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Reactions of Bis(cyclopentadienyl)- and Bis(pentamethylcyclopentadienyl)titanium and Bis(cyclopentadienyl)- and Bis(pentamethylcyclopentadienyl)zirconium Dicarbonyls with Water and Dihydrogen Sulfide: Evolution of Dihydrogen and Formation of Oxo or Sulfido Monomers, Dimers, or Clusters

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The reaction between H_2O and $Cp_2Ti(CO)_2$ ($Cp = \eta^5\text{-}C_5H_5$) gave $Cp_6Ti_6O_8$ in quantitative yield. On reaction with H_2O, $Cp_2Zr(CO)_2$ yielded only ZrO_2. There was no reaction between H_2O and $Cp^*{}_2M(CO)_2$ ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$; M = Ti, Zr). The reaction between H_2S and $Cp_2Ti(CO)_2$ gave the cluster $Cp_5Ti_5S_6$; from the reaction between H_2S and $Cp^*{}_2Ti(CO)_2$, $Cp^*{}_2Ti(SH)_2$ was obtained. The reactions between H_2S and $Cp'_2Zr(CO)_2$ (Cp' = Cp or Cp*) gave $[Cp'_2Zr(\mu\text{-}S)]_2$. All reactions were conducted in toluene at 80 °C with the reagent and complex in a 1:1 mole ratio. In all cases the $Cp'_2M(CO)_2$ complex was oxidized with liberation of CO and concomitant reduction of H_2O or H_2S to H_2. The identity of all the products was determined, quantitatively and qualitatively, by a combination of analysis, spectroscopy, and X-ray diffraction. The crystal structures of $Cp^*{}_2Ti(SH)_2$ and $[Cp_2Zr(\mu\text{-}S)]_2$ are reported in detail. In $Cp^*{}_2Ti(SH)_2$ (a = 31.140 (6) Å, c = 8.350 (1) Å; space group $I4_1/a$; Z = 16; R = 0.038) the average Ti–S distance is 2.413 (3) Å and the S–Ti–S angle 94.8 (1)°. In $[Cp_2Zr(\mu\text{-}S)]_2$ (a = 8.391 (1) Å, b = 8.250 (1) Å, c = 13.668 (1) Å; β = 94.69 (1)°; space group $P2_1/n$, Z = 2; R = 0.040) the $Zr(\mu\text{-}S)_2Zr$ core is an almost exact square (Zr–S = 2.490 (3), 2.482 (3) Å; S–Zr–S = 89.6 (1)°; Zr–S–Zr = 90.4 (1)°).

Introduction

The chemistry of the group 4 metals titanium and zirconium is dominated by their tendency, especially in the oxidation state IV, to form strong bonds to "hard" ligands, particularly oxygen.[1] As a result many complexes of these metals are sensitive to water, and numerous investigations of the reactions between H_2O and Ti(IV) or Zr(IV) complexes have been made; those investigations involving Cp'_2M derivatives (Cp' = Cp or Cp*; $Cp = \eta^5\text{-}C_5H_5$; $Cp^* = \eta^5\text{-}C_5(CH_3)_5$; M = Ti, Zr) are relevant to the present work.[1-10] Two of these investigations included reactions between water and Cp'_2M derivatives in which the metal was in the oxidization state II.[2,3] Since these are particularly important to the present work they will be discussed in more detail.

In 1977 Coulton and co-workers obtained the octahedral cluster $Cp_6Ti_6O_8$ during the homogeneous hydrogenation of the carbon monoxide in $Cp_2Ti(CO)_2$.[2] These workers suggested that the source of the oxygen atoms in $Cp_6Ti_6O_8$ was water produced from H_2 and CO.[2] That this suggestion was correct was clear to one of us, who had reacted water with $Cp_2Ti(CO)_2$ and obtained a product which proved to be the blue $Cp_6Ti_6O_8$ at about the same time.[11] We were very interested in this reaction since it offered another route to the $(CpM)_m(\mu_3\text{-}O)_n$ clusters which we have been preparing from the reactions between nitrogen oxides and Cp_2M (M = V, Cr).[12,13] It also appeared likely that the reaction could be extended to the dihydrides of the heavier elements in group 16 and thus provide a route to $(CpM)_m(\mu_3\text{-}A)_n$ clusters (A = S, Se, or Te).

In their investigation of the reactions between water and $Cp^*{}_2Zr$ derivatives, Hillhouse and Bercaw found that $[Cp^*{}_2Zr(N_2)]_2(\mu\text{-}N_2)$ gave $[Cp^*{}_2Zr(H)]_2(\mu\text{-}O)$ (reaction 1),

$$[Cp^*{}_2Zr(N_2)]_2(\mu\text{-}N_2) + H_2O \rightarrow [Cp^*{}_2Zr(H)]_2(\mu\text{-}O) + 3N_2 \quad (1)$$

and this complex gave $Cp^*{}_2Zr(OH)_2$ and dihydrogen on further treatment with water (reaction 2).[3] They also

$$[Cp^*{}_2Zr(H)]_2(\mu\text{-}O) + 3H_2O \rightarrow 2Cp^*{}_2Zr(OH)_2 + 2H_2 \quad (2)$$

noted that $Cp^*{}_2Zr(CO)_2$ was inert to water.[3] We wished to explore the different behavior of Cp'_2Ti and Cp'_2Zr complexes in the oxidation state II and to extend the reactions to the heavier members of group 16. Whereas the metallacyclosulfanes Cp'_2MS_n are a very active area of research,[14-19] the only reactions of H_2S which have been explored are those with Cp_2MCl_2.[14,17,19]

We report here our investigations on the reactions of H_2O and H_2S with $Cp'_2M(CO)_2$. A brief report on the

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synthesis of $Cp_5Ti_5S_6$ from H_2S and $Cp_2Ti(CO)_2$ has appeared previously.[20]

Results

Reaction between H_2O and $Cp_2Ti(CO)_2$. There was a smooth reaction between H_2O and $Cp_2Ti(CO)_2$ in toluene solution at 80 °C over 72 h to give $Cp_6Ti_6O_8$. The stoichiometry of the reaction is given by reaction 3. As for

$$6Cp_2Ti(CO)_2 + 8H_2O \rightarrow Cp_6Ti_6O_8 + 5H_2 + 12CO + 6C_5H_6 \quad (3)$$

all the reactions described here, the reactants were initially in a 1:1 mole ratio and the amounts of H_2 and CO produced were determined quantitatively. Distillation of the liquid phase after reaction gave only toluene and C_5H_6, as judged by the NMR spectrum;[21] the C_5H_6 dimerized with time in the known manner.[22] The very air- and water-sensitive cluster $Cp_6Ti_6O_8$[2] was isolated in 80% yield; no other product containing titanium was observed. In this respect the mass spectrum of the product is very informative. We have shown elsewhere that the clusters $Cp_4Ti_4O_4$ and $Cp_5Ti_5O_6$ can be expected to exist.[23] Our experience with vanadium, for which we have prepared all three clusters ($Cp_4V_4O_4$, $Cp_5V_5O_6$ and $Cp_6V_6O_8$), is that any of the three can be detected by mass spectrometry and that the smaller clusters do not occur as fragments of the larger ones. The observation or nonobservations of a peak corresponding to a particular cluster is therefore clear evidence of its presence or absence. In the case of $Cp_6Ti_6O_8$ obtained by reaction 3, the mass spectrum showed neither $[Cp_5Ti_5O_6]^+$ (*m/e* 661) nor $[Cp_4Ti_4O_4]^+$ (*m/e* 516). The only possible additional products of the reaction are therefore involatile derivatives of $Cp_6Ti_6O_8$ with higher molecular weight (e.g., the titanium equivalents of $[Cp_5V_6O_8]_2(\mu\text{-}O)$ or $[Cp_5V_6O_8]_2(\mu\text{-}Cp_4V_4O_8)$[13]) or involatile organic compounds. However the weight of the evidence is that reaction 3 is quantitatively complete as written. There was no measurable reaction between H_2O and $Cp_2Ti(CO)_2$ at 20 °C.

Reactions between H_2O and $Cp_2Zr(CO)_2$, $Cp^*{}_2Ti(CO)_2$, or $Cp^*{}_2Zr(CO)_2$. The reaction between H_2O and $Cp_2Zr(CO)_2$ gave ZrO_2 as the only identifiable product which contained zirconium, regardless of the conditions of the reaction. The stoichiometry can be described by reaction 4, but the amount of H_2 evolved was always lower

$$Cp_2Zr(CO)_2 + 2H_2O \rightarrow ZrO_2 + H_2 + 2CO + 2C_5H_6 \quad (4)$$

than expected, and the infrared spectrum of the crude "ZrO_2" showed bands ascribable to ν(O–H) and/or ν(C–H) vibrations. Since the product was intractable this result was not pursued.

There was no reaction between water and $Cp^*{}_2Ti(CO)_2$ in toluene at temperatures up to 80 °C for periods of up to 7 days. Hillhouse and Bercaw reported the same unreactivity for $Cp^*{}_2Zr(CO)_2$.[3]

Reaction between H_2S and $Cp_2Ti(CO)_2$. There was a smooth reaction between H_2S and $Cp_2Ti(CO)_2$ in toluene at 80 °C over 72 h to give the moderately air-sensitive dark green-brown cluster $Cp_5Ti_5S_6$. The stoichiometry of the reaction was as in eq 5. However, although the ratios of

$$10Cp_2Ti(CO)_2 + 12H_2S \rightarrow 2Cp_5Ti_5S_6 + 7H_2 + 20CO + 10C_5H_6 \quad (5)$$

the gaseous products to each other and to the reactants and the yield of $Cp_5Ti_5S_6$ (73%) were as described by reaction 5, two caveats are necessary. The first is that the vile smell of the toluene solution after completion of the reaction testified eloquently to the presence of organic sulfur compounds; because of these compounds the amount of C_5H_6 produced could not be determined. The second caveat is that the mass spectrum of the $Cp_5Ti_5S_6$ produced showed traces of $Cp_6Ti_6S_8$ and perhaps $Cp_4Ti_4S_4$ as well as fragmentation patterns from $Cp_6Ti_6S_nO_{8-n}$ and $Cp_5Ti_5S_nO_{6-n}$. The substitution of O for S during the mass spectral analysis of $(Cp_2ZrS)_2$ has been observed elsewhere.[14] The other clusters were not evident in the molecular spectra or analytical data for $Cp_5Ti_5S_6$ (which was also characterized by X-ray diffraction[20]), but the mass spectrum indicates that (5) does not represent the reaction between H_2S and $Cp_2Ti(CO)_2$ completely. The reaction proceeded very slowly, but observably, at 20 °C.

Reaction between H_2S and $Cp^*{}_2Ti(CO)_2$. There was a smooth reaction between H_2S and $Cp^*{}_2Ti(CO)_2$ in toluene at 80 °C over 72 h to give $Cp^*{}_2Ti(SH)_2$. The stoichiometry of the reaction, as determined, is given by reaction 6. $Cp^*{}_2Ti(SH)_2$ was identified by X-ray diffraction

$$Cp^*{}_2Ti(CO)_2 + 2H_2S \rightarrow Cp^*{}_2Ti(SH)_2 + H_2 + 2CO \quad (6)$$

and spectroscopy. The properties of $Cp^*{}_2Ti(SH)_2$ were similar to those of $Cp_2Ti(SH)_2$ and $(\eta\text{-}C_5H_4CH_3)_2Ti(SH)_2$ which have been described previously.[14,17,19] No other product containing titanium was identified. In the solid state $Cp^*{}_2Ti(SH)_2$ was air-stable, but in solution it was quite rapidly oxidized, giving a yellow insoluble material.

Reaction between H_2S and $Cp_2Zr(CO)_2$ or $Cp^*{}_2Zr(CO)_2$. The reactions between H_2S and $Cp'_2Zr(CO)_2$ followed the same course at 80 °C in toluene over 72 h giving $[Cp'_2Zr(\mu\text{-}S)]_2$. The stoichiometry was as in reaction 7.

$$2Cp'_2Zr(CO)_2 + 2H_2S \rightarrow [Cp'_2Zr(\mu\text{-}S)]_2 + 2H_2 + 4CO \quad (7)$$

The yield of $[Cp_2Zr(\mu\text{-}S)]_2$ was 79% but that of $[Cp^*{}_2Zr(\mu\text{-}S)]_2$ only 46% due to the extremely high solubility of this complex in toluene. No other products containing zirconium were observed. The complex $[Cp_2Zr(\mu\text{-}S)]_2$ has been briefly mentioned by Shaver and McCall;[14] we proved it to be a dimer by X-ray diffraction. The molecular weight of $[Cp^*{}_2Zr(\mu\text{-}S)]_2$ was determined by osmometry to be 769, which is in agreement with the calculated value of 786 for the dimeric formulation. However the ^1H NMR spectrum showed two singlets in the $C_5(CH_3)_5$ region, at 1.97 and 1.92 ppm with relative intensities of 10:1. We believe the signal at 1.92 ppm is due to a small amount of an oligomer other than $[Cp^*{}_2Zr(\mu\text{-}S)]_2$. The dimer $[Cp^*{}_2Zr(\mu\text{-}S)]_2$ must be an extremely crowded molecular, but the ^1H NMR indicates that twisting of the $Zr(\mu\text{-}S)_2Zr$ plane does not occur. This would lead to two $C_5(CH_3)_5$ signals of equal intensity, as was observed in $[Cp^*{}_2Zr(H)]_2(\mu\text{-}O)$.[3] Monomeric $Cp^*{}_2ZrS$ is unlikely, so that only trimers or higher oligomers remain as possibilities. Both $[Cp'_2Zr(\mu\text{-}S)]_2$ complexes are air stable.

Discussion

It must be stressed that in the present work the initial mole ratio of H_2O or H_2S to $Cp'_2M(CO)_2$ was 1:1 and the reactions were conducted in such a way that the involatile $Cp'_2M(CO)_2$ was effectively in excess over H_2O or H_2S during the course of the reaction. Toney and Marks have shown that hydrolysis of Cp_2MCl_2 in water as solvent leads to loss of Cp and formation of intractable CpTiO(OH) polymers.[7] We also found that large excesses of H_2O or H_2S gave intractable products but that under the condi-

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tions described here no polymers were observed. Where loss of Cp did occur (in the formation of $Cp_6Ti_6O_8$ and $Cp_5Ti_5S_6$), it was in a controlled manner. The preparation of $[Cp'_2Zr(\mu\text{-}S)]_2$ from $Cp'_2Zr(CO)_2$ and H_2S represents a convenient synthesis of these complexes; $[Cp_2Zr(\mu\text{-}S)]_2$ was previously available as a byproduct of the reaction between H_2S and Cp_2ZrCl_2 which gives mainly $Cp_2Zr(SH)_2$.[14]

The organometallic products obtained in the reactions between H_2O or H_2S and $Cp'_2M(CO)_2$ were characterized primarily by X-ray diffraction. The structure of $Cp_6Ti_6O_8$ was determined by Caulton and co-workers[2] and is discussed in detail elsewhere.[2,12,23] The details of the structure and magnetism of $Cp_5Ti_5S_6$[20] will be the subject of a future publication in which this cluster will be compared to other $(CpM)_m(\mu_3\text{-}A)_n$ clusters. The structures of $Cp^*_2Ti(SH)_2$ and $[Cp_2Zr(\mu\text{-}S)]_2$ are discussed below. In the case of $Cp^*_2Ti(SH)_2$ two crystalline forms were found. Crystallization at room temperature gave a monoclinic form (space group *Cm*) whose structure could only be refined to $R = 0.12$. The refinement gave unacceptably large thermal parameters to all the carbon atoms of the $C_5(CH_3)_5$ rings but was sufficiently accurate to establish the formula and stereochemistry of $Cp^*_2Ti(SH)_2$. Subsequent recrystallization at −30 °C gave the tetragonal form whose structure is reported in detail here.

The clusters $Cp_6Ti_6O_8$ and $Cp_5Ti_5S_6$ both contain mixtures of the formal oxidation states Ti(III) and Ti(IV). Since the Zr(III) oxidation state is very rare and Zr(III) would be readily oxidized by H_2O or H_2S, it is not surprising (though disappointing) that $(CpZr)_m(\mu_3\text{-}A)_n$ clusters are not formed in the reactions of $Cp_2Zr(CO)_2$ with H_2O or H_2S. Reaction 3 is remarkably specific giving only one product containing titanium, the unique cluster $Cp_6Ti_6O_8$.[2] Since no intermediate has been detected, we cannot even speculate on the mechanism of this remarkable reaction.

The relative reactivities of the $Cp'_2M(CO)_2$ complexes toward water are exactly the same as toward N_2O, and equally difficult to understand. For $Cp_2Ti(CO)_2$ and water reaction 3 applied and for N_2O reaction 8.[24] The reaction

$$4Cp_2Ti(CO)_2 + 4N_2O \rightarrow [(Cp_2Ti)_4(CO_3)_2] + 4N_2 + 6CO \qquad (8)$$

between $Cp_2Zr(CO)_2$ and H_2O or N_2O gives ZrO_2 as the only identifiable product. Neither H_2O nor N_2O react with $Cp^*_2M(CO)_2$ (M = Ti, Zr). Given the strength of group 4 metal–oxygen bonds (Ti–O, 666 kJ mol^{-1}; Zr–O, 760 kJ mol^{-1} [25]) and the fact that they are readily formed in reactions 1–4 and 8, there can be no thermodynamic reason for the unreactivity of the $Cp^*_2M(CO)_2$ complexes. Among kinetic arguments, steric hindrance cannot be a factor with such small reagents as N_2O and H_2O, given that H_2S reacts with all $Cp'_2M(CO)_2$ complexes. Hillhouse and Bercaw suggested that H_2O could react with $[Cp^*_2Zr(N_2)]_2(\mu\text{-}N_2)$ (reaction 1) but not $Cp^*_2Zr(CO)_2$ because in the dinitrogen complex the terminal N_2 ligands can dissociate to provide a coordination site for H_2O.[3] If this explanation is correct, it leads to the conclusions that the dissociation (9) is not

$$Cp'_2M(CO)_2 \rightleftharpoons Cp'_2M(CO) + CO \qquad (9)$$

the first step in the reactions found here. If (9) were the first step, similar initial reactivity of $Cp'_2M(CO)_2$ toward H_2O, N_2O, and H_2S would be expected. This is not observed; H_2S reacts with $Cp^*_2M(CO)_2$ whereas H_2O and N_2O do not. We therefore conclude that there is an initial bimolecular step in all reactions involving $Cp'_2M(CO)_2$.

Table I. Important Bond Distances (Å) and Angles (deg) in $Cp^*_2Ti(SH)_2$

Ti–S(1)[a]	2.409 (2)[b]	S(1)–Ti–S(2)	94.8 (1)
Ti–S(2)	2.418 (3)	Cp*(1)–Ti–Cp*(2)	135.3[e]
Ti–Cp*(1)[c]	2.150[d]	H(1)–S(1)–Ti	106 (3)
Ti–Cp*(2)[c]	2.135[d]	H(2)–S(2)–Ti	116 (3)
S(1)–H(1)	1.40 (7)		
S(2)–H(2)	1.21 (8)		

[a] For numbering scheme see Figure 1. [b] Estimated standard deviations are in parentheses. [c] Carbon atoms C(1)–C(5) define Cp*(1); C(11)–C(15) define Cp*(2). [d] Perpendicular distance to Cp*(1) or Cp*(2) plane. [E] Angle between the two Ti–Cp* vectors.

In the overall reactions N_2O, H_2O, and H_2S function as electrophiles. The initial attack is expected to be electrophilic also, since $Cp'_2M(CO)_2$ have 18 electrons. Simple electrophilic attack of H_2A at $Cp'_2M(CO)_2$ does not, however, explain why derivatives of the less basic Cp are more reactive than those of Cp*. We believe that a two-term rate law involving dissociation and protonation is operative. In accord with this we have found that whereas H_2O only reacts with $Cp_2Ti(CO)_2$ at 80 °C, H_2S does so at 20 °C, albeit very slowly, and H_2Se reacts quite rapidly at 20 °C.[26]

In all of the reactions (3)–(7) dihydrogen is evolved. Although the reduction of H_2O to H_2 is a relatively common phenomenon for low valent complexes of the transition metals, reduction of H_2S to H_2 and S^{2-}, as occurs on $Cp'_2M(CO)_2$ (reactions 5 and 7), is rare.[17,27] The driving force for the reactions is the Zr(IV)–S bond strength (575 kJ mol^{-1} [28]) combined with the strong H_2 bond (436 kJ mol^{-1} [29]) and rather weak H–S bond (344 kJ mol^{-1} [29]). The analogous reaction with water (reaction 10) would be

$$2Cp'_2M(CO)_2 + 2H_2O \rightarrow [Cp'_2M(\mu\text{-}O)]_2 + 2H_2 + 4CO \qquad (10)$$

thermodynamically even more favorable. The trimer $[Cp_2Zr(\mu\text{-}O)]_3$ is known but was obtained from $Cp_2Zr(CO)_2$ and CO_2,[30] not H_2O.

Reactions 1 and 2 described by Hillhouse and Bercaw[3] may be combined to the overall equation (11) which is the

$$[Cp^*_2Zr(N_2)]_2(\mu\text{-}N_2) + 4H_2O \rightarrow 2Cp^*_2Zr(OH)_2 + 2H_2 + 3N_2 \qquad (11)$$

direct analogue of (6) if allowance for the different constitution of the Zr(II) starting materials is made. In the reaction of $Cp^*_2Ti(CO)_2$ with H_2S we observed neither $Cp^*_2Ti(H)(SH)$ nor $[Cp^*_2Ti(H)]_2(\mu\text{-}S)$, the sulfido analogues of the oxo complexes obtained in the reactions with water.[3] The analogue of $Cp^*_2Ti(SH)_2$ in the oxo series ($Cp'_2Ti(OH)_2$) has not been observed.

The possibility that $Cp^*_2Ti(SH)_2$ might lose dihydrogen to form $[Cp^*_2Ti(\mu\text{-}S_2)]_2$ has been suggested (eq 12).[17] We

$$2Cp^*_2Ti(SH)_2 \rightarrow [Cp^*_2Ti(\mu\text{-}S_2)]_2 + 2H_2 \qquad (12)$$

observed no such conversion. Our reaction conditions would be favorable to such a dimerization since much of the isolation and crystallization procedure was conducted with high concentrations of $Cp^*_2Ti(SH)_2$ and under vacuum.

Structure of $Cp^*_2Ti(SH)_2$. The important distances and angles are given in Table I and the numbering scheme

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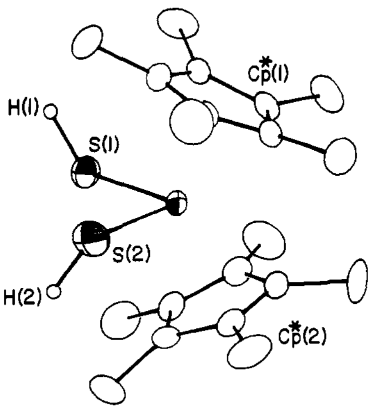

Figure 1. The molecular structure of $Cp^*_2Ti(SH)_2$.

Table II. Important Bond Distances (Å) and Angles (deg) in $[Cp_2Zr(\mu\text{-}S)]_2$

Zr–S(1)[a]	2.490 (3)[b]	S–Zr–S(1′)	89.6 (1)
Zr–S(1′)	2.482 (3)	Zr–S–Zr(1′)	90.4 (1)
Zr–Cp(1)[c]	2.235[d]	Cp(1)–Zr–Cp(2)	122.7
Zr–Cp(2)[c]	2.239		
Zr–Zr(1′)	3.530 (2)		
S–S(1′)	3.503 (3)		

[a] For numbering scheme see Figure 2. [b] Estimated standard deviations are in parentheses. [c] Cp(1) is defined by carbon atoms C(11)–C(15) and Cp(2) by C(21)–C(25). [d] Perpendicular distance to Cp(1) or Cp(2) plane. [e] Angle defined by the two Zr–Cp vectors.

in Figure 1. The unit cell contains well-separated molecules of $Cp^*_2Ti(SH)_2$ with a minimum intermolecular S–S distance of 5.66 Å. The Ti–S distances 2.409 (2) and 2.418 (3) Å are identical with those in $Cp^*_2TiS_3$ (2.413 (4) Å[15]) but shorter than the Ti(IV)–S distances in other 8-coordinate $Cp'_2Ti(SR)_2$ derivatives, which range from 2.42 to 2.49 Å.[31-33] This shortening is due to π-bonding between the S and Ti atoms. Further evidence for this π-bonding is provided by the position of the hydrogen atoms attached to sulfur; these were easily located in a difference Fourier map, and their positions were successfully refined, giving reasonable S–H distances and Ti–S–H angles. The two hydrogen atoms are on opposite sides of the Ti–S(1)–S(2) plane, and the Ti–S–H torsion angles with respect to this plane are 66° and 64.5°. This allows a filled pπ orbital on each S atom to overlap with the empty $1a_1$ orbital on Ti, creating a π bond.[34] The S–T–S angle of 94.8 (1)° is in the range normally observed for Cp_2MX_2 complexes of d^0 metals.[34] The CH_3 groups of the Cp* ligands are bent out of the plane of the C_5 ring away from the titanium. The average distance from the plane is 0.26 Å in Cp*(1) and 0.24 Å in Cp*(2).

Structure of $[Cp_2Zr(\mu\text{-}S)]_2$. The important distances and angles are given in Table II and the numbering scheme in Figure 2. The molecule consists of two Cp_2Zr units bridged by S atoms. The $\overline{\text{ZrSZrS}}$ core is exactly planar by symmetry and almost exactly square (Zr–S(1) = 2.490 (3) Å, Zr–S(1′) = 2.482 (3) Å; Zr(1)–S–Zr(1′) = 90.4 (1)°, S(1)–Zr–S(1′) = 89.6 (1)°). The Zr–S distances are extremely short compared to others in the literature,[35-40] only the terminal Zr–S-*t*-Bu in $Zr_3(S)(S\text{-}t\text{-}Bu)_{10}$ at 2.423 (8) Å being shorter.[35] One general reason for shortness is the coordination number. If Cp or Cp* is regarded as occupying three coordination sites, the Zr atom in $[Cp_2Zr(\mu\text{-}S)]_2$ is 8-coordinate and the Zr atoms in $Zr_3(S)(t\text{-}BuS)_{10}$ are 6-coordinate. In the 9-coordinate mono- and dithiocarbamates of Cp_2Zr the Zr–S distances are 2.63–2.72 Å.[35,36] However in $[Cp_2Zr(SC_6H_5)]_2(\mu\text{-}O)$ which is 8-coordinate and comparable to $[Cp_2Zr(\mu\text{-}S)]_2$ the average Zr–S distance is 2.548 (2) Å, 0.06 Å longer than the average found here. The short Zr–S distance in $[Cp_2Zr(\mu\text{-}S)]_2$ implies some double-bond character, achieved by donation of electrons from the filled pπ orbitals on S to the empty $1a_1$ orbital of the Cp^*_2Zr(IV) fragment as outlined above.[34,37] The Zr–Zr distance 3.529 (2) Å is longer than any reasonable bonding distance, as expected for d^0 metals.

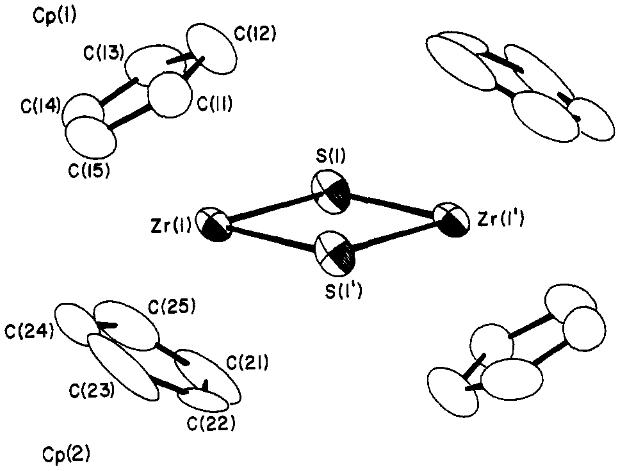

Figure 2. The molecular structure of $[Cp_2Zr(\mu\text{-}S)]_2$.

The Cp–Zr–Cp angle of 122.7° is the smallest yet observed. With the exception of $[Cp_2Zr(\mu\text{-}O)]_3$, which has an average Cp–Zr–Cp angle of 123.8,[30] other Cp_2Zr complexes have this angle close to 130°.[8,35,36,41] The observation that the Cp–Zr–Cp angle is small in $[Cp_2Zr(\mu\text{-}E)]_n$ ($E = O$, $n = 3$; $E = S$, $n = 2$) contradicts the prediction of Lauher and Hoffmann that acute angles would be associated with ligands which are good π-acceptors and poor σ-donors.[34] However no trend in the angles which would allow an alternative prediction is evident.

Experimental Section

General Techniques and Reagents. All experiments were carried out under argon or vacuum by using standard vacuum line techniques. Volumes of gaseous reactants and products were measured by using manometers and calibrated bulbs; mixtures of gaseous products were separated by using a Toepler pump with traps at different temperatures and a Cu/CuO bed at 300 °C. Solvents were predried, stored over CH_3Li, and distilled under vacuum. $Cp_2Ti(CO)_2$,[42] $Cp^*_2Ti(CO)_2$,[43] $Cp_2Zr(CO)_2$,[43] and $Cp^*_2Zr(CO)_2$[43] were prepared by literature methods; H_2S was passed through silica gel at −70 °C and subjected to several freeze–thaw cycles before use. All other chemicals were reagent grade and used as received.

Instruments used in this work were a Perkin-Elmer 683 infrared spectrophotometer (spectra measured as Nujol mulls between KBr plates), a locally modified version of the Varian E4 ESR spectrometer, and a Varian XL-200 NMR spectrometer. Micro-

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Table III. Crystal Data and Details of Refinement of $Cp^*_2Ti(SH)_2$ and $[Cp_2Zr(\mu\text{-}S)]_2$

	$(\eta^5\text{-}C_5(CH_3)_5)_2Ti(SH)_2$	$[(\eta^5\text{-}C_5H_5)_2Zr(\mu\text{-}S)]_2$
formula	$C_{20}H_{32}S_2Ti$	$C_{20}H_{20}S_2Zr_2$
M, daltons	384.54	506.96
crystal class	tetragonal	monoclinic
space group	$I4_1/a$	$P2_1/n$
λ(Mo K$\bar{\alpha}$), Å	0.710 73	0.710 73
a, Å	31.140 (6)	8.3912 (5)
b, Å	31.140 (6)	8.2498 (7)
c, Å	8.350 (1)	13.6683 (9)
β, deg	90	94.69 (1)
V, Å^3	8097 (2)	943 (1)
Z	16	2
D_{calcd} mg m^{-3}	1.26	1.78
F(000), electrons	3296	504
μ(Mo K$\bar{\alpha}$), cm^{-1}	5.85	12.70
R ($\sum\Delta\|F\|/\sum\|F\|$)	0.038	0.039
R_w (($\sum w(\Delta F)^2/\sum wF^2)^{1/2}$)	0.041	0.038
no. of independent reflections	3780	1779
scan type	ω–2θ	ω–2θ
$2\theta_{(max)}$, deg	50	50
no. of obsd reflections ($I > 3\sigma(I)$)	1221	1130
no. of variables	215	120
max residual intensity, e Å^{-3}	0.20	0.67
min residual intensity, e Å^{-3}	–0.23	–0.69

analyses were by Beller Laboratorium, Göttingen, West Germany.

Reaction of Bis(cyclopentadienyl)titanium Dicarbonyl with Water: Formation of Octakis(μ_3-oxo)hexakis[(η-cyclopentadienyl)titanium], $[((\eta\text{-}C_5H_5)Ti)_6(\mu_3\text{-}O)_8]$. A solution of $Cp_2Ti(CO)_2$ (1.3 g, 5.56 mM) in toluene (100 cm^3) containing water (0.1 cm^3, 5.56 mM) was heated at 80 °C with stirring for 72 h. During this time the solution changed color from purple-brown to royal blue. The gaseous products were CO (8.52 mM) and H_2 (3.55 mM). The solvent was removed from the blue mixture under vacuum and the excess $Cp_2Ti(CO)_2$ (0.30 g, 1.28 mM) sublimed out of the residue at 50 °C under vacuum. The royal blue residue was extracted with toluene (60 cm^3), the extract concentrated to 20 cm^3, and hexane (30 cm^3) added to precipitate $Cp_6Ti_6O_8$; yield 0.46 g, 80% based on the $Cp_2Ti(CO)_2$ actually consumed in the reaction. Anal. Calcd for $C_{30}H_{30}O_8Ti_6$: C, 44.7; H, 3.8. Found: C, 44.9; H, 4.7. Infrared: 730 and 595 cm^{-1} (vw) assigned to vibrations of the Ti_6O_8 core (lit. 728, 598 cm^{-1}[2]). Mass spectrum: m/e 805 ($[(C_5H_5)_5(C_5H_4)Ti_6O_8]^+$), 739 ($[(C_5H_5)_3(C_5H_4)_2Ti_6O_8]^+$), 675 ($[(C_5H_5)_3(C_5H_4)Ti_6O_8]^+$), 610 ($[(C_5H_5)_2(C_5H_4)Ti_6O_8]^+$), 546 ($[(C_5H_5)_2Ti_6O_8]^+$); no peaks around m/e 661 ($Cp_5Ti_5O_6$) or 516 ($Cp_4Ti_4O_4$).

Reaction of Bis(cyclopentadienyl)titanium Dicarbonyl with Dihydrogen Sulfide: Formation of Hexakis(μ_3-thio)pentakis[(η-cyclopentadienyl)titanium], $[((\eta\text{-}C_5H_5)Ti)_5(\mu_3\text{-}S)_6]$. A solution of $Cp_2Ti(CO)_2$ (1.5 g, 6.4 mM) in toluene (100 cm^3) was incubated with stirring under gaseous H_2S (7.7 mM) at 80 °C for 72 h, during which time the red-brown of the initial solution changed to dark green. The gaseous products were CO (12.3 mM) and H_2 (4.49 mM). The solvent was removed under vacuum and the residue washed with hexane (50 cm^3). On extraction of the residue with toluene, concentration of the extract to 20 cm^3 and addition of hexane (30 cm^3), dark green-brown $Cp_5Ti_5S_6$ precipitated. This was collected by filtration and recrystallized from toluene/hexane (1:2 v/w) to give 0.71 g (73%) of the moderately air-sensitive product. Anal. Calcd for $C_{32}H_{33}S_6Ti_5(Cp_5Ti_5S_6{\cdot}C_6H_5CH_3)$: C, 45.2; H, 3.9; S, 22.6; Ti, 28.2. Found (two separate analyses of different samples): C, 45.7, 45.2; H, 4.2, 4.3; S, 15.2, 10.8; Ti (as TiO_2), 27.7, 28.7. The problem of incorrect sulfur analyses in cyclopentadienyl–metal–sulfur complexes has been discussed by others.[14] The ESR spectrum (toluene solution, 20 °C) showed a single line at $g = 1.993$, with weak satellites due to ^{47}Ti and ^{49}Ti. The bulk magnetic susceptibility at 20 °C was 6.525×10^{-4} cm^3 M^{-1}, corresponding to a magnetic moment of 1.25 μB (uncorrected) and 1.67 μB (corrected).[44] The cluster showed weak absorption bands at 400 and 375 cm^{-1} in the infrared spectrum, attributable to vibrations of the Ti_5S_6 core. The mass spectrum showed the most intense peak at m/e 757 ($[Cp_5Ti_5S_6]^+$) with a trace peak at m/e 934 [($Cp_6Ti_6S_8]^+$) and a complicated fragmentation pattern of traces of all possible derivatives of $[Cp_6Ti_6S_nO_{8-n}]^+$ and $[Cp_5Ti_5S_nO_{6-n}]^+$. There was also weak peak at m/e 580 ($[Cp_4Ti_4S_4]^+$). It is assumed that the oxygen arises on handling and/or inside the mass spectrometer. The ^1H NMR spectrum showed two broad singlets at 9.4 and 14.6 ppm, assigned to the protons of the axial and equatorial ($\eta^5\text{-}C_5H_5$) rings, respectively. The intensity ratio was 1:1.45.

Reaction of Bis(pentamethylcyclopentadienyl)titanium Dicarbonyl with Dihydrogen Sulfide: Formation of Bis(pentamethylcyclopentadienyl)dimercaptotitanium, $Cp^*_2Ti(SH)_2$. A solution of $Cp^*_2Ti(CO)_2$ (0.55 g, 1.47 mM) in toluene (70 cm^3) was incubated with stirring under H_2S (1.45 mM) at 80 °C for 72 h during which time the color of the solution changed from red-brown to blood-red. The gaseous products were CO (1.39 mM) and H_2 (0.69 mM). The solvent was removed under vacuum and excess $Cp^*_2Ti(CO)_2$ (0.27 g, 0.74 mM) sublimed out of the residue at 80 °C under vacuum. The red residue was dissolved in toluene (50 cm^3) and filtered and the filtrate concentrated to 20 cm^3. Addition of hexane (30 cm^3) precipitated red crystals of $Cp^*_2Ti(SH)_2$. These were collected by filtration, washed with hexane, and dried in vacuo; yield 0.16 g, 60% based on the $Cp^*_2Ti(CO)_2$ actually consumed in the reaction. Anal. Calcd for $C_{20}H_{32}S_2Ti$: C, 62.5; H, 8.4; S, 16.7; Ti, 12.5. Found: C, 61.2; H, 8.3; S, 16.5; Ti (as TiO_2), 12.8. Infrared: 2580 cm^{-1} (vw) (ν(S–H)); 405 (w), 365 (s); 330 cm^{-1} (w) (ν(Ti–S)). NMR (^1H, $CDCl_3$ solution): 1.84 (s, 30 H, $C_5(CH_3)_5$), 2.73 ppm (s, 2 H, SH). When toluene solutions were set aside at room temperature for 7 days, the complex crystallized in the monoclinic system with $a = 8.202$ (1) Å, $b = 14.941$ (1) Å, $c = 9.255$ (1) Å, $\beta = 116.29$ (1)°, space group Cm, and $Z = 2$ for M_r 384.5. On setting similar solutions aside at –30 °C for 30 days, crystals belonging to the tetragonal class formed (see Table III for details).

Reaction of Bis(cyclopentadienyl)zirconium Dicarbonyl with Dihydrogen Sulfide: Formation of Bis[bis(cyclopentadienyl)(μ-sulfido)zirconium], $[Cp_2Zr(\mu\text{-}S)]_2$. A solution of $Cp_2Zr(CO)_2$ (1.04 g, 3.75 mM) in toluene (100 cm^3) was incubated with stirring under H_2S (3.75 mM) at 80 °C for 72 h. The color of the solution changed from violet to turquoise, and some green solid was deposited. The gaseous products were CO (7.35 mM) and H_2 (3.69 mM). The mixture was concentrated to 30 cm^3; addition of hexane (30 cm^3) precipitated green $[Cp_2Zr(\mu\text{-}S)]_2$. This was collected by filtration and recrystallized from hot toluene/hexane; yield 0.75 g, 79%. Anal. Calcd. for $C_{20}H_{20}S_2Zr_2$: C, 47.4; H, 4.0; S, 12.6; Zr, 36.0. Found: C, 45.5; H, 3.9; S, 12.7; Zr (as ZrO_2), 35.6. Infrared (KBr pellet): 335 cm^{-1} (vs) (ν(Zr–S)). NMR (^1H, $CDCl_3$ solution): 6.49 ppm (s, C_5H_5). The literature

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(44) For the diamagnetic correction values of -50.9×10^{-6} cm^{-3} M^{-1} per $C_5H_5^-$ ring, -38.0×10^{-6} per S^{2-}, -5.0×10^{-6} for each of two Ti^{4+} and -9.2×10^{-6} for each of three Ti^{3+} ions were used. See: Weiss, A.; Witte, H. *Magnetochemie*, Verlag Chemie: Weinheim, FRG, 1973; pp 93–95.

Table IV. Atomic Positions ($\times10^4$) for the Non-Hydrogen Atoms of $Cp^*_2Ti(SH)_2$

atom[a]	x/a	y/b	z/c
Ti	6500.6 (4)[b]	1508.6 (4)	6037 (1)
S(1)	6415 (1)	1028 (1)	8276 (2)
H(1)	6022 (24)	1136 (22)	8972 (95)
S(2)	6559 (1)	2148 (1)	7665 (3)
H(2)	6870 (24)	2167 (23)	8539 (95)
C(1)	5720 (2)	1647 (2)	6268 (8)
C(2)	5876 (2)	1951 (2)	5164 (8)
C(3)	6034 (2)	1731 (2)	3803 (7)
C(4)	5970 (2)	1286 (2)	4045 (8)
C(5)	5775 (2)	1235 (2)	5555 (8)
C(6)	5491 (2)	1752 (2)	7783 (8)
C(7)	5815 (2)	2420 (2)	5254 (10)
C(8)	6131 (2)	1947 (2)	2200 (8)
C(9)	5978 (2)	941 (2)	2806 (8)
C(10)	5582 (1)	828 (1)	6160 (3)
C(11)	7209 (1)	1144 (1)	6399 (3)
C(12)	7028 (1)	1016 (1)	4922 (3)
C(13)	7025 (1)	1380 (1)	3915 (3)
C(14)	7162 (1)	1745 (1)	4814 (3)
C(15)	7286 (1)	1586 (1)	6345 (3)
C(16)	7365 (2)	849 (2)	7695 (9)
C(17)	6948 (2)	562 (2)	4481 (10)
C(18)	7010 (2)	1367 (3)	2100 (8)
C(19)	7225 (2)	2189 (2)	4239 (9)
C(20)	7542 (2)	1823 (2)	7572 (9)

[a] For numbering scheme see Figure 1. [b] Estimated standard deviations referring to the last digits are given in parentheses. [c] C(1)–C(5) define Cp*(1), and C(6)–C(10) are the methyl groups attached to C(1)–C(5) in rotation. C(11)–C(15) define Cp*(2), and C(16)–C(20) are the methyl groups attached to C(11)–C(15) in rotation.

value is 6.44 ppm.[14] The formulation of the product as a dimer is based on the X-ray diffraction results (see below). Crystals were obtained by slowly cooling a toluene solution from 80 °C to room temperature.

Reaction of Bis(pentamethylcyclopentadienyl)zirconium Dicarbonyl with Dihydrogen Sulfide: Formation of Bis[bis(pentamethylcyclopentadienyl)(μ-sulfido)zirconium], $[Cp^*_2Zr(\mu\text{-}S)]_2$. A solution of $Cp^*_2Zr(CO)_2$ (0.65 g, 1.56 mM) in toluene (75 cm^3) was incubated with stirring under H_2S (1.5 mM) at 80 °C for 72 h. During this time the color of the solution changed from deep violet to pale yellow. The gaseous products were CO (3.08 mM) and H_2 (1.6 mM). The solution was concentrated to 20 cm^3 and hexane (30 cm^3) added to precipitate pale yellow $[Cp^*_2Zr(\mu\text{-}S)]_2$. This was collected by filtration and washed with cold hexane; yield 0.28 g, 46%. The low yield is mainly due to the very high solubility of $[Cp^*_2Zr(\mu\text{-}S)]_2$ in organic solvents. Anal. Calcd for $C_{40}H_{60}S_2Zr_2$: C, 61.0; H, 7.7; S, 8.1; Zr, 23.2. Found: C, 57.8; H, 8.3; S, 8.0; Zr (as ZrO_2), 24.2. The relatively poor analysis results are mainly due to the impossibility of recrystallizing the complex because of its high solubility in all organic solvents, including hexane. Infrared: 330 cm^{-1} (m) (ν(Zr–S)). NMR (^{1}H in $CDCl_3$ solution): 1.97, 1.92 ppm (s, $C_5(CH_3)_5$). Mass spectrum: m/e 392 ($[(C_5(CH_3)_5)_2{}^{90}ZrS]^+$). Molecular weight by osmometry in toluene solution: 769, calcd for $(Cp^*_2ZrS)_2$ 786.

Crystallography. Crystals of $[Cp_2Zr(\mu\text{-}S)]_2$ and $Cp^*_2Ti(SH)_2$ were obtained as described above. They were coated in "Apiezon" grease and mounted in sealed tubes under argon. Cell dimensions and space group were determined by a combination of precession photography and cell reduction on the diffractometer. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer. Crystal data are given in Table III. Because of the low values of μ no absorption corrections were applied. In the case of $Cp^*_2Ti(SH)_2$ the crystallinity of the sample was not optimal, a common situation with crystals having very large unit cells. The ratio of observed to the total number of independent reflections was therefore rather poor.

Table V. Atomic Positions ($\times10^4$) for the Non-Hydrogen Atoms of $[Cp_2Zr(\mu\text{-}S)]_2$

atom[a]	x/a	y/b	z/c
Zr	568 (1)[b]	1536 (1)	857 (1)
S	879 (3)	−1464 (3)	800 (1)
C(11)[c]	−2080 (11)	2675 (12)	1334 (6)
C(12)	−2064 (14)	1101 (12)	1674 (8)
C(13)	−755 (14)	1011 (15)	2421 (7)
C(14)	−70 (11)	2482 (16)	2534 (7)
C(15)	−829 (11)	3513 (14)	1849 (7)
C(21)[c]	3462 (11)	1505 (15)	447 (10)
C(22)	2775 (12)	2675 (15)	−122 (7)
C(23)	2316 (15)	3902 (13)	476 (12)
C(24)	2734 (13)	3540 (16)	1411 (8)
C(25)	3408 (11)	2046 (17)	1462 (8)

[a] For numbering scheme see Figure 2. [b] Estimated standard deviations in parentheses. [c] C(11)–C(21) define Cp(1); C(21)–C(25) define Cp(2).

Preliminary positions for the metal and sulfur atoms were derived by using MULTAN-80.[45] The positions of these atoms were used in the phasing of Fourier syntheses and the position of all non-hydrogen atoms determined by successive Fourier, difference Fourier, and partial refinement techniques. The structures were refined by standard methods, minimizing the function $\sum w(\Delta F)^2$ with a weighting scheme of the form $w = 1/(\sigma(F)^2 + kF^2)$ with σ based on counting statistics. Scattering factors were taken from ref 46 and were corrected for both the real and the imaginary parts of the anomalous dispersion where appropriate. The hydrogen atoms in the C_5H_5 and $C_5(CH_3)_5$ rings were included with their positions calculated by using sp^2 or sp^3 hybridization at the C atom as appropriate and a fixed C–H distance of 0.97 Å. In the case of $[Cp_2Zr(\mu\text{-}S)]_2$ the isotropic thermal parameter for each hydrogen atom was refined. In the case of $Cp^*_2Ti(SH)_2$ a single thermal parameter for all hydrogen atoms was refined, and in a preliminary refinement cycle the hydrogen atoms were allowed to rotate about the C–C axis. The positions of the hydrogen atoms attached to the S atoms in $Cp^*_2Ti(SH)_2$ were allowed to vary freely. Final refinement in both cases was with all non-hydrogen atoms anisotropic. For $[Cp_2Zr(\mu\text{-}S)]_2$ an extinction parameter was included. The SHELX-76[47] program package was used for refinements. Figures 1 and 2 were drawn by using ORTEP-II.[48] The details of the final refinements are included in Table III. The positional parameters for the non-hydrogen atoms of $Cp^*_2Ti(SH)_2$ are given in Table IV and the important bond distances and angles in Table I; for $[Cp_2Zr(\mu\text{-}S)]_2$ the same information is contained in Tables V and II, respectively. Tables of hydrogen atom positions, thermal parameters, equations of some mean planes, comprehensive lists of bond distances and angles, and tables of $|F_o|$ and $|F_c|$ for both compounds are available as supplementary material for this paper.

Acknowledgment. We thank Tracy Bell for performing some of the reactions between water and $Cp_2Zr(CO)_2$ and the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Natural Sciences and Engineering Research Council of Canada for financial support of this work. G.O.E. wishes to thank the University of Ife, Nigeria for grant of a study leave.

Registry No. $Cp_2Ti(CO)_2$, 12129-51-0; $[(\eta\text{-}C_5H_5)_6Ti_6(\mu_3\text{-}O)_8]$, 83114-88-9; $[\eta\text{-}C_5H_5)_5Ti_5(\mu_3\text{-}O)_6]$, 96807-22-6; $Cp^*_2Ti(CO)_2$, 11136-40-6; $Cp^*_2Ti(SH)_2$, 102869-71-6; $Cp_2Zr(CO)_2$, 59487-85-3; $[Cp_2Zr(\mu\text{-}S)]_2$, 92097-09-1; $Cp^*_2Zr(CO)_2$, 61396-31-4; $[Cp^*_2Zr(\mu\text{-}S)]_2$, 102869-72-7; H_2O, 7732-18-5; H_2, 1333-74-0; H_2S, 7783-06-4; Ti, 7440-32-6.

Supplementary Material Available: Tables of hydrogen atoms coordinates, thermal parameters of all atoms, bond distances and angles, least squares planes, and observed and calculated structure factors (42 pages). Ordering information is given on any current masthead page.

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