

## Synthesis, Structure, and Reactivity of Monomeric Titanocene Sulfido and Disulfide Complexes. Reaction of H<sub>2</sub> with a Terminal M=S Bond

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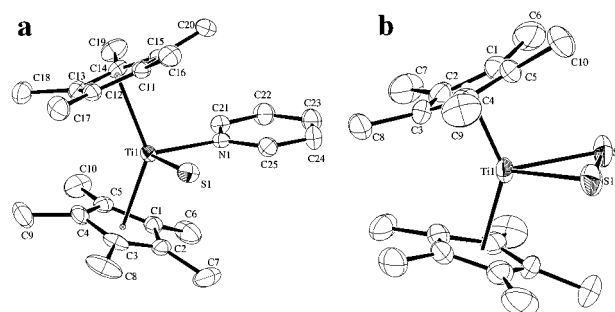
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The catalytic desulfurization of some organosulfur compounds has been proposed to proceed through an intermediate containing a metal–sulfur multiple bond which reacts with H<sub>2</sub>.<sup>1–5</sup> However, the activation of H<sub>2</sub> by a terminal M=S bond has not been observed in a discrete homogenous system.<sup>6</sup> In this communication, we report the synthesis of the terminal decamethyltitanocene sulfido complex Cp\*<sub>2</sub>Ti(S)py (**1**, py = pyridine) and its reactivity toward H–H and H–Si bonds. We also report the synthesis of the corresponding disulfide complex Cp\*<sub>2</sub>Ti(S<sub>2</sub>) (**2**) and describe its reactivity toward dihydrogen.

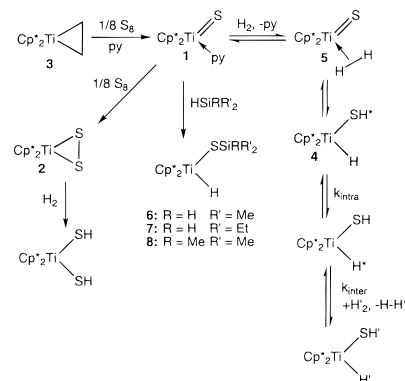
The decamethyltitanocene ethylene complex Cp\*<sub>2</sub>Ti(CH<sub>2</sub>CH<sub>2</sub>)<sup>7</sup> (**3**) is a useful starting material for the synthesis of titanocene oxo,<sup>8</sup> imido,<sup>9</sup> and diazoalkane<sup>10</sup> complexes. This compound is also an excellent synthon for **1**. Addition of a suspension of S<sub>8</sub> (1/8 equiv) to a toluene solution of **3** and py (5 equiv) results in an immediate color change from green to red. Subsequent reduction of the solvent volume, addition of pentane, and cooling to –40 °C produce red crystals of **1** in 76% yield. Alternatively, **1** can be synthesized by addition of H<sub>2</sub>S (1 equiv) to a cold solution of **3** and py in THF, although in this case the product is isolated in much lower (*ca.* 30%) yields. The structure of **1** has been determined by X-ray diffraction; an ORTEP diagram is shown in Figure 1. The Ti–S bond length of 2.217(1) Å is longer than that found for other terminal titanium sulfido bonds<sup>11–13</sup> and is slightly longer than the value predicted for [Cp<sub>2</sub>TiS] using *ab initio* methods.<sup>14,15</sup> The geometry about the titanium center is very similar to that found in the analogous oxo compound,<sup>8</sup> although the Ti–N bond length is slightly longer (2.245(3) vs 2.215(4) Å) and the E–Ti–N bond angle is slightly wider (93.91(7)° vs 90.8(1)°) in the sulfido complex. At room temperature, the 300 MHz <sup>1</sup>H NMR spectrum shows a sharp Cp\* resonance and two broadened peaks assigned to the *meta* and *para* pyridine proton resonances; the *ortho* proton resonances are broadened into the baseline. The broad pyridine resonances indicate that the pyridine ligand is dissociating reversibly from the metal center on the NMR time scale.

Placing a degassed toluene-*d*<sub>8</sub> solution of **1** under H<sub>2</sub> (1 atm) results in a color change from red to yellow. The room temperature 300 MHz <sup>1</sup>H NMR spectrum of the yellow solution



**Figure 1.** ORTEP drawings of (a) **1** and (b) **2**. Bond distances and angles for **1** and **2** are included in the Supporting Information.

### Scheme 1



shows only a new Cp\* resonance and peaks assignable to free py. Attempts to isolate the reaction product by removal of solvent from the yellow solution have resulted only in recovery of **1**, indicating that the reaction is readily reversible.<sup>16,17</sup> However, cooling the solution to 273 K results in the decoalescence of resonances assignable to free py, free H<sub>2</sub>, and the hydride and hydrosulfido protons of Cp\*<sub>2</sub>Ti(SH)H (**4**) (Scheme 1).<sup>18</sup>

The 2D EXSY <sup>1</sup>H NMR spectrum<sup>19</sup> of this solution at 253 K (Figure 2) shows that exchange is occurring between the H<sub>2</sub>, hydride, and hydrosulfido protons. Interestingly, the cross peaks between the hydride and hydrosulfido resonances are more intense than the cross peaks between the H<sub>2</sub> resonance and the hydride or hydrosulfido resonances, suggesting that *intramolecular* hydrogen exchange (exchange between the hydrosulfido and hydride protons) is faster than *intermolecular* hydrogen exchange (exchange of the hydrosulfido or hydride protons with H<sub>2</sub>). The similar intensities of the cross peaks due to exchange of the hydrosulfido and hydride protons with H<sub>2</sub> indicate that the rates of chemical exchange of these protons with H<sub>2</sub> are nearly identical. These qualitative assessments were confirmed by a kinetic matrix analysis of the cross peak intensities using the D2DNMR program developed by Orrell and co-workers.<sup>20</sup> This analysis provides the first-order rate constants for multisite

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(16) Dihydrogen also reacts reversibly with Cp\*<sub>2</sub>TiNPh to form the anilide hydride Cp\*<sub>2</sub>Ti(H)NPh. EXSY experiments indicate that in this system intramolecular hydrogen exchange is slower than exchange with H<sub>2</sub> and that there is no long-lived η<sup>2</sup>-H<sub>2</sub> species along the reaction coordinate. See ref 7.

(17) Attempts to synthesize the product of this reaction independently have led only to mixtures of products. These efforts will be described in detail in a future publication.

(18) Representative <sup>1</sup>H NMR spectra are included in the Supporting Information.

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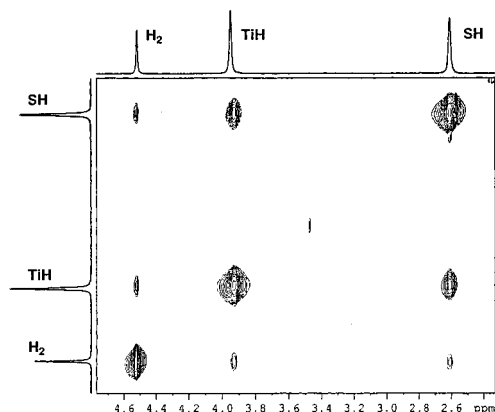
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**Figure 2.** 2D EXSY  $^1\text{H}$  spectrum of **4** showing exchange between  $\text{H}_2$ , TiH, and SH protons.

exchange directly from the 2D EXSY spectrum peak volumes. The kinetic matrix for this exchange indicates that at 243 K the rate constant for TiH–SH proton exchange is  $1.2 \pm 0.2 \text{ s}^{-1}$ , while the rate constants for TiH– $\text{H}_2$  and SH– $\text{H}_2$  proton exchange are  $0.2 \pm 0.2 \text{ s}^{-1}$ . Since elimination of  $\text{H}_2$  from **4** and exchange of the hydrosulfido and hydride protons are first-order processes, these rate constants are equivalent to the rate constants for intermolecular and intramolecular hydrogen exchange.

The differences in these exchange rates, the reversibility of the formation of the hydrosulfido–hydride complex, and the nearly identical rates of exchange of the hydrosulfido and hydride protons with  $\text{H}_2$  can best be explained by the postulate of an  $\eta^2\text{-H}_2$  complex (**5**) as an intermediate in the elimination of  $\text{H}_2$  from **4** and the formation of **4** from **1** and  $\text{H}_2$ . Formation of an  $\eta^2\text{-H}_2$  ligand from  $\text{M}(\text{RSH})(\text{H})$  complexes has recently been observed by Morris et al. for cationic late-metal species,<sup>21</sup> and  $\eta^2\text{-H}_2$  adducts have been implicated as intermediates in hydrogen metathesis reactions of  $d^0$  metals.<sup>22,23</sup> If **5** is an intermediate in the hydrogen exchange reactions shown in Scheme 1,  $k_{\text{intra}}$  must be larger than  $k_{\text{inter}}$  because the barrier to formation of **5** and rotation of the  $\eta^2\text{-H}_2$  ligand is lower in energy than the barrier to dissociation of  $\text{H}_2$  from the  $\text{Cp}^*_2\text{Ti}(\text{S})$  metal fragment.<sup>24</sup> This mechanism for intramolecular hydrogen exchange also requires that the actual rate of formation of the  $\eta^2\text{-H}_2$  intermediate from **4** be twice the observed rate of magnetization transfer between the hydrosulfido and hydride protons (*ca.*  $2.4 \text{ s}^{-1}$ ) since elimination and readdition will occur 50% of the time without exchanging the hydrosulfido and hydride protons.<sup>25</sup>

Silanes and  $\text{H}_2$  often exhibit similar reactivity toward organometallic compounds.<sup>26</sup> As shown in Scheme 1, silanes add across the Ti–S bond of **1** to form complexes of the type  $\text{Cp}^*_2\text{Ti}(\text{H})\text{SSiRR}'_2$  (**6–8**).<sup>27</sup> The structure of **7** has been confirmed by X-ray diffraction.<sup>28</sup> The kinetic isotope effect for the reaction

of **1** with  $(\text{H}/\text{D})\text{SiMe}_3$  at  $25^\circ\text{C}$  was measured by competition experiments to be  $1.3 \pm 0.1$ . This modest value of  $k_{\text{H}}/k_{\text{D}}$  is consistent with hydride transfer from a silane *via* a four-centered transition state. Most surprisingly, we have also found that the reaction of **1** with silanes is reversible. For example, heating a benzene solution of **8** to  $75^\circ\text{C}$  in the presence of 3 equiv of dimethylsilane results in the formation of **6** and trimethylsilane (identified by  $^1\text{H}$  NMR spectroscopy). Similarly, heating a solution of  $\text{Cp}^*_2\text{Ti}(\text{D})\text{SSiMe}_3$  (**8-D**) in the presence of  $\text{H}_2\text{SiMe}_2$  results in the formation of an equilibrium mixture of **8-D**,  $\text{HSiMe}_3$ , **6**, and  $\text{H}_2\text{SiMe}_2$ . These results suggest that exchange occurs via elimination of silane from the metal complex to form a Ti–S species (presumably  $\text{Cp}^*_2\text{Ti}=\text{S}$ ) which is then trapped by another silane.

Addition of 1 equiv of elemental sulfur to **1** results in formation of the titanocene disulfide complex **2** in 67% isolated yield. This compound is stable in benzene solution at  $75^\circ\text{C}$  for several days. An ORTEP diagram of **2** is shown in Figure 1. The S–S bond distance of  $2.069(3) \text{ \AA}$  is close to the S–S bond distance in elemental sulfur<sup>29</sup> and indicates that there is extensive back-bonding from the titanocene fragment into the  $\pi^*$  orbital of the  $\text{S}_2$  ligand. Piers et al. have recently reported the synthesis of the dichalcogenides  $\text{Cp}^*_2\text{Ti}(\eta^2\text{-Se}_2)$  and  $\text{Cp}^*_2\text{Ti}(\eta^2\text{-Te}_2)$ ,<sup>14,30</sup> and Howard and Parkin have synthesized the carbon monoxide adducts of zirconocene and hafnocene disulfides.<sup>31</sup> Thus far, however, studies of the reaction chemistry of early metal dichalcogenides has largely been limited to examination of their behavior as atom transfer reagents.<sup>14,32,33</sup> We have discovered that **2** reacts with  $\text{H}_2$  to form the previously reported titanocene bis(hydrosulfido) species  $\text{Cp}^*_2\text{Ti}(\text{SH})_2$ <sup>34</sup> in 79% isolated yield. To our knowledge, this is the first example of apparently direct addition of  $\text{H}_2$  to a nonbridging metal disulfide complex.<sup>4,35</sup> No intermediates in the reaction are observed by  $^1\text{H}$  NMR, although a small amount of  $\text{Cp}^*_2\text{Ti}(\text{S}_3)$ <sup>36</sup> does form during the course of the reaction. Experiments designed to elucidate the mechanism of this transformation are currently underway.

In conclusion, we have synthesized monomeric titanocene sulfido and disulfide complexes and studied their reactivity toward  $\text{H}_2$ . The reaction of  $\text{H}_2$  with **1** constitutes the first example of  $\text{H}_2$  activation by a terminal metal sulfur bond. Silanes appear to behave analogously. The relative rates of intramolecular and intermolecular hydrogen exchange of **3** under an atmosphere of  $\text{H}_2$  suggest that hydrogen exchange may occur via a  $\eta^2\text{-H}_2$  complex. Further studies of the reaction chemistry of **1** and **2** are in progress.

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**Supporting Information Available:** See refs 18, 27, and 28 for description (30 pages). See any current masthead page for ordering and Internet access instructions.

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