in the formation of two diastereomers of the dimeric product $[CpTi(SCH(C(CH_3)(C_4H_9)O)CH_2CH_2S)]_2$ (**16a**,**b**), in a ratio of 2:1. NOE experiments were consistent with a geometry of the major isomer in which the butyl substituents are oriented away from the cyclopentadienyl rings. This relieves steric congestion in a manner similar to that observed for **13** and **14**.

Reactions with Imines. Compound **3** reacts with the imine PhCH═NPh to yield two diastereomers of $CpTi(SCH(CHPhNPh)CH_2CH_2S)$ (**17**) in a ratio of 81:19 (Scheme 4). Similarly two diastereomers of the analogous species **18** derived from $PhCH═N(C_6H_4OMe)$- and **3** are observed in a 65:35 ratio. The more abundant isomer was confirmed crystallographically to have the *SR*/*RS* configuration at the chiral carbon atoms (Figure 9), consistent with the assignment of geometry for the more abundant isomer of **19** based on coupling constant and NOE data. Analogous reactions with (C_6H_4OMe)-CH═NPh and $(C_6H_4OMe)CH═(C_6H_4OMe)$ gave similar ratios of the diastereomeric products **19** and **20**. NMR data for the reaction of the imine PhCH═NPr showed formation of a single monomeric product with traces of a dimeric isomer. Successive recrystallization afforded

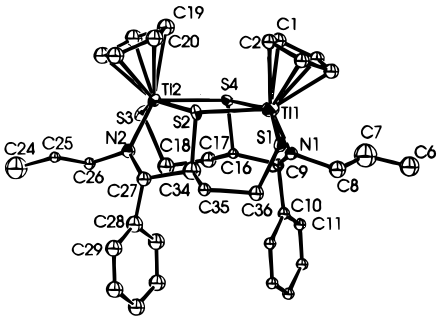


Figure 10. ORTEP drawing of **21b**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Distances and angles: Ti(1)−S(1) 2.38(1) Å, Ti(1)−S(2) 2.52(2) Å, Ti(1)−S(4) 2.59(1) Å, Ti(1)−N(1) 1.98(3) Å, Ti(2)−S(2) 2.49(1) Å, Ti(2)−S(3) 2.41(2) Å, Ti(2)−S(4) 2.52(2) Å, Ti(2)−N(2) 1.95(2) Å, S(1)−Ti(1)−S(2) 82.0(4)°, S(2)−Ti(1)−S(4) 74.2(4)°, S(1)−Ti(1)−N(1) 98(1)°, S(2)−Ti(1)−N(1) 118.4(9)°, S(2)−Ti(2)−S(4) 75.9(5)°, S(3)−Ti(2)−S(4) 80.3(5)°, S(2)−Ti(2)−N(2) 79(1)°, S(4)−Ti(2)−N(2) 121.3(7)°, Ti(1)−S(2)−Ti(2) 106.3(6)°, Ti(1)−S(4)−Ti(2) 103.5(6)°.

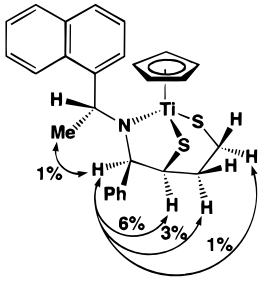


Figure 11. NOE observed for **22**.

a few crystals of the dimeric species **21b**. X-ray data for **21b** confirmed the dimeric formulation (Figure 10) with the relative configurations at the chiral carbons being *SS*/*RR*.

The relative stereochemistry of chiral carbons of major isomers of **17**−**21** appears to be dictated by a minimization of the steric congestion in the interaction between imine substituents and Ti fragment. Use of a chiral substrate, *rac*-(Naphth)CH(CH_3)N=CHPh, resulted in the formation of a 50:50 mixture of two diastereomers of CpTi(SC(CHPhNCHMe(Napth))CH_2-CH_2S) (**22a**,**b**). In contrast to **17**−**21**, NOE data (Figure 11) reveal that the phenyl groups on the imine carbons in **22** are oriented toward the cyclopentadienyl rings. This implies that the steric demands of the substituent on N in **22** cause the inversion of the preferred relative stereochemistry of the imino and methine carbons.

Reactions with Nitriles and Heteroallenes. Reaction of **3** with benzonitrile, valeronitrile, and methyl thiocyanate proceed in similar fashions yielding purple-black products **23**−**25**, formulated as mononuclear products of the form CpTi(SC=(C(R)NH)CH_2CH_2S) (Scheme 4). The NMR data reveal the presence of amido protons consistent with the enolization of the methine protons to N. Similar, but much slower, proton migrations were observed by Buchwald et al. in reactions of acetonitrile with the thioformaldehyde adduct of zirconocene.[5−7] Structural data obtained for the benzonitrile product **23** confirmed the presence of the olefinic C−C bond and the amido nitrogen (Figure 12). The interaction of the olefinic bond with the Ti is indicated by the Ti−C distances of 2.319(5) and 2.387(5) Å. A C to N proton migration is observed in the

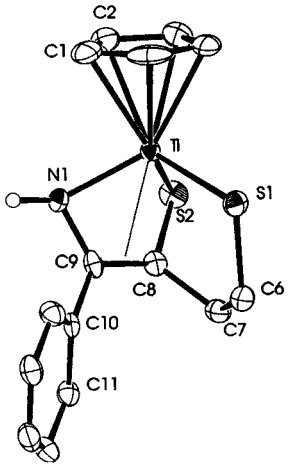


Figure 12. ORTEP drawing of **23**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Distances and angles: Ti−S(1) 2.358(2) Å, Ti−S(2) 2.280(2) Å, Ti−N(1) 1.956(4) Å, S(1)−Ti−S(2) 105.75(6)°, S(1)−Ti−N(1) 113.7(1)°, S(2)−Ti−N(1) 88.3(1)°.

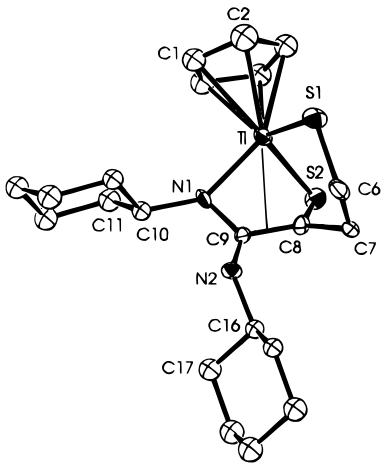


Figure 13. ORTEP drawing of **26**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Distances and angles: Ti−S(1) 2.362(4) Å, Ti−S(2) 2.287(4) Å, Ti−N(1) 2.033(7) Å, S(1)−Ti−S(2) 108.1(1)°, S(1)−Ti−N(1) 110.5(3)°, S(2)−Ti−N(1) 89.5(3)°.

product derived from DCC, CpTi(SC=(C(NHCy)NCy)-CH_2CH_2S) (**26**) (Scheme 4), but in this case, the proton migrates to the exocyclic nitrogen atom producing an exocyclic amino group (Figure 13).

The reaction of **3** with phenyl isocyanate and phenyl isothiocyanate results in the formation of the compounds CpTi(SC(PhNCO)CH_2CH_2S)TiCp($SCH_2CH_2CH_2$S) (**27**) and CpTi(SCH(PhNCS)CH_2CH_2S) (**28**), respectively (Scheme 4). The formulation of **27** was confirmed crystallographically (Figure 14). It is thought that these reactions proceed in a similar fashion. However, in the case of the phenyl isocyanate reaction, enolization of the methine proton to the exocyclic oxygen atom takes place affording an intermediate analogous to **28**. The resulting alcohol functionality is subsequently quenched by a second 1 equiv of **3**, affording **27**.

Mechanistic Considerations. The formation of both monomeric and dimeric products from the thiatitanacycles **3** and **4** is consistent with kinetically competitive reaction pathways. Monitoring of the reactions of **3** or **4** with cyclohexanone by NMR spectroscopy revealed the initial formation of a ketone adduct and subsequent transformation to the products **11** and **12**,

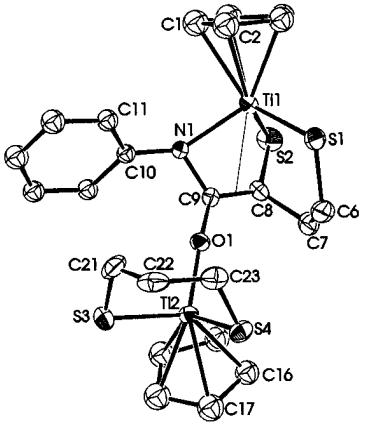
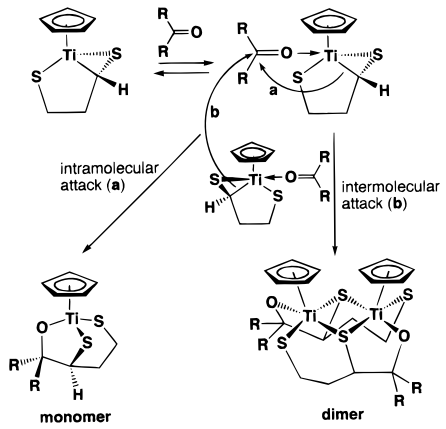


Figure 14. ORTEP drawing of **27**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Distances and angles: Ti(1)−S(1) 2.356(3) Å, Ti(1)−S(2) 2.267(3) Å, Ti(1)−N(1) 2.012(7) Å, Ti(2)−S(3) 2.265(3) Å, Ti(2)−S(4) 2.284(3) Å, Ti(2)−O(1) 1.839(6) Å, S(1)−Ti(1)−S(2) 106.6(1)°, S(1)−Ti(1)−N(1) 110.8(2)°, S(1)−Ti(1)−N(1) 90.6(2)°, S(3)−Ti(2)−S(4) 99.9(1)°, S(3)−Ti(2)−O(1) 104.9-(2)°, S(4)−Ti(2)−O(1) 103.6(2)°.

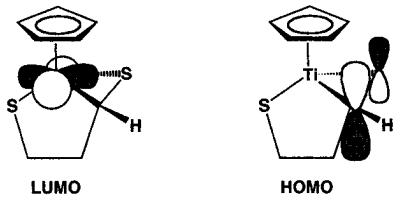
Scheme 5



respectively (Scheme 5). The ketone adducts are formed rapidly in THF but more slowly in benzene. Kinetic data reveal that, in benzene, the ketone adduct derived from **4** is formed in a reaction which is first order in **4** ($k = 7.2 \times 10^{-3}$ s^{-1}). The conversion to **12** appears to proceed through a number of intermediates suggesting a complex mechanism. However, kinetic data for the reaction in THF are approximately second order in the ketone adduct suggesting the mechanism is dominated by a bimolecular process ($k = 1.7 \times 10^{-3}$ Lmol^{-1} s^{-1}). For the reaction of **4** with benzophenone, no ketone complex was observed. In THF the reaction was too fast to monitor, although in benzene the reaction is first order in Ti ($k = 2.4 \times 10^{-4}$ s^{-1}) suggesting that the rate-determining step is ketone complexation followed by rapid intramolecular C−C bond formation.

EHMO calculations done for the fragment CpTi(SCHCH$_2$CH$_2$S) show the LUMO is a vacant metal-based d orbital (Chart 1). This Lewis acidic orbital is

Chart 1



responsible for the initial coordination of substrate. The HOMO of CpTi(SCHCH$_2$CH$_2$S) is predominently the C-based p-orbital of thiacyclopropane ring, and this orbital is responsible for subsequent attack of the coordinated substrate resulting in the new C−C bond. Intramolecular attack is operative in the formation of the mononuclear complexes **9**, **10**, and **17**−**28**, while an intermolecular attack accounts for the formation of the dimeric products such as **11**−**14**, **15c**, **16**, and **21b**. The course of the reaction appears to be a subtle result of steric and electronic factors. In the case of reactions involving ketones, the accessibility of the ketonic carbon appears to be a determining factor as dimeric products prevail when the substrate is more accessible to attack. Of course, the preferred course of the reaction may be altered by the conditions as was observed for **15**. The increased donor ability and steric demands of imines are thought to encourage proximity of the imine carbon and the thiatitanacycle in the coordination adduct, thus favoring intramolecular C−C bond formation.

Summary. The present study provides a facile and convenient route to thiametallacyclopropane derivatives of monocyclopentadienyltitanium. A wide range of reactivity with organic unsaturates is demonstrated herein, affirming that in the absence of steric crowding, as in Cp$_2$Ti(SCH$_2$), thiatitanacyclopropanes are, indeed, highly reactive. These results augur well for utility of thiametallacyclopropanes in the preparation of a variety of organosulfur derivatives. Furthermore, the observation of varying degrees of diastereoselectivity in reactions with prochiral and chiral substrates is attributed to a synergism between the molecular dissymmetry of these thiatitanacyclopropanes and the steric demands of the substrate. The development of related enantioselective systems is currently under study.

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Supporting Information Available: Tables of crystallographic data, positional and thermal parameters, and selected bond distances and angles (44 pages). Ordering information is given on any current masthead page.

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