

## Synthesis and Structure of an Unusual Zirconium Hydride Amide Complex. Mechanistic Studies of the Reactions of Transition-Metal Amides with Silanes

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The reactions of transition-metal amides with proton- or hydride-containing compounds are known to yield amines (H–NR<sub>2</sub>).<sup>1</sup> Such reactions include those with H<sub>2</sub>O, HSnPh<sub>3</sub>,<sup>2</sup> and a silane HSi(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.<sup>3</sup> Recently patents were issued for the chemical vapor deposition (CVD) of TiSi<sub>x</sub>/TiN films from the reactions of Ti(NR<sub>2</sub>)<sub>4</sub> with silanes.<sup>4</sup> In addition, the reactions of Ti(NR<sub>2</sub>)<sub>4</sub> with SiH<sub>4</sub> and NH<sub>3</sub> were found to give Ti–Si–N films.<sup>5</sup> These patents and reports prompted us to investigate the nature of the reactions between amide ligands (M–NR<sub>2</sub>) and silanes (H–Si). We found that the reactions of Zr(NMe<sub>2</sub>)<sub>4</sub> and (Me<sub>3</sub>Si)<sub>3</sub>Si–Zr(NMe<sub>2</sub>)<sub>3</sub> (**1**) with silanes yielded aminosilanes, H<sub>2</sub> and amide hydrides such as an unusual trinuclear complex [(Me<sub>2</sub>N)<sub>3</sub>Zr(μ-H)(μ-NMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>-Zr (**2**) (Figure 1). We report here our preliminary experimental and theoretical studies of these reactions.

When M(NMe<sub>2</sub>)<sub>4</sub> (M = Ti, Zr) was exposed to excess SiH<sub>4</sub> (5% in Ar) or H<sub>2</sub>SiR'<sub>2</sub> (R' = HPh, Ph<sub>2</sub>, MePh) at 23 °C, instantaneous reactions occurred yielding aminosilanes [HSi(NMe<sub>2</sub>)<sub>3</sub>, HSi(NMe<sub>2</sub>)<sub>2</sub>Ph, HSi(NMe<sub>2</sub>)Ph<sub>2</sub>, and HSi(NMe<sub>2</sub>)MePh, respectively], H<sub>2</sub>, and unknown black solids.<sup>6</sup> No HNMe<sub>2</sub> was detected. The formation of aminosilanes was found to be stepwise: H<sub>2</sub>Si(NMe<sub>2</sub>)<sub>2</sub> and H<sub>2</sub>Si(NMe<sub>2</sub>)Ph were observed as intermediates. The reactions of Zr(NMe<sub>2</sub>)<sub>4</sub> with less than 1 equiv of H<sub>3</sub>SiPh, H<sub>2</sub>SiPh<sub>2</sub>, H<sub>2</sub>SiMePh or HSi(NMe<sub>2</sub>)Ph<sub>2</sub> were found to yield an amide hydride [(Me<sub>2</sub>N)<sub>3</sub>Zr(μ-H)(μ-NMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>-Zr (**2**),<sup>6</sup> a trinuclear complex of yet unobserved HZr(NMe<sub>2</sub>)<sub>3</sub> (**3**) or H<sub>2</sub>Zr(NMe<sub>2</sub>)<sub>2</sub> (**4**) and Zr(NMe<sub>2</sub>)<sub>4</sub> (Scheme 1). **2** reacted further with H<sub>2</sub>SiR'<sub>2</sub> and HSi(NMe<sub>2</sub>)R'<sub>2</sub> to give H<sub>2</sub>, HSi(NMe<sub>2</sub>)R'<sub>2</sub>, and Si(NMe<sub>2</sub>)<sub>2</sub>R'<sub>2</sub>, respectively, and unidentified species.

These results suggest two interesting roles<sup>7</sup> that silanes play in their reactions with amides such as Ti(NMe<sub>2</sub>)<sub>4</sub> to form TiSi<sub>x</sub>/

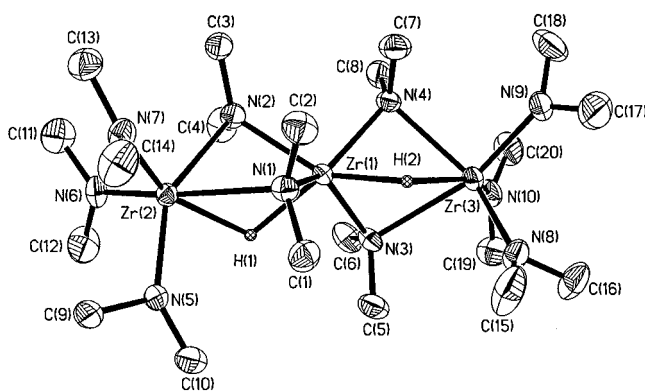
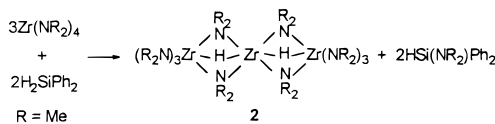
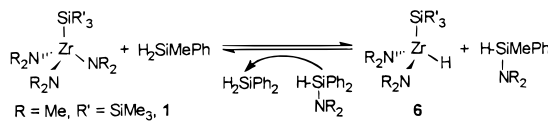


Figure 1. ORTEP of **2**, showing 50% thermal ellipsoids.

### Scheme 1



### Scheme 2



TiN.<sup>4</sup> Some SiH<sub>4</sub> molecules remove amide ligands as aminosilanes to give metal hydrides, and other SiH<sub>4</sub> molecules (or polysilanes, possible products in this reaction) may react with these metal hydrides to form M–Si bonds which lead to solid metal silicides. There are two possible pathways for **2** (or **3**) in its reactions with silanes to give either H<sub>2</sub>Zr(NMe<sub>2</sub>)<sub>2</sub> (**4**) or (Me<sub>2</sub>N)<sub>3</sub>ZrSiHR'<sub>2</sub> (**5**). We have not been able to directly observe **4** or **5** and have thus studied the reactions of (Me<sub>3</sub>Si)<sub>3</sub>Si–Zr(NMe<sub>2</sub>)<sub>3</sub> (**1**),<sup>8</sup> a model for **5**, with H<sub>2</sub>SiR'<sub>2</sub> (R' = HPh, Ph<sub>2</sub>, MePh). These reactions were found to give an unstable hydride complex (Me<sub>2</sub>N)<sub>2</sub>Zr(H)Si(SiMe<sub>3</sub>)<sub>3</sub> (**6**) and HSi(NMe<sub>2</sub>)R'<sub>2</sub>, and to reach equilibria. The equilibrium **1** + H<sub>2</sub>SiPh<sub>2</sub> ⇌ **6** + HSi(NMe<sub>2</sub>)Ph<sub>2</sub> was found to favor **1** and H<sub>2</sub>SiPh<sub>2</sub> at 0 °C, as shown in the equilibrium constant K<sub>eq</sub> [0.11(0.01)] and ΔG° [1.20(0.05) kcal/mol] at this temperature. The addition of HSi(NMe<sub>2</sub>)Ph<sub>2</sub> to the equilibrium involving H<sub>2</sub>-SiMePh in Scheme 2 yielded H<sub>2</sub>SiPh<sub>2</sub>. This observation confirmed that the reactions of these d<sup>0</sup> amide complexes with silanes to form hydrides and aminosilanes were reversible.

Ab initio MO calculations were conducted on the reaction of a model complex Ti(NH<sub>2</sub>)<sub>4</sub> with SiH<sub>4</sub>.<sup>6</sup> These studies showed that the energy of the transition state **A** (Figure 2) is lower than that of **B** by 18.8 kcal/mol. Additional calculations indicated that Ti(NH<sub>2</sub>)<sub>4</sub> and Ti(NMe<sub>2</sub>)<sub>4</sub> have similar reactivities.<sup>6</sup> If such reactions proceed through **B**, the amine HNR<sub>2</sub> (or NH<sub>3</sub>) thus produced could further react with silanes to form aminosilanes and H<sub>2</sub> in the

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(2) M(NR<sub>2</sub>)<sub>4</sub> + 4HSnPh<sub>3</sub> → M(SnPh<sub>3</sub>)<sub>4</sub> + 4HNR<sub>2</sub> (M = Ti, R = Me; M = Zr, R = Et). Creemers, H. M. J. C.; Verbeek, F.; Noltes, J. G. *J. Organomet. Chem.* **1968**, *15*, 125. A radical mechanism here is also possible.

(3) M(NR<sub>2</sub>)<sub>2</sub> + 2HSiR'<sub>3</sub> → M(SiR'<sub>3</sub>)<sub>2</sub> + 2HNR<sub>2</sub> (M = Cd, Hg; R = SiMe<sub>3</sub>; R' = C<sub>6</sub>F<sub>5</sub>). Kalinina, G. S.; Petrov, B. I.; Kruglaya, O. A.; Vyazankin, N. S. *J. Gen. Chem. USSR (Engl. Transl.)* **1972**, *42*, 144.

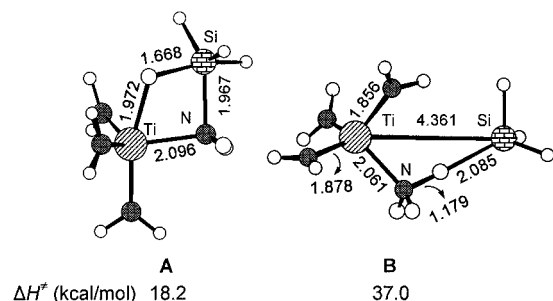
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(8) Wu, Z.; Diminnie, J. B.; Xue, Z. *Inorg. Chem.* **1998**, *37*, 6366. For other related d<sup>0</sup> Cp-free silyl complexes, see: Xue, Z.; Li, L.; Hoyt, L. K.; Diminnie, J. B.; Pollitte, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 2169. Li, L.; Diminnie, J. B.; Liu, X.; Pollitte, J. L.; Xue, Z. *Organometallics* **1996**, *15*, 3520. McAlexander, L. H.; Hung, M.; Li, L.; Diminnie, J. B.; Xue, Z.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1996**, *15*, 5231. Wu, Z.; Diminnie, J. B.; Xue, Z. *Organometallics* **1998**, *17*, 2917. Liu, X.; Li, L.; Diminnie, J. B.; Yap, G. P. A.; Rheingold, A. L.; Xue, Z. *Organometallics* **1998**, *17*, 4597. Chen, T.; Wu, Z.; Li, L.; Sorasane, K. R.; Diminnie, J. B.; Pan, H.; Guzei, I. A.; Rheingold, A. L.; Xue, Z. *J. Am. Chem. Soc.* **1998**, *120*, 13519. Wu, Z.; Diminnie, J. B.; Xue, Z. *J. Am. Chem. Soc.* **1999**, *121*, 4300. Xue, Z. *Comments Inorg. Chem.* **1996**, *18*, 223.



**Figure 2.** Transition structures (HF/HW3) and activation enthalpies (MP2/HW3) for the reaction of  $\text{Ti}(\text{NH}_2)_4$  with  $\text{SiH}_4$ .

presence of a catalyst.<sup>9</sup> We investigated whether  $\text{HNMe}_2$  could survive the conditions of the reaction between  $\text{Zr}(\text{NMe}_2)_4$  and  $\text{H}_2\text{SiPh}_2$  and found that the reaction of  $\text{HNMe}_2$  with  $\text{H}_2\text{SiPh}_2$ , if it occurred, was much slower than that of  $\text{Zr}(\text{NMe}_2)_4$  with  $\text{H}_2\text{-SiPh}_2$ .<sup>6</sup> Although we cannot rule out the transition state **B**, the isolation of **2**, the observation of **6**, and the ab initio MO calculations indicate that **A** is more likely and favored. Such preference for **A** in these metathesis reactions between  $\text{M}^{\delta+}-\text{N}^{\delta-}\text{Me}_2$  ( $\text{M} = \text{Ti}, \text{Zr}$ ) and  $\text{H}^{\delta-}-\text{Si}^{\delta+}$  bonds could perhaps also be explained by the electronegativity differences between  $\text{M}$  and  $\text{N}$  as well as between  $\text{H}$  and  $\text{Si}$ .<sup>10</sup>

To our knowledge, the current study represents the first direct observation of hydrides in the reactions of transition-metal amides with silanes through unusual equilibria.<sup>11</sup> Buchwald et al. proposed a catalytic cycle involving reactions between  $\text{Cp}'_2\text{Ti}-\text{NR}^*$  ( $\text{Cp}' = (S,S)\text{-ethylenebis}(\eta^5\text{-tetrahydroindenyl})$ ) and  $\text{H}_3\text{SiPh}$  to give  $\text{Cp}'_2\text{Ti}-\text{H}$  and  $\text{PhH}_2\text{Si}-\text{NR}^*$  ( $\text{Cp}'_2\text{Ti}-\text{H}$  and  $\text{PhH}_2\text{Si}-\text{NR}^*$ ).<sup>12</sup> The reactions of  $\text{Cp}_2\text{MRR}'$  ( $\text{M} = \text{Ti}, \text{Zr}$ ;  $\text{R}, \text{R}' = \text{H}, \text{alkyl}, \text{silyl}$ )<sup>13a-d</sup> and  $\text{Cp}_2\text{Ti}(\text{OPh})_2$  (**7**)<sup>13e</sup> with silanes were found to give  $\text{HR}$  ( $\text{HR}'$ ), disilanes, alkoxysilanes, and proposed  $\text{M}-\text{H}$  catalysts<sup>13f</sup> for polysilane synthesis. Such hydrides are believed to catalyze alkoxy- and siloxy-silane redistributions as well.<sup>14</sup>

The structure of the hydride-amide complex **2** (Figure 1) shows two terminal  $\text{Zr}(\text{NMe}_2)_3$  units, one central Zr atom, and two triply bridging units, each consisting of two amides and one hydride.<sup>6</sup> The hydride ligands were located from an electron

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density map and independently refined.<sup>6</sup> To our knowledge, **2** is one of the few structurally characterized Cp-free Group 4 hydrides.<sup>15-17</sup> Others are  $[\text{P}_2\text{N}_2]\text{Zr}(\mu\text{-}\eta^2\text{-N}_2\text{H})(\mu\text{-H})\text{Zr}[\text{P}_2\text{N}_2]$  [ $\text{P}_2\text{N}_2 = \text{PhP}(\text{CH}_2\text{SiMe}_2\text{NSiMe}_2\text{CH}_2)_2\text{PPh}$ ],<sup>16a</sup>  $(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3\text{O})_3\text{TiH}(\text{PMe}_3)$ ,<sup>16b</sup> an adduct of  $\text{NaH}$  to a Zr porphyrinogen  $[(\eta^5\text{-}\eta^1\text{-}\eta^1\text{-}\eta^1\text{-Et}_8\text{N}_4)\text{Zr}]_2(\mu\text{-NaH})_2$ ,<sup>16c</sup> and  $\text{BH}_4^-$  complexes.<sup>17</sup> Some other known Cp-free group 4 hydrides include  $\text{MH}_2$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ ),<sup>18</sup> silica-supported  $(\equiv\text{SiO})_3\text{Zr}-\text{H}$ ,<sup>19a</sup> and  $\text{HTi}[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]$ .<sup>19b</sup> The average Zr- -Zr distance of 3.232 Å in **2** reflects the constraints imposed by the bridging ligands.<sup>17a-b</sup> It is interesting to note that, in the structure of the only other known trinuclear Zr complex  $\text{Zr}_3\text{H}_6(\text{BH}_4)_6(\text{PMe}_3)_4$ ,<sup>17b</sup> the Zr atoms are arranged in a nonlinear fashion with the Zr- -Zr- -Zr angle of 124.14(1)°. In contrast, the Zr atoms in **2** are almost linear with the Zr- -Zr- -Zr angle of 170.48(2)°. The middle and two terminal Zr atoms in **2** adopt a trigonal prismatic and trigonal antiprismatic geometries, respectively. The hydride ligands are closer to the central [av Zr-(1)-H = 1.91(4) Å] than to the terminal Zr atoms [av Zr-H = 2.15(4) Å]. The Zr-H and Zr-N lengths are similar to those in other bridging Zr hydrides<sup>13f,16a,17a-d,20</sup> and Zr amide complexes, respectively.<sup>21</sup>

It should be pointed out that the CVD of  $\text{TiSi}_x/\text{TiN}$  in Doan and Sandhu's process involving  $\text{SiH}_4$  was conducted at 100–500 °C<sup>4</sup> and our studies were performed at 23 °C. It is possible that intermediates different from **2** may be active in the CVD processes. Studies are currently underway to probe the fate of **2** in our system.

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**Supporting Information Available:** Details of experiments and theoretical calculations and a complete list of the crystallographic data for **2** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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