Organometallics **1993,** *12,* 2363-2366

Interconversion of Hydrosulfido and Sulfido Ligands in Permethylzirconocene Complexes

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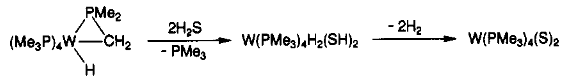
Received November 13, 1992

Summary: The bis(hydrosulfido) complex $Cp^*_2Zr(SH)_2$ is dehydrogenated by $Cp^*_2Zr(CO)_2$ to give $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$, but further dehydrogenation to give $[Cp^*_2Zr(\mu\text{-}S)]_2$ is not observed. Together with other studies, these results indicate that, contrary to the original report, the product of the reaction between $Cp^*_2Zr(CO)_2$ and H_2S is the hydrosulfido complex $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$ and not the sulfido complex $[Cp^*_2Zr(\mu\text{-}S)]_2$.

Introduction

The interconversion of hydrosulfido [M–SH] and sulfido [M═S or M–S–M] ligands may be expected to play an important role in hydrodesulfurization processes.[1] We have recently described the facile dehydrogenation of hydrogen sulfide by $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ to give the terminal bis(sulfido) complex *trans*-$W(PMe_3)_4(S)_2$, *via* the bis(hydrosulfido) intermediate $W(PMe_3)_4H_2(SH)_2$ (eq 1).[2]

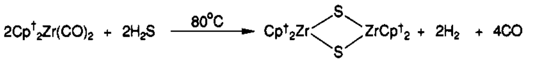


(1)

The facile dehydrogenation of H_2S by transition metal complexes is rare and typically gives bridging sulfido complexes.[3,4] In order to obtain more information concerning the nature of such transformations, we have examined other systems that are known to dehydrogenate H_2S. Here we (*i*) report the interconversion of hydrosulfido and sulfido ligands within the permethylzirconocene system and (*ii*) offer a new perspective on the previously studied dehydrogenation of H_2S by $Cp^*_2Zr(CO)_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$).[4]

Results and Discussion

The zirconocene carbonyl derivatives $Cp_2Zr(CO)_2$ ($Cp = \eta^5\text{-}C_5H_5$) and $Cp^*_2Zr(CO)_2$ were recently reported to dehydrogenate H_2S to give the bridging sulfido complexes $[Cp_2Zr(\mu\text{-}S)]_2$ and $[Cp^*_2Zr(\mu\text{-}S)]_2$, respectively (eq 2; $Cp^\dagger = Cp$ or Cp^*).[4,5] Although the zirconium products were reported to be dimeric with bridging sulfido ligands, our specific interest was to determine to what extent the dehydrogenation reaction occurred at a single zirconium center. For example, a possible pathway for dehydrogenation could involve the formation of a bis(hydrosulfido) intermediate $Cp^\dagger_2Zr(SH)_2$ prior to formation of the observed μ-sulfido dimer $[Cp^\dagger_2Zr(\mu\text{-}S)]_2$. Such a pathway has precedence for the cyclopentadienyl system, since it is known that $Cp_2Zr(SH)_2$ is in equilibrium with $[Cp_2Zr(\mu\text{-}S)]_2$ and H_2S (eq 3).[6] However, for the related permethylzirconocene system, the increased steric interactions between the Cp* ligands on adjacent zirconium centers in $[Cp^*_2Zr(\mu\text{-}S)]_2$ suggests that the proposed equilibrium (eq 4) would lie more in favor of the bis(hydrosulfido) complex $Cp^*_2Zr(SH)_2$, compared with the equilibrium for the cyclopentadienyl system (*i.e.* $K_{Cp^*} < K_{Cp}$). If the equilibrium were to be shifted completely towards $Cp^*_2Zr(SH)_2$, isolation of $[Cp^*_2Zr(\mu\text{-}S)]_2$ from the reaction of $Cp^*_2Zr(CO)_2$ with H_2S would signal that the dehydrogenation sequence did not occur *via* the intermediacy of $Cp^*_2Zr(SH)_2$. Therefore, one of our objectives was to determine whether or not $Cp^*_2Zr(SH)_2$ could be converted to the bridging sulfido dimer $[Cp^*_2Zr(\mu\text{-}S)]_2$.



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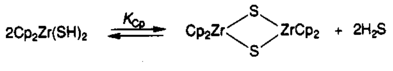

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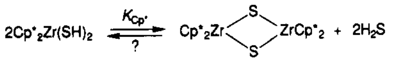

(4)

The bis(hydrosulfido) complex $Cp^*_2Zr(SH)_2$ is conveniently obtained by the reaction of $Cp^*_2Zr(CH_3)_2$ with H_2S at 60 °C (eq 5).[7] The molecular structure of $Cp^*_2Zr(SH)_2$ was determined by X-ray diffraction (Figure 1) and selected bond lengths and angles are presented in Table I. As expected, the structure of $Cp^*_2Zr(SH)_2$ is closely related to those of the titanium analogue $Cp^*_2Ti(SH)_2$[4] and the hydroxy derivative $Cp^*_2Zr(OH)_2$.[8] Although the hydrogen atoms of the hydrosulfido group were not located in the X-ray diffraction study, evidence for their presence is readily provided by ^1H NMR ($\delta_{SH} = 1.59$ ppm) and IR ($\nu_{S\text{-}H} = 2596\ cm^{-1}$) spectroscopies.

$$Cp^*_2Zr(CH_3)_2 + 2H_2S \xrightarrow{60\ °C} Cp^*_2Zr(SH)_2 + 2CH_4 \qquad (5)$$

Preliminary observations indicated that $Cp^*_2Zr(SH)_2$ is substantially more stable than its $Cp_2Zr(SH)_2$ counterpart with respect to elimination of H_2S and formation of the sulfido-bridged dimer. For example, whereas $Cp_2Zr(SH)_2$ may be quantitatively transformed to the dimer

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[1] (a) Angelici, R. J. *Acc. Chem. Res.* **1988,** *21,* 387–394. (b) Wachter, J. *Angew. Chem. Int. Ed. Engl.* **1989,** *28,* 1613–1626. (c) Rakowski DuBois, M. *Chem. Rev.* **1989,** *89,* 1–9.

[2] Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1991,** *113,* 5904–5905.

[3] (a) Besenyei, G.; Lee, C.-L., Gulinski, J.; Rettig, S. J.; James, B. R.; Nelson, D. A.; Lilga, M. A. *Inorg. Chem.* **1987,** *26,* 3622–3628. (b) Lee, C.-L.; Besenyei, G.; James, B. R.; Nelson, D. A.; Lilga, M. A. *J. Chem. Soc., Chem. Commun.* **1985,** 1175–1176.

[4] Bottomley, F.; Drummond, D. F.; Egharevba, G. O.; White, P. S. *Organometallics* **1986,** *5,* 1620–1625.

[5] The molecular structure of $[Cp_2Zr(\mu\text{-}S)]_2$, but not $[Cp^*_2Zr(\mu\text{-}S)]_2$, has been determined by X-ray diffraction. See: reference 4 and Hey, E.; Lappert, M. F.; Atwood, J. L.; Bott, S. G. *J. Chem. Soc., Chem. Commun.* **1987,** 421–422.

[6] Shaver, A.; McCall, J. M. *Organometallics* **1984,** *3,* 1823–1829.

[7] $Cp^*_2Zr(SH)_2$ has been cited previously (ref 9) but details of synthesis and characterization were not reported.

[8] Bortolin, R.; Patel, V.; Munday, I.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1985,** 456–458.

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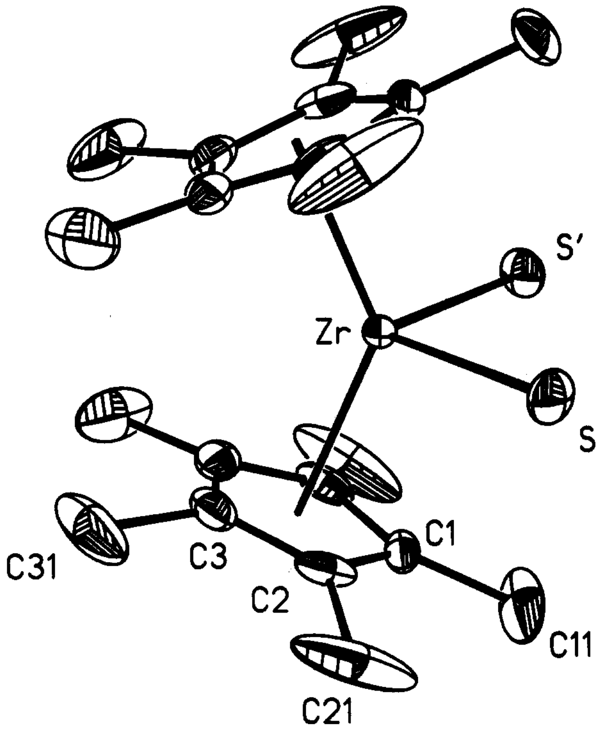
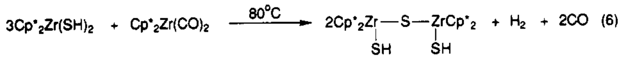


Figure 1. Molecular structure of $Cp^*_2Zr(SH)_2$.

Table I. Selected Bond Lengths (Å) and Angles (deg) for $Cp^*_2Zr(SH)_2$

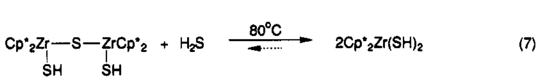
Zr–S	2.518(2)
Zr–S′	2.518(2)
Zr–C(1)	2.555(6)
Zr–C(2)	2.555(5)
Zr–C(3)	2.553(5)
S–Zr–S′	97.7(1)

$[Cp_2Zr(\mu\text{-}S)]_2$ at 80 °C by periodic removal of H_2S, the corresponding permethylzirconocene derivative $Cp^*_2Zr(SH)_2$ is completely stable under similar conditions. However, the proposed equilibrium (eq 4) for the permethylzirconocene system could be kinetically facile. Therefore, we decided to add a reagent that would trap H_2S in an attempt to shift the equilibrium (eq 4) toward the sulfido dimer. A suitable H_2S trap for this system appeared to be $Cp^*_2Zr(CO)_2$, since this complex is known to react with H_2S.[4] Indeed, we observed that $Cp^*_2Zr(CO)_2$ reacts with $Cp^*_2Zr(SH)_2$ at 80 °C to give the singly-bridged sulfido derivative $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$ (eq 6), a complex recently



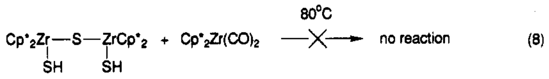
$$3Cp^*_2Zr(SH)_2 + Cp^*_2Zr(CO)_2 \xrightarrow{80°C} 2Cp^*_2\underset{SH}{Zr}—S—\underset{SH}{Zr}Cp^*_2 + H_2 + 2CO \quad (6)$$

reported by Bergman.[9] Furthermore, the sulfido-bridged complex $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$ reacts with H_2S at 80 °C to give the bis(hydrosulfido) complex $Cp^*_2Zr(SH)_2$, supporting the notion that the equilibrium (eq 7) favors $Cp^*_2Zr(SH)_2$. It is important to note, however, that although



$$Cp^*_2\underset{SH}{Zr}—S—\underset{SH}{Zr}Cp^*_2 + H_2S \overset{80°C}{\rightleftharpoons} 2Cp^*_2Zr(SH)_2 \quad (7)$$

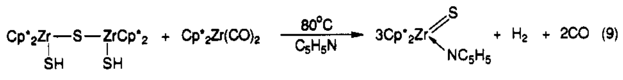
the formation of $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$ in the reaction of $Cp^*_2Zr(SH)_2$ with $Cp^*_2Zr(CO)_2$ (eq 6) provides support for elimination of H_2S from $Cp^*_2Zr(SH)_2$ (either *via* a unimolecular or bimolecular mechanism), such an observation cannot rule out the possibility that the formation of $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$ involves a direct reaction between $Cp^*_2Zr(SH)_2$ and $Cp^*_2Zr(CO)_2$.[10] Nevertheless, regardless of the mechanism, the results do indicate that $Cp^*_2Zr(SH)_2$ is not intrinsically inert toward the formation of a *single* sulfido bridge between two zirconium centers. However, the question of whether it is possible to eliminate the second equivalent of H_2S to generate the doubly-bridged sulfido dimer $[Cp^*_2Zr(\mu\text{-}S)]_2$ remained. In an attempt to answer this question, the reaction of $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$ with $Cp^*_2Zr(CO)_2$ at 80 °C (2 weeks) was examined, but no evidence for the formation of $[Cp^*_2Zr(\mu\text{-}S)]_2$ was obtained (eq 8). Therefore, neither of the



$$Cp^*_2\underset{SH}{Zr}—S—\underset{SH}{Zr}Cp^*_2 + Cp^*_2Zr(CO)_2 \xrightarrow[\times]{80°C} \text{no reaction} \quad (8)$$

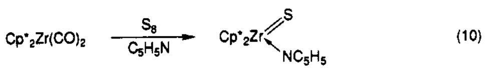
hydrosulfido derivatives, $Cp^*_2Zr(SH)_2$ nor $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$, could be possible intermediates in the formation of the sulfido dimer $[Cp^*_2Zr(\mu\text{-}S)]_2$ from the reaction of $Cp^*_2Zr(CO)_2$ with H_2S at 80 °C.[4]

Although $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$ does not react with $Cp^*_2Zr(CO)_2$ alone, in the presence of pyridine reaction occurs resulting in the formation of the monomeric sulfido complex $Cp^*_2Zr(S)(NC_5H_5)$ (eq 9). The sulfido complex



$$Cp^*_2\underset{SH}{Zr}—S—\underset{SH}{Zr}Cp^*_2 + Cp^*_2Zr(CO)_2 \xrightarrow[C_5H_5N]{80°C} 3Cp^*_2Zr(=S)(NC_5H_5) + H_2 + 2CO \quad (9)$$

$Cp^*_2Zr(S)(NC_5H_5)$ has been previously reported by Bergman,[9] and we have also found that it may be obtained directly by the reaction between $Cp^*_2Zr(CO)_2$ and sulfur in the presence of pyridine at 145 °C (eq 10). We also note



$$Cp^*_2Zr(CO)_2 \xrightarrow[C_5H_5N]{S_8} Cp^*_2Zr(=S)(NC_5H_5) \quad (10)$$

that the above synthesis of $Cp^*_2Zr(S)(NC_5H_5)$ may be applied to other chalcogenido derivatives. Thus, the terminal selenido and tellurido complexes $Cp^*_2Zr(Se)(NC_5H_5)$ and $Cp^*_2Zr(Te)(NC_5H_5)$ have been obtained by the corresponding reactions with selenium and tellurium, respectively.[11]

In order to obtain more information concerning the proposed formation of the sulfido dimer $[Cp^*_2Zr(\mu\text{-}S)]_2$ in this system,[4] the reaction between $Cp^*_2Zr(CO)_2$ and H_2S was monitored by ^1H NMR spectroscopy. Firstly, the reaction between $Cp^*_2Zr(CO)_2$ and *excess* H_2S at 80 °C cleanly gives the bis(hydrosulfido) derivative $Cp^*_2Zr(SH)_2$ (eq 11). In this regard we also note that for the

$$Cp^*_2Zr(CO)_2 + 2H_2S \xrightarrow{80°C} Cp^*_2Zr(SH)_2 + H_2 + 2CO \quad (11)$$

related titanium system, the bis(hydrosulfido) derivative $Cp^*_2Ti(SH)_2$ is the product of the reaction between $Cp^*_2Ti(CO)_2$ and H_2S.[4] Secondly, under conditions in which $Cp^*_2Zr(CO)_2$ is in excess, $Cp^*_2Zr(SH)_2$ is also formed at early stages of the reaction. However, as the reaction progresses, the singly-bridged sulfido derivative $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$ is formed, and is the final product of the reaction. In contrast to the original report,[4] there is no

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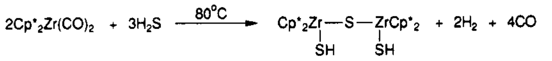
(9) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1992**, *11*, 761–777.

(10) In fact, on the basis that we observe an intermediate which is tentatively characterized as the hydrido–hydrosulfido complex $[Cp^*_2Zr(H)](\mu\text{-}S)[Zr(SH)Cp^*_2]$, we favor a mechanism involving direct reaction between $Cp^*_2Zr(SH)_2$ and $Cp^*_2Zr(CO)_2$.

(11) Howard, W. A.; Parkin, G. Unpublished results.

evidence for the presence of the sulfido dimer $[Cp^*_2Zr(\mu\text{-}S)]_2$ in the system, and it is possible that the hydrosulfido derivative $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$ was incorrectly formulated as the sulfido derivative $[Cp^*_2Zr(\mu\text{-}S)]_2$ in the earlier work. In support of this suggestion, the ^1H NMR resonance of the Cp* ligands of $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$ in $CDCl_3$ (δ 1.97 ppm) is identical to that reported previously for $[Cp^*_2Zr(\mu\text{-}S)]_2$.[4,12] Moreover, the required stoichiometry of the CO and H_2 eliminated for formation of $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$, is identical to that required for $[Cp^*_2Zr(\mu\text{-}S)]_2$. Therefore, under conditions in which H_2S is the limiting reagent, the product of the reaction between $Cp^*_2Zr(CO)_2$ and H_2S is $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$, and not $[Cp^*_2Zr(\mu\text{-}S)]_2$ (eq 12).

 (12)

$$2Cp^*_2Zr(CO)_2 + 3H_2S \xrightarrow{80^\circ C} Cp^*_2\underset{SH}{Zr}\text{—}S\text{—}\underset{SH}{Zr}Cp^*_2 + 2H_2 + 4CO \quad (12)$$

It is likely that the difference between the zirconocene and permethylzirconocene systems derives from the larger size of the Cp* *versus* Cp ligands. A double sulfido bridge would produce excessive steric interactions between Cp* ligands on adjacent Zr centers. In contrast, the presence of a *single* sulfido bridge, as in $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$, allows both (*i*) the Zr centers to be further separated and (*ii*) the molecule to adopt a configuration in which the Cp* ligands can occupy more spacious positions.[13]

Finally, although our results indicate that $[Cp^*_2Zr(\mu\text{-}S)]_2$ is not obtained by the reaction of $Cp^*_2Zr(CO)_2$ with H_2S, it is possible that $[Cp^*_2Zr(\mu\text{-}S)]_2$ could be obtained by a different synthetic method. Thus, we note that $[Cp^*_2Zr(\mu\text{-}S)]_2$ has also been proposed to be a product of the reaction of $Cp^*_2Zr(CH{=}CH_2)_2$ with sulfur,[14] although the structure has not been confirmed by X-ray diffraction.

Conclusion

In conclusion, whereas the sulfido-bridged dimer $[Cp_2Zr(\mu\text{-}S)]_2$ may be obtained by the reaction of $Cp_2Zr(CO)_2$ with H_2S, the corresponding permethylzirconocene system yields the singly-bridged sulfido complex $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$.

Experimental Section

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, or Schlenk techniques.[15] Solvents were purified and degassed by standard procedures. ^1H and ^{13}C NMR spectra were measured on Varian VXR 200, 300, and 400 spectrometers. IR spectra were recorded as KBr pellets on a Perkin-Elmer 1420 spectrophotometer and the data are reported in cm^{-1}. Elemental analyses were measured using a Perkin-Elmer 2400 CHN Elemental Analyzer. $Cp^*_2Zr(CO)_2$[16] and $Cp^*_2Zr(CH_3)_2$[17] were prepared as reported previously. The stoichiometry of the gaseous products of the reactions studied were not measured, although the formation of H_2 was confirmed by ^1H NMR spectroscopy. Hence, the stoichiometries of the gaseous products indicated by the equations in the text are those required to balance the zirconium-containing products.

Preparation of $Cp^*_2Zr(SH)_2$. A solution of $Cp^*_2Zr(CH_3)_2$ (0.28 g, 0.71 mmol) in benzene was treated with H_2S (1 atm) and the mixture was heated at 60 °C for 1.5 days. The volatile components were removed under reduced pressure giving yellow $Cp^*_2Zr(SH)_2$ (0.27 g, 88%). ^1H NMR (C_6D_6): 1.82 [s, 30H, 2 $\{\eta^5\text{-}C_5(CH_3)_5\}$], 1.59 [s, 2H, 2 Zr-S*H*]. ^{13}C NMR (C_6D_6): 12.2 [q, $^1J_{C-H}$ = 127 Hz, 2 $\{\eta^5\text{-}C_5(CH_3)_5\}$], 119.9 [s, 2 $\{\eta^5\text{-}C_5(CH_3)_5\}$]. IR (KBr): 2596 cm^{-1} [ν(S–H)]. Anal. (Found/calcd): %C 56.4 (56.2), % H 6.1 (7.5).

Preparation of $Cp_2Zr(SH)_2$. $Cp_2Zr(SH)_2$ was prepared by an alternative procedure to the literature method.[6] A solution of $Cp_2Zr(CH_3)_2$ (0.5 g, 2.0 mmol) in C_6H_6 (5 mL) was stirred under excess H_2S (*ca.* 2 atm) at room temperature giving a bright yellow solution (observation of a slight green tint indicates the presence of the dimer $[Cp_2Zr(\mu\text{-}S)]_2$, therefore requiring addition of more H_2S). After 30 min the mixture was frozen and the volatile components removed under reduced pressure giving $[Cp_2Zr(SH)_2$ as a bright yellow powder (0.45g, 78%) that was identified by ^1H NMR spectroscopy.

Interconversion of $Cp_2Zr(SH)_2$ and $[Cp_2Zr(\mu\text{-}S)]_2$. A solution of $Cp_2Zr(SH)_2$ (30 mg, 0.1 mmol) in C_6D_6 (1 mL) was heated at 80 °C and the volatile components were removed periodically. Monitoring the reaction by ^1H NMR spectroscopy demonstrated complete conversion to the sulfido dimer $[Cp_2Zr(\mu\text{-}S)]_2$ after 6 h. Addition of H_2S (1 atm) to a sample of $[Cp_2Zr(\mu\text{-}S)]_2$ in C_6D_6 resulted in conversion to $Cp_2Zr(SH)_2$ over a period of *ca.* 6 h at room temperature, as demonstrated by ^1H NMR spectroscopy.[6]

Reaction of $Cp^*_2Zr(SH)_2$ with $Cp^*_2Zr(CO)_2$. The reaction between $Cp^*_2Zr(SH)_2$ and $Cp^*_2Zr(CO)_2$ was monitored by ^1H NMR spectroscopy. A solution of $Cp^*_2Zr(SH)_2$ and $Cp^*_2Zr(CO)_2$ (1:1 molar ratio) in C_6D_6 was heated at 80 °C. $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$ was formed over a period of 3 days, as demonstrated by comparison of the ^1H NMR spectrum with that of the literature.[9]

Reaction of $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$ with H_2S. A solution of $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$ (*ca.* 30 mg, 0.04 mmol) in C_6D_6 (1 mL) was treated with H_2S. $Cp^*_2Zr(SH)_2$ was formed over 2 h at 80 °C, as demonstrated by ^1H NMR spectroscopy.

Reaction of $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$ with $Cp^*_2Zr(CO)_2$. The reaction between $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$ and $Cp^*_2Zr(CO)_2$ was monitored by ^1H NMR spectroscopy. A solution of $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$ and $Cp^*_2Zr(CO)_2$ (1:1 molar ratio and also *ca.* 1:10 molar ratio) in C_6D_6 (1 mL) was heated at 80 °C. No significant change was observed by ^1H NMR spectroscopy after a period of 2 weeks.

Reaction of $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$ with $Cp^*_2Zr(CO)_2$ in the Presence of C_5H_5N. The reaction between $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$ and $Cp^*_2Zr(CO)_2$ in the presence of pyridine was monitored by ^1H NMR spectroscopy. A mixture of $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$, $Cp^*_2Zr(CO)_2$ and pyridine (molar ratio *ca.* 1:10:10) in C_6D_6 (1.5 mL) was heated at 80 °C giving $Cp^*_2Zr(S)(NC_5H_5)$ over a period of 2 days.

Synthesis of $Cp^*_2Zr(S)(NC_5H_5)$. A solution of $Cp^*_2Zr(CO)_2$ (0.40 g, 0.96 mmol) and sulfur (0.03 g, 0.94 mmol) in toluene (5 mL) was heated at 145 °C for 3 h. The solvent was removed under reduced pressure and the orange solid was washed with pentane and dried *in vacuo* (0.32 g, 71%). $Cp^*_2Zr(S)(NC_5H_5)$ was identified by comparison of the ^1H NMR spectrum with that of the literature.[9]

Reaction of $Cp^*_2Zr(CO)_2$ with H_2S. The reaction between $Cp^*_2Zr(CO)_2$ and H_2S at 80 °C was monitored periodically by ^1H NMR spectroscopy. In the presence of excess H_2S (1 atm) the final product was $Cp^*_2Zr(SH)_2$ after 5 days, whereas with $Cp^*_2Zr(CO)_2$ in excess, $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$ was the final product.

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[12] Furthermore, whereas $Cp^*_2Zr(S)(NC_5H_5)$ is obtained by dehydrohalogenation of $Cp^*_2Zr(SH)I$ in the presence of pyridine, Bergman was also unable to obtain $[Cp^*_2Zr(\mu\text{-}S)]_2$ in the absence of a trapping ligand. See ref 9.

[13] Such a suggestion is supported by the fact that Cp* ligands on each zirconium center of $[Cp^*_2Zr(SH)]_2(\mu\text{-}S)$ are observed to be diastereoscopic by ^1H NMR spectroscopy in C_6D_6 solution (see ref 9). Also note that in $CDCl_3$ solution the Cp* resonances are coincidentally equivalent (δ 1.97).

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Table II. Crystal and Intensity Collection Data

formula	$C_{20}H_{32}S_2Zr$
formula weight	427.8
lattice	orthorhombic
a, Å	8.218(1)
b, Å	15.032(3)
c, Å	16.957(2)
V, Å^3	2094.8(5)
Z	4
$F(000)$, electrons	896
λ (Mo Kα), Å	0.71073
space group	*F*2*mm* (No. 42)
2θ range	3–55°
ρ (calcd), g cm^{-1}	1.36
μ (Mo Kα), cm^{-1}	7.1
no. of reflections with $F > 6\sigma(F)$	855
no. of parameters varied	59
goodness of fit	1.213
R	0.0338
R_w	0.0441
final residual electron density, e Å^{-3}	0.51
weighting scheme	$w = [\sigma^2(F) + 0.0008F^2]^{-1}$

Table III. Atom Coordinates (×10^4) for Non-Hydrogen Atoms of $Cp^*{}_2Zr(SH)_2$

atom	x	y	z
Zr	0	0	0
S	2015(3)	1261(1)	0
C(1)	319(7)	0	1499(3)
C(11)	1924(15)	0	1886(6)
C(2)	−694(8)	750(3)	1310(3)
C(21)	−362(22)	1705(5)	1521(6)
C(3)	−2130(7)	441(4)	1024(3)
C(31)	−3603(16)	1045(10)	917(5)

X-ray Structure Determination of $Cp^*{}_2Zr(SH)_2$. Crystal data, data collection, and refinement parameters for $Cp^*{}_2Zr(SH)_2$ are summarized in Table II. A single crystal of $Cp^*{}_2Zr(SH)_2$ was mounted in a glass capillary and placed on a Nicolet R3m diffractometer. The unit cell was determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photographs. Intensity data were collected using graphite monochromated Mo Kα X-radiation (λ = 0.71073 Å). Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization, and absorption effects. The structure was solved using Patterson and standard differnce map techniques on a Data General NOVA 4 computer using SHELXTL.[18] Systematic absences were consistent with several space groups, of which the choice *F*2*mm* (No. 42) was made since this is also the space group for the isomorphous complexes $Cp^*{}_2Zr(CO)_2$ and $Cp^*{}_2Hf(CO)_2$.[16] Hydrogen atoms on carbon were included in calculated positions (d_{C-H} = 0.96Å; $U_{iso}(H) = 1.2U_{iso}(CO)$). Atomic coordinates and selected bond lengths and angles for $Cp^*{}_2Zr(SH)_2$ are given in Tables I and III.

Acknowledgment. We are very grateful to Professors R.G. Bergman and F. Bottomley for valuable discussions, and we thank the reviewers for helpful comments. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. G.P. is the recipient of an A.P. Sloan Research Fellowship (1991–1993), a Camille and Henry Dreyfus Teacher–Scholar Award (1991–1996), and a Presidential Faculty Fellowship Award (1992–1997).

Supplementary Material Available: Tables of crystal and intensity data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters (7 pages). Ordering information is given on any current masthead page.

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