

**Reactions of Bis(cyclopentadienyl)- and  
Bis(pentamethylcyclopentadienyl)titanium and  
Bis(cyclopentadienyl)- and  
Bis(pentamethylcyclopentadienyl)zirconium Dicarbonyls with  
Dihydrogen Selenide: Evolution of Dihydrogen and Formation of  
Hydroselenides and Selenides. Comparison with the Analogous  
Reactions of Dihydrogen Sulfide and Oxide**

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Peter S. White

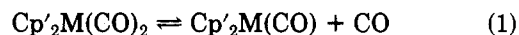
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The reaction between  $\text{Cp}_2\text{Ti}(\text{CO})_2$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) and  $\text{H}_2\text{Se}$  at 0 °C in hexane or toluene gave  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})]_2$ ; at 20 °C the same reaction in toluene gave  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})_2\text{TiCp}]_2(\mu\text{-Se})$ ; at 80 °C the major product was the cluster  $[\text{CpTi}]_6\text{Se}_8$  with traces of  $[\text{CpTiSe}]_4$  and  $[\text{CpTi}]_5\text{Se}_6$ . The reaction between  $\text{Cp}^*\text{Ti}(\text{CO})_2$  ( $\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$ ) and  $\text{H}_2\text{Se}$  in a 1:4 mole ratio in toluene at 20 °C gave  $\text{Cp}^*\text{Ti}(\text{SeH})_2$ . At a lower mole ratio a mixture of  $\text{Cp}^*\text{Ti}(\text{SeH})_2$  and  $[\text{Cp}^*\text{Ti}(\mu\text{-Se})]_2$  was obtained. The reactions between  $\text{Cp}'_2\text{Zr}(\text{CO})_2$  ( $\text{Cp}' = \text{Cp}$  or  $\text{Cp}^*$ ) and  $\text{H}_2\text{Se}$  at 80 °C in toluene gave  $[\text{Cp}'_2\text{Zr}(\mu\text{-Se})]_2$ . In all of the reactions CO and  $\text{H}_2$  were evolved. From a comparison of the reactions of  $\text{H}_2\text{Se}$  with the analogous reactions between  $\text{Cp}'_2\text{M}(\text{CO})_2$  and  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{O}$ , or  $\text{N}_2\text{O}$  it is concluded that the initial step is protonation of  $\text{Cp}'_2\text{M}(\text{CO})_2$  by  $\text{H}_2\text{A}$  ( $\text{A} = \text{O}, \text{S},$  or  $\text{Se}$ ) giving  $[\text{Cp}'_2\text{M}(\text{H})(\text{CO})_2]^+$ . This loses CO and coordinates  $\text{AH}^-$  to give  $\text{Cp}'_2\text{M}(\text{H})(\text{AH})$ , which in turn reacts with either  $\text{Cp}'_2\text{M}(\text{CO})_2$  to give  $[\text{Cp}'_2\text{M}(\text{H})]_2(\mu\text{-A})$  or with  $\text{H}_2\text{A}$  to give  $\text{Cp}'_2\text{M}(\text{AH})_2$ ; reaction with  $\text{Cp}'_2\text{M}(\text{CO})_2$  is considered to be the more probable route. The structure of  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})_2\text{TiCp}]_2(\mu\text{-Se})$  was determined by X-ray diffraction. Crystal data for  $\text{C}_{30}\text{H}_{30}\text{Se}_5\text{Ti}_4 \cdot 0.25(\text{C}_6\text{H}_5\text{CH}_3)$ :  $P\bar{1}$ ,  $a = 11.329$  (1),  $b = 12.572$  (1),  $c = 23.769$  (2) Å;  $\alpha = 88.587$  (7),  $\beta = 86.481$  (8),  $\gamma = 89.217$  (7)°;  $Z = 4$ ;  $R = 0.056$  for 416 variables and 6237 observed reflections. The average distance between  $\text{Cp}_2\text{Ti}$  and Se is 2.580 (3) Å, between  $\text{CpTi}$  and Se within the  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})_2\text{TiCp}]$  unit 2.392 (3) Å, and between  $\text{CpTi}$  and the central Se 2.467 (3) Å. The differences in the Ti-Se distances are ascribed to a combination of the coordination number of the Ti atoms and  $\pi$ -bonding between Ti and Se.

### Introduction

We have described previously the reactions between  $\text{Cp}'_2\text{M}(\text{CO})_2$  ( $\text{Cp}' = \text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ;  $\text{Cp}' = \text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$ ;  $\text{M} = \text{Ti}, \text{Zr}$ ) and  $\text{H}_2\text{O}$  or  $\text{H}_2\text{S}$ .<sup>1</sup> In the case of  $\text{H}_2\text{O}$ , the cluster  $[\text{CpTi}]_6(\mu_3\text{-O})_8$ <sup>2</sup> is obtained from  $\text{Cp}_2\text{Ti}(\text{CO})_2$ ;  $\text{ZrO}_2$  is obtained from  $\text{Cp}_2\text{Zr}(\text{CO})_2$  and there is no reaction with  $\text{Cp}^*\text{Zr}(\text{CO})_2$ . The absence of a reaction between  $\text{Cp}^*\text{Zr}(\text{CO})_2$  and  $\text{H}_2\text{O}$  was also noted by Hillhouse and Bercaw.<sup>3</sup> In the case of  $\text{H}_2\text{S}$ , the cluster  $[\text{CpTi}]_5(\mu_3\text{-S})_6$  is obtained from  $\text{Cp}_2\text{Ti}(\text{CO})_2$ <sup>4</sup> and  $\text{Cp}^*\text{Ti}(\text{SH})_2$  from  $\text{Cp}^*\text{Ti}(\text{CO})_2$ ; with  $\text{Cp}'_2\text{Zr}(\text{CO})_2$  the dimers  $[\text{Cp}'_2\text{Zr}(\mu\text{-S})]_2$  are obtained.<sup>1</sup> A marked difference in reactivity on going from  $\text{H}_2\text{O}$  to  $\text{H}_2\text{S}$  is apparent in both the products obtained and rates of the reactions. Therefore it was desirable to extend the reactions to those between  $\text{H}_2\text{Se}$  and  $\text{Cp}'_2\text{M}(\text{CO})_2$  in order to investigate the trend in reactivity further. A second reason for turning to the next member of group 16 was to provide evidence for the mechanisms of the initial reaction between  $\text{Cp}'_2\text{M}(\text{CO})_2$  and  $\text{H}_2\text{A}$  ( $\text{A} = \text{O}, \text{S},$  or  $\text{Se}$ ). Hillhouse and Bercaw had suggested that the unreactivity of  $\text{Cp}^*\text{Zr}(\text{CO})_2$  toward  $\text{H}_2\text{O}$ , compared to the reactivity of  $[\text{Cp}^*\text{Zr}(\text{N}_2)]_2(\mu\text{-N}_2)$  which gave  $[\text{Cp}^*\text{Zr}(\text{H})]_2(\mu\text{-O})$ , was due to the inability of  $\text{Cp}^*\text{Zr}(\text{CO})_2$  to dissociate a CO ligand.<sup>3</sup> This implies that the initial step in the reactions of  $\text{Cp}'_2\text{M}(\text{CO})_2$  with  $\text{H}_2\text{A}$  is dissociation (reaction 1). It has been shown that carbonyl substitution



reactions of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  take place by such a dissociation but that those of  $\text{Cp}_2\text{Zr}(\text{CO})_2$  are associative.<sup>5</sup> The postulate that dissociation is the important step does not explain the difference in reactivity of  $\text{Cp}'_2\text{M}(\text{CO})_2$  toward  $\text{H}_2\text{O}$  or  $\text{H}_2\text{S}$ .

A third reason for investigating the reactions of  $\text{H}_2\text{Se}$  relates to the formation of clusters of type  $[\text{CpTi}]_m(\mu_3\text{-A})_n$  from  $\text{Cp}_2\text{Ti}(\text{CO})_2$  and  $\text{H}_2\text{A}$ . With  $\text{H}_2\text{O}$ , only  $[\text{CpTi}]_6(\mu_3\text{-O})_8$  is observed; with  $\text{H}_2\text{S}$ , the product is  $[\text{CpTi}]_5(\mu_3\text{-S})_6$ , although traces of  $[\text{CpTi}]_6\text{S}_8$  are observed in the mass spectrum of the product. In neither case is there any evidence of how these remarkable clusters are formed, nor why one should predominate in a particular case. Investigation of the clusters formed by  $\text{H}_2\text{Se}$  might provide information on the formation of clusters in general, and it was obviously of interest to see which of the possible clusters,<sup>6</sup>  $[\text{CpTiSe}]_4$ ,  $[\text{CpTi}]_5\text{Se}_6$ , or  $[\text{CpTi}]_6\text{Se}_8$ , would predominate.

### Results

**Reaction between  $\text{Cp}_2\text{Ti}(\text{CO})_2$  and  $\text{H}_2\text{Se}$ .** The reaction between  $\text{Cp}_2\text{Ti}(\text{CO})_2$  and  $\text{H}_2\text{Se}$  in a 1:1 mole ratio proceeded smoothly at 0 °C in hexane over 5 days to produce purple  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})]_2$  according to eq 2. The use



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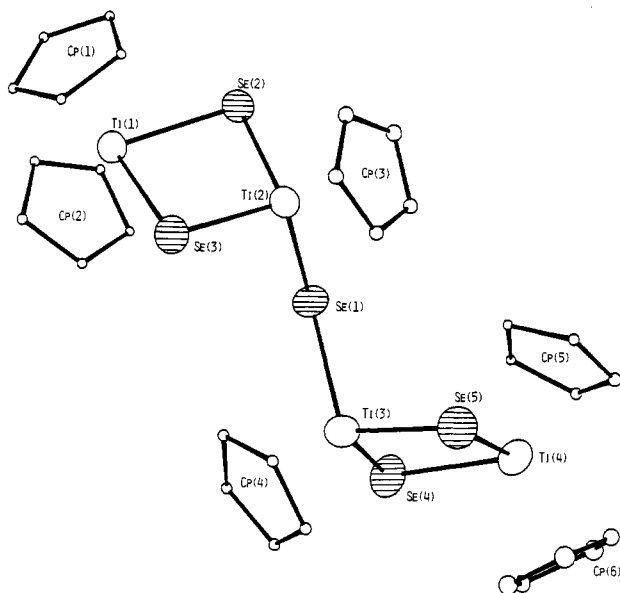
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**Figure 1.** The molecular structure and numbering scheme for  $[Cp_2Ti(\mu-Se)_2TiCp]_2(\mu-Se)$ .

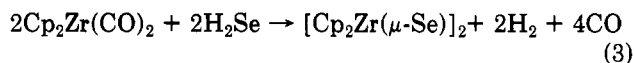
of hexane as reaction medium was important, since  $[Cp_2Ti(\mu-Se)]_2$  was insoluble in hexane and precipitated from solution, thus preventing further reaction. The identity of  $[Cp_2Ti(\mu-Se)]_2$  was proved by mass and NMR spectroscopies, by osmometric molecular weight determination in  $CHCl_3$  solution, and by comparison with the reported properties of the analogous Zr and Hf complexes.<sup>7,8</sup> When the reaction between  $Cp_2Ti(CO)_2$  and  $H_2Se$  was conducted in toluene at 20 °C, dark purple  $[Cp_2Ti(\mu-Se)_2TiCp]_2(\mu-Se)$  was the major product, though traces of the clusters  $[CpTiSe]_4$ ,  $[CpTi]_5Se_6$ , and  $[CpTi]_6Se_3$  were found by mass spectrometry. The identity of  $[Cp_2Ti(\mu-Se)_2TiCp]_2(\mu-Se)$  was determined by X-ray diffraction, and its structure is discussed below (Figure 1). It had a marked tendency to polymerize further in solution, depositing a red-brown material which was insoluble in all common solvents but which had an analysis corresponding to the same empirical formula,  $Cp_6Ti_4Se_5$ .

When the reaction between  $Cp_2Ti(CO)_2$  and  $H_2Se$  was conducted at 80 °C or higher, in toluene or xylene, some  $[Cp_2Ti(\mu-Se)_2TiCp]_2(\mu-Se)$  was formed, but the major product was the cluster  $[CpTi]_6Se_3$ . The identity of this product was determined by mass spectrometry. The spectra showed the parent ion peak ( $[Cp_6^{49}Ti_6^{80}Se_3]^+$ ,  $m/e$  1318) and peaks for ions obtained by successive loss of Cp from the parent. Similar behavior was observed for other clusters of the  $[CpM]_mAn$  type.<sup>1,4,9</sup> There were traces of  $[CpTiSe]_4$  and  $[CpTi]_5Se_6$  in the mass spectra of the crude product. There was no evidence (infrared, NMR, or mass spectroscopies) in any of the reactions for the presence of compounds containing Ti-H bonds.

**Reaction between  $Cp^*_2Ti(CO)_2$  and  $H_2Se$ .** The reaction between  $Cp^*_2Ti(CO)_2$  and  $H_2Se$  (1:2 mole ratio in toluene) produced, over 7 days at 20 °C, a mixture consisting of purple-brown  $Cp^*_2Ti(SeH)_2$  as the major product and brown-purple  $[Cp^*_2Ti(\mu-Se)]_2$  as the minor one. The two products could be separated since  $[Cp^*_2Ti(\mu-Se)]_2$  was much more soluble in hexane than  $Cp^*_2Ti(SeH)_2$ . The two

complexes were identified by spectroscopy (note  $\nu(\text{Se-H})$  at 2300  $\text{cm}^{-1}$ ) and analysis and by comparison with their various  $Cp'_2M(AH)_2$  and  $[Cp'_2M(\mu-A)]_2$  analogues.<sup>1,7,8,10-15</sup> When the reaction between  $Cp^*_2Ti(CO)_2$  and  $H_2Se$  was conducted in a 1:4 mole ratio in toluene, the results were essentially the same as for the 1:2 case. In a 1:1 mole ratio at 0 °C in hexane solution the product was  $[Cp^*_2Ti(\mu-Se)]_2$ . However, in a 1:1 mole ratio at 20 °C in toluene solution only traces of  $[Cp^*_2Ti(\mu-Se)]_2$  or  $Cp^*_2Ti(SeH)_2$  were obtained. The major product was a red material which was insoluble in all common solvents and showed no bands attributable to  $\nu(\text{Se-H})$  in the infrared spectrum. The same material was obtained when a toluene solution of  $Cp^*_2Ti(SeH)_2$  was set aside in a sealed, evacuated NMR tube. The solution initially turned brown and then slowly precipitated the red material.

**Reaction between  $Cp_2Zr(CO)_2$  or  $Cp^*_2Zr(CO)_2$  and  $H_2Se$ .** The reaction between  $Cp_2Zr(CO)_2$  and  $H_2Se$  proceeded smoothly and cleanly at 20 °C in toluene over 5 days to give  $[Cp_2Zr(\mu-Se)]_2$  according to eq 3. An analo-



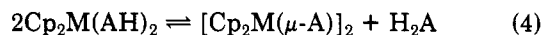
gous reaction took place with  $Cp^*_2Zr(CO)_2$  but was not quite so clean due to the ready oxidation of  $Cp^*_2Zr(CO)_2$  and the difficulty of isolating the product, which was extremely soluble in all solvents.

The  $[Cp'_2Zr(\mu-Se)]_2$  complexes were proven to be dimeric by mass spectrometry and osmometric molecular weight determination. The properties of  $[Cp^*_2Zr(\mu-Se)]_2$  are similar to those of the closely related complex  $[(\eta^5-t\text{-BuC}_5\text{H}_4)_2Zr(\mu-Se)]_2$  prepared previously.<sup>7,16</sup> The  $^1\text{H}$  NMR spectrum of  $[Cp_2Zr(\mu-Se)]_2$  showed, as its main feature, an intense sharp singlet at 6.53 ppm due to  $C_5H_5$ , but also a weak sharp singlet at 6.12 ppm and an extremely weak sharp singlet at 6.21 ppm were present. The  $^{13}\text{C}$  NMR showed a singlet at 114.35 ppm, with a weak singlet at 111.81 ppm also present. The subsidiary resonances in the  $^1\text{H}$  and  $^{13}\text{C}$  spectra may be due to  $[Cp_2Zr(\mu-Se)]_n$  oligomers with  $n > 2$ .

## Discussion

**Formation of  $Cp'_2M(AH)_2$  and  $[Cp'_2M(\mu-A)]_2$ .** In all reactions reported in this work stoichiometric amounts of  $H_2Se$  were reacted with  $Cp'_2M(CO)_2$ . We have not investigated the effect of large excesses of  $H_2Se$ . The complexes  $Cp'_2M(SeH)_2$  and  $[Cp'_2M(\mu-Se)]_2$  were not markedly air-sensitive and showed no tendency to oxidize at selenium; it has been reported that  $[PdCl(\mu-(PPh_2)_2CHR)]_2(\mu-Se)$  (R = H,  $CH_3$ ) are readily oxidized to  $[PdCl(\mu-(PPh_2)_2CHR)]_2(\mu-SeO)$ .<sup>17</sup>

Shaver and McCall showed that  $Cp_2Zr(SH)_2$  and  $[Cp_2Zr(\mu-S)]_2$  are in equilibrium according to eq 4.<sup>10</sup> This



equilibrium is facile at room temperature. On the other

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Table I. Bond Energies (kJ mol<sup>-1</sup>) of Group 4 Oxides, Sulfides, and Selenides<sup>a</sup>

Ti-O	665	O-H	425
Zr-O	760	S-H	345
Ti-S	425	Se-H	305
Zr-S	575	H-H	435
Ti-Se	380	Ti-CO	100 <sup>c</sup>
Zr-Se	490 <sup>b</sup>	Zr-CO	150 <sup>c</sup>

<sup>a</sup>From ref 24 unless noted. <sup>b</sup>Estimated from data in ref 24. <sup>c</sup>Estimated from data in ref 25.

hand, the analogous ( $\eta^5$ -*t*-BuC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Zr(SH)<sub>2</sub> only loses H<sub>2</sub>S according to eq 4 on boiling in toluene for 30 h.<sup>16</sup> In the present investigations the reactions between Cp'<sub>2</sub>Zr(CO)<sub>2</sub> and H<sub>2</sub>S or H<sub>2</sub>Se produced only [Cp'<sub>2</sub>Zr( $\mu$ -A)]<sub>2</sub>. Under the conditions used, namely, low ratios of H<sub>2</sub>A to Cp'<sub>2</sub>Zr(CO)<sub>2</sub>, it is unlikely that Cp'<sub>2</sub>Zr(AH)<sub>2</sub> would be observed unless the equilibrium constant for reaction 4 favored it very heavily. However, the reaction between Cp'<sub>2</sub>Ti(CO)<sub>2</sub> and H<sub>2</sub>Se gave a mixture of Cp'<sub>2</sub>Ti(SeH)<sub>2</sub> and [Cp'<sub>2</sub>Ti( $\mu$ -Se)]<sub>2</sub>, with the former predominating. In toluene solution under vacuum Cp'<sub>2</sub>Ti(SeH)<sub>2</sub> lost H<sub>2</sub>Se forming [Cp'<sub>2</sub>Ti( $\mu$ -Se)]<sub>2</sub>.

The reaction between Cp'<sub>2</sub>Ti(CO)<sub>2</sub> and H<sub>2</sub>S gives only Cp'<sub>2</sub>Ti(SH)<sub>2</sub>.<sup>1</sup> Direct comparison with oxygen is not possible since there is no reaction between Cp'<sub>2</sub>Ti(CO)<sub>2</sub> and H<sub>2</sub>O. Hillhouse and Bercaw prepared Cp'<sub>2</sub>M(OH)<sub>2</sub> from [Cp'<sub>2</sub>M(H)]<sub>2</sub>( $\mu$ -O);<sup>3</sup> it has been suggested that Cp'<sub>2</sub>M(OH)<sub>2</sub> complexes do not eliminate H<sub>2</sub>O to form [Cp'<sub>2</sub>M( $\mu$ -O)]<sub>2</sub> (M = Zr, Hf) because of steric factors.<sup>18</sup> The trimers [Cp'<sub>2</sub>M( $\mu$ -O)]<sub>3</sub> (M = Zr,<sup>19</sup> Hf<sup>20</sup>) are known, but their conversion to Cp'<sub>2</sub>M(OH)<sub>2</sub> is not reported. A rationalization of the results is that equilibrium 4 favors [Cp'<sub>2</sub>M( $\mu$ -A)]<sub>2</sub> except when these are sterically prohibited. Steric crowding will be greatest in Cp'<sub>2</sub>Ti derivatives with oxygen as the bridging ligand. The larger Zr can accommodate Cp\* and form [Cp\*<sub>2</sub>Zr( $\mu$ -A)]<sub>2</sub>. With Se as the bridging ligand it is just possible to accommodate Cp'<sub>2</sub>Ti.

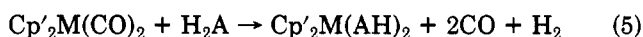
**Aggregation of Cp'<sub>2</sub>M(SeH)<sub>2</sub> and [Cp'<sub>2</sub>M( $\mu$ -Se)]<sub>2</sub>.** In contrast to the sulfur derivatives the [Cp'<sub>2</sub>Ti( $\mu$ -Se)]<sub>2</sub> compounds showed a marked tendency to aggregate, particularly in the presence of H<sub>2</sub>Se. For example, [Cp'<sub>2</sub>Ti( $\mu$ -Se)]<sub>2</sub> gave [Cp'<sub>2</sub>Ti( $\mu$ -Se)<sub>2</sub>TiCp]<sub>2</sub>( $\mu$ -Se) (Figure 1). This polymerized in toluene solution to a material that was totally insoluble in all common solvents. One way that [Cp'<sub>2</sub>Ti( $\mu$ -Se)<sub>2</sub>TiCp]<sub>2</sub>( $\mu$ -Se) can polymerize is by ring expansion, initially to an octamer and then further to an infinite sheet. Aggregation is well-known when large excesses of H<sub>2</sub>O react with Cp'<sub>2</sub>M derivatives<sup>1,21-23</sup> but is not observed in reactions involving stoichiometric amounts of either H<sub>2</sub>O or H<sub>2</sub>S.<sup>1,3</sup> The reason for the aggregation with selenium is not thermodynamic, since the formation of M-A bonds at the expense of H-A is energetically most favorable for oxygen. One reason for the difference between Se and S or O may be steric; aggregates require close approach of Cp'M units when these are bridged by A. The larger size

Table II. Estimated Enthalpies (kJ mol<sup>-1</sup>) for the Reaction Cp'<sub>2</sub>M(CO)<sub>2</sub> + H<sub>2</sub>A → Cp'<sub>2</sub>M(AH)<sub>2</sub> + 2CO + H<sub>2</sub>

A	M	
	Ti	Zr
O	-690	-805
S	-395	-595
Se	-385	-505

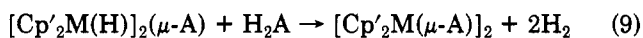
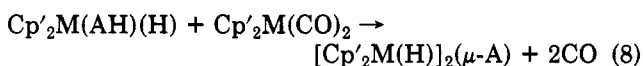
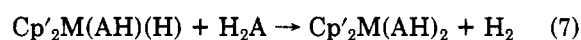
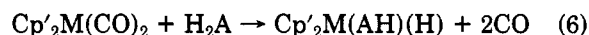
of selenium allows such an approach.

**Thermodynamic Considerations in the Formation of Cp'<sub>2</sub>M(AH)<sub>2</sub> and [Cp'<sub>2</sub>M( $\mu$ -A)]<sub>2</sub>.** The driving force for the reactions between Cp'<sub>2</sub>M(CO)<sub>2</sub> and H<sub>2</sub>A is the strong M-A bond formed at the expense of a considerably weaker H-A bond. Table I gives the relevant information. The M-CO bond strengths are unknown, but estimates of 100 kJ mol<sup>-1</sup> for Ti-CO and 150 kJ mol<sup>-1</sup> for Zr-CO are reasonable on the basis of data for other carbonyls.<sup>25</sup> On the basis of the bond strengths, the enthalpies of reaction 5 are given in Table II. The thermodynamic advantage of oxygen is readily apparent.



In Table III are shown the products and conditions of all the reactions between Cp'<sub>2</sub>M(CO)<sub>2</sub> and H<sub>2</sub>O, H<sub>2</sub>S, or H<sub>2</sub>Se. It is seen that the order of reactivity is H<sub>2</sub>O < H<sub>2</sub>S ≤ H<sub>2</sub>Se, though the difference is less marked for Cp'<sub>2</sub>Zr(CO)<sub>2</sub> than for Cp'<sub>2</sub>Ti(CO)<sub>2</sub>. It is also seen that Cp'<sub>2</sub>Ti(CO)<sub>2</sub> is more reactive than Cp'<sub>2</sub>Zr(CO)<sub>2</sub> and that Cp'<sub>2</sub>M(CO)<sub>2</sub> is more reactive than Cp\*<sub>2</sub>M(CO)<sub>2</sub>. This order is exactly the same for the reactions between Cp'<sub>2</sub>M(CO)<sub>2</sub> and N<sub>2</sub>O, also given in Table III. The order is the opposite to that suggested by bond strengths, and therefore the reactivities must be related to the mechanism of the reactions.

**Mechanism of the Formation of Cp'<sub>2</sub>M(AH)<sub>2</sub> and [Cp'<sub>2</sub>M( $\mu$ -A)]<sub>2</sub>.** Reactions 6-9 can be suggested for the formation of Cp'<sub>2</sub>M(AH)<sub>2</sub> or [Cp'<sub>2</sub>M( $\mu$ -A)]<sub>2</sub> using the work of Hillhouse and Bercaw<sup>3</sup> as a basis. The reactions gen-



erally were conducted with a mole ratio of H<sub>2</sub>A to Cp'<sub>2</sub>M(CO)<sub>2</sub> of 1:1 at 80 °C in toluene solution. In the case of H<sub>2</sub>O, which has a vapor pressure only slightly greater than that of the solvent, the initial mole ratio of Cp'<sub>2</sub>M(CO)<sub>2</sub> to H<sub>2</sub>O is 1:1, and after reaction 6 has taken place, reaction 7 or 8 is equally likely. With H<sub>2</sub>S and H<sub>2</sub>Se, which have vapor pressures much greater than the solvent, the initial ratio of H<sub>2</sub>A to Cp'<sub>2</sub>M(CO)<sub>2</sub> must be much less than 1:1. The Henry's law constants are not available over the temperature range used in the experiments described here. With use of values at 20 °C it is estimated that the mole ratio of Cp'<sub>2</sub>M(CO)<sub>2</sub> to H<sub>2</sub>S in solution was between 7 and 9 to 1 and of Cp'<sub>2</sub>M(CO)<sub>2</sub> to H<sub>2</sub>Se between 2.5 and 10 to 1.<sup>28</sup> Under these conditions reaction 7 is much less likely than reaction 8. We conclude that for H<sub>2</sub>S and H<sub>2</sub>Se the product of the reaction with Cp'<sub>2</sub>M(CO)<sub>2</sub> is [Cp'<sub>2</sub>M( $\mu$ -A)]<sub>2</sub>.

(28) The only Henry's law constant for H<sub>2</sub>S or H<sub>2</sub>Se that we have been able to find in the literature is for H<sub>2</sub>S in aniline, 0.61 (mol/L)/atm at 22 °C (Bancroft, W. D.; Belden, B. C. *J. Phys. Chem.* 1930, 34, 2123). B. R. James and F. Barnabas have determined the constant for H<sub>2</sub>S in CH<sub>2</sub>Cl<sub>2</sub> as 1.15 (mol/L)/atm at 25 °C and for H<sub>2</sub>S in CHCl<sub>3</sub> as 1.36 (mol/L)/atm at 20 °C. We thank Prof. James for these unpublished results.

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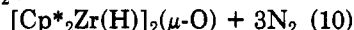
Table III. Products and Conditions of the Reactions between  $H_2O$ ,  $H_2S$ ,  $H_2Se$ , or  $N_2O$  and  $Cp'_2M(CO)_2$  in Toluene Solution

complex	reactant			
	$H_2O^{a,b}$	$H_2S^c$	$H_2Se^c$	$N_2O^d$
$Cp_2Ti(CO)_2$ $\nu(CO)^e$ 1977, 1899	$Cp_6Ti_6O_8$ 80 °C <sup>f</sup>	$Cp_5Ti_5S_6$ , $Cp_6Ti_6S_8$ 80 °C <sup>g</sup>	$[Cp_2Ti(\mu-Se)]_2$ 0 °C (hexane) $[Cp_2Ti(\mu-Se)_2TiCp]_2(\mu-Se)$ 20 °C $Cp_6Ti_6Se_8$ , $Cp_5Ti_5Se_6$ , $Cp_4Ti_4Se_4$ 80 °C	$[(P_2Ti)_2CO_3]_2$ 20 °C
$Cp^*_2Ti(CO)_2$ $\nu(CO)^e$ 1940, 1858	no reaction 80 °C	$Cp^*_2Ti(SH)_2$ 80 °C <sup>f</sup>	$Cp^*_2Ti(SeH)_2$ , $[Cp^*_2Ti(\mu-Se)]_2$ 20 °C	no reaction 20 °C
$Cp_2Zr(CO)_2$ $\nu(CO)^e$ 1975, 1885	$ZrO_2$ 80 °C <sup>f</sup>	$[Cp_2Zr(\mu-S)]_2$ 80 °C <sup>f</sup>	$[Cp_2Zr(\mu-Se)]_2$ 80 °C <sup>f</sup>	$ZrO_2$ 20 °C
$Cp^*_2Zr(CO)_2$ $\nu(CO)^e$ 1945, 1852	no reaction 80 °C	$[Cp^*_2Zr(\mu-S)]_2$ 80 °C <sup>f</sup>	$[Cp^*_2Zr(\mu-Se)]_2$ 80 °C <sup>f</sup>	no reaction 20 °C

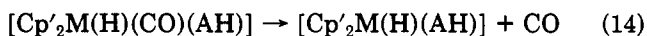
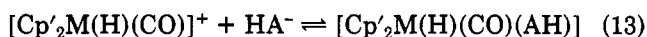
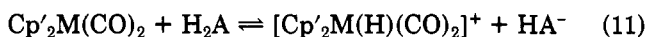
<sup>a</sup> Reference 1. <sup>b</sup> Reference 3. <sup>c</sup> This work. <sup>d</sup> Reference 26. <sup>e</sup>  $cm^{-1}$ ; ref 27. <sup>f</sup> No reaction at 20 °C. <sup>g</sup> Very slow reaction at 20 °C.

A caveat must be made in the case of the reactions of  $Cp^*_2Ti(CO)_2$ , where steric factors prevent formation of  $[Cp^*_2Ti(\mu-A)]_2$ . In this case reaction 7 will take place.

The initial step in the reaction sequence is formation of  $Cp'_2M(AH)(H)$  by reaction 6. Hillhouse and Bercaw suggested that  $[Cp^*_2Zr(N_2)]_2(\mu-N_2)$  reacts with  $H_2O$  according to eq 10 because  $[Cp^*_2Zr(N_2)]_2(\mu-N_2)$  dissociates  $[Cp^*_2Zr(N_2)]_2(\mu-N_2) + H_2O \rightarrow$



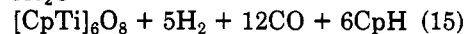
a terminal  $N_2$ , leaving a free coordination site at which  $H_2O$  reacts.<sup>3</sup> They found that  $Cp^*_2Zr(CO)_2$  does not react with water and suggested that this is because this complex does not lose CO. This implies that the dissociation 1 is the important step in all reactions of  $Cp'_2M(CO)_2$  with  $H_2A$ . However, this does not explain the different reactivities of  $H_2O$ ,  $H_2S$ ,  $H_2Se$ , and  $N_2O$  shown in Table III. Dissociation is also at variance with the mechanism of substitution of CO in  $Cp_2Zr(CO)_2$ .<sup>5</sup> We propose a two-term mechanism in which the dissociation is assisted by protonation, giving the reaction sequence 11–14.



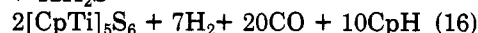
The combination of reactions 1 and 11–14 explains the reactivity patterns in Table III well. Since  $Cp_2Ti(CO)_2$  dissociates CO, all reagents (including  $N_2O$ , which cannot protonate  $Cp'_2M(CO)_2$ ) will react with it. The fact that  $Cp_2Zr(CO)_2$  reacts (under forcing conditions) with all reagents, including  $N_2O$ , suggests that it too can dissociate CO. However, associative attack of  $H_2A$  or  $N_2O$  may be operating, in line with the mechanism of CO substitution found for this carbonyl.<sup>5,29</sup> Neither of the  $Cp^*_2M(CO)_2$  complexes dissociate CO (due to the increased basicity of  $Cp^*$ ) and need assistance from the protonation step 11. Protonation depends on the relative acidities of  $H_2O$ ,  $H_2S$ , and  $H_2Se$  and cannot take place when  $N_2O$  is the reagent. Since all reactions were conducted in dilute solution in toluene, the best measure of the relative acidities is the proton affinity of  $HA^-$  in the gas phase. These are 1632  $kJ\ mol^{-1}$  for  $OH^-$ , 1464  $kJ\ mol^{-1}$  for  $SH^-$ , and 1418  $kJ\ mol^{-1}$  for  $SeH^-$ ;<sup>30</sup> acid dissociation constants in aqueous solution and A–H bond strengths show the same trend; i.e., the ability to protonate lies in the order  $H_2O < H_2S < H_2Se$ . In summary, we expect the reactivity of  $Cp'_2M(CO)_2$  to-

ward  $H_2A$  to lie in the order  $Cp_2Ti(CO)_2 > Cp_2Zr(CO)_2 > Cp^*_2Ti(CO)_2 > Cp^*_2Zr(CO)_2$ , this being the order of ease of CO loss; the order of reactivity of  $H_2A$  will be  $H_2Se > H_2S > H_2O > N_2O$ , this being the order of their ability to protonate  $Cp'_2M(CO)_2$ .

**Formation of  $[CpM]_m(\mu_3-A)_n$  Clusters.** The reaction between  $Cp_2Ti(CO)_2$  and  $H_2Se$  throws light on the formation of the  $[CpM]_m(\mu_3-A)_n$  clusters. In the reaction between  $Cp_2Ti(CO)_2$  and  $H_2O$  the only product observed is  $[CpTi]_6O_8$ , according to eq 15.<sup>1,2</sup> In the case of  $H_2S$  a  $6Cp_2Ti(CO)_2 + 8H_2O \rightarrow$



similar reaction takes place, but the major product is  $[CpTi]_5S_6$  (eq 16), with only traces of  $[CpTi]_6S_8$ .<sup>1,4</sup> Neither  $10Cp_2Ti(CO)_2 + 12H_2S \rightarrow$



$[Cp_2Ti(\mu-A)]_2$  nor  $Cp_2Ti(AH)_2$  is observed. On the other hand,  $[Cp_2Ti(\mu-Se)]_2$  was obtained when the reaction between  $Cp_2Ti(CO)_2$  and  $H_2Se$  was conducted in hexane at 0 °C,  $[Cp_2Ti(\mu-Se)_2TiCp]_2(\mu-Se)$  was obtained in toluene at 20 °C, and a mixture of  $[CpTi]_mSe_n$  clusters, with  $[CpTi]_6Se_8$  predominating, was obtained at 80 °C. As discussed above, the initial reaction between  $Cp_2Ti(CO)_2$  and  $H_2A$  is loss of CO, with or without protonation (reaction 1 or 12). The nature of the final product is not determined at this stage. Both  $[Cp_2Ti(\mu-Se)]_2$  and  $[Cp_2Ti(\mu-Se)_2TiCp]_2(\mu-Se)$  can be converted into  $[CpTi]_6Se_8$  or one of the other clusters (e.g. via the symmetrical  $[CpTi(\mu-Se)_2TiCp(\mu-Se)]_2$  shown in Figure 2), but the clusters cannot be converted into  $[Cp_2Ti(\mu-Se)]_2$  or  $[Cp_2Ti(\mu-Se)_2TiCp]_2(\mu-Se)$  because they have only one Cp ring per titanium.

The nature of the initial reaction between  $H_2Se$  and  $Cp_2Ti(CO)_2$  and the appearance of  $[Cp_2Ti(\mu-Se)]_2$  at low,  $[Cp_2Ti(\mu-Se)_2TiCp]_2(\mu-Se)$  at intermediate, and the  $[Cp_2Ti]_mSe_n$  clusters at high temperature strongly suggest that  $[Cp_2Ti(\mu-Se)]_2$  and  $[Cp_2Ti(\mu-Se)_2TiCp]_2(\mu-Se)$  are intermediates in the formation of the clusters. We note in this respect that Floriani and co-workers were able to assemble clusters of the type  $[CpTi]_6Cl_nO_{(8-n)}$  ( $n = 0, 2, 4$ ) by reductive aggregation of  $[CpTiCl(\mu-O)]_4$  or  $[CpTiCl_2(\mu-O)]_2$ <sup>31</sup> and Rauchfuss and co-workers were able to desulfurize the dimer  $[(\eta^5-C_5H_4Me)V]_2(\mu-S_2)(\mu-S)_2$  to give  $[(\eta^5-C_5H_4Me)VS]_4$  and  $[(\eta^5-C_5H_4Me)V]_5S_6$ .<sup>32</sup>

**Structure of  $[Cp_2Ti(\mu-Se)_2TiCp]_2(\mu-Se)$ .** There are two independent molecules in the unit cell. The equivalent distances and angles are the same within experimental error in the two molecules (see Tables IV and V and Figure

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**Table IV. Important Distances (Å) in the Two Independent Molecules of  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})_2\text{TiCp}]_2(\mu\text{-Se})$** 

distance	molecule 1	molecule 2
Ti(1)-Se(2) <sup>a</sup>	2.570 (3) <sup>b</sup>	2.569 (3)
Ti(1)-Se(3)	2.605 (3)	2.584 (3)
Ti(2)-Se(2)	2.394 (3)	2.403 (3)
Ti(2)-Se(3)	2.385 (3)	2.387 (3)
Ti(2)-Se(1)	2.469 (3)	2.475 (3)
Ti(3)-Se(1)	2.454 (3)	2.470 (3)
Ti(3)-Se(4)	2.407 (3)	2.392 (3)
Ti(3)-Se(5)	2.383 (4)	2.392 (3)
Ti(4)-Se(4)	2.581 (4)	2.569 (3)
Ti(4)-Se(5)	2.583 (4)	2.582 (3)
Ti(1)-Cp(1) <sup>c</sup>	2.060 (7)	2.064 (8)
Ti(1)-Cp(2)	2.065 (8)	2.058 (11)
Ti(2)-Cp(3)	2.070 (8)	2.046 (8)
Ti(3)-Cp(4)	2.046 (8)	2.057 (10)
Ti(4)-Cp(5)	2.067 (8)	2.076 (7)
Ti(4)-Cp(6)	2.068 (11)	2.048 (7)

<sup>a</sup> For the numbering scheme see Figure 1. <sup>b</sup> Estimated standard deviations in parentheses. <sup>c</sup> Cp is the centroid of the  $\text{C}_5\text{H}_5$  ring.

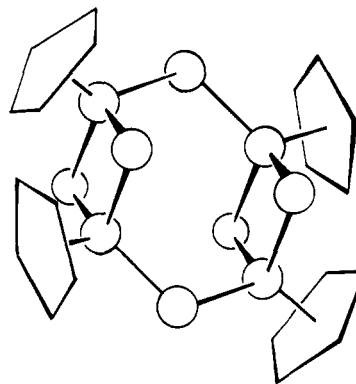
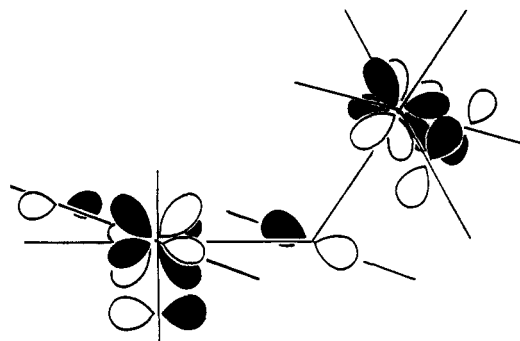
**Table V. Important Angles (deg) in the Two Independent Molecules of  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})_2\text{TiCp}]_2(\mu\text{-Se})$** 

angle	molecule 1	molecule 2
Se(2)-Ti(1)-Se(3) <sup>a</sup>	87.7 (1) <sup>b</sup>	88.2 (1)
Se(4)-Ti(4)-Se(5)	87.3 (1)	87.6 (1)
Se(2)-Ti(2)-Se(3)	97.2 (1)	96.9 (1)
Se(4)-Ti(3)-Se(5)	96.2 (1)	96.4 (1)
Se(1)-Ti(2)-Se(2)	106.9 (1)	107.7 (1)
Se(1)-Ti(2)-Se(3)	100.1 (1)	101.7 (1)
Se(1)-Ti(3)-Se(4)	108.6 (1)	103.2 (1)
Se(1)-Ti(3)-Se(5)	100.8 (1)	106.7 (1)
Ti(1)-Se(2)-Ti(2)	86.9 (1)	86.9 (1)
Ti(1)-Se(3)-Ti(2)	86.3 (1)	86.9 (1)
Ti(3)-Se(4)-Ti(4)	86.2 (1)	87.6 (1)
Ti(3)-Se(5)-Ti(4)	86.6 (1)	87.2 (1)
Ti(2)-Se(1)-Ti(3)	124.5 (1)	123.3 (1)
Cp(1)-Ti(1)-Cp(2) <sup>c</sup>	129.3 (7)	129.5 (9)
Cp(5)-Ti(4)-Cp(6) <sup>c</sup>	130.4 (9)	130.4 (7)

<sup>a</sup> For the numbering scheme see Figure 1. <sup>b</sup> Estimated standard deviations in parentheses. <sup>c</sup> Cp is the centroid of the  $\text{C}_5\text{H}_5$  ring.

1). There are three different groups of Ti-Se distances: those involving the  $\text{Cp}_2\text{Ti}(1,4)$  unit, which average 2.580 (3) Å; those between  $\text{CpTi}(2,3)$  and the  $\mu\text{-Se}(2-5)$  atoms in the  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})_2\text{TiCp}]$  units, which average 2.392 (3) Å; and the  $\text{CpTi}(2)\text{-Se}(1)\text{-Ti}(3)\text{Cp}$  distances to the central Se atom, which average 2.467 (3) Å. For comparison, the Ti-Se distance in  $\text{TiSe}_2$ , which has the  $\text{CdI}_2$  structure with six-coordination about Ti, is 2.554 (1) Å.<sup>33</sup> The angles in the  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})_2\text{TiCp}]$  group average 86.8 (1)° at the Se(2-5) atoms, 87.7(1)° at  $\text{Cp}_2\text{Ti}(1,4)$ , and 96.7(1)° at  $\text{CpTi}(2,3)$  (see Table V). The longer Ti-Se distances and smaller Se-Ti-Se angles at the  $\text{Cp}_2\text{Ti}(1,4)$  group, compared to those at  $\text{CpTi}(2,3)$ , are mainly due to the difference in the coordination number of the two Ti atoms (eight at the  $\text{Cp}_2\text{Ti}(\mu\text{-Se})_2$  versus six at  $\text{CpTi}(\mu\text{-Se})_3$ ). The Ti-Cp distances average 2.060 (8) Å, with a maximum deviation from the average of only 0.016 Å, independent of the coordination number of the Ti atom.

The  $\text{Ti}(\mu\text{-Se})_2\text{Ti}$  units in the  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})_2\text{TiCp}]$  fragments are approximately planar and almost rectangular (Tables IV-VI). Two comparable  $\text{M}(\mu\text{-A})_2\text{M}$  units are  $\text{Zr}(\mu\text{-S})_2\text{Zr}$  in  $[\text{Cp}_2\text{Zr}(\mu\text{-S})_2]_2^{1,15}$  and  $\text{Zr}(\mu\text{-Te})_2\text{Zr}$  in  $[(\eta^5\text{-C}_5\text{H}_4\text{-}t\text{-Bu})_2\text{Zr}(\mu\text{-Te})_2]_2^{13}$ . Both are square-planar, with identical MAM and AMA angles which are very close to 90°. Some surprise has been expressed that the  $\text{M}(\mu\text{-A})_2\text{M}$  rings in these molecules are square-planar.<sup>13,15</sup> However,

**Figure 2.** Proposed structure for the initial stage of the aggregation of  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})_2\text{TiCp}]_2(\mu\text{-Se})$ .**Figure 3.** The  $\pi$ -orbitals of  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})_2\text{TiCp}]_2(\mu\text{-Se})$ .

an A-M-A angle of close to 90° would be expected for a  $\text{Cp}_2\text{MA}_2$  unit with zero d electrons.<sup>34</sup> There is also a tendency for the s electrons to be more diffuse and less stereochemically active in the heavier members of group 16. This results in  $p^3$  hybridization and an M-A-M angle of 90°. It is interesting to note that in  $\text{TiSe}_2$  the Ti-Se-Ti angle is 87.72 (3)° and the Se-Ti-Se angle 85.60 (3)°.<sup>34</sup> The deviations of the angles within the  $\text{Ti}(\mu\text{-Se})_2\text{Ti}$  units of  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})_2\text{TiCp}]_2(\mu\text{-Se})$  from 90° is ascribed to the different coordination numbers of the Ti atoms. The average Se...Se and Ti...Ti distances across the rectangles are 3.575 and 3.615 Å, respectively, indicating no interaction. The planes of the two  $\text{Ti}(\mu\text{-Se})_2\text{Ti}$  rectangles make a dihedral angle of 118.7 (5)° with each other. This dihedral is determined by the Ti(2)-Se(1)-Ti(3) angle, which averages 123.9 (1)°. The difference between the dihedral angle and the angle at Se(1) is due to small variations in the angles around Ti(2) compared to Ti(3) (see Table V) and the fact that the  $\text{Ti}(\mu\text{-Se})_2\text{Ti}$  units are not exactly planar (Table VI). The 124° angle at Se(1) must be due to electronic effects since an angle of 180° would be most favorable on steric grounds. The torsion angle of the four Ti atoms defines the rotation of the  $\text{Ti}(\mu\text{-Se})_2\text{Ti}$  rectangles with respect to one another. This is the only parameter that is significantly different in the two independent molecules, being 124.8° in one and 147.2° in the other. This marked difference indicates that there is little steric or electronic hindrance to rotation about the Ti(2)-Se(1) or Ti(3)-Se(1) bonds, at least over a considerable angle. The electronic reasons for this freedom are discussed below.

The average CpTi-Se distance within the  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})_2\text{TiCp}]$  units is 2.392 (3) Å, which is much shorter than the average distance between the  $\text{CpTi}(2,3)$  and the central Se(1) atom, 2.467 (3) Å. The difference in the distances

**Table VI. Important Planes and Deviations (Å) in  $[Cp_2Ti(\mu-Se)_2TiCp]_2(\mu-Se)$** 

atom	dev	atom	dev
Plane 1: Ti(1)Se(2)Se(3)Ti(2) <sup>1</sup>			
11.3225 (3)X - 0.096 (12)Y + 2.061 (14)Z = 9.955 (2)			
Ti(1)	0.132 (3)	Se(2)	-0.063 (2)
Ti(2)	0.184 (3)	Se(3)	-0.067 (2)
Plane 2: Ti(3)Se(4)Se(5)Ti(4)			
-5.935 (7)Z + 4.733 (10)Y + 17.489 (16)Z = 7.664 (13)			
Ti(3)	0.230 (3)	Se(4)	-0.091 (2)
Ti(4)	0.214 (3)	Se(5)	-0.098 (2)
Plane 3: Ti(1A)Se(2A)Se(3A)Ti(2A)			
10.605 (3)Z - 1.437 (13)Y + 9.070 (14)Z = 9.440 (19)			
Ti(1A)	-0.117 (3)	Se(2A)	0.049 (2)
Ti(2A)	-0.116 (3)	Se(3A)	0.048 (2)
Plane 4: Ti(3A)Se(4A)Se(5A)Ti(4A)			
-8.295 (5)X - 1.945 (11)Y + 14.634 (14)Z = 0.709 (15)			
Ti(3A)	-0.133 (3)	Se(4A)	0.046 (2)
Ti(4A)	-0.122 (3)	Se(5A)	0.052 (2)
Dihedral angle between Planes 1 and 2 = 120.8 (1) and between Planes 3 and 4 = 116.7 (5).			

<sup>a</sup> For the numbering scheme see Figure 1.

is due to the differing extent of  $\pi$ -bonding between the  $CpTi(2,3)$  and the two types of Se atom (one type being the Se(2-5) atoms bridging  $CpTi$  to  $Cp_2Ti$  and the other being the central Se(1) atom). As shown in Figure 3, the  $p\pi$  orbitals of one of the Se atoms in the  $[Cp_2Ti(\mu-Se)_2TiCp]$  units overlaps uniquely with a  $d\pi$  orbital on  $CpTi$ . The  $p\pi$  orbital of the other Se atom in this unit overlaps with a  $d\pi$  orbital which can also be overlapped by a  $p\pi$  orbital of the central Se(1) atom. There is a set of orbitals, related by symmetry to those shown in Figure 2, in which the Se atoms in the  $[Cp_2Ti(\mu-Se)_2TiCp]$  and the  $d\pi$  orbitals on the  $CpTi$  units are interchanged and the  $\pi$  orbital on the bridging Se(1) atoms is an  $sp^2$  hybrid. The  $\pi$ -overlap between  $CpTi$  and the Se atoms in the  $[Cp_2Ti(\mu-Se)_2TiCp]$  has the capacity to be twice as large as that between  $CpTi$  and the bridging Se(1) atom. There is also the possibility of a delocalized  $\pi$ -overlap in the plane of, and including, all four atoms of the  $Ti(\mu-Se)_2Ti$  unit. The overlap would use the  $1a^1$  orbital on the  $Cp_2Ti$  fragment,<sup>34</sup> an  $sp^2$  hybrid on each of the Se atoms, and a  $d\pi$  orbital on the  $TiCp$  unit. This  $d\pi$  orbital is forbidden by symmetry from being involved in any of the interactions discussed previously. In summary, there is  $\pi$ -bonding between  $CpTi$  and the Se atoms in the  $[Cp_2Ti(\mu-Se)_2TiCp]$  unit but not between  $CpTi$  and the bridging Se(1) atom, and the Ti-Se distances reflect this difference in bonding. The marked variation in the torsion angles (124.8 and 147.2°) of the two independent molecules also indicates that the Ti(2)-Se(1)-Ti(3) bridge has only single Ti-Se bonds, since the torsion angle is a measure of the rotation of the  $[Cp_2Ti(\mu-Se)_2TiCp]$  units about the Ti-Se(1) axis.

### 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.  $Cp_2Ti(CO)_2$ ,<sup>35</sup>  $Cp^*_2Ti(CO)_2$ ,<sup>27</sup>  $Cp_2Zr(CO)_2$ ,<sup>27</sup> and

$Cp^*_2Zr(CO)_2$ <sup>27</sup> were prepared by literature methods.  $H_2Se$  was purchased from Matheson, Toronto. All other chemicals were reagent grade and were used as received.

Instruments used in this work were a Perkin-Elmer 683 infrared spectrophotometer (spectra measured as Nujol mulls between KBr plates or as KBr disks) and a Varian XL-200 NMR spectrometer. Microanalyses were by Beller Laboratorium, Göttingen, West Germany, molecular weights using the osmometric method by Microanalytisches Laboratorium, Engelskirchen, West Germany, and mass spectra by the University of Alberta Mass Spectrometric Facility.

**Reaction of Bis(cyclopentadienyl)dicarbonyltitanium with Dihydrogen Selenide: Formation of Bis[bis(cyclopentadienyl)( $\mu$ -seleno)titanium],  $[Cp_2Ti(\mu-Se)]_2$ .** A solution of  $Cp_2Ti(CO)_2$  (1.57 g, 6.71 mM) in hexane (100 cm<sup>3</sup>) was incubated with  $H_2Se$  (6.71 mM) and stirred at 0 °C for 120 h. The color of the solution changed from reddish brown to dark purple during this time, and a purple solid precipitated. The solid was recrystallized from toluene/hexane to give 0.91 g (49%) of purple, moderately air-sensitive  $[Cp_2Ti(\mu-Se)]_2$ . Anal. Calcd for  $C_{20}H_{20}Se_2Ti_2$ : C, 46.7; H, 3.9; Ti, 18.6. Found: C, 46.4; H, 4.3; Ti (as  $TiO_2$ ), 19.3. Infrared (KBr pellet): 403 cm<sup>-1</sup> (s) ( $\nu(Ti-Se)$ ). <sup>1</sup>H NMR ( $CDCl_3$ ): 6.39 ppm (s,  $C_5H_5$ ). Mass spectrum:  $m/e$  516 ( $[(C_5H_5)_2^{48}Ti^{80}Se]_2^+$ ), 451 ( $[(C_5H_5)_3Ti_2Se_2]^+$ ), 386 ( $[(C_5H_5)_2Ti_2Se_2]^+$ ), 321 ( $[(C_5H_5)Ti_2Se_2]^+$ ). Molecular weight by osmometry in  $CHCl_3$  solution: 500; calcd for  $[Cp_2TiSe]_2$  514.

**Reaction of Bis(cyclopentadienyl)dicarbonyltitanium with Dihydrogen Selenide: Formation of ( $\mu$ -Seleno)bis[bis(cyclopentadienyl)titanium]bis( $\mu$ -seleno)(cyclopentadienyl)titanium  $[Cp_2Ti(\mu-Se)_2TiCp]_2(\mu-Se)$ .** A solution of  $Cp_2Ti(CO)_2$  (1.40 g, 5.98 mM) in toluene (90 cm<sup>3</sup>) was incubated with  $H_2Se$  (6.00 mM) over 48 h at room temperature. The solution was not stirred or otherwise disturbed during the course of the reaction. After 12 h the original red-brown color of the solution had changed to purple, and after 48 h purple crystals of  $[Cp_2Ti(\mu-Se)_2TiCp]_2(\mu-Se)$  had deposited; yield 1.5 g, 25%. The product was characterized by X-ray crystallography (see below). Anal. Calcd for  $C_{30}H_{30}Se_5Ti_4$ : C, 36.9; H, 3.1. Found: C, 36.2; H, 3.6. Infrared: 400 cm<sup>-1</sup> ( $\nu(Ti-Se)$ ). The compound did not sublime, and the mass spectrum showed no parent ion or interpretable fragments. Attempts to obtain NMR spectra were frustrated by the formation of insoluble materials.

**Reaction of Bis(cyclopentadienyl)dicarbonyltitanium with Dihydrogen Selenide: Formation of Hexakis((cyclopentadienyl)titanium) Octaselenide,  $[CpTi]_6Se_8$ .** A solution of  $Cp_2Ti(CO)_2$  (1.54 g, 6.58 mM) in toluene (100 cm<sup>3</sup>) was incubated with  $H_2Se$  (6.60 mM) at 80 °C for 150 h with vigorous stirring. Over this period a small quantity of black precipitate deposited and was removed by filtration. The solvent was removed from the filtrate, and unreacted  $Cp_2Ti(CO)_2$  (trace) was sublimed out of the residue at 80 °C under vacuum. The residue was then recrystallized from toluene/hexane three times. At each stage infrared and mass spectra were obtained. The crude product showed mass spectral peaks assignable to  $[Cp_2TiSe]_2^+$  ( $m/e$  516),  $Cp_4Ti_4Se_4^+$  ( $m/e$  772),  $Cp_5Ti_5Se_6^+$  ( $m/e$  1045), and  $Cp_6Ti_6Se_8^+$  ( $m/e$  1318). After the third recrystallization the product was pure  $Cp_6Ti_6Se_8$  (as determined by mass spectrometry), yield 1.5 g, 18%. Infrared: 400 cm<sup>-1</sup> ( $[Ti_6(\mu_3-Se)_8]$ ). <sup>1</sup>H NMR: 5.95 ppm ( $C_5H_5$ ). Anal. Calcd for  $C_{30}H_{30}Se_8Ti_6$ : C, 27.5; H, 2.3. Found: C, 27.0; H, 2.1.

The reaction was repeated at 90 and 130 °C using xylene as solvent. Similar results to those described above were obtained, with the exception that the amounts of  $[Cp_2Ti(\mu-Se)]_2$ ,  $Cp_4Ti_4Se_4$ , and  $Cp_5Ti_5Se_6$  in the crude product decreased.

**Reaction of Bis(pentamethylcyclopentadienyl)dicarbonyltitanium with Dihydrogen Selenide: Formation of Bis(pentamethylcyclopentadienyl)titanium Bis(hydro-selenide),  $Cp^*_2Ti(SeH)_2$ , and Bis[bis(pentamethylcyclopentadienyl)( $\mu$ -seleno)titanium],  $[Cp^*_2Ti(\mu-Se)]_2$ .** A solution of  $Cp^*_2Ti(CO)_2$  (1.01 g, 2.70 mM) in toluene (70 cm<sup>3</sup>) was incubated with stirring under  $H_2Se$  (5.40 mM) at 20 °C for 4 days. During this time the color of the solution changed from reddish brown to violet. The gaseous products were  $CO$  (4.42 mM) and  $H_2$  (1.26 mM). The solvent was removed from the mixture under vacuum, and the residue was extracted with hexane, giving a purple solid ( $Cp^*_2Ti(SeH)_2$ ) and a purple-brown solution. On

(35) Demerseman, B.; Bouquet, G.; Bignorgne, M. *J. Organomet. Chem.* 1975, 101, C24.

Table VII. Atomic Parameters for the Non-Hydrogen atoms of  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})_2\text{TiCp}]_2(\mu\text{-Se})$ 

atom <sup>a</sup>	x	y	z	atom <sup>a</sup>	x	y	z
Ti(1)	0.86350 (20)	0.04520 (18)	0.15248 (9)	Ti(3A)	0.36094 (20)	1.13759 (17)	0.39515 (9)
Ti(2)	0.86764 (22)	-0.22548 (19)	0.14243 (10)	Ti(4A)	0.29469 (20)	0.90908 (17)	0.32801 (9)
Ti(3)	1.19970 (22)	-0.37669 (18)	0.08399 (10)	Se(1A)	0.53028 (12)	1.21770 (11)	0.33986 (6)
Ti(4)	1.30402 (23)	-0.57107 (19)	0.17111 (11)	Se(2A)	0.69403 (14)	1.37515 (12)	0.45261 (6)
Se(1)	1.07850 (13)	-0.27067 (11)	0.15151 (6)	Se(3A)	0.81489 (14)	1.36628 (12)	0.30978 (6)
Se(2)	0.85987 (13)	-0.08688 (11)	0.07181 (5)	Se(4A)	0.22383 (12)	1.10400 (10)	0.32526 (6)
Se(3)	0.83183 (14)	-0.11612 (11)	0.22242 (6)	Se(5A)	0.41325 (13)	0.95551 (10)	0.41330 (6)
Se(4)	1.14624 (14)	-0.56066 (11)	0.09726 (6)	C(71)	0.5566 (14)	1.5154 (12)	0.3562 (6)
Se(5)	1.38015 (13)	-0.39065 (13)	0.13028 (7)	C(72)	0.5664 (15)	1.5885 (13)	0.3995 (7)
C(11)	0.6849 (13)	0.0996 (11)	0.2049 (6)	C(73)	0.6333 (18)	1.6710 (16)	0.3798 (8)
C(12)	0.6505 (14)	0.0437 (12)	0.1574 (6)	C(74)	0.6729 (16)	1.6508 (14)	0.3248 (7)
C(13)	0.6894 (12)	0.1031 (11)	0.1082 (6)	C(75)	0.6232 (13)	1.5547 (12)	0.3090 (6)
C(14)	0.7481 (13)	0.1900 (11)	0.1253 (6)	C(81)	0.8685 (19)	1.6385 (17)	0.4258 (9)
C(15)	0.7440 (13)	0.1906 (12)	0.1849 (6)	C(82)	0.9094 (23)	1.6494 (20)	0.3734 (11)
C(21)	1.0028 (15)	0.1845 (14)	0.1467 (7)	C(83)	0.9660 (20)	1.5461 (18)	0.3624 (9)
C(22)	1.0388 (15)	0.1137 (13)	0.1053 (7)	C(84)	0.9531 (22)	1.4915 (19)	0.4091 (10)
C(23)	1.0726 (15)	0.0188 (13)	0.1350 (7)	C(85)	0.8945 (23)	1.5475 (21)	0.4490 (11)
C(24)	1.0536 (17)	0.0330 (15)	0.1890 (8)	C(91)	0.8253 (15)	1.0883 (13)	0.3530 (7)
C(25)	1.0093 (17)	0.1332 (15)	0.2000 (8)	C(92)	0.7306 (16)	1.0601 (14)	0.3899 (7)
C(31)	0.7827 (16)	-0.3516 (14)	0.0837 (7)	C(93)	0.7567 (15)	1.1059 (13)	0.4414 (7)
C(32)	0.8413 (16)	-0.4088 (14)	0.1214 (7)	C(94)	0.8614 (16)	1.1610 (14)	0.4361 (7)
C(33)	0.7892 (14)	-0.3908 (12)	0.1753 (7)	C(95)	0.9052 (16)	1.1498 (14)	0.3813 (7)
C(34)	0.6932 (16)	-0.3214 (14)	0.1686 (7)	C(101)	0.3566 (18)	1.2960 (15)	0.4474 (8)
C(35)	0.6917 (17)	-0.2980 (15)	0.1093 (8)	C(102)	0.3906 (17)	1.2208 (15)	0.4819 (8)
C(41)	1.2073 (17)	-0.2357 (15)	0.0178 (8)	C(103)	0.2978 (19)	1.1513 (17)	0.4926 (9)
C(42)	1.1070 (16)	-0.2933 (14)	0.0082 (7)	C(104)	0.2074 (20)	1.1834 (17)	0.4599 (9)
C(43)	1.1386 (14)	-0.3882 (12)	-0.0097 (6)	C(105)	0.2425 (20)	1.2778 (18)	0.4323 (9)
C(44)	1.2632 (15)	-0.3952 (13)	-0.0118 (7)	C(111)	0.2058 (14)	0.7880 (12)	0.3984 (7)
C(45)	1.3021 (16)	-0.3015 (14)	0.0052 (7)	C(112)	0.1353 (13)	0.8782 (11)	0.3979 (6)
C(51)	1.2884 (14)	-0.6136 (12)	0.2701 (6)	C(113)	0.0875 (14)	0.8875 (12)	0.3461 (6)
C(52)	1.3100 (15)	-0.5047 (13)	0.2646 (7)	C(114)	0.1285 (14)	0.8054 (12)	0.3147 (6)
C(53)	1.2130 (13)	-0.4583 (12)	0.2396 (6)	C(115)	0.2038 (14)	0.7415 (12)	0.3464 (6)
C(54)	1.1300 (15)	-0.5347 (13)	0.2298 (7)	C(121)	0.4252 (15)	0.7993 (13)	0.2734 (7)
C(55)	1.1811 (16)	-0.6314 (14)	0.2489 (7)	C(122)	0.3408 (14)	0.8368 (13)	0.2386 (7)
C(61)	1.3488 (23)	-0.7285 (21)	0.1234 (11)	C(123)	0.3500 (14)	0.9451 (12)	0.2319 (6)
C(62)	1.4170 (20)	-0.6541 (18)	0.0961 (9)	C(124)	0.4411 (13)	0.9790 (11)	0.2625 (6)
C(63)	1.4989 (19)	-0.6207 (16)	0.1335 (9)	C(125)	0.4912 (14)	0.8877 (12)	0.2887 (6)
C(64)	1.4741 (19)	-0.6773 (17)	0.1837 (8)	C(1)	0.5360 (18)	0.9151 (16)	1.0203 (9)
C(65)	1.3909 (23)	-0.7424 (20)	0.1764 (10)	C(2)	0.567 (3)	0.977 (3)	0.9759 (14)
Ti(1A)	0.76089 (23)	1.51776 (20)	0.37863 (11)	C(3)	0.6241 (21)	1.0068 (18)	0.9281 (10)
Ti(2A)	0.72404 (21)	1.24801 (19)	0.37912 (10)				

<sup>a</sup> For numbering scheme see Figure 1. <sup>b</sup> Estimated standard deviations are given in parentheses.

reduction of the volume of the solution a purple-brown precipitate  $[\text{Cp}^*\text{Ti}(\mu\text{-Se})_2]$  was obtained. Yields:  $\text{Cp}^*\text{Ti}(\text{SeH})_2$ , 0.65 g, 50%;  $[\text{Cp}^*\text{Ti}(\mu\text{-Se})_2]$ , 0.32 g, 30%.

**Characterization of  $\text{Cp}^*\text{Ti}(\text{SeH})_2$ .** Anal. Calcd for  $\text{C}_{20}\text{H}_{30}\text{Se}_2\text{Ti}$ : C, 50.2; H, 6.8. Found: C, 50.1; H, 6.6. Mass spectrum:  $m/e$  478  $[(\text{Cp}^*\text{TiSe}_2)^+]$ , 399  $[(\text{Cp}^*\text{TiSeH})^+]$ , 343  $[(\text{Cp}^*\text{TiSe}_2)^+]$ . Infrared (KBr pellet): 2320 (w) ( $\nu(\text{Se-H})$ ), 395  $\text{cm}^{-1}$  (w) ( $\nu(\text{Ti-Se})$ ).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_5\text{CD}_3$ ): 1.88 (s, 30 H,  $\text{C}_5(\text{CH}_3)_5$ ), 1.36 ppm (s, 2 H,  $\text{SeH}$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_5\text{CD}_3$ ): 13.64 ( $\text{C}_5(\text{CH}_3)_5$ ), 122.49 ppm ( $\text{C}_5(\text{CH}_3)_5$ ).  $^{77}\text{Se}$  NMR ( $\text{C}_6\text{H}_5\text{CD}_3$ ): 622.1 ppm with  $J(\text{Se-H}) = 27.2$  Hz ( $(\text{CH}_3)_2\text{Se}$  as reference).

**Characterization of  $[\text{Cp}^*\text{Ti}(\mu\text{-Se})_2]$ .** Anal. Calcd for  $\text{C}_{40}\text{H}_{60}\text{Se}_2\text{Ti}_2$ : C, 60.4; H, 7.6. Found: C, 59.8; H, 7.2. Mass spectrum:  $m/e$  796  $[(\text{Cp}^*\text{TiSe}_2)^+]$ . Infrared (KBr pellet): 395  $\text{cm}^{-1}$  ( $\nu(\text{Ti-Se})$ ).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_5\text{CD}_3$  solution): 1.87 ppm (s). Solutions of  $\text{Cp}^*\text{Ti}(\text{SeH})_2$  or  $[\text{Cp}^*\text{Ti}(\mu\text{-Se})_2]$  when  $\text{H}_2\text{Se}$  was present slowly turned red and precipitated a bright red solid. This solid was insoluble in all common solvents and could not be sublimed. It was purified by washing with toluene. The mass spectrum showed, as the highest attainable peak,  $m/e$  1150  $[(\text{Cp}^*\text{Ti}_2\text{Se}_3)^+]$ . There were only absorptions attributable to  $\text{Cp}^*$  and Ti-Se vibrations in the infrared spectrum. Anal. Calcd for  $\text{C}_{20}\text{H}_{30}\text{Ti}_2\text{Se}_3$ : C, 21.0; H, 2.6. Found: C, 19.3; H, 2.5.

**Reaction of Bis(cyclopentadienyl)dicarbonylzirconium with Dihydrogen Selenide: Formation of Bis[bis(cyclopentadienyl)( $\mu$ -seleno)zirconium],  $[\text{Cp}_2\text{Zr}(\mu\text{-Se})_2]$ .** A solution of  $\text{Cp}_2\text{Zr}(\text{CO})_2$  (0.83 g, 2.99 mM) in toluene (70  $\text{cm}^3$ ) was incubated, with stirring, with  $\text{H}_2\text{Se}$  (2.99 mM) at 80 °C for 5 days. During this time the color of the solution changed from black to light green, and a bright green solid precipitated. The gaseous products were CO (4.37 mM) and  $\text{H}_2$  (2.44 mM). The green solid was collected by filtration, washed with hexane, and recrystallized from

toluene/hexane to give 0.56 g (62%) of bright green, air-stable  $[\text{Cp}_2\text{Zr}(\mu\text{-Se})_2]$ . Anal. Calcd for  $\text{C}_{20}\text{H}_{20}\text{Se}_2\text{Zr}_2$ : C, 40.0; H, 3.4. Found: C, 38.7; H, 3.5. Infrared (KBr pellet): 332 and 310  $\text{cm}^{-1}$  (m) ( $\nu(\text{Zr-Se})$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 6.53 ppm (s,  $\text{C}_5\text{H}_5$ ) (lit. 6.34 ppm in  $\text{C}_6\text{D}_6$  solution<sup>8</sup>).  $^{13}\text{C}$  NMR: 114.35 ppm (s,  $\text{C}_5\text{H}_5$ ).  $^{77}\text{Se}$  NMR 1100 ppm (relative to  $(\text{CH}_3)_2\text{Se}$ ). Mass spectrum:  $m/e$  600  $[(\text{C}_5\text{H}_5)_2\text{Zr}^{80}\text{Se}_2]^+$ , 535  $[(\text{C}_5\text{H}_5)_3\text{Zr}_2\text{Se}_2]^+$ , 470  $[(\text{C}_5\text{H}_5)_2\text{Zr}_2\text{Se}_2]^+$ , 300  $[(\text{C}_5\text{H}_5)_2\text{ZrSe}]^+$ ; relative intensities 56:100:36:8. Molecular weight (by osmometry in  $\text{CHCl}_3$ ): 635; calcd for  $[\text{Cp}_2\text{ZrSe}_2]$  600.

**Reaction of Bis(pentamethylcyclopentadienyl)dicarbonylzirconium with Dihydrogen Selenide: Formation of Bis[bis(pentamethylcyclopentadienyl)( $\mu$ -seleno)zirconium],  $[\text{Cp}^*\text{Zr}(\mu\text{-Se})_2]$ .** A solution of  $\text{Cp}^*\text{Zr}(\text{CO})_2$  (0.88 g, 2.11 mM) in toluene (50  $\text{cm}^3$ ) was incubated, with stirring, under  $\text{H}_2\text{Se}$  (2.1 mM) at 80 °C for 8 days. During this time the color of the solution changed from black to light yellow, and a light yellow precipitate formed. The gaseous products were CO (2.0 mM) and  $\text{H}_2$  (1.6 mM). The light yellow precipitate was collected by filtration, washed with hexane, and recrystallized from toluene/hexane to give 0.45 g (50%) of light yellow  $[\text{Cp}^*\text{Zr}(\mu\text{-Se})_2]$ . Anal. Calcd for  $\text{C}_{40}\text{H}_{60}\text{Se}_2\text{Zr}_2$ : C, 54.5; H, 6.9. Found: C, 54.2; H, 6.7. Infrared (KBr pellet): 355  $\text{cm}^{-1}$  (w) ( $\nu(\text{Zr-Se})$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 2.03 ppm. Mass spectrum:  $m/e$  440  $[(\text{C}_5(\text{CH}_3)_5)_2\text{Zr}^{80}\text{Se}]^+$ . Molecular weight by osmometry in solution 840; calcd for  $[\text{Cp}^*\text{ZrSe}_2]$  880.

**X-ray Crystallography.** Large, well-formed crystals of  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})_2\text{TiCp}]_2(\mu\text{-Se})$  were obtained as described above. They were coated with "Apiezon" grease and mounted in sealed tubes. Cell dimensions and space group symmetry were determined by a combination of precession photography and cell reduction on an Enraf-Nonius CAD-4 diffractometer, which was

also used to collect the intensity data. The diffractometer was run under the control of the NRCCAD software.<sup>36</sup> Crystal data for  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})_2\text{TiCp}]_2(\mu\text{-Se})\cdot 0.25(\text{C}_6\text{H}_5\text{CH}_3)$ :  $M$ , 1000.04 daltons; triclinic,  $P\bar{1}$ ;  $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$ ;  $a = 11.329(1)$ ,  $b = 12.572(1)$ ,  $c = 23.769(2) \text{ \AA}$ ;  $\alpha = 88.587(7)$ ,  $\beta = 86.481(8)$ ,  $\gamma = 89.217(7)^\circ$ ;  $V = 3377.70 \text{ \AA}^3$ ;  $Z = 4$ ;  $D_{\text{calc}} = 1.97 \text{ Mg m}^{-3}$ ;  $F(000) = 1922$ ;  $\mu(\text{Mo K}\alpha) = 0.99 \text{ cm}^{-1}$ . A total of 8799 reflections with a  $2\theta \leq 45^\circ$  were measured by the  $\omega$ - $2\theta$  scan technique, of which 6237 were judged as being observed by the criterion that  $I > 2.5\sigma(I)$ .

Preliminary positions for the metal and selenium atoms were derived by using MULTAN direct methods.<sup>37</sup> The positions of these atoms were used in the phasing of a Fourier synthesis, and the positions of all non-hydrogen atoms of the  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})_2\text{TiCp}]_2(\mu\text{-Se})$  unit were obtained by successive Fourier, difference Fourier, and partial refinement techniques. The structure was refined by standard methods,<sup>38</sup> minimizing the function  $\sum w(\Delta F)^2$  with a weighting scheme of the form  $w = 1/(\sigma(F)^2 + kF^2)$  with  $\sigma$  based on counting statistics. Scattering factors were taken from ref 39 and were corrected for both the real and the imaginary parts of the anomalous dispersion where appropriate. An absorption correction of an empirical nature<sup>40</sup> was made. The hydrogen atoms in the  $\text{C}_6\text{H}_5$  rings were included with their positions calculated by using  $sp^2$  hybridization at the C atom and a fixed C-H distance of 0.96  $\text{\AA}$ . The  $\text{C}_6\text{H}_5\text{CH}_3$  molecule was disordered in a very complicated fashion, and only the six carbon atoms of the ring could be seen in difference Fourier maps. It is assumed that the  $\text{CH}_3$  group is disordered over all six positions. This carbon was not included in the final refinement, which used anisotropic thermal parameters for the Ti and Se atoms and isotropic for the C atoms. The H atoms were fixed with a C-H distance of 0.96  $\text{\AA}$  and  $sp^2$  hybridization at the C atom.

The total number of parameters was 416; the final  $R$  ( $= \sum \Delta|F|/\sum |F|$ ) was 0.056,  $R_w$  ( $= (\sum w(\Delta F)^2/\sum wF^2)^{1/2}$ ) was 0.092 and the goodness of fit ( $= \sum w(\Delta F)^2/(\text{number of reflections} - \text{number$

of parameters)) 1.13. A final difference Fourier had a minimum residual intensity of  $-0.79 \text{ e \AA}^{-3}$  and a maximum of  $1.72 \text{ e \AA}^{-3}$  in the region of the toluene of crystallization. The positional parameters for the non-hydrogen atoms of  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})_2\text{TiCp}]_2(\mu\text{-Se})$  are given in Table VII, the important distances in Table IV, the angles in Table V, and the planes in Table VI. Figure 1, which was drawn by ORTEP-II,<sup>41</sup> gives the numbering scheme.

## Conclusions

The reactivities of  $\text{Cp}'_2\text{M}(\text{CO})_2$  in reaction with  $\text{H}_2\text{A}$  or  $\text{N}_2\text{O}$  lie in the order  $\text{Cp}_2\text{Ti}(\text{CO})_2 > \text{Cp}_2\text{Zr}(\text{CO})_2 > \text{Cp}^*\text{Ti}(\text{CO})_2 > \text{Cp}^*\text{Zr}(\text{CO})_2$  and  $\text{H}_2\text{Se} > \text{H}_2\text{S} > \text{H}_2\text{O} \approx \text{N}_2\text{O}$ . The reactivities are consistent with a mechanism in which initial loss of CO from  $\text{Cp}'_2\text{M}(\text{CO})_2$  is assisted by protonation. The primary product of the reactions is  $[\text{Cp}'_2\text{M}(\mu\text{-A})]_2$  unless steric factors prevent formation of this dimer, in which case the primary product is  $\text{Cp}'_2\text{M}(\text{AH})_2$ . For  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})]_2$  further reaction with  $\text{H}_2\text{Se}$  gives  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})_2\text{TiCp}]_2(\mu\text{-Se})$  which is an intermediate in the formation of the clusters  $[\text{CpTi}]_m\text{Se}_n$ .

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**Registry No.**  $\text{Cp}_2\text{Ti}(\text{CO})_2$ , 12129-51-0;  $\text{H}_2\text{Se}$ , 7783-07-5;  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})]_2$ , 113725-89-6;  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})_2\text{TiCp}]_2(\mu\text{-Se})$ , 113704-80-6;  $[\text{CpTi}]_6\text{Se}_8$ , 113747-40-3;  $[\text{CpTi}]_5\text{Se}_8$ , 113747-41-4;  $[\text{CpTi}]_4\text{Se}_4$ , 113704-85-1;  $\text{Cp}^*\text{Ti}(\text{CO})_2$ , 11136-40-6;  $\text{Cp}^*\text{Ti}(\text{SeH})_2$ , 113704-81-7;  $\text{Cp}^*\text{Zr}(\text{CO})_2$ , 59487-85-3;  $[\text{Cp}_2\text{Zr}(\mu\text{-Se})]_2$ , 100581-44-0;  $\text{Cp}^*\text{Zr}(\text{CO})_2$ , 61396-31-4;  $[\text{Cp}^*\text{Zr}(\mu\text{-Se})]_2$ , 113704-83-9;  $[\text{Cp}_2\text{Ti}(\mu\text{-Se})_2\text{TiCp}]_2(\mu\text{-Se})\cdot 0.25(\text{C}_6\text{H}_5\text{CH}_3)$ , 113704-84-0;  $\text{H}_2\text{O}$ , 7732-18-5;  $\text{H}_2\text{S}$ , 7783-06-4;  $\text{N}_2\text{O}$ , 10024-97-2.

**Supplementary Material Available:** Tables of hydrogen atom positions, thermal parameters, and equations of some mean planes and comprehensive lists of bond distances and angles (21 pages); a table of  $|F_o|$  and  $|F_c|$  (57 pages). Ordering information is given on any current masthead page.

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# Communications

## C-F Bond Activation and Vicinal Defluorination by $(\text{OC})_3\text{Mn}^-$

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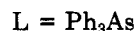
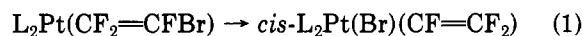
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**Summary:** C-F bond activation and vicinal defluorination of  $\text{F}_2\text{C}=\text{CF}_2$ ,  $\text{F}_2\text{C}=\text{CHF}$ ,  $\text{FCH}=\text{CHF}$ , and  $\text{F}_3\text{CCF}_3$  were accomplished in the gas phase by reactions with  $(\text{OC})_3\text{Mn}^-$ . The product ions were shown to have the general structure  $\text{F}_2\text{Mn}(\text{XC}_2\text{Y})^-$  where X and Y are F or H.

The large dissociation energies of C-F bonds in fluorinated alkanes ( $D^0(\text{CF}_3\text{CF}_2-\text{F}) = 126.8 \pm 1.8 \text{ kcal mol}^{-1}$ )<sup>1</sup>

and alkenes ( $D^0(\text{CH}_2=\text{CH}-\text{F}) = 118.7 \text{ kcal mol}^{-1}$ )<sup>2</sup> are associated with the low reactivity of these compounds under various conditions. For example, a number of organometallic  $d^{10}$  Ni(0), Pd(0), and Pt(0) complexes readily react with vinyl halides to yield oxidation adducts via their  $\pi$ -complexes<sup>3</sup> (eq 1)<sup>4</sup> with the oxidative insertion occurring



exclusively in the non-CF bond. In the vicinal dehalo-

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