Coordination Chemistry of *N*-Alkylbenzamide-2,3-dithiolates as an Approach to Poly(dithiolate) Ligands: 1,4-Bis[(2,3-dimercaptobenzamido)methyl]benzene and Its Chelate Complex with the $(C_5H_5)Ti$ Fragment†

Wolfram W. Seidel, F. Ekkehardt Hahn,* and Thomas Lügger

Institut für Anorganische und Analytische Chemie der Freien Universität Berlin, Fabeckstrasse 34-36, D-14195 Berlin, Germany

Received May 30, 1997

The bidentate dithiolate ligands *N*,*N*-diethyl-2,3-dimercaptobenzamide (H_2-**1**), bis(*N*,*N*-diethyl-2,3-dimercaptoterephthalamide (H_2-**2**), and 1,4-bis(hydroxymethyl)-2,3-dimercaptobenzene (H_4-**3**) were synthesized from 2,3-dimercaptobenzoic acid or 2,3-dimercaptoterephthalic acid. The air-sensitive ligands form metallocene complexes of the type $[(\eta^5\text{-}C_5H_5)_2Ti(\mathbf{1})]$ (**13**), $[(\eta^5\text{-}C_5H_5)_2Mo(\mathbf{1})]$ (**15**), $[(\eta^5\text{-}C_5H_5)_2Ti(\mathbf{3})]$ (**16**), and $[(\eta^5\text{-}C_5H_5)_2Ti(\mathbf{2})]$ (**17**). Complexes **15** and **16** were characterized by X-ray diffraction. Selected crystallographic details for **15** are as follows: formula $C_{21}H_{23}MoNOS_2$; $M = 465.49$; *Pbca*; $a = 12.536(3)$, $b = 14.313(3)$, $c = 22.463(3)$ Å; $V = 4031(2)$ Å^3; $Z = 8$; $R = 3.56$ and $R_w = 4.49$ for 2111 structure factors ($F_o^2 \geq 3\sigma(F_o^2)$) and 254 refined parameters. The molybdenum complex **15** shows an almost planar $Mo(\mu\text{-}S)_2C_2$ chelate ring. Selected crystallographic details for **16** are as follows: formula $C_{18}H_{18}O_2S_2Ti$; $M = 378.35$; $P\bar{1}$; $a = 10.1778(11)$, $b = 11.5806(14)$, $c = 22.967(3)$ Å; $\alpha = 96.42(1)$, $\beta = 101.74(1)$, $\gamma = 108.82(1)°$; $V = 2462.3(5)$ Å^3; $Z = 6$; $R = 4.79$ and $R_w = 13.27$ for 5426 structure factors ($I \geq 2\sigma(I)$) and 766 refined parameters. All titanocene derivatives assume the envelope conformation. The free activation energy for the flip around the S−S axis was determined for **13** to be 69 kJ/mol. The bis(dithiolate) ligand 1,4-bis[(2,3-dimercaptobenzamido)methyl]benzene (H_4-**4**) was prepared from 2,3-dimercaptobenzoic acid and converted into the dinuclear air-stable titanocene complex $[\{(\eta^5\text{-}C_5H_5)_2Ti\}_2(\mathbf{4})]$ (**19**). Complex **19** reacts with $HCl/CHCl_3$ with liberation of free H_4-**4** while reaction with NMe_4Cl results in an intramolecular dithiolate shift under formal liberation of $[(C_5H_5)_3TiCl]$ and formation of the square-pyramidal chelate complex $(NMe_4)[(\eta^5\text{-}C_5H_5)Ti(\mathbf{4})]$, $(NMe_4)[\mathbf{20}]$. Crystallographic details for $(NMe_4)[\mathbf{20}]\cdot CH_2Cl_2$ are as follows: formula $C_{32}H_{35}Cl_2N_3O_2S_4Ti$; $M = 740.67$; $P\bar{1}$; $a = 11.579(4)$, $b = 12.210(4)$, $c = 14.016(4)$ Å; $\alpha = 112.28(2)$, $\beta = 94.46(3)$, $\gamma = 104.22(3)°$; $V = 1744.9(10)$ Å^3; $Z = 2$; $R = 5.35$ and $R_w = 12.84$ for 2870 structure factors ($I \geq 2\sigma(I)$) and 397 refined parameters. The chelate rings in $[\mathbf{20}]^-$ assume an endo/exo conformation.

Introduction

The coordination chemistry of unsaturated 1,2-dithiolate ligands has been investigated thoroughly during the past decades and has been reviewed regularly.[1] Particularly dithiolenes have attracted academic interest owing to the "non innocent" behavior of the dithiolate ligands in these complexes.[1,2] On the other hand, much effort has been dedicated toward practical applications for dithiolene complexes.[3]

Whereas numerous symmetrically substituted 1,2-dithiolate ligands are known,[4] unsymmetrically functionalized 1,2-dithiolate ligands remained comparatively rare[5] and poly(1,2-dithiolate) chelate ligands were unknown until recently. A first report on the synthesis and coordination chemistry of a tripodal tris(dithiolate) ligand appeared in 1995.[6] Multidentate, sulfur-rich ligands of type **A** (Figure 1), based on benzene-1,2-dithiol, have been used successfully in the preparation of model

† Dedicated to Professor Bernt Krebs on the occasion of his 60th birthday.

(1) (a) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49. (b) Schrauzer, G. N. *Acc. Chem. Res.* **1969**, *2*, 72. (c) Eisenberg, R. *Prog. Inorg. Chem.* **1970**, *12*, 295. (d) Burns, R. P.; McAuliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 303. (e) Mahadevan, C. *J. Crystallogr. Spectrosc. Res.* **1986**, *16*, 347.

(2) (a) Stiefel, E. I.; Eisenberg, R.; Rosenberg, R. C.; Gray, H. B. *J. Am. Chem. Soc.* **1966**, *88*, 2956. (b) Davison, A.; Edelstein, N.; Holm, R. H.; Maki, A. H. *Inorg. Chem.* **1963**, *2*, 1227. (c) For EPR studies see: Maki A. H.; Edelstein, N.; Davison, A.; Holm, R. H. *J. Am. Chem. Soc.* **1964**, *86*, 4580. Kirmse, R.; Stach, J.; Dietzsch, W.; Steimecke, G.; Hoyer, E. *Inorg. Chem.* **1980**, *19*, 2679.

(3) (a) For a review see: Mueller-Westerhoff, U. T.; Vance, B. *Comprehensive Coordination Chemistry*; Pergamon Press: Oxford, U.K., 1987; Vol 2, p 595. (b) Dithiolene dyes with strong near-IR absorption: Mueller-Westerhoff, U. T.; Vance, B.; Yoon, D. I. *Tetrahedron* **1991**, *47*, 909. Oliver, S.; Winter, C. *Adv. Mater.* **1992**, *4*, 119. (c) Building blocks in conducting and superconducting salts: Cassoux, P.; Valade, L.; Kobayashi, H.; Kobayashi, A.; Clark, R. A.; Underhill, A. E. *Coord. Chem. Rev.* **1991**, *110*, 115.

(4) For example, see the following. (a) Maleonitrile-1,2-dithiolate (mnt^{2-}): Gray, H. B.; Williams, R.; Bernal, I.; Billig, E. *J. Am. Chem. Soc.* **1962**, *84*, 3596 and Eisenberg, R.; Ibers, J. A.; Clark, R. J. H.; Gray, H. B. *J. Am. Chem. Soc.* **1964**, *86*, 113. (b) Bis(trifluormethyl)ethylene-1,2-dithiolate (tfd^{2-}): Enemark, J. H.; Lipscomb, W. N. *Inorg. Chem.* **1965**, *4*, 1729. Schulz, A. J.; Eisenberg, R. *Inorg. Chem.* **1973**, *12*, 518. (c) Stilbene-1,2-dithiolate: Schrauzer, G. N.; Mayweg, V.; Finck, H. W.; Müller-Westerhoff, U.; Heinrich W. *Angew. Chem.* **1964**, *76*, 345. Mahadevan, C.; Seshasayee, M.; Kuppusamy, P.; Manoharan, P. T. *J. Crystallogr. Spectrosc. Res.* **1984**, *14*, 179. (d) Isotrithionedithiolate (itd^{2-}): Lindqvist, O.; Sjölin, L.; Sieler, J.; Steimecke, G.; Hoyer, E. *Acta Chem. Scand.* **1979**, *A33*, 445. (e) 1,2-Dicarbomethoxyethylene-1,2-dithiolate: Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947. Coucouvanis, D.; Hadjikyriacou, A.; Toupadakis, A.; Koo, S.-M.; Ileperuma, O.; Draganjac, M.; Salifoglou, A. *Inorg. Chem.* **1991**, *30*, 754. (f) Two of the few unsymmetrically substituted dithiolate ligands are the following. (4-Phenyloctyl)ethylene-1,2-dithiolate: Cotrait, M.; Gaultier, J.; Polycarpe, C.; Giroud, A. M.; Mueller-Westerhoff, U. T. *Acta Crystallogr.* **1983**, *C39*, 833. Trithionedithiolate (ttd^{-2}): Lindqvist, O.; Sjölin, L.; Sieler, J.; Steimecke, G.; Hoyer, E. *Acta Chem. Scand.* **1982**, *A36*, 853.

(5) Pilato, R. S.; Eriksen, K. A.; Greaney, M. A.; Stiefel, E. I.; Goswami, S.; Kilpatrick, L.; Spiro, T. G.; Taylor, E. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1991**, *113*, 9372.

10.1021/ic9706616 CCC: $15.00
Published on Web 12/01/1998

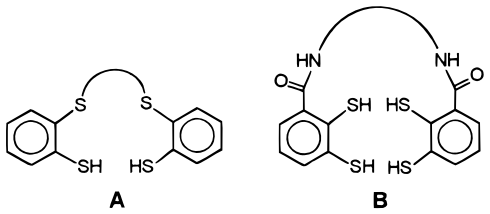


Figure 1. Topology of bis(thioether−thiol) (**A**) and bis(dithiol) ligands (**B**).

compounds for the active sites in nitrogenase[7] and for certain nickel enzymes.[8] In the ligands of type **A**, two aromatic dithiolate units are bridged via a thioether link which leads to a tetradentate ligand with two thiolate and two thioether sulfur donor atoms. The formation of the thioether links leads, in spite of the superb properties of ligands of type **A**, to a loss of the dithiolene character in the bidentate binding unit.

Our approach to sulfur-rich multidentate ligands was directed at the utilization of the dithiolene-like metal-binding capacity of benzene-1,2-dithiolates, which differs from the benzene−thiolate−thioether ligation in **A**. We aimed to prepare tetradentate ligands with two benzene-1,2-dithiolate donors of type **B** (Figure 1) in which the bidentate binding unit might retain some dithiolene character upon coordination.

For the preparation of ligands of type **B** a suitably ortho-functionalized benzene-1,2-dithiol was needed. We decided to base our ligand design on 2,3-dimercaptobenzoic acid[6] and to bridge two such molecules by suitable diamines under formation of stable amide bonds. A similar approach was used previously by Raymond et al. for the preparation and evaluation of a multitude of poly(catechoylamide) ligands.[9]

Ligands of type **B** not only offer the opportunity for the preparation of new model complexes for the active sites in sulfur-containing metalloenzymes but might also allow an investigation of how geometric constraints originating comparatively far from the metal center in the organic backbone of the ligand affect the properties of the coordinated metal center. This might lead to interesting dithiolene complexes for metals known to change their coordination geometry during redox reactions.[10]

In this contribution, we describe the synthesis of the new ortho-functionalized dithiolate ligands H_2-**1**, H_2-**2**, and H_4-**3** (Figure 2) from 2,3-dimercaptobenzoic acid or 2,3-dimercaptoterephthalic acid, respectively, as well as their coordination chemistry with metallocene fragments. In addition, we present the synthesis and the purification of the bridged bis(dithiolate) ligand H_4-**4** and the crystal structure of the chelate complex $(NMe_4)[(\eta^5\text{-}C_5H_5)Ti(\mathbf{4})]$.

Experimental Section

Materials and Methods. If not noted otherwise, all manipulations were performed in an atmosphere of dry argon by using standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM 250 and AM 270 spectrometers, respectively. Elemental analyses (C, H, N, S) were performed at the Freie Universität Berlin on a Perkin-Elmer 240 C elemental analyzer. Mass spectra (FAB, EI) were recorded on Varian MAT 311A and Varian MAT 711 instruments, respectively. Benzene-1,2-dithiol was prepared from thiophenol.[11] 1,4-Bis(aminomethyl)benzene was obtained from Aldrich.

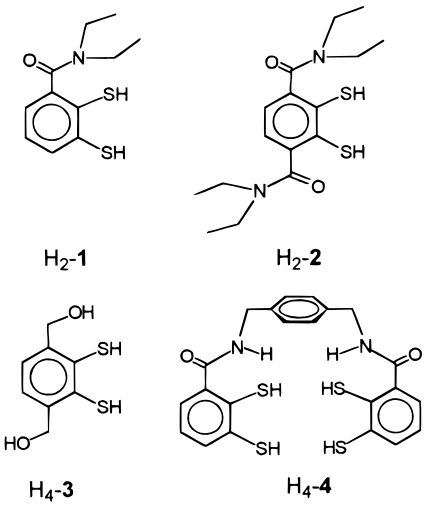


Figure 2. Novel bridged and unbridged dithiolate ligands.

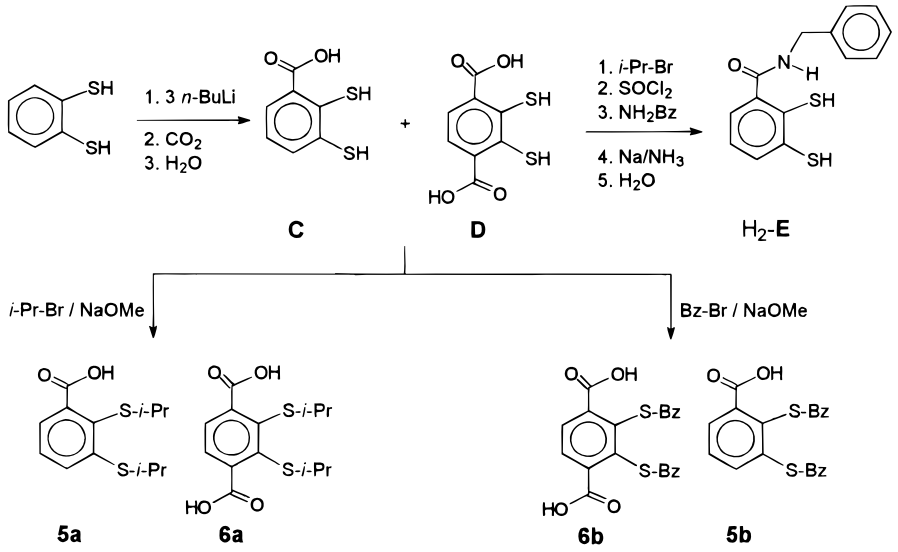
The preparation of 2,3-dimercaptobenzoic acid, **C** (Scheme 1), has been reported.[6,12] Our preparation from benzene-1,2-dithiol followed the reported synthesis of mercaptobenzoic acid from thiophenol.[13] We observed the formation of **C** together with the terephthalic acid derivative **D** (Scheme 1). Alkylation of the thiol functions leads to more stable compounds which can be purified chromatographically. The isolation of the benzoic acid **5a** has been described earlier.[6] The benzoic acid **5b** was synthesized similarly to **5a** from a mixture of **C** and **D** by using benzyl bromide as the alkylating agent. The 2,3-bis-(alkylthio)terephthalic acids (R = isopropyl, **6a**; R = benzyl, **6b**) are formed as byproducts (5−20%) during the preparation of **5a** and **5b**.[6] The purification of **5a**, **5b**, **6a** and **6b** was achieved by column chromatography on SiO_2 using diethyl ether/petroleum ether (bp 40−60 °C) as the eluent.

Synthesis of *N*,*N*-Diethyl-2,3-bis(benzylthio)benzamide (7b). The conversion of **5a**,**b** and **6a**,**b** into the benzamides **7a**,**b** and **8a**,**b** was achieved by routine procedures (Scheme 2). The preparation of **7b** is described as an example. A mixture of 500 mg of **5b** (1.37 mmol) in 10 mL of $CHCl_3$, 0.2 mL of $SOCl_2$, and a few drops of DMF (DMF = dimethylformamide) was heated under reflux for 2 h. The oily benzoic acid chloride obtained after removal of the solvent was dissolved in 10 mL of THF (THF = tetrahydrofuran), and this solution was added to a solution of diethylamine (0.3 mL, 2.9 mmol) in 20 mL of THF. After being stirred at ambient temperature for 12 h, the solution was reduced to dryness. The residue was redissolved in Et_2O (Et_2O = diethyl ether), and the solution was filtered through SiO_2. After removal of the solvent, 496 mg (86%) of **7b** was obtained as a colorless oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.40−7.18 (m, 12 H, Ar *H*), 7.02 (dd, 1 H, Ar *H*), 4.24 (d, 1 H, SCH_2), 4.14 (s, 2 H, SCH_2), 4.12 (d, 1 H, SCH_2), 3.84 (dq, 1 H, NCH_2), 3.34 (dq, 1 H, NCH_2), 3.00 (m, 2 H, NCH_2), 1.32 (dd, 3 H, CH_2CH_3), 1.00 (dd, 3H, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 62.90 MHz): δ 168.7 (*C*ON), 145.9, 144.5, 136.9, 125.7 (Ar *C*), 129.4−126.7 (total of eight signals, Ar *C*), 124.8, 122.0 (Ar *C*), 42.4 (NCH_2), 40.3 (SCH_2), 38.8 (NCH_2), 36.8 (SCH_2), 13.5, 12.2 (NCH_2CH_3).

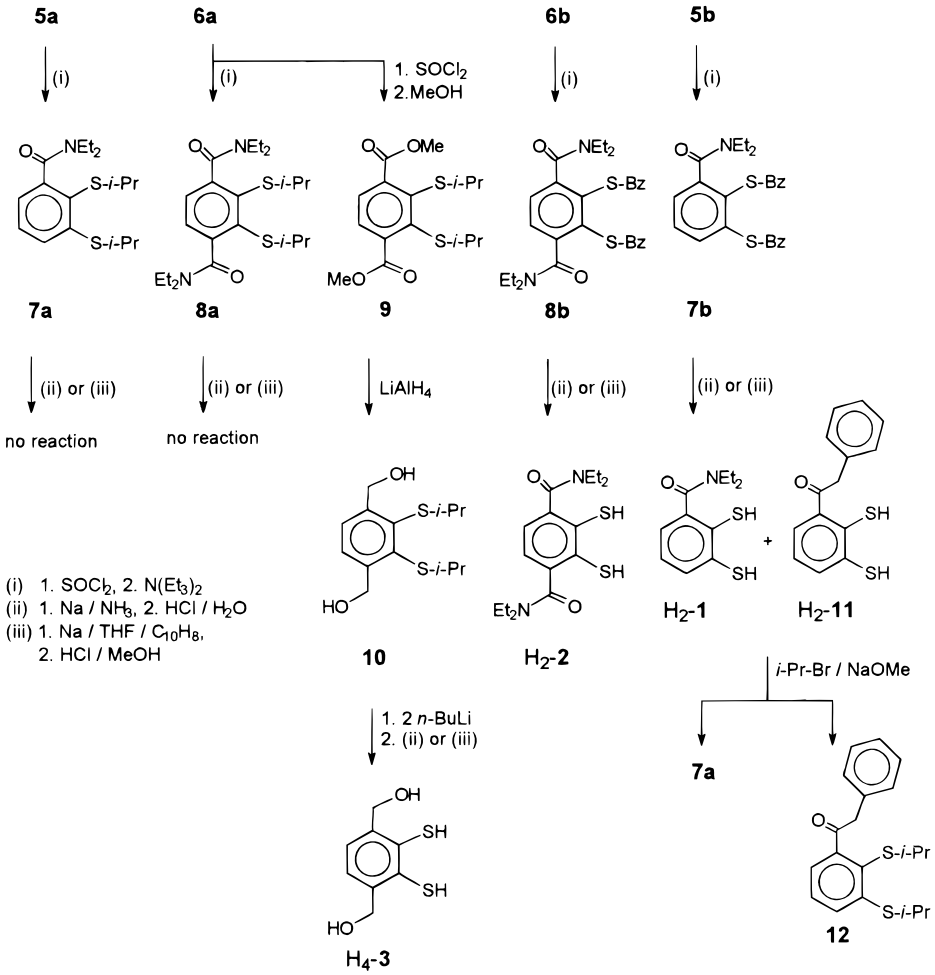
***N*,*N*-Diethyl-2,3-bis(isopropylthio)benzamide (7a).** Yield: 80%; colorless oil. IR (KBr, cm^{-1}): ν = 1633 (vs, C=O). ^{1}H NMR ($CDCl_3$,

(6) Hahn, F. E.; Seidel, W. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2700.
(7) (a) Sellmann, D.; Soglowek, W.; Knoch, F.; Moll, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1271. (b) Sellmann, D.; Soglowek, W.; Knoch, F.; Ritter, G.; Dengler, J. *Inorg. Chem.* **1992**, *31*, 3711.
(8) Sellmann, D.; Fünfgelder, S.; Pöhlmann, G.; Knoch, F.; Moll, M. *Inorg. Chem.* **1990**, *29*, 4772.
(9) Garrett, T. M.; McMurry, T. J.; Hossaini, M. W.; Reyes, Z. E.; Hahn, F. E.; Raymond, K. N. *J. Am. Chem. Soc.* **1991**, *113*, 2965.
(10) Henkel, G.; Greiwe, K.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 117.
(11) Giolando, D. M.; Kirschbaum, K. *Synthesis* **1992**, 451.
(12) Sellmann, D.; Becker, T.; Knoch, F. *Chem. Ber.* **1996**, *129*, 509.
(13) (a) Figuly, G. D.; Loop, C. K.; Martin, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 654. (b) Block, E.; Eswarakrishnan, V.; Gernon, M.; Ofori-Okai, G.; Saha, C.; Tang, K.: Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 658. (c) Smith, K.; Lindsay, C. M.; Pritchard, G. J. *J. Am. Chem. Soc.* **1989**, *111*, 665.

Scheme 1. Functionalization of Benzene-1,2-dithiol



Scheme 2. Synthesis of Ortho-Functionalized Dithiols H_2-**1**, H_2-**2**, H_4-**3**, and H_2-**11**



250 MHz): δ 7.28 (m, 2 H, Ar *H*), 7.04 (dd, 1 H, Ar *H*), 4.80 (dq, 1 H, NCH*H*CH_3), 3.55 (m, 2 H, SC*H*$(CH_3)_2$), 3.20 (dq, 1 H, NCH*H*CH_3), 3.08 (m, 2 H, NCH_2CH_3), 1.44 (m, 6 H, CH(C$H_3)_2$), 1.25 (m, 9 H, NCH_2CH_3 and CH(C$H_3)_2$), 1.04 (t, 3 H, NCH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.90 MHz): δ 168.9 (*C*ON), 145.5, 144.6, 128.9, 128.0, 125.8, 122.4 (Ar *C*), 42.8 (NCH_2), 38.5 (NCH_2), 40.1 (S*C*H), 35.5 (S*C*H), 23.2, 22.9, 22.4, 22.2 (SCH(*C*$H_3)_2$), 13.6, 12.1 (NCH_2CH_3).

***N,N,N′,N′*-Tetraethyl-2,3-bis(isopropylthio)terephthalamide (8a).** Pure **8a** and **8b** were obtained after column chromatography (SiO_2, eluent Et_2O). Yield: 8% based on $C_6H_4(SH)_2$; colorless crystals (mp 67 °C). Anal. Calcd (found) for $C_{22}H_{36}N_2O_2S_2$ (fw = 424.66): C, 62.22 (62.07); H, 8.54 (8.49); N, 6.60 (6.53). ^1H NMR ($CDCl_3$, 250 MHz): δ 7.25 (s, 2 H, Ar *H*), 3.90 (dq, 2 H, NCH*H*CH_3), 3.65 (sept, 2 H, SC*H*), 3.30 (dq, 2 H, NCH*H*CH_3), 3.05 (m, 4 H, 2 × NCH*H*CH_3), 1.30 (t, 6 H, NCH_2CH_3), 1.25 (m, 12 H, CH(C$H_3)_2$), 1.05 (t, 6 H, NCH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.90 MHz): δ 168.4 (*C*ON), 144.6, 137.8, 126.7 (Ar *C*), 42.4, 41.1 (NCH_2), 38.5 (S*C*H), 23.0 22.6 (CH(*C*$H_3)_2$), 13.6, 11.9 ($NCCH_3$).

***N,N,N′,N′*-Tetraethyl-2,3-bis(benzylthio)terephthalamide (8b).** Yield: 5% based on $C_6H_4(SH)_2$. Recrystallization from Et_2O/hexane yielded colorless crystals (mp 135 °C) of **8b**. Anal. Calcd (found) for $C_{30}H_{36}N_2O_2S_2$ (fw = 520.75): C, 69.19 (69.66); H, 6.97 (6.71); N, 5.38 (5.48). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.32−7.12 (m, 12 H, Ar *H*), 4.20 (d, 2 H, SCH*H*Ph), 4.00 (d, 2 H, SCH*H*Ph), 3.80 (dq, 2 H, NCH*H*CH_3), 3.26 (dq, 2 H, NCH*H*CH_3), 2.84 (dq, 2 H, NCH*H*CH_3), 2.74 (dq, 2 H, NCH*H*CH_3), 1.24 (dd, 6 H, C*H*$_3$), 0.94 (dd, 6 H, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 62.90 MHz): δ 168.4 (*C*ON), 144.7, 137.3, 137.0, 129.3, 128.0, 126.9, 126.8 (Ar *C*), 42.5, 41.3 (N*C*H_2), 38.7 (S*C*H_2Ph), 13.6, 12.1 (NC*C*H_3).

Synthesis of 1,4-Bis(hydroxymethyl)-2,3-bis(isopropylthio)benzene (10). The crude acid **6a** (3.0 g) was treated with $SOCl_2$ as described above. The reaction product was dissolved in 5 mL of pyridine, and methanol (10 mL) was added. After being stirred overnight, the mixture was poured into water (50 mL) and extracted with Et_2O (3 time 30 mL). The diester **9** could be isolated after stripping of the solvent by column chromatography (SiO_2, eluent petroleum ether (bp 40−60 °C)/Et_2O, 5:1). Yield: 1.91 g (10% based on $C_6H_4(SH)_2$). A 500 mg (1.46 mmol) sample of **9** was dissolved in 20 mL of diethyl ether, and this solution was added dropwise to a suspension of 89 mg (2.34 mmol) $LiAlH_4$ in 10 mL of diethyl ether. The reaction mixture was stirred at room temperature for 16 h. Hydrolysis with water and sulfuric acid resulted in the formation of two phases. The organic layer was isolated, washed with $NaHCO_3$/H_2O and water, and dried over $MgSO_4$. Removal of the solvent and column chromatography (SiO_2, eluent Et_2O/petroleum ether (bp 40−60 °C), 2:1) yielded 330 mg (78% relative to **9**) of **10** as an analytically pure white powder. Anal. Calcd (found) for $C_{14}H_{22}O_2S_2$ (fw = 286.45): C, 58.70 (58.21); H, 7.74 (7.65). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.34 (s, 2 H, Ar *H*), 4.80 (s, 4 H, C*H*$_2$OH), 3.56 (sept, 2 H, C*H*$(CH_3)_2$), 3.18 (s, 2 H, O*H*), 1.20 (d, 12 H, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 62.90 MHz): δ 145.4, 138.7, 127.7 (Ar *C*), 63.8 (*C*H_2-OH), 40.6 (S*C*H$(CH_3)_2$), 22.8 (CH(*C*$H_3)_2$).

Removal of the Protection Groups at Sulfur in 7b, 8b, and 10. The dealkylation of **7b** is described as an example.

Method A. A solution of 421 mg (1 mmol) of **7b** in 10 mL of THF was added to a solution of 92 mg (4 mmol) of sodium in 30 mL of liquid ammonia. After 15 min, the reaction was quenched with 107 mg (2 mmol) of NH_4Cl. Upon quenching, the mixture became clear and the color turned from blue to orange. The solvents were removed, and the residue was redissolved in 20 mL of water saturated with argon. The resulting orange solution was washed with 20 mL of diethyl ether. Acidification with hydrochloric acid (2 mL of a 36% solution) led to a white precipitate which was extracted with diethyl ether (3 times, 10 mL each). The combined organic phases were dried over $MgSO_4$, and after removal of the solvent, crude H_2-**1** was obtained as an off-white solid.

The dealkylation of the diol **10** required the previous deprotonation of the hydroxy functions with 2 equiv of *n*-BuLi in THF at −78 °C in order to avoid Birch reductions of the aromatic ring during S−C(isopropyl) bond cleavage. For completion of the reaction of deprotonated **10** with sodium in NH_3, a distinctly prolonged reaction time of 90 min was necessary. The workup was carried out as described for **7b**.

Method B. A solution of 200 mg (0.47 mmol) of **7b** and 270 mg (2.11 mmol) of naphthalene in 20 mL of THF was treated with 44 mg (1.92 mmol) of sodium (pieces), and the mixture was stirred for 12 h at ambient temperature. The reaction in the reddish brown mixture was quenched with 2 mL of MeOH, and the resulting mixture was acidified with 10 mL of HCl (1 M solution in diethyl ether), causing the formation of a white precipitate. After removal of the solvents, crude H_2-**1** was obtained as an off-white solid. Dealkylation of **7b** yielded as a side product the ketone H_2-**11**. H_2-**11** was characterized as the titanocene complex **14**. Reaction of the H_2-**1**/H_2-**11** mixture with isopropyl bromide led to re-formation of **7a** and of the S-alkylated ketone **12**. **12** could be separated chromatographically from **7a**.

2,3-Bis(isopropylthio)phenyl Benzyl Ketone (12). Yield: 12% (based on **7b**); colorless oil. IR (KBr, cm^{-1}): ν = 1702 (vs, C═O). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.25 (m, 7 H, Ar *H*), 6.80 (dd, 1 H, Ar *H*), 4.20 (s, 2 H, C(O)C*H*$_2$Ph), 3.52 (sept, 1 H, SC*H*$(CH_3)_2$), 3.44 (sept, 1 H, SC*H*$(CH_3)_2$), 1.41 (d, 6 H, CH(C*H*$_3)_2$), 1.16 (d, 6 H, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 62.90 MHz): δ 203.0 (*C*O), 149.2, 145.5, 128.8, 127.8, 126.8, 122.6 (S_2Ar *C*), 133.9, 129.4, 128.3, 127.4 (Bz−Ar *C*), 50.9 (*C*H_2Ph), 40.7, 35.9 (S*C*H$(CH_3)_2$), 22.9, 22.6 (SCH-(*C*$H_3)_2$).

Titanocene Complexes 13, 14, 16, and 17. The preparation of **13** is described as an example. A sample of 249 mg (1.0 mmol) of [(η^5-$C_5H_5)_2TiCl_2$] was mixed with crude H_2-**1** (the reaction product of method A dealkylation of 1 mmol of **7b**) in 30 mL of THF. The resulting red solution was treated with 0.28 mL (2 mmol) of NEt_3, causing the solution to turn green. After 2 h of stirring, the solvent was removed and the air-stable green residue was purified chromatographically (SiO_2, eluents CH_2Cl_2/diethyl ether, 1:1, for **13** and **14**, CH_2Cl_2/MeOH, 7:1, for **16**, CH_2Cl_2/MeOH, 20:1, for **17**).

Bis(η^5-cyclopentadienyl)(*N,N*-diethylbenzamide-2,3-dithiolato)titanium(IV) (13). Yield: 241 mg (58% relative to crude H_2-**1**). Anal. Calcd (found) for $C_{21}H_{23}NOS_2Ti$ (fw = 417.42): C, 60.43 (60.68); H, 5.55 (5.69); N, 3.36 (3.23). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.44 (dd, 1 H, Ar *H*), 7.12 (t, 1 H, Ar *H*), 7.00 (dd, 1 H, Ar *H*), 6.24 (s, br, 5 H, C_5H_5), 5.80 (s, br, 5 H, C_5H_5), 3.64 (m, 1 H, NCH*H*CH_3), 3.48 (m, 1 H, NCH*H*CH_3), 3.20 (m, 2 H, NCH_2CH_3), 1.20 (dd, 3 H, CH_2CH_3), 1.04 (dd, 3 H, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 62.90 MHz): δ 170.2 (*C*ON), 158.4, 151.7, 138.0, 129.6, 124.6, 121.4 (Ar *C*), 113.5, 112.2 (C_5H_5), 42.7 (N*C*H_2), 38.5 (NCH_2), 14.2 (NCH$_2$*C*H_3), 12.8 (NCH$_2$*C*H_3).

Bis(η^5-cyclopentadienyl)[(2-phenyl-1-oxoethyl)benzene-2,3-dithiolato]titanium(IV) (14). Complex **14** was a side product in the reaction of crude H_2-**1** (containing some H_2-**11**) with titanocene dichloride. The yield of **14** was especially high if crude H_2-**1** obtained via method B was used, while method A yielded H_2-**1** with little or no H_2-**11** and therefore almost no **14**. Yield: 131 mg of **14** (30% based on method B dealkylation of 1 mmol of **7b**). Compound **14** crystallized from a toluene/hexane solution as dark green needles. Anal. Calcd (found) for $C_{24}H_{20}OS_2Ti$ (fw = 436.42): C, 66.05 (66.41); H, 4.62 (4.45). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.55 (dd, 1 H, Ar *H*), 7.32−7.12 (m, 7 H, Ar *H*), 5.96 (s, br, 10 H, C_5H_5), 4.28 (s, 2 H, CH_2).

Bis(η^5-cyclopentadienyl)[1,4-bis(hydroxymethyl)benzene-2,3-dithiolato]titanium(IV) (16). Yield: 60% (based on crude H_4-**3**). Deep green crystals (mp 163 °C dec) were grown by slow cooling of a solution of **16** in toluene/dioxane from 80 °C to ambient temperature. Anal. Calcd (found) for $C_{18}H_{18}O_2S_2Ti$ (fw = 378.34): C, 57.14 (57.17); H, 4.80 (4.83); S, 16.95 (16.78). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.24 (s, 2 H, Ar *H*), 6.10 (s, br, 10 H, C_5H_5), 4.85 (d, 4 H, CH_2), 2.80 (t, 2 H, O*H*). MS (EI, 70 eV), *m*/*e* (relative intensity, assignment): 378 (1, M^+), 295 (1, $M^+ - C_5H_5 - H_2O$), 183 (3, $M^+ - (C_5H_5)_2Ti - OH$), 66 (100, $C_5H_6^+$).

Bis(η^5-cyclopentadienyl)(*N,N,N′,N′*-tetraethylterephthalamide-2,3-dithiolato)titanium(IV) (17). Diffusion of pentane into a solution of crude **17** in toluene yielded thin green needles that were collected to yield pure **17** (53% based on crude H_2-**2**). Anal. Calcd (found) for $C_{26}H_{32}N_2O_2S_2Ti$ (fw = 516.55): C, 60.46 (60.74); H, 6.24 (6.36); N, 5.42 (5.28). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.28 (s, 2 H, Ar *H*), 7.06, 6.34, 6.10, 5.92 (s, br, 10 H, C_5H_5), 3.68 (m, 2 H, NCH_2), 3.54 (m, 2 H, NCH_2), 3.28 (m, 4 H, NCH_2), 1.30 (t, 6 H, CH_2CH_3), 1.12 (t, 6 H, CH_2CH_3).

Bis(η^5-cyclopentadienyl)(*N,N*-diethylbenzamide-2,3-dithiolato)molybdenum(IV) (15). The disodium salt Na_2-**1** was used for the preparation of **15**. This salt was obtained from **7b** by method A without acidification of the reaction product. A solution of Na_2-**1** (obtained from 497 mg of **7b**, 1.18 mmol) in 15 mL of water was added to a suspension of 350 mg (1.18 mmol) of [(η^5-$C_5H_5)_2MoCl_2$] in 30 mL of benzene. After 1 h of stirring, the reddish brown benzene phase was isolated and reduced to 10 mL. Column chromatography (Florisil, eluent benzene/MeOH, 10:1) gave 208 mg (38% relative to **7b**) of **15**. Crystals were obtained by cooling a CH_3CN solution of **15** to −30 °C. Anal. Calcd (found) for $C_{21}H_{23}NOS_2Mo$ (fw = 465.48): C, 54.19 (54.46); H, 4.98 (5.13); N, 3.01 (2.89); S, 13.78 (13.03). IR (KBr, cm^{-1}): ν = 1617 (vs, C═O). ^{1}H NMR (CD_3CN, 250 MHz): δ 7.23 (d, 1 H, Ar *H*), 6.65 (t, 1 H, Ar *H*), 6.45 (d, 1 H, Ar *H*), 5.30 (s, 10 H, C_5H_5), 3.45 (m, 2 H, NCH_2CH_3), 3.17 (m, 2 H, NCH_2CH_3), 1.21 (t, 3 H, NCH_2CH_3), 1.00 (t, 3 H, NCH_2CH_3). MS (EI, 80 eV), *m*/*e* (relative intensity, assignment): 467 (100, M^+), 395 (13, $M^+ - NEt_2$), 367 (9, $M^+ - CONEt_2$), 302 (13, [367 − C_5H_5]$^+$), 228 (41, [$(C_5H_5)_2Mo$]$^+$).

Table 1. Summary of Crystallographic Data for **15**, **16**, and (NMe_4)[**20**]·CH_2Cl_2

parameter	**15**	**16**	(NMe_4)[**20**]·CH_2Cl_2
cryst size, mm	0.40 × 0.25 × 0.15	0.50 × 0.13 × 0.08	0.6 × 0.4 × 0.02
formula	$C_{21}H_{23}MoNOS_2$	$C_{18}H_{18}O_2S_2Ti$	$C_{32}H_{35}Cl_2N_3O_2S_4Ti$
mol wt	465.49	378.35	740.67
a, Å	12.536(3)	10.1778(11)	11.579(4)
b, Å	14.313(3)	11.5806(14)	12.210(4)
c, Å	22.463(3)	22.967(3)	14.016(4)
α, deg	90.0	96.42(1)	112.28(2)
β, deg	90.0	101.74(1)	94.46(3)
γ, deg	90.0	108.82(1)	104.22(3)
V, Å^3	4031(2)	2462.3(5)	1744.9(10)
Z	8	6	2
space group	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
ρ_{exp}, g/cm^3	1.56	not measd	not measd
ρ_{calc}, g/cm^3	1.534	1.531	1.410
μ, cm^{-1}	8.43	7.81	6.71
radiation; λ, Å	Mo Kα; 0.710 73	Mo Kα; 0.710 73	Mo Kα; 0.710 73
data collcn temp, K	293(2)	293(2)	193(2)
2θ range, deg	$2 \le 2\theta \le 45$	$3 \le 2\theta \le 45$	$5 \le 2\theta \le 45$
no. of unique data	3535	6419	4539
no. of obsd data	2111 ($F_o^2 \ge 3\sigma(F_o^2)$)	5426 ($I \ge 2\sigma(I)$)	2870 ($I \ge 2\sigma(I)$)
R, %[a]	3.56	4.79	5.35
R_w, %[a]	4.49	13.27	12.84
GOF	1.207	1.122	1.149
no. of variables	254	766	397

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$. **15** was refined with MolEN against *F*; **16** and (NMe_4)[**20**]·CH_2Cl_2 were refined against F^2 with SHELXL-93. All refinement parameters were calculated for observed data only.

1,4-Bis{[2,3-bis(isopropylthio)benzamido]methyl}benzene (18). A solution of the acid chloride of **5a** (7.22 mmol, synthesized from 1.95 g of **5a** as described above) in 10 mL of THF was added to a solution of 465 mg (3.42 mmol) of 1,4-bis(aminomethyl)benzene and 1 mL of NEt_3 (7.2 mmol) in 40 mL of THF. The suspension obtained was stirred for 24 h at ambient temperature. Subsequently, the solvent was removed and the product was purified chromatographically (SiO_2, eluent $CH_3C(O)OC_2H_5/CH_2Cl_2$, 1:3). Yield: 1.77 g (81%, relative to 1,4-bis(aminomethyl)benzene); off-white powder (mp 164 °C). Anal. Calcd (found) for $C_{34}H_{44}N_2O_2S_4$ (fw = 640.98): C, 63.71 (63.55); H, 6.92 (6.50); N, 4.37 (4.21); S, 20.01 (19.16). IR (KBr, cm^{-1}): ν = 1643 (vs, C═O). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.44 (m, 2 H, S_2Ar *H*), 7.40 (s, 4 H, Ar *H*), 7.30 (m, 4 H, S_2Ar *H*), 7.04 (t, 2 H, N*H*), 4.62 (d, 4 H, NCH_2Ar), 3.48 (m, 4 H, $SCH(CH_3)_2$), 1.36 (d, 12 H, $CH(CH_3)_2$), 1.18 (d, 12 H, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 62.90 MHz): δ 168.2 (*C*O), 145.6, 142.6, 137.2, 128.8, 128.3, 127.7, 125.3 (Ar *C*), 43.7 (NCH_2), 40.5, 35.9 ($SCH(CH_3)_2$), 22.8, 22.5 ($CH(CH_3)_2$).

Crude H_4-4 and {1,4-Phenylenebis[[(methylamino)carbonyl]-benzene-2,3-dithiolato]}bis[bis(η^5-cyclopentadienyl)titanium(IV)] (19). A solution of 200 mg (0.31 mmol) of **18** and 416 mg (3.25 mmol) of naphthalene in 30 mL of THF was treated with 71 mg (3.09 mmol) of sodium (pieces), and the mixture was then stirred for 12 h at ambient temperature (method B). The reaction in the resulting brownish mixture was quenched with 2 mL of MeOH and 10 mL of a 1 M solution of HCl in Et_2O. A white precipitate formed upon quenching. All solvents were removed, and 154 mg (0.62 mmol) of solid [(η^5-C_5H_5)$_2$$TiCl_2$] was added to the residue. To this mixture were added 30 mL of THF and 0.28 mL (2 mmol) of NEt_3. A green solution was obtained. After 2 h of stirring, the solvent was almost completely removed and the residue was put on a chromatographic column (SiO_2). The dinuclear complex **19** was eluted with CH_2Cl_2/MeOH (25:1). Yield: 166 mg (65% based on **18**); dark green powder. Anal. Calcd (found) for $C_{42}H_{36}N_2O_2S_4Ti_2$ (fw = 824.76): C, 61.16 (60.55); H, 4.40 (4.55); N, 3.40 (3.30); S, 15.55 (14.87). IR (KBr, cm^{-1}): ν = 3291 (m, NH), 1655 (s, C═O). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.90 (t, 2 H, N*H*), 7.65 (d, 2 H, Ar *H*), 7.53 (d, 2 H, Ar *H*), 7.35 (s, 4 H, Ar *H*), 7.17 (t, 2 H, Ar *H*), 6.00 (s, br, 20 H, C_5H_5), 4.55 (d, 4 H, NCH_2Ar). ^{13}C{^{1}H} NMR ($CDCl_3$, 62.90 MHz): δ 168.2 (*C*ON), 158.9, 152.5, 134.8, 131.5, 125.5, 124.1 (S_2Ar *C*), 137.3, 127.5 (Ar *C*), 112.9 (C_5H_5), 43.3 (NCH_2-Ar).

1,4-Bis[(2,3-dimercaptobenzamido)methyl]benzene (H_4-4). Dry $CHCl_3$ was saturated with dry, gaseous HCl. A solution of 124 mg (0.15 mmol) of **19** in 10 mL of $CHCl_3$ was treated with 20 mL of the HCl/$CHCl_3$ solution. Immediately, the green color caused by **19** disappeared and the solution turned red (formation of [(η^5-C_5H_5)$_2$$TiCl_2$]) with formation of a white precipitate (pure, chloroform-insoluble H_4-**4**). The volume was reduced to 10 mL, and the white precipitate was collected by filtration, after which it was washed twice with HCl/$CHCl_3$ (5 mL each) and dried in vacuo. Yield: 67 mg (94%); white powder. Anal. Calcd (found) for $C_{22}H_{20}N_2O_2S_4$ (fw = 472.65): C, 55.91 (55.23); H, 4.27 (4.39); N, 5.93 (5.64). ^{1}H NMR ($(CD_3)_2SO$, 270 MHz): δ 9.15 (s, br, 2 H, N*H*), 7.51 (d, 2 H, Ar *H*), 7.28 (m, 6 H, Ar *H*), 7.12 (t, 2 H, Ar *H*), 4.42 (s, 4 H, NCH_2Ar), 4.5−3.5 (s, br, 4 H, S*H*).

Tetramethylammonium {1,4-Phenylenebis[[(methylamino)carbonyl]benzene-2,3-dithiolato]}(η^5-cyclopentadienyl)titanate(IV) ((NMe_4)[20]). A 70 mg (0.085 mmol) sample of **19** and 19 mg (0.17 mmol) of NMe_4Cl were dissolved in 20 mL of acetonitrile. The intensely green reaction mixture was heated under reflux for 36 h. During this time, the color of the solution turned purple. The solvent was removed, the residue was redissolved in 15 mL of CH_2Cl_2, and the solution was filtered. Vapor diffusion of Et_2O into the filtrate yielded after 2 days a crystalline sample of purple (NMe_4)[**20**] (10 mg, 18%). Anal. Calcd (found) for $C_{31}H_{33}N_3O_2S_4Ti$ (fw = 655.74): C, 56.78 (57.06); H, 5.07 (5.48); N, 6.41 (6.14). ^{1}H NMR (CD_2Cl_2, 250 MHz): δ 9.28 (s, br, 1 H, N*H*), 8.72 (s, br, 1 H, N*H*), 7.80 (d, 1 H, Ar *H*), 7.70 (d, 1 H, Ar *H*), 7.60−7.00 (m, 6 H, Ar *H*), 6.88 (m, 2 H, Ar *H*), 6.25 (s, 5 H, C_5H_5), 4.76−4.56 (m, 3 H, $NHCH_2Ar$), 4.40 (dd, 1 H, $NHCH_2Ar$), 2.48 (s, 12 H, $N(CH_3)_4^+$). MS (FAB, negative ions, 3-nitrobenzyl alcohol/dimethyl sulfoxide), *m*/*e* (relative intensity, assignment): 581 (1, [**20**]$^-$).

Crystal Structure Analyses. Air-stable dark green crystals of **16** were obtained by cooling a toluene/dioxane solution from 80 °C to room temperature. Red crystals of **15** formed upon cooling an acetonitrile solution to −30 °C. Diffusion of diethyl ether into to a dichloromethane solution of (NMe_4)[**20**] at room temperature yielded air-sensitive (loss of dichloromethane) purple crystals of (NMe_4)[**20**]·CH_2Cl_2. Suitable specimens were mounted at room temperature (**15** and **16**) or at 193 K ((NMe_4)[**20**]·CH_2Cl_2) on an Enraf-Nonius CAD-4 diffractometer. Routine search and autoindexing procedures yielded the dimensions of the unit cells for all three compounds. Important crystal and data collection details are listed in Table 1. Diffraction data were collected at 293(2) K for **15** and **16** and at 193 K for (NMe_4)[**20**]·CH_2Cl_2 using $\omega-2\Theta$ scans. Raw data were reduced to structure factors[14] (and their esd's) by correcting for scan speed and for Lorentz and polarization effects. No decay or absorption corrections

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **15**[a]

	Distances		
Mo−S1	2.431(1)	Mo−Cp2	2.000(7)
Mo−S2	2.424(2)	S1−C1	1.743(5)
Mo−Cp1	2.000(7)	S2−C2	1.746(5)
	Angles		
S1−Mo−S2	81.99(4)	S2−Mo−Cp1	106.5(2)
S1−Mo−Cp1	106.4(2)	S2−Mo−Cp2	108.6(2)
S1−Mo−Cp2	108.2(2)	Cp1−Mo−Cp2	133.2(3)

[a] Cp denotes the centroids of the cyclopentadienyl rings.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **16**[a]

	Distances		
TiA−S1A	2.4151(13)	TiA−Cp2A	2.043(5)
TiA−S2A	2.4037(14)	S1A−C1A	1.756(4)
TiA−Cp1A	2.071(5)	S2A−C6A	1.757(4)
	Angles		
S1A−TiA−S2A	81.72(4)	S2A−TiA−Cp1A	107.8(2)
S1A−TiA−Cp1A	109.9(2)	S2A−TiA−Cp2A	106.6(2)
S1A−TiA−Cp2A	105.9(2)	Cp1A−TiA−Cp2A	132.9(3)

[a] Cp denotes the centroids of the cyclopentadienyl rings. Molecular parameters for molecule A are listed. They do not differ significantly from those of the other two independent molecules in the asymmetric unit.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for the Anion in (NMe_4)[**20**]·CH_2Cl_2

	Distances		
Ti−S1	2.390(2)	S1−C1	1.753(6)
Ti−S2	2.406(2)	S2−C2	1.759(6)
Ti−S3	2.423(2)	S3−C19	1.764(6)
Ti−S4	2.409(2)		
	Angles		
S1−Ti−S2	82.58(7)	S2−Ti−S3	83.42(7)
S1−Ti−S3	134.80(7)	S2−Ti−S4	133.38(7)
S1−Ti−S4	79.11(7)	S3−Ti−S4	80.02(6)

were necessary. The space groups were found to be *Pbca* for **15** and $P\bar{1}$ for **16** and (NMe_4)[**20**]·CH_2Cl_2. The structures were solved by standard Patterson methods. The positional parameters for all non-hydrogen atoms were refined with anisotropic thermal parameters. Difference Fourier maps calculated at this stage showed the positional parameters of the hydrogen atoms. However, hydrogen atoms were added to the structure models on calculated positions [d(C−H) = 0.95 Å, d(N−H) = 0.87 Å][15] and are unrefined. No hydrogen positions were calculated for the hydroxyl functions in **16**. The isotropic temperature factors for hydrogen atoms were fixed to be 1.3 times the U_{eq} or B_{eq}, respectively, of the parent atom. Calculations were carried out with the MolEN package[16] (refinement on F) for **15** and with SHELXL-93[17] (refinement on F^2) for **16** and (NMe_4)[**20**]·CH_2Cl_2. ORTEP[18] was used for all molecular drawings. One of the ethyl groups of the amide in **15** is disordered. The asymmetric unit for **16** contains three independent molecules. These are held together by a network of hydrogen bonds (O−H···O) in the asymmetric unit. Tables 2−4 list selected bond distances and angles for **15**, **16**, and (NMe_4)[**20**]·CH_2Cl_2, respectively. ORTEP drawings of **15** and **16** and of the anion [**20**]$^-$ are presented in Figures 3 and 5, respectively.

(14) Neutral-atom scattering factors were used: *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B. Terms of anomalous dispersion were taken from: *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.
(15) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.
(16) *MolEN: Molecular Structure Solution Procedures. Program Descriptions*; Enraf-Nonius: Delft, The Netherlands, 1990.
(17) Sheldrick, G. M. *SHELX-93: Program for the Solution of Crystal Structures*; Universität Göttingen: Göttingen, Germany, 1993.
(18) Johnson, C. K. *ORTEP II*; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1971.

Results and Discussion

Synthetic Strategy and Preparation of the Ligands. The goal of our study was the preparation of chelate complexes with bridged bis(dithiolate) ligands of type **B** (Figure 1). The investigation of the coordination chemistry of such ligands (for example, H_4-**4**) was hindered by their poor solubility in most organic solvents (exceptions DMF and DMSO), their sensibility to air oxidation, and their pronounced tendency to form polynuclear complexes when completely deprotonated and reacted with metal halides. To overcome these problems, we decided to start with an investigation of simple 2,3-dimercaptobenzamides which exhibit all features of H_4-**4** and to study their preparation and coordination chemistry. In the course of this study, we found efficient procedures for the preparation and purification of bis(dithiolate) ligands such as H_4-**4** and a versatile reaction for the preparation of their metal complexes.

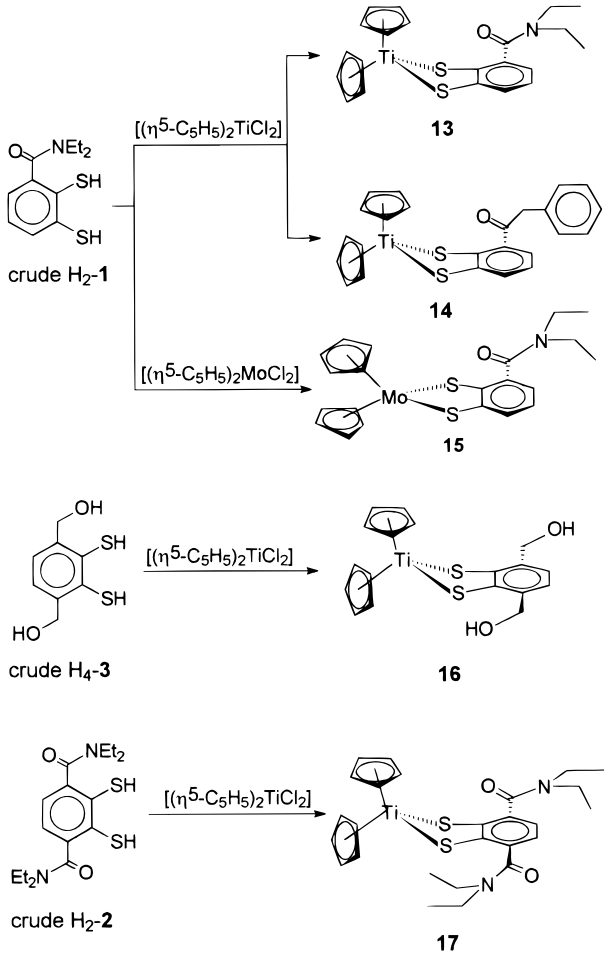
Our strategy for the preparation of 2,3-dimercaptobenzamides involves the protection of the thiolate functions in 2,3-dimercaptobenzoic acid, **C**,[6,12] with isopropyl groups, the conversion of the carboxylic acid into an amide, and finally the removal of the protection groups at the sulfur atoms. As we showed in a preliminary report[6] this strategy turned out to be successful for the synthesis of the secondary amide H_2-**E** (Scheme 1) and a tris(dithiolate) ligand, respectively. Here we report extended investigations that resulted in the preparation of the new dithiolate ligands H_2-**1**, H_2-**2**, H_4-**3**, and H_4-**4**. The study comprises the use of tertiary amide functions instead of secondary ones forcing the replacement of the S-protection groups in **C** and **D** and the isolation of different derivatives of 2,3-dimercaptoterephthalic acid, **D**, which has been found to be a byproduct in the synthesis of **C**.

The isopropyl- and benzyl-protected compounds **5a**/**6a** and **5b**/**6b** were obtained from a mixture of **C**/**D** by reactions with isopropyl bromide/NaOMe and benzyl bromide/NaOMe, respectively (Scheme 1). In contrast to **C** and **D**, the alkylated derivatives **5a**/**6a** and **5b**/**6b** can be isolated by column chromatography. Standard procedures via the acid chlorides led to the tertiary amides **7a,b**/**8a,b**. The terephthalic acid **6a** can be converted into the terephthalic diester **9**, which can be reduced to yield the diol **10** (Scheme 2).

For the subsequent reductive cleavage of the S−alkyl bonds, we used two methods: (i) sodium in liquid ammonia (method A)[19] and (ii) naphthalene/sodium in THF (method B). The latter in combination with a water-free workup has been proved to be more convenient because the use of ammonia is avoided. We found that the isopropyl groups in **7a** and **8a** could not be removed using either method A or method B. Apparently the presence of tertiary amides prevents the S−C(isopropyl) bond cleavage. When tertiary benzamides or terephthalamides are employed, the S-protecting group cannot be isopropyl but must be benzyl instead. The S−C(benzyl) bonds in **7b** and **8b** are readily cleaved by either method A or method B, leading to the crude dithiols H_2-**1** and H_2-**2**. While the removal of the benzyl groups proceeds satisfactorily, these protecting groups pose another problem. In the debenzylation reaction of **7b**, we noted a side product, which was identified as H_2-**11** after realkylation of the H_2-**1**/H_2-**11** mixture with isopropyl bromide and chromatographic isolation of **12** (Scheme 2). The formation of H_2-**11** is surprising, and we think that benzyl radicals attack the amide function under ketone formation.

(19) (a) Block, E. In *The chemistry of ethers, crown ethers, hydroxyl groups and their sulfur analogues*; Patai, S., Ed.; John Wiley: New York, 1980; Supplement E, p 587 ff. (b) Ferretti, A. *Org. Synth.* **1962**, *42*, 54.

Scheme 3. Preparation of Mononuclear Dithiolate Metal Complexes



In light of these results we decided (i) to prepare only secondary amides during the synthesis of bis(dithiolate) ligands and (ii) to use exclusively isopropyl protecting groups in order to avoid radical side reactions on the bridge. However, H_2-**1**, H_2-**2**, H_4-**3**, and H_4-**4** could not be obtained analytically pure and were used in further coordination attempts as crude products.

Synthesis of Metallocene−Dithiolate Complexes (Metal = Ti, Mo). Seeking purification procedures for our ligands, we chose the formation of neutral complexes with metallocene fragments. These complexes proved to be advantageous because they allow chromatographic purification. The crude ligands H_2-**1**, H_2-**2**, and H_4-**3** react with 1 equivalent of $[(\eta^5\text{-}C_5H_5)_2TiCl_2]$ in THF in the presence of triethylamine to yield the intensly green complexes **13**, **14**, **16**, and **17** (Scheme 3). In contrast to the free ligands, these complexes are air-stable and are readily purified by chromatography. Complex formation allowed also for the separation of H_2-**1** and H_2-**11** via formation and purification of the titanocene complexes **13** and **14**. Reaction of the titanium complexes **13**, **14**, **16**, and **17** with dry HCl in $CHCl_3$ yielded $[(\eta^5\text{-}C_5H_5)_2TiCl_2]$ together with the free ligands as monitored by ^{1}H NMR spectroscopy. This complex degradation turned out to be crucial for the purification of H_4-**4** (vide infra).

Description of the Molecular Structures of 15 and 16. The molecular structure of **15** is depicted in Figure 3 (top). The bond distances and angles for **15** fall in the range observed previously for $[(\eta^5\text{-}C_5H_5)_2Mo(bdt)]$ (bdt^{2-} = benzene-1,2-dithiolate)[20] and $[(\eta^5\text{-}C_5H_5)_2Mo(tdt)]$ (tdt^{2-} = toluene-3,4-dithiolate).[21] The angle between the MoS_2 and the C_6S_2 planes

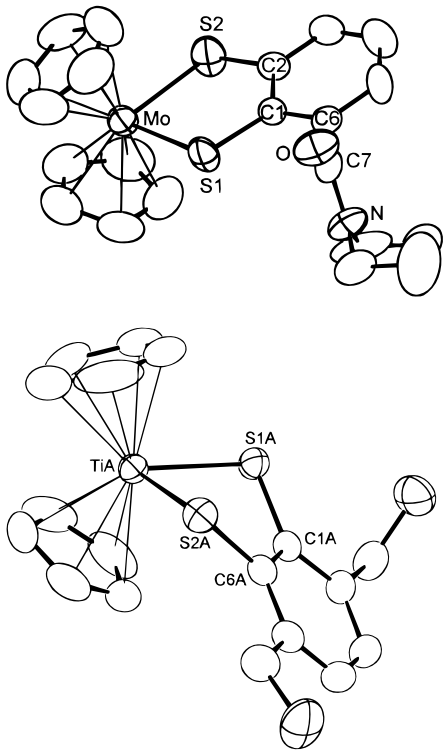


Figure 3. ORTEP plots of complexes **15** (top) and **16** (bottom). Only one of the three molecules on the asymmetric unit of **16** is shown.

measures 4.5(6)° and is only slightly smaller than that in $[(\eta^5\text{-}C_5H_5)_2Mo(bdt)]$ (9°).[20] As expected for a tertiary amide, the amide plane is strongly twisted against the benzene plane (torsion angle C1−C6−C7−O = 91.8(6)°). Steric rather than electronic effects must be made responsible for this observation.[22]

The corresponding torsion angle in the complex $[(\eta^5\text{-}C_5H_5)_2Ti(\mathbf{E})]$ with a nonplanar TiS_2C_2 ring and the sterically less demanding secondary benzamide is only half as large (45.9-(15)°)[6] as that in **15**. From this it appears that least substituted benzamides are particularly useful for the preparation of chelating bis(dithiolates).

The S−C(aryl) bond distances in **15** (1.743(5) and 1.746(5) Å) are slightly shorter than those in the corresponding 2,3-bis-(alkylthio)benzoic acid.[6] They fall, however, in the range observed for benzene-1,2-dithiolate complexes and are significantly longer than those measured for dithiolenes with thioketo character, where S−C distances of around 1.70 Å are typical.[1e]

The molecular structure of **16** (Figure 3, bottom) resembles that of the prototype complex $[(\eta^5\text{-}C_5H_5)_2Ti(S_2C_6H_4)]$[23] and of some other 1,2-enedithiolates of $(\eta^5\text{-}C_5H_5)_2Ti$, which have been characterized crystallographically.[4e,24] The asymmetric unit of **16** contains three independent molecules, which do not differ significantly in their molecular parameters. Surprisingly for the oxophilic titanium, the hydroxy groups are turned away from the titanium center and are connected together by hydrogen bridges (shortest oxygen−oxygen contacts are 2.779−2.903 Å).

(20) Kutoglu, A.; Köpf, H. *J. Organomet. Chem.* **1970**, *25*, 455.
(21) (a) Knox, J. R.; Prout, C. K. *J. Chem. Soc., Chem. Commun.* **1967**, 1277. (b) Knox, J. R.; Prout, C. K. *Acta Crystallogr.* **1969**, *B25*, 2013.
(22) Chakrabarti, P.; Dunitz, J. D. *Helv. Chim. Acta* **1982**, *65*, 1555.
(23) (a) Kutoglu, A. *Z. Anorg. Allg. Chem.* **1972**, *390*, 195. (b) Kutoglu, A. *Acta Crystallogr.* **1973**, *B29*, 2891.
(24) (a) Chiesi Villa, A.; Gaetani Manfredotti, A.; Guastini, C. *Acta Crystallogr.* **1976**, *B32*, 909. (b) Guyon, F.; Lenoir, C.; Formigue, M.; Larsen, J.; Amaudrut, J. *Bull. Soc. Chim. Fr.* **1994**, *131*, 217.

Table 5. ^{1}H NMR Data and Calculated Activation Enthalpies for Dithiolate Complexes[a]

complex	solvent	T_c, °C	$\Delta\nu_{Cp}$, Hz	ΔG_c*, kJ/mol	ref
$[(Cp)_2Ti(\mathbf{E})]$[6]	$CDCl_3$	10	165	55	6
13	toluene-d_8	55	22.5	69	this work
$[(Cp)_2Ti(S_2C_6H_4)]$	toluene-d_8	−20	25.0	53	26a
$[(Cp)_2Ti(S_2C_6H_3\text{-}4\text{-}Me)]$	toluene-d_8	−15	25.0	54	26a
$[(Cp)_2Ti(Se_2C_6H_4)]$	toluene-d_8	−9	13.5	57	26b
$[(Cp)_2Ti(Te_2C_6H_4)]$	toluene-d_8	−38	10.0	51	26c

[a] Frequencies: $[(Cp)_2Ti(\mathbf{E})]$, 300 MHz; **13**, 89.55 MHz. Cp = η^5-C_5H_5.

The angle between the planes containing TiS_2 and S_2C_6 measures 45.3° (for the depicted molecule A). Thus the chelate ring of **16** shows about the same folding as those in $[(\eta^5\text{-}C_5H_5)_2Ti(\mathbf{E})]$ (48.5(3)°),[6] $[(\eta^5\text{-}C_5H_5)_2Ti(S_2C_6H_4)]$ (46.4 and 45.5° for the two independent molecules in the asymmetric unit),[23] and $[(\eta^5\text{-}CH_3C_5H_4)_2Ti(S_2C_2(CO_2CH_3)_2)]$ (44°).[4e] The S−C(aryl) bond distances in **16** (1.756(4) and 1.757(4) Å) compare well with equivalent distances in the molybdenum complex **15** and show that the ligand is coordinated as a dithiolate.

Variable-Temperature ^{1}H NMR Studies. Titanocene dithiolate complexes assume the so-called envelope conformation with the chelate ring folded along the S···S axis (Figure 3). As a consequence of the chelate ring folding, the cyclopentadienyl ligands do not have the same environment. As shown by Köpf,[25] Rauchfuss,[4e] and others[24b] the free activation enthalpy for the flip around the S···S axis falls in the range that can be estimated by variable-temperature ^{1}H NMR spectroscopy. To evaluate the relevance of the amide function for the flipping process, we carried out variable-temperature ^{1}H NMR studies with **13**.

At ambient temperature, only one slightly broadened signal for the cyclopentadienyl protons was found in the ^{1}H NMR spectrum of the complex $[(\eta^5\text{-}C_5H_5)_2Ti(\mathbf{E})]$ with a secondary amide function.[6] Both conformational isomers were observed at low temperature, which is illustrated by two signals for the cyclopentadienyl protons together with two signals for the diastereotypical benzyl protons.[6] In contrast to that observation, two signals for the cyclopentadienyl protons were already found at ambient temperature for complex **13** with the bulkier tertiary amide substituent. Only at elevated temperature (55 °C, in toluene-d_8) did coalescence occur.

The free activation enthalpy for the flip around the S···S axis in **13** was estimated from the difference in the chemical shift of the cyclopentadienyl protons and from the coalescence temperature. In Table 5 the value obtained is compared to the free activation enthalpy for the flip in the known complexes $[(\eta^5\text{-}C_5H_5)_2Ti(\mathbf{E})]$[6] and $[(\eta^5\text{-}C_5H_5)_2Ti(X_2C_6H_4)]$ (X = S,[26a] Se,[26b] Te[26c]). While the barriers for $[(\eta^5\text{-}C_5H_5)_2Ti(\mathbf{E})]$ and $[(\eta^5\text{-}C_5H_5)_2Ti(Se_2C_6H_4)]$ are only slightly raised compared with that for $[(\eta^5C_5H_5)_2Ti(S_2C_6H_4)]$, the activation enthalpy for **13** lies more than 10 kJ/mol higher.

It appears that the activation enthalpy for the flip depends strongly on the nature of substitution at the amide nitrogen atom. The transition from a secondary amide in $[(\eta^5\text{-}C_5H_5)_2Ti(\mathbf{E})]$[6] to a tertiary amide in **13** has a stronger influence on the activation enthalpy than the substitution of the dithiolate in general (compare $[(\eta^5\text{-}C_5H_5)_2Ti(S_2C_6H_4)]$ to $[(\eta^5\text{-}C_5H_5)_2Ti(\mathbf{E})]$) or the substitution of sulfur against other group 16 elements (compare $[(\eta^5\text{-}C_5H_5)_2Ti(S_2C_6H_4)]$ to $[(\eta^5\text{-}C_5H_5)_2Ti(X_2C_6H_4)]$ (X = Se, Te)).

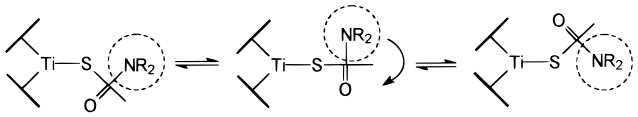


Figure 4. Schematic representation of the combined amide/chelate ring motion during the flip around the S···S axis.

Figure 4 illustrates how the flipping process around the S···S axis is likely combined with a rotation of the amide function around the C(aryl)−C(amide) bond in order to avoid interaction of the substituents at nitrogen with the $(\eta^5\text{-}C_5H_5)_2Ti$ moiety. This complex motion is probably rendered more difficult in complexes such as **13** with a tertiary amide function. This explanation is corroborated by the observation that the NHR unit in the envelope structure of $[(\eta^5\text{-}C_5H_5)_2Ti(\mathbf{E})]$ points away from the $(\eta^5\text{-}C_5H_5)_2Ti$ moiety while the torsion angle C1−C6−C7−O measures about 90° in the essentially planar complex **15**.

Further evidence for an interaction of the amide substituents with the cyclopentadienyl rings can be drawn from the ^{1}H NMR data of complex **17** with two bulky diethylamide substituents. If the ligand assumes the trans geometry as depicted in Scheme 3, one cyclopentadienyl ring will most likely interact with one of the diethylamide functions, which explains the observation of four cyclopentadienyl proton signals in the ^{1}H NMR spectrum of **17** at room temperature. Thus it appears very likely that, in complexes with envelope geometry and only one amide ligand, the amide switches over to the other side of the aromatic ring during the flip around the S···S axis.

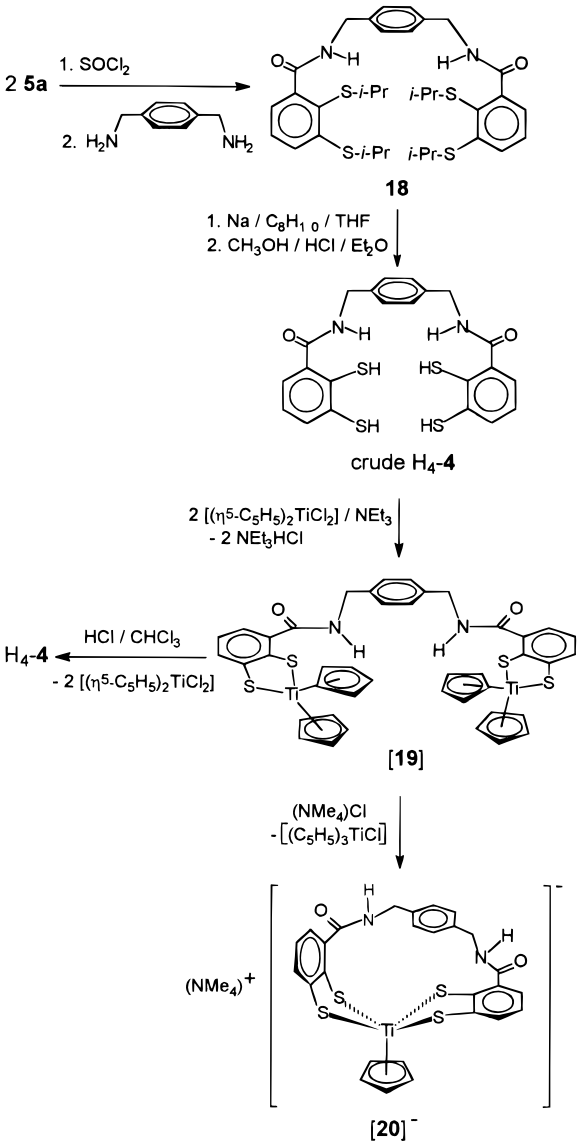
Synthesis and Purification of the Bis(dithiolate) Ligand H_4-4. By utilizing the reactivity of the bis(titanocene) complex **19**, a simple purification procedure for the bis(dithiolate) ligand H_4-**4** was developed (Scheme 4). Compared with the case of H_4-**4**, not only is the dinuclear complex **19** air-stable but its solubility in organic solvents such as CH_2Cl_2 is extremely improved over that of the free ligand. After chromatography, **19** can be subjected to acidic degradation with $HCl/CHCl_3$ to give within seconds a deep red chloroform solution of $[(\eta^5\text{-}C_5H_5)_2TiCl_2]$ and the analytically pure H_4-**4**, which precipitates and can be isolated by filtration. The overall yield of 60% for the reaction sequence from crude H_4-**4** via **19** to analytically pure H_4-**4** confirms the necessity of this purification step.

The driving force for the complex degradation is apparently the high stability of $[(\eta^5\text{-}C_5H_5)_2TiCl_2]$. The halophilicity of the $(\eta^5\text{-}C_5H_5)_2Ti$ moiety has been exploited previously in transmetalation reactions between titanocene−dithiolate complexes and late transition metal halides to give dithiolate complexes of the late transition metals and $[(\eta^5\text{-}C_5H_5)_2TiCl_2]$.[4e,27] This type of transfer has been demonstrated with non-metal halides, which allowed for the preparation of cyclic sulfur derivatives from $[(\eta^5\text{-}C_5H_5)_2TiS_5]$ and S_xCl_2,[28] and the corresponding transfer of selenates has also been reported.[29]

Synthesis and Molecular Structure of the (Cyclopentadienyl)bis(dithiolato)titanate(IV) Complex Anion [20]$^-$. One

(25) Köpf, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 134.
(26) (a) Köpf, H.; Klapötke, T. *Z. Naturforsch.* **1986**, *41B*, 667. (b) Köpf, H.; Klapötke, T. *J. Organomet. Chem.* **1986**, *310*, 303. (c) Köpf, H.; Klapötke, T. *J. Chem. Soc., Chem. Commun.* **1986**, 1192.
(27) (a) Osakada, K.; Kawaguchi, Y.; Yamamoto, T. *Organometallics* **1995**, *14*, 4542. (b) Wark, T. A.; Stephan, D. W. *Can. J. Chem.* **1990**, *68*, 565.
(28) (a) Schmidt, M.; Block, B.; Block, H. D.; Köpf, H.; Wilhelm, E. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 632. (b) Roesky, H. W.; Zamankhan, H.; Bats, J. W.; Fuess, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 125.
(29) Giolando, D. M.; Papavassiliou, M.; Pickardt, J.; Rauchfuss, T. B.; Steudel, R. *Inorg. Chem.* **1988**, *27*, 2596.

Scheme 4. Preparation of the Bis(dithiolate) Ligand H_4-**4** and Its Titanium(IV) Chelate Complex (NMe_4)[**20**]



possibility for the synthesis of the anion $[(\eta^5\text{-}C_5H_5)Ti(\mathbf{4})]^-$, [**20**]$^-$, involves the metathesis reaction of $[(\eta^5\text{-}C_5H_5)TiCl_3]$ with Li_4-**4**. This strategy was used in the preparation of $(Ph_4P)[(\eta^5\text{-}C_5H_5)Ti(S_2C_6H_4)_2]$ from $[(\eta^5\text{-}C_5H_5)TiCl_3]$ and 2 equiv of 1,2-$(LiS)_2C_6H_4$ by Köpf et al.[30] The application of this method to the bis(dithiolate) ligand $\mathbf{4}^{4-}$ has been proved unsuccessful, at least in our hands, apparently because the reaction suffers from the high charge at the ligand and its tendency to form polynuclear species. However, titanocene dithiolate complexes are known to react with an excess of dithiolate ligand under displacement of one C_5H_5 ring to yield the corresponding (cyclopentadienyl)bis(dithiolato)titanate anions.[31]

In our preparation of (NMe_4)[**20**] from **19**, we utilized the halophilicity of the titanocene moiety together with the attack of an enedithiolate on a titanocene dithiolate under substitution of a C_5H_5 ligand, avoiding the highly charged intermediate $\mathbf{4}^{4-}$. The reaction of the bis(titanocene) complex **19** with tetramethylammonium chloride in acetonitrile under reflux conditions

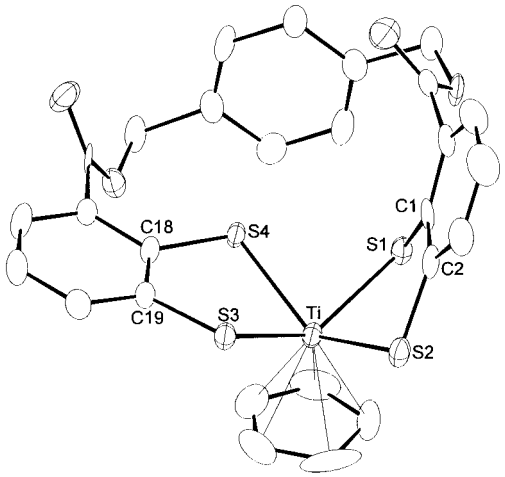


Figure 5. ORTEP plot of the anion [**20**]$^-$.

yielded the purple bis(dithiolate) complex (NMe_4)[**20**] (Scheme 4). The solvate (NMe_4)[**20**]·CH_2Cl_2 was crystallized by vapor diffusion of diethyl ether into a dichloromethane solution of (NMe_4)[**20**]. The reactivity of **19** with chloride ions is readily explained by the halophilic character of the titanocene fragment. The substitution of at least one thiolate function at one titanium center of **19** by a chloride ion probably initiates the reaction. Several reaction pathways are conceivable for the following substitution of a cyclopentadienyl ring at the other titanium center by the released dithiolate donor and the formal elimination of unstable $[(C_5H_5)_3TiCl]$.

The ^{1}H NMR spectrum of (NMe_4)[**20**] in CD_2Cl_2 reveals that the N−H protons and all four benzyl protons are inequivalent, and the complex is consequently rigid. This result can be explained with the bend of the dithiolate chelate rings about the S···S axis in an exo/endo conformation. This exo/endo structure was also found for the prototypical complex (Ph_4P)-$[(\eta^5\text{-}C_5H_5)Ti(S_2C_6H_4)_2]$[30] and leads in [**20**]$^-$ to the formation of enantiomers, which crystallize together in a centrosymmetric space group.

The determination of the molecular structure by X-ray diffraction proves the identity of (NMe_4)[**20**]·CH_2Cl_2 as a chelate complex (Figure 5). The titanium center is coordinated in a distorted tetragonal-pyramidal fashion. The four thiolate donors take the basal positions, whereas the cyclopentadienyl ligand assumes the apical position. The bond lengths and bond angles in the organic backbone are found to be normal within experimental error. However, the coordination geometry around the titanium center in the anion [**20**]$^-$ is distorted compared with that in $[(\eta^5\text{-}C_5H_5)Ti(S_2C_6H_4)_2]^-$, with unbridged benzene-1,2-dithiolate ligands.[30]

The Ti−S bond lengths (Table 4) ortho to the amide groups (S1 and S4) are slightly shorter than the meta Ti−S bonds for each dithiolate unit. Combined with the very small S−Ti−S angle involving the ortho sulfur atoms (S1−Ti−S4 = 79.11-(7)°), this leads to a distinctly shorter inter-dithiolate separation on one side of the bridge (S1···S4 = 3.057 Å, S2···S3 = 3.213 Å).

Regarding the exo/endo bend of the chelate rings around the S···S axis, the anion [**20**]$^-$ resembles the complex anion $[(\eta^5\text{-}C_5H_5)Ti(S_2C_6H_4)_2]^-$.[30] However, the angles describing this folding are larger in [**20**]$^-$ (27.5° exo and 44° endo, relative to the C_5H_5 ligand) than in $[(\eta^5\text{-}C_5H_5)Ti(S_2C_6H_4)_2]^-$ (36.3° exo and 23.3° endo, relative to the C_5H_5 ligand). Owing to the requirements of the bridge in [**20**]$^-$, the endo bend is larger

(30) Köpf, H.; Lange, K.; Pickardt, J. *J. Organomet. Chem.* **1991**, *420*, 345.
(31) (a) Locke, J.; McCleverty, J. A. *Inorg. Chem.* **1966**, *5*, 1157. (b) James, T. A.; McCleverty, J. A. *J. Chem. Soc. A* **1970**, 3318.

than the exo bend, which is the inverse of the situation found in the anion $[(\eta^5\text{-}C_5H_5)Ti(S_2C_6H_4)_2]^-$.

The steric constraints of the xylylene bridge probably account both for the distortion and for the magnitude and direction of the folding. The exo/endo bend of the chelate rings in [**20**]$^-$ is essential as it reduces the mutual distance of the amide groups to be bridged and allows the amide functions to assume the favored twist out of the aromatic planes.

Concluding Remarks. We have shown that benzene-1,2-dithiol can be ortho-functionalized and that this allows bridging of two benzene-1,2-dithiol units. The problems during purification of such air-sensitive and poorly soluble ligands were overcome by preparation of the titanocene complexes which are soluble in most common solvents and which are air-stable enough for chromatographic purification. Protonolysis of such complexes with $HCl/CHCl_3$ utilizes the well-established halophilicity of the titanocene moiety and leads to the free ligands H_2-**1**, H_2-**2**, H_4-**3**, and H_4-**4**. These ligands coordinate as dithiolates in their metal complexes.

Our experiments indicate that large multidentate ligands with many degrees of freedom do not favor the formation of chelate complexes in a fast reaction like metal halogenide sodium thiolate metathesis owing to the necessary rearrangement of the ligand during complex formation. In contrast to the fast metathesis reaction, the release of a benzene-1,2-dithiolate in **19** by reaction with NMe_4Cl and the subsequent dithiolate transfer reaction described for the preparation of [**20**]$^-$ proceeds under reflux conditions in the course of hours. The comparatively low reaction rate reveals a high activation enthalpy, which turns out to be advantageous for the formation of the chelate complex (NMe_4)[**20**], because the rearrangement barriers for the ligand become negligible under these conditions.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support. We thank reviewers A and C for useful comments on an earlier draft of this paper.

Supporting Information Available: X-ray crystallographic files, in CIF format, for the structures of **15**, **16**, and (NMe_4)[**20**]·CH_2Cl_2 are available on the Internet only. Access information is given on any current masthead page.

IC9706616