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Preparation and Variable-Temperature NMR Studies of the Metallacyclosulfanes Cp_2MS_5 and $(Me_5Cp)_2MS_3$, Where M = Ti, Zr, and Hf

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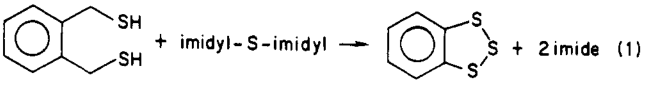
The complexes $Cp_2M(SH)_2$, where M = Ti and Zr, have been prepared and treated with S_8 and imidyl–S_x–imidyl, where imidyl = benzimidazolyl and phthalimidyl and $x = 1$ and 2, to give the metallacyclohexasulfanes Cp_2MS_5. Treatment of the complexes Cp_2MCl_2 with anhydrous solutions of Li_2E_x gave the complexes Cp_2ME_5, where M = Ti, Zr, and Hf, E = S and Se, and $x = 2$ and 5. The compounds $(RCp)_2TiS_5$ (R = Me, $SiMe_3$), $CH_2Cp_2TiS_5$, and $(Me_5Cp)CpTiS_5$ were prepared similarly. Reaction of Li_2S_x with $(Me_5Cp)_2MCl_2$, where M = Ti, Zr, and Hf and $x = 5$, gave the metallacyclotetrasulfanes $(Me_5Cp)_2MS_3$. The factors that affect the size of the MS_x ring are discussed. Comparison of the barriers ($\Delta G^\ddagger$) for ME_x ring reversal for the complexes Cp_2ME_5, where M = Ti, Zr, and Hf and E = S and Se, and $(Me_5Cp)_2MS_3$, where M = Ti, Zr, and Hf, revealed the following: (a) that the barrier is higher for M = Ti (approximately 80 kJ mol^{-1}) than for M = Zr (approximately 50 kJ mol^{-1}) or for M = Hf (approximately 60 kJ mol^{-1}) for the ME_5 series; (b) the barriers for the MS_3 series are similar for M = Ti (40.6 kJ mol^{-1}) and M = Zr (39.3 kJ mol^{-1}), which are less than those for the ME_5 series; (c) monosubstitution of the Cp rings with CH_3 or $Si(CH_3)_3$ does not appreciably affect the barrier for TiS_5 ring reversal; however, bridging the Cp rings in $CH_2(C_5H_4)_2TiS_5$ reduced the barrier to 66.5 kJ mol^{-1}.

As recently as 1973, the nature of the sulfur–sulfur bond was considered to "constitute an important, still unsolved problem".[1] One of the most interesting classes of metal–sulfur complexes are those which contain cyclic catenated sulfur chelates of the type MS_x. Complex anions of the type $M(S_5)_3^{2-}$, where M = Pt[2] and Ir,[3] were prepared at the turn of the century while complexes of the type Cp_2MS_5, where M = Ti[4] and V,[5] and Cp_2MS_4, where M = Mo[6] and W,[7] were reported in the late 1960s. There has been a revival of interest in catenated polysulfur ligands within the last few years;[8] however, surprisingly little is known about the factors that affect the length of the sulfur chain.

Organic chemists have developed reagents and techniques to systematically prepare organopolysulfanes with great control over the length of the chain. Sulfur transfer reagents of the type imidyl–S_x–imidyl, where imidyl is a nitrogen base such as phthalimidyl or benzimidazolyl and $x = 1$ and 2, react with thiols to give tri- and tetrasulfides, respectively, in high yield under mild conditions.[9] The organic dithiol α,α-dimercapto-*o*-xylene reacts with imidyl–S–imidyl, where imidyl = benzimidazolyl to give the monomeric cyclic trisulfide 2,3,4-benzotrithiepin in high yield[10] (eq 1). In addition, it has been reported that sulfur transfer via the reaction of anhydrous solutions of Li_2S_x, where $x = 1$ and 2, with organic halides leads to mono- and disulfides.[11a]



Thus, the compounds Cp_2TiCl_2 and $Cp_2Ti(SH)_2$[12] were chosen as possible precursors to the target complexes Cp_2TiS_x, where $x = 2$, 3, and 4, via reaction with the appropriate sulfur transfer reagents. The complexes where $x = 3$ and 4 have been reported,[13] but others[14] were unable to duplicate their synthesis. Our studies into the synthesis of such systems are reported here; preliminary accounts of some of the results have appeared.[15a] We found that only MS_5 rings were isolated for bis Cp complexes of group 4B metals, while for the relatively electron-rich permethylated bis Me_5Cp systems, only MS_3 rings were isolated.[15b] In this paper we also report the DNMR properties of these rings and compare the barriers for MS_x ring inversion as a function of M = Ti, Zr, and Hf and of $x = 3$ and 5.

Results

Preparations. The complexes $Cp_2M(SH)_2$, where M = Ti (**1**) and Zr (**2**), were easily prepared via treatment of the dichlorides with H_2S in THF in the presence of Et_3N (eq 2).

$$Cp_2MCl_2 + 2H_2S + 2Et_3N \xrightarrow{\text{THF}} Cp_2M(SH)_2 + 2Et_3NHCl \quad (2)$$

Rapid reaction occurred with immediate precipitation of Et_3NHCl that was removed by filtration. Incomplete dissolution of the Cp_2TiCl_2 prior to the addition of H_2S gave a crude product that contained large amounts of cyclopentadienyltitanium-containing impurities (detected

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(1) Schmidt, M. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 445–455.

(2) Hofmann, K. A.; Höchtlen, F. *Chem. Ber.* **1903**, *36*, 3090–3092.

(3) Hofmann, K. A.; Höchtlen, F. *Chem. Ber.* **1904**, *37*, 245–249.

(4) (a) Samuel, E. *Bull. Soc. Chim. Fr.* **1966**, 3548. (b) McHugh, K. L.; Smith, J. O. U.S. Patent 3242081, 1966; *Chem. Abstr.* **1966**, *64*, 17333.

(5) Köpf, H.; Wirl, A.; Kahl, W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 137–138.

(6) Köpf, H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 375.

(7) Köpf, H.; Kahl, W.; Wirl, A. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 801–802.

(8) (a) Koch, S. A.; Chebolu, V. *Organometallics* **1983**, *2*, 350–351. (b) Dudis, D.; Fackler, J. P., Jr. *Inorg. Chem.* **1982**, *21*, 3578–3580. (c) Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947–3954. (d) Simhon, E. D.; Baenziger, N. C.; Kanatzidis, M.; Draganjac, M.; Coucouvanis, D. *J. Am. Chem. Soc.* **1981**, *103*, 1218–1219.

(9) Harpp, D. N.; Steliou, K.; Chan, T. H. *J. Am. Chem. Soc.* **1978**, *100*, 1222–1228.

(10) Steliou, K. Ph.D. Thesis, McGill University, Montreal, Quebec, 1978.

(11) (a) Gladysz, J. A.; Wong, V. K.; Jick, B. S. *Tetrahedron* **1979**, *35*, 2329–2335. (b) Gladysz, J. A.; Hornby, J. L.; Garbe, J. E. *J. Org. Chem.* **1978**, *43*, 1204–1208.

(12) Köpf, H.; Schmidt, M. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 953.

(13) Ralea, R.; Ungurenasu, C.; Cihodaru, S. *Rev. Roum. Chim.* **1967**, *12*, 861.

(14) Köpf, H.; Block, B. *Chem. Ber.* **1969**, *102*, 1504–1508.

(15) (a) McCall, J. M.; Shaver, A. *J. Organomet. Chem.* **1980**, *193*, C37–C39. (b) Bird, P. H.; McCall, J. M.; Shaver, A.; Siriwardane, U. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 384–385.

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in the ^1H NMR spectrum) which were difficult to remove since recrystallization of 1 resulted in excessive loss of compound. Storage of 1 at room temperature for several months resulted in partial decomposition;[12] however, some 1 could be recovered by extraction with CH_2Cl_2. A sample stored at −20 °C showed no evidence of decomposition after 1 year. The complex $Cp_2Zr(SH)_2$ appeared to decompose upon storage for a few months, even at −20 °C. The preparation of **2** was accompanied by the isolation of complex **3** that was formulated as $(Cp_2ZrS)_2$ on the basis of spectral and microanalytical data. Complex **3** appears

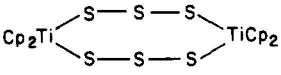
$$\underset{\mathbf{2}}{2Cp_2Zr(SH)_2} \rightleftharpoons \underset{\mathbf{3}}{(Cp_2ZrS)_2} + 2H_2S \qquad (3)$$

to be in equilibrium with **2** since treatment of **3** in $CDCl_3$ with H_2S discharged the turquoise color and the ^1H NMR signal of **3** was replaced by those of **2**. Under the conditions used to prepare **2** it is unlikely that **3** is formed. However, during evaporation of solutions of **2** in vacuo, the yellow color is replaced by the emerald green color of **3**. Complex **3** tends to decompose in solution, and its formulation as a dimer is based on its mass spectrum. Thus, other oligomeric structures cannot be completely ruled out. The hafnium analogue of **1** and **2** was not accessible via this route. Unreacted $(Me_5Cp)_2TiCl_2$ was recovered after treatment with H_2S and Et_3N in THF at room temperature.[16]

Complex **1** reacts with the suulfur transfer reagents imidyl–S_x–imidyl, where imidyl = benzimidazolyl[9] and phthalimidyl[18] and x = 1 and 2, to give Cp_2TiS_5 (**4**) as the major and, in most cases, the only product, regardless of the reaction conditions (eq 4). The yield ranged from 33

$$\underset{\mathbf{1,\,2}}{Cp_2M(SH)_2} + \text{imidyl–}S_x\text{–imidyl} \rightarrow \underset{\mathbf{4,\,5}}{Cp_2MS_5} + 2\text{imidyl–H} \qquad (4)$$

to 70% on the basis of the limiting sulfur reagent. In the case of imidyl = benzimidazolyl and x = 1, the complex $[Cp_2Ti(\mu\text{-}S_3)]_2$[19] was isolated in low yield (1%). Complex



2 reacts with sulfur or 1,1′-dithiobisbenzimidazole to give Cp_2ZrS_5 (**5**) (12% and 32%, respectively). Thus, these reactions that were designed to give MS_3 and MS_4 rings resulted in isolation of complexes containing MS_5 rings.

Treatment of Cp_2TiCl_2 with an equimolar quantity of Li_2S_2, generated in situ from treatment[11a] of sulfur with $LiEt_3BH$ in THF, gave an intractable brown product in which some **4** was detected by TLC. However, **4** in 98% yield was isolated from the reaction if sufficient sulfur is present to give a formal stoichiometry of $Cp_2TiCl_2/Li_2S_2/S$ = 1:1:3. The reaction is general (eq 5); thus, complexes

$$Cp_2MCl_2 + 2LiEt_3BH + 5S \rightarrow \underset{\mathbf{4\text{–}6}}{Cp_2MS_5} + 2LiCl \qquad (5)$$

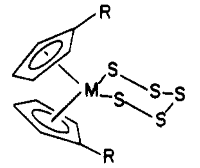
$$(Me_5Cp)_2MCl_2 + 2LiEt_3BH + 5S \rightarrow \underset{\mathbf{11,\,12}}{(Me_5Cp)_2MS_3} + 2LiCl \qquad (6)$$

4–10[20] were prepared in the same way from the appropriate dichlorides. Their formulation as metallacyclohexasulfanes with a chair-like conformation is consistent with their spectroscopic and microanalytical data and, in the case of **4**,[21] **5**,[22] and **6**,[22] confirmed by X-ray analysis.

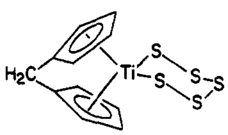
On the other hand complete methylation of both Cp rings led to a contraction of the ring size. The complexes **11–13** were prepared via treatment of the dichlorides with Li_2S_5 (**11**, **12**) or Li_2S_3 (**13**) (eq 6). These are high melting solids and are air stable in solution. Solution molecular weight determinations of **11** and **12** indicate they are monomeric. The structure of **11** has been determined.[15b]

Since Li_2S_5 solutions were used for the preparation of **4–13**, the nature of the species present was investigated. A solution of Li_2S_5 was treated dropwise with 2 equiv of $PhCH_2Cl$ in THF. After being stirred for 4 h at room temperature, the solution was evaporated to leave an oily residue. In the ^1H NMR spectrum the CH_2 signals are easily distinguished for $(PhCH_2)_2S_x$ where x = 2–5, and are diagnostic since a progressive downfield shift occurs as x increases.[23] The residue in CCl_4 gave the following signals (lit. value[23b] in parentheses): δ 3.51 (x = 2, 3.51), 3.95 (x = 3, 3.94), 4.07 (x = 4, 4.04), and 4.12 (x = 5, 4.14). The relative amounts of the species was determined by integration to be 2.6:1.4:1.0:4.6 for x = 2:3:4:5.

The general method of preparation of the polysulfanes **4–13** can be extended to prepare selenanes. The complexes Cp_2MSe_5, where M = Ti (**14**),[24] Zr (**15**), and Hf (**16**), were prepared by treating the appropriate dichlorides with a solution of Li_2Se_5 prepared in situ.[11b] Complexes **15** and **16** appeared somewhat light sensitive and **16** tended to decompose upon recrystallization.



4, M = Ti, R = H
5, M = Zr, R = H
6, M = Hf, R = H
7, M = Ti, R = CH₃
8, M = Ti, R = Si(CH₃)₃



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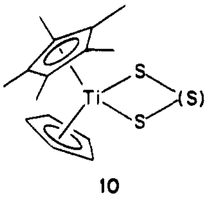

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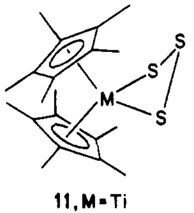

11, M = Ti
12, M = Zr
13, M = Hf

The preparation of $Cp_2Ti[S(CH_2)_3S]$ was undertaken for comparative purposes. Treatment of Cp_2TiCl_2 with dilithio-1,3-propanedithiolate gave the desired monomer **17** (solution molecular weight 281, calcd 284). Attempts to prepare $Cp_2M[S(CH_2)_2S]$, where M = Ti and Zr, failed.[25–27]

The infrared spectra of complexes **4–16** were dominated by bands characteristic of the type of cyclopentadienyl

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[16] The complex $(MeCp)_2Ti(SH)_2$ was recently prepared[17] according to this route.

[17] Bolinger, C. M.; Hoots, J. E.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 223–227.

[18] Kalnins, M. V. *Can. J. Chem.* **1966**, *44*, 2111–2112.

[19] Bolinger, C. M.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 5620–5621.

[20] Compound 7 has been reported: Chandra, K.; Soni, P.; Garg, B. S.; Singh, R. P. *J. Indian Chem. Soc.* **1981**, *58*, 10.

[21] (a) Epstein, E. F.; Bernal, I.; Köpf, H. *J. Organomet. Chem.* **1971**, *26*, 229–245. (b) Muller, E. G.; Petersen, J. L.; Dahl, L. F. *Ibid.* **1976**, *111*, 91–112.

[22] Day, V.; Vollmer, S.; Shaver, A.; McCall, J. M., manuscript in preparation.

[23] (a) van Wazer, J. R.; Grant, D. *J. Am. Chem. Soc.* **1964**, *86*, 1450–1451. (b) Voronkov, M. G.; Pereferkovich, A. N.; Pestanovich, V. A. *Zh. Strukt. Khim.* **1968**, *9*, 627.

[24] Köpf, H.; Block, B.; Schmidt, M. *Chem. Ber.* **1968**, *101*, 272–276.

[25] Köpf, H.; Schmidt, M. *J. Organomet. Chem.* **1965**, *4*, 426–429.

[26] Sen, D. N.; Kantak, U. N. *Indian J. Chem.* **1971**, *9*, 254–257.

[27] Chaudhari, M. A.; Stone, F. G. A. *J. Chem. Soc. A* **1966**, 838–841.

ligand present. Thus, the spectra of **4**–**6** are very similar to each other, as expected, as are those for the sets **11**–**13** and **14**–**16**. Studies of the infrared and Raman spectra of these complexes and of Cp_2MoS_4 and Cp_2MoS_2 are in progress[28] in an attempt to correlate features of the spectra with ring size. Molecular ions were observed in the mass spectrum for all the complexes except **8**. Metastable ion peaks corresponding to loss of S_2 and Se_2 were observed for several of the ME_5 compounds but not for the MS_3 complexes.

Variable-Temperature NMR Spectra. The complexes **4**–**9** and **11**–**16** show temperature-dependent ^1H NMR spectra and the free energy of activation for these processes has been measured (Table I). The DNMR properties of **4** have been reported[24,29] and are consistent with inversion of the TiS_5 ring. The ΔG^* values of 48.6 and 58.0 kJ mol^{-1} for **5** and **6**, respectively, reflect a decrease in the free energy of activation as compared to **4** (76.3 kJ mol^{-1}). The same trend was observed in the MSe_5 complexes **14**–**16**. High-temperature studies of **14** were hampered by decomposition at elevated temperatures; however, at 90 °C in toluene-d_8 some broadening of the signals was evident. The complex decomposes at lower temperatures in Me_2SO-d_6 and DMF. If T_c is estimated to be greater than 90 °C, then ΔG^* must be greater than 76.5 kJ mol^{-1}. The values of ΔG^* calculated for **15** and **16** (49.9 and 61.6 kJ mol^{-1}, respectively) were lower than that for **14**. Thus, the zirconium and hafnium complexes Cp_2ME_5, where E = S and Se, have lower ΔG^* values than the titanium compounds. The presence of either one methyl group (**7**) or one trimethylsilyl group (**8**) on each ring had little effect. However, bridging the two rings with a methylene group (**9**) did significantly lower the value of ΔG^* to 66.5 kJ mol^{-1}. The NMR study of $(Me_5Cp)CpTiS_5$ (**10**) was interesting because in CD_2Cl_2 and toluene-d_8 no changes occurred in the spectrum over the temperature range −101 to +124 °C, except for some slight viscosity broadening at the lowest temperatures. Similarly, no significant line-shape changes occurred in the spectrum of $Cp_2Ti[S(CH_2)_3S]$.

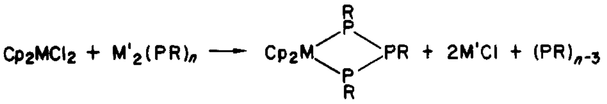
The values of ΔG^* for the MS_3 complexes **11**–**13** were significantly lower than those of the MS_5 compounds. Complexes **11**–**13** exhibited a sharp singlet for the methyl groups at room temperature that broadened as the temperature was lowered. At about −80 °C the signal for **11** and **12** appeared as a symmetrical broad singlet. Between −85 and −110 °C the spectra consisted of two overlapping singlets of unequal intensity. Further cooling caused the overlapping signals to broaden and collapse. However, by −120 °C new peaks in the spectrum of **11** began to appear. At very low temperature (−130 °C) several broad peaks appear in the spectrum of **11**. A value of $\Delta G^* = 40.6$ kJ mol^{-1} was calculated for **11** for the first broadening process. The spectra of **12** were better resolved than those of **11**, and at −100 °C two singlets were present. The signal at lower field became more intense below the coalescence temperature. At −125 °C the higher field signal was barely resolved as a shoulder of the lower field peak. The spectrum had not sharpened appreciably by −130 °C. The ΔG^* for the first broadening process was calculated to be 39.3 kJ mol^{-1}. The spectrum of $(Me_5Cp)_2HfS_3$ in the range of −110 to −130 °C showed a broad singlet with a half-height width of 10 Hz at −110 °C and about 14 Hz at −130 °C. Assuming a coalescence temperature of <−130 °C and a value of $\Delta < 14$ Hz, ΔG^* is estimated to be less than 30 kJ mol^{-1}.

Discussion

The literature method[12] for the preparation of **1** specifies extraction with water to remove the Et_3NHCl byproduct. However, **1** is moisture sensitive; thus the anhydrous conditions described here gave much better results. Whereas complex **1** was the only organometallic product isolated from the reaction of Cp_2TiCl_2, the analogous reaction with Cp_2ZrCl_2 gave two products **2** and **3**. The NMR experiment demonstrated that **3** was converted to **2** under an atmosphere of H_2S. It is reasonable to conclude that **2** undergoes loss of H_2S to give **3**.

The reactions of **1** and **2** with imidyl–S_x–imidyl, where x = 1 and 2, gave Cp_2MS_5, where M = Ti and Zr, as the isolated products together with $[Cp_2Ti(\mu\text{-}S_3)]_2$ as a low yield additional product. One can assume that a mechanism similar to that proposed for the reactions of organic thiols is operative[9] for the first step(s) of the reaction but clearly additional steps occur. The isolation of $[Cp_2Ti(\mu\text{-}S_3)]_2$ is of interest since this dimer was found to be unstable in $CDCl_3$ solution and to chromatography on Florisil, converting in part to **4**. The tendancy of the dimer to give **4** plus an insoluble residue upon heating in benzene has been noted.[19]

The appropriate metallocene dichlorides reacted with lithium polysulfide solutions to give complexes **4**–**10** containing the six-membered ring regardless of the substituents on the Cp rings. Full methyl substitution, however, leads to the complexes **11**–**13** that contain the four-membered MS_3 ring. It is important to note that regardless of the conditions or the polysulfur anion used only these products were isolated. The preparative routes to **4** and **11** were the same but the resulting ring sizes differ. Kopf has noted a similar selectivity in that the reactions of Cp_2TiCl_2 with Na_2S_x (x = 2–7)[14] and the treatment of $Cp_2Ti(SH)_2$ with sulfenyl chlorides S_xCl_2 (x = 1–3) in the presence of pyridine[30] gave only Cp_2TiS_5. The latter is also formed via treatment of **1** with elemental sulfur[24] and by photolysis of Cp_2TiR_2 where R = CH_3 and CH_2Ph in the presence of elemental sulfur.[31,32] Selectivity of ring size is also observed in reaction of Cp_2TiCl_2 with group 5 elements. Metallacyclophosphines of the type $Cp_2M(PR)_3$, where M = Ti, Zr, and Hf and R = Me, Et, t-Bu, and Ph, have been prepared according to eq 7, where M′ = Li, Na,


(7)

$$Cp_2MCl_2 + M'_2(PR)_n \longrightarrow Cp_2M(PR)_3 + 2M'Cl + (PR)_{n-3} \quad (7)$$

and K and n = 2–5.[33,34] A similar reaction with $K_2(AsEt)_x$ gave only $Cp_2Ti(AsEt)_3$ whether x = 2 or 5.[35] On the other hand the complexes $Cp_2Ti(CH_2)_x$, where x = 3–5,[36,37]

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(28) Harvey, P.; Butler, I. S.; McCall, J. M.; Shaver, A., manuscript in preparation.

(29) Abel, E. W.; Booth, M.; Orrell, K. G. *J. Organomet. Chem.* **1978**, *160*, 75–79.

(30) Köpf, H. *Chem. Ber.* **1969**, *102*, 1509–1512.

(31) Samuel, E.; Giannotti, C. *J. Organomet. Chem.* **1976**, *113*, C17–C18.

(32) The analogous reaction of Cp_2ZrMe_2 gave a yellow product that lost sulfur during recrystallization or sublimation.[31] The reported ^1H NMR spectrum is consistent with the absence of methyl groups displaying only a single peak at δ 6.38 corresponding to Cp protons. This chemical shift does not agree with that found for **5** (δ 6.20).

(33) Issleib, K.; Wille, G.; Krech, F. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 527.

(34) Köpf, H.; Voigtländer, R. *Chem. Ber.* **1981**, *114*, 2731–2743.

(35) Köpf, H.; Görges, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 1205–1207.

(36) Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7358–7361.

(37) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529–6536.

Table I. $\Delta G^{\ddagger}$ Values (kJ mol^{-1}) for Ring Inversion of the Complexes 4-16[a]

complex	$\Delta G^{\ddagger}$	complex	$\Delta G^{\ddagger}$
Cp_2TiS_5 (**4**)	76.3[29]	Cp_2TiSe_5 (**14**)	>76.5
Cp_2ZrS_5 (**5**)	48.6	Cp_2ZrSe_5 (**15**)	49.9
Cp_2HfS_5 (**6**)	58.0	Cp_2HfSe_5 (**16**)	61.6
$(MeCp)_2TiS_5$ (**7**)	75.6	$(Me_5Cp)_2TiS_3$ (**11**)	40.6
$(Me_3SiCp)_2TiS_5$ (**8**)	82.0	$(Me_5Cp)_2ZrS_3$ (**12**)	39.3
$CH_2Cp_2TiS_5$ (**9**)	66.5	$(Me_5Cp)_2HfS_3$ (**13**)	<30
$Pt(S_5)_3{}^{2-}$	50.5[41]		

[a] Table II, an expanded version of Table I, is included in the supplementary material. It contains information on the solvents, chemical shifts, coupling constants, slow-exchange limiting temperatures, coalescence temperatures, and details of the DNMR analysis.

$Cp_2Zr(CH_2)_4$,[37] $(Me_5Cp)_2M(CH_2)_4$, where M = Ti[37] and Zr,[38] and $Cp_2Ti(SiPh_2)_4$[39] were prepared from the appropriate lithium salts.

The constitution of the lithium polysulfide solutions used to obtain the metallacyclopolysulfanes reported here is important with respect to the MS_x ring size "selected" by these complexes. The reactions of alkylating agents with Li_2S and Li_2S_2 prepared in situ gave only the organic sulfides and disulfides, respectively.[11a] However, the products from the reaction of a Li_2S_3 solution with Ph_2CHBr or $PhCH_2Br$ were consistent with disproportionation of Li_2S_3 to Li_2S_x (x = 2–5) prior to reaction.[11a] Our results indicate that solutions of Li_2S_5 can supply a similar range of polysulfide dianions.

The isolation of complexes **7**–**10** indicates that substitution of the Cp ring has no apparent effect on the final ring size. Only when both Cp rings are permethylated does the ring size contract. The Me_5Cp ring is much bulkier than the Cp ring but it is difficult to predict how this might affect the ring size. Certainly a good deal of crowding exists in the coordination sphere of **11**.[15b] However, the increase in electron density at the metal upon permethylation of the Cp rings[40] may be the factor that most determines the size of the MS_x ring. Recently, the complex $(Me_5Cp)_2VS_2$[8a] was reported, whereas the parent complex is Cp_2VS_5.[5,21b] The complexes Cp_2MS_4, where M = Mo and W, are d^2 systems as compared to the d^0 system in the compounds Cp_2MS_5, where M = Ti, Zr, and Hf. Thus, there may be an inverse relationship between the size of the MS_x ring isolated and the electron density at the metal in compounds of this type.

The variable-temperature ^1H NMR spectra of **4**–**9** and **14**–**16** are consistent with ME_5 ring flipping. The barriers follow the order Ti > Hf > Zr for E = S and Se with those for the selenanes being slightly greater than those for the sulfanes. The barrier for inversion of one PtS_5 chair in $Pt(S_5)_3{}^{2-}$ is 50.5 ± 1.3 kJ mol^{-1} [41] which is close to those found for Cp_2MS_5, where M = Zr and Hf, but lower than that for M = Ti. The structures of **4**–**6** are very similar, and the reason for the relatively high values for the titanium compounds is not obvious. However, it is interesting to note that the mean M–S bond lengths in the complexes Cp_2MS_5 increase in the order Ti < Hf < Zr and the S–M–S bond angles also increase in the same order.[22] While the CH_3 substituent in **7** has a shielding effect[42,43] and the Me_3Si group in **8** has a deshielding effect,[44] the barriers for these complexes are similar to that of **4**. On the other hand "tying-back" the Cp rings with a bridging methylene group, as in **9**, significantly lowers the barrier. The Cp–Ti–Cp angle in $CH_2Cp_2TiCl_2$ (121°[45]) is smaller than in Cp_2TiCl_2 (131°[46]). This should lead to a reduction of the ring carbon to sulfur interactions observed[21] in **4**. The Cp ligand occupies the axial position in the structure of $CpCo(PMe_3)S_5$[47] despite the fact that its cone angle (ca. 136°) is larger than that of PMe_3 (118°[48]). These observations are consistent with an attractive interaction between axial Cp groups and MS_5 rings although the origin of such a effect is not obvious. The ^1H NMR spectrum of $(Me_5Cp)CpTiS_5$ was unchanged from −101 to 124 °C. This is consistent with two possibilities, namely, that the molecule is locked in one conformation over this temperature range or that the TiS_5 ring is flipping rapidly on the NMR times scale even at −101 °C. The high barriers found for the other complexes containing TiS_5 rings argue against the latter possibility. Thus the molecule appears to be fixed in a chair conformation. The data, however, cannot assign the position of either ring with respect to being axial or equatorial.

The variable-temperature NMR results for the MS_3 complexes **11**–**13** are consistent with the occurrence of two processes. The TiS_3 ring of **11** is highly puckered,[15b] and the two Me_5Cp rings are inequivalent; thus, the observation of only one peak in the room-temperature spectrum is consistent with rapid ring inversion. Cooling slows the exchange and the spectrum displays two peaks; however, at very low temperatures further collapse occurs. This may be due to the slowing of the rotation of the Me_5Cp rings. The crystal structure of $(Me_5Cp)_2TiS_3$ indicated a possible steric interaction between the central sulfur atom and the pseudoaxial Me_5Cp group. In both **11** and **12** the peak to higher field broadens most rapidly with a concurrent reduction in intensity. On this basis the peak to higher field is assigned to the pseudoaxial Me_5Cp ligand. While the barriers to MS_3 ring inversion in complexes **11**–**13** are similar, for **11** the broadening of the upfield signal occurs at a much higher temperature than for **12**. This observation is consistent with the greater congestion anticipated for the titanium complex.[49] Interactions of a similar nature have been proposed in complexes of the type $Cp_2M(PR)_3$, where M = Ti, Zr, and Hf and R = alkyl or aryl.[50]

By analogy to the ME_5 systems and dithiolene complexes[51-53] of Cp_2Ti^{IV}, the exchange of the Me_5Cp ring environments in **11**–**13** is consistent with simple ring flipping. However, a weak bonding interaction between the titanium atom and the central sulfur atom could not be ruled out.[15b] Thus, it is interesting to note that the NMR data is also consistent with rotation of the $S_3{}^{2-}$ ligand

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(38) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716–2724.

(39) Holtman, M. S.; Schram, E. P. *J. Organomet. Chem.* **1980**, *187*, 147–155.

(40) (a) Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, *2*, 1470–1472. (b) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1983**, *105*, 6188–6189.

(41) Riddell, F. G.; Gillard, R. D.; Wimmer, F. L. *J. Chem. Soc., Chem. Commun.* **1982**, 332–333.

(42) Martin, H. A.; van Gorkom, M.; de Jongh, R. O. *J. Organomet. Chem.* **1972**, *36*, 93–100.

(43) Rosenblum, M. "Chemistry of the Iron Group Metallocenes"; Wiley: New York, 1965; p 44.

(44) Lappert, M. F.; Pickett, C. J.; Riley, P. I.; Yarrow, P. I. W. *J. Chem. Soc., Dalton Trans.* **1981**, 805–813.

(45) Smith, J. A.; von Seyerl, J.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *173*, 175–185.

(46) Clearfield, A.; Warner, D. K.; Saldarriaga-Molina, C. H.; Ropal, R.; Bernal, I. *Can. J. Chem.* **1975**, *53*, 1622–1629.

(47) Burschka, D. H.; Leonhard, K.; Werner, H. *Z. Anorg. Allg. Chem.* **1980**, *464*, 30–36.

(48) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.

(49) McKenzie, T. C.; Sanner, R. D.; Bercaw, J. E. *J. Organomet. Chem.* **1975**, *102*, 457–466.

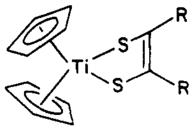
(50) Köpf, H.; Voightänder, R. *Chem. Ber.* **1981**, *114*, 2731–2743.

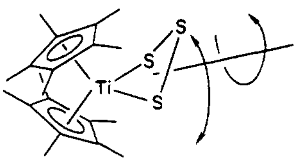
(51) Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947–3954.

(52) Köpf, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 134–135.

(53) Kutoglu, A. *Acta Crystallogr., Sect. B* **1973**, *29B*, 2891–2897.

about an axis through it and the titanium atom.





Experimental Section

Methods and Materials. Unless otherwise noted, all procedures were conducted under an atmosphere of nitrogen (Linde, prepurified) using conventional round-bottomed flasks and established inert-atmosphere bench-top techniques.[54] Solvents were dried and deoxygenated by distillation under nitrogen from the appropriate desiccant. All reactions generated compounds that were malodorous to varying degrees and consequently were conducted in a fume hood. This precaution was especially important in the syntheses of the selenium derivatives.

Titanium trichloride (Alfa, 98+%, H_2 reduced), titanium tetrachloride (J.T. Baker, purified), zirconium tetrachloride (Alfa, reaction grade, 99.6%), and hafnium tetrachloride (Alfa) were used as received. Powdered selenium metal (99.5%) was obtained from Anachemia. The metallocene dichlorides Cp_2MCl_2, where M = Ti, Zr (Alfa), and Hf (Strem) were used as received, as was $CpTiCl_3$(Strem). The substituted metallocene dichlorides $(MeCp)_2TiCl_2$,[44,55] $(Me_3SiCp)_2TiCl_2$,[44] and $CH_2Cp_2TiCl_2$[56] were prepared according to published procedures[57,58] with minor modifications. The compound $CH_2Cp_2TiCl_2$ could not be purified by the literature method, and the crude product was used in subsequent reactions. Literature procedures gave $Cp(Me_5Cp)TiCl_2$[59] and $(Me_5Cp)_2MCl_2$, where M = Ti,[60,61] Zr,[62] and Hf.[63]

Hydrogen sulfide gas (Linde) was dried by passing it through a short column of calcium chloride prior to use. Effluent vapors were passed through three scrubbing towers containing (1) 5 M aqueous sodium hydroxide, (2) saturated aqueous lead acetate, and (3) 5 M aqueous sodium hydroxide before venting into an efficient fume hood.

Solutions of lithium polysulfides[11a] or polyselenides[11b] were prepared as follows: Super Hydride (Aldrich, 1 M in THF) was slowly added by syringe to stirred sulfur powder (or a stirred suspension in a small volume of THF) or to gray selenium powder. The resulting exothermic effervescent reaction was stirred for ca. 20 min. before a solution of the metallocene dichloride was added dropwise. In most cases the final molar ratio of the reactants was metallocene dichloride/$LiEt_3BH$/sulfur = 1:2:5. In the preparations of the MS_3 complexes the sulfur was in excess and was isolated later in the workup.

Physical and Analytical Measurements. ^1H NMR spectra were recorded by using a Varian T-60 or T-60A, a Bruker WH-90, or a Varian XL-200 instrument. Routine spectra were recorded at 35 °C (T-60, T-60A) or 23 °C (XL-200). All ^1H chemical shifts (δ, ppm) are reported relative to internal tetramethylsilane unless otherwise noted and are considered accurate to ±0.05 ppm (T-60, T60A) and ±0.005 ppm (WH-90, XL-200). Deuterated chlorinated solvents were dried over type 4A molecular sieves. Other NMR solvents were used as received from Merck, Sharp and Dohme Canada Ltd. Air-sensitive samples were dissolved and transferred under nitrogen to a NMR tube that had been previously evacuated and filled with nitrogen. Variable-temperature ^1H NMR experiments were conducted on a Varian XL-200 spectrometer except for those studies of the complexes Cp_2MS_5, where M = Zr and Hf, which were done on the Bruker WH-90. Variable-temperature controllers calibrated with methanol and ethylene glycol gave temperatures that are considered accurate to ±0.5 °C. The coalescence temperatures were estimated visually from the recorded spectra and are probably accurate to within ±3 K of their true values. This was taken into account in the estimation of error limits for the calculated ΔG^* values.

Infrared spectra of samples prepared as KBr disks were recorded on a Perkin-Elmer 297 spectrometer. All band positions are reported relative to the 1601 cm^{-1} peak of polystyrene. Visible spectra in the 400–700 nm region were recorded on a Cary 17 instrument.

Mass spectra were recorded on a Hewlett-Packard HP 5980A [$(MeCp)_2TiS_5$ and $(Me_5Cp)_2HfS_3$], and an LKB 9000 (for all compounds) spectrometer operating at 70 eV and using direct sample inlet. The reported m/z value for a metal-containing species corresponds to the principal ion of the parent ion cluster unless otherwise stated.

Elemental analyses were performed by Midwest Microlab, Ltd., Indianapolis, IN, Guelph Chemical Laboratories, Guelph, Ontario, or Galbraith Laboratories, Inc., Knoxville, TN. In some instances poor analytical results were obtained despite repeated recrystallizations and submission of samples to more than one analytical company. Such discrepancies have been noted for other cyclopentadienyl metal complexes with sulfur-containing ligands[64,65] and with (polysulfane)platinum complexes.[66] Solution molecular weights were determined by Spang Microanalytical Laboratory, Eagle Harbour, MI. Melting points were determined for samples sealed in air in capillary tubes on a Thomas-Hoover melting point apparatus and are uncorrected.

Preparations. Bis(η-cyclopentadienyl)bis(hydrosulfido)titanium(IV), $Cp_2Ti(SH)_2$ (1). A red solution of Cp_2TiCl_2 (6.04 g, 24.3 mmol) in THF (500 mL) was treated with H_2S for 10 min. Slow addition of Et_3N (6.90 mL, 49.6 mmol) caused the solution to darken. Hydrogen sulfide was passed through the solution for 90 min. In order to remove excess H_2S, nitrogen gas was bubbled through the red-black solution for 30 min. Rapid filtration in air through Celite followed by washing the filter cake with THF (4 × 10 mL) gave a red-black solution while an off-white insoluble residue remained on the fritte. The combined filtrate and washings were stripped to dryness by rotary evaporation, and the malodorous brown powder (5.55 g, 93%; decomp ca. 130 °C) (lit.[12] decomp 150–160 °C) was dried by pumping on it overnight. Since excessive loss of compound occurred during recrystallization, the crude product was the analytical sample and was used in all subsequent reactions: ^1H NMR ($CDCl_3$) δ 6.28 (s, 10 H, C_5H_5), 3.38 (s, 2 H, SH); IR ν(SH) 2530 (w) cm^{-1} (KBr); mass spectrum, m/z (relative intensity) $M^{+\cdot}$, 244 (3.8); Visible spectrum, maximum (CH_2Cl_2) 476 nm (ϵ 3.0 × 10^3 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{10}H_{12}S_2Ti$: C, 49.18; H, 4.95; S, 26.26. Found: C, 49.97; H, 5.18; S, 23.18; 23.41.

Bis(η-cyclopentadienyl)bis(hydrosulfido)zirconium(IV), $Cp_2Zr(SH)_2$ (2), and 1,3-Bis[bis(η-cyclopentadienyl)zircona(Zr^{IV})]cyclotetrasulfane,[67] $(Cp_2ZrS)_2$ (3). A solution of

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[54] Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969.

[55] Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6422–6433.

[56] Katz, T. J.; Acton, N.; Martin, G. *J. Am. Chem. Soc.* **1973**, *95*, 2934–2939.

[57] Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1156–1160.

[58] Schaltegger, H.; Nuenschwander, M.; Meuche, D. *Helv. Chim. Acta* **1965**, *48*, 955–961.

[59] Nesmeyanov, A. N.; Nogina, O. V.; Dubovitskii, V. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, 527.

[60] Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219–1238.

[61] Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087–5095.

[62] Manriquez, J. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 6229–6230.

[63] Fryzuk, M. D.; Seidler, P. R.; Bercaw, J. E. "Abstracts of Papers", 63rd Canadian Chemical Conference, Ottawa, Ontario, May 1980; The Chemical Institute of Canada: Ottawa, Ontario, 1980; IN 46.

[64] Coutts, R. S. P.; Surtees, J. R.; Swan, J. M.; Wailes, P. C. *Aust. J. Chem.* **1966**, *19*, 1377–1380.

[65] Hartgerink, J. M.Sc. Thesis, McGill University, Montreal, Quebec, 1981.

[66] Gillard, R. D., private communication, Apr 1984.

[67] The IUPAC convention for polysulfur compounds is that they be named polysulfanes.[68] When extended to metal–polysulfur rings, the use of sulfane terminology presents an improvement over current nomenclature that fails to distinguish between three different cases: (i) covalently bound organopolysulfanes, (ii) polysulfur chelates, S_x^{2-}, and (iii) species such as the tetrathiomolybdate dianion MoS_4^{2-}, which does not contain catenated sulfur but has a tetrahedral structure with four Mo–S bonds. Thus, Cp_2TiS_5, may be called "bis(cyclopentadienyl)titanacyclohexasulfane". The numerary prefix for sulfane refers to ring size rather than the number of sulfur atoms contained in it, as with metallacycloalkanes. Similarly, the recently synthesized[19] complex $Cp_2Ti(\mu\text{-}S_3)_2TiCp_2$ could be called "tetrakis(cyclopentadienyl)-1,5-dititanacyclooctasulfane". An alternative name might use "μ-trisulfane" to describe the bridge.

Cp_2ZrCl_2 (4.38 g, 15.0 mmol) in THF (130 mL) was treated with H_2S for about 10 min followed by slow addition of Et_3N (4.20 mL, 30.2 mmol). After being stirred for 1 h, the slurry was filtered and the filter cake was washed with 20 mL of solvent. Removal in vacuo of the volatiles from the clear yellow filtrate gave a yellow-green microcrystalline solid. This was recrystallized from THF (−20 °C) to give large yellow-green crystals of $Cp_2Zr(SH)_2$ (2; 1.70 g, 45%; decomp 45 °C). Concentrating the mother liquors gave additional 2 (0.26 g). Refluxing the mother liquors for 4 h followed by cooling (−20 °C) gave turquoise microcrystals (3; 0.60 g, 16%; decomp 210–215 °C) contaminated by a few very small yellow crystals. For 2: ^1H NMR ($CDCl_3$) δ 6.28 (s, 10 H, C_5H_5), 1.94 (s, 2 H, SH); IR ν(SH) 2550 (br, vw) cm^{-1} (KBr); mass spectrum, m/z (relative intensity), the mass spectrum was consistent with the presence of a small amount of $(Cp_2ZrS)_2$ and possibly $(Cp_2Zr)_2OS$; however, a molecular ion was observed at m/z 286 as well as the fragments $M^{+\cdot} - H\cdot - S\cdot$ (m/z 253) and $M^{+\cdot} - 2H\cdot - S\cdot$ (m/z 252). Anal. Calcd for $C_{10}H_{12}S_2Zr$: C, 41.77; H, 4.21; S, 22.30. Found: C, 42.17; H, 4.49; S, 21.72.

For 3: ^1H NMR ($CDCl_3$) δ 6.44 (s, C_5H_5); mass spectrum, m/z (relative intensity) $M^{+\cdot}$, 504 (47.9); visible spectrum, maximum (CH_2Cl_2) 594 nm (ϵ 70 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{10}H_{10}SZr$: C, 47.39; H, 3.98; S, 12.65. Found: C, 46.79; H, 4.26; S, 12.85.

Bis(η-cyclopentadienyl)titana(*Ti*^{IV})cyclohexasulfane, Cp_2TiS_5 (4). The preparation of 4 is typical of that of the other polysulfane and polyselenane complexes reported. A solution of lithium polysulfides (15.0 mmol of sulfur; 6.0 mmol of $LiEt_3BH$) was treated dropwise with a THF (75 mL) solution of Cp_2TiCl_2 (3.0 mmol) and stirred at room temperature overnight to give a deep red solution. The volatiles were removed in vacuo, and the residue was extracted with CH_2Cl_2 (100 mL). Filtration through Celite and removal of the solvent by rotary evaporation gave the product as dark red microcrystals (0.994 g, 98%). The crude product was pure by TLC and was the analytical sample: mp 196–198 °C (lit.[24] mp 201–202 °C); ^1H NMR ($CDCl_3$) δ 6.32 (s, 5 H, C_5H_5), 6.03 (s, 5 H, C_5H_5); mass spectrum, m/z (relative intensity) $M^{+\cdot}$, 338 (24.2); visible spectrum, maximum (CH_2Cl_2) 491 nm (ϵ 1.7 × 10^3 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{10}H_{10}S_5Ti$: C, 35.49; H, 2.98; S, 47.37. Found: C, 35.22; H, 3.34; S, 47.27.

Bis(η-cyclopentadienyl)zircona(*Zr*^{IV})cyclohexasulfane, Cp_2ZrS_5 (5). The reaction solution was filtered, concentrated, and cooled (−20 °) to crystallize excess sulfur, which was removed by filtration. The filtrate was dried in vacuo, extracted with toluene, and filtered. The residue, upon drying, was recrystallized (−20 °C) from a minimum of CH_2Cl_2 to give 5 as large orange crystals (1.12 g, 30%; decomp 165–170 °C): ^1H NMR ($CDCl_3$) δ 6.20 (s, C_5H_5); mass spectrum, m/z (relative intensity) $M^{+\cdot}$, 380 (12.3). Anal. Calcd for $C_{10}H_{10}S_5Zr$: C, 31.46; H, 2.64; S, 42.00; mol wt (CH_2Cl_2), 381.73. Found: C, 31.46; H, 2.98; S, 41.98; mol wt, 375.

Bis(η-cyclopentadienyl)hafna(*Hf*^{IV})cyclohexasulfane, Cp_2HfS_5 (6). Complex 6 was recrystallized from CH_2Cl_2 (0.33 g, 53%; decomp 150–155 °C). Satisfactory elemental analysis could not be obtained despite recrystallization and the submission of the X-ray structural analysis crystals:[22] ^1H NMR ($CDCl_3$) δ 6.18 (s, C_5H_5), minor impurity δ 6.23; mass spectrum, m/z (relative intensity) $M^{+\cdot}$, 470 (10.8). Anal. Calcd for $C_{10}H_{10}HfS_5$: C, 25.61; H, 2.15; S, 34.18. Found: C, 22.37, 24.93; H, 2.56, 2.42; S, 34.23, 33.27.

Bis(η-methylcyclopentadienyl)titana(*Ti*^{IV})cyclohexasulfane, $(MeCp)_2TiS_5$ (7). Recrystallization from CH_2Cl_2/pentane at −20 °C gave 7 (0.566 g, 85%; mp 171–172 °C) (lit.[20] decomp 200 °C): ^1H NMR (toluene-d_8, 200 MHz) δ 5.62 (t, 2 H, J = 2.6 Hz, C_5H_4), 5.59 (t, 2 H, J = 2.6 Hz, C_5H_4), 5.45 (t, 2 H, J = 2.6 Hz, C_5H_4), 5.32 (t, 2 H, J = 2.6 Hz, C_5H_4), 1.97 (s, 3 H, Me), 1.65 (s, 3 H, Me); mass spectrum, m/z (relative intensity) $M^{+\cdot}$, 366 (10.2); visible spectrum, maximum (CH_2Cl_2) 488 nm (ϵ 1.9 × 10^3 L mol^{-1} cm^{-1}), 434 (sh, 1.0 × 10^3). Anal. Calcd for $C_{12}H_{14}S_5Ti$: C, 39.33; H, 3.85; S, 43.75. Found: C, 38.96; H, 4.10; S, 43.92.

Bis(η-(trimethylsilyl)cyclopentadienyl)titana(*Ti*^{IV})-cyclohexasulfane, $(Me_3SiCp)_2TiS_5$ (8). The compound was recrystallized from hexanes at −20 °C to give deep red crystals (0.31 g, 64%; mp 106–107 °C): ^1H NMR (toluene-d_8, 200 MHz) δ 6.09 (t, 2 H, J = 2.4 Hz, C_5H_4), 6.04 (t, 2 H, J = 2.4 Hz, C_5H_4), 5.76 (overlapping pair of triplets, 4 H, J = 2.4 Hz, C_5H_4), 0.21 (s, 9 H, Me), 0.08 (s, 9 H, Me); mass spectrum, m/z (relative intensity) $M^{+\cdot} - S\cdot$, 418 (17.3); visible spectrum, maximum (CH_2Cl_2) 504 nm (ϵ 2.0 × 10^3 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{16}H_{26}S_5Si_2Ti$: C, 39.81; H, 5.43; S, 33.21. Found: C, 39.98; H, 5.83; S, 32.64.

1,1′-Methylenebis(η-cyclopentadienyl)titana(*Ti*^{IV})cyclohexasulfane, $CH_2Cp_2TiS_5$ (9). Chromatography on silica gel gave (1:2 hexanes/CH_2Cl_2) an orange band that gave red $CH_2Cp_2TiS_5$ (0.030 g, 9%; decomp ca. 180 °C) upon evaporation to dryness: ^1H NMR (toluene-d_8, 200 MHz) δ 6.51 (s, br, 2 H, C_5H_4), 6.30 (s, br, 2 H, C_5H_4), 4.71 (s, br, 2 H, C_5H_4), 4.28 (s, br, 2 H, C_5H_4), 2.53 (s, 2 H, CH_2); mass spectrum, m/z (relative intensity) $M^{+\cdot}$, 350 (9.6). Anal. Calcd for $C_{11}H_{10}S_5Ti$: C, 37.70; H, 2.89; S, 45.75. Found: C, 39.69; H, 3.13; S, 41.57. Calcd for $C_{11}H_{10}S_5Ti\cdot{}^1/_5CH_2Cl_2\cdot{}^1/_4C_6H_{14}$: C, 39.22; H, 3.60; S, 41.22. The appropriate amounts (integration) of both methylene chloride and hexanes were observed in the ^1H NMR spectrum.

(η-Cyclopentadienyl)(η-pentamethylcyclopentadienyl)titana(*Ti*^{IV})cyclohexasulfane, $Cp(Me_5Cp)TiS_5$ (10). The analytical sample was recrystallized from hot (1:1) hexanes/toluene to give irregular needles (0.058 g, 92%; mp 212–213 °C); ^1H NMR ($CDCl_3$) δ 5.90 (s, 5 H, C_5H_5), 2.05 (s, 15 H, C_5Me_5); mass spectrum, m/z (relative intensity) $M^{+\cdot}$, 408 (2.5); visible spectrum, maximum (CH_2Cl_2) 476 nm (ϵ 1.4 × 10^3 L mol^{-1} cm^{-1}), 445 (1.4 × 10^3). Anal. Calcd for $C_{15}H_{20}S_5Ti$: C, 44.10; H, 4.93; S, 39.94. Found: C, 44.15; H, 4.88; S, 28.85, 29.57, 35.51.

Bis(η-pentamethylcyclopentadienyl)titana(*Ti*^{IV})cyclotetrasulfane, $(Me_5Cp)_2TiS_3$ (11). Powdered sulfur (0.160 g, 5.00 mmol), Super Hydride (2.0 mmol), and $(Me_5Cp)_2TiCl_2$ (0.399 g, 1.00 mmol) were combined as for 4 and refluxed for 10.5 h. The volatiles were removed in vacuo, and the residue was extracted with CH_2Cl_2 (2 × 25 mL plus 2 × 10 mL) and filtered through Celite. Removal of the solvent from the purple filtrate gave the product as a black microcrystalline solid (sole product by ^1H NMR). Recrystallization from THF/pentane at −20 °C gave black crystals (0.228 g, 55%; mp 149–152 °C). The moderate yield is in part due to the high solubility of the compound. Crystals suitable for X-ray structure determination were grown from CH_2Cl_2/pentane at −20 °C: ^1H NMR ($CDCl_3$) δ 1.83 (s, C_5Me_5); mass spectrum, m/z (relative intensity) $M^{+\cdot}$, 414 (25.2); visible spectrum, maximum (CH_2Cl_2) 504 nm (ϵ 5.2 × 10^2 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{20}H_{30}S_3Ti$: C, 57.95; H, 7.29; S, 23.20; mol wt (CH_2Cl_2), 414.55. Found: C, 57.43; H, 7.40; S, 22.83; mol wt, 407.

Bis(η-pentamethylcyclopentadienyl)zircona(*Zr*^{IV})cyclotetrasulfane, $(Me_5Cp)_2ZrS_3$ (12). The orange CH_2Cl_2 extract was concentrated to 5 mL and cooled (−20 °C) to give 0.246 g of deep orange crystals, mp 182–185 °C. The mother liquor was evaporated to dryness in vacuo, and the residue was recrystallized from hexanes to give 0.101 g of orange microcrystals for a combined yield of 0.347 g (76%): ^1H NMR ($CDCl_3$) δ 1.87 (s, C_5Me_5); mass spectrum, m/z (relative intensity) $M^{+\cdot}$, 456 (92.5). Anal. Calcd for $C_{20}H_{30}S_3Zr$: C, 52.46; H, 6.60; S, 21.01; mol wt (CH_2Cl_2), 457.87. Found: C, 52.18; H, 6.78; S, 21.04; mol wt, 439.

Bis(η-pentamethylcyclopentadienyl)hafna(*Hf*^{IV})cyclotetrasulfane, $(Me_5Cp)_2HfS_3$ (13). The reaction residue was extracted and the solution filtered to give, upon evaporation, a light orange solid (0.077 g contaminated with sulfur (TLC)). This was recrystallized from CH_2Cl_2 to give the product as an orange solid (0.015 g, 9%; mp 169–173 °C). As with Cp_2HfS_5 a satisfactory analysis was not obtained. The product was pure in the NMR spectrum, had an infrared spectrum identical with 11 and 12, and gave a molecular ion peak as the most intense in the mass spectrum: ^1H NMR ($CDCl_3$) δ 1.92 (s, C_5Me_5); mass spectrum, m/z (relative intensity) $M^{+\cdot}$, 546 (100.0). Anal. Calcd for $C_{20}H_{30}HfS_3$: C, 44.07; H, 5.55; S, 17.65. Found: C, 42.77; H, 5,83; S, 13.88.

Bis(η-cyclopentadienyl)titana(*T*^{IV})cyclohexaselenane, Cp_2TiSe_5 (14). Powdered gray selenium (1.182 g, 14.97 mmol) was treated with Super Hydride (6.0 mL of a 1 M solution of $LiEt_3BH$ in THF, 6.0 mmol) to give a brown solution of lithium polyselenides. A suspension of Cp_2TiCl_2 (0.746 g, 3.00 mmol) in THF (50 mL) was added dropwise. The color of the reaction

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(68) Leoning, K. L. In "Sulfur in Organic and Inorganic Chemistry"; Senning, A., Ed.; Marcel Dekker: New York, 1972; Vol. 3, pp 339–354.

mixture became purple. The reaction mixture was stirred at ambient temperature for 4.75 h. Removal of the volatiles in vacuo gave a black residue that was extracted with CH_2Cl_2 (6 × 50 mL plus 2 × 100 mL) and filtered through Celite. The purple filtrate was concentrated in vacuo to ca. 50 mL and stored at −20 °C overnight. Air-stable purple crystals of **14** were collected by filtration from successive concentration of the mother liquors (1.227 g, 72%). The product foamed without melting at 209–211 °C (lit.[24] mp 211 °C): ^1H NMR ($CDCl_3$) δ 6.34 (s, 5 H, C_5H_5), 5.92 (s, 5 H, C_5H_5); mass spectrum, *m/z* (relative intensity) $M^{+\cdot}$, 574 (2.4). Anal. Calcd for $C_{10}H_{10}Se_5Ti$: C, 20.97; H, 1.76. Found: C, 21.13; H, 1.77.

Bis(η-cyclopentadienyl)zircona(*Zr*^{IV})cyclohexaselenane, Cp_2ZrSe_5 (15). Evaporation of the CH_2Cl_2 extract in vacuo gave the product as a brick-red microcrystalline solid (1.55 g, 50%). The analytical sample was recrystallized from CH_2Cl_2 at −20 °C in an aluminum foil wrapped vessel and was obtained as orange flakes that decomposed without melting at 135–140 °C: ^1H NMR ($CDCl_3$) δ 6.15 (s, C_5H_5); mass spectrum, *m/z* (relative intensity) $M^{+\cdot}$, 618 (1.5). Anal. Calcd for $C_{10}H_{10}Se_5Zr$: C, 19.49; H, 1.64. Found: C, 19.47; H, 1.66.

Bis(η-cyclopentadienyl)hafna(*Hf*^{IV})cyclohexaselenane, Cp_2HfSe_5 (16). The product was crystallized from the CH_2Cl_2 extract to give an orange microcrystalline solid (0.355 g, 52%; decomp 130 °C): ^1H NMR ($CDCl_3$) δ 6.08 (s, C_5H_5); mass spectrum, *m/z* (relative intensity) $M^{+\cdot}$, 704 (1.9). Anal. Calcd for $C_{10}H_{10}HfSe_5$: C, 17.07; H, 1.43. Found: C, 17.14; H, 1.51.

Bis(η-cyclopentadienyl)titana(*Ti*^{IV})-2,6-dithiacyclohexane, $Cp_2Ti[S(CH_2)_3S]$ (17). To a stirred THF solution (40 mL) of 1,3-propanedithiol (0.50 mL, 5.0 mmol) was added methyllithium (5.5 mL of a 1.8 M ether solution, 9.9 mmol) slowly by syringe. Stirring was continued for 2 h after which all volatiles were removed in vacuo. A suspension of Cp_2TiCl_2 (1.233 g, 4.95 mmol) in THF (70 mL) was added dropwise to the solid dilithium salt in an exothermic reaction to give a deep purple mixture that was stirred for 2.75 h. Removal of the solvent in vacuo gave a purple residue. The product may be isolated by extraction at ambient temperature with CH_2Cl_2 or, more efficiently, by using a Soxhlet apparatus. The solvent was removed from the purple extract by rotary evaporation until the onset of crystallization whereupon cooling at −20 °C overnight gave the product as small, deep purple needles (0.531 g, 38%; mp 207–208 °C dec): ^1H NMR ($CDCl_3$) δ 6.11 (s, 10 H, C_5H_5), 3.08 (t, 4 H, J = 6.0 Hz, CH_2), 1.93 (quintet, 2 H, J = 6.0 Hz, CH_2); mass spectrum, *m/z* (relative intensity) $M^{+\cdot}$, 284 (59.2). Anal. Calcd for $C_{13}H_{16}S_2Ti$: C, 54.92; H, 5.67; S, 22.56; mol wt ($CHCl_3$), 284.30. Found: C, 52.89; H, 5.66; S, 21.73; mol wt, 281. Calcd for $C_{13}H_{16}S_2Ti\cdot{}^1/_6CH_2Cl_2$: C, 53.02; H, 5.52; S, 21.49. The appropriate amount of methylene chloride was observed in the ^1H NMR spectrum.

Reaction of $Cp_2Ti(SH)_2$ with 1,1′-Thiobisbenzimidazole. The compound 1,1′-thiobisbenzimidazole,[9] (Bz–S–Bz) (0.545 g, 2.05 mmol), was suspended in toluene (20 mL) and treated dropwise with a suspension of **1** (0.500 g, 2.04 mmol) in toluene (50 mL). After the solution was stirred for 3 h at room temperature, all volatiles were removed in vacuo. The residue was extracted with CH_2Cl_2 (2 × 20 mL) and the extracts were filtered. The filtrate was evaporated to dryness to give a black residue. This was dissolved in CH_2Cl_2 and chromatographed on Florisil. Toluene eluted a red band that was evaporated in vacuo to give **4** (0.147 g, 64% based on Bz–S–Bz). Elution with 1:1 toluene/CH_2Cl_2 gave a blue band (strongly overlapped by the red band due to **4**). The fractions in which the blue product was most highly concentrated (TLC) were collected and reduced in volume to about 5 mL whereupon a dark solid began to precipitate. Cooling at −20 °C for 11 h gave a dark blue solid (0.0023 g, 1% based on Bz–S–Bz) which was free of **4** (TLC). The blue product was identified as 1,5-$(Cp_2TiS_3)_2$ by comparison of its color, ^1H NMR spectrum, and electronic spectrum with those reported in the literature.[19]

Reaction of $Cp_2Zr(SH)_2$ with Sulfur. Toluene (50 mL) was added to an ice-cold solid mixture of **2** (0.64 g, 2.2 mmol) and sulfur (0.51 g, 16 mmol). The mixture was stirred for 4 h during which time it was allowed to warm to ambient temperature. The mixture was filtered and its volume reduced in vacuo and cooled at −20 °C. The product consisted of a mixture of small orange and large pale yellow crystals. The yellow product was sulfur by TLC and the orange crystals (0.104 g, 12%) were subsequently identified as **5** by its NMR spectrum.

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Supplementary Material Available: Table II and DNMR spectral assignments for **7**, **8**, **9**, and $Cp_2Ti[S(CH_2)_3S]$ (5 pages). Ordering information is given on any current masthead page.