Redox-Active Macrocycles as Metalloligands: Synthesis, Electrochemistry, and Structure of Silver(I) and Copper(I) Complexes of $Cp_2Ti(\mu\text{-}S(CH_2)_nS)_2TiCp_2$ ($n = 2, 3$)

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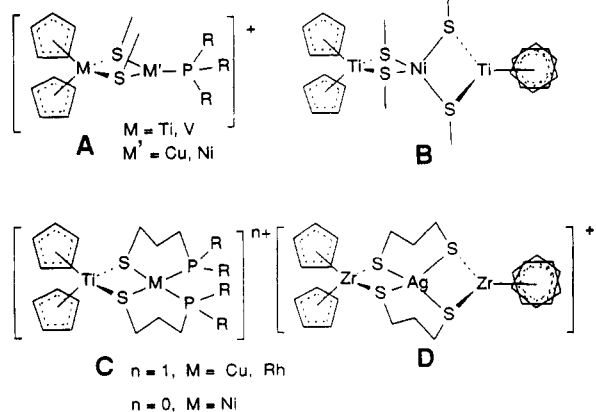*Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4*

The reactions of Cp_2TiCl_2 with the dithiols $HS(CH_2)_nSH$ ($n = 2, 3$) in the presence of imidazole proceed with formation of imidazole hydrochloride, affording insoluble titanocene dithiolate derivatives 1 and 2, respectively. In the case of propanedithiol, the product 2 can also be synthesized via reaction of Cp_2TiCl_2 with Mg and $(SCH_2CH_2CH_2S)_2$ or by reaction of $Cp_2Ti(PMe_3)_2$ with $(SCH_2CH_2CH_2S)_2$. Alternatively, 2 can be prepared via the reaction of Cp_2TiPh_2 with dithiols. The spectroscopic and analytical data are consistent with the formulation of 1 and 2 as the bimetallic compounds $Cp_2Ti(\mu\text{-}S(CH_2)_nS)_2TiCp_2$ ($n = 2, 1; n = 3, 2$). The ^1H NMR data suggest an open macrocyclic structure for 2. In contrast, the temperature dependence of the ^1H NMR spectra for 1 is consistent with a fluxional process involving the twisted conformations of 1 in which two of the four sulfur atoms bridge the two Ti centers. Molecules 1 and 2 are shown to act as metalloligands and react with $AgBPh_4$ and $[Cu(NCMe)_4]BF_4$ to yield the complexes $[(Cp_2Ti(\mu\text{-}S(CH_2)_nS)_2TiCp_2)M]^+X^-$ ($n = 2, M = Cu(I), 3; n = 3, M = Ag(I), 4$). A crystallographic study of 4 confirms the formulation of 4 in which 2 acts as a macrocyclic metalloligand presenting a four-sulfur coordination sphere to the encapsulated silver ion. The complex $[(Cp_2Ti(\mu\text{-}SCH_2CH_2CH_2S)_2TiCp_2)Ag]BPh_4$ (4) crystallizes as $4 \cdot H_2O \cdot 0.75CH_2Cl_2$ in the space group $P2_1/n$ with $a = 24.610$ (9) Å, $b = 17.098$ (5) Å, $c = 25.453$ (15) Å, $\beta = 111.76$ (3)°, $Z = 8$, and $V = 9947$ (14) $Å^3$. Electrochemical studies of 1–4 by cyclic voltammetry are reported. The macrocycles exhibit only irreversible reductions. In contrast, the complexes 3 and 4 undergo quasi-reversible one-electron reductions at −0.93 and −1.26 V vs Ag/AgCl, respectively. A second irreversible wave is also observed at −1.56 and −1.53 V for 3 and 4, respectively. This redox behavior is interpreted in terms of Ti(IV)/Ti(III) redox couples. The chemical generation of the one-electron-reduction products, i.e. $[(Cp_2Ti(\mu\text{-}S(CH_2)_nS)_2TiCp_2)M]^0$ ($n = 2, M = Cu(I), 5; n = 3, M = Ag(I), 6$) is achieved via reactions of 3 and 4 with Cp_2Co. The EPR spectrum of 5 reveals $^{63}Cu,^{65}Cu$ hyperfine coupling, while $^{107}Ag,^{109}Ag$ hyperfine coupling is seen for 6. The results of these studies are discussed, and the implications of the data are considered.

Introduction

Recent interest in early–late heterobimetallics (ELHB) stems, in part, from the perspective of synthetic methodology development. Moreover, the potential for new reactivity patterns arising from such metal combinations has established precedent in heterogeneous catalysis systems.[1-3] In attempts to study related homogeneous systems containing early- and late-metal centers, we and others have adopted an approach in which an early-metal species is employed as a "metalloligand" for a late-metal species. For example, we have employed early-metal phosphides,[4-10] thiolates,[11-13] (A, B), and pendant chelating

metalloligands[14-16] (C) in the synthesis of ELHB species. In the case of thiolate-bridged ELHB complexes, we have previously described a variety of Ti/Cu,[11] Ti/Ni,[12] and V/Cu[13] species. Such compounds have proved difficult to isolate as a result of their inherent instability. Recently, we have reported related species based on macrocyclic metalloligands.[17-19] The species, $Cp_2Zr(\mu\text{-}S(CH_2)_nS)_2ZrCp_2$ ($n = 2, 3; D$), offer the four sulfur donors for complexation of Ag(I), while providing the stability of a macrocycle. While the chemistry of these and other metal complexes of this new class of macrocycles is of ongoing interest, we have also sought to broaden the scope of potential reactivity by the incorporation of redox-active metal centers in the macrocyclic backbone. We have previously shown that Ti/Cu or Ti/Rh complexes, in which chelating phosphinethiolate ligands link the two metal centers, tolerate chemical reduction at Ti. Thus, the inclusion of Ti centers in a macrocyclic system offers the possibility that the macrocyclic metalloligand may act potentially as an electron reservoir. Such systems also offer a unique

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approach in attempts to incorporate a redox center whose potential will be dependent on metal ion binding. Previous approaches to such systems have typically been to incorporate pendant redox centers such as ferrocene on a macrocyclic ligand.[20] Herein, we describe several synthetic routes to new redox-active macrocyclic metalloligands which incorporate titanocene moieties in the ring. These systems complex Cu(I) and Ag(I). Structural, spectral, and electrochemical studies of these species are described. The potential for applications of these redox-active macrocyclic systems are considered in light of these data.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 employing a Vacuum Atmospheres inert-atmosphere glovebox. Solvents were reagent grade, were distilled from the appropriate drying agents under N_2, and were degassed by the freeze–thaw method at least three times prior to use. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer operating at 300 and 75 MHz, respectively. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to $SiMe_4$. For variable-temperature NMR data for 1, the activation barrier was estimated on the basis of the coalescence temperature.[21] Cyclic voltammetric experiments were recorded by employing a BAS potentiometer having a Pt disk as the working electrode, Ag/AgCl as the reference electrode, and Bu_4NBF_4 as the supporting electrolyte. EPR spectra were recorded using a Varian E-12 EPR spectrometer employing DPPH as the external reference. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, TN, and Schwarzkopf Laboratories, Woodside, NY. Cp_2TiCl_2, 1,2-ethanediol, and 1,3-propanedithiol were purchased from the Aldrich Chemical Co. PMe_3 was purchased from the Strem Chemical Co. $AgBPh_4$,[22] $[Cu(NCMe)_4]BF_4$,[11] $Cp_2Ti(PMe_3)_2$,[23] Cp_2TiPh_2[24] and $(SCH_2CH_2CH_2S)_2$[26] were prepared by the literature methods.

Synthesis of $(SCH_2CH_2CH_2S)_2$. $NCSCH_2CH_2CH_2SCN$ was prepared by the literature method.[25] ^1H NMR (δ, 298 K, $CDCl_3$): 3.30 (4 H, t), 2.38 (2 H, q, $|J_{H-H}| = 6$ Hz). This was converted to $(SCH_2CH_2CH_2S)_2$ by oxidation with hydrazine hydrate employing a published procedure.[26] ^1H NMR (δ, 298 K, $CDCl_3$): 2.77 (8 H, t), 2.06 (4 H, q, $|J_{H-H}| = 9$ Hz).

Synthesis of $Cp_2Ti(\mu$-$SCH_2CH_2S)_2TiCp_2$ (1). Ethanedithiol (0.189 g, 2.08 mmol) and imidazole (273 mg, 4.01 mmol) were suspended in 25 mL of benzene. This was added to a benzene suspension containing Cp_2TiCl_2 (0.50 g, 2.01 mmol). The mixture was stirred for 18 h, during which time it became deep purple. The solution was filtered to remove imidazole hydrochloride. The solvent was removed in vacuo and the residue extracted into 20 mL of CH_2Cl_2. Vapor diffusion of diethyl ether into this solution afforded the purple crystalline solid 1, yield 75%. ^1H NMR (δ, 298 K, CD_2Cl_2): C_5H_5, 6.07 (s, 20 H); CH_2, 2.85 (br s, 8 H). ^1H NMR (δ, 188 K, CD_2Cl_2): C_5H_5, 6.07 (s, 20 H); CH_2, 2.07, 3.38 (br, t, 8 H). $^{13}C\{^1H\}$ NMR (δ, 298 K, CD_2Cl_2): C_5H_5, 111.7; CH_2, 48.3. Anal. Calcd for $C_{24}H_{28}S_4Ti_2$: C, 53.33; H, 5.22. Found: C, 53.00; H, 5.00.

Synthesis of $Cp_2Ti(\mu$-$SCH_2CH_2CH_2S)_2TiCp_2$ (2). (i) From Cp_2TiCl_2 and Dithiol. Propanedithiol (0.869 g, 8.03 mmol) and imidazole (1.640 g, 24.09 mmol) were dissolved in 25 mL of THF. This was added to a THF solution of Cp_2TiCl_2 (2.00 g, 8.03 mmol). The mixture was stirred for 24 h, during which time it became deep black-purple. The solvent was removed in vacuo and the residue extracted 10 times, each time with 50 mL of benzene. The

benzene extracts were combined, and the volume was reduced to about 30 mL. When this solution stood, the black-purple crystalline solid 2 precipitated, yield 50%. ^1H NMR (δ, 298 K, CD_2Cl_2): C_5H_5, 6.07 (s, 20 H); CH_2, 3.05 (t, 8 H, $|J_{H-H}| = 6.5$ Hz), 1.82 (q, 4 H). $^{13}C\{^1H\}$ NMR (δ, 298 K, $CDCl_3$): C_5H_5 111.4; CH_2, 42.6, 42.6, 33.5. Anal. Calcd for $C_{26}H_{32}S_4Ti_2$: C, 55.00; H, 5.67. Found: C, 55.14; H, 5.76.

(ii) From $Cp_2Ti(PMe_3)_2$ and $(SCH_2CH_2CH_2S)_2$. $Cp_2Ti(PMe_3)_2$ (0.50 g, 0.15 mmol) and $(SCH_2CH_2CH_2S)_2$ (0.017 g, 0.08 mmol) were combined and suspended in THF (5 mL). The mixture was stirred for 24 h, the solvent removed under vacuum, and the residue extracted into $CDCl_3$; yield (by NMR) 95%.

(iii) From Cp_2TiCl_2/Mg and $(SCH_2CH_2CH_2S)_2$. Cp_2TiCl_2 (0.469 g, 1.88 mmol), Mg (0.160 g, 6.59 mmol), and $(SCH_2CH_2CH_2S)_2$ (0.200 g, 0.94 mmol) were combined and suspended in THF (5 mL). The mixture was stirred for 1 h, the solution was filtered, and the solvent was removed under vacuum. The residue was extracted into CD_2Cl_2; yield (NMR) 50%.

(iv) From Cp_2TiPh_2 and Dithiol. Cp_2TiPh_2 (0.048 g, 0.14 mmol) and $HSCH_2CH_2CH_2SH$ (0.016 g, 0.14 mmol) were combined and suspended in benzene (5 mL). The mixture was stirred and irradiated with UV light for 3 h. The solution was filtered and the solvent removed under vacuum. The residue was extracted into CD_2Cl_2; yield (NMR) 30%.

Synthesis of $[(Cp_2Ti(\mu$-$SCH_2CH_2S)_2TiCp_2)Cu]BF_4$ (3). The compound 1 (10 mg, 0.0185 mmol) and $[Cu(NCMe)_4]BF_4$ (5.82 mg, 0.185 mmol) were combined and dissolved in CH_2Cl_2. The solution immediately became green-brown. The mixture was stirred for 3 h, the solution was filtered, and the solvent was replaced with CD_2Cl_2; yield (isolated) >95%. ^1H NMR (δ, 298 K, CD_2Cl_2): C_5H_5, 6.11 (s, 20 H), 3.82, 3.24 (d, 8 H, $|J_{H-H}| = 7.9$ Hz). $^{13}C\{^1H\}$ NMR (δ, 298 K, CD_2Cl_2): C_5H_5, 112.7; CH_2 47.4. Anal. Calcd for $C_{24}H_{28}BCuF_4S_4Ti_2$: C, 41.72; H, 4.08. Found: C, 42.00; H, 4.00.

Synthesis of $[(Cp_2Ti(\mu$-$SCH_2CH_2CH_2S)_2TiCp_2)Ag]BPh_4$ (4). The compound 2 (50 mg, 0.0876 mmol) and $AgBPh_4$ (37.5 mg, 0.0876 mmol) were combined and dissolved in THF. The solution became red-brown upon stirring for 2 h. The solvent was removed and the residue extracted into CH_2Cl_2. Red-black crystals precipitated from solution upon standing; yield (NMR) >95%. ^1H NMR (δ, 298 K, CD_2Cl_2): C_6H_5, 7.02 (t), 7.31 (m), 6.8 (t) (20 H); C_5H_5, 6.17 (s, 20 H); CH_2 3.24 (t, 8 H), 2.07 (q, 4 H, $|J_{H-H}| = 6.6$ Hz). $^{13}C\{^1H\}$ NMR (δ, 298 K, CD_2Cl_2): C_5H_5, 113.5; CH_2 39.9, 32.3. Anal. Calcd for $C_{50}H_{52}AgBS_4Ti_2$ (vacuum dried): C, 60.32; H, 5.26. Found: C, 60.10; H, 5.10.

Generation of $[(Cp_2Ti(\mu$-$SCH_2CH_2S)_2TiCp_2)Cu]$ (5) and $[(Cp_2Ti(\mu$-$SCH_2CH_2CH_2S)_2TiCp_2)Ag]$ (6). Since these compounds were generated in a similar manner from 3 and 4, respectively, only one procedure is described. The compound 3 (0.010 g, 0.0117 mmol) and Cp_2Co (0.0022 g, 0.0116 mmol) were combined and dissolved in 5 mL of CH_2Cl_2. The mixture stood for 1 h, and then the solution was filtered into a quartz EPR tube and sealed under an inert atmosphere. 5: EPR (CH_2Cl_2, 298 K) $g = 1.9821$, $\langle a_{Cu}\rangle = 3.5$ G, $\langle a_{Ti}\rangle = 10.5$ G. 6: EPR (CH_2Cl_2, 298 K) $g = 1.9817$, $\langle a_{Ag}\rangle = 5.0$ G, $\langle a_{Ti}\rangle = 11.0$ G.

X-ray Data Collection and Reduction. X-ray-quality crystals of 4 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-S four-circle diffractometer with graphite-monochromatized Mo Kα radiation. The initial orientation matrices were obtained from 20 reflections located by an auto-search routine. These data were used to determine the crystal system. An automated check of the Laue symmetry confirmed the crystal system as monoclinic. Ultimately, 25 reflections ($15° < 2\theta < 35°$) were used to obtain the final lattice parameters and the orientation matrix. Machine parameters, crystal data, and data collection parameters are summarized in Table I. The observed extinctions confirmed the space group $P2_1/n$. The data sets were collected in four shells ($4.5° < 2\theta < 50.0°$), and three standard reflections were recorded every 150 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 software program package on a VAX 3420 workstation located in the Department of Chemistry and Biochemistry at the University of

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Table I. Crystallographic Parameters for
[(Cp₂Ti(μ-SCH₂CH₂CH₂S)₂TiCp₂)Ag]BPh₄•H₂O•0.75CH₂Cl₂

Table I. Crystallographic Parameters for $[(Cp_2Ti(\mu\text{-}SCH_2CH_2CH_2S)_2TiCp_2)Ag]BPh_4 \cdot H_2O \cdot 0.75CH_2Cl_2$

formula	$C_{50}H_{52}BS_4AgTi_2 \cdot H_2O \cdot 0.75CH_2Cl_2$
cryst color, form	black blocks
a, Å	24.610 (9)
b, Å	17.098 (5)
c, Å	25.453 (14)
β, deg	111.76 (3)
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
vol, Å³	9947 (14)
density (calcd), g cm⁻³	1.439
Z	8
cryst dimens, mm	0.55 × 0.35 × 0.30
abs coeff, μ, cm⁻¹	9.74
radiation, λ, Å	Mo $K\alpha$ (0.710 69)
temp, °C	24
scan speed, deg min⁻¹	32.0 ($\theta/2\theta$)
scan range, deg	1.0 below $K\alpha_1$ to 1.0 above $K\alpha_2$
bkgd/scan time ratio	0.5
2θ range, deg	4.5–50.0
index range	$h,k,\pm l$
no. of data collected	15 419
no. of unique data $F_o^2 > 3\sigma(F_o^2)$	3891
no. of variables	491
R, %	9.00
R_w, %	9.10
max shift/error in final cycle	0.000
goodness of fit	2.035
max residual (associated atom), e Å⁻³	1.0 (O(2))

Windsor. The reflections with $F_o^2 > 3\sigma F_o^2$ were used in each of the refinements.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[27,28] The heavy-atom positions for each structure were determined using direct methods employing the Mithril option of the TEXSAN package. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix, least-squares techniques on F, minimizing the function $w(|F_o| - |F_c|)^2$, where the weight, w, is defined as $1/\sigma^2(F_o)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of refinement all the Ag, Ti, and S atoms were refined as individual anisotropic atoms. The remaining atoms of the cation and all the atoms of the anion were refined isotropically. In all cases, hydrogen atom positions were calculated 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. Solvent molecules of crystallization were revealed by difference Fourier calculations. The hydrogen atoms of the H₂O molecules of crystallization were not located. One of the CH₂Cl₂ molecules was present in only partial site occupancy. Refinement of the site occupancy factor for this molecule converged at 0.50. The hydrogen atoms of the CH₂Cl₂ molecules of crystallization were calculated. The final refinement data are given in Table I. The largest peaks in the final difference Fourier map calculation showed residual electron densities of no chemical significance. The following data are tabulated: positional parameters (Table II) and selected bond distances and angles (Table III). Thermal parameters (Table S1), hydrogen atom parameters (Table S2), and values of $10F_o$ and $10F_c$ (Table S3) have been deposited as supplementary material.

Results and Discussion

Previous reports showed that reactions of Cp₂TiCl₂ with dithiols and NEt₃ led to uncharacterized products.[29,30] We

Scheme I
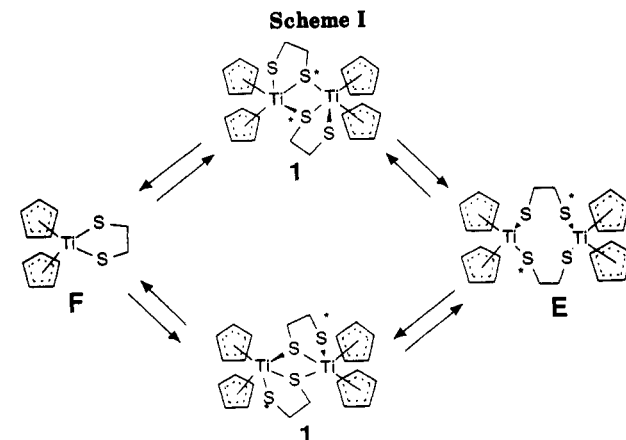
have found that the reactions of Cp₂TiCl₂ with dithiols in the presence of imidazole proceed with the formation of imidazole hydrochloride and a purple product which is slightly soluble in THF or benzene. In the case of the reaction using 1,2-ethanedithiol, the purple product 1 exhibits a ¹H NMR spectrum at 25 °C which is comprised of resonances at 6.07 and 2.85 ppm attributable to the cyclopentadienyl and ethylene protons, respectively. These data together with the ¹³C{¹H} NMR spectrum and analytical data are consistent with the empirical formulation of 1 as [Cp₂Ti(μ-SCH₂CH₂S)]ₙ.

More structural information is derived from an examination of the temperature dependence of the ¹H NMR spectra of 1. At 185 K, two broad resonances attributable to the ethylene protons are seen at 2.07 and 3.38 ppm. The low temperature inequivalence of the methylene protons suggests a dimeric formulation in which adjacent ethylene protons are inequivalent as a result of inequivalent sulfur atoms. Such a conformation for 1 is depicted in Scheme I. A similar geometry has been crystallographically established for Cp₂Zr(μ-SCH₂CH₂S)₂ZrCp₂.[17,18] As the temperature is raised, the ethylene proton resonances broaden and coalesce at 2.85 ppm at 298 K. The temperature range of the solvent precludes the observation of either limiting spectrum. Nonetheless, these data suggest a dynamic process in which the methylene resonances are averaged. This may occur via an untwisting of 1 to give a macrocyclic intermediate (E). Alternatively, the mononuclear intermediate (F) is also possible. In the absence of limiting spectra, the activation energy for the fluxional process was approximated to be 56 kJ/mol. These data for 1 are similar to those seen by Erker and Noe[31] for related Zr–alkoxide macrocycles, thus suggesting the fluxional process involves the twisting and untwisting of the macrocycle (Scheme I). This is also consistent with the complexation chemistry of 1 (vide infra).

The similar reaction involving 1,3-propanedithiol also proceeds to yield the tractable purple product 2. The ¹H and ¹³C{¹H} NMR spectra of 2 exhibit resonances at 6.07, 3.05, and 1.82 ppm and 111.4, 42.6, and 33.5 ppm, respectively. These are attributable to cyclopentadienyl and methylene protons and are consistent with the empirical formulation [Cp₂Ti(SCH₂CH₂CH₂S)]ₙ. The poor solubility in common organic solvents is not typical of mononuclear metallocenedithiolates,[12] suggesting that the present complexes are higher oligomers. By analogy to the results previously described for the analogous dimeric zirconoc-

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Table II. Positional Parameters

atom	x	y	z	atom	x	y	z
Ag(1)	0.7337 (1)	0.0269 (1)	0.2746 (1)	C(32)	0.123 (1)	0.352 (2)	0.017 (1)
Ag(2)	0.0906 (1)	0.3249 (1)	0.1500 (1)	C(33)	0.141 (1)	0.414 (2)	0.061 (1)
Ti(1)	0.7260 (3)	0.0586 (3)	0.1479 (2)	C(34)	0.070 (1)	0.235 (2)	0.255 (1)
Ti(2)	0.7543 (2)	-0.0235 (3)	0.4035 (2)	C(35)	0.042 (1)	0.297 (2)	0.273 (1)
Ti(3)	0.0846 (2)	0.1349 (3)	0.1313 (2)	C(36)	0.035 (1)	0.374 (2)	0.240 (1)
Ti(4)	0.1012 (2)	0.5132 (3)	0.1725 (2)	C(41)	-0.016 (1)	0.109 (2)	0.085 (1)
Cl(1)	0.1620 (5)	0.2076 (6)	0.9142 (5)	C(42)	-0.000 (1)	0.153 (2)	0.051 (1)
Cl(2)	0.0427 (5)	0.1587 (9)	0.8828 (5)	C(43)	0.039 (1)	0.108 (2)	0.030 (1)
Cl(3)	0.3351 (8)	0.171 (1)	0.9754 (8)	C(44)	0.046 (1)	0.039 (2)	0.060 (1)
Cl(4)	0.443 (1)	0.136 (2)	0.977 (2)	C(45)	0.012 (1)	0.038 (2)	0.090 (1)
S(1)	0.6897 (3)	-0.0534 (4)	0.1859 (3)	C(46)	0.129 (1)	0.082 (2)	0.226 (1)
S(2)	0.7513 (3)	0.1574 (5)	0.2251 (3)	C(47)	0.129 (1)	0.024 (2)	0.190 (1)
S(3)	0.8158 (3)	0.0582 (5)	0.3665 (3)	C(48)	0.159 (1)	0.039 (2)	0.157 (1)
S(4)	0.6602 (3)	-0.0323 (5)	0.3214 (3)	C(49)	0.187 (1)	0.111 (2)	0.175 (1)
S(5)	0.1352 (3)	0.2352 (5)	0.0958 (3)	C(50)	0.170 (1)	0.138 (2)	0.216 (1)
S(6)	0.0328 (3)	0.2140 (4)	0.1788 (3)	C(51)	0.173 (1)	0.612 (2)	0.184 (1)
S(7)	0.1035 (3)	0.4067 (4)	0.2384 (3)	C(52)	0.180 (1)	0.585 (2)	0.240 (1)
S(8)	0.0796 (3)	0.4449 (5)	0.0820 (3)	C(53)	0.199 (1)	0.505 (2)	0.245 (1)
O(1)	0.4625 (9)	0.052 (1)	0.1442 (9)	C(54)	0.202 (1)	0.479 (2)	0.195 (1)
O(2)	0.0407 (8)	0.416 (1)	0.4142 (8)	C(55)	0.189 (1)	0.547 (2)	0.158 (1)
C(1)	0.619 (1)	-0.042 (2)	0.184 (1)	C(56)	0.009 (2)	0.556 (2)	0.111 (2)
C(2)	0.602 (1)	-0.106 (2)	0.221 (1)	C(57)	-0.001 (2)	0.521 (2)	0.157 (2)
C(3)	0.646 (1)	-0.122 (2)	0.277 (1)	C(58)	0.028 (1)	0.559 (2)	0.203 (1)
C(4)	0.828 (1)	0.165 (2)	0.273 (1)	C(59)	0.053 (1)	0.627 (2)	0.187 (1)
C(5)	0.832 (1)	0.206 (2)	0.325 (1)	C(60)	0.044 (1)	0.621 (2)	0.131 (1)
C(6)	0.800 (1)	0.164 (2)	0.362 (1)	C(119)	0.100 (2)	0.162 (2)	0.863 (2)
C(11)	0.662 (1)	0.171 (2)	0.113 (1)	C(120)	0.402 (3)	0.198 (4)	0.987 (3)
C(12)	0.687 (1)	0.152 (2)	0.070 (1)	C(99)	0.8808 (6)	0.179 (1)	0.8294 (8)
C(13)	0.663 (2)	0.072 (2)	0.052 (2)	C(100)	0.8639 (7)	0.183 (1)	0.8758 (6)
C(14)	0.627 (1)	0.051 (2)	0.080 (1)	C(101)	0.7825 (9)	0.1026 (8)	0.9398 (8)
C(15)	0.627 (1)	0.111 (2)	0.118 (1)	C(102)	0.8293 (7)	0.063 (1)	0.9797 (7)
C(16)	0.770 (2)	-0.023 (2)	0.103 (2)	C(103)	0.8262 (7)	-0.018 (1)	0.9866 (7)
C(17)	0.796 (2)	0.054 (2)	0.108 (2)	C(104)	0.776 (1)	-0.0586 (8)	0.9536 (9)
C(18)	0.828 (2)	0.077 (2)	0.161 (2)	C(105)	0.7294 (7)	-0.019 (1)	0.9137 (7)
C(19)	0.825 (1)	0.010 (2)	0.196 (1)	C(106)	0.7326 (7)	0.061 (1)	0.9068 (6)
C(20)	0.791 (1)	-0.048 (2)	0.158 (1)	C(107)	0.7243 (7)	0.245 (1)	0.9123 (7)
C(21)	0.784 (2)	-0.135 (2)	0.362 (1)	C(108)	0.7196 (7)	0.320 (1)	0.8883 (7)
C(22)	0.834 (1)	-0.102 (2)	0.401 (1)	C(109)	0.6709 (9)	0.3662 (8)	0.8816 (7)
C(23)	0.832 (1)	-0.106 (2)	0.455 (1)	C(110)	0.6269 (7)	0.339 (1)	0.8990 (8)
C(24)	0.782 (2)	-0.145 (2)	0.449 (1)	C(111)	0.6316 (7)	0.264 (1)	0.9230 (8)
C(25)	0.750 (1)	-0.161 (2)	0.391 (1)	C(112)	0.6803 (8)	0.2178 (9)	0.9297 (7)
C(26)	0.684 (2)	0.030 (2)	0.435 (2)	C(113)	0.8363 (7)	0.247 (1)	0.9786 (7)
C(27)	0.715 (1)	-0.017 (2)	0.476 (1)	C(114)	0.8703 (8)	0.306 (1)	0.9677 (6)
C(28)	0.770 (1)	0.017 (2)	0.498 (1)	C(115)	0.9088 (8)	0.350 (1)	1.0122 (9)
C(29)	0.775 (1)	0.080 (2)	0.470 (1)	C(116)	0.9134 (7)	0.335 (1)	1.0676 (7)
C(30)	0.722 (2)	0.091 (2)	0.429 (2)	C(117)	0.8794 (8)	0.277 (1)	1.0785 (6)
C(31)	0.091 (1)	0.284 (2)	0.026 (1)	C(118)	0.8409 (7)	0.233 (1)	1.0340 (9)

enedithiolate and zirconocene dialkoxide complexes, a formulation of 2 as $Cp_2Ti(\mu\text{-}SCH_2CH_2CH_2S)_2TiCp_2$ is suggested. This formulation has been confirmed by an X-ray crystallographic study (vide infra).

We have previously described the formation of macrocyclic zirconocene dialkoxides and zirconocenedithiolates from the reactions of Cp_2ZrMe_2 with diols and dithiols, respectively.[18,19] In an analogous reaction of Cp_2TiPh_2 with 1,3-propanedithiol, benzene is eliminated. Among the products is the purple compound 2, which is obtained in 30% yield. While nucleophilic substitutions and acidolysis of Ti–C bonds do provide viable routes to these macrocyclic species, the yields are generally fair at best, presumably as a result of the formation of both mononuclear and higher oligomeric side products. Thus, in efforts to develop specific, high-yield routes to these macrocycles, we sought to employ the oxidation of Ti(II) reagents by disulfides. In such a reaction, $Cp_2Ti(PMe_3)_2$ reacts with the bis(disulfide) $(SCH_2CH_2CH_2S)_2$, affording a convenient, virtually quantitative route to 2. In this case, the macrocyclic bis(disulfide) acts as a template for the formation of 2, thus eliminating undesirable mononuclear or oligomeric byproducts. The preparation and isolation of the costly precursor (time and money) $Cp_2Ti(PMe_3)_2$ can be avoided by the reaction of Cp_2TiCl_2 with excess Mg in

Scheme II
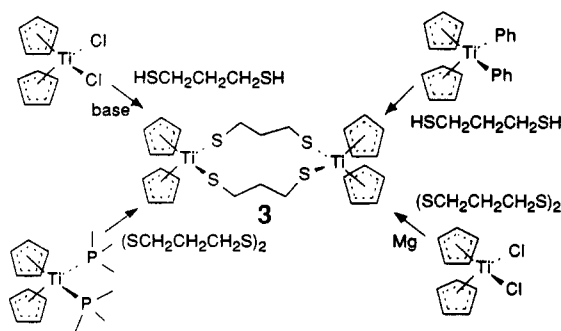
THF in the presence of $(SCH_2CH_2CH_2S)_2$. This affords 2 in 50% yield. (Scheme II). Although the nature of the intermediate has not been established. Ti(II) species are isolated from the Mg reduction of Cp_2TiCl_2,[23] suggesting that this one-pot synthesis proceeds via the disulfide oxidation of the reaction equivalent of "Cp_2Ti". The diminished yield of 2 via this route may be associated with the inability to generate "Cp_2Ti" cleanly, although reduction of the bis(disulfide) $(SCH_2CH_2CH_2S)_2$ template by Mg may also occur. The various synthetic routes are shown in Scheme II.

**Table III. Selected Bond Distances and Angles Involving the Non-Hydrogen Atoms**[a]

Ag(1)–S(1)	2.518 (8)	Ag(1)–S(2)	2.676 (9)
Ag(1)–S(3)	2.517 (7)	Ag(1)–S(4)	2.70 (1)
Ag(2)–S(5)	2.56 (1)	Ag(2)–S(6)	2.634 (9)
Ag(2)–S(7)	2.568 (9)	Ag(2)–S(8)	2.632 (9)
Ti(1)–S(1)	2.46 (1)	Ti(1)–S(2)	2.49 (1)
Ti(2)–S(3)	2.49 (1)	Ti(2)–S(4)	2.483 (8)
Ti(3)–S(5)	2.48 (1)	Ti(3)–S(6)	2.46 (1)
Ti(4)–S(7)	2.46 (1)	Ti(4)–S(8)	2.46 (1)
S(1)–C(1)	1.75 (4)	S(2)–C(4)	1.83 (2)
S(3)–C(6)	1.84 (3)	S(4)–C(3)	1.87 (3)
S(5)–C(31)	1.89 (3)	S(6)–C(34)	1.84 (3)
S(7)–C(36)	1.80 (3)	S(8)–C(33)	1.85 (4)
C(1)–C(2)	1.58 (5)	C(2)–C(3)	1.46 (4)
C(4)–C(5)	1.48 (4)	C(5)–C(6)	1.60 (5)
C(31)–C(32)	1.47 (4)	C(32)–C(33)	1.49 (4)
C(34)–C(35)	1.43 (5)	C(35)–C(36)	1.53 (4)
S(1)–Ag(1)–S(2)	97.1 (3)	S(1)–Ag(1)–S(3)	151.5 (3)
S(1)–Ag(1)–S(4)	93.2 (3)	S(2)–Ag(1)–S(3)	92.6 (3)
S(2)–Ag(1)–S(4)	140.4 (3)	S(3)–Ag(1)–S(4)	96.2 (3)
S(5)–Ag(2)–S(6)	95.8 (3)	S(5)–Ag(2)–S(7)	149.1 (2)
S(5)–Ag(2)–S(8)	94.2 (3)	S(6)–Ag(2)–S(7)	92.9 (3)
S(6)–Ag(2)–S(8)	144.1 (2)	S(7)–Ag(2)–S(8)	95.8 (3)
S(1)–Ti(1)–S(2)	103.8 (4)	S(3)–Ti(2)–S(4)	102.9 (3)
S(5)–Ti(3)–S(6)	102.7 (3)	S(7)–Ti(4)–S(8)	103.3 (3)
Ag(1)–S(1)–Ti(1)	80.2 (3)	Ag(1)–S(1)–C(1)	93 (1)
Ti(1)–S(1)–C(1)	114 (1)	Ag(1)–S(2)–Ti(1)	76.6 (3)
Ag(1)–S(2)–C(4)	93.2 (9)	Ti(1)–S(2)–C(4)	118 (1)
Ag(1)–S(3)–Ti(2)	80.8 (3)	Ag(1)–S(3)–C(6)	94.3 (8)
Ti(2)–S(3)–C(6)	115 (1)	Ag(1)–S(4)–Ti(2)	77.4 (3)
Ag(1)–S(4)–C(3)	93 (1)	Ti(2)–S(4)–C(3)	118.1 (9)
Ag(2)–S(5)–Ti(3)	81.1 (3)	Ag(2)–S(5)–C(31)	91 (1)
Ti(3)–S(5)–C(31)	117 (1)	Ag(2)–S(6)–Ti(3)	80.0 (3)
Ag(2)–S(6)–C(34)	92 (1)	Ti(3)–S(6)–C(34)	119 (1)
Ag(2)–S(7)–Ti(4)	80.8 (3)	Ag(2)–S(7)–C(36)	92.6 (9)
Ti(4)–S(7)–C(36)	117.6 (5)	Ag(2)–S(8)–Ti(4)	79.7 (3)
Ag(2)–S(8)–C(33)	94 (1)	Ti(4)–S(8)–C(33)	119 (1)
S(1)–C(1)–C(2)	112 (2)	C(1)–C(2)–C(3)	117 (3)
S(4)–C(3)–C(2)	110 (2)	S(2)–C(4)–C(5)	110 (2)
C(4)–C(5)–C(6)	116 (2)	S(3)–C(6)–C(5)	109 (2)
S(5)–C(31)–C(32	110 (2)	C(31)–C(32)–C(33)	118 (3)
S(8)–C(33)–C(32)	112 (2)	S(6)–C(34)–C(35)	112 (2)
C(34)–C(35)–C(36)	116 (3)	S(7)–C(36)–C(35)	111 (2)

[a] Distances are in angstroms and angles in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Complexation. The reaction of 1 with 1 equiv of [Cu(NCMe)₄][BF₄] proceeds in dichloromethane with the gradual and complete dissolution of the crystals of 1 and a change from red-purple to green-black. Addition of THF and hexane yields, on standing, the dark crystalline product 3. The ¹H NMR data for 3 are consistent with the inclusion of the metalloligand 1. The shift of the cyclopentadienyl resonance and the observation of resonances attributable to the geminally coupled methylene protons, as well as combustion analysis data, are consistent with the formulation of 3 as the 1:1 salt complex of 1 with CuBF₄, i.e. [(Cp₂Ti(μ-SCH₂CH₂S)₂TiCp₂)Cu]BF₄ (3).

Reaction of 2 with AgBPh₄ proceeds in THF to afford dark crystals of the product 4. ¹H NMR and analytical data suggest the formulation of 4 as [(Cp₂Ti(μ-SCH₂CH₂CH₂S)₂TiCp₂)Ag]BPh₄ (Scheme III). This formulation has been confirmed crystallographically (vide infra).

Structural Study of 4. The compound 4 crystallizes from methylene chloride as 4·H₂O·0.75CH₂Cl₂. The water of crystallization is derived from the incomplete drying of the reagent AgBPh₄. Two pairs of cations and anions as well as 1.5 molecules of CH₂Cl₂ and two H₂O molecules comprise the asymmetric unit of the monoclinic cell. OR-TEP drawings of the two independent cations of 4 are shown in Figure 1. The bond distances and angles within
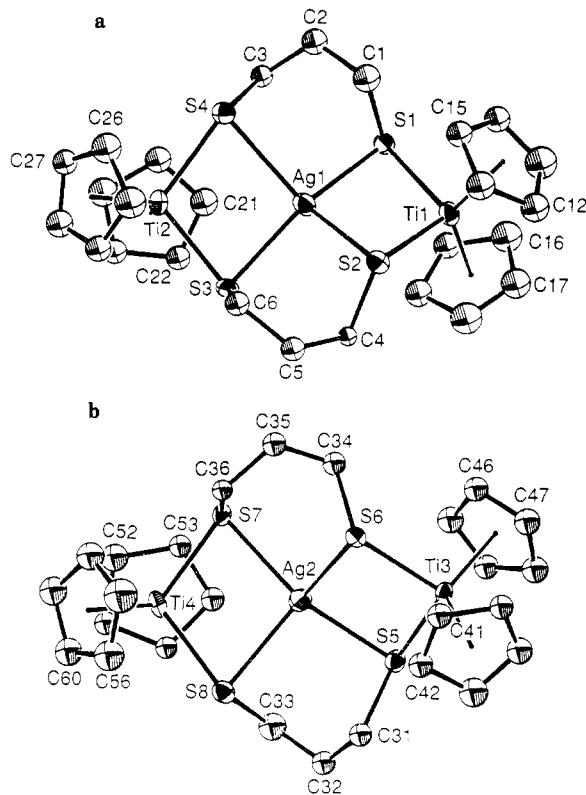

Figure 1. ORTEP drawings of the two crystallographically independent cations of 4 (a and b). Thermal ellipsoids are shown at the 30% level; hydrogen atoms are omitted for clarity.

Scheme III
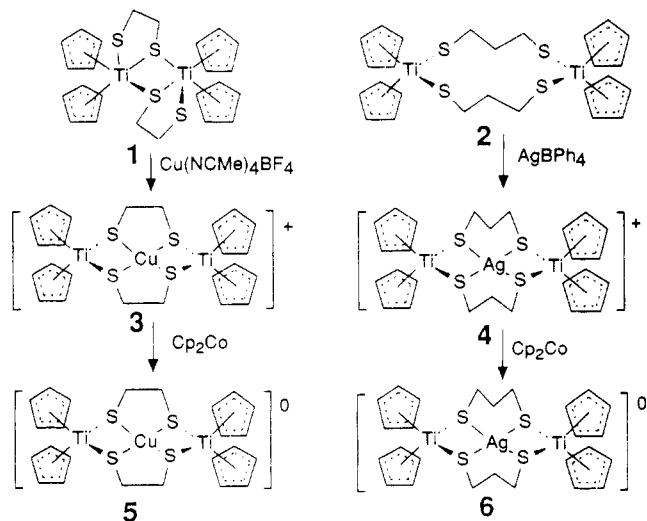
the solvent molecules and the anions, as well as the cyclopentadienyl groups of the cation, are typical and require no further comment. The two crystallographically independent cations of 4 are similar. The central Ag ion is coordinated to four sulfur atoms. Each sulfur atom bridges the Ag and a Ti center. Each of the two Ti centers is bonded to two sulfurs in addition to two π-bonded cyclopentadienyl ligands. Thus, in either case, the titanocenedithiolate acts as a macrocyclic metalloligand to encapsulate the silver ion.
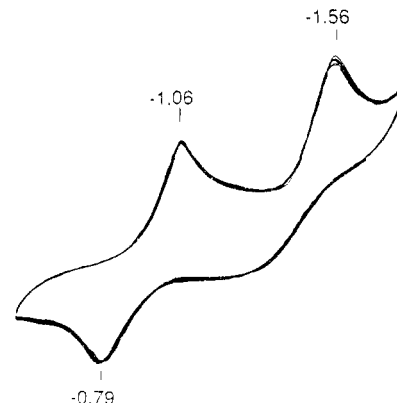
The structural details of the Ti(μ-S)₂Ag(μ-S)₂Ti cores of 4 are illustrated in Figure 2. The Ti–Ag–Ti chains are approximately linear, forming angles of 172.2 (2) and 177.9 (1)° at the respective silver centers, while the angles between the pairs of TiS₂ planes are 125.5 and 133.4°, respectively. These structural features are similar to those
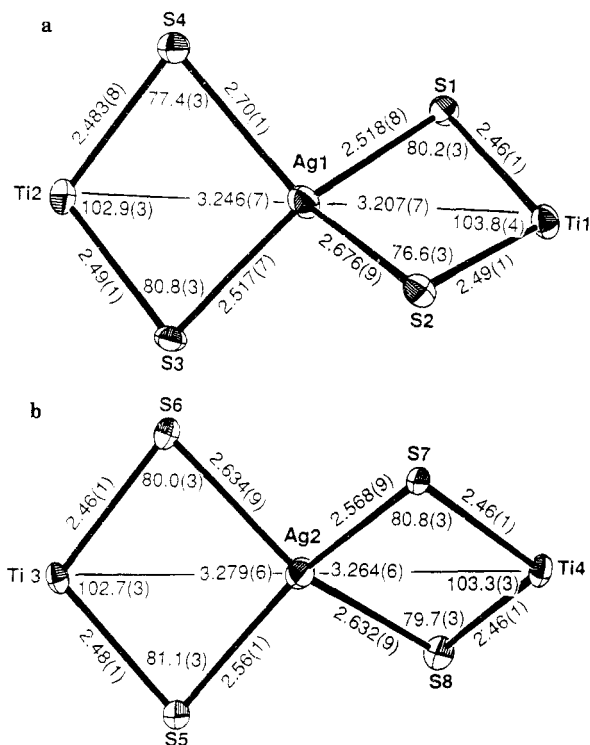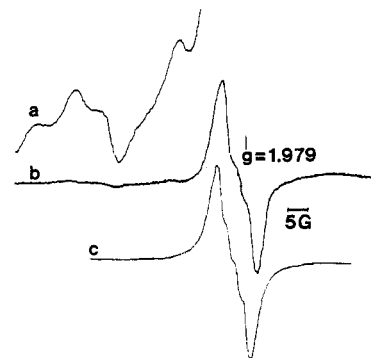
Figure 2. Structural details of the Ti(μ-S)$_2$Ag(μ-S)$_2$Ti cores of the two independent cations of 4 (a and b). Distances are given in angstroms and angles in degrees.

Figure 3. Cyclic voltammogram of 3 in CH$_2$Cl$_2$ with Bu$_4$NBF$_4$ as the supporting electrolyte and a Pt-disk electrode. The potentials shown are referenced to the Ag/AgCl electrode. The scan rate was 100 mV/s.

Figure 4. EPR spectra of 5 in THF: (a) expanded view of a portion of the Ti hyperfine signals; (b) complete observed EPR spectrum for 5; (c) simulated EPR spectrum for 5.

observed in the related Zr$_2$Ag macrocycles.[17,18] The rotation of the Cp$_2$Ti groups with respect to each other both accommodates the required pseudotetrahedral geometry for the central Ag ion and minimizes transannular steric interactions.

The Ti–S distances in 4 are longer than those found in titanocenedithiolates such as Cp$_2$Ti(SMe)$_2$ (2.400 (1) Å),[12] Cp$_2$Ti(SPh)$_2$ (2.439 (8), 2.424 (8) Å),[32] Cp*Ti(SH)$_2$ (2.409 (2), 2.418 (3) Å),[33] and Cp$_2$Ti(SPCy$_2$)$_2$ (2.420 (3), 2.427 (3) Å).[34] In addition, the Ti–S distances in 4 are similar in length to those found in the related thiolato-bridged early–late heterobimetallic complexes depicted in A–C.[11-18] The longer Ti–S distances in 4 compared to those found in simple titanocenedithiolates are consistent with the bridging nature of the sulfur atoms in the present compound. The Ag–S distances found in 4 range from 2.517 (7) to 2.70 (1) Å. A similar variation in the distances was seen in the related zirconocene-based macrocyclic complexes.[17,18] As well, in the only other cases where homoleptic pseudotetrahedral AgS$_4$ coordination spheres have been established, namely [Ag$_3$([9]aneS$_3$)$_3$]$^{3+}$ and [Ag([16]aneS$_6$)]$^+$, similar ranges and averages are observed for the Ag–S distances.[35,36] The angles about the Ag atoms fall into three pairs of about 93, 96, and 145°. Thus, the geometry about silver is best described as that of a flattened tetrahedron. This feature was also observed in the Zr analogue.[17,18] The S–Ti–S angles and the Ti–S–Ag angles in 4 average 103.2 (4) and 79.6 (4)°, respectively. The Ti···Ag distances are found to be 3.207 (7), 3.246 (7), 3.279 (6), and 3.264 (6) Å. In related thiolato-bridged ELHB complexes, structural[11-18] and theoretical studies[37]

imply a dative metal–metal interaction between d^{10} late-metal centers and d^0 early metals. In the present compound 4, the two Ti(IV) centers compete to accept electron density from the central Ag ion. Thus, the fact that the Ti···Ag distances in 4 are longer than the Ti···M distances seen in related thiolate-bridged heterobimetallics suggests that the metal–metal dative interaction is weaker in 4. A more detailed discussion of such metal–metal interactions appears elsewhere.[11-18,37]

Redox Properties. Cyclic voltammetric studies of 1–4 were performed in CH$_2$Cl$_2$ by employing Bu$_4$NBF$_4$ as the supporting electrolyte and a Pt-disk electrode with a Ag/AgCl electrode as the reference. The metalloligands 1 and 2 exhibit irreversible waves at −1.20 and −1.25 V vs Ag/AgCl, respectively. The potentials are typical of titanocenedithiolates and are attributed to Ti(IV) to Ti(III) reduction. In contrast, the complexes 3 and 4 exhibit quasi-reversible waves at −0.93 and −1.26 V vs Ag/AgCl, respectively. The peak to peak separations were observed to be about 270 mV in each case. Under similar conditions (i.e. concentration, solvent, electrolyte) the Cp$_2$Fe/[Cp$_2$Fe]$^+$ couple showed peak to peak separations of approximately 200 mV. These data suggest that the reversible waves are attributable to a one-electron reduction. Chemical reductions of 3 and 4 using 1 equiv of Cp$_2$Co allows the generation of the reduced species formulated formally as the Ti(III)/M(I)/Ti(IV) analogues of 3 and 4. The EPR spectrum of the product of the reduction of 3, i.e. [(Cp$_2$Ti(μ-SCH$_2$CH$_2$S)$_2$TiCp$_2$)Cu]^0 (5), exhibits an EPR signal at g = 1.9821 with ^{47}Ti,^{49}Ti hyperfine coupling of 10.5 G. Simulation of the center band of this EPR spec-

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(35) Küppers, H.-J.; Wieghardt, K.; Tsay, Y.-H.; Krüger, C.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* 1987, 26, 575.

(36) de Groot, B.; Loeb, S. J. *Inorg. Chem.* 1991, *30*, 3103.

(37) Rousseau, R.; Stephan, D. W. *Organometallics* 1991, *10*, 3399.

trum is consistent with $^{65}Cu,^{63}Cu$ hyperfine coupling of 3.5 G. In a similar fashion, **4** undergoes chemical reduction to give the species $[(Cp_2Ti(\mu\text{-}SCH_2CH_2CH_2S)_2TiCp_2)Ag]^0$ (**6**). The EPR signal for **6** is centered at $g = 1.9817$. In addition, hyperfine couplings to $^{107}Ag,^{109}Ag$ and $^{47}Ti,^{49}Ti$ of 5.0 and 11.0 G respectively are observed. These g values and Ti hyperfine parameters are typical of Ti-based radicals. The hyperfine coupling to the encapsulated metal ions in **5** and **6** compare with the $^{65}Cu,^{63}Cu$ hyperfine couplings of 9.5 G seen in $[Cp_2V(\mu\text{-}SEt)_2CuPR_3]^+$ and the ^{103}Rh hyperfine coupling of 2.8 G seen in $[Cp_2Ti(\mu\text{-}SCH_2CH_2CH_2PPh_2)_2Rh]^0$.[13,15] Solutions of the reduced species **5** and **6** are unstable, and thus, isolation of the reduced compounds was not achieved. A minor additional EPR signal is also observed at $g = 1.9791$ and $g = 1.9794$ in the EPR spectra of **5** and **6**, respectively. These signals could be reproduced via reduction of the free metalloligands **1** and **2**, and thus, these signals are attributed to the demetalated degradation products of **5** and **6**. Similar instability has been observed for related reduced ELHB complexes.[13,15] Further reduction to what is potentially a Ti(III)/M(I)/Ti(III) species proceeds with complex degradation, as evidenced by the irreversible reduction waves observed at –1.56 and –1.53 V vs Ag/AgCl for **3** and **4**, respectively. As well, an irreversible oxidation wave, presumably attributable to Cu(I)/Cu(II) oxidation, is observed at 1.13 V for **3**. Although Cu(II) complexes of organic S_4 macrocycles have been described by several authors,[38] for reasons that are not clear a square-planar

environment about Cu(II) presented by the macrocycle **3** is not stable. However, studies in which the titanocene macrocycle **2** and its zirconocene analogue accommodate the square-planar coordination spheres for Rh(I) and Ir(I) are ongoing.

Summary. The present results offer synthetic routes to a new class of redox-active, macrocyclic ligands. Further, the data confirm that these early-metal macrocycles act as effective metalloligands for the encapsulation of late metals. The electrochemical and EPR data indicate that such early-metal macrocycles are capable of acting as electron reservoirs, and thus, work is continuing both to stabilize the reduced complexes and to examine the participation of the early metal in reactions centered on the late metal.

(38) A recent reference in this area is: Desper, J. M.; Gellman, S. H. *J. Am. Chem. Soc.* **1991**, *113*, 704.

# Synthesis and Structure of Two Organozirconocenes with α Nitrogen Substituents

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Two zirconocene derivatives with organic ligands containing α nitrogen substituents have been prepared, and their structures have been determined by single-crystal X-ray diffractometry. The reaction of Cp$_2$Zr(Me)(η^2-CHPhNMe$_2$) with CF$_3$CO$_2$H yields Cp$_2$Zr(O$_2$CCF$_3$)(η^2-CHPhNMe$_2$) (**8**). The reaction of Cp$_2$Zr(CMeN^{t}Bu)(O$_2$CCF$_3$) with Cp$_2$Zr(Me)H yields Cp$_2$Zr(η^2-CMeN^{t}Bu)(μ-O,O'-O$_2$CHCF$_3$)Zr(Me)Cp$_2$ (**9**). The structure of **8** was determined at –125 °C; it crystallizes in space group $P2_1/n$, with $a = 8.839$ (2) Å, $b = 16.491$ (4) Å, $c = 13.887$ (5) Å, $\beta = 103.22$ (2)°, and $Z = 4$. The structure of **9** was determined at –130 °C; it crystallizes in space group $P2_1/n$, with $a = 12.085$ (2) Å, $b = 14.922$ (3) Å, $c = 15.927$ (2) Å, $\beta = 91.50$ (1)°, and $Z = 4$. In both **8** and **9** the nitrogen is coordinated inside the carbon and oxygen ligand atoms.

It is difficult to determine spectroscopically whether a donor atom E attached to an organic ligand R in a metallocene complex Cp$_2$M(R)X is bound "inside" (A) or "outside" (B).[1]

inside
A
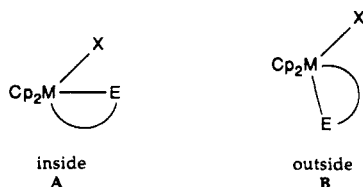
outside
B

Zirconocene chemistry offers examples of both structural types. For example, acyl ligands, with E being oxygen, have their oxygen atoms coordinated outside when they are generated by the carbonylation of organozirconocenes but eventually rearrange so that their oxygen atoms are coordinated inside.[2] When E is nitrogen, X-ray crystallography has usually shown the nitrogen atom to be coordinated inside, for example in the aldimine ligand in **1**[3] and in the iminoacyl ligand in **2**.[4]

(1) The "inside" and "outside" terminology is due to: Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440.

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