## Crystal Structure of TaCl(NMe<sub>2</sub>)<sub>4</sub> and Its Reactions with Lithium Amides and Water. Indirect Observation of an Equilibrium among TaCl(NMe<sub>2</sub>)<sub>4</sub>, Ta(NMe<sub>2</sub>)<sub>5</sub> and Ta<sub>2</sub>(µ-Cl)<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub>Cl<sub>2</sub>

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Reactions of  $TaCl(NMe_2)_4$  (2) with  $LiNR_2$  (R = SiMe\_3, Et), yielding  $Ta(NMe_2)_4(NR_2)$  (R = SiMe\_3, 4;

Et, 7), Ta(NMe<sub>2</sub>)<sub>5</sub> (1), (Me<sub>2</sub>N)<sub>3</sub>TaN(SiMe<sub>3</sub>)SiMe<sub>2</sub>CH<sub>2</sub> (5), and Ta(NMe<sub>2</sub>)<sub>3</sub>(NEt<sub>2</sub>)<sub>2</sub> (8), respectively, suggest the presence of an equilibrium among TaCl(NMe<sub>2</sub>)<sub>4</sub> (2), Ta(NMe<sub>2</sub>)<sub>5</sub> (1), and Ta<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub>Cl<sub>2</sub> (3): 2 **2**  $\approx$  **1** + 0.5 **3**. New products Ta(NMe<sub>2</sub>)<sub>4</sub>(NR<sub>2</sub>) have been characterized. Ta(NMe<sub>2</sub>)<sub>4</sub>(NEt<sub>2</sub>) (7), Ta(NMe<sub>2</sub>)<sub>5</sub> (1), and Ta(NMe<sub>2</sub>)<sub>3</sub>(NEt<sub>2</sub>)<sub>2</sub> (8) are in a slow exchange: 2 **7**  $\approx$  **1** + **8** with an equilibrium constant of  $K_{eq}$ = 0.25(0.01) at 90 °C. The following are also reported: X-ray crystal structure and a one-step synthesis of TaCl(NMe<sub>2</sub>)<sub>4</sub> (2), reaction of **2** with H<sub>2</sub>O giving Ta<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>( $\mu$ -O)(NMe<sub>2</sub>)<sub>6</sub> (9), X-ray structure of **9**, and preparation of LiNEt<sub>2</sub> solid.

## Introduction

Early transition metal amides are of intense interest as precursors to microelectronic materials.<sup>1</sup> They have been used in chemical vapor deposition (CVD) processes to make metal oxide thin films as gate insulators<sup>1a-d</sup> and metal nitride (M-Si-N ternary) films as diffusion barriers.<sup>1e-g</sup> Ta(NMe<sub>2</sub>)<sub>5</sub> (1), a CVD precursor to Ta<sub>2</sub>O<sub>5</sub> films,<sup>2</sup> was first reported by Bradley in 1962. <sup>3</sup> TaCl(NMe<sub>2</sub>)<sub>4</sub> (**2**), a precursor to Ta(NMe<sub>2</sub>)<sub>5</sub> (**1**), was later prepared by Chisholm and co-workers using a metathesis reaction between Ta(NMe<sub>2</sub>)<sub>5</sub> (**1**) and Ta<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub>Cl<sub>2</sub> (**3**).<sup>4</sup> Monochloride TaCl(NMe<sub>2</sub>)<sub>4</sub> (**2**) is a precursor to amide, alkyl,<sup>4</sup> silyl,<sup>5</sup> guanidinate,<sup>6</sup> and aminoxy<sup>3</sup> derivatives. Such derivatives are often precursors to microelectronic materials or intermediates in the formation of these materials.<sup>3</sup> The crystal structure of **2** remains unknown in large part because of its high solubility in many organic solvents. Chisholm and co-workers reported the crystal structure of  $TaCl_2(NMe_2)_3$  as a dimer  $Ta_2(\mu$ -Cl)<sub>2</sub> $(NMe_2)_6Cl_2$  (3).<sup>7</sup> It is not clear if  $TaCl(NMe_2)_4$  (2) is a monomer or dimer. In our current studies of the reactions of metal amides complexes with  $O_2^{3.5.8}$  and silanes,<sup>1g,9</sup> we have prepared 2 through reaction of  $TaCl_5$  with 4 equiv of LiNMe<sub>2</sub> and obtained crystals of 2 through sublimation at 85 °C. Its X-ray crystal structure revealed that it is a monomer in pseudo trigonal bipyramidal geometry with an axial Cl ligand. The reaction of  $TaCl(NMe_2)_4$  (2) with LiN-(SiMe<sub>3</sub>)<sub>2</sub> yields  $Ta(NMe_2)_4[N(SiMe_3)_2]$  (4) as well as  $Ta(NMe_2)_5$ 

(1) and  $(Me_2N)_3$ TaN(SiMe\_3)SiMe\_2CH<sub>2</sub> (5),<sup>10</sup> suggesting an equilibrium among 2, 1 and 3 (Scheme 1). 5 has been prepared from Ta<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub>Cl<sub>2</sub> (3) and LiN(SiMe<sub>3</sub>)<sub>2</sub>.<sup>10</sup> Additional studies revealed that the reaction of TaCl(NMe<sub>2</sub>)<sub>4</sub> (2) with LiNEt<sub>2</sub> gave Ta(NMe<sub>2</sub>)<sub>4</sub>(NEt<sub>2</sub>) (7), Ta(NMe<sub>2</sub>)<sub>5</sub> (1) and Ta(NMe<sub>2</sub>)<sub>3</sub>(NEt<sub>2</sub>)<sub>2</sub> (8). 7, 1, and 8 are involved in a slow exchange (Scheme 2). Our studies of 2 and its reactivities are reported here.

## **Results and Discussion**

TaCl(NMe<sub>2</sub>)<sub>4</sub> (**2**) had been prepared earlier from TaCl<sub>5</sub> in three steps.<sup>4</sup> In the current work, it was prepared in one step in 66% yield from the reaction of TaCl<sub>5</sub> with 4 equiv of LiNMe<sub>2</sub>. Our earlier, repeated attempts to grow crystals of **2** from its solution failed, either because of its high solubility in most solvents or because of the noncyrstalline nature of its solid obtained from the solvents. Pale-yellow crystals of **2** were later obtained on a coldfinger during the sublimation of **2** at 85 °C from the reaction between TaCl<sub>5</sub> and 4 equiv of LiNMe<sub>2</sub>.

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Scheme 1. Equilibria among 2, 1, 3 (Solution), and 3 (Solid) as Well as Reaction of 2 with LiN(SiMe<sub>3</sub>)<sub>2</sub> To Give 4, 1, and 5







crystals were carefully removed from the coldfinger, and one was cut into a suitable size for X-ray diffraction. The crystals of 2 were very sensitive to air, decomposing readily in paratone oil which was used to coat crystals for protection.

Crystal structure of Ta<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub>Cl<sub>2</sub> (**3**),<sup>7</sup> reported by Chrisholm and co-workers, displays a dimer, where two chlorides bridge two Ta atoms to give a four-member ring with two other chlorides and all amides as terminal ligands. In comparison, crystal structure of **2** reveals a monomer (Figure 1) as a distorted trigonal bipyramid. This suggests monomer is more thermally and sterically stable for the monochloride **2**. It should be noted that Ta(NMe<sub>2</sub>)<sub>5</sub> (**1**) and Ta(NEt<sub>2</sub>)<sub>5</sub> adopt a distorted square pyramidal and trigonal bipyramidal structure, respectively.<sup>11</sup> The chloride in TaCl(NMe<sub>2</sub>)<sub>4</sub> (**2**) takes the axial position with a Ta-Cl bond length of 2.5077(13) Å, slightly



Figure 1. Crystal structure of  $TaCl(NMe_2)_4$  (2). Selected bond lengths (Å) and angles (deg): Ta(1)-N(1) 1.951(4), Ta(1)-N(2)1.974(4), Ta(1)-N(3) 1.988(3), Ta(1)-N(4) 2.008(4), Ta(1)-Cl(1)2.5077(13), N(1)-Ta(1)-N(2) 122.05(17), N(1)-Ta(1)-N(3)118.09(17), N(2)-Ta(1)-N(3) 119.46(14), N(1)-Ta(1)-N(4)90.38(16),N(2)-Ta(1)-N(4) 92.14(18),N(3)-Ta(1)-N(4) 93.87(15), N(1)-Ta(1)-Cl(1) 88.58(11), N(2)-Ta(1)-Cl(1) 87.99(13), N(3)-Ta(1)-Cl(1) 87.06(11), N(4)-Ta(1)-Cl(1) 178.85(11).

longer than those of the axial Ta-Cl bond [2.454(4) Å] in  $(Me_2N)_3Ta(SiPh_2Bu')Cl^5$  and the terminal Ta-Cl bond in 3 [2.463(1) Å].<sup>7</sup> In **2**, the axial Ta(1)–N(4) bond [2.008(4) Å] is longer than equatorial Ta-N bonds [1.974(4)-1.988(3) Å]. Such a difference was also observed in the structures of (Me<sub>2</sub>N)<sub>3</sub>Ta[Si(SiMe<sub>3</sub>)<sub>3</sub>]Cl/ (Me<sub>2</sub>N)<sub>3</sub>Ta(SiPh<sub>2</sub>Bu<sup>t</sup>)Cl and (Me<sub>2</sub>N)<sub>3</sub>Ta[Si(SiMe<sub>3</sub>)<sub>3</sub>]Br.<sup>5</sup> These Ta-N bond lengths are similar to those [1.965(5)-2.038(8) Å] in Ta(NMe<sub>2</sub>)<sub>5</sub> (1).<sup>11</sup> The Cl(1)-Ta(1)-N(4) angle of 178.85(11)° shows that the two axial ligands are nearly linear. The angles of the axial chloride to equatorial N atoms are 87.06(11)-88.58(11)°, smaller than those of the axial N(4) to the N atoms  $[90.38(16)-93.87(15)^{\circ}]$ , probably as a result of the repulsion by bulkier axial -NMe<sub>2</sub> ligand.

Direct reaction of Ta(NMe<sub>2</sub>)<sub>5</sub> with Me<sub>3</sub>SiCl gave Ta<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub>Cl<sub>2</sub> (**3**), rather than TaCl(NMe<sub>2</sub>)<sub>4</sub> (**1**), because of the facile ligand redistribution and the lower solubility of **3**.<sup>7</sup> Our studies further reveal that there is an equilibrium among TaCl(NMe<sub>2</sub>)<sub>4</sub> (**2**), Ta(NMe<sub>2</sub>)<sub>5</sub> (**1**), and Ta<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub>Cl<sub>2</sub> (**3**) in toluene-*d*<sub>8</sub>. In <sup>1</sup>H NMR at 23 °C, the equilibrium 2 **2** = **1** + 0.5 **3** is not directly observed.<sup>12</sup> Although **3** is not observed, its presence is inferred from the formation of **5** (Scheme 1) and HN(SiMe<sub>3</sub>)<sub>2</sub>, when LiN(SiMe<sub>3</sub>)<sub>2</sub> is added to **2**. Reaction of **3** with LiN(SiMe<sub>3</sub>)<sub>2</sub> is known to give **5** and HN(SiMe<sub>3</sub>)<sub>2</sub>, with Ta(NMe<sub>2</sub>)<sub>3</sub>[N(SiMe<sub>3</sub>)<sub>2</sub>]Cl as an intermediate.<sup>10</sup> Other products from the reaction between TaCl(NMe<sub>2</sub>)<sub>4</sub> (**2**) and LiN(SiMe<sub>3</sub>)<sub>2</sub> at 23 °C are Ta(NMe<sub>2</sub>)<sub>4</sub>[N(SiMe<sub>3</sub>)<sub>2</sub>] (**4**), Ta(NMe<sub>2</sub>)<sub>5</sub> (**1**) with a molar ratio of **4**: **1**: **5**: HN(SiMe<sub>3</sub>)<sub>2</sub> ≈ **5**: 1: 1: 1.

The observation that significant amounts of both 1 and 5 are yielded in the reaction of 2 with LiN(SiMe<sub>3</sub>)<sub>2</sub> suggests that the reaction of 3 with LiN(SiMe<sub>3</sub>)<sub>2</sub> is faster than that of 2 with LiN(SiMe<sub>3</sub>)<sub>2</sub>, thus shifting the equilibrium to the formation of 1 and 3. In other words, although the concentration of 3 is below the <sup>1</sup>H NMR detection limit, its fast reaction with LiN(SiMe<sub>3</sub>)<sub>2</sub> eventually increases concentrations of 1, 5 and HN(SiMe<sub>3</sub>)<sub>2</sub> to 20% of that of 4 at the end of the reaction. The indirect observation of the equilibrium 2  $2 \Rightarrow 1 + 0.5$  3 here is unusual.

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(12) (a) Both <sup>1</sup>H and <sup>13</sup>C -NMe<sub>2</sub> peaks of Ta(NMe<sub>2</sub>)<sub>5</sub> (1) and

<sup>(12) (</sup>a) Both <sup>1</sup>H and <sup>13</sup>C -NMe<sub>2</sub> peaks of Ta(NMe<sub>2</sub>)<sub>5</sub> (1) and TaCl(NMe<sub>2</sub>)<sub>4</sub> (2) overlap in toluene- $d_8$ . The presence of 1 in the equilibrium mixture could not be independently confirmed. (b) A small amount of Ta<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>( $\mu$ -O)(NMe<sub>2</sub>)<sub>6</sub> (9) is often present in the equilibrium mixture, and its -NMe<sub>2</sub> peak in <sup>1</sup>H NMR at 3.57 ppm is close to that of Ta<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>(Me<sub>2</sub>)<sub>6</sub>Cl<sub>2</sub> (3) at 3.56 ppm in toluene- $d_8$ .

Reverse reaction in the equilibrium  $2 \ 2 = 1 + 0.5 \ 3$  (Scheme 1) was also observed. Mixing Ta(NMe<sub>2</sub>)<sub>5</sub> (1) and 0.5 equiv of Ta<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub>Cl<sub>2</sub> (3) in toluene- $d_8$  at 23 °C led to the formation of **2**, although the low solubility (1.5 mg/mL estimated by <sup>1</sup>H NMR) and slow dissolvation of **3** in toluene- $d_8$  [3 (solution) = **3** (solid), Scheme 1] at 23 °C make the formation of **2** slow. Heating the solution to 80 °C increases the solubility of **3** and makes the formation of TaCl(NMe<sub>2</sub>)<sub>4</sub> (**2**) faster. After the formation of **2**, the solution showed no detectable amount of Ta<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub>Cl<sub>2</sub> (**3**) by <sup>1</sup>H NMR, <sup>12</sup> indicating the equilibrium 2 **2** = **1** + 0.5 **3** (Scheme 1) is shifted exclusively to the left at 23 °C.

Ta(NMe<sub>2</sub>)<sub>4</sub>[N(SiMe<sub>3</sub>)<sub>2</sub>] (4) does not convert to 1 and (Me<sub>2</sub>N)<sub>3</sub>TaN(SiMe<sub>3</sub>)SiMe<sub>2</sub>CH<sub>2</sub> (5) in toluene- $d_8$  at 23 °C for a few days. Heating the solution at 86 °C for 24 h led to the decomposition of 4 to unknown species. The result rules out a pathway in which 4 is yielded initially in the reaction of TaCl(NMe<sub>2</sub>)<sub>4</sub> (2) with LiN(SiMe<sub>3</sub>)<sub>2</sub>, and then it converts to 1 and 5.

Reactions of TaCl(NMe<sub>2</sub>)<sub>4</sub> (**2**) with LiN(SiMe<sub>3</sub>)<sub>2</sub> was found to be complete in 4 h at 10 °C and in 2.5 h at 15 °C, respectively. Slow formation of **1** and **5** was observed in the process. Ta<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub>Cl<sub>2</sub> (**3**) was not, however, detected during monitoring of the reaction, suggesting that the equilibrium 2 **2**  $\approx$  **1** + 0.5 **3** (Scheme 1) is shifted exclusively to the left. Reaction of **3** with LiN(SiMe<sub>3</sub>)<sub>2</sub> further decreases the likeliness of the observation of **3** in the reaction.

Reaction of TaCl(NMe<sub>2</sub>)<sub>4</sub> (**2**) with 1 equiv of LiNEt<sub>2</sub> was also investigated. This reaction at 23 °C was found to yield Ta(NMe<sub>2</sub>)<sub>4</sub>(NEt<sub>2</sub>) (**7**) as well as Ta(NMe<sub>2</sub>)<sub>3</sub>(NEt<sub>2</sub>)<sub>2</sub> (**8**) and Ta(NMe<sub>2</sub>)<sub>5</sub> (**1**) in a molar ratio of about 2.8:1:1 (Scheme 2). Ta(NMe<sub>2</sub>)<sub>3</sub>(NEt<sub>2</sub>)<sub>2</sub> (**8**) has been reported earlier in a patent by Chen and co-workers.<sup>13</sup> Ta(NMe<sub>2</sub>)<sub>4</sub>(NEt<sub>2</sub>) (**7**) is a new product, and it was characterized by <sup>1</sup>H and <sup>13</sup>C NMR and elemental analysis. **7** is a pale-yellow solid at 23 °C. One set of peaks were observed for both -NMe<sub>2</sub> and -NEt<sub>2</sub> ligands in <sup>1</sup>H and <sup>13</sup>C NMR spectra. The structure of **7** is not clear. If it is trigonal bipyramidal, the NMR observations suggest there is perhaps a fast exchange of the axial and equatorial ligands in **7**.

We also found that there is an exchange among 7, 1 and 8:  $27 \Rightarrow 1 + 8$  (Scheme 2).

Two tests were conducted. In the first test, **1** was added to a mixture of **7** and **8** in toluene- $d_8$  at 23 °C, and peaks of **7** *slowly* grew up while peaks of **1** and **8** dropped. In the absence of **1**, no change was observed of a mixture of **7** and **8** in toluene- $d_8$  at 23 °C for 9 days. In a second test, a solution of Ta(NMe<sub>2</sub>)<sub>4</sub>(NEt<sub>2</sub>) (**7**) in toluene- $d_8$  was monitored and found to yield Ta(NMe<sub>2</sub>)<sub>3</sub>(NEt<sub>2</sub>)<sub>2</sub> (**8**) and Ta(NMe<sub>2</sub>)<sub>5</sub> (**1**). The exchange 2 **7**  $\Rightarrow$  **1** + **8** (Scheme 2) at 90 °C is faster, but it still took 4–5 days to reach an equilibrium with  $K_{eq} = 0.25(0.01)$  at 90 °C. Given that the exchange of the products 2 **7**  $\Rightarrow$  **1** + **8** (Scheme 2) is very slow, it is unlikely that this exchange would change the ratio of the three products (**7**: **1**: **8** = 2.8: 1: 1) from the reaction of TaCl(NMe<sub>2</sub>)<sub>4</sub> (**2**) with 1 equiv of LiNEt<sub>2</sub>. In other

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words, the exchange of the starting materials 2 = 1 + 0.5 3 led to the observation of the three products 7, 1 and 8 in this reaction.

The new complex  $Ta(NMe_2)_4[N(SiMe_3)_2]$  (4) was characterized by <sup>1</sup>H and <sup>13</sup>C NMR and elemental analysis. Repeated attempts to obtain the crystal structure of 4 were not successful. Crystal-like solids gave poor reflections on an X-ray diffractometer.



Complex  $TaCl(NMe_2)_4$  (2) in THF was found to react with



Figure 2. Crystal structure of  $Ta_2(\mu$ -Cl)<sub>2</sub>( $\mu$ -O)(NMe<sub>2</sub>)<sub>6</sub> (9). Selected bond lengths (Å) and angles (deg): Cl(1)-Ta(1) 2.7571(15), Cl(1)-Ta(2) 2.8214(15), Cl(2)-Ta(2) 2.7128(17), Cl(2)-Ta(1) 2.7618(16), N(1)-Ta(1) 1.965(7), N(2)-Ta(1) 1.995(7), N(3)-Ta(1) 1.943(7), N(4)-Ta(2) 1.951(7), N(5)-Ta(2) 1.993(7), N(6)-Ta(2) 1.961(7), O-Ta(1) 1.931(5), O-Ta(2) 1.936(5), Ta(1)-Cl(1)-Ta(2) 73.92(4), Ta(2)-Cl(2)-Ta(1) 75.57(4), Ta(1)-O-Ta(2) 120.3(3), O-Ta(1)-Cl(1) 74.04(16), O-Ta(1)-Cl(2) 72.96(16).

H<sub>2</sub>O (0.5 equiv in THF), yielding Ta<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>( $\mu$ -O)(NMe<sub>2</sub>)<sub>6</sub> (9) and  $HNMe_2$  (eq 1). One -NMe<sub>2</sub> ligand in 2 was removed as  $HNMe_2$  in the reaction, followed by dimerization to give 9. The X-ray structure of 9 in Figure 2 reveals that, of the two bridging Ta-Cl-Ta bonds, Cl(1)-Ta(1) bond length [2.7571(15) Å] is smaller than that of the Cl(1)-Ta(2) bond [2.8214(15) Å]. However, both bridging Ta-Cl bond lengths [2.7128(17)-2.8214(15) Å] in 9 are longer than that of the terminal Ta-Cl bond [2.5077(13) Å] in **2**. The difference here is similar to those in  $Ta_2(\mu-Cl)_2(NMe_2)_6Cl_2$  (3)<sup>7</sup> and  $Cl(Me_2N)_2Zr(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-Cl)_2(\mu-$ NMe<sub>2</sub>)Zr(NMe<sub>2</sub>)<sub>2</sub>(THF).<sup>14</sup> In 3, the bridging Ta-Cl bonds [2.586(1) and 2.635(2) Å] are longer than that of the terminal Ta-Cl bond [2.463(1) Å].<sup>7</sup> The bridging Zr-Cl bond lengths of 2.6130(12) - 2.7214(12) Å in the Zr complex<sup>14</sup> are also longer than that of the terminal Zr-Cl bond [2.4409(12) Å]. The Ta(1)-O-Ta(2) bond angle  $[120.3(3)^{\circ}]$  is much larger than two Ta(1)-Cl-Ta(2) bond angles [73.92(4) and 75.57(4)°] in 9.



Chisholm and co-workers have also reported a Ta dimeric complex  $Ta_2(\mu$ -O)Cl<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub>(HNMe<sub>2</sub>)<sub>2</sub> (**10**) containing a single bridging oxo ligand.<sup>7</sup> It is interesting to compare **9** with **10**. Complex **9** is a derivative of **10** without the HNMe<sub>2</sub> ligand.

<sup>(13)</sup> Chen, T.; Xu, C.; Baum, T. H. U.S. Patent 2005079290,2005, "Tantalum amide complexes for depositing tantalum-containing films, and method of making same." Preparation, NMR chemical shifts, and elemental analysis of  $Ta(NMe_2)_3(NEt_2)_2$  (8) were given.

<sup>(15) (</sup>a) Sheldrick, G. M. SADABS, A Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen: Göttingen, Germany, 2000. (b) Sheldrick, G. M. SHELXL-97, A Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997.

The Ta atoms in 10 adopt an octahedron coordination sphere using terminal chloride and HNMe<sub>2</sub> as ligands. Loss of lone pair electrons in HNMe<sub>2</sub> in 9 leads to the formation of the two bridging chloride ligands so that their lone pair electrons could be used to remediate electron deficiency in 9. The Ta-O bond length of 1.928(6) Å in **10** is nearly identical to those [1.931(5) and 1.936(5) Å] in 9. The Ta-O-Ta bond [174.3(3)°] in 10 is nearly linear, while that  $[120.3(3)^{\circ}]$  in Ta<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>( $\mu$ -O)(NMe<sub>2</sub>)<sub>6</sub> (9) is, however, much smaller. The two Ta atoms in 9 are closer [Ta(1)-to-Ta(2) distance: 3.3545 Å] than those in, e.g., Ta<sub>2</sub>( $\mu$ - $Cl_2(NMe_2)_6Cl_2$  (3) [Ta(1)-to-Ta(2) distance: 4.1 Å]<sup>7</sup> probably to accommodate one oxo and two bridging ligands. In addition to the smaller Ta-O-Ta bond angle in 9 (than in 10), the Ta-Cl-Ta [73.92(4) and 75.57(4)°] bond angles in 9 are also much smaller than that  $[103.7(0)^{\circ}]$  in Ta<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub>Cl<sub>2</sub> (**3**).<sup>7</sup> The Ta-N bond lengths [1.943(7)-1.995(7) Å] are close to those in, e.g.,  $TaCl(NMe_2)_4$  (2) [1.951(4) to 2.008(4) Å].

## **Experimental Section**

**General Procedures.** All manipulations were carried out under a dry and oxygen-free nitrogen atmosphere with the use of glovebox or Schlenk techniques. All solvents were purified by distillation from potassium/benzophenone ketyl. Benzene- $d_6$  and toluene- $d_8$ were dried and stored over activated molecular sieves under nitrogen. TaCl<sub>5</sub> (Strem), LiNMe<sub>2</sub> (Aldrich), and LiN(SiMe<sub>3</sub>)<sub>2</sub> (Aldrich) were used as received. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AMX-400 Fourier transform spectrometer. Elemental analysis was conducted by Complete Analysis Laboratories, Inc., Parsippany, NJ.

**Synthesis of LiNEt<sub>2</sub>.** HNEt<sub>2</sub> was dried over NaOH pellets at 23 °C for 24 h and then distilled at 72 °C under nitrogen. HNEt<sub>2</sub> (12.590 g, 0.172 mmol) in hexanes (30 mL) at 0 °C was treated with 1 equiv of *n*-BuLi (0.173 mmol, 108.0 mL, 1.6 M in hexane) over a period of 1 h. The mixture was stirred at 23 °C for additional 2.5 h. Volatiles were removed in vacuo to give white powders of LiNEt<sub>2</sub> (12.920 g, 0.163 mmol, 95% yield).

Synthesis of TaCl(NMe<sub>2</sub>)<sub>4</sub> (2). Hexanes (100 mL) were added to a solid mixture of TaCl<sub>5</sub> (7.660 g, 21.38 mmol) and LiNMe<sub>2</sub> (4.363 g, 85.52 mmol) at -40 °C with vigorous stirring. The mixture was slowly warmed to 23 °C, and the solution was then refluxed at 72 °C for 22 h. The deep brown solution was filtered, and the residue was extracted with hexanes for 3 times (3 × 60 mL). Volatiles were removed from the filtrate in vacuo, and subsequent sublimation at 85 °C yielded 5.567 g (14.18 mmol, 66%) of yellow crystalline TaCl(NMe<sub>2</sub>)<sub>4</sub> (2). <sup>1</sup>H NMR of **2**(benzene-*d*<sub>6</sub>, 399.88 MHz, 23 °C)  $\delta$  3.24 (s, 24H, N*Me*<sub>2</sub>). <sup>13</sup>C NMR (benzene*d*<sub>6</sub>, 100.55 MHz, 23 °C)  $\delta$  45.93 (s, N*Me*<sub>2</sub>). The crystals were used directly in the subsequent X-ray diffraction to be discussed below.

Synthesis of Ta(NMe<sub>2</sub>)<sub>4</sub>[N(SiMe<sub>3</sub>)<sub>2</sub>] (4). Toluene (20 mL) was added to a solid mixture of TaCl(NMe<sub>2</sub>)<sub>4</sub> (2, 0.684 g, 1.74 mmol) and LiN(SiMe<sub>3</sub>)<sub>2</sub> (0.291 g, 1.74 mmol) at -78 °C with vigorous stirring. The mixture was slowly warmed to 23 °C and stirred for 15 h. Volatiles were removed from the mixture in vacuo, and the residue was extracted with n-pentane. Filtration and crystallization yielded a pale-yellow solid of 4 (0.423 g, 0.817 mmol, 47% yield) at -32 °C. <sup>1</sup>H NMR of 4 (benzene-*d*<sub>6</sub>, 399.79 MHz, 23 °C)  $\delta$  3.26 (s, 24H, NM*e*<sub>2</sub>), 0.33 (s, 18H, SiM*e*<sub>3</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>, 100.54 MHz, 23 °C)  $\delta$  48.28 (s, NM*e*<sub>2</sub>), 5.17 (s, SiM*e*<sub>3</sub>). Anal. calcd for C<sub>14</sub>H<sub>42</sub>N<sub>5</sub>Si<sub>2</sub>Ta: C, 32.48; H, 8.18. Found: C, 32.41; H, 8.13.

Synthesis of Ta(NMe<sub>2</sub>)<sub>4</sub>(NEt<sub>2</sub>) (7). To TaCl(NMe<sub>2</sub>)<sub>4</sub> (2, 2.330 g, 5.932 mmol) in n-pentane (15 mL) at 0 °C was added slowly 1 equiv of LiNEt<sub>2</sub> (0.460 g, 5.932 mmol) in Et<sub>2</sub>O (15 mL). The solution was then stirred at 0–13 °C for 2 h. The solution was settled and filtered. Volatiles were removed from the filtrate in vacuo and n-pentane was added to the residue. The solution was concentrated and then put in a freezer (-32 °C) for crystallization.

A pale-yellow solid (0.700 g, 1.630 mmol, 27.5%) of Ta(NMe<sub>2</sub>)<sub>4</sub>(NEt<sub>2</sub>) (**7**) was isolated in one day. <sup>1</sup>H NMR (benzened<sub>6</sub>, 399.79 MHz, 23 °C)  $\delta$  3.49 (q, 4H, NCH<sub>2</sub>CH<sub>3</sub>), 3.28 (s, 24H, NCH<sub>3</sub>), 1.12 (t, 6H, NCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (benzene-d<sub>6</sub>, 100.53 MHz, 23 °C)  $\delta$  47.57 (s, NCH<sub>2</sub>CH<sub>3</sub>), 46.60 (s, NCH<sub>3</sub>), 17.01 (s, NCH<sub>2</sub>CH<sub>3</sub>). Anal. calcd for C<sub>12</sub>H<sub>34</sub>N<sub>5</sub>Ta: C, 33.57; H, 7.98. Found: C 33.36, H 7.84.

Heating of Ta(NMe<sub>2</sub>)<sub>4</sub>[N(SiMe<sub>3</sub>)<sub>2</sub>] (4) at 86 °C. The solution of Ta(NMe<sub>2</sub>)<sub>4</sub>[N(SiMe<sub>3</sub>)<sub>2</sub>] (4) (16.7 mg, 0.0323 mmol) and bibenzyl (internal standard, 11.3 mg, 0.0620 mmol) in toluene (0.46 mL) in a Young tube was heated at 86 °C for 50 h. <sup>1</sup>H NMR spectrum of the solution revealed that 4 had decomposed to unknown species.

Indirect Observation of the Equilibrium among TaCl(NMe<sub>2</sub>)<sub>4</sub> (2), Ta(NMe<sub>2</sub>)<sub>5</sub> (1), and Ta<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub>Cl<sub>2</sub> (3). TaCl(NMe<sub>2</sub>)<sub>4</sub> (2, 35.7 mg, 0.0914 mmol), LiN(SiMe<sub>3</sub>)<sub>2</sub> (15.3 mg, 0.0914 mmol), and bibenzyl (internal standard, 15.9 mg, 0.0872 mmol) were dissolved in toluene- $d_8$  in a Young tube. The reaction yielded Ta(NMe<sub>2</sub>)<sub>4</sub>[N(SiMe<sub>3</sub>)<sub>2</sub>] (4, 0.0592 mmol, 65% yield), Ta(NMe<sub>2</sub>)<sub>5</sub> (1, 0.0123 mmol, 13% yield), **6** (0.0113 mmol, 12% yield), and HN(SiMe<sub>3</sub>)<sub>2</sub> (0.0115 mmol, 13% yield), suggesting that there is an equilibrium as shown in Scheme 1.

Reaction of TaCl(NMe<sub>2</sub>)<sub>4</sub> (2) with 1 equiv of LiN(SiMe<sub>3</sub>)<sub>2</sub> at 10 and 15 °C. Reaction at 10 °C. LiN(SiMe<sub>3</sub>)<sub>2</sub> (12.7 mg, 0.0760 mmol) and bibenzyl (internal standard, 20.4 mg, 0.112 mmol) were dissolved in toluene- $d_8$  in a Young tube and the solution was cooled to -78 °C. TaCl(NMe<sub>2</sub>)<sub>4</sub> (2, 29.7 mg, 0.0760 mmol) was added at -78 °C, and the solution was then warmed to 10 °C. <sup>1</sup>H NMR was used to follow the reaction, and it revealed that the reaction was completed in 4 h.

**Reaction at 15** °C. LiN(SiMe<sub>3</sub>)<sub>2</sub> (12.7 mg, 0.0760 mmol) and bibenzyl (internal standard, 13.3 mg, 0.0729 mmol) were dissolved in toluene- $d_8$  in a Young tube and the solution was cooled to -78°C. TaCl(NMe<sub>2</sub>)<sub>4</sub> (**2**, 29.7 mg, 0.0760 mmol) was added at -78°C, and the solution was then warmed to 15 °C. <sup>1</sup>H NMR was used to follow the reaction, and it revealed that the reaction was completed in 2.5 h.

The reaction at both 10 and 15 °C gave the same products  $Ta(NMe_2)_4[N(SiMe_3)_2]$  (4),  $Ta(NMe_2)_5$  (1), 5, and  $HN(SiMe_3)_2$  in ratios of 4:1:1:1 and 3:1:1:1, respectively.

Reaction of TaCl(NMe<sub>2</sub>)<sub>4</sub> (2) with 1 equiv of LiNEt<sub>2</sub>. TaCl(NMe<sub>2</sub>)<sub>4</sub> (2, 53.4 mg, 0.137 mmol) and LiNEt<sub>2</sub> (10.8 mg, 0.137 mmol) were mixed in benzene- $d_6$  (0.46 mL) in a Young tube and the solution was shaken for 10 min. The reaction yielded Ta(NMe<sub>2</sub>)<sub>4</sub>(NEt<sub>2</sub>) (7), Ta(NMe<sub>2</sub>)<sub>3</sub>(NEt<sub>2</sub>)<sub>2</sub> (8), and Ta(NMe<sub>2</sub>)<sub>5</sub> (1) in a molar ratio 2.8:1:1.

Exchange of Ta(NMe<sub>2</sub>)<sub>4</sub>(NEt<sub>2</sub>) (7), Ta(NMe<sub>2</sub>)<sub>3</sub>(NEt<sub>2</sub>)<sub>2</sub> (8), and Ta(NMe<sub>2</sub>)<sub>5</sub> (1). Exchange at 23 °C. Ta(NMe<sub>2</sub>)<sub>5</sub> (1, 22.3 mg, 0.0556 mmol) was added to a mixture of Ta(NMe<sub>2</sub>)<sub>4</sub>(NEt<sub>2</sub>) (7) and Ta(NMe<sub>2</sub>)<sub>3</sub>(NEt<sub>2</sub>)<sub>2</sub> (8, total 19.3 mg; 26 mol% 7 and 74 mol% 8) and bibenzyl (internal standard, 10.6 mg, 0.0576 mmol) in toluene $d_8$  (0.46 mL). The solution was kept at 23 °C for over 160 h. <sup>1</sup>H NMR revealed that the peaks of 7 slowly grew up. A similar slow exchange was observed with a solution of 1 (8.7 mg, 0.0218 mmol), 7 and 8 (total 18.8 mg; 29 mol% 7 and 71 mol% 8) and bibenzyl (internal standard, 10.3 mg, 0.0565 mmol) in toluene- $d_8$  (0.46 mL).

**Exchange at 90** °C. A solution of **1** (9.1 mg, 0.0227 mmol), **7** and **8** (total 18.8 mg; 29 mol% **7** and 71 mol% **8**) and bibenzyl (internal standard, 10.0 mg, 0.0549 mmol) in toluene- $d_8$  (0.46 mL) was initially heated at 60 °C and then at 90 °C. The solution was monitored by <sup>1</sup>H NMR at 23 °C. The heating at 90 °C lasted about 4–5 days until no change in concentrations of the three complexes was observed. Since the exchange at 23 °C was very slow and the time needed for a <sup>1</sup>H NMR spectrum was short (about 10 min), cooling the solution to 23 °C for 10 min essentially "quenched" the exchange. In a second test, a solution of Ta(NMe<sub>2</sub>)<sub>4</sub>(NEt<sub>2</sub>) (**7**, 12.3 mg, 0.0287 mmol) and bibenzyl (internal standard, 10.1 mg, 0.0554 mmol) in toluene- $d_8$  was heated at 90 °C. The solution was

periodically cooled to 23 °C to take <sup>1</sup>H NMR spectra. The heating was found to yield  $Ta(NMe_2)_3(NEt_2)_2$  (8) and  $Ta(NMe_2)_5$  (1) over a period of 4–5 days to reach an equilibrium.

When a mixture (19.9 mg total) of **7**, **8** and bibenzyl (internal standard, 10.5 mg, 0.0576 mmol) in toluene- $d_8$  (0.46 mL) was kept at 23 °C for 9 days, no change was observed.

**Reactions of TaCl(NMe<sub>2</sub>)<sub>4</sub> with H<sub>2</sub>O.** Ta<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>( $\mu$ -O)(NMe<sub>2</sub>)<sub>6</sub> (**9**) has been isolated from the reaction of TaCl(NMe<sub>2</sub>)<sub>4</sub> (**2**) with 1 equiv of H<sub>2</sub>O. To TaCl(NMe<sub>2</sub>)<sub>4</sub> (**2**, 1.000 g, 2.546 mmol) in THF (10 mL) with vigorous stirring at -30 °C was added slowly 1 equiv of H<sub>2</sub>O (46.0  $\mu$ L) in 5 mL of THF. After temperature was raised to 23 °C, solution was stirred for additional 1 h. Volatiles were removed under reduced pressure and pale yellow residue was extracted with hexanes. Filtrate was concentrated for crystallization at -32 °C. Yellow crystals of **9** (0.463 g, 0.649 mmol, 51% yield) were collected in a few days. <sup>1</sup>H NMR of **9** (benzene-*d*<sub>6</sub>, 399.87 MHz, 23 °C)  $\delta$  3.57 (s, 36H, 6N*M*e<sub>2</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>, 100.56 MHz, 23 °C)  $\delta$  47.36 (s, 6N*M*e<sub>2</sub>). Anal. calcd for C<sub>12</sub>H<sub>36</sub>N<sub>6</sub>OCl<sub>2</sub>Ta<sub>2</sub>: C, 20.21; H, 5.09. Found: C, 20.14; H, 5.07.

Determination of X-Ray Crystal Structures of 2 and 9. The data were collected at -100 °C on a Bruker-AXS APEX diffractometer with a Kryoflex low temperature device, a CCD area

detector fitted with an upgraded Nicolet LT-2 low temperature device, and a graphite-monochromated Mo source ( $K_{\alpha}$  radiation, 0.71073 Å). Suitable crystals were coated with paratone oil (Exxon) and mounted on loops under a stream of nitrogen at the data collection temperature. The structures were solved by direct methods. Non-hydrogen atoms were anisotropically refined. All hydrogen atoms were treated as idealized contributions. Empirical absorption correction was performed with SADABS.<sup>15a</sup> In addition the global refinements for the unit cells and data reductions of the two structures were performed using the Saint program (version 6.02). All calculations were package.<sup>15b</sup>

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**Supporting Information Available:** Crystallographic data of **2** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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