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Dihydrogen Activation by Titanium Sulfide Complexes

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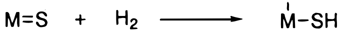
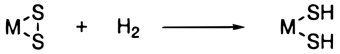
The titanocene sulfido complex Cp*$_2$Ti(S)py (**1**, Cp* = pentamethylcyclopentadienyl; py = pyridine) is synthesized by addition of a suspension of S$_8$ to a toluene solution of Cp*$_2$Ti(CH$_2$CH$_2$) (**2**) and py. The rate of rotation of the pyridine ligand in solution was determined by ^{1}H NMR spectroscopy, and the structure of **1** was determined by X-ray crystallography. Complex **1** reacts reversibly with dihydrogen to give Cp*$_2$Ti(H)SH (**6**) and py. Reaction of **1** with HD gives an equilibrium mixture of Cp*$_2$Ti(D)SH and Cp*$_2$Ti(H)SD; H$_2$ and D$_2$ are not formed in this reaction. 1D ^{1}H NMR magnetization transfer spectra and 2D EXSY ^{1}H NMR spectra of **6** in the presence of H$_2$ show that in solution the H$_2$, hydride, and hydrosulfido hydrogen atoms exchange. A four-center mechanism for this exchange is proposed. The EXSY studies show that the Ti−H and S−H hydrogens exchange with each other more rapidly than either of those hydrogens exchanges with external H$_2$. A transient dihydrogen complex intermediate is proposed to explain this observation. The infrared spectrum of **6** shows an absorption assigned to the Ti−H stretching mode at 1591 cm^{-1} that shifts upon deuteration to 1154 cm^{-1}. Reaction of **1** with trimethylsilane, diethylsilane, or dimethylsilane gives Cp*$_2$Ti(H)SSiMe$_3$ (**7**), Cp*$_2$Ti(H)SSiHEt$_2$ (**8**), or Cp*$_2$Ti(H)SSiHMe$_2$ (**9**), respectively. The isotope effect for the reaction producing **7** has been measured, and a mechanism is proposed. Treatment of **1** with an additional equivalent of S$_8$ results in the formation of the disulfide Cp*$_2$Ti(S$_2$) (**4**). Acetylene inserts into the Ti−S bond of **4** to produce the vinyl disulfide complex **5**. The structures of **4** and **5** have been determined by X-ray diffraction. Compound **4** reacts with **2** in the presence of py to produce **1.** Phosphines react with **4** in the presence of H$_2$ to provide **6** and the corresponding phosphine sulfide. Reaction of hydrogen with **4** gives Cp*$_2$Ti(SH)$_2$ (**3**). The reactions of **1** and **4** with dihydrogen provide a model for possible mechanisms of H$_2$ activation by metal−sulfide hydrodesulfurization catalysts.

Introduction

Although the reactions of dihydrogen with metal−sulfide surfaces have been explored theoretically and experimentally, the process by which H$_2$ is activated on hydrodesulfurization catalysts is still unclear.[1−5] A number of different mechanisms have been proposed for this step, including reaction of H$_2$ with a metal−sulfide bond (eq 1a)[6,7] and H$_2$ addition across the disulfide bond of a metal−disulfide complex (eq 1b).[8,9]



$$M{=}S + H_2 \longrightarrow \overset{H}{M}{-}SH \qquad (1a)$$



(1b)

Evidence for surface disulfide (S$_2$$^{2-}$) groups comes from infrared emission,[10] Raman,[11,12] and X-ray photoelectron spectroscopic[13] investigations. Some of these studies indicate that there are both bridging and nonbridging disulfide groups on the catalyst surface.[14] There is less evidence for the existence of nonbridging sulfide (S^{2-}) groups, although these species have been observed as intermediates during the sulfiding of metal oxide surfaces and could arise from oxidation of the reduced metal surface during the desulfurization process.[15] The original suggestion for the presence of M═S groups on the catalyst surface was based on the production of butadiene during the desulfurization of thiophene and by an apparent requirement for metal "anion vacancies" for catalytic activity (Scheme 1).[6]

Mechanistic insight into the activation and hydrogenation of organosulfur species on surfaces has increas-

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[1] Clausen, B. S.; Topsoe, H.; Massoth, F. E. *Hydrotreating Catalysis*; Anderson, J., Boudart, M., Eds.; Springer: Berlin, 1996; Vol. 11.

[2] Sánchez-Delgado, R. A. *J. Mol. Catal.* **1994**, *86*, 287.

[3] Prins, R.; De Beer, V. H. J.; Somorjai, G. A. *Catal. Rev.-Sci. Eng.* **1989**, *31*, 1.

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[9] Startsev, A. N. *Catal. Rev.-Sci. Eng.* **1995**, *37*, 353.

[10] Weber, T.; Muijsers, J. C.; van Wolput, J. H. M. C.; Verhagen, C. P. J.; Niemantsverdriet, J. W. *J. Phys. Chem.* **1996**, *100*, 14144.

[11] Payen, E.; Kasztelan, S.; Grimblot, J. *J. Mol. Struct.* **1988**, *174*, 71.

[12] Schrader, G. L.; Cheng, C. P. *J. Catal.* **1983**, *80*, 369.

[13] Nagai, M.; Irisawa, A.; Omi, S. *J. Phys. Chem. B* **1998**, *102*, 7619.

[14] Muijsers, J. C.; Weber, T.; van Hardeveld, R. M.; Zandbergen, H. W.; Niemantsverdriet, J. W. *J. Catal.* **1995**, *157*, 698.

[15] X-ray photoelectron spectroscopic studies are consistent with the presence of S^{2-} ligands, although most of these probably bridge metal atoms.

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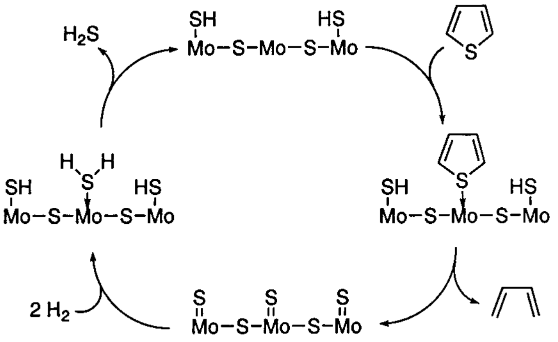
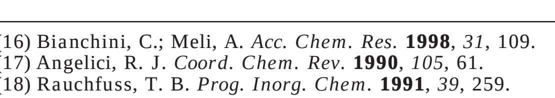
Scheme 1



ingly come from investigations of the solution phase reactions of thiophenes with soluble monomeric metal compounds.[16–18] However, little is known as yet about the processes by which hydrogen could be activated on the catalyst surface. There is no direct evidence for the processes illustrated in eq 1a and eq 1b, as neither the activation of dihydrogen by a terminal metal sulfide complex nor the reaction of dihydrogen with a monomeric metal disulfide complex has been observed in a homogeneous system.[19] In this report, we describe the synthesis of monomeric titanocene sulfide and disulfide complexes that react with dihydrogen and other small molecules.[20]

Results

Synthesis of $Cp^*_2Ti(S)py$ (1). Previous work in our laboratory had shown that the terminal titanocene oxo complex $Cp^*_2Ti(O)py$ (py = pyridine, Cp* = pentamethylcyclopentadienyl) can be synthesized by the careful addition of 1 equiv of H_2O to THF solutions of $Cp^*_2Ti(C_2H_4)$ (**2**) and py.[21] Our initial efforts toward the synthesis of $Cp^*_2Ti(S)py$ (**1**) therefore focused on using H_2S as a sulfur atom source. Condensation of 1 equiv of H_2S onto THF solutions of **2** and py does provide complex **1** in low yield. However, inspection of the crude reaction mixture by ^1H NMR spectroscopy indicated that significant amounts of $Cp^*_2Ti(SH)_2$ (**3**)[22] also formed during the reaction. When this procedure was performed on a small scale in a sealed tube, ^1H NMR spectroscopic analysis showed that **1**, **2**, and **3** were present in the product mixture along with ethane and a small amount of ethylene (eq 2). We therefore sought an improved method for sulfur atom transfer.



$$\underset{\mathbf{2}}{Cp^*_2Ti(C_2H_4)} + H_2S \xrightarrow{py} \underset{\mathbf{1}}{Cp^*_2(py)Ti{=}S} + \underset{\mathbf{3}}{Cp^*_2Ti(SH)_2} + CH_3CH_3 + CH_2CH_2 \qquad (2)$$

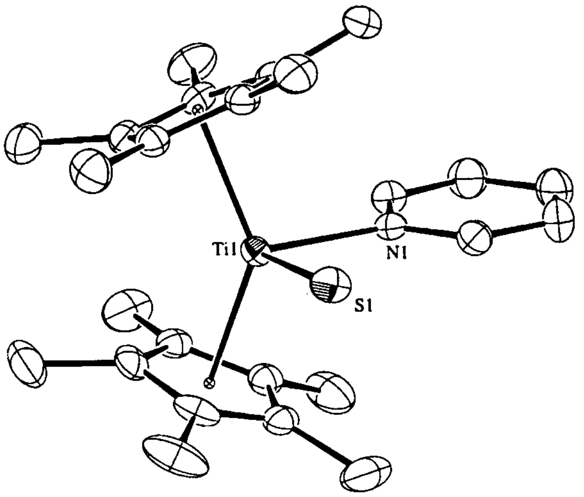
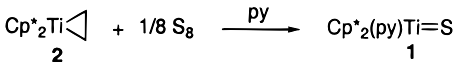


Figure 1. ORTEP diagram of $Cp^*_2Ti(S)py$ (**1**). Selected distances (Å) and angles (deg): Ti–S 2.217(1), Ti–N 2.245(3), N–Ti–S 93.9(7), Cp*–Ti–Cp* 136.1(3).

Elemental sulfur has been used as a sulfur atom source in the synthesis of early metal–sulfide complexes by several workers. Westphal and Steudel treated the titanium(II) complex $Cp_2Ti(CO)_2$ with elemental sulfur in their syntheses of various titanocene polysulfides.[23] Parkin and co-workers have also reported that $Cp^*_2Zr(S)py$[24] and $Cp^*_2Hf(S)py$ can be synthesized by treatment of $Cp^*_2Zr(CO)_2$ or $Cp^*_2Hf(CO)_2$ with S_8 in the presence of py.[25,26] Similarly, **1** is formed quantitatively when a toluene solution of **2**, py, and S_8 is stirred overnight (eq 3). When this reaction was monitored by ^1H NMR spectroscopy, an intermediate was observed in the reaction mixture. Mass spectral analysis indicated that this intermediate was the disulfide complex $Cp^*_2Ti(\eta^2\text{-}S_2)$ (**4**).



$$\underset{\mathbf{2}}{Cp^*_2Ti(C_2H_4)} + 1/8\,S_8 \xrightarrow{py} \underset{\mathbf{1}}{Cp^*_2(py)Ti{=}S} \qquad (3)$$

The structure of **1** was determined by an X-ray diffraction study. An ORTEP diagram and selected bond lengths and angles are shown in Figure 1. The general structure of **1** is similar to that of other $Cp^*_2M(E)py$ complexes (M = Ti, Zr, Hf; E = chalcogen), where the pyridine ligand lies in the plane bisecting the Cp rings.[27] The Ti–S bond distance of 2.216(1) Å is consistent with the presence of a Ti–S multiple bond.[28] The ^1H NMR spectrum of **1** at 25 °C in toluene-d_8 shows only a single resonance for the meta protons of the pyridine ligand, while the ortho protons are broadened into the baseline. Cooling this solution to 243 K results in the appearance of five inequivalent pyridine resonances. From the coalescence temperature of the meta protons of the pyridine ring (267 K) and the difference in chemical shift of these resonances at the slow exchange limit (34 ± 5 Hz) an exchange rate of 75 ± 11 s^{-1} at 267 K was

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[16] Bianchini, C.; Meli, A. *Acc. Chem. Res.* **1998**, *31*, 109.

[17] Angelici, R. J. *Coord. Chem. Rev.* **1990**, *105*, 61.

[18] Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 259.

[19] Rakowski Dubois, M.; Jagirdar, B.; Noll, B.; Dietz, S. *Syntheses, Structures, and Reactions of Cyclopentadienyl Metal Complexes with Bridging Sulfur Ligands*; Stiefel, E. I., Matsumoto, K., Eds.; American Chemical Society: Washington D.C., 1996.

[20] Some of these results have been communicated: Sweeney, Z. K.; Polse, J. L.; Andersen, R. A.; Bergman, R. G.; Kubinec, M. G. *J. Am. Chem. Soc.* **1997**, *119*, 4543.

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[24] Carney, M. J.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 6426.

[25] Howard, W. A.; Parkin, G. *J. Am. Chem. Soc.* **1994**, *116*, 606.

[26] Howard, W. A.; Parkin, G. *J. Organomet. Chem.* **1994**, *472*, C1.

[27] Parkin, G. *Prog. Inorg. Chem.* **1998**, *47*, 1.

[28] Hagadorn, J. R.; Arnold, J. *Inorg. Chem.* **1997**, *36*, 2928.

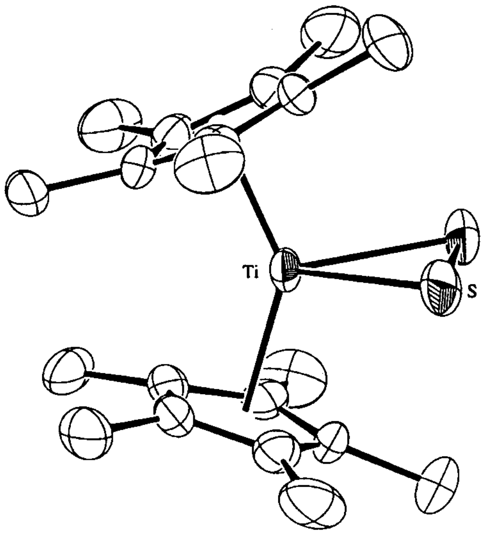
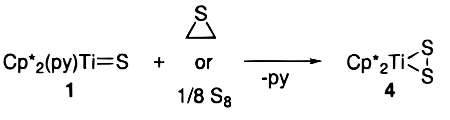


Figure 2. ORTEP diagram of $Cp^*_2Ti(S_2)$ (**4**). Selected distances (Å) and angles (deg): Ti−S 2.413(2), S−S 2.069(3), S−Ti−S 50.8(1), Ti−S−S 64.6(1).

determined.[29,30] We have previously found that the rate of dissociation of pyridine from **1** at 293 K is approximately $2.2 \times 10^{-2}\ s^{-1}$.[31] Apparently, there are two exchange processes involving the pyridine ligand of **1**: fast rotation about the Ti−N bond and relatively slow dissociation of pyridine from the metal center.

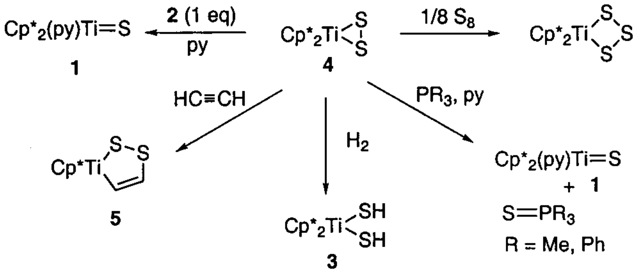
Synthesis and Reactivity of $Cp^*_2Ti(\eta^2\text{-}S_2)$ (4). Parkin and co-workers have speculated that dichalcogenides may function as intermediates in the synthesis of terminal zirconocene chalcogenide complexes, and the identification of disulfide complex **4** during the synthesis of **1** (vide supra) prompted us to synthesize this compound and explore its reactivity.[32] Although we found that **4** can be prepared simply by addition of 2 equiv of elemental sulfur to toluene solutions of **2**, this synthetic route results in the formation of small amounts of $Cp^*_2Ti(\eta^2\text{-}S_3)$,[33] which is difficult to separate from the disulfide by crystallization. Therefore, **4** is best prepared by the reaction of 1 equiv of ethylene sulfide or elemental sulfur with **1** (eq 4).



(4)

The structure of **4** was confirmed by X-ray crystallography. An ORTEP diagram and selected bond lengths and angles are shown in Figure 2. The molecule crystallizes in the space group *Fdd*2 and lies on a crystallographic 2-fold axis. The Ti−S bond length (2.413(2) Å) is 0.2 Å longer than the Ti−S distance in **1** and is similar to the Ti−S bond lengths in other titanium disulfide complexes.[34−36] The S−S bond distance of 2.069(3) Å is intermediate between that found for S_2^{2-} and S_2^{-} and is indicative of a considerable amount of electron density localized on the disulfide ligand.[37]

Scheme 2



As expected, **4** reacts with ethylene complex **2** in the presence of pyridine to provide **1** (Scheme 2). This transformation confirms that **4** is a viable intermediate in the synthesis of **1** from **2**. Other sulfur atom transfer reactions were also attempted. While **4** did not react with mercury at 25 °C, treatment of benzene solutions of **4** and pyridine with either trimethylphosphine or triphenylphosphine produces **1** and the corresponding phosphine sulfide. The disulfide can also serve as a precursor for larger titanocene−sulfur rings. For example, addition of several equivalents of sulfur to benzene solutions of **4** provides the trisulfide metallacycle $Cp^*_2Ti(\eta^2\text{-}S_3)$.

Vinyl disulfide **5** is formed upon treatment of solutions of **4** with acetylene (Scheme 2). The ^1H NMR spectrum of **5** in benzene-d_6 shows coupled proton resonances at 6.78 and 5.71 ppm ($J = 9.0$ Hz), and the ^{13}C NMR spectrum features a downfield methine resonance at 201.5 ppm that is characteristic of vinylic carbon bound to titanium.[31,38] The connectivity of **5** was confirmed by X-ray diffraction. Although there is disorder in the metallacyle, the structure was solved by modeling two different ligand orientations such that the sum of the occupancies is 1 and the minority components were refined with isotropic thermal parameters. This analysis resulted in a reasonable least-squares refinement. As shown in Figure 3, the thiametallacycle is nonplanar. The Cp* ligands are staggered with respect to each other, and the sulfur ligand is bent away from the Cp* methyl group located between the ligating S and C atoms. This appears to be purely a result of internal steric interaction, as there are no apparent short intermolecular contacts. Only a single Cp* resonance is observed by ^1H NMR spectroscopy in solutions of **5** at 25 °C, suggesting that rapid ring flipping of the vinyl disulfide ligand must be occurring in solution. Rauchfuss has shown that similar vinyl disulfide complexes are highly fluxional.[39]

The known bis(hydrosulfido) complex **3** is gradually produced when solutions of **4** are heated to 70 °C under

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[29] Binsch, G. *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975.

[30] The corresponding free energy of activation is $\Delta G^{\ddagger}_{267} = 13.3$ kcal mol^{-1}. This value is close to the $\Delta G^{\ddagger}_{267}$ of 12.2 kcal mol^{-1} measured by Mountford et al. for pyridine rotation in $[Tp^{Me2}Ti(NBu^t)Cl(py\text{-}Bu^t)]$: Dunn, S. C.; Mountford, P.; Shishkin, O. V. *Inorg. Chem.* **1996**, *35*, 1006.

[31] Sweeney, Z. K.; Polse, J. L.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 7825.

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[33] Shaver, A.; McCall, J. M. *Organometallics* **1984**, *3*, 1823.

[34] Verma, A. K.; Chou, J.-H.; Rauchfuss, T. B. *Inorg. Chem.* **1998**, *37*, 5960.

[35] Hagadorn, J. R.; Arnold, J. *Organometallics* **1998**, *17*, 1355.

[36] Guilard, R.; Ratti, C.; Tabard, A.; Richard, P.; Dubois, D.; Kadish, K. M. *Inorg. Chem.* **1990**, *29*, 2532.

[37] Müller, A.; Jaegermann, W.; Enemark, J. H. *Coord. Chem. Rev.* **1982**, *46*, 245.

[38] Polse, J. L.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 5393.

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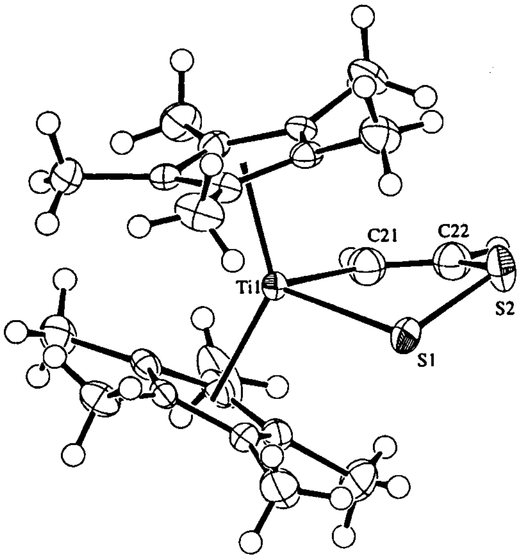
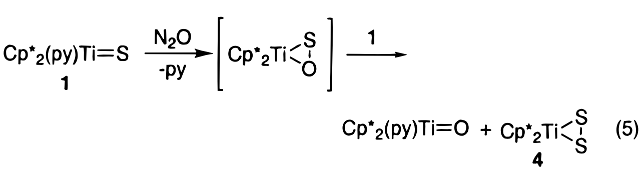


Figure 3. ORTEP diagram of $Cp^*_2Ti(\eta^2\text{-}SSC(H){=}C(H))$ (**5**). See the Supporting Information for details of structure solution and tables of bond lengths and angles.

1 atm of H_2. After crystallization from a toluene/pentane mixture, **3** can be isolated in 80% yield. The identity of **3** was confirmed by ^1H NMR spectroscopy and elemental analysis of the recrystallized product. No intermediates were observed when the reaction was monitored by ^1H NMR spectroscopy, although a small amount of $Cp^*_2Ti(\eta^2\text{-}S_3)$ formed during the course of the reaction. When **3** was heated to 105 °C in benzene-d_6 under 1 atm of D_2 for several days, no deuterium was incorporated into **3** (as judged by ^1H and ^2H NMR spectroscopy). This suggests that the reduction of **4** with dihydrogen is not reversible.

We also attempted to use atom transfer chemistry to produce oxygen- and sulfur-containing heterocycles such as $Cp^*_2Ti(\eta^2\text{-}SO)$. Sulfur–oxygen heterocycles of titanocene have been synthesized previously; however, to our knowledge there are no reported examples of three-membered metallacycles of this type.[40] Upon treatment of **1** with several equivalents of N_2O, equal amounts of $Cp^*_2Ti(O)py$ and disulfide **4** are formed (eq 5).[41] No intermediates were identified when this reaction was monitored at 193 K by ^1H NMR spectroscopy.



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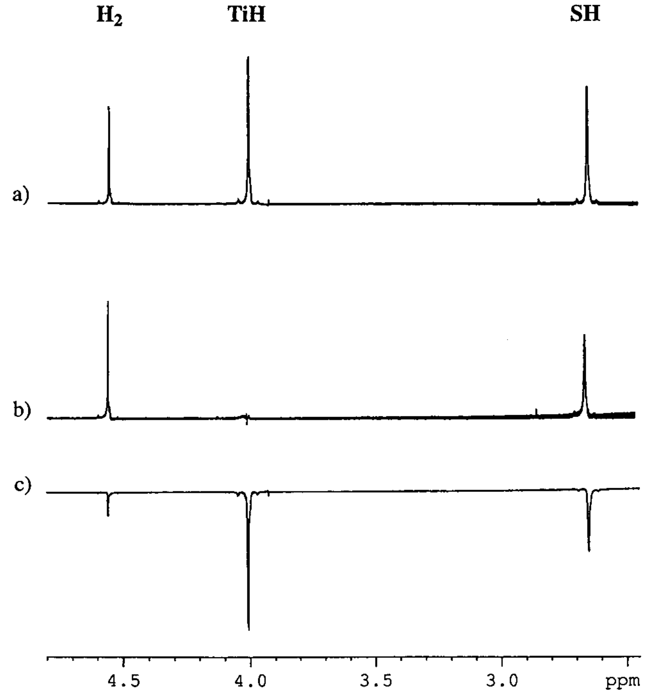
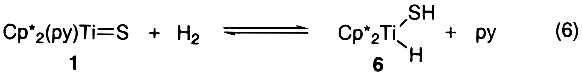


Figure 4. ^1H NMR spectra (500 MHz, 233 K) of **6** showing results of spin saturation transfer experiments: (a) control spectrum, (b) spectrum with saturation of TiH resonance, (c) difference spectrum (b − a).

Reactions of 1 with H_2. An immediate color change from red to yellow is observed upon addition of 1 atm of H_2 to a degassed toluene solution of **1**. The ^1H NMR spectrum of the yellow solution at 25 °C shows only a single Cp* resonance and slightly broadened pyridine resonances. The chemical shifts of the pyridine resonances indicate that the pyridine ligand is no longer bound to the metal center. As the temperature of the solution is lowered to −30 °C, the pyridine resonances sharpen and peaks assigned to free H_2 and the Ti−H and S−H protons of the hydrosulfido-hydride **6** become well resolved (eq 6).[42]



$$\underset{\mathbf{1}}{Cp^*_2(py)Ti{=}S} + H_2 \rightleftharpoons \underset{\mathbf{6}}{Cp^*_2Ti(SH)(H)} + py \qquad (6)$$

The variation of the ^1H NMR spectrum of **6** with temperature suggests that the dihydrogen, hydrosulfido, and metal−hydride protons are exchanging with one another, and the exchange process was initially investigated by spin saturation transfer experiments. Upon irradiation of the H_2 resonance at −50 °C, the intensities of both the Ti−H and S−H resonances decreased. The intensities of the S−H and H_2 resonances also decreased upon irradiation of the Ti−H resonance. Interestingly, upon irradiation of the Ti−H resonance we observed considerable magnetization transfer to the hydrosulfido proton but only a relatively small amount of magnetization transfer to H_2 (Figure 4).

This exchange process was also investigated using ^1H EXSY NMR spectroscopy,[43] which provides quantitative information regarding the rate of proton transfer in multisite exchange systems. The 2D ^1H EXSY spectrum (mixing time = 100 ms) of the solution at −30 °C is shown in Figure 5. The spectrum confirms that exchange is occurring between all three proton sites (H_2, Ti−H, and SH), and the first-order rate constants for each exchange process were calculated from a kinetic

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[40] Steudel, R.; Prenzel, A.; Pickardt, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 552.

[41] Parkin et al. have observed that treatment of $Cp^*_2Zr(Te)py$ with N_2O results in formation of $Cp^*_2Zr(O)py$ and elemental Te. See: Howard, W. A.; Trnka, T. M.; Parkin, G. *J. Organomet. Chem.* **1997**, *528*, 95.

[42] The resonances for the hydride and hydrosulfido protons in ^1H NMR spectra of **6** were assigned on the basis of the shifts of the hydride resonances in **7**−**9** and the shifts of the hydrosulfido resonance in **3** and related compounds.

[43] Perrin, C.; Dwyer, T. J. *Chem. Rev.* **1990**, *90*, 935.

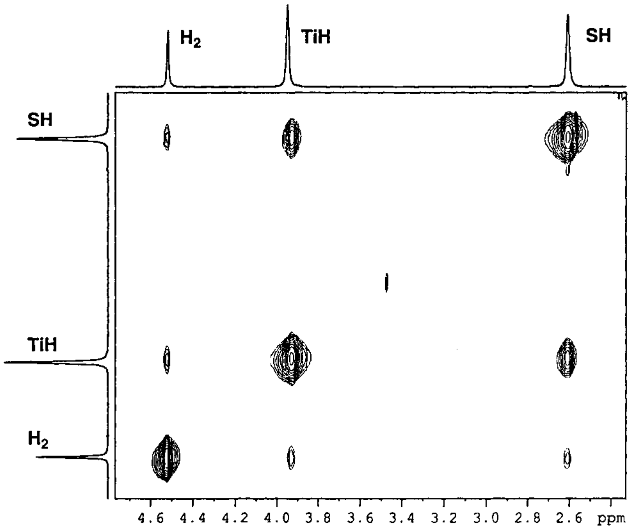


Figure 5. 2D ^{1}H EXSY spectrum of **6**.

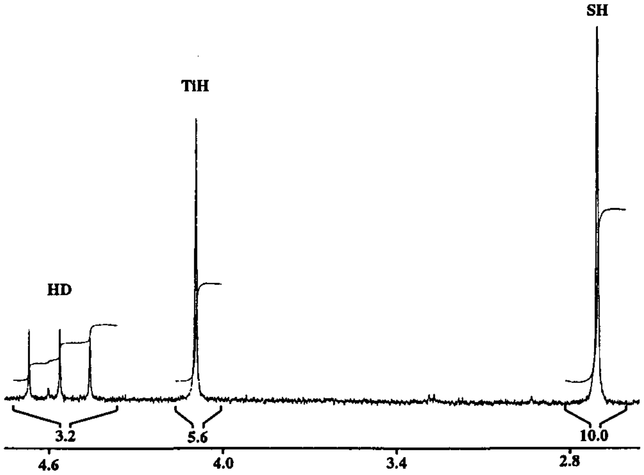
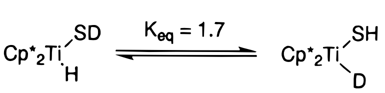


Figure 6. ^{1}H NMR spectrum of **6-HD** (400 MHz, 243 K) showing SH and TiH resonances of unequal intensity.

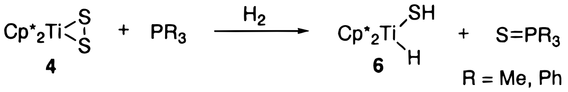
matrix analysis of the peak volumes.[44] The rate constants for TiH/H_2 and SH/H_2 exchange are both 0.2 ± 0.2 s^{-1}, and the rate constant for TiH/SH exchange is 1.2 ± 0.2 s^{-1}.

Reaction of HD with **1** does not result in the formation of H_2 or D_2.[45] The fact that H/D exchange is not catalyzed by **1** or **6** indicates that the addition and elimination of H_2 from the metal center proceeds strictly in a pairwise fashion and that potential metathesis processes such as reaction of dihydrogen with the hydride ligand of **6** are not operative. The ^{1}H NMR spectrum of **6-HD** is identical to the spectrum of **6-H$_2$** except that integration of the hydride and hydrosulfido resonances is no longer equal (Figure 6). Instead, the relative intensities of the SH:TiH resonances is 1.7:1. This ratio is essentially constant between 213 and 270 K and appears to be the result of an equilibrium isotope effect (EIE) in which the deuterium atom prefers to occupy the metal−hydride site of **6-HD** (eq 7).



$$\mathrm{Cp^*{}_2Ti(SD)(H)} \xrightleftharpoons{K_{eq} = 1.7} \mathrm{Cp^*{}_2Ti(SH)(D)} \qquad (7)$$

We have made several attempts to isolate **6** from the reaction of **1** with H_2. Unfortunately, only sulfide **1** is isolated following removal of the volatile materials under reduced pressure from a solution containing **6** and py. Addition of pentane to concentrated toluene solutions of **6** and py results only in the precipitation of **1**, which is apparently less soluble than hydrosulfido−hydride **6**, with which it is in equilibrium. Compound **6** can be prepared by other synthetic routes, however. Addition of 1 equiv of H_2S or disulfide **4** to $Cp^*{}_2TiH_2$ under an atmosphere of H_2 provides **6** along with varying amounts of the bis(hydrosulfido) species **3**. Complex **6** is also produced quantitatively from the reactions of phosphines with **4** in the presence of H_2 (eq 8). When the products of the phosphine reaction are exposed to dynamic vacuum, the color of the solution changes from yellow to dark red and a number of Cp*-containing compounds are observed by ^{1}H NMR spectroscopy. Attempts to obtain **6** as a solid from this synthetic route therefore avoided exposure to vacuum. Treatment of disulfide **4** with 1 equiv of triphenylphososphine followed by removal of the solvent under a stream of argon and dihydrogen provides a reddish solid that can be redissolved in benzene-d_6 under H_2 and can be shown by ^{1}H NMR spectroscopy to be a mixture of **6** and S=PPh$_3$. The IR spectrum of this solid shows a strong absorption at 1591 cm^{-1} assigned to the Ti−H stretching mode that shifts to 1154 cm^{-1} when the complex is prepared using D_2. A weak band at 2609 cm^{-1} is assigned to the SH stretching mode of the material prepared using H_2. This absorption is absent in the deuterated analogue; however, the SD absorption is obscured by aryl overtone bands in the 2000−1800 cm^{-1} region, preventing conclusive assignment of this feature.[46] Other workers have observed similar frequencies for hydride and hydrosulfido stretching modes in early metal metallocene complexes. For example, the Ti−H stretching frequency in $Cp^*{}_2TiH_2$[47] is 1560 cm^{-1}, and the SH stretching frequency in **3** was determined to be 2580 cm^{-1}.[22] The intramolecular EIE in **6-HD** (eq 7) is unexpected in light of the observed stretching frequencies for the hydrosulfido and hydride protons in **6**. Due to the large contribution of the zero-point energy difference in determining the EIE, the position with the higher stretching frequency is usually the preferred binding site for the heavier isotope.[48] Intermolecular EIEs that are not predicted by stretching force constants are usually attributed to metal−hydride bending modes.[49,50] It is possible that bending modes are respon-



$$\underset{\mathbf{4}}{\mathrm{Cp^*{}_2TiS_2}} + \mathrm{PR_3} \xrightarrow{H_2} \underset{\mathbf{6}}{\mathrm{Cp^*{}_2Ti(SH)(H)}} + \mathrm{S{=}PR_3} \qquad \text{R = Me, Ph} \qquad (8)$$

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[44] Abel, E. W.; Coston, T. P. J.; Orrell, K. G.; Sik, V.; Stephenson, D. J. *J. Magn. Reson.* **1986**, *70*, 34.

[45] If **1** was recrystallized only once, rapid formation of an equilibrium mixture of H_2, HD, and D_2 is observed. This exchange is probably catalyzed by traces of **2**, which is converted to $Cp^*{}_2TiH_2$ and $Cp^*{}_2TiH$ upon reaction with dihydrogen. See ref 89.

[46] A weak stretch was observed at 1885 cm^{-1} (calculated for Ti−S−D: 1872 cm^{-1}).

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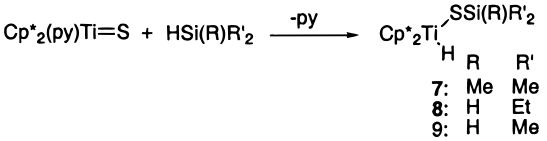
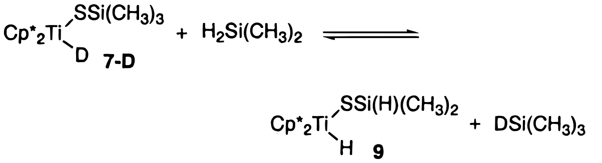
sible for the EIE in **6-HD**; however, further analysis of this effect is precluded by our inability to unambiguously assign bending modes associated with the hydride or hydrosulfido protons.

Reaction of 1 with Silanes. We have also found that **1** reacts cleanly with silanes. An immediate color change from red to orange and the production of a single compound in nearly quantitative yield are observed upon addition of trimethylsilane to a benzene solution of **1**. The ^{1}H NMR spectrum of the product in benzene-d_6 shows a singlet at δ 4.13 assigned to the Ti−H proton of **7** (eq 9). This resonance is not present in the ^{1}H NMR spectrum when the monodeuterated analogue (**7-D**) is prepared from the reaction of **1** with trimethylsilane-d_1. To confirm the connectivity of the complex, **7** was independently synthesized from the reaction of Cp*$_2$Ti(H)Cl with NaSSi(CH$_3$)$_3$. An X-ray diffraction study has also confirmed the structure of **8**.[51]



$$Cp^*_2(py)Ti{=}S + HSi(R)R'_2 \xrightarrow{-py} Cp^*_2Ti(H)SSi(R)R'_2 \quad (9)$$

Silane addition to the Ti═S bond is reversible. For example, thermolysis of **7** at 75 °C in the presence of 3 equiv of H$_2$SiMe$_2$ gave a mixture of HSiMe$_3$, H$_2$SiMe$_2$, **7**, and **9**. To establish that this exchange involved the intramolecular 1,2-elimination of silane, a benzene-d_6 solution of Cp*$_2$Ti(D)SSiMe$_3$ and H$_2$SiMe$_2$ was heated to 75 °C for 2 days. Inspection of the reaction mixture by ^{1}H and ^{2}H NMR spectroscopy showed only the reactants, **9**, and DSiMe$_3$ (eq 10). This result demonstrates that, as in the reaction of **1** with H$_2$, addition and elimination of the Si−H bond occur strictly in a pairwise fashion. To gain further insight into the transition state for these processes, the kinetic isotope effect for the reaction of **1** with HSiMe$_3$ was measured. The k_H/k_D was determined to be 1.3 ± 0.1 at 298 K.



$$Cp^*_2Ti(D)SSi(CH_3)_3 + H_2Si(CH_3)_2 \rightleftharpoons Cp^*_2Ti(H)SSi(H)(CH_3)_2 + DSi(CH_3)_3 \quad (10)$$

Discussion

Processes in which a sulfur ligand functions as a proton acceptor in the heterolytic cleavage of dihydrogen are of interest,[19,52−58] as this is thought to be an important step in the activation of dihydrogen by hydrogenases and hydrodesulfurization catalysts.[59] However, since the sulfur atom has a tendency to bridge two metal centers, most complexes containing sulfur ligands are either coordinatively or electronically saturated, and potential reaction partners cannot be activated by coordination to the metal center. Transformations involving sulfide complexes are therefore often limited to reactions that take advantage of the localization of electron density on the sulfide ligand (i.e., ligand oxidation, adduct formation with Lewis acids).[60]

Terminal titanium sulfide complexes have been reported, and reactivity studies of some of these compounds have been performed. Geoffroy et al. found that the macrocycle-supported complex [η^4-Me$_4$taa]Ti═S reacted with strong electrophiles such as hexafluoroacetone.[61,62] The syntheses and structures of the salts [NR$_4$]$_2$[Ti(S)Cl$_4$] (R = Ph, Et)[63] and Na$_2$[CpTi(μ-S)(S)]$_2$[64] have also been described. More recently, Hagadorn and Arnold prepared and structurally characterized the benzamidinate complex (PhC(NSiMe$_3$)$_2$)$_2$Ti(S)py.[28,35] These compounds are all apparently unreactive toward nonpolar substrates such as dihydrogen and silanes.[65]

Several unsaturated group IV imido complexes have been shown to react with dihydrogen to produce anilide−hydride complexes.[66,67] In some cases, these reactions have been found to be reversible. For example, Smith et al. showed that Cp*$_2$Ti═N(C$_6$H$_5$) reacts reversibly with H$_2$ to form Cp*$_2$Ti(H)N(H)C$_6$H$_5$ (**10**).[68,69] Zirconocene oxo and titanocene oxo complexes also react with dihydrogen, although these reactions do not cleanly produce products resulting from simple addition of H$_2$ across the metal−oxygen bond. Instead, treatment of Cp*$_2$Ti(O)py with 1 atm of H$_2$ provides a mixture of products including Cp*$_2$Ti(OH)$_2$ and Cp*$_2$Ti(H)(OH), and heating Cp*$_2$Zr(O)py to 80 °C in the presence of dihydrogen forms dinuclear [Cp*$_2$Zr(H)](μ-O)[Cp*$_2$Zr(OH)].[70]

The production of **6** by treatment of **1** with dihydrogen (eq 6) constitutes the first direct observation of the activation of dihydrogen by a terminal sulfide species, and the labeling experiments and kinetic studies that

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(51) In the crystal, the molecule possesses a crystallographic 2-fold axis that passes through the Ti atom and the Si atom, disordering the sulfur and the methylene carbons. While this disorder reduces the accuracy of the bond distances and angles, it does confirm the structural assignment of the product. See the Supporting Information for details.

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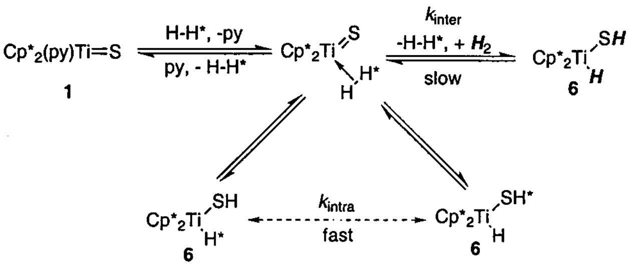
Scheme 3

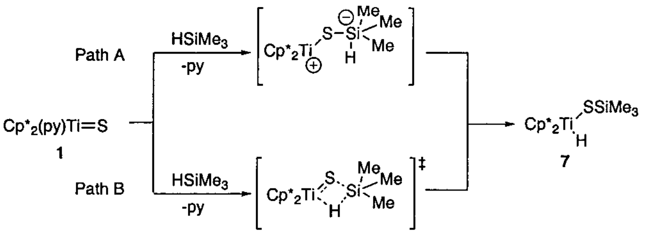


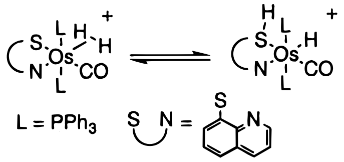
were performed provide a detailed picture of the mechanism of this reaction. Given the fact that **1** is an 18-electron complex and contains a labile pyridine ligand, it is reasonable to assume that the initial stage of the reaction of **1** with H_2 involves dissociation of pyridine from the metal center and formation of the 16-electron complex [$Cp^*_2Ti{=}S$]. Addition of H_2 to the metal–sulfur bond could then proceed via a polarized four-membered transition state, as is commonly postulated for σ-bond metathesis reactions.[71] The principle of microscopic reversibility dictates that the 1,2-elimination of H_2 from **6** should also occur via a four-centered transition state. This mechanistic hypothesis is consistent with the result from the reaction of **1** with HD, which demonstrates that addition and elimination of H_2 occur strictly in a pairwise fashion. It is also supported by the 2D ^{1}H EXSY studies of **1**, which show that the rates of exchange of H_2 with the Ti–H and SH protons are identical.

Since the discovery of stable molecular hydrogen complexes, it has been widely recognized that such species can function as intermediates along the pathway to homolytic or heterolytic dihydrogen activation.[72] Although d^0 metal complexes are formally incapable of stabilizing molecular hydrogen adducts by "back donation", calculations have nevertheless suggested that d^0 metal–dihydrogen complexes can be intermediates in hydride exchange reactions.[73–75] Schwartz et al. have also proposed that dihydrogen complexes are intermediates in the activation of H_2 by d^0 zirconocene alkyl complexes.[76] The 1D and 2D NMR studies of solutions of **1** and H_2 that we have performed are consistent with the intermediacy of a molecular dihydrogen complex in the hydrogen exchange reactions of **6** (Scheme 3). In particular, the observation that *intra*molecular proton exchange is faster than *inter*molecular proton exchange indicates the transient [$Cp^*_2Ti(S)\cdot(H_2)$] is formed and undergoes rotation and readdition of H_2 significantly faster than the H_2 molecule leaves the coordination sphere.

The intermediacy of a dihydrogen complex has also been postulated for a number of other heterolytic activations of H_2 where a proton is transferred to a sulfur ligand. For example, Sellmann et al. have suggested that a dihydrogen complex is an intermediate in the heterolytic activation of H_2 by an unsaturated rhodium thiolate complex.[54,55] Schlaf and Morris have also reported an osmium system in which a hydrido–thiolate complex is in equilibrium with a dihydrogen complex (eq 11).[58,77]

Scheme 4





(11)

The reactions of **1** with silanes provide a model for the reaction of **1** with dihydrogen. Given the expected nucleophilicity of the [$Cp^*_2Ti{=}S$] species,[31] we have considered two possible mechanisms for the addition of silanes to **1**. The first mechanism involves attack of the sulfide ligand on the silane to form a pentacoordinate silicon center followed by rapid transfer of the hydride to the metal center (Scheme 4, path A).[78] The second mechanistic postulate involves a single four-centered transition state similar to the transition states proposed for silane metathesis reactions (Scheme 4, path B).[79] Rate-determining formation of a pentacoordinate silicon intermediate as shown in path A should result in an inverse isotope effect.[78] Conversely, a normal isotope effect would be expected for the process shown for path B, since the Si–H bond should be considerably weakened in the transition state.[80] Our observation of a normal isotope effect in the reaction of **1** with $HSiMe_3$ suggests that the rate-determining step involves a concerted [2+2] addition as shown in path B.

Reactivity of Disulfide 4. The chemistry of titanocene polysulfides has been explored extensively because these complexes participate in atom transfer reactions and serve as precursors for a variety of interesting carbon- and heteroatom-containing metallacycles.[81] Monomeric titanocene disulfides have not been prepared however, since compounds of the stoichiometry $(C_5H_4R)_2TiS_2$ form the sulfur-bridged dimers 1,4-$[(C_5H_4R)_2Ti]_2S_4$.[39] The atom transfer reactions of **4** and the presumed intermediate [$Cp_2Ti(\eta^2\text{-}SO)$] are characteristic of the kinetic lability of chalcogen metallacycles.[82] The atom transfer reaction between **4** and **2** in the presence of pyridine has precedent both in Woo's studies of the reactions of titanium porphyrin complexes

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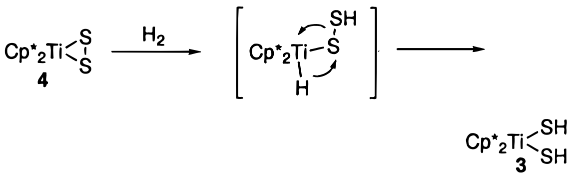
and in the reactivity of CO complexes of bis(permethylcyclopentadienyl)zirconocene dichalcogenides.[32,83] Abstraction of a sulfur atom by tertiary phosphines is not unexpected in light of the strength of the resulting phosphorus−sulfur bond.[84,85] This transformation is synthetically useful however, since it provides a way to generate [$Cp^*_2Ti{=}S$] in the absence of pyridine.

The reaction of **4** with dihydrogen to produce $Cp^*_2Ti(SH)_2$ is relevant to proposed mechanisms for hydrogen activation on metal sulfide surfaces. As the metal center in **4** is electronically unsaturated and undergoes insertion of acetylene into the metal−sulfur bond (vide supra), it seems reasonable to propose that formation of $Cp^*_2Ti(SH)_2$ from the reaction between **4** and H_2 occurs via initial addition of H_2 across a metal−sulfur bond as shown in eq 12. This mechanism has precedent in the formation of hydrosulfido ligands by sulfur atom transfer into metal−hydride bonds,[86] and it is consistent with the ability of titanocene disulfide complexes to rapidly rearrange.[39] Previous studies have shown that bridging disulfide ligands activate H_2,[56] and this work suggests that the nonbridging disulfide moieties present on catalyst surfaces may also be capable of reacting with dihydrogen.



(12)

Conclusion

We have synthesized and crystallographically characterized monomeric titanium sulfide and disulfide complexes. The reactions of these model compounds with dihydrogen support the postulate that dihydrogen could be activated by nonbridging disulfide or sulfide groups on hydrodesulfurization catalysts. The reaction of the sulfide complex with dihydrogen is reversible, and NMR studies suggest that this transformation proceeds via an η^2-H_2 intermediate. The titanocene disulfide complex $Cp^*_2Ti(\eta^2\text{-}S_2)$ also participates in atom transfer reactions and reacts with acetylene to form an unusual vinyl disulfide complex. We are currently attempting to synthesize early metal sulfido complexes that do not require stabilization by donor ligands such as pyridine.

Experimental Section

General Procedures. Unless otherwise noted, reactions and manipulations were performed in an inert atmosphere (N_2) glovebox or using standard Schlenk and high vacuum line techniques. Glassware was dried overnight at 150 °C before use. Except where noted, all NMR spectra were acquired at 25 °C. In cases where assignment of $^{13}C\{^1H\}$ NMR resonances from the initial $^{13}C\{^1H\}$ NMR spectrum was ambiguous, resonances were assigned using standard DEPT 45, 90, and/or 135 pulse sequences. 2D ^1H EXSY spectra were aquired at 243 K in phase-sensitive mode using the Bruker pulse program noesytp (see Supporting Information for further details). Mass spectrometric (MS) analyses were obtained at the University of California, Berkeley Mass Spectrometry Facility. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility. Reactions with gases and low-boiling liquids involved condensation of a calculated pressure of gas from a bulb of known volume into the reaction vessel at −196 °C. These vacuum transfers were accomplished with a digital MKS Baratron gauge attached to a high-vacuum line.

Materials. Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. All nondeuterated solvents (Fisher) were either distilled from sodium metal under N_2 or passed through a column of activated alumina under nitrogen pressure and sparged with N_2 prior to use. Deuterated solvents (Cambridge Isotope Laboratories) were purified by vacuum transfer from sodium prior to use. Pyridine was distilled from sodium under dinitrogen. Elemental sulfur was purified by recrystallization from dry benzene. Acetylene was purified by passing the gas through two cold (−78 °C) traps separated by a trap containing concentrated sulfuric acid. H_2 (Matheson) and HD (99%, Cambridge Isotope Laboratories) were used as received. $(Cp^*_2Ti(H)Cl$,[87] $NaSSiMe_3$,[88] and **1**[31] were prepared by literature methods. $Cp^*_2Ti(C_2H_4)$ (**2**)[89] was prepared by the literature method except that Cp^*_2TiCl[90] was used instead of $Cp^*_2TiCl_2$.

$Cp^*_2Ti(SH)_2$ (3) from 4. This compound has been previously reported by Bottomley et al. from reaction of $Cp^*_2Ti(CO)_2$ with H_2S.[22] Hydrogen (1 atm) was added to a frozen benzene (5 mL) solution of **4** (80 mg, 0.21 mmol) at −196 °C. The solution was thawed and heated to 70 °C for 4 days, during which time the solution color changed from deep red to red-orange. The solvent was removed in vacuo, and the remaining solid was crystallized from toluene/pentane to yield 64 mg (80%) of **3**. ^1H NMR (C_6D_6): δ 2.85 (2H), 1.83 (30H) ppm. Anal. Calcd for $C_{20}H_{32}S_2Ti$: C, 62.48; H, 8.40. Found: C, 62.29; H, 8.47.

$Cp^*_2Ti(\eta^2\text{-}S_2)$ (4). A suspension of elemental sulfur (18.1 mg, 0.56 mmol) in toluene (5 mL) was added dropwise to a stirred solution of **1** (243 mg, 0.56 mmol) in toluene (10 mL). The solution immediately turned red and was stirred for 2 days at 25 °C. The volatile materials were removed in vacuo, and residue was recrystallized from toluene to yield purple crystals of **4** (145 mg, 67%). ^1H NMR (C_6D_6): δ 1.80 (s) ppm. $^{13}C\{^1H\}$ NMR: δ 124.8 ($C{-}CH_3$), 12.3 ($C{-}CH_3$) ppm. IR (KBr): 2903 (s), 1489 (w), 1435 (m), 1375 (s), 1141 (m), 1019 (w), 737 (s) cm^{-1}. MS (EI): m/z 382 (M+). Anal. Calcd for $C_{20}H_{30}S_2Ti$: C, 62.81; H, 7.91. Found: C, 62.68; H, 7.78.

$Cp^*_2Ti(SSC(H)CH)$ (5). Compound **4** (55 mg, 0.14 mmol) was dissolved in benzene (5 mL) and placed in a resealable glass ampule fitted with a septum. Acetylene was bubbled through the solution for 5 min, and the ampule was resealed. After 1 week, the volatile materials were removed to give a solid that was crystallized from toluene/pentane to give orange crystals of **5** (33 mg, 56%). ^1H NMR (C_6D_6): δ 6.78 (d, $J = 9.0$ Hz, 1H), 5.77 (d, $J = 9.0$ Hz, H), 1.82 (s, 30H) ppm. $^{13}C\{^1H\}$ NMR: δ 201.5 (CH), 136.5 (CH), 123.6 ($C{-}CH_3$), 12.3 ($C{-}CH_3$) ppm. IR (KBr): 2907 (s), 2715 (w), 1490 (w), 1432 (m), 1377 (s), 1260 (w), 1019 (s), 803 (w) cm^{-1}. MS (EI): m/z 408 (M+). Anal. Calcd for $C_{22}H_{32}S_2Ti$: C, 64.69; H, 7.90. Found: C, 64.49; H, 7.92.

$Cp^*_2Ti(H)(SH)$ (6). Method A: An NMR tube containing a solution of **1** (4.0 mg, 0.093 mmol) in toluene-d_8 (0.5 mL) was degassed and charged with approximately 1 atm of H_2 at −196

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°C. Upon thawing, the color of the solution immediately changed from red to yellow. Method B: An ampule was charged with 74 mg (0.19 mmol) of **4** and 51 mg (0.19 mmol) of triphenylphosphine. Et_2O (5 mL) was condensed onto the solids at −196 °C, and 1 atm of H_2 was added. The solution was thawed and stirred at 25 °C for 4 h and then transferred by cannula (under a H_2/Ar mixture) to a Schlenk tube. Storing this solution at −80 °C overnight resulted in the precipitation of 38 mg (0.13 mmol) of white triphenylphosphine sulfide (identified by IR spectroscopy). The supernatant was filtered at −78 °C to another Schlenk flask, and the solvent was removed under a H_2/Ar stream at 25 °C. Analysis of this solid by ^{1}H NMR spectroscopy under H_2 showed it to be a mixture of triphenylphosphine sulfide and **6**. Spectroscopic data for **6**: ^{1}H NMR, 252 K, (C_7D_8): δ 3.96 (s, 1H), 2.62 (s, 1H), 1.86 (s, 30H) ppm. $^{13}C\{^1H\}$ NMR, 252 K, (C_7H_8): δ 118.4 (*C*−CH$_3$), 12.6 (C−*C*H$_3$) ppm. IR (Nujol): 1591 cm^{-1} (Ti−H).

Cp*$_2$Ti(H)(SSiMe$_3$) (7). Trimethylsilane (0.36 mmol) was condensed into an evacuated resealable ampule containing a frozen solution of **1** (79 mg, 0.18 mmol) in benzene (5 mL). The solution was thawed and allowed to stand for several hours. The solvent was then removed in vacuo to yield **7** as an analytically pure orange solid (68 mg, 94%). ^{1}H NMR (C_6D_6): δ 4.13 (s, 1H), 1.90 (s, 30H), 0.51 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR: δ 121.9 (*C*−CH$_3$), 13.3 (C−*C*H$_3$), 8.2 (Si−*C*H$_3$) ppm. IR (Nujol): 2721 (w), 1679 (w), 1606 (m), 1238 (s), 1022 (m), 952 (w), 825 (s) 746 (m), 676 (m), 636 (s) cm^{-1}. MS (EI): *m*/*z* 423 (M − H$^+$). Anal. Calcd for $C_{23}H_{40}SSiTi$: C, 65.06; H, 9.50. Found: C, 64.99; H, 9.51.

Cp*$_2$Ti(H)(SSiHEt$_2$) (8). A resealable glass ampule was charged with a solution of **1** (192 mg, 0.45 mmol) in benzene (5 mL). The solution was frozen, and diethylsilane (0.67 mmol) was condensed into the ampule. The solution was thawed and allowed to stand at 25 °C for 1 h. The volatile materials were removed in vacuo, and the resulting solid was recrystallized from pentane to yield **8** (105 mg, 53%) as orange crystals. ^{1}H NMR (C_6D_6): δ 5.11 (m, 1H), 1.92 (s, 30H), 1.20 (t, 6H), 0.89 (m, 4H) ppm. $^{13}C\{^1H\}$ NMR: δ 121.6 (*C*−CH$_3$), 12.9 (C−*C*H$_3$), 10.8 (CH$_3$), 8.5 (CH$_2$) ppm. IR (cyclohexane): 2994 (s), 2750 (w), 2036 (s), 1604 (s), 1463 (m), 1326 (s), 1020 (m), 927 (s), 848 (s), 708 (m), 590 (m) cm^{-1}. MS (EI): *m*/*z* 437 (M+). Anal. Calcd for $C_{24}H_{42}SSiTi$: C, 65.87; H, 9.44. Found: C, 65.92; H, 9.62.

Cp*$_2$Ti(H)(SSiHMe$_2$) (9). Dimethylsilane (0.187 mmol) was condensed into an evacuated resealable ampule containing a frozen solution of **1** (80 mg, 0.187 mmol) in benzene (5 mL) at −196 °C. The solution was thawed and allowed to stand for 30 min. The solvent was removed in vacuo, and **9** (70 mg, 92%) was collected as an analytically pure orange solid. ^{1}H NMR (C_6D_6): δ 5.30 (m, 1H), 4.01 (s, 1H), 1.92 (s, 30H), 0.44 (d, 6H) ppm. $^{13}C\{^1H\}$ NMR: δ 122.0 (*C*−CH$_3$), 13.1 (C−*C*H$_3$), 5.2 (Si−*C*H$_3$) ppm. IR (Nujol): 2723 (w), 2096 (s), 1600 (m), 1234 (m), 1022 (m), 877 (s), 831 (m) cm^{-1}. MS (EI): *m*/*z* 409 (M − H$^+$). Anal. Calcd for $C_{22}H_{38}SSiTi$: C, 64.36; H, 9.34. Found: C, 64.44; H, 9.33.

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Supporting Information Available: Tables giving details of the data collection, data reduction and structure solution and refinement, positional and thermal parameters, bond lengths, bond angles, and torsion angles for **1**, **4**, **5**, and **8** and details of the 2D EXSY NMR study of **6**.

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