

Macrocyclic Titanium Thiolate Metalloligands: Complexation and Thiolate-Transfer Reactions with Copper(I), Nickel(II), Palladium(II)

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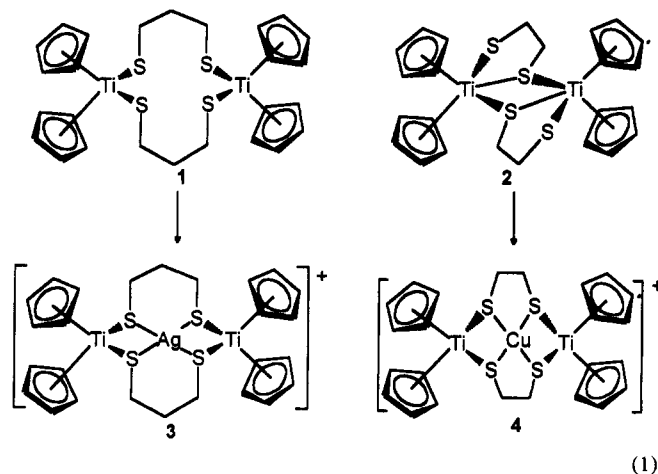
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The reaction of Cp_2ZrMe_2 with $(\text{HSCH}_2\text{CH}_2)_2\text{S}$ affords the S_6 macrocyclic complex $[\text{Cp}_2\text{Zr}(\text{SCH}_2\text{CH}_2)_2\text{S}]_2$ (**5**). This compound crystallizes in the orthorhombic space group $Pbcn$ with $a = 15.463(5)$ Å, $b = 14.049(5)$ Å, $c = 14.399(5)$ Å, $V = 3128(3)$ Å³, and $Z = 8$. Related titanocene derivatives were prepared via the reaction of Cp_2TiCl_2 with extended dithiols in the presence of base. In these cases, both monometallic and bimetallic macrocycles were formed and separated via column chromatography. In this way the following compounds were purified and characterized: $\text{Cp}_2\text{Ti}(\text{SCH}_2\text{CH}_2)_2\text{S}$ (**6**), $[\text{Cp}_2\text{Ti}(\text{SCH}_2\text{CH}_2)_2\text{S}]_2$ (**7**), $[\text{Cp}_2\text{TiCl}]_2(\text{SCH}_2\text{CH}_2)_2\text{S}$ (**8**), $\text{Cp}_2\text{Ti}((\text{SCH}_2\text{CH}_2)_2\text{S})_2$ (**9**), $[\text{Cp}_2\text{Ti}(\text{SCH}_2\text{CH}_2\text{CH}_2)_2\text{S}]_2$ (**10**), $\text{Cp}_2\text{Ti}((\text{SCH}_2\text{CH}_2\text{SCH}_2)_2\text{CH}_2)$ (**11**), $[\text{Cp}_2\text{Ti}((\text{SCH}_2\text{CH}_2\text{SCH}_2)_2\text{CH}_2)]_2$ (**12**), and $\text{Cp}_2\text{Ti}(\text{SCH}_2\text{CH}_2\text{SCH}_2\text{R})_2$ ($\text{R} = \text{CH}_3$ (**13**), Ph (**14**)). The interaction of these macrocycles with Cu(I) demonstrates their varying ability to act as metalloligands. In the case of **6**, **7**, and **9–12**, binding of Cu(I) is weak at best. In contrast, the S_4 macrocycle **11** complexes Cu(I) effectively to give the heterobimetallic complex $[\text{Cp}_2\text{Ti}(\text{SCH}_2\text{CH}_2\text{SCH}_2)_2\text{CH}_2\text{Cu}][\text{PF}_6]$ (**15**). Complex **15** crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.526(5)$ Å, $b = 10.952(3)$ Å, $c = 10.154(4)$ Å, $\alpha = 95.84(4)^\circ$, $\beta = 103.75(4)^\circ$, $\gamma = 99.02(3)^\circ$, $V = 1111.2(8)$ Å³, and $Z = 2$. An electrochemical study of **15** shows that it undergoes an irreversible reduction at -0.90 V vs the Ag/AgCl electrode. This is in contrast to that observed for related Ti–Cu macrocyclic species. Extended Huckel and Fenske–Hall molecular orbital calculations are consistent with dative metal–metal interactions in **15**. Further, they suggest that the Ti–S bonds are weakened by reduction. Similar bonding of Cu(I) by **13** affords the species $[\text{Cp}_2\text{Ti}(\text{SCH}_2\text{CH}_2\text{SCH}_2\text{Me})_2\text{Cu}][\text{PF}_6]$ (**18**) while the 24-membered-ring S_8 macrocycle **12** interacts with 1 equiv of Cu(I) to give the species $[(\text{Cp}_2\text{Ti}(\text{SCH}_2\text{CH}_2\text{SCH}_2)_2\text{CH}_2)_2\text{Cu}][\text{PF}_6]$ (**16**), in which Cu(I) binds the central four sulfur atoms. Further reaction of **16** with additional Cu(I) leads to Ti–S bond cleavage and affords 2 equiv of **15**. The observation of this rearrangement prompted an examination of thiolate-transfer reactions. Reaction of **7** with the Ni(II) salts $[\text{Ni}(\text{H}_2\text{O})_6][\text{BF}_4]_2$ and NiCl_2 results in the formation of $[\text{Ni}_2(\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2)_2]$ (**19**) and Cp_2TiF_2 or Cp_2TiCl_2 , respectively. Similarly, the reaction of **14** with $[\text{Pd}(\text{NCMe})_4][\text{BF}_4]_2$ affords the species $[\text{Pd}_6(\text{SCH}_2\text{CH}_2\text{SCH}_2\text{Ph})_8][\text{BF}_4]_4$ (**20**). The complex **20**· $0.5\text{C}_6\text{H}_6$ · 2NCCH_3 crystallizes in the triclinic space group $P\bar{1}$ with $a = 14.605(5)$ Å, $b = 15.110(4)$ Å, $c = 13.248(4)$ Å, $\alpha = 110.86(2)^\circ$, $\beta = 98.71(3)^\circ$, $\gamma = 98.53(3)^\circ$, $V = 2635(4)$ Å³, and $Z = 2$. The chemistry described herein indicates that while titanocenedithiolate macrocycles are capable of complexation of late metals in some cases, ring size and the Lewis acidity of the late metal may act to destabilize the Ti–S bonds, resulting in thiolate-transfer reactions.

Introduction

Much of the interest in heterobimetallic complexes stems from the view that new reactivity patterns will emerge from the combination of disparate metals in a single species.¹ Most recently, we pursued such complexes from a different standpoint. The first-row early metals have several easily accessible oxidation states. On formation of an early–late heterobimetallic complex, one might expect a significant perturbation of the redox properties of the early metal center. This reasoning suggests the possibility that early metal complexes could act as redox-responsive sensors for the complexation of late metals. In developing this line of research, we recently described the syntheses and structures of a series of Ti- and Zr-based macrocyclic metalloligands of the form $\text{Cp}_2\text{M}(\text{S}(\text{CH}_2)_n\text{S})_2\text{MCp}_2$ ($n = 2, 3$) and we showed that these systems bind late metals such as Ag(I) and Cu(I) (eq 1).^{2–4} In the case of the Ti-based systems, the Ag and Cu derivatives exhibit reversible electrochemical reductions, with redox potentials differing by almost 400 mV.⁴ These initial results augur well for potential application of such systems in chemical sensor technology; however, questions regarding the range of utility and chemical stability remain unanswered. In this paper, we address such questions. We describe the complexation of Cu(I) by a series of new, larger S_6 and S_8 macrocycles which provide some



insight regarding the relationship between structure and redox properties. The chemical instability of the large-ring complexes is evidenced both in reactions where Cu(I) is present in excess and in reactions with Ni(II). Related reactions involving Pd(II) also result in thiolate transfer, yielding late metal thiolate aggregates. Together, the studies presented herein help to define the chemistry of macrocyclic titanocenedithiolate derivatives.

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

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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. 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 $SiMe_4$. Cyclic voltammetric experiments were performed on a BAS CV-27 electrochemical unit employing a Pt disk working electrode and a Ag/AgCl reference electrode. Bu_4NPF_6 was used as the supporting electrolyte in THF solvent. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, TN, and Schwarzkopf Laboratories, Woodside, NY. Cp_2TiCl_2 and Cp_2ZrCl_2 were purchased from the Aldrich Chemical Co. Cp_2ZrMe_2 was prepared by the literature method.⁵

Synthesis of $[Cp_2Zr(SCH_2CH_2)_2S]_2$ (5). Cp_2ZrMe_2 (100 mg, 0.38 mmol) was dissolved in 2 mL of THF, and $S(CH_2CH_2SH)_2$ (60 mg, 0.40 mmol) was added. The mixture was stirred for 1 h and allowed to stand overnight. Subsequent addition of 1 mL of hexane and further standing at 25 °C for 48 h afforded a white-yellow solid. Yield: 62 mg, 42%. The product was recrystallized from CH_2Cl_2 /hexane. 1H NMR ($CDCl_3$, 25 °C, δ): 6.18 (s, 20H, Cp), 3.05 (m, 8H, CH_2), 2.58 (m, 8H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, δ): 110.86, 37.81, 34.67. Anal. Calcd: C, 45.00; H, 4.85. Found: C, 44.60; H, 4.50.

Synthesis of $[Cp_2Ti(SCH_2CH_2)_2S]$ (6). To Cp_2TiCl_2 (500 mg, 2.0 mmol) and imidazole (400 mg, 6 mmol) in 20 mL of benzene was added $S(CH_2CH_2SH)_2$ (300 mg, 2.0 mmol). The mixture was stirred for 0.5 h and then allowed to stand at 25 °C for 48 h. After solvent removal, the purple residue was separated from the mixture by column chromatography on neutral alumina under a N_2 atmosphere employing hexane and ethyl acetate as the eluents. The purple product was obtained in 20% yield. 1H NMR ($CDCl_3$, 25 °C, δ): 6.17 (s, 10H, Cp), 3.62 (t, 4H, CH_2 , $|J_{H-H}| = 5.4$ Hz), 2.59 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, δ): 112.56, 43.63, 32.32. Anal. Calcd: C, 50.90; H, 5.49. Found: C, 50.85; H, 5.35.

Synthesis of $[Cp_2Ti(SCH_2CH_2)_2S]_2$ (7). To Cp_2TiCl_2 (1.0 g, 4.0 mmol) in 30 mL of benzene were added $S(CH_2CH_2SH)_2$ (600 mg, 4.0 mmol) and Et_3N (900 mg, 8.9 mmol). The mixture was stirred for 2 h and then allowed to stand at 25 °C for 24 h. After solvent removal, the purple residue was separated from the mixture by column chromatography on neutral alumina under a N_2 atmosphere employing THF and hexane as the eluents. The purple products 6 and 7 were obtained in 1% and 39% yields respectively. 1H NMR ($CDCl_3$, 25 °C, δ): 6.11 (s, 20H, Cp), 3.17 (t, 8H, CH_2 , $|J_{H-H}| = 9.0$ Hz), 2.48 (t, 8H, CH_2 , $|J_{H-H}| = 9.0$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, δ): 111.84, 43.89, 36.87. Anal. Calcd: C, 50.90; H, 5.49. Found: C, 50.75; H, 5.30.

Synthesis of $[Cp_2TiCl_2(SCH_2CH_2)_2S]$ (8). To Cp_2TiCl_2 (100 mg, 0.4 mmol) and imidazole (100 mg, 1.5 mmol) in 4 mL of benzene was added $S(CH_2CH_2SH)_2$ (30 mg, 0.2 mmol). The mixture was stirred overnight at 25 °C. After solvent removal, the red residue was washed with 3×2 mL of hexane and then extracted with 3×15 mL of benzene. The solvent was removed from the extracts, affording the product in 78% yield. 1H NMR ($CDCl_3$, 25 °C, δ): 6.35 (s, 20H, Cp), 3.73 (t, 4H, CH_2 , $|J_{H-H}| = 7.2$ Hz), 2.72 (t, 4H, CH_2 , $|J_{H-H}| = 7.2$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, δ): 115.54, 44.00, 34.32. Anal. Calcd: C, 49.76; H, 4.87. Found: C, 49.60; H, 4.80.

Synthesis of $Cp_2Ti(SCH_2CH_2CH_2)_2S$ (9) and $[Cp_2Ti(SCH_2CH_2CH_2)_2S]_2$ (10). The procedure was identical to that employed above for 7 with the appropriate substitution of $S(CH_2CH_2CH_2SH)_2$ for $S(CH_2CH_2SH)_2$. The two compounds were eluted from the column in 8% and 30% yields, respectively. Data for 9 are as follows. 1H NMR ($CDCl_3$, 25 °C, δ): 6.15 (s, 10H, Cp), 3.39 (t, 4H, CH_2 , $|J_{H-H}| = 6.0$ Hz), 2.54 (t, 4H, CH_2 , $|J_{H-H}| = 6.9$ Hz), 2.04 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, δ): 111.83, 43.51, 32.80, 31.36. Anal. Calcd: C, 53.62; H, 6.19. Found: 53.50; H, 6.00. Data for 10 are as follows. 1H NMR ($CDCl_3$, 25 °C, δ): 6.11 (s, 20H, Cp), 3.09 (t, 8H, CH_2 , $|J_{H-H}| = 7.0$ Hz), 2.57 (t, 8H, CH_2 , $|J_{H-H}| = 6.9$ Hz), 1.74 (m, 8H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, δ): 111.80, 40.15, 30.28, 27.79. Anal. Calcd: C, 53.62; H, 6.19. Found: C, 53.45; H, 6.10.

Synthesis of $Cp_2Ti(SCH_2CH_2SCH_2)_2CH_2$ (11) and $[Cp_2Ti(SCH_2CH_2SCH_2)_2CH_2]_2$ (12). The synthesis was identical to that used above for 9 and 10 with the use of $CH_2(CH_2S(CH_2CH_2SH))_2$. Column chromatography on neutral alumina under N_2 atmosphere employing hexane and ethyl acetate as the eluents afforded a separation of the two products in 8% and 26% yields, respectively. Data for 11 are as follows. 1H NMR ($CDCl_3$, 25 °C, δ): 6.14 (s, 10H, Cp), 3.28 (t, 4H, CH_2 , $|J_{H-H}|$

= 6.6 Hz), 2.68 (t, 4H, CH_2 , $|J_{H-H}| = 7.2$ Hz), 2.62 (t, 4H, CH_2 , $|J_{H-H}| = 6.6$ Hz), 1.75 (q, 2H, CH_2 , $|J_{H-H}| = 7.2$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, δ): 111.80, 43.89, 34.44, 29.74, 28.75. Anal. Calcd: C, 50.48; H, 5.98. Found: C, 50.80; H, 5.80. Data for 12 are as follows. 1H NMR ($CDCl_3$, 25 °C, δ): 6.12 (s, 20H, Cp), 3.23 (t, 8H, CH_2 , $|J_{H-H}| = 8.1$ Hz), 2.5–2.7 (m, 16H, CH_2), 1.83 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, δ): 111.88, 43.98, 34.53, 31.35, 29.65. Anal. Calcd: C, 50.48; H, 5.98. Found: C, 50.35; H, 5.85.

Synthesis of $Cp_2Ti(SCH_2CH_2SCH_2)_2$ (R = CH_3 (13), Ph (14)). These two products were prepared in a similar manner. To Cp_2TiCl_2 (1.0 g, 4.0 mmol) in 40 mL of THF was added $NaSCH_2CH_2SPh$ (1.20 g, 8.3 mmol). The mixture was stirred for 1 h and then filtered. After solvent removal, the residue was dried and washed with 2×10 mL of pentane. The red-purple solid 14 was dried in vacuo (yield 1.46 g, 87%). In the case of 13, the process was identical except that hexane was employed to wash the residue (yield 1.90 g, 85%). Data for 13 are as follows. 1H NMR ($CDCl_3$, 25 °C, δ): 6.12 (s, 10H, Cp), 3.23 (t, 4H, CH_2 , $|J_{H-H}| = 6.1$ Hz), 2.56 (t, 4H, CH_2 , $|J_{H-H}| = 6.1$ Hz), 2.53 (t, 4H, CH_2 , $|J_{H-H}| = 7.5$ Hz), 1.23 (t, 6H, CH_3 , $|J_{H-H}| = 7.5$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, δ): 111.86, 43.89, 34.15, 26.36, 15.01. Anal. Calcd: C, 51.41; H, 6.71. Found: C, 51.30; H, 6.50. Data for 14 are as follows. 1H NMR ($CDCl_3$, 25 °C, δ): 7.28 (m, 10H, C_6H_5), 6.06 (s, 10H, Cp), 3.70 (s, 4H, CH_2), 3.13 (t, 4H, CH_2 , $|J_{H-H}| = 6.0$ Hz), 2.49 (t, 4H, CH_2 , $|J_{H-H}| = 6.0$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, δ): 138.74, 128.94, 127.06, 111.80, 43.66, 36.90, 34.15. Analysis Calcd: C, 61.74; H, 5.92; Found C: 61.60; H: 5.88.

Synthesis of $[Cp_2Ti(SCH_2CH_2SCH_2)_2CH_2Cu][PF_6]$ (15). (i) To a THF (1.0 mL) solution of 11 (20 mg, 0.05 mmol) was added $[Cu(NCCH_3)_4][PF_6]$ (19 mg, 0.05 mmol) suspended in 2 mL of THF (or 2 mL of CH_3CN). The mixture was stirred for 0.5 h, during which a black precipitate formed. The solvent was removed in vacuo and washed with 2×3 mL of benzene. The black solid was isolated in 93% yield.

(ii) To a THF (1.0 mL) solution of 12 (10 mg, 0.01 mmol) was added excess $[Cu(NCCH_3)_4][PF_6]$ suspended in 2 mL of THF (or 2 mL of CH_3CN). The mixture was stirred for 0.5 h, during which a red-black precipitate formed. The solvent was removed in vacuo and washed with 2×3 mL of benzene. The black solid isolated in 65% yield. 1H NMR (CD_3CN , 25 °C, δ): 6.16 (s, 10H, Cp), 3.88 (ddd, 2H, CH_2 , $|J_{H-H}| = 2.0$ Hz, $|J_{H-H}| = 2.4$ Hz, $|J_{H-H}| = 6.3$ Hz), 3.69 (ddd, 2H, CH_2 , $|J_{H-H}| = 2.0$ Hz, $|J_{H-H}| = 2.4$ Hz, $|J_{H-H}| = 7.2$ Hz), 3.33 (dt, 2H, CH_2 , $|J_{H-H}| = 13.0$ Hz, $|J_{H-H}| = 6.0$ Hz), 2.93 (dd, 2H, CH_2 , $|J_{H-H}| = 2.4$ Hz, $|J_{H-H}| = 6.3$ Hz), 2.92 (dd, 2H, CH_2 , $|J_{H-H}| = 2.4$ Hz, $|J_{H-H}| = 6.3$ Hz), 2.75 (dt, 2H, CH_2 , $|J_{H-H}| = 13.0$ Hz, $|J_{H-H}| = 6.0$ Hz), 2.0 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, δ): 111.68, 44.91, 38.01, 34.81, 23.39. Anal. Calcd: C, 33.31; H, 3.95. Found: C, 33.10; H, 3.70.

Synthesis of $[(Cp_2Ti(SCH_2CH_2SCH_2)_2CH_2)_2Cu][PF_6]$ (16) and $[Cp_2Ti(SCH_2CH_2SCH_2Me)_2Cu][PF_6]$ (18). These products were prepared by employing method i described above for 15 with the use of the appropriate Ti metalloligand precursor and 1 equiv of Cu(I). Data for 16 (red black solid) are as follows. Yield: 76%. 1H NMR (CD_3CN , 25 °C, δ): 6.20 (s, 20H, Cp), 3.35 (m, 8H, CH_2), 3.15 (m, 8H, CH_2), 2.80 (m, 8H, CH_2), 2.08 (m, 4H, CH_2). Anal. Calcd: 38.69; H, 4.87. Found: C, 38.50; H, 4.75. Data for 18 are as follows. Yield: 68%. 1H NMR ($CDCl_3$, 25 °C, δ): 6.06 (s, 10H, Cp), 3.62 (br d, 2H, CH_2 , $|J_{H-H}| = 12.0$ Hz), 3.50 (br d, 2H, CH_2 , $|J_{H-H}| = 12.0$ Hz), 2.86 (m, 4H, CH_2), 2.63 (q, 4H, CH_2 , $|J_{H-H}| = 7.1$ Hz), 1.34 (t, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, δ): 112.08, 42.47, 38.10, 29.73, 14.19. Anal. Calcd: C, 34.37; H, 4.49. Found: C, 34.05; H, 4.40.

Synthesis of $[Ni_2(SCH_2CH_2SCH_2CH_2S)_2]$ (19). (i) To 7 (66 mg, 0.1 mmol) in 1 mL of THF was added $NiCl_2$ (26 mg, 0.2 mmol) suspended in 2 mL of THF. The mixture was stirred for 5 h at 25 °C. After removal of the solvent, the residue was washed with benzene (3×3 mL) and dried in vacuo. The black product was obtained in 90% yield and was recrystallized from CH_3CN to give X-ray-quality crystals. Removal of the solvent from the benzene washings afforded Cp_2TiCl_2 in 74% yield.

(ii) To 7 (66 mg, 0.1 mmol) in 1 mL of THF was added $NiCl_2$ (13 mg, 0.1 mmol) suspended in 2 mL of THF. The workup was as above. $[Ni_2(SCH_2CH_2SCH_2CH_2S)_2]$ was obtained in 85% yield. The Ti-containing products were shown to be 7, 8, and Cp_2TiCl_2 in a 1:8:2 ratio, with a yield of $[Cp_2TiCl_2(SCH_2CH_2)_2S]$ of 51%. 1H NMR ($CDCl_3$, 25 °C, δ): 4.3 (m, 2H), 3.4–3.6 (m, 2H), 3.15–3.25 (m, 4H).

Synthesis of $[Pd_4(SCH_2CH_2SCH_2Ph)_4][BF_4] \cdot 0.5C_6H_6 \cdot 2NCCH_3$ (20). To a THF solution (1 mL) of 14 (0.1 mmol, 56 mg) was added $[Pd(NCCH_3)_4][BF_4]$ (66 mg, 1.5 mmol) suspended in CH_3CN (2 mL). The mixture was stirred overnight at 25 °C. The color of the solution changed from purple to yellow. After solvent removal, the residue was washed

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Table I. Crystallographic Parameters

	5	15	20
formula	C ₁₀ H ₁₆ S ₃ Zr	C ₁₇ H ₂₄ CuF ₆ PS ₄ Ti	C ₄₃ H ₅₃ B ₂ F ₆ N ₂ Pd ₃ S ₆
cryst syst	orthorhombic	triclinic	triclinic
space group	<i>Pbcn</i> (No. 60)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> (Å)	15.463(5)	10.526(5)	14.605(5)
<i>b</i> (Å)	14.049(5)	10.952(3)	15.110(4)
<i>c</i> (Å)	14.399(5)	10.154(4)	13.248(4)
α (deg)		95.84(4)	110.86(2)
β (deg)		103.75(4)	98.71(3)
γ (deg)		99.02(3)	98.53(3)
<i>V</i> (Å ³)	3128(3)	1111.2(8)	2635(4)
<i>Z</i>	8	2	2
abs coeff,	10.58	18.01	13.65
μ (cm ⁻¹)			
<i>T</i> (°C)	24	24	24
<i>R</i> (%) ^a	3.88	5.72	5.81
<i>R_w</i> (%) ^b	4.08	5.74	6.13

$$^a R = \sum |k|F_o| - |F_c| / \sum |k|F_o, \quad ^b R_w = [\sum w(k|F_o| - |F_c|)^2 / \sum w k^2 F_o^2]^{1/2}.$$

with three portions of benzene (3 mL) was dried under vacuum. The yellow product was obtained in 72% yield. Crystals of **20** were obtained by recrystallization from MeCN and benzene. The solvent was removed from the benzene washings. The residue was washed with methanol and identified as Cp₂TiF₂ by NMR. ¹H NMR (CD₃CN, 25 °C, δ): 7.78 (m), 7.62 (m), 7.30 (m), 7.20 (m), 4.4–4.0 (m), 4.8–4.7 (m), 3.8 (m), 3.5 (m), 3.1 (m), 2.7 (m). Anal. Calcd: C, 36.87; H, 3.80. Found: C, 36.60; H, 3.60.

Molecular Orbital Calculations. Extended Huckel⁶ and Fenske–Hall⁷ molecular orbital calculations were performed by employing suitably simplified models derived from the crystallographic data. Details of the methodology have been previously described.⁸

X-ray Data Collection and Reduction. X-ray-quality crystals of **5**, **15**, and **20** were obtained directly from the preparations as described above. The crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O₂-free environment for each crystal. Diffraction experiments were performed on a Rigaku AFC6 diffractometer equipped with graphite-monochromatized Mo K α 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 I. Ultimately, 25 reflections (20° < 2 θ < 25°) were used to obtain the final lattice parameters and the orientation matrices. Machine parameters, crystal data, and data collection parameters are summarized in Table I. The observed extinctions were consistent with the space groups given in Table I. The data sets were collected in one shell (4.5° < 2 θ < 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 3520 workstation. The reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinements.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.^{9,10} The heavy-atom positions were determined using direct methods employing either the SHELX-86 or MITHRIL direct methods routines. In each case, the remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F*, minimizing the function $w(|F_o| - |F_c|)^2$ where the weight *w* is defined as $4F_o^2/2\sigma(F_o^2)$ and *F_o* and *F_c* are the observed and calculated structure factor amplitudes. In the final cycles of refinement, all heavy atoms were assigned anisotropic temperature factors. The number of carbon atoms assigned anisotropic thermal parameters varied among the five structures and was set so as to maintain a reasonable data:variable ratio in each case. Hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded by assuming a C–H bond length of 0.95 Å. Hydrogen

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

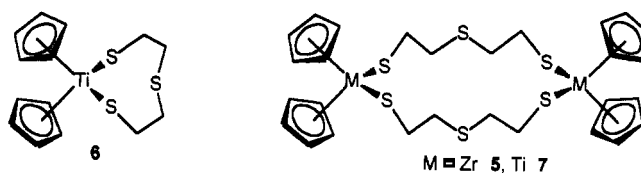
Results

Macrocyclic Titanocenedithiolates. The synthetic details for macrocyclic titanocenedithiolates **5–14** and the metal complexes **15–18** are presented in the Experimental Section. The results of crystallographic studies of compounds **5** and **15** are illustrated in Figures 1 and 2, and the numerical and metric data are tabulated in Tables I–III. Pertinent spectroscopic, electrochemical, and theoretical data will be introduced and discussed at the appropriate places in the Discussion.

Thiolate-Transfer Reactions. Compounds **19** and **20** are derived from thiolate-transfer reactions involving titanocenedithiolate derivatives and the appropriate Ni and Pd precursors. The synthetic details as well as the spectral and structural data are presented in the Experimental Section. The results of crystallographic study of compound **20** are illustrated in Figure 3, and the numerical and metric data are tabulated in Tables I–III. Pertinent data will be introduced and discussed at the appropriate places in the Discussion.

Discussion

Macrocyclic Titanocenedithiolates. Previously established synthetic routes to Ti and Zr S₄ macrocycles involve either thiololysis of an early metal alkyl, thiolate displacement of halide, or oxidative addition of disulfide to M(II).^{2–4} In a similar vein, S₆ macrocycles can be prepared. The reaction of Cp₂ZrMe₂ with (HSCH₂CH₂)₂S proceeds cleanly with the evolution of CH₄ and a slight yellowing of the solution, affording the S₆ macrocycle [Cp₂Zr(SCH₂CH₂)₂S]₂ (**5**) in 42% yield. The bimetallic nature



of complex **5** was confirmed crystallographically (vide infra). An ORTEP drawing of **5** is shown in Figure 1. The two bis-(cyclopentadienyl)zirconium fragments of **5** are linked by the two dithiolate chains, yielding a 16-membered ring. The central thioether sulfur atoms adopt an exodentate conformation while the thiolate sulfur atoms are endodentate to the macrocyclic ring. The Zr–S distances average 2.504(3) Å while the S–Zr–S angle is 99.99(7)°. This is typical of zirconocenedithiolates. The Zr···Zr distance is 7.608(3) Å, substantially larger than that seen in the Zr analogs of **1** and **2**, as expected.^{2,3}

The Ti analog of **5** is prepared by reaction of Cp₂TiCl₂ with (HSCH₂CH₂)₂S in the presence of base. Monitoring of the purple reaction mixture reveals at least three Ti-containing products. Chromatography on neutral alumina effects a clean separation of two purple products. The product most readily eluted from the column was formulated as the monometallic eight-membered-ring product Cp₂Ti(SCH₂CH₂)₂S (**6**). Such elution properties have been previously demonstrated for simple titanocenedithiolate derivatives.^{4,11–16} ¹H NMR data were also consistent with the

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Table II. Selected Positional Parameters

atom	x	y	z
Complex 5			
Zr(1)	0.17047(4)	0.24880(6)	0.02596(5)
S(1)	0.0388(1)	0.3422(1)	-0.0161(2)
S(2)	0.1931(1)	0.1581(2)	-0.1224(1)
S(3)	0	0.5387(2)	-1/4
S(4)	0	0.1978(2)	-1/4
C(1)	0.0638(6)	0.4176(6)	-0.1148(6)
C(2)	-0.0196(6)	0.4563(6)	-0.1547(6)
C(3)	0.1077(6)	0.0736(6)	-0.1491(6)
C(4)	0.0162(5)	0.1165(5)	-0.1568(6)
C(5)	0.0544(6)	0.1487(7)	0.0989(7)
C(6)	0.1251(6)	0.0905(6)	0.0913(6)
C(7)	0.1866(6)	0.1281(8)	0.1485(7)
C(8)	0.155(1)	0.207(1)	0.1932(7)
C(9)	0.072(1)	0.2192(7)	0.1602(8)
C(10)	0.2737(7)	0.360(1)	-0.0552(7)
C(11)	0.2404(6)	0.4092(7)	0.0187(9)
C(12)	0.2676(8)	0.367(1)	0.1009(7)
Complex 15			
Cu(1)	0.1294(1)	0.2607(1)	-0.0172(2)
Ti(1)	0.2902(2)	0.2188(2)	-0.1986(2)
S(1)	0.1022(3)	0.0769(3)	-0.1504(3)
S(2)	-0.0921(3)	0.2779(3)	-0.0778(3)
S(3)	0.1943(3)	0.2847(3)	0.2199(3)
S(4)	0.2954(3)	0.4087(3)	-0.0385(3)
C(1)	-0.070(1)	0.076(1)	-0.247(1)
C(2)	-0.154(1)	0.115(1)	-0.156(1)
C(3)	-0.136(1)	0.281(1)	0.086(1)
C(4)	-0.044(1)	0.384(1)	0.194(1)
C(5)	0.065(1)	0.335(1)	0.291(1)
C(6)	0.307(1)	0.433(1)	0.240(1)
C(7)	0.392(1)	0.427(1)	0.141(1)
C(8)	0.383(1)	0.044(1)	-0.122(1)
C(9)	0.419(1)	0.141(1)	-0.012(1)
C(10)	0.503(1)	0.235(1)	-0.043(1)
C(11)	0.516(1)	0.202(1)	-0.175(1)
C(12)	0.441(1)	0.083(1)	-0.226(1)
C(13)	0.251(1)	0.379(1)	-0.339(1)
C(14)	0.131(1)	0.297(1)	-0.352(1)
C(15)	0.139(1)	0.180(1)	-0.418(1)
C(16)	0.267(1)	0.186(1)	-0.438(1)
C(17)	0.336(1)	0.311(1)	-0.390(1)
Complex 20			
Pd(1)	0.54214(8)	0.06271(7)	0.44101(9)
Pd(2)	0.45108(8)	-0.21131(8)	0.24485(9)
Pd(3)	0.27849(8)	0.05932(8)	0.4548(1)
S(1)	0.4759(3)	-0.2052(2)	0.4233(3)
S(2)	0.3522(3)	-0.3639(2)	0.1891(3)
S(3)	0.3879(3)	0.0427(3)	0.3443(3)
S(4)	0.2646(3)	0.2012(3)	0.4289(3)
S(5)	0.5611(3)	-0.0690(2)	0.2943(3)
S(6)	0.4296(3)	-0.2255(3)	0.0623(3)
S(7)	0.3002(3)	-0.0837(3)	0.4705(3)
S(8)	0.1524(3)	0.0570(3)	0.5418(3)
C(1)	0.377(1)	-0.302(1)	0.410(1)
C(2)	0.378(1)	-0.390(1)	0.312(1)
C(3)	0.404(1)	-0.450(1)	0.093(1)
C(4)	0.394(1)	0.149(1)	0.308(1)
C(5)	0.296(1)	0.172(1)	0.294(1)
C(6)	0.140(1)	0.210(1)	0.397(1)
C(7)	0.536(1)	-0.040(1)	0.172(1)
C(8)	0.521(1)	-0.128(1)	0.070(1)
C(9)	0.323(1)	-0.180(1)	0.046(1)
C(10)	0.228(1)	-0.092(1)	0.571(1)
C(11)	0.137(1)	-0.063(1)	0.543(1)
C(12)	0.198(1)	0.136(1)	0.687(1)

formulation of 6. A second purple product which eluted more slowly from the column was formulated as $[\text{Cp}_2\text{Ti}(\text{SCH}_2\text{CH}_2)_2\text{S}]_2$ (7) on the basis of both the ^1H NMR data and the similarity of

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Table III. Selected Bond Distances and Angles

Complex 5			
Zr(1)-S(1)	2.496(2)	Zr(1)-S(2)	2.512(2)
Zr(1)-C(5)	2.510(8)	Zr(1)-C(6)	2.514(8)
Zr(1)-C(7)	2.460(9)	Zr(1)-C(8)	2.49(1)
Zr(1)-C(9)	2.498(9)	Zr(1)-C(10)	2.518(9)
Zr(1)-C(11)	2.502(9)	Zr(1)-C(12)	2.487(9)
Zr(1)-C(13)	2.487(9)	Zr(1)-C(14)	2.519(9)
S(1)-C(1)	1.813(8)	S(2)-C(3)	1.816(9)
S(3)-C(2)	1.821(9)	S(3)-C(2)	1.821(9)
S(4)-C(4)	1.780(8)	S(4)-C(4)	1.780(8)
S(1)-Zr(1)-S(2)	99.99(7)	Zr(1)-S(1)-C(1)	108.9(3)
Zr(1)-S(2)-C(3)	114.2(3)	C(2)-S(3)-C(2)	101.0(5)
C(4)-S(4)-C(4)	100.2(5)		
Complex 15			
Cu(1)-Ti(1)	2.832(3)	Cu(1)-S(1)	2.246(4)
Cu(1)-S(2)	2.308(4)	Cu(1)-S(3)	2.316(4)
Cu(1)-S(4)	2.255(4)	Ti(1)-S(1)	2.494(4)
Ti(1)-S(4)	2.491(4)	Ti(1)-C(8)	2.40(1)
Ti(1)-C(9)	2.37(1)	Ti(1)-C(10)	2.38(1)
Ti(1)-C(11)	2.37(1)	Ti(1)-C(12)	2.38(1)
Ti(1)-C(13)	2.40(1)	Ti(1)-C(14)	2.34(1)
Ti(1)-C(15)	2.36(1)	Ti(1)-C(16)	2.37(1)
Ti(1)-C(17)	2.39(1)		
Ti(1)-Cu(1)-S(2)	126.4(1)	Ti(1)-Cu(1)-S(3)	126.8(1)
S(1)-Cu(1)-S(2)	95.5(1)	S(1)-Cu(1)-S(3)	123.1(1)
S(1)-Cu(1)-S(4)	114.7(1)	S(2)-Cu(1)-S(3)	106.8(1)
S(2)-Cu(1)-S(4)	123.2(1)	S(3)-Cu(1)-S(4)	95.5(1)
S(1)-Ti(1)-S(4)	99.0(1)	Cu(1)-S(1)-Ti(1)	73.2(1)
Cu(1)-S(4)-Ti(1)	73.1(1)		
Complex 20			
Pd(1)-S(1)	2.343(4)	Pd(1)-S(3)	2.335(4)
Pd(1)-S(5)	2.321(4)	Pd(1)-S(7)	2.341(4)
Pd(2)-S(1)	2.303(4)	Pd(2)-S(2)	2.328(4)
Pd(2)-S(5)	2.300(4)	Pd(2)-S(6)	2.319(4)
Pd(3)-S(3)	2.308(4)	Pd(3)-S(4)	2.321(4)
Pd(3)-S(7)	2.306(4)	Pd(3)-S(8)	2.318(4)
S(1)-Pd(1)-S(3)	89.1(1)	S(1)-Pd(1)-S(5)	173.7(1)
S(1)-Pd(1)-S(7)	92.3(1)	S(3)-Pd(1)-S(5)	89.0(1)
S(3)-Pd(1)-S(7)	176.8(1)	S(5)-Pd(1)-S(7)	89.2(1)
S(1)-Pd(2)-S(2)	88.0(1)	S(1)-Pd(2)-S(5)	92.7(1)
S(1)-Pd(2)-S(6)	176.7(1)	S(2)-Pd(2)-S(5)	174.0(1)
S(2)-Pd(2)-S(6)	90.3(1)	S(5)-Pd(2)-S(6)	88.7(1)
S(3)-Pd(3)-S(4)	87.4(1)	S(3)-Pd(3)-S(7)	88.1(1)
S(3)-Pd(3)-S(8)	171.0(1)	S(4)-Pd(3)-S(7)	175.4(1)
S(4)-Pd(3)-S(8)	94.9(1)	S(7)-Pd(3)-S(8)	89.6(1)
Pd(1)-S(1)-Pd(2)	116.0(1)	Pd(1)-S(1)-C(1)	106.5(5)
Pd(2)-S(1)-C(1)	100.8(5)	Pd(2)-S(2)-C(2)	101.5(5)
Pd(2)-S(2)-C(3)	107.1(5)	C(2)-S(2)-C(3)	102.1(7)
Pd(1)-S(3)-Pd(3)	113.2(1)	Pd(1)-S(3)-C(4)	103.8(5)
Pd(3)-S(3)-C(4)	103.4(4)	Pd(3)-S(4)-C(5)	99.3(4)
Pd(3)-S(4)-C(6)	112.1(5)	C(5)-S(4)-C(6)	102.2(7)
Pd(1)-S(5)-Pd(2)	115.8(1)	Pd(1)-S(5)-C(7)	106.0(5)
Pd(2)-S(5)-C(7)	102.0(5)	Pd(2)-S(6)-C(8)	102.5(5)
Pd(2)-S(6)-C(9)	101.4(5)	C(8)-S(6)-C(9)	103.0(8)
Pd(1)-S(7)-Pd(3)	109.0(1)	Pd(1)-S(7)-C(10)	106.0(5)
Pd(3)-S(7)-C(10)	101.9(5)	Pd(3)-S(8)-C(11)	100.9(5)
Pd(3)-S(8)-C(12)	107.0(5)	C(11)-S(8)-C(12)	103.3(7)

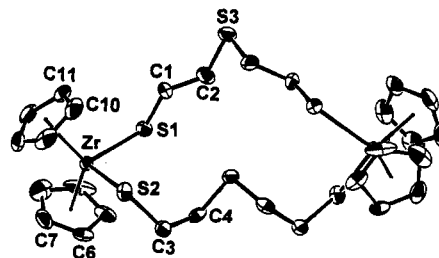


Figure 1. ORTEP drawing of molecule 5. 30% thermal ellipsoids are shown; hydrogen atoms are omitted for clarity.

the elution and solubility properties to those of 5. Residues which were not eluted from the column are presumed to be either

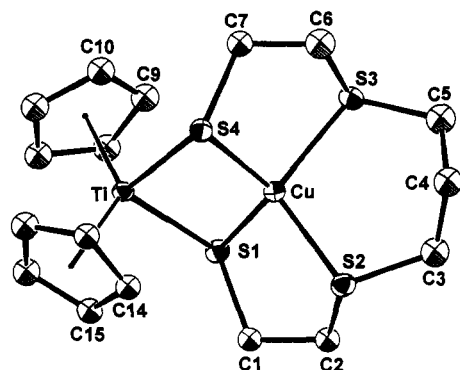


Figure 2. ORTEP drawing of cation of molecule 15. 30% thermal ellipsoids are shown; hydrogen atoms are omitted for clarity.

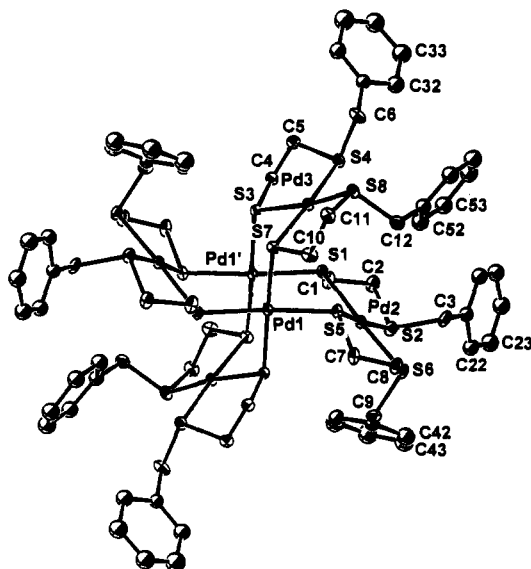
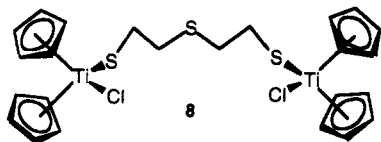


Figure 3. ORTEP drawing of the cation of molecule 20. 30% thermal ellipsoids are shown; hydrogen atoms are omitted for clarity.

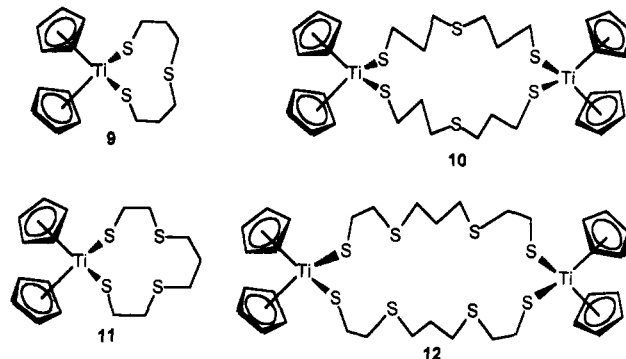
monosubstitution products or higher oligomeric materials of the forms $\text{Cp}_2\text{TiCl}(\text{SR})$ and $[\text{Cp}_2\text{Ti}(\text{SR})_2]_n$, respectively.

Reaction of Cp_2TiCl_2 with $(\text{HSCH}_2\text{CH}_2)_2\text{S}$ in a 2:1 ratio in the presence of a large excess of imidazole affords a red-purple solid 8, which is purified by successive washings with benzene.



The ^1H NMR data for 8 are consistent with the formulation $[\text{Cp}_2\text{TiCl}]_2(\text{SCH}_2\text{CH}_2)_2\text{S}$. The compound is also observed in the reaction mixture in the preparation of 7, consistent with its being an intermediate in the formation of the macrocyclic species 7.

In a similar fashion, the larger ring compounds have been prepared, separated, and formulated as the 10- S_3 -, 20- S_6 -, and 24- S_8 -membered ring complexes, 9–12, respectively. Although the structures of 9–12 have not been confirmed crystallographically, the trends in the chemical shifts for the cyclopentadienyl and methylene resonances, the solubility properties, and relative retention times on neutral alumina for 9 and 11 and for 10 and 12 parallel those of 6 and 7, respectively.⁴ These are consistent with the mononuclear formulas for 6, 9, and 11 and the binuclear formulations of 7, 10, and 12. Similar synthetic procedures were employed to prepare and purify the pendant thioether titanocenedithiolate derivatives $\text{Cp}_2\text{Ti}(\text{SCH}_2\text{CH}_2\text{SCH}_2\text{R})_2$ (R = Me (13), Ph (14)).

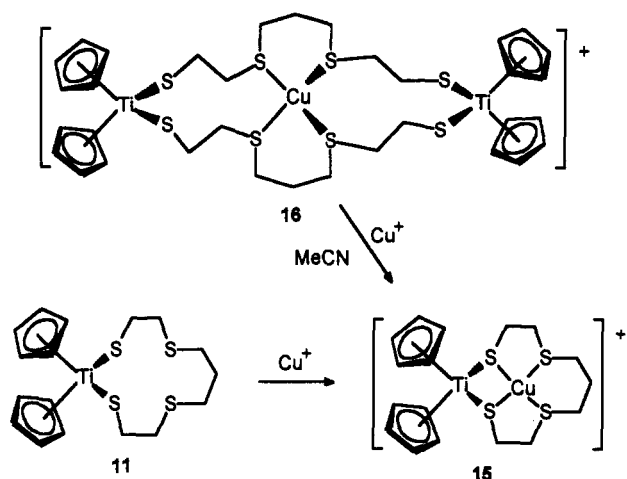


Complexation. We have previously shown that the macrocycles 1 and 2 will bind late transition metals in the central cavity of the ring such that the four sulfur atoms bridge the Ti and late metal centers.^{2–4} An initial screening of this capability of the new macrocycles described herein was presented by an examination of the reactions of these Ti complexes with Cu(I). Addition of Cu(I) to solutions of the three-sulfur, monometallic derivatives 6 and 9 resulted in no detectable reactions. This is expected as, intuitively, the small eight- and ten-membered rings appear too small to encapsulate Cu(I) ions. In the absence of the macrocyclic effect, binding of Cu(I) to these Ti dithiolate derivatives is weak and thus presumably competitive with solvent.

The S_4 macrocycle 11 contains a 12-membered ring, one that readily accommodates the inclusion of a Cu(I) metal in the central cavity. Reaction of 11 with $[\text{Cu}(\text{NCCCH}_3)_4]^+$ is rapid, affording a color change from purple to red-black, and ultimately, after workup, affording the new product 15. The ^1H NMR of 15 shows shifts in the cyclopentadienyl and methylene resonances consistent with the complexation of Cu(I) and thus leads to the formulation of 15 as $[(\text{Cp}_2\text{Ti}(\text{SCH}_2\text{CH}_2\text{SCH}_2)_2\text{CH}_2)_2\text{Cu}][\text{PF}_6]$. This formulation was confirmed by a crystallographic study of 15. An ORTEP drawing of 15 is shown in Figure 2. The structural data confirm the presence of a single titanium atom in a 12-membered macrocyclic complex which encapsulates Cu(I). Two thiolate sulfur atoms bridge the titanocene fragment and the Cu(I) center while two thioether sulfur atoms complete the coordination sphere of Cu(I). The charge of this heterobimetallic cation is balanced by the anion $[\text{PF}_6]^-$. The Ti–S distances average 2.493(4) Å and are comparable to those seen in 3. The pseudotetrahedral S_4 environment about Cu is characterized by Cu–S distances which average 2.250(4) and 2.312 Å for the bridging and thioether sulfur atoms, respectively. The Ti–Cu distance in 15 of 2.832(3) Å compares with the Ti–Cu distances of 2.846(2), 2.803(1), and 2.840(1) Å found in $[\text{Cp}_2\text{Ti}(\text{SMe})_2\text{Cu}(\text{NCMe})_2]^+$, $[\text{Cp}_2\text{Ti}(\text{SMe})_2\text{Cu}(\text{PPh}_3)]^+$, and $[\text{Cp}_2\text{Ti}(\text{SMe})_2\text{Cu}(\text{PCy}_3)]^+$, respectively.^{14,15} Previous spectroscopic, structural, and theoretical work has been shown to be consistent with dative bonding between the d^0 and d^{10} metal centers of such heterobimetallic systems.⁸ Similar metal–metal interactions are suggested by the geometry of the TiS_2Cu core in 15.

Initial cyclic voltammetry experiments employing 15 in THF with NEt_4PF_6 as the supporting electrolyte showed an irreversible reduction at a potential of -0.90 V vs Ag/AgCl. Similar irreversible redox behavior was reported for $[\text{Cp}_2\text{Ti}(\text{SMe})_2\text{CuL}_n]^+$ ($n = 1, 2$).^{14,15} Such electrochemical behavior is in marked contrast to that of 3 and 4, which have been shown to exhibit reversible one-electron reductions. Superficially one might attribute the stability of reduced analogs of 3 and 4 to the possibility of delocalization of electron density over the two Ti centers. However, the related Ti/Cu heterobimetallic complex $[\text{Cp}_2\text{Ti}(\text{SCH}_2\text{CH}_2\text{PPh}_2)_2\text{Cu}]^+$, which only contains a single early metal center, also exhibits reversible redox behavior.¹¹ These differing observations for structurally related compounds prompted a theoretical molecular orbital study.

Scheme I



Molecular Orbital Calculations. EHMO and FHMO calculations were performed for models of the cations of **15** and **4**. The model for **15** was derived directly from crystallographic data while the model of **4** was derived by suitable perturbation of the structural data for **3**.⁴ The basic electronic structures of these models are similar to those described previously for $[\text{Cp}_2\text{Ti}(\text{SH})_2\text{CuL}_2]^+$ ($\text{L} = \text{NH}_3, \text{PH}_3$).⁸ The Ti...Cu interactions in **15** and **4** are indicated by the net overlap populations (NOP) of 0.032 and 0.024, respectively. The lesser overlap in **4** is consistent with the structural data and suggests dative interactions with both Ti centers.

In the case of **15**, the LUMO is essentially the Ti-based d_{z^2} orbital while in **4** it is an admixture of both Ti d_{z^2} orbitals with minor contributions from Cu and S atoms. These orbitals correspond to the $1a_1$ frontier orbitals of the Cp_2Ti molecular fragment.¹⁷ Although the limitations are recognized, calculations in which species **4** and **15** were reduced by one electron provide at least some indication of the effect of reduction. The trends that emerge suggest that both the Ti-S and the metal-metal interactions are reduced in strength and that these effects appear more significant in **15** than in **4**. This appears to be consistent with the electrochemical observations in that reduction of **15** results in a species that is not stable, presumably degrading via Ti-S bond cleavage.⁴ The possibility of delocalization of a single electron in the reduced analog of **4** presumably accounts for its stability and thus the reversible electrochemical behavior.

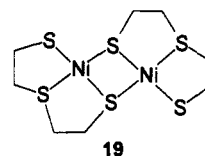
The reactions of Cu(I) with the six sulfur macrocycles **7** and **10** are similar. Weak binding is indicated by the observation of broad resonances in the ¹H NMR spectra even at low temperature. This is consistent with the proposition of a fluxional process in which the four sulfur atoms constituting the Cu(I) coordination sphere are rapidly exchanging among the six sulfurs within the macrocycles. Exchange involving coordination of solvent is also a possibility and is one that may account for the inability to isolate clean Cu(I) complexes of these macrocycles.

Cu(I) also interacts with the S_8 macrocycle **12**. Addition of 1 equiv of Cu(I) to a solution of **12** results in an ¹H NMR spectrum that is consistent with the coordination of Cu(I) by the central four thioether sulfur atoms of **12**, thus giving the complex $[(\text{Cp}_2\text{Ti}(\text{SCH}_2\text{CH}_2\text{SCH}_2)_2\text{CH}_2)_2\text{Cu}]^+$ (**16**). Addition of a second equivalent of Cu(I) to this solution results in further reaction. This is expected, as one might expect that the macrocycle **12** should be capable of binding two Cu(I) atoms. However, the ¹H NMR data as well as crystallographic information confirm that, upon addition of a second equivalent to **16**, a rearrangement occurs, affording 2 equiv of **15** (Scheme I). The mechanism of this rearrangement is now known although the intermediacy of a species in which two Cu(I) atoms are bound to the 24-membered-

ring metalloligand, that is $[(\text{Cp}_2\text{Ti}(\text{SCH}_2\text{CH}_2\text{SCH}_2)_2\text{CH}_2)_2\text{Cu}_2]^{2+}$ (**17**), is reasonable.

The open-chain heterobimetallic $[\text{Cp}_2\text{Ti}(\text{SCH}_2\text{CH}_2\text{SCH}_2\text{Me})_2\text{Cu}][\text{PF}_6]$ (**18**) was also prepared in a similar manner by reaction of **13** with Cu(I). In contrast, reactions of **14** with Cu(I) led to a mixture of products that were not readily purified; however preliminary NMR data suggest that Ti-S bond rupture may have occurred to some extent.

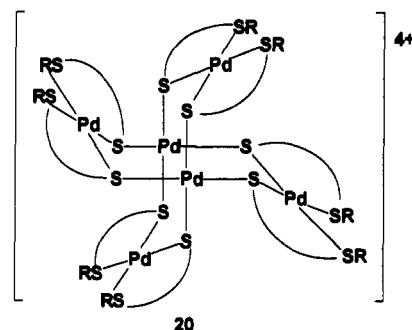
Thiolate-Transfer Reactions. The formation of **15** from the larger macrocyclic complex **16** requires the transfer of a thiolate ligand from one Ti center to another. While the resulting heterobimetallic complex, i.e. **16** is stable, this subsequent rearrangement suggests that Ti-S bonds are susceptible to cleavage and thus may effect transfer of thiolate moieties to other metal centers. Such transfers have been demonstrated for the reaction of **7** with $[\text{Ni}(\text{H}_2\text{O})_6][\text{BF}_4]_2$ or NiCl_2 . In these cases, the reactions proceed smoothly with a color change from purple to yellow. Crystals of the yellow product **19** were formed upon



standing. This product exhibited only methylene resonances in the ¹H NMR spectrum, suggesting the absence of the titanocene fragments. ¹H NMR data for the mother liquors showed the presence of Cp_2TiF_2 and Cp_2TiCl_2 for the $[\text{Ni}(\text{H}_2\text{O})_6][\text{BF}_4]_2$ and NiCl_2 reactions, respectively. As well, the species **8** was observed in the NiCl_2 reaction mixture. X-ray diffraction data for **19** identified the product as the bimetallic species $[\text{Ni}_2(\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{S})_2]$ in which two thiolate sulfurs bridge the two Ni centers.¹⁸

The formation of Cu(I) heterobimetallics described herein and elsewhere^{2-4,11-16} suggests that the formation of **19** proceeds through an initial interaction of Ni(II) with **7**, affording a Ti-Ni heterobimetallic species. FHMO calculations for the Ni(II) analog of **15** show a marked decrease in the Ti-S NOP. Thus it appears that the Lewis acidity of Ni(II) facilitates Ti-S bond cleavage; however, the observation of compound **8** in the formation of **19** from NiCl_2 suggests a role of the counterion (i.e. BF_4^- or Cl^-) as a nucleophile. It is noteworthy that while the Ni(0) complex $(\text{Cp}_2\text{Ti}(\text{SMe})_2)_2\text{Ni}$ was previously prepared and structurally characterized, attempts to prepare similar related Ni(II) species led to degradation via Ti-S bond cleavage.^{13,16}

In a similar fashion, the reaction of **14** with $[\text{Pd}(\text{NCMe})_4][\text{BF}_4]_2$ led to Ti-S bond cleavage and the formation of Cp_2TiF_2 .¹⁹ The resulting Pd-thiolate species **20** crystallized from the reaction



as red blocks. While the ¹H NMR data confirmed the presence of the $-\text{SCH}_2\text{CH}_2\text{SCH}_2\text{Ph}$ ligand, X-ray crystallography was

(18) The identity of **19** was confirmed via X-ray crystallographic methods. The cell parameters determined were within experimental error of those reported for **19** in: Baker, D. J.; Goodall, D. C.; Moss, D. S. *J. Chem. Soc., Chem. Commun.* 1969, 325.

(19) Clark, H. C.; Shaver, A. *Coord. Chem.* 1975, 4, 243.

(17) Lauher, J.; Hoffmann, R. *J. Am. Chem. Soc.* 1976, 98, 1729.

required to identify the product **20**. An ORTEP drawing of the tetracation of **20** is shown in Figure 3. This cation comprises six Pd atoms, each of which are held in a pseudo square planar coordination sphere. The two central Pd atoms (Pd(1) and Pd(1')) are each bonded to four thiolate sulfurs. These sulfur atoms are also coordinated in a pairwise fashion (i.e. one from each of the central Pd atoms) to the four more Pd atoms. The thioether sulfurs from each of the thiolate ligands chelate to the respective Pd atoms, thus completing the coordination sphere of the four peripheral Pd atoms. The entire cation has $\bar{1}$ symmetry. The Pd-S distances for the central Pd atoms average 2.335(5) Å, while the Pd-S distances for the peripheral Pd atoms average 2.304(4) and 2.322(4) Å for the bridging thiolate and thioether sulfur atoms, respectively. These compare to those seen in Pd₃((SCH₂CH₂)₂S)₃.²⁰

Summary. A series of macrocyclic titanocenedithiolate com-

plexes have been prepared and characterized. While such compounds act as metalloligands for Cu(I), the Ti-S bonds in such species are susceptible to cleavage. This may result in ligand redistribution reactions affording thermodynamically stable species, or it may lead to thiolate-ligand-transfer reactions. The electrochemical properties of heterobimetallic complexes derived from such systems remain of ongoing interest while the use of titanocenedithiolates in the synthesis of new transition metal thiolate derivatives is under investigation.

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Supplementary Material Available: Tables of crystallographic parameters and complete positional parameters, hydrogen atom parameters, and thermal parameters for **5**, **15**, and **20** (12 pages). Ordering information is given on any current masthead page.

(20) McPartlin, E. M.; Stephenson, N. C. *Acta Crystallogr.* **1969**, *25*, 1659.