

# Reviews

## Transition-Metal Silyl Complexes and Chemistry in the Reactions of Silanes with Transition-Metal Complexes

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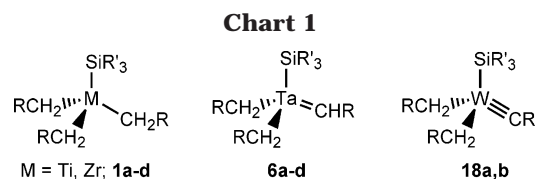
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Studies from the authors' group of early-transition-metal silyl complexes and pathways in the reactions of silanes with transition-metal complexes are reviewed. Cyclopentadienyl-free, group 4 alkyl silyl, group 5 alkylidene silyl, group 6 alkylidyne silyl, and groups 4 and 5 amide and imide silyl complexes have been prepared and characterized. In the reactions of silanes with alkylidene and amide complexes, the  $M=CH-\pi$  bonds and  $d-p \pi$  bonds in  $M=NR_2$  were found to attack Si in silanes. The mechanistic studies here help in understanding the formation of mixtures of TiN and  $Si_3N_4$  from the reactions of  $Ti(NMe_2)_4$  and  $SiH_4$  as microelectronic diffusion barrier materials.

$Cp(CO)_2Fe-SiMe_3$  ( $Cp$  = cyclopentadienyl), the first complex known to contain a transition-metal–silicon bond, was reported by Wilkinson and co-workers in 1956.<sup>1</sup> Since then, transition-metal silyl chemistry has become a field of intense study.<sup>2</sup> Many complexes involve late-transition-metal elements containing metal–silicon bonds; they are usually coordinatively saturated and electron-rich.<sup>2</sup> Early-transition-metal silyl chemistry had been mostly focused on complexes with stabilizing ligands such as  $Cp$ ,  $CO$ ,  $-OR$ ,  $-NR_2$ , and  $PR_3$ .<sup>3</sup> The presence of such donating ligands in silyl complexes is believed to contribute to their enhanced stability.

Our studies of early-transition-metal silyl complexes and reactions of silanes with metal complexes started when one of us (Z.-L.X.) began his faculty appointment at the University of Tennessee in 1992. He had been attracted to these areas when he was developing ideas for his future independent research during his postdoctoral appointment at Indiana University. With interest in the uses of transition metals in microelectronics, he chose to study chemistry related to molecular approaches to metal–silicon-based materials. Our initial interest was in the Cp-free alkyl, alkylidene, and alkylidyne silyl complexes shown in Chart 1. These complexes were chosen as they were then unknown, and in molecular approaches such as chemical vapor deposi-

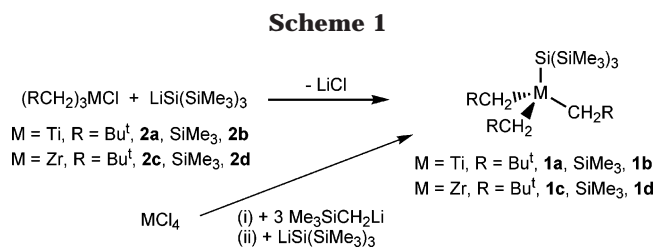


tion of metal–silicon materials, Cp-free complexes are often more volatile and are thus desirable. We were interested in the fundamental chemistry—the synthesis, characterization, and reactivities of these novel silyl complexes—and their potential applications. After these complexes were successfully prepared and characterized, we investigated groups 4 and 5 silyl amide and imide complexes and the reactions of silanes with alkylidene and amide complexes. Our studies of these complexes and reactions are summarized.

(1) Piper, T. S.; Lemal, D.; Wilkinson, G. *Naturwissenschaften* **1956**, *43*, 129.

(2) (a) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p. 1415. (b) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; pp 245, 309. (c) Eisen, M. S. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, Part 3, p 2037. (d) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37. (e) Harrod, J. F.; Mu, Y.; Samuel, E. *Polyhedron* **1991**, *10*, 1239. (f) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175. (g) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22. (h) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351. (i) Xue, Z.-L. *Comments Inorg. Chem.* **1996**, *18*, 223. (j) Chen, T.-N.; Xue, Z.-L. *Chinese J. Inorg. Chem.* **1999**, *15*, 413.

(3) (a)  $V(CO)_6SiH_3$ : Allinson, J. S.; Aylett, B. J.; Colquhoun, H. M. *J. Organomet. Chem.* **1976**, *112*, C7. (b)  $[R_2SiM(CO)_5]^-$  (M = Cr, Mo, W): Isaacs, E. E.; Graham, W. A. G. *Can. J. Chem.* **1975**, *53*, 467. Darendsberg, D. J.; Bauch, C. G.; Reibenspies, J. H.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 4203. (c)  $C_6H_6(CO)_2Cr(H)SiCl_3$ : Jetz, W.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 4.  $C_6Me_6(CO)_2Cr(H)SiHPh_2$ : Schubert, U.; Muller, J.; Alt, H. G. *Organometallics* **1987**, *6*, 469. (d)  $W_2(CO)_{10}(SiEt_2)_2$  and  $W_2(CO)_6H_2(SiEt_2)_2$ : Hoyano, J. K. Ph.D. dissertation, University of Alberta, Canada, 1971. Bennett, M. J.; Simpson, K. A. *J. Am. Chem. Soc.* **1971**, *93*, 7156. (e) (dppe)(CO)<sub>3</sub>M(H)SiCl<sub>3</sub> (M = Cr, Mo, W): Schubert, U.; Kirchgassner, U.; Gronen, J.; Piana, H. *Polyhedron* **1989**, *8*, 1589. (f) (2-Ph<sub>2</sub>PCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Si=Cr(CO)<sub>5</sub>: Handwerker, H.; Paul, M.; Blumel, J.; Zybill, C. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1313. (g)  $[NEt_4][[CO)_5MSi(SnMe_3)_3]$  (M = Cr, Mo, W): Heyn, R. H.; Tilley, T. D. *Inorg. Chem.* **1990**, *29*, 4051. (h) *cis*-Mo( $\eta^2$ -H-SiHR'<sub>2</sub>)(CO)(R<sub>2</sub>PC<sub>2</sub>H<sub>4</sub>PR'<sub>2</sub>)<sub>2</sub> (R' = Ph, *n*-C<sub>6</sub>H<sub>13</sub>): Luo, X.-L.; Kubas, G. J.; Bryan, J. C.; Burns, C. J.; Unkefer, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 10312. (i) (Me<sub>3</sub>P)<sub>3</sub>W(H)<sub>2</sub>I(SiMe<sub>3</sub>): Barron, A. R.; Wilkinson, G.; Motevall, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 837. (j) Mo<sub>2</sub>(Si(SiMe<sub>3</sub>)<sub>3</sub>)<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub>: Chisholm, M. H.; Chiu, H.-T.; Foltling, K.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 4097. (k) (R<sub>2</sub>N)<sub>3</sub>Ti-Si(SiMe<sub>3</sub>)<sub>3</sub> (R = Me, Et): Ustinov, M. V.; Bravo-Zhivotoskii, D. A.; Kalikhman, I. D.; Vitkovskii, V. Yu.; Vyazankin, N. S.; Voronkov, M. G. *Organomet. Chem. USSR* **1989**, *2*, 664. Ovchinnikov, Yu. E.; Struchkov, Yu. T.; Ustinov, M. V.; Voronkov, M. G. *Russ. Chem. Bull.* **1993**, *8*, 1411. (l) (Me<sub>3</sub>P)<sub>3</sub>W(H)<sub>2</sub>(SiH<sub>3</sub>)<sub>2</sub>: Green, M. L. H.; Parkin, G.; Chen, M.-Q.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1986**, 2227.



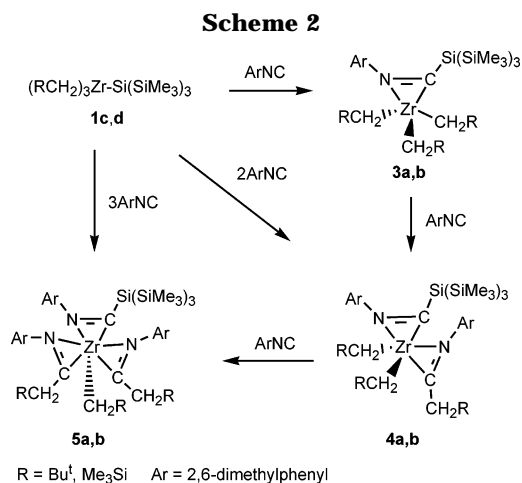
### I. Cp-Free Alkyl, Alkylidene, and Alkylidyne Silyl Complexes

The complexes in Chart 1 are essentially silyl analogues of d<sup>0</sup> high-oxidation-state peralkyl,<sup>4</sup> Schrock-type alkyl alkylidene,<sup>5</sup> and alkyl alkylidyne complexes.<sup>5</sup> Our initial interest in these complexes also originated in part from our desire to compare the silyl and alkyl complexes. The complexes in Chart 1 would provide a unique opportunity to compare the reactivities of alkyl and silyl ligands free of the influence of ancillary ligands. In the first section of this review, our work on the d<sup>0</sup> high-oxidation-state alkyl, alkylidene, and alkylidyne silyl complexes in Chart 1 is discussed.

**1. Alkyl Silyl Complexes (RCH<sub>2</sub>)<sub>3</sub>MSi(SiMe<sub>3</sub>)<sub>3</sub>.**<sup>6,7</sup> The reactions to prepare (RCH<sub>2</sub>)<sub>3</sub>MSi(SiMe<sub>3</sub>)<sub>3</sub> (M = Ti, R = Me<sub>3</sub>C (**1a**), Me<sub>3</sub>Si (**1b**); M = Zr, R = Me<sub>3</sub>C (**1c**), Me<sub>3</sub>Si (**1d**)) are shown in Scheme 1. In solution, the Zr complexes are significantly more thermally stable than the Ti analogues. However, they are all slightly light sensitive. As solids, they can be stored in the dark at room temperature for several weeks with little degradation.

There is no evidence in the NMR spectra of these complexes to suggest an agostic interaction. The X-ray structures of (Me<sub>3</sub>CCH<sub>2</sub>)<sub>3</sub>Ti-Si(SiMe<sub>3</sub>)<sub>3</sub> (**1a**), (Me<sub>3</sub>-SiCH<sub>2</sub>)<sub>3</sub>Ti-Si(SiMe<sub>3</sub>)<sub>3</sub> (**1b**), and (Me<sub>3</sub>CCH<sub>2</sub>)<sub>3</sub>Zr-Si(SiMe<sub>3</sub>)<sub>3</sub> (**1c**) show a staggered conformation of the alkyl ligands with respect to the SiMe<sub>3</sub> groups in the silyl ligand and pseudo-tetrahedral geometry around the metal centers.

The alkyl silyl complexes (RCH<sub>2</sub>)<sub>3</sub>Zr-Si(SiMe<sub>3</sub>)<sub>3</sub> (R = Me<sub>3</sub>C (**1c**), Me<sub>3</sub>Si (**1d**)) undergo ArNC (Ar = 2,6-dimethylphenyl) insertion reactions (Scheme 2).<sup>8</sup> The isocyanide inserts first into the Zr-Si bonds to give the monoinsertion products **3a,b**, followed by two additional insertions into the Zr-C bonds. **3a,b** were isolated through crystallization and are stable under nitrogen at room temperature. The diinsertion products **4a,b** were only identifiable by NMR spectrometry in situ; attempts to isolate pure products were unsuccessful. The triinsertion products **5a,b** are prepared either by the reaction of (RCH<sub>2</sub>)<sub>3</sub>Zr-Si(SiMe<sub>3</sub>)<sub>3</sub> (**1c,d**) with 3 equiv of ArNC or by the reaction of 1 equiv of ArNC with the diinsertion products. They were crystallized from toluene. The triinsertion products **5a,b** are inert to further insertion, most likely due to steric hindrance, and are less susceptible to air oxidation than the monoinsertion



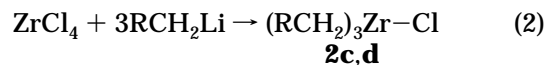
products **3a,b**. The preferential insertion of the first isocyanide into the Zr-Si bonds in **1c,d** and its comparison with the reactions of ArNC with Zr amide silyl complexes (R<sub>2</sub>N)<sub>3</sub>ZrSiR'<sub>3</sub> (**21b,c**) are discussed in section II.1.

The trialkyl chloride complexes (RCH<sub>2</sub>)<sub>3</sub>M-Cl (**2a-d**) were prepared as starting materials for the alkyl silyl complexes (RCH<sub>2</sub>)<sub>3</sub>M-Si(SiMe<sub>3</sub>)<sub>3</sub> (**1a-d**).<sup>9</sup> (Me<sub>3</sub>CCH<sub>2</sub>)<sub>3</sub>Zr-Cl (**2c**) was first prepared by Wengrovius and Schrock through the reaction of (Bu<sup>t</sup>CH<sub>2</sub>)<sub>2</sub>Mg with (Bu<sup>t</sup>-CH<sub>2</sub>)<sub>2</sub>ZrCl<sub>2</sub>(Et<sub>2</sub>O)<sub>2</sub>.<sup>10</sup> We subsequently developed several new methods to prepare (RCH<sub>2</sub>)<sub>3</sub>M-Cl (**2a-d**; eqs 1-4).<sup>9</sup>

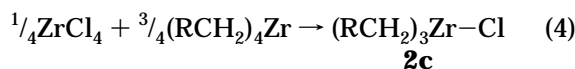
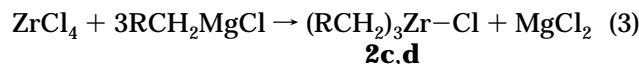


M = Ti, R = Bu<sup>t</sup> (**2a**), Me<sub>3</sub>Si (**2b**);

M = Zr, R = Bu<sup>t</sup> (**2c**)



R = Bu<sup>t</sup> (**2c**), Me<sub>3</sub>Si (**2d**)



In the studies of (Bu<sup>t</sup>CH<sub>2</sub>)<sub>3</sub>Zr-Cl (**2c**), we were surprised to find that it crystallizes in polymeric chains with a linear, symmetric Zr-Cl-Zr repeating unit (Figure 1). Linear M-Cl-M configurations are rare, as the halide bridges normally have M-X-M angles around 109°, consistent with sp<sup>3</sup> hybridization of the halide bridge. Some linear chloride-bridged compounds have been reported for late transition metals with d<sup>0</sup> configurations.<sup>11</sup> The ligands around each zirconium are arranged in a trigonal bipyramid. The Zr-Cl-Zr-Cl-chain is linear, and the C-Zr-Cl angle is 90°, as defined by the crystallographic symmetry. The zirconium and three carbon atoms are coplanar, and this plane is

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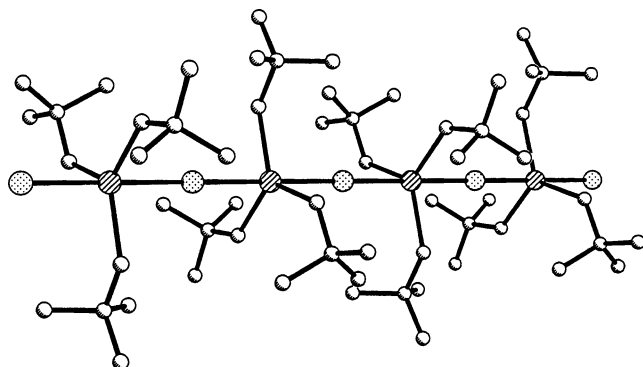
(6) Xue, Z.-L.; Li, L.-T.; Hoyt, L. K.; Diminnie, J. B.; Pollitte, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 2169.

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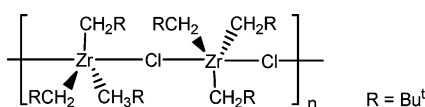
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(10) Wengrovius, J. H.; Schrock, R. R. *J. Organomet. Chem.* **1981**, *205*, 319.

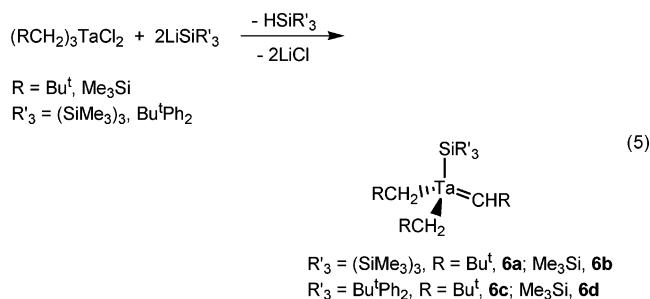


**Figure 1.** Drawing of the linear polymeric chain in **2c** from X-ray single-crystal diffraction.<sup>9</sup>

perpendicular to the Zr–Cl–Zr–Cl– chain. Adjacent (Bu<sup>t</sup>CH<sub>2</sub>)<sub>3</sub>Zr moieties are staggered to reduce steric strain (Figure 1).



**2. Alkylidene Silyl Complexes (RCH<sub>2</sub>)<sub>2</sub>Ta(=CHR)-(SiR<sub>3</sub>) (R = Bu<sup>t</sup> (**6a**), Me<sub>3</sub>Si (**6b**)).**<sup>6,12</sup> The first stable group 5 silyl alkylidenes were prepared by the reactions in eq 5. To our knowledge, this was the first reported



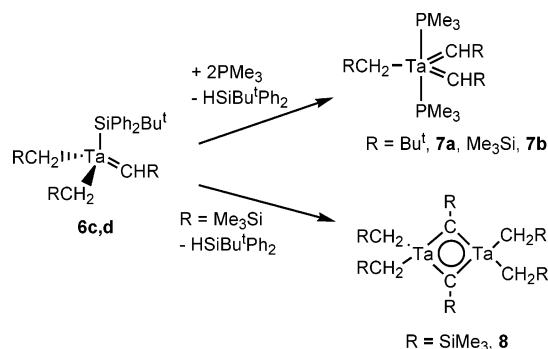
*preferential* silane elimination to form alkylidene bonds. The diastereotopic protons, H<sub>a</sub> and H<sub>b</sub>, of the methylene moiety in both complexes show large chemical shift differences in their <sup>1</sup>H NMR spectra. This is attributed to the diamagnetic anisotropy of the M–C multiple bonds.

X-ray crystal structures of the alkylidene complexes (RCH<sub>2</sub>)<sub>2</sub>Ta(=CHR)[Si(SiMe<sub>3</sub>)<sub>3</sub>] (**6a,b**) with the –Si(SiMe<sub>3</sub>)<sub>3</sub> ligand show a 3-fold disorder, thus giving an average alkylidene/alkyl bond length of 1.97(3) Å in **6a** and 2.03(4) Å in **6b**, respectively. In comparison, Ta–C and Ta=C bond lengths in [Ta(=CHBu<sup>t</sup>)(CH<sub>2</sub>Bu<sup>t</sup>)(PMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(μ-N<sub>2</sub>) are 2.285(10) and 1.932(9) Å, respectively.<sup>13</sup> The Ta–Si distances of 2.559(16)–2.680(15) Å in **6a** and 2.611(7) Å in **6b** are similar to other reported Ta–Si distances.<sup>14</sup>

(11) (a) Bino, A.; Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1979**, *18*, 2599. (b) Butler, L. G.; Zietlow, M. H.; Che, C.-M.; Schaefer, W. P.; Sridhar, S.; Grunthaler, P. J.; Swanson, B. I.; Clark, R. J. H.; Gray, H. B. *J. Am. Chem. Soc.* **1988**, *110*, 1155. (c) Jin, S.; Ito, T.; Toriumi, K.; Yamashita, M. *Acta Crystallogr.* **1989**, *C45*, 1415. (d) Clark, R. J. H.; Kurmoo, M.; Dawes, H. M.; Hursthouse, M. B. *Inorg. Chem.* **1986**, *25*, 409. (e) Yamashita, M.; Toriumi, K. *Inorg. Chim. Acta* **1990**, *178*, 143. (f) Bellitto, C.; Dessy, G.; Fares, V. *Inorg. Chem.* **1985**, *24*, 2815. (g) O'Connor, C. J.; Romananch, R. J.; Robertson, D. M.; Eduok, E. E.; Fronczek, F. R. *Inorg. Chem.* **1983**, *22*, 449.

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**Scheme 3**



The alkylidene complexes (RCH<sub>2</sub>)<sub>2</sub>Ta(=CHR)(SiBu<sup>t</sup>Ph<sub>2</sub>) (**6c,d**), with the –SiBu<sup>t</sup>Ph<sub>2</sub> ligand, are thermally unstable. They undergo preferential silane eliminations through α-H abstraction, as in the formation of silyl alkylidenes, to give the bis(alkylidene) bis(phosphine) complexes (RCH<sub>2</sub>)<sub>2</sub>Ta(=CHR)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (R = Bu<sup>t</sup> (**7a**), Me<sub>3</sub>Si (**7b**)) in the presence of PMe<sub>3</sub> and, for **6d**, the bridging dimeric bis(alkylidene) complex (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>4</sub>Ta<sub>2</sub>(μ-CSiMe<sub>3</sub>)<sub>2</sub> (**8**) in the absence of PMe<sub>3</sub> (Scheme 3).<sup>15</sup> **6d** decomposes within minutes to **8**. The d<sup>0</sup> alkylidene complex **8** was first reported by Wilkinson and co-workers.<sup>16</sup> The silyl neopentylidene (Bu<sup>t</sup>CH<sub>2</sub>)<sub>2</sub>Ta(=CHBu<sup>t</sup>)(SiBu<sup>t</sup>Ph<sub>2</sub>) (**6c**), as observed by NMR spectrometry, decomposes slowly over several hours to give unidentified products.

The reasons for the silane elimination to be preferred over alkane elimination are not clear. Earlier studies show that early-transition-metal (especially d<sup>0</sup>)–silicon bonds are weaker than metal–hydrocarbyl bonds.<sup>17</sup> Our thermodynamic analysis of silane vs alkane elimination from (RCH<sub>2</sub>)<sub>3</sub>Ta(Cl)[Si(SiMe<sub>3</sub>)<sub>3</sub>] suggests that the silane elimination may be slightly thermodynamically less favored, mainly because H–Si bonds are much weaker than H–C bonds. Preferential silane elimination could be attributed to a kinetic effect. Silane elimination is preferred over methane elimination by ca. 4–5 kcal/mol in the calculated activation free energy.

Addition of 2 equiv of HCl to the alkylidene complex (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>4</sub>Ta<sub>2</sub>(μ-CSiMe<sub>3</sub>)<sub>2</sub> (**8**) gives the unstable bis(alkylidene) complex (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>4</sub>(Cl)<sub>2</sub>Ta<sub>2</sub>(=CHSiMe<sub>3</sub>)<sub>2</sub> (**9a**).<sup>18</sup> Addition of excess PMe<sub>3</sub> to the solution containing this unstable bridging bis(alkylidene) complex leads to the stable nonsymmetric bis(alkylidene) complex

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(14) See the following examples. (a) 2.624(12)–2.633(2) Å in Cp<sub>2</sub>Ta(H)(SiMe<sub>2</sub>H) and 2.639(4) Å in Cp<sub>2</sub>Ta(PMe<sub>3</sub>)(SiMe<sub>3</sub>); Jiang, Q.; Carroll, P. J.; Berry, D. H. *Organometallics* **1991**, *10*, 3648. (b) 2.651(4) Å in Cp<sub>2</sub>Ta(H)<sub>2</sub>SiPhMe<sub>2</sub>; Curtis, M. D.; Bell, L. G.; Butler, W. M. *Organometallics* **1985**, *4*, 701. (c) 2.669(4) Å in (C<sub>5</sub>Me<sub>5</sub>)Ta(SiMe<sub>3</sub>)Cl<sub>3</sub>; Arnold, J.; Shina, D. N.; Tilley, T. D.; Arif, A. M. *Organometallics* **1986**, *5*, 2037.

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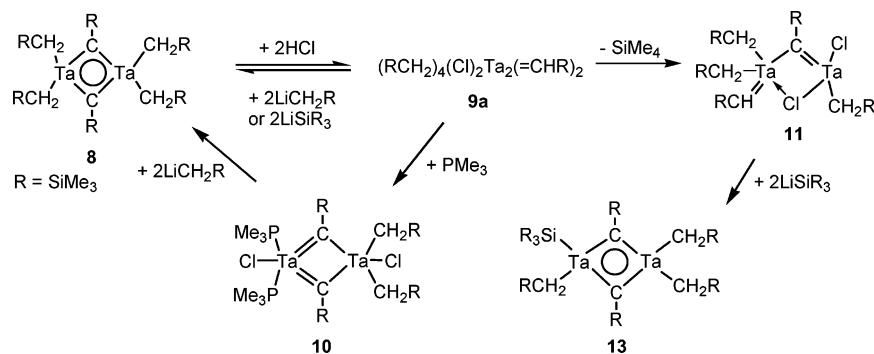
(16) Mowat, W.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 1120.

(17) (a) King, W. A.; Marks, T. J. *Inorg. Chim. Acta* **1995**, *229*, 343. (b) Jiang, Q.; Pestana, D. C.; Carroll, P. J.; Berry, D. H. *Organometallics* **1994**, *13*, 3679. (c) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1993**, *115*, 6883.

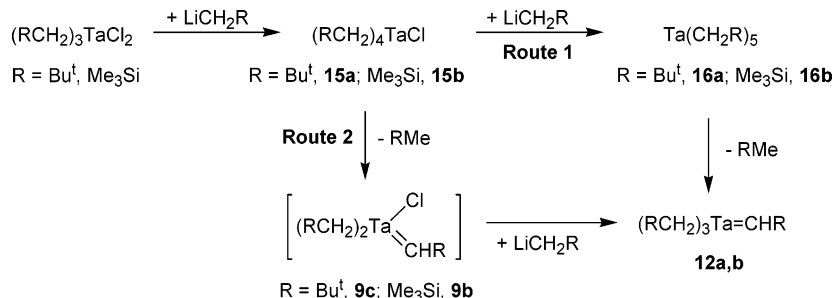
(18) (a) Li, L.-T.; Xue, Z.-L.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1995**, *14*, 4992. (b) Liu, X.-Z.; Li, L.-T.; Diminnie, J. B.; Yap, G. P. A.; Rheingold, A. L.; Xue, Z.-L. *Organometallics* **1998**, *17*, 4597.



Scheme 4



Scheme 5. Possible Pathways to Alkyl Alkylidene Complexes



( $\text{Me}_3\text{P}$ )<sub>2</sub>(Cl)Ta( $\mu$ -CSiMe<sub>3</sub>)<sub>2</sub>Ta(Cl)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (**10**). Substitution of the chlorides in the bis(alkylidene) complex **9a** by LiSi(SiMe<sub>3</sub>)<sub>3</sub> or LiCH<sub>2</sub>SiMe<sub>3</sub> and in the bis(alkylidene) complex **10** by LiCH<sub>2</sub>SiMe<sub>3</sub> converts them back to ( $\text{Me}_3\text{SiCH}_2$ )<sub>4</sub>Ta<sub>2</sub>( $\mu$ -CSiMe<sub>3</sub>)<sub>2</sub> (**8**; Scheme 4).

The unstable bis(alkylidene) complex **9a** decomposes by the elimination of 1 equiv of SiMe<sub>4</sub> to give the alkylidene alkylidene complex ( $\text{Me}_3\text{SiCH}_2$ )<sub>3</sub>(Cl)<sub>2</sub>Ta<sub>2</sub>(=CHSiMe<sub>3</sub>)(=CSiMe<sub>3</sub>) (**11**). NOESY studies suggest that the most likely structure of this complex has bridging chloride and alkylidene ligands (Scheme 4). The  $\alpha$ -H abstraction reaction to give this complex was found to follow first-order kinetics with rate constants ranging between  $[4.00(0.13)] \times 10^{-5} \text{ s}^{-1}$  at 217(1) K to  $[1.58(0.05)] \times 10^{-3} \text{ s}^{-1}$  at 244(1) K. Kinetic studies of this alkylidene (**9a**)  $\rightarrow$  alkylidene (**11**) conversion give an activation enthalpy of  $\Delta H^\ddagger = 14.1(0.8) \text{ kcal/mol}$  and an activation entropy of  $\Delta S^\ddagger = -12(3) \text{ eu}$ . The work here is, to our knowledge, the second kinetic study of the alkylidene  $\rightarrow$  alkylidene conversion after our earlier study of the conversion of ( $\text{Me}_3\text{SiCH}_2$ )<sub>3</sub>Ta=CHSiMe<sub>3</sub> (**12b**) to ( $\text{Me}_3\text{SiCH}_2$ )<sub>4</sub>Ta<sub>2</sub>( $\mu$ -CSiMe<sub>3</sub>)<sub>2</sub> (**8**), to be discussed below.<sup>19</sup> The negative  $\Delta S^\ddagger$  value indicates a transition state where rotation of the bonds involved in the reaction is restricted and the symmetry of the molecule descends. Such negative  $\Delta S^\ddagger$  values have been observed in other C–H bond activation processes and are attributed to concerted four-center transition states, especially those involving cyclometalation.<sup>20</sup>

The reaction of the alkylidene alkylidene complex ( $\text{Me}_3\text{SiCH}_2$ )<sub>3</sub>(Cl)<sub>2</sub>Ta<sub>2</sub>(=CHSiMe<sub>3</sub>)(=CSiMe<sub>3</sub>) (**11**) with 2

equiv of LiSi(SiMe<sub>3</sub>)<sub>3</sub> gives the silyl alkylidene ( $\text{Me}_3\text{SiCH}_2$ )<sub>3</sub>( $\text{Me}_3\text{Si}$ )<sub>3</sub>Si]Ta<sub>2</sub>( $\mu$ -CSiMe<sub>3</sub>)<sub>2</sub> (**13**). This is a silyl analogue of the bridging alkyl alkylidene complex **8**. These results are summarized in Scheme 4.

At  $-78^\circ\text{C}$ , ( $\text{RCH}_2$ )<sub>2</sub>Ta(=CHR)[Si(SiMe<sub>3</sub>)<sub>3</sub>] (R = Bu<sup>t</sup> (**6a**), Me<sub>3</sub>Si (**6b**)) were found to react with 1 equiv of HCl to form the unstable purple complexes ( $\text{RCH}_2$ )<sub>3</sub>Ta(Cl)[Si(SiMe<sub>3</sub>)<sub>3</sub>] (R = Bu<sup>t</sup> (**14a**), Me<sub>3</sub>Si (**14b**)). In the reaction of ( $\text{Me}_3\text{SiCH}_2$ )<sub>3</sub>TaCl<sub>2</sub> with LiSi(SiMe<sub>3</sub>)<sub>3</sub> to give **6b** at  $-78^\circ\text{C}$  discussed earlier, the purple alkyl chloride complex **14b** was observed. Reactions of the purple **14b** with LiSi(SiMe<sub>3</sub>)<sub>3</sub> and LiCH<sub>2</sub>SiMe<sub>3</sub> form ( $\text{Me}_3\text{SiCH}_2$ )<sub>2</sub>-Ta(=CHSiMe<sub>3</sub>)[Si(SiMe<sub>3</sub>)<sub>3</sub>] (**6b**) and ( $\text{Me}_3\text{SiCH}_2$ )<sub>3</sub>Ta=CHSiMe<sub>3</sub> (**12b**), respectively.<sup>12</sup> Decomposition of the deep purple complex via preferential silane elimination gives the unstable bis(alkylidene) complex ( $\text{Me}_3\text{SiCH}_2$ )<sub>4</sub>(Cl)<sub>2</sub>Ta<sub>2</sub>(=CHSiMe<sub>3</sub>)<sub>2</sub> (**9a**). Kinetic and mechanistic studies of these reactions will be presented in the next section.

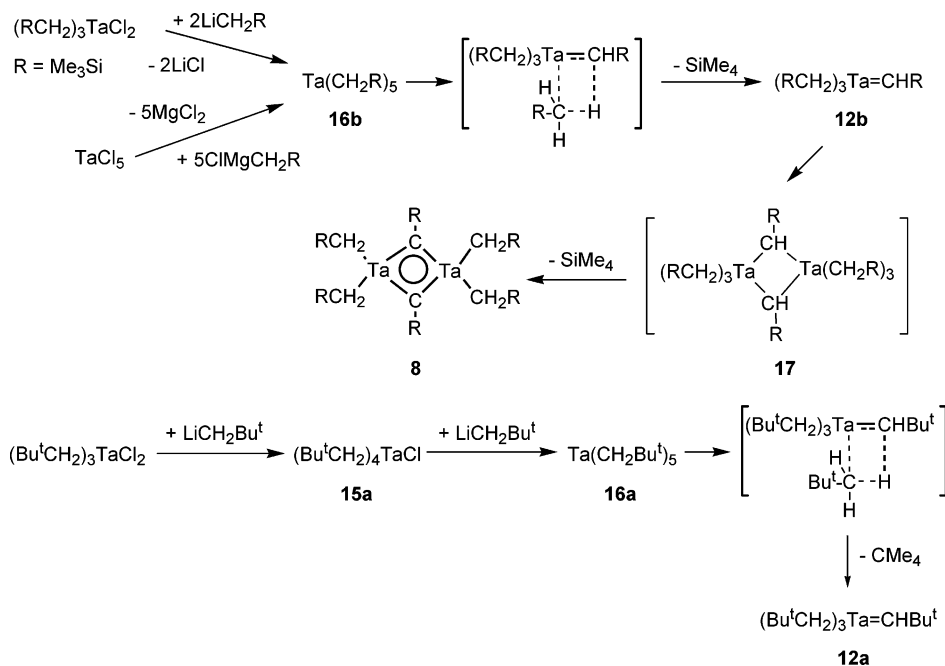
**3. Kinetic and Mechanistic Studies of the Formation of ( $\text{RCH}_2$ )<sub>3</sub>Ta=CHR (R = Bu<sup>t</sup> (**12a**), Me<sub>3</sub>Si (**12b**))<sup>19</sup> and ( $\text{Me}_3\text{SiCH}_2$ )<sub>2</sub>Ta(=CHSiMe<sub>3</sub>)[Si(SiMe<sub>3</sub>)<sub>3</sub>] (**6b**):<sup>12</sup> Comparison of Alkyl Alkylidenes and Silyl Alkylidenes.** Alkyl alkylidene complexes ( $\text{RCH}_2$ )<sub>3</sub>Ta=CHR (R = Bu<sup>t</sup> (**12a**), Me<sub>3</sub>Si (**12b**)) and their silyl analogues, the silyl alkylidene complexes ( $\text{Me}_3\text{SiCH}_2$ )<sub>2</sub>-Ta(=CHSiMe<sub>3</sub>)[Si(SiMe<sub>3</sub>)<sub>3</sub>] (**6b**), make an ideal case to compare the reactivities of alkyl and silyl ligands and the formation of alkyl and silyl alkylidene complexes.

Routes 1 and 2 in Scheme 5 have been among the possible pathways considered in the formation of the archetypical alkyl alkylidene complexes ( $\text{RCH}_2$ )<sub>3</sub>Ta=CHR (**12a,b**) from ( $\text{RCH}_2$ )<sub>3</sub>TaCl<sub>2</sub>.<sup>21</sup> In the first step, one chloride ligand in ( $\text{RCH}_2$ )<sub>3</sub>TaCl<sub>2</sub> is replaced to give the tetraalkyl chloro complexes ( $\text{RCH}_2$ )<sub>4</sub>TaCl (**15a,b**). In route 1, the remaining chloride ligand in **15a,b** is

(19) (a) Li, L.-T.; Hung, M.-L.; Xue, Z.-L. *J. Am. Chem. Soc.* **1995**, *117*, 12746. See also ab initio quantum-chemical studies of the decompositions of peralkyl complexes M(CH<sub>2</sub>Bu<sup>t</sup>)<sub>4</sub> (Ti, Zr, Hf) and MMe<sub>5</sub> (M = Nb, Ta). (b) Wu, Y.-D.; Peng, Z.-H.; Xue, Z.-L. *J. Am. Chem. Soc.* **1996**, *118*, 9772. (c) Wu, Y.-D.; Peng, Z.-H.; Chan, K. W. K.; Liu, X.-Z.; Tuinman, A. A.; Xue, Z.-L. *Organometallics* **1999**, *18*, 2081. (d) Wu, Y.-D.; Chan, K. W. K.; Xue, Z.-L. *J. Am. Chem. Soc.* **1995**, *117*, 9259.

(20) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177.

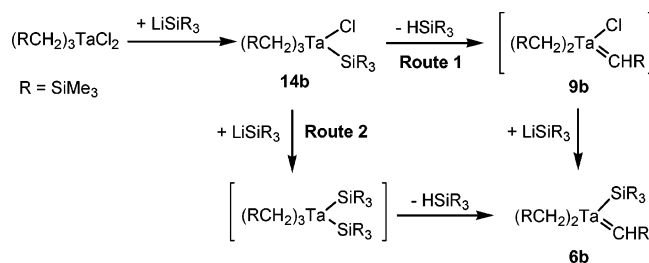
(21) See, e.g.: Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; Wiley: New York, 2001; pp 301–302.

**Scheme 6. Mechanistic Pathways in the Alkyl → Alkylidene → Alkylidyne Conversions**

replaced to give the pentaalkyl complexes **16a,b**, followed by  $\alpha$ -H abstraction to give the alkylidene ligands in **12a,b**. In other words, the formation of the alkylidene ligands is preceded by the substitution of chlorides in **15a,b**. In route 2,  $(\text{RCH}_2)_4\text{TaCl}$  (**15a,b**) undergoes  $\alpha$ -H abstraction reactions to give the alkylidene bonds in **9b,c** prior to the substitution of the chloride ligands to yield **12a,b**.<sup>19</sup>

We started our studies of the mechanistic pathways in the formation of alkylidene complexes when we were confirming the formation of a small amount of  $(\text{Me}_3\text{SiCH}_2)_4\text{Ta}_2(\mu\text{-CSiMe}_3)_2$  (**8**) as a byproduct in the preparation of  $(\text{Me}_3\text{SiCH}_2)_2\text{Ta}(\text{=CHSiMe}_3)[\text{Si}(\text{SiMe}_3)_3]$  (**6b**) from the reaction of  $(\text{Me}_3\text{SiCH}_2)_3\text{TaCl}_2$  with  $\text{LiSi}(\text{SiMe}_3)_3$ . **8** was prepared earlier from  $\text{TaCl}_5$  and  $\text{LiCH}_2\text{SiMe}_3$ .<sup>16</sup> In the preparation of this bis(alkylidyne) complex, we noticed two peaks in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the reaction mixture, which disappeared with time. Further studies confirmed that these peaks were those of  $\text{Ta}(\text{CH}_2\text{SiMe}_3)_5$  (**16b**), an unstable pentaalkyl intermediate.<sup>19</sup> **16b** converts first to the alkyl alkylidene complex  $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}=\text{CHSiMe}_3$  (**12b**). This  $\alpha$ -H abstraction reaction follows first-order kinetics, with rate constants ranging from  $[1.028(0.008)] \times 10^{-4} \text{ s}^{-1}$  at 301(1) K to  $[1.83(0.02)] \times 10^{-3} \text{ s}^{-1}$  at 326(1) K. The activation parameters thus derived for this conversion are  $\Delta H^\ddagger = 21.6(1.4) \text{ kcal/mol}$  and  $\Delta S^\ddagger = -5(5) \text{ eu}$ .

$(\text{Me}_3\text{SiCH}_2)_3\text{Ta}=\text{CHSiMe}_3$  (**12b**) is unstable and decomposes to the bridging alkyldiyne complex  $(\text{Me}_3\text{SiCH}_2)_4\text{Ta}_2(\mu\text{-CSiMe}_3)_2$  (**8**) through the abstraction of the  $\alpha$ -alkylidene hydrogen atom to give  $\text{SiMe}_4$ . This conversion follows second-order kinetics with rate constants ranging from  $[9.75(0.11)] \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$  at 313.2(0.1) K to  $[6.02(0.6)] \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$  at 373.2(0.1) K. The activation parameters for this second-order reaction are  $\Delta H^\ddagger = 6.2(0.3) \text{ kcal/mol}$  and  $\Delta S^\ddagger = -61.5(0.8) \text{ eu}$ . Small activation enthalpy and large, negative activation entropy values have been observed in associative reactions that follow second-order kinetics. These results are consistent with the dimerization of **12b** to give  $[(\text{Me}_3\text{-}$

**Scheme 7. Possible Pathways in the Formation of Silyl Alkylidene Complexes**

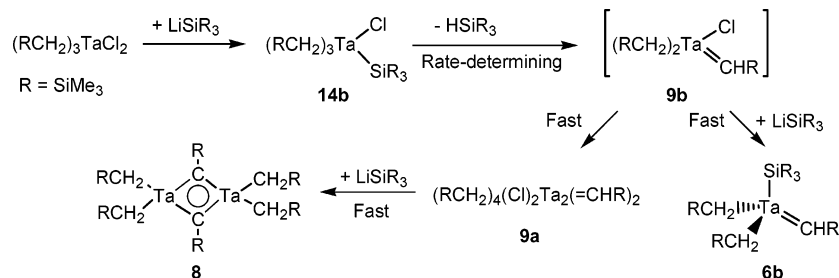
$\text{SiCH}_2)_6\text{Ta}_2(\mu\text{-CHSiMe}_3)_2$  (**17**) in the transition state, followed by fast elimination of  $\text{SiMe}_4$ . The alkyl  $\text{Ta}(\text{CH}_2\text{SiMe}_3)_5$  (**16b**) → alkylidene  $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}=\text{CHSiMe}_3$  (**12b**) → alkyldiyne  $(\text{Me}_3\text{SiCH}_2)_4\text{Ta}_2(\mu\text{-CSiMe}_3)_2$  (**8**) conversions are summarized in Scheme 6.

We subsequently investigated the formation of the neopentylidene species  $(\text{Bu}^t\text{CH}_2)_3\text{Ta}=\text{CHBu}^t$  (**12a**) and whether  $\text{Ta}(\text{CH}_2\text{Bu}^t)_5$  (**16a**) is the intermediate to **12a**. We thought that **16a**, which was more crowded than  $\text{Ta}(\text{CH}_2\text{SiMe}_3)_5$  (**16b**), would be perhaps too unstable to be observed at room temperature. We thus decided to prepare deuterium-labeled  $\text{Ta}(\text{CD}_2\text{Bu}^t)_5$  (**16a-d**), and the kinetic isotope effect in  $\alpha$ -H/D abstraction reactions was expected to make the half-life of **16a-d** longer than that of  $\text{Ta}(\text{CH}_2\text{Bu}^t)_5$  (**16a**). The reaction of  $\text{LiCD}_2\text{Bu}^t$  with  $(\text{Bu}^t\text{CD}_2)_2\text{TaCl}_3$ , which was prepared from  $\text{TaCl}_5$  and  $\text{Zn}(\text{CD}_2\text{Bu}^t)_2$ , gave  $\text{Ta}(\text{CD}_2\text{Bu}^t)_5$  (**16a-d**). **16a-d** was identified in the  $^1\text{H}$  NMR spectrum of the reaction mixture at 23 °C, which decomposed to  $(\text{Bu}^t\text{CD}_2)_3\text{Ta}=\text{CHBu}^t$  (**12a-d**).<sup>22</sup>

We then investigated the reaction of  $(\text{Bu}^t\text{CH}_2)_4\text{TaCl}$  with  $\text{LiCH}_2\text{Bu}^t$  at  $-40$  °C, as the low temperature was expected to slow the  $\alpha$ -H abstraction reaction in  $\text{Ta}(\text{CH}_2\text{Bu}^t)_5$  (**16a**) to give  $(\text{Bu}^t\text{CH}_2)_3\text{Ta}=\text{CHBu}^t$  (**12a**). **16a** was observed in the reaction mixture, and it decomposed to **12a**.<sup>19</sup> The mechanistic pathways in the formation of

(22) Xue, Z.-L. Unpublished results.

## Scheme 8. Mechanistic Pathway in the Formation of Silyl Alkylidene Complex 6b



the Schrock-type alkylidene complexes  $(\text{RCH}_2)_3\text{Ta}=\text{CHR}$  (**12a,b**) are summarized in Scheme 6.

In the formation of silyl analogues of alkyl alkylidene complexes  $(\text{RCH}_2)_2\text{Ta}(=\text{CHR})[\text{Si}(\text{SiMe}_3)_3]$  (**6a,b**), the deep purple intermediates  $(\text{RCH}_2)_3\text{Ta}(\text{Cl})[\text{Si}(\text{SiMe}_3)_3]$  (**14a,b**) were observed. **14b** was further studied to probe the mechanistic pathway to the silyl alkylidene complex **6b**. We considered the two possible pathways shown in Scheme 7.

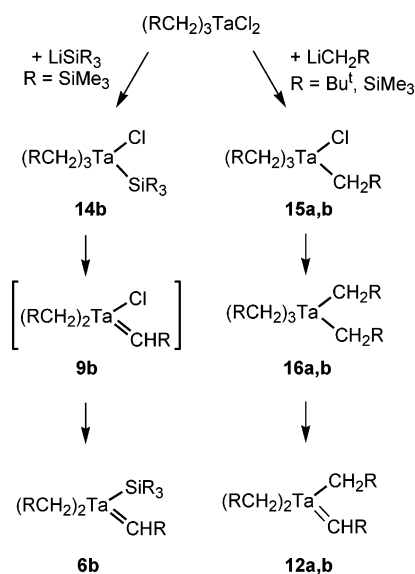
The unstable purple intermediate  $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}(\text{Cl})[\text{Si}(\text{SiMe}_3)_3]$  (**14b**) could also be prepared from the addition of HCl to  $(\text{Me}_3\text{SiCH}_2)_2\text{Ta}(=\text{CHSiMe}_3)[\text{Si}(\text{SiMe}_3)_3]$  (**6b**).<sup>12</sup> It decomposes above  $-90^\circ\text{C}$  to give  $\text{HSi}(\text{SiMe}_3)_3$  and  $(\text{Me}_3\text{SiCH}_2)_4(\text{Cl})_2\text{Ta}_2(=\text{CHSiMe}_3)_2$  (**9a**), the dimer of the chloro alkylidene “ $(\text{Me}_3\text{SiCH}_2)_2\text{Ta}(=\text{CHSiMe}_3)\text{Cl}$ ” (**9b**). Thermal decomposition of **14b** was monitored by variable-temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR and was found to follow first-order kinetics with rate constants ranging from  $[1.92(0.05)] \times 10^{-5} \text{ s}^{-1}$  at 227(1) K to  $[1.20(0.04)] \times 10^{-3} \text{ s}^{-1}$  at 255(1) K. The activation parameters for this  $\alpha$ -H abstraction by the silyl ligand in  $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}(\text{Cl})[\text{Si}(\text{SiMe}_3)_3]$  (**14b**) are  $\Delta H^\ddagger = 17.2(1.0) \text{ kcal/mol}$  and  $\Delta S^\ddagger = -4(4) \text{ eu}$ .

The reaction of  $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}(\text{Cl})[\text{Si}(\text{SiMe}_3)_3]$  (**14b**) with  $\text{LiSi}(\text{SiMe}_3)_3$  gives  $(\text{Me}_3\text{SiCH}_2)_2\text{Ta}(=\text{CHSiMe}_3)[\text{Si}(\text{SiMe}_3)_3]$  (**6b**) and  $\text{HSi}(\text{SiMe}_3)_3$ . The rates of this reaction were found to be the same as those of the decomposition of **14b** to  $(\text{Me}_3\text{SiCH}_2)_4(\text{Cl})_2\text{Ta}_2(=\text{CHSiMe}_3)_2$  (**9a**).

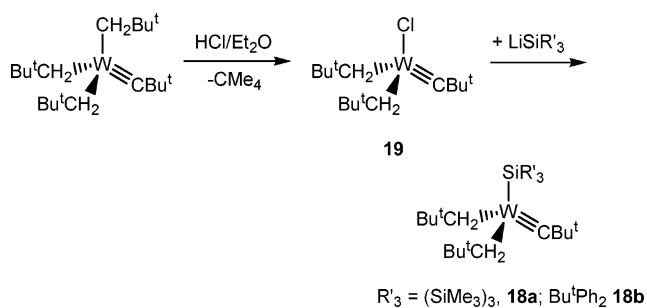
These observations suggest that the  $\alpha$ -H abstraction by the silyl ligand in  $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}(\text{Cl})[\text{Si}(\text{SiMe}_3)_3]$  (**14b**) to give the chloro alkylidene species “ $(\text{Me}_3\text{SiCH}_2)_2\text{Ta}(=\text{CHSiMe}_3)\text{Cl}$ ” (**9b**) is the rate-determining step. **9b** then either reacts with  $\text{LiSi}(\text{SiMe}_3)_3$  to yield  $(\text{Me}_3\text{SiCH}_2)_2\text{Ta}(=\text{CHSiMe}_3)[\text{Si}(\text{SiMe}_3)_3]$  (**6b**) or dimerizes to give  $(\text{Me}_3\text{SiCH}_2)_4(\text{Cl})_2\text{Ta}_2(=\text{CHSiMe}_3)_2$  (**9a**), which we had prepared independently from the reaction of  $(\text{Me}_3\text{SiCH}_2)_4\text{Ta}_2(\mu\text{-CSiMe}_3)_2$  (**8**) with HCl (Scheme 4). **9a** further reacts with  $\text{LiSi}(\text{SiMe}_3)_3$  to give **8**. The formations of both **6b** and **8** share the same rate-determining step, followed by fast reactions with  $\text{LiSi}(\text{SiMe}_3)_3$  to give these two complexes, which were observed as the major (**6b**) and minor (**8**) products, respectively, in the reaction of  $(\text{Me}_3\text{SiCH}_2)_3\text{TaCl}_2$  and 2 equiv of  $\text{LiSi}(\text{SiMe}_3)_3$ . These findings are summarized in Scheme 8.

It is interesting to note that the alkyl alkylidenes  $(\text{RCH}_2)_3\text{Ta}=\text{CHR}$  (**12a,b**, Scheme 6) and the silyl alkylidene  $(\text{Me}_3\text{SiCH}_2)_2\text{Ta}(=\text{CHSiMe}_3)[\text{Si}(\text{SiMe}_3)_3]$  (**6b**, Scheme 8) adopt different pathways in their formation.  $(\text{RCH}_2)_4\text{TaCl}$  (**15a,b**) undergo chloride substitution first to give the pentaalkyls  $\text{Ta}(\text{CH}_2\text{R})_5$  (**16a,b**), followed by  $\alpha$ -H abstraction to give the alkylidene ligands in **12a,b** (Scheme 9). In contrast,  $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}(\text{Cl})[\text{Si}(\text{SiMe}_3)_3]$  (**14b**) undergoes  $\alpha$ -H abstraction to give the alkylidene

## Scheme 9



## Scheme 10

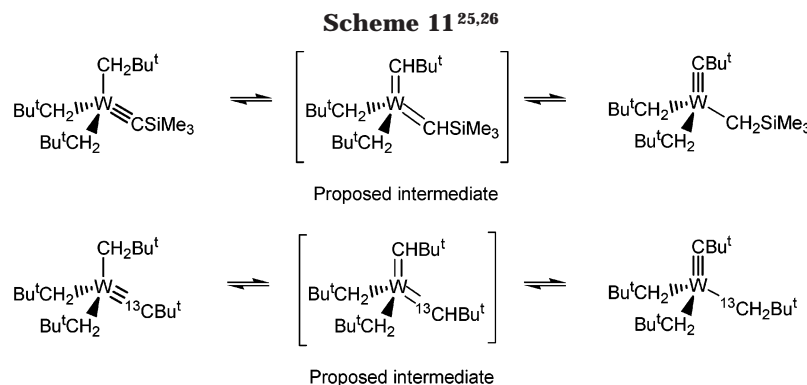


ligand in “ $(\text{Me}_3\text{SiCH}_2)_2\text{Ta}(\text{Cl})(=\text{CHSiMe}_3)$ ” (**9b**) prior to the substitution of chloride ligand by  $\text{Si}(\text{SiMe}_3)_3^-$  in the second step to give **6b** (Scheme 9).

**4. Alkylidene Silyl Complexes  $(\text{Bu}^t\text{CH}_2)_2\text{W}(=\text{C}-\text{Bu}^t)\text{SiR}'_3$  and an Unusual Equilibrium between Alkylidene and Bis(alkylidene) Complexes.**<sup>23</sup> Alkylidene silyl complexes discussed in Section I.2 are prepared primarily through abstraction of  $\alpha$ -H atoms in alkyl ligands by silyl ligands. The alkylidene complexes  $(\text{Bu}^t\text{CH}_2)_2\text{W}(=\text{CBu}^t)\text{SiR}'_3$  ( $\text{R}'_3 = (\text{SiMe}_3)_3$ , **18a**;  $\text{Bu}^t\text{Ph}_2$ , **18b**) are prepared using  $(\text{Bu}^t\text{CH}_2)_3\text{W}=\text{CBu}^t$  as a starting material, and the  $\text{W}=\text{CR}$  moiety is retained during the synthesis.<sup>6,23</sup> Addition of a HCl/Et<sub>2</sub>O solution to  $(\text{Bu}^t\text{CH}_2)_3\text{W}=\text{CBu}^t$  gives  $(\text{Bu}^t\text{CH}_2)_2\text{W}(=\text{CBu}^t)\text{Cl}$  (**19**), and this chloro alkylidene complex is subsequently used in situ to yield the silyl alkylidene complexes **18a,b** through its reactions with  $\text{LiSiR}'_3$  (Scheme 10).

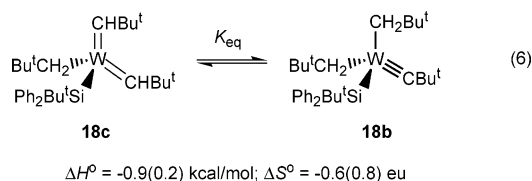
Both **18a** and **18b** were characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR and elemental analysis. Attempts to obtain





the X-ray structures of these two alkyldiene silyl complexes were not successful. Both structures are severely disordered.<sup>24</sup>

An unusual equilibrium was observed between the alkyldiene  $(\text{Bu}^t\text{CH}_2)_2\text{W}(\equiv\text{CBu}^t)(\text{SiBu}^t\text{Ph}_2)$  (**18b**) and its bis(alkylidene) tautomer  $(\text{Bu}^t\text{CH}_2)\text{W}(\equiv\text{CHBu}^t)_2(\text{SiBu}^t\text{Ph}_2)$  (**18c**, eq 6).<sup>23</sup> Exchange of two  $\alpha$ -hydrogen atoms



has been observed when  $(\text{Bu}^t\text{CH}_2)_3\text{W}\equiv\text{CSiMe}_3$  is converted to  $(\text{Bu}^t\text{CH}_2)_2\text{W}(\text{CH}_2\text{SiMe}_3)(\equiv\text{CBu}^t)$  with heating.<sup>25</sup> Deuterium-labeling and kinetic studies indicate that such an exchange is stepwise, and the two migrating  $\alpha$ -hydrogen atoms are from the same  $\text{Bu}^t\text{CH}_2$  ligand. The bis(alkylidene) intermediate “ $(\text{Bu}^t\text{CH}_2)_2\text{W}(\equiv\text{CHSiMe}_3)(\equiv\text{CHBu}^t)$ ” was thus proposed as an intermediate in the transfer (Scheme 11). It was, however, not observed in the exchange, presumably because its energy is much higher than those of the two alkyldiene complexes. A similar exchange was observed in  $(\text{Bu}^t\text{CH}_2)_3\text{W}\equiv^{13}\text{CBu}^t$ .<sup>26</sup> The  $^{13}\text{C}$ -labeled alkyldiene carbon atom was found to quickly scramble among the four  $\alpha$ -carbon atoms with a nearly statistical distribution of 25%  $^{13}\text{C}$  labeling on each  $\alpha$ -carbon atom. This exchange is also believed to involve a bis(alkylidene) intermediate (Scheme 11). In the  $d^2$  bis(alkylidene) complex  $\text{Os}(\equiv\text{CHBu}^t)_2(\text{CD}_2\text{Bu}^t)_2$ , deuterium-scrambled products were observed in the NMR spectra, and the exchange is believed to involve an alkyldiene intermediate.<sup>27</sup> However, direct observation of such an exchange between bis(alkylidene) and alkyldiene complexes had not been reported.

The equilibrium between the silyl alkyldiene complex  $(\text{Bu}^t\text{CH}_2)_2\text{W}(\equiv\text{CBu}^t)(\text{SiBu}^t\text{Ph}_2)$  (**18b**) and its silyl bis(alkylidene) tautomer  $(\text{Bu}^t\text{CH}_2)\text{W}(\equiv\text{CHBu}^t)_2(\text{SiBu}^t\text{Ph}_2)$  (**18c**) (eq 6) is, to our knowledge, the first direct observation of such an exchange. Thermodynamic stud-

ies of the equilibrium gave the equilibrium constants  $K_{\text{eq}} = [\mathbf{18b}]/[\mathbf{18c}]$ , which range from 4.590(0.006) at 237(1) K to 3.34(0.05) at 287(1) K, indicating that the alkyldiene tautomer is favored and that increasing the temperature shifts the equilibrium toward bis(alkylidene) tautomer **18c**. The enthalpy and entropy of the exchange  $\mathbf{18c} \rightleftharpoons \mathbf{18b}$  (eq 6) that are obtained from the equilibrium constants  $K_{\text{eq}}$  indicate that the conversion of the bis(alkylidene) to the alkyldiene is slightly exothermic, and it outweighs the entropy change ( $\Delta S^\circ = -0.6(0.8) \text{ eu}$ ) to give  $\Delta G^\circ = -0.7(0.4) \text{ kcal/mol}$  at 287(1) K in favor of **18b**.

It is interesting to note that the silyl alkyldiene complex **18b** is thermodynamically close in energy to its silyl bis(alkylidene) isomer **18c**. In the  $\alpha$ -H exchange in the *alkyl* alkyldiene  $(\text{Bu}^t\text{CH}_2)_3\text{W}\equiv\text{CSiMe}_3 \rightleftharpoons (\text{Bu}^t\text{CH}_2)_2\text{W}(\text{CH}_2\text{SiMe}_3)(\equiv\text{CBu}^t)$  (Scheme 11), the proposed *alkyl* bis(alkylidene) intermediate “ $(\text{Bu}^t\text{CH}_2)_2\text{W}(\equiv\text{CHSiMe}_3)(\equiv\text{CHBu}^t)$ ” is so much higher in energy than the ground-state alkyldiene structure that this intermediate is not observed.<sup>25–27</sup>

Professor Zhen-Yang Lin of the Hong Kong University of Science and Technology and co-workers have conducted density functional molecular orbital calculations at the B3LYP level of the relative stabilities of the tautomeric pairs of transition-metal alkyldiene  $(\text{CH}_3)_2\text{M}(\equiv\text{CH})(\text{X})$  and bis(alkylidene)  $(\text{CH}_3)_2\text{M}(\equiv\text{CH}_2)_2(\text{X})$  complexes ( $\text{M} = \text{W}, \text{Mo}, \text{Os}, \text{Ru}; \text{X} = \text{Cl}, \text{CH}_3, \text{CF}_3, \text{SiH}_3, \text{SiF}_3$ ).<sup>28</sup> The calculations indicate that the relative stabilities of the bis(alkylidene) tautomers increase with the increasing  $\pi$ -accepting ability of X for the  $d^0$  W and Mo complexes.<sup>25,26</sup> When X is a silyl ligand, it is found that the W or Mo tautomeric pairs have similar stabilities. These results have been explained in terms of  $\pi$  interaction between the ligand X and the electron density in the metal–alkylidene/alkylidene bonds. For the  $d^2$  Os and Ru complexes, the bis(alkylidene) tautomers are more stable no matter what X is.<sup>27</sup> The stabilities of the bis(alkylidene) tautomers for these  $d^2$  metal complexes have been related to the bonding characteristics of the orbital that accommodates the two metal d electrons.

**5. Reaction of  $\text{O}_2$  with the Tautomers  $(\text{Bu}^t\text{CH}_2)\text{W}(\equiv\text{CHBu}^t)_2(\text{SiBu}^t\text{Ph}_2)$  (**18c**)  $\rightleftharpoons$   $(\text{Bu}^t\text{CH}_2)_2\text{W}(\equiv\text{CBu}^t)(\text{SiBu}^t\text{Ph}_2)$  (**18b**).**<sup>23</sup> Reactions of oxygen with metal complexes play important roles in biological and catalytic processes.<sup>29</sup> These reactions usually involve  $d^0$  metals, and oxidations of metals are often the key steps

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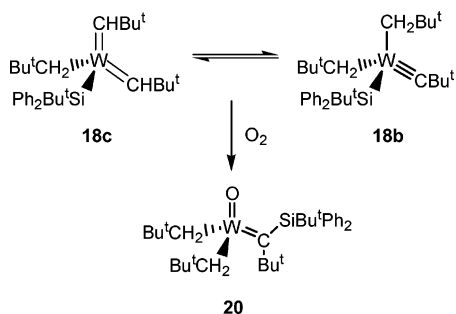
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Scheme 12



in the reaction. There have been few studies of reactions of  $\text{O}_2$  with  $d^0$  metal complexes.<sup>30</sup> Recently, reactions of  $\text{O}_2$  with  $d^0$  metal complexes have been shown to yield metal oxide thin films with high dielectric constants as microelectronic gate materials.<sup>31</sup> The mechanistic pathways in these reactions are, however, not known.

We are particularly interested in the reaction of  $\text{O}_2$  with  $d^0$  silyl complexes, where both the metal and silicon are oxophilic. An equilibrium mixture of  $(\text{Bu}^t\text{CH}_2)_2\text{W}(=\text{CHBu}^t)_2(\text{SiBu}^t\text{Ph}_2)$  (**18c**)  $\rightleftharpoons$   $(\text{Bu}^t\text{CH}_2)_2\text{W}(=\text{CBu}^t)(\text{SiBu}^t\text{Ph}_2)$  (**18b**) was found to react with  $\text{O}_2$  to give  $(\text{Bu}^t\text{CH}_2)_2\text{W}(=\text{O})[\text{C}(\text{SiBu}^t\text{Ph}_2)]$  (**20**) (Scheme 12).<sup>23</sup>

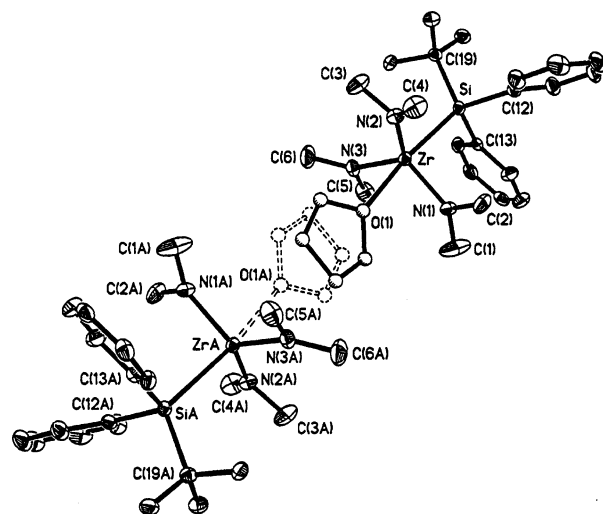
In this reaction with  $\text{O}_2$ , the silyl ligand in **18b,c** migrates to the  $\alpha$ -C of the alkylidyne ligand to give a substituted alkylidene complex (Scheme 12). To our knowledge, such a silyl migration reaction has not been reported. The product **20** is thermally stable at room temperature and undergoes further reaction with  $\text{O}_2$  to give unknown products. The siloxy complex  $(\text{Bu}^t\text{CH}_2)_2\text{W}(=\text{CBu}^t)(\text{OSiBu}^t\text{Ph}_2)$  was prepared from  $(\text{Bu}^t\text{CH}_2)_2\text{W}(=\text{CBu}^t)\text{Cl}$  and  $\text{LiOSiBu}^t\text{Ph}_2$ .<sup>24</sup> It is stable and does not convert to  $(\text{Bu}^t\text{CH}_2)_2\text{W}(=\text{O})[\text{C}(\text{SiBu}^t\text{Ph}_2)]$  (**20**).  $(\text{Bu}^t\text{CH}_2)_2\text{W}(=\text{CBu}^t)(\text{OSiBu}^t\text{Ph}_2)$  as an intermediate to **20** could thus be ruled out. The mechanism of this reaction is not clear.

## II. Cp-Free Amide and Imide Silyl Complexes

Our focus expanded to include new  $d^0$  early-transition-metal amide and imide silyl complexes.<sup>32–34</sup> Few

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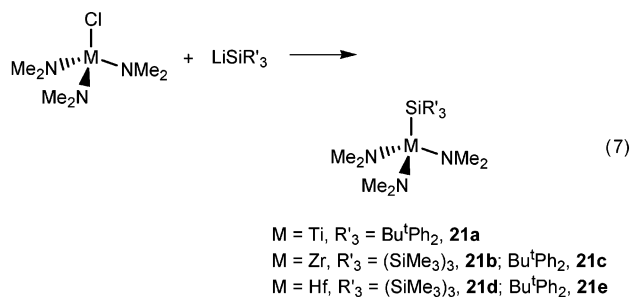
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**Figure 2.** Molecular drawing of **21c**·0.5THF from X-ray single-crystal diffraction.<sup>32</sup>

$d^0$  Cp-free amide/imide silyl complexes have been reported. The metal amide and imide silyl complexes have been studied to compare them with alkyl and alkylidene silyl complexes. Their reactivities toward  $\text{O}_2$  and isocyanides have also been investigated.

**1. Group 4 Amide Silyl and Disilyl Complexes.**<sup>32,34</sup>  $(\text{R}_2\text{N})_3\text{Ti}-\text{Si}(\text{SiMe}_3)_3$  complexes ( $\text{R} = \text{Me}, \text{Et}$ ) have been reported by Ustinov, Ovchinnikov, and co-workers.<sup>3k</sup> Reactions of  $(\text{Me}_2\text{N})_3\text{M}-\text{Cl}$ <sup>35</sup> with  $\text{LiSiR}'_3$  yield  $(\text{Me}_2\text{N})_3\text{M}-\text{SiR}'_3$  ( $\text{M} = \text{Ti}, \text{R}'_3 = \text{Bu}^t\text{Ph}_2$  (**21a**);  $\text{M} = \text{Zr}, \text{R}'_3 = (\text{SiMe}_3)_3$  (**21b**),  $\text{Bu}^t\text{Ph}_2$  (**21c**);  $\text{M} = \text{Hf}, \text{R}'_3 = (\text{SiMe}_3)_3$  (**21d**),  $\text{Bu}^t\text{Ph}_2$  (**21e**)) in our preparation of these amide silyl complexes (eq 7).<sup>32</sup> **21c,e**, which are less bulky than



**21b,d**, exist as the THF adducts  $(\text{Me}_2\text{N})_3\text{Zr}-\text{SiBu}^t\text{Ph}_2 \cdot 0.5\text{THF}$  (**21c**·0.5THF) and  $(\text{Me}_2\text{N})_3\text{Hf}-\text{SiBu}^t\text{Ph}_2 \cdot n\text{THF}$  ( $n = 0.5, 1$ , **21e**· $n\text{THF}$ ). The X-ray crystal structure of **21c**·0.5THF shows that two back-to-back molecules share one THF molecule which coordinates to the Zr atoms (Figure 2). The THF ligand is in a position trans to the silyl ligand in this distorted trigonal-bipyramidal structure. The structure of **21e**·THF is similar to that of **21c**·0.5THF, except that there is one THF ligand per complex.

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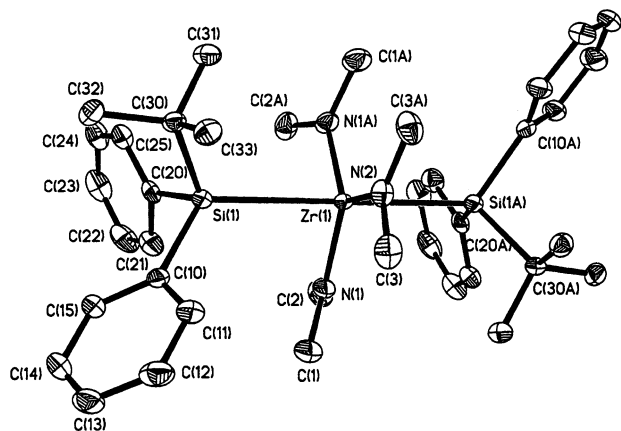
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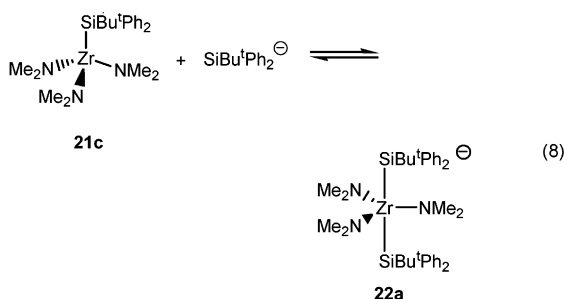
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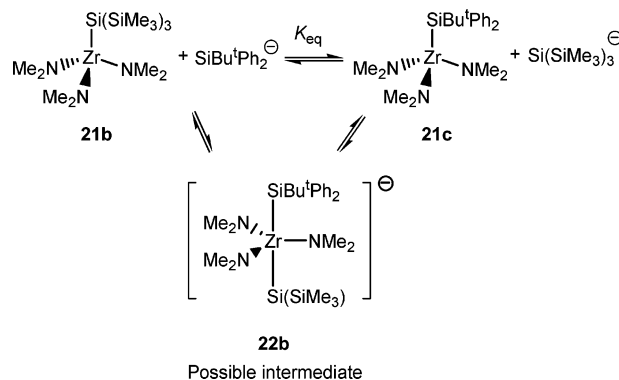


**Figure 3.** Molecular drawing of **22a** from X-ray single-crystal diffraction.<sup>34</sup>

The addition of  $(\text{Me}_2\text{N})_3\text{Zr}-\text{SiBu}^t\text{Ph}_2$  (**21c**) to a solution of  $\text{LiSiBu}^t\text{Ph}_2$  in a small amount of toluene at room temperature gives the anionic bis(silyl) complex  $(\text{Me}_2\text{N})_3\text{Zr}(\text{SiBu}^t\text{Ph}_2)_2^-$  (**22a**; Figure 3) as a crystalline solid.<sup>34</sup> **22a** is, to our knowledge, the first reported Cp-free  $d^0$  bis(silyl) complex. It is involved in an exchange with **21c** and  $\text{SiBu}^t\text{Ph}_2^-$  (eq 8). The dynamic NMR of this



**Scheme 13**



**22b**

Possible intermediate

The alkoxy silyl complex  $(\text{Me}_3\text{SiO})_2\text{Zr}(\text{SiBu}^t\text{Ph}_2)\text{Cl}\cdot 2\text{THF}$  was also prepared from the reaction of  $\text{ZrCl}_4$  with 2 equiv of  $\text{NaOSiMe}_3$  and then 1 equiv of  $\text{LiSiBu}^t\text{Ph}_2$ .<sup>38</sup> The Zr–Si bond distance of 2.848(3) Å in this silyl complex was then the longest reported Zr–Si bond.

In the multiinsertion reactions of the isocyanide  $\text{ArNC}$  ( $\text{Ar} = 2,6\text{-dimethylphenyl}$ ) with alkyl silyl complexes  $(\text{RCH}_2)_3\text{Zr}-\text{Si}(\text{SiMe}_3)_3$  ( $\text{R} = \text{Me}_3\text{C}$  (**1c**),  $\text{Me}_3\text{Si}$  (**1d**)), the first  $\text{ArNC}$  inserts into the Zr–Si bonds in **1c,d**, as discussed in Section I.1. A subsequent second and third  $\text{ArNC}$  insert into the Zr–C bonds.

The isocyanide  $\text{ArNC}$  reacts with the amide silyl complexes  $(\text{Me}_2\text{N})_3\text{Zr}-\text{SiBu}^t\text{Ph}_2\cdot 0.5\text{THF}$  (**21c}\cdot 0.5\text{THF}) and  $(\text{Me}_2\text{N})_3\text{Zr}-\text{Si}(\text{SiMe}_3)_3$  (**21b**) as well, leading to multiinsertion of  $\text{ArNC}$  into Zr–N and Zr–Si bonds.<sup>39</sup> The reaction of **21c}\cdot 0.5\text{THF} with  $\text{ArNC}$  was fast, and only the tetrainsertion product  $\text{Zr}[\eta^2\text{-C}(\text{NMe}_2)=\text{NAr}]_3\text{-}[\eta^2\text{-C}(\text{SiBu}^t\text{Ph}_2)=\text{NAr}]$  (**23**) was isolated. In the reaction of  $\text{ArNC}$  with  $(\text{Me}_2\text{N})_3\text{ZrSi}(\text{SiMe}_3)_3$  (**21b**), the first and second equivalents of isocyanide insert into the Zr–N bonds to give **24** and **25**, respectively. The third equivalent of isocyanide inserts into the Zr–Si bond to yield **26**. **21b** reacts with 4 equiv of isocyanide at room temperature to give the tetrainsertion product **27**. These insertion reactions are summarized in Scheme 14.****

The reactions in Scheme 14 are, to our knowledge, the first isocyanide insertions involving complexes containing both amido and silyl ligands.<sup>39</sup> As indicated earlier, the first  $\text{ArNC}$  inserts into a Zr–N bond in the amide silyl complex  $(\text{Me}_2\text{N})_3\text{Zr}-\text{Si}(\text{SiMe}_3)_3$  (**21b**). In contrast, the first  $\text{ArNC}$  inserts exclusively into the Zr–Si bond in the alkyl silyl complexes  $(\text{RCH}_2)_3\text{Zr}-\text{Si}(\text{SiMe}_3)_3$  ( $\text{R} = \text{Me}_3\text{C}$  (**1c**),  $\text{Me}_3\text{Si}$  (**1d**); section I.1).<sup>8</sup> Space-filling drawings of **21b** suggest that the largest open area of the Zr atom in **21b** for the  $\text{ArNC}$  attack is between the amide ligands and is trans to the silyl ligand. The addition of the first  $\text{ArNC}$  to **21b** may thus take place exclusively trans to the silyl ligand, and subsequently the coordinated  $\text{ArNC}$  inserts into a Zr–N bond (Scheme 14). Such an attack trans to the silyl ligand may also be preferred for the second equivalent of isocyanide. However, after two insertions, the attack trans to the silyl ligand may become hindered, and the third isocyanide attack occurs cis to the silyl ligand.

exchange reaction gives the estimated free energy of activation  $\Delta G^\ddagger = 14.1(0.5)$  kcal/mol for the exchange at the coalescence temperature of 20 °C. The exchange in eq 8 is a rare example of the observation and isolation of an intermediate in the associative ligand substitution of a  $d^0$  complex. The structure of the bis(silyl) anion **22a** adopts a trigonal-bipyramidal (TBP) geometry with the silyl ligands in axial positions. The Si–Zr–Si bond angle of 177.93(5)° is close to linear. The Zr–Si bond length of 2.9331(14) Å is, to our knowledge, the longest reported Zr–Si bond.

A similar silyl exchange was also observed when  $\text{SiBu}^t\text{Ph}_2^-$  was added to  $(\text{Me}_2\text{N})_3\text{Zr}-\text{Si}(\text{SiMe}_3)_3$  (**21b**) to give **21c** and  $\text{Si}(\text{SiMe}_3)_3^-$  (Scheme 13). The  $K_{\text{eq}}$  value at 20 °C was found to be 82.83(2) in favor of **21c** and  $\text{Si}(\text{SiMe}_3)_3^-$ , and thermodynamic parameters for this exchange are  $\Delta H^\circ = -4.6(5)$  kcal/mol and  $\Delta S^\circ = -7(2)$  eu. The silyl exchange in Scheme 13 likely proceeds through an associative ligand substitution mechanism involving the five-coordinated anionic disilyl intermediate **22b**, as in the exchange in eq 8.

The reaction of  $(\text{Me}_2\text{N})_3\text{ZrCl}$  with the chelating disilyl dianion  $[\text{R}_2\text{Si}-(\text{CH}_2)_2-\text{SiR}_2]^{2-}$  ( $\text{R} = \text{SiMe}_3$ )<sup>36</sup> yields an analogue of **22a**, the disilyl anion  $\{(\text{Me}_2\text{N})_3\text{Zr}[\eta^2\text{-R}_2\text{Si}-(\text{CH}_2)_2-\text{SiR}_2]\}^-$  (**22c**), as a distorted trigonal bipyramid with the two Si atoms in equatorial positions.<sup>37</sup>

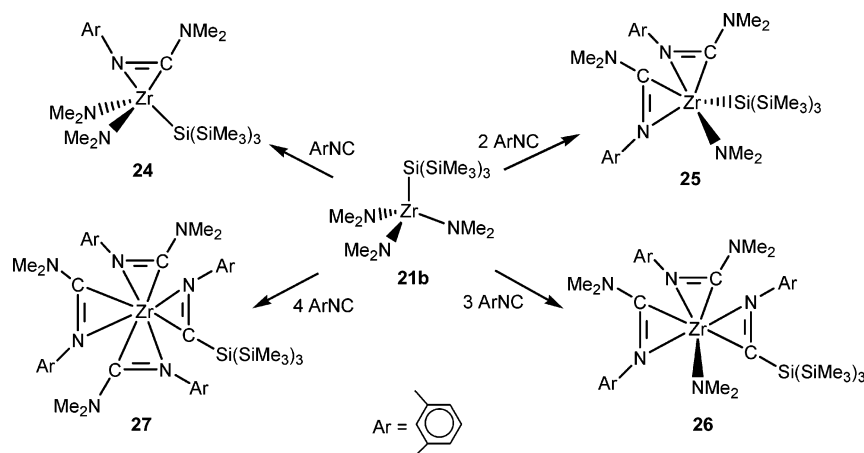
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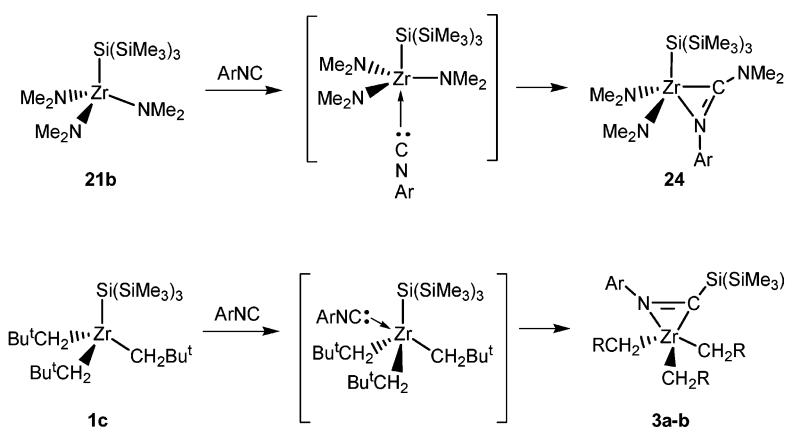
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Scheme 14



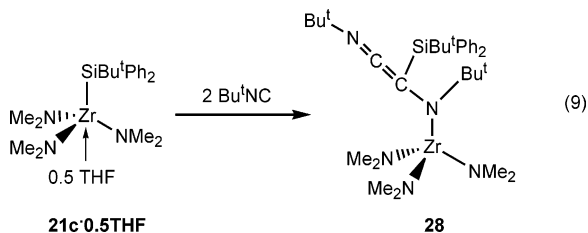
Scheme 15



Space-filling drawings of  $(\text{Me}_3\text{CCH}_2)_3\text{Zr}-\text{Si}(\text{SiMe}_3)_3$  (**1c**)<sup>39</sup> indicate that the space between the alkyl ligands is much more crowded than that in **21b**. The isocyanide addition between the alkyl and silyl ligands may thus be preferred (Scheme 15). This addition is followed by a migration of the bulky  $\text{Si}(\text{SiMe}_3)_3$  group onto the isocyanide carbon.

The reaction of  $(\text{Me}_2\text{N})_2[(\text{Me}_3\text{Si})_2\text{N}]\text{ZrSi}(\text{SiMe}_3)_3$  with  $\text{ArNC}$  was very fast at both room and low temperature. Only the diinsertion complex was isolated and characterized. The NMR data clearly indicate that the first equivalent of  $\text{ArNC}$  inserts into the  $\text{Zr}-\text{Si}$  bond and the second equivalent inserts into a  $\text{Zr}-\text{N}$  bond.

The insertion reactions of  $\text{Bu}^t\text{NC}$  with  $(\text{Me}_2\text{N})_3\text{ZrSiR}'_3$  (**21b,c**) are much slower than those with  $\text{ArNC}$ . No reaction was observed between  $(\text{Me}_2\text{N})_3\text{ZrSi}(\text{SiMe}_3)_3$  (**21b**) and  $\text{Bu}^t\text{NC}$ . Excess  $\text{Bu}^t\text{NC}$  reacts with  $(\text{Me}_2\text{N})_3\text{Zr}-\text{SiBu}^t\text{Ph}_2 \cdot 0.5\text{THF}$  (**21c**·0.5THF) to give the diisocyanide addition product (**28**; eq 9) containing a keten-

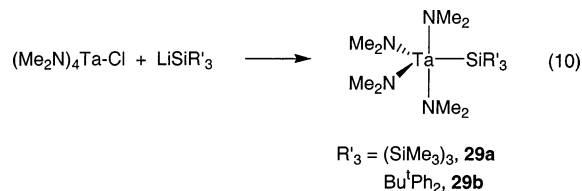


imine functionality. This diisocyanide adduct is inert to further insertion by  $\text{Bu}^t\text{NC}$ .

Although no insertion of  $\text{Bu}^t\text{NC}$  into the amide ligand was found in the reaction of **21c**·0.5THF with  $\text{Bu}^t\text{NC}$ , it was observed in the reaction of  $\text{Zr}(\text{NMe}_2)_4$  with  $\text{Bu}^t\text{NC}$ . Tetrainsertion products of both  $\text{ArNC}$  and  $\text{Bu}^t\text{NC}$  were observed in the reactions of 4 equiv of  $\text{ArNC}$  and  $\text{Bu}^t\text{NC}$  with  $\text{Zr}(\text{NMe}_2)_4$ . It takes about 1 week for the tetrainsertion reaction of  $\text{Bu}^t\text{NC}$  to go to completion, whereas the reaction of  $\text{Zr}(\text{NMe}_2)_4$  with  $\text{ArNC}$  is instantaneous.

## 2. Tantalum Amide Silyl and Disilyl Complexes.

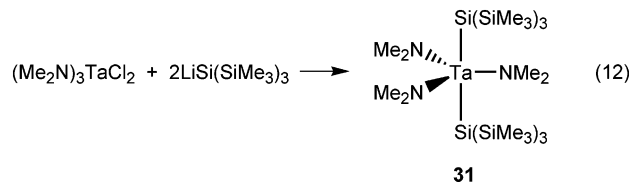
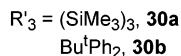
The Ta amide silyl complexes  $\text{Ta}(\text{NMe}_2)_4(\text{SiR}'_3)$  ( $\text{R}'_3 = (\text{SiMe}_3)_3$  (**29a**),  $\text{Bu}^t\text{Ph}_2$  (**29b**)) were prepared from the reactions of  $\text{Ta}(\text{NMe}_2)_4\text{Cl}$  with  $\text{LiSiR}'_3$  (eq 10). The X-ray



crystal structure of **29b** shows that the silyl ligand is in the equatorial position, as expected from the VSEPR theory.<sup>40</sup>  $\text{Ta}(\text{NMe}_2)_4[\text{Si}(\text{SiMe}_3)_3]$  (**29a**) was found to be too unstable, and it was identified by NMR and the product of its reaction with  $\text{O}_2$ , which is discussed below.  $\text{Ta}(\text{NMe}_2)_4(\text{SiR}'_3)$  (**29a,b**) decomposed rapidly to  $\text{HNMe}_2$ ,  $\text{HSiR}'_3$ , and metal oxides once they were exposed to  $\text{H}_2\text{O}$ .

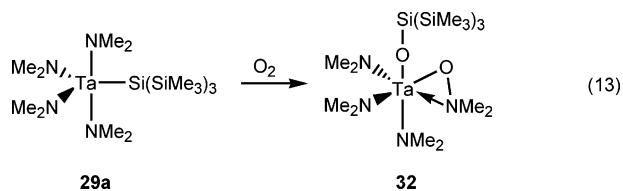
(40) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; HarperCollins: New York, pp 203–206.

Reactions of  $(\text{Me}_2\text{N})_3\text{TaCl}_2$  with 1 equiv of silyl anions  $\text{SiR}'_3^-$  yields the chloro silyl complexes  $(\text{Me}_2\text{N})_3\text{TaCl}(\text{SiR}'_3)$  ( $\text{R}'_3 = (\text{SiMe}_3)_3$  (**30a**),  $\text{Bu}^t\text{Ph}_2$  (**30b**); eq 11).



Subsequent reaction of **30a** with  $\text{LiSi}(\text{SiMe}_3)_3$  or the reaction of  $(\text{Me}_2\text{N})_3\text{TaCl}_2$  with 2 equiv of  $\text{LiSi}(\text{SiMe}_3)_3$  gives the disilyl complex  $(\text{Me}_2\text{N})_3\text{Ta}[\text{Si}(\text{SiMe}_3)_3]_2$  (**31**; eq 12).<sup>34</sup> The disilyl complex was prepared as a neutral analogue of  $\text{Zr}(\text{NMe}_2)_3[\text{Si}(\text{SiMe}_3)_3]_2^-$  (**22a**). NMR spectra of  $\text{Ta}(\text{NMe}_2)_3[\text{Si}(\text{SiMe}_3)_3]_2$  (**31**) shows only one set of resonances for amide and silyl ligands between  $-60$  and  $27$  °C, suggesting that **31** adopts a trigonal-bipyramidal structure with two silyl ligands in the axial positions.

The Ta amide silyl complex  $\text{Ta}(\text{NMe}_2)_4[\text{Si}(\text{SiMe}_3)_3]$  (**29a**) is sensitive to air. Its reaction with  $\text{O}_2$  at room temperature leads to  $(\text{Me}_2\text{N})_3\text{Ta}(\eta^2\text{-ONMe}_2)[\text{OSi}(\text{SiMe}_3)_3]$  (**32**; eq 13).<sup>31</sup> In the reaction, two oxygen atoms insert

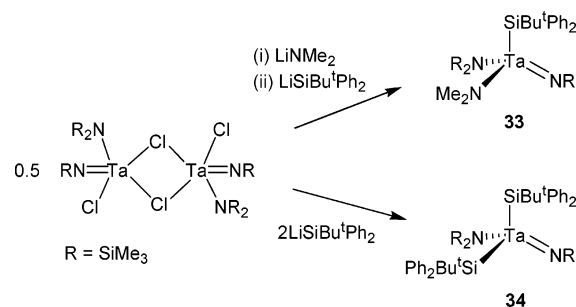


into Ta–Si and Ta–N bonds, respectively, in **29a**. **32** is inert to excess  $\text{O}_2$ . The oxidation of the M– $\text{NMe}_2$  bond in the reaction is, to our knowledge, unprecedented. The  $\text{R}_2\text{NO}$  ligands are usually prepared from the hydroxyamines  $\text{R}_2\text{NOH}$ .<sup>41</sup>

Reactions of  $\text{O}_2$  with  $\text{Ta}(\text{NMe}_2)_5$  or  $(\text{Et}_2\text{N})_3\text{Ta}=\text{NBU}^t$  have been studied to yield high- $\kappa$  (dielectric constant)  $\text{Ta}_2\text{O}_5$  thin films as gate insulating materials in microelectronic transistors.<sup>31</sup> The mechanistic pathways in these reactions are not clear. Our studies help shed light on the mechanisms of the reactions of  $\text{O}_2$  with  $d^0$  metal amide complexes.

**3. Tantalum Amide Imide Silyl and Bis(silyl) Complexes.** Tilley and co-workers have reported the Cp-free group 6 imido silyl complexes  $(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3\text{-N}=\text{M}(\text{R}))[\text{Si}(\text{SiMe}_3)_3]$  ( $\text{M} = \text{Mo}, \text{W}; \text{R} = \text{Cl}, \text{CH}_2\text{Bu}^t, \text{H}$ ).<sup>42</sup> We prepared the Ta imide silyl and disilyl complexes  $[(\text{Me}_3\text{Si})_2\text{N}](\text{Me}_2\text{N})(\text{Me}_3\text{SiN}=\text{TaSiBu}^t\text{Ph}_2)$  (**33**) and  $[(\text{Me}_3\text{Si})_2\text{N}](\text{Me}_3\text{SiN}=\text{Ta}(\text{SiBu}^t\text{Ph}_2)_2)$  (**34**) from  $\{\text{Ta}(\mu\text{-Cl})\text{Cl}(\text{N}=\text{SiMe}_3)[\text{N}(\text{SiMe}_3)_2]\}_2$  by the reactions shown in Scheme 16.<sup>33</sup> These two complexes are, to our

Scheme 16



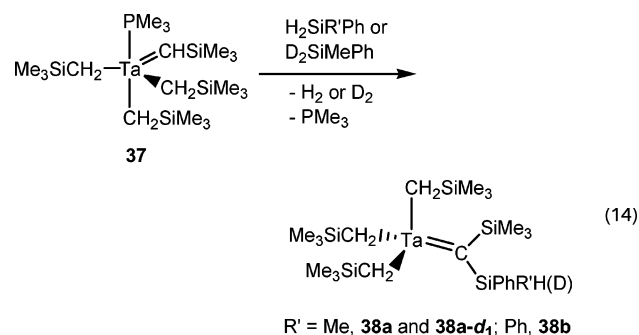
knowledge, the first Cp-free group 5 imido disilyl and silyl complexes.

The Mo amide imide silyl complex  $(\text{ArN}=\text{M})(\text{NMe}_2)[\text{Si}(\text{SiMe}_3)_3]$  (**35**;  $\text{Ar} = 2,6\text{-Pr}^i_2\text{C}_6\text{H}_3$ ) was also prepared from the reaction of  $(\text{ArN}=\text{M})\text{OCl}_2(\text{DME})$  with  $\text{LiNMe}_2$  and  $\text{LiSi}(\text{SiMe}_3)_3$  (Scheme 17). The diamide diimides  $(\text{ArN}=\text{M})(\text{NMe}_2)_2$  (**36**; Scheme 17) and  $(\text{Ar-N}=\text{M})(\text{NMe}_2)[\text{N}(\text{SiMe}_3)_2]$  were similarly prepared.<sup>43</sup>

### III. Reactions of Silanes with Alkylidene and Amide Complexes

The reactions of hydrosilanes with coordinated ligands are of particular interest to us. We have studied how H–Si bonds in silanes react with the  $\pi$  bonds in the  $\text{M}=\text{CHR}$  and with the  $d\text{-p}$   $\pi$  bonds in the  $\text{M-NR}_2$  moieties and mechanisms in these reactions. In the former, we chose the Cp-free  $d^0$  high-oxidation-state alkylidene complexes  $(\text{RCH}_2)\text{Ta}(\text{PMe}_3)_2(=\text{CHR})_2$ , containing phosphine ligands, in the hope that such ligands would help stabilize the resulting reaction products.<sup>44,45</sup> In the latter, Cp-free  $d^0$  high-oxidation-state amide complexes  $\text{M}(\text{NMe}_2)_n$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{Ta}$ ) were used.<sup>46–48</sup> The reactions of metal amides with silanes have also played an important role in the formation of M–Si–N ternary films as diffusion barrier materials in very-large-scale-integrated microelectronic devices, as discussed below.

**1. Reactions of Tantalum Alkylidene Complexes with Silanes.**<sup>44,45</sup> An immediate reaction was observed between  $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}(\text{PMe}_3)(=\text{CHSiMe}_3)$  (**37**)<sup>49</sup> and  $\text{H}_2\text{SiR}'\text{Ph}$  ( $\text{R}' = \text{Me}, \text{Ph}$ ), yielding  $\text{H}_2$  and nearly quantitatively  $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}[\text{C}(\text{SiMe}_3)\text{SiHR}'\text{Ph}]$  ( $\text{R}' = \text{Me}$  (**38a**),  $\text{Ph}$  (**38b**); eq 14). **37** does not react with  $\text{HSiPh}_3$  at room temperature.



Kinetic studies of the reactions of **37** with  $\text{H}_2\text{SiMePh}$  and  $\text{D}_2\text{SiMePh}$  at  $10$  °C show that a dissociative mechanism is operative in this reaction.<sup>44,45</sup> This path-

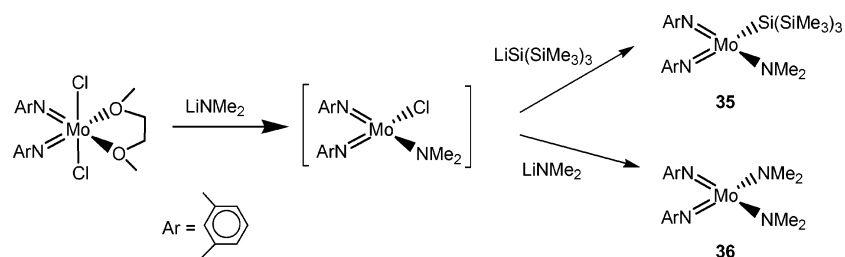
(41) Mehrotra, R. C.; Rai, A. K.; Singh, A.; Bohra, R. *Inorg. Chim. Acta* **1975**, *13*, 91.

(42) Casty, G. L.; Tilley, T. D.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1997**, *16*, 4746.

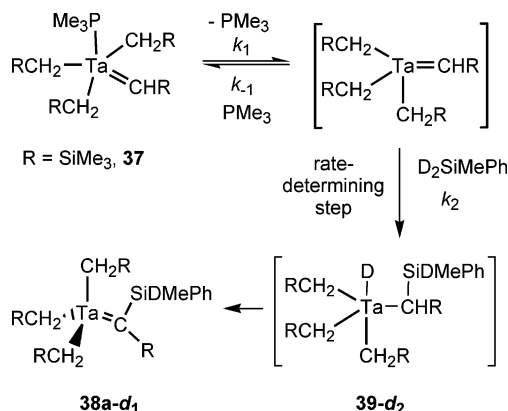
(43) Chen, T.-N.; Sorasaene, K. R.; Wu, Z.-Z.; Diminnie, J. B.; Xue, Z.-L. *Inorg. Chim. Acta* **2003**, *345*, 113.



## Scheme 17



## Scheme 18



way involves the loss of a PMe<sub>3</sub> ligand to open a coordination site on the Ta center, followed by rate-determining addition of the silane to the Ta=C bond to give **39** (Scheme 18). For example, a steady-state approximation gives eqs 15 and 16.<sup>44b</sup> Under conditions

$$v = -d[\mathbf{37}]/dt = \frac{k_1 k_2 [\text{H}_2\text{SiMePh}][\mathbf{37}]}{k_{-1} [\text{PMe}_3] + k_2 [\text{H}_2\text{SiMePh}]} \quad (15)$$

$$\frac{1}{k_{\text{obs}}} = \frac{k_{-1} [\text{PMe}_3]_{\text{av}}}{k_1 k_2 [\text{H}_2\text{SiMePh}]_{\text{av}}} + \frac{1}{k_1} \quad (16)$$

of excess H<sub>2</sub>SiMePh, pseudo-first-order kinetics in **37** was observed, as eq 15 suggests. Plots of 1/k<sub>obs</sub> vs [PMe<sub>3</sub>]<sub>av</sub>/[H<sub>2</sub>SiMePh]<sub>av</sub> and [PMe<sub>3</sub>]<sub>av</sub>/[D<sub>2</sub>SiMePh]<sub>av</sub> were found to fit eq 16 (Figure 4) with k<sub>1</sub> = [5.45(10)] × 10<sup>-2</sup> min<sup>-1</sup> and a kinetic isotope effect (k<sub>2H</sub>/k<sub>2D</sub>) of 1.87.

In the reactions of the excess deuterium-labeled silane D<sub>2</sub>SiMePh with **37**, the formation of HDSiMePh and H<sub>2</sub>-SiMePh was also observed. Analyses by mass spectrometry (MS) of the gaseous products show that D<sub>2</sub> is the major product in the reaction, and the ratios of D<sub>2</sub>, HD,

and H<sub>2</sub> are in the range from [86.6(0.3)–89.6(1.2)]:[12.5(0.3)–9.1(1.1)]:[0.86(0.03)–1.26(0.01)]. When the reaction with 4.5 equiv of D<sub>2</sub>SiMePh was conducted under excess H<sub>2</sub>, the MS showed the products to be D<sub>2</sub>, HD, and H<sub>2</sub> in a 24.5(0.1):13.4(0.1):62.1(0.1) ratio, indicating that the products and H<sub>2</sub> added to the system undergo hydrogen scrambling. The mechanism in the conversion of **39** to the product **38a** is not clear, and three possible pathways may operate here.<sup>44b</sup>

The addition of H<sub>2</sub>SiR'Ph (R' = Me, Ph) to bis-(alkylidene) complexes (Me<sub>3</sub>SiCH<sub>2</sub>)Ta(PMe<sub>3</sub>)<sub>2</sub>(=CHR)<sub>2</sub> (R = SiMe<sub>3</sub> (**7a**), Bu<sup>t</sup> (**7c**)) gives the 1,1'-metalla-3-silacyclobutadiene complexes **40a–c** (Scheme 19) and H<sub>2</sub>. The reaction with the silane (PhH<sub>2</sub>Si)<sub>2</sub>CH<sub>2</sub>, containing more than one silyl group, yields the metalladisi-lacyclohexadiene complex **41**. The X-ray crystal structure of **41** showed that it adopted the structure of a meso isomer.

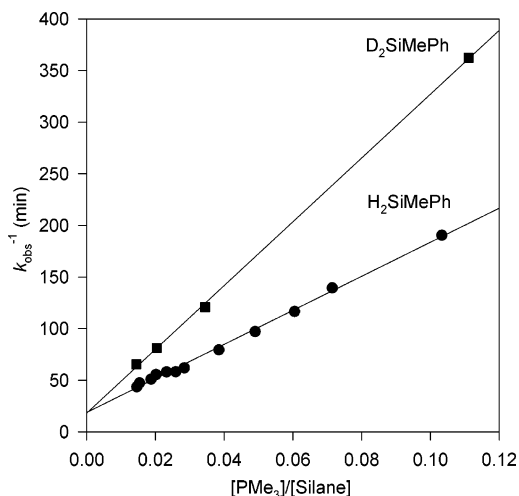
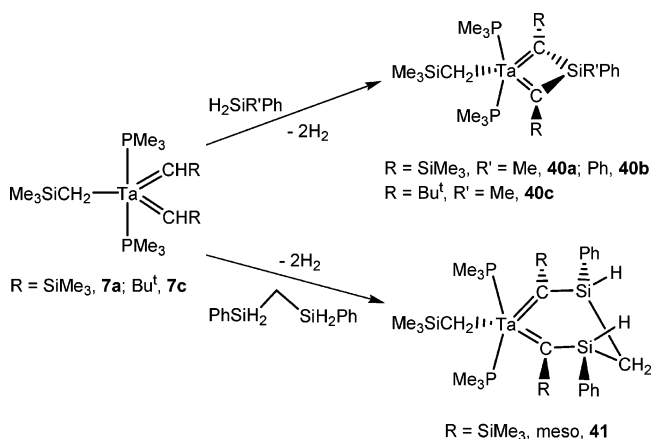


Figure 4. Plot of 1/k<sub>obs</sub> vs [PMe<sub>3</sub>]<sub>av</sub>/[silane]<sub>av</sub>.<sup>44b</sup>

## Scheme 19



(44) (a) Diminnie, J. B.; Xue, Z.-L. *J. Am. Chem. Soc.* **1997**, *119*, 12657. (b) Diminnie, J. B.; Blanton, J. R.; Cai, H.; Quisenberry, K. T.; Xue, Z.-L. *Organometallics* **2001**, *20*, 1504.

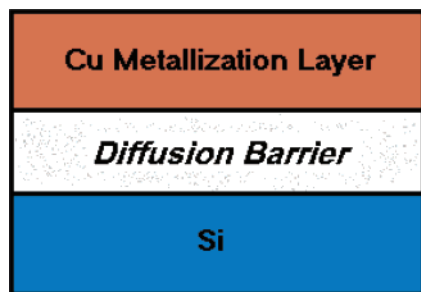
(45) (a) Blanton, J. R.; Chen, T.-N.; Diminnie, J. B.; Cai, H.; Wu, Z.-Z.; Li, L.-T.; Sorasaene, K. R.; Quisenberry, K. T.; Pan, H.-J.; Wang, C.-S.; Choi, S.-H.; Wu, Y.-D.; Lin, Z.-Y.; Guzei, I. A.; Rheingold, A. L.; Xue, Z.-L. *J. Mol. Catal. A: Chem.* **2002**, *190*, 101. (b) Diminnie, J. B.; Liu, X.-Z.; Cai, H.; Wu, Z.-Z.; Blanton, J. R.; Tuinman, A. A.; Quisenberry, K. T.; Vallet, C. E.; Zuhr, R. A.; Beach, D. B.; Peng, Z.-H.; Wu, Y.-D.; Concolino, T. E.; Rheingold, A. L.; Xue, Z.-L. *Pure Appl. Chem.* **2001**, *73*, 331.

(46) Liu, X.-Z.; Wu, Z.-Z.; Peng, Z.-H.; Wu, Y.-D.; Xue, Z.-L. *J. Am. Chem. Soc.* **1999**, *121*, 5350.

(47) Liu, X.-Z.; Wu, Z.-Z.; Cai, H.; Yang, Y.-H.; Chen, T.-N.; Vallet, C. E.; Zuhr, R. A.; Beach, D. B.; Peng, Z.-H.; Wu, Y.-D.; Concolino, T. E.; Rheingold, A. L.; Xue, Z.-L. *J. Am. Chem. Soc.* **2001**, *123*, 8011.

(48) Cai, H.; Chen, T.-N.; Wang, X.-P.; Schultz, A. J.; Koetzle, T. F.; Xue, Z.-L. *Chem. Commun.* **2002**, 230 and references therein.

(49) Rupprecht, G. A. Ph.D. dissertation, Massachusetts Institute of Technology, 1979.

**Chart 2. Diffusion Barrier between the Metalization Layer and Si**

**2. Reactions of  $d^0$  Metal Amide Complexes with Silanes.** Transition-metal amide ligands are known to react with proton- or hydride-containing compounds to yield amines ( $H-NR_2$ ).<sup>50</sup> Reactions of  $Ti(NR_2)_4$  with  $SiH_4$  and  $NH_3$  through chemical vapor deposition have recently been studied to give Ti–Si–N ternary materials as barriers (Chart 2) between Cu and Si in integrated circuits to prevent solid-state reactions/diffusion between Cu and Si (to form copper silicides  $CuSi_n$ ) and the degradation of the devices.<sup>51</sup> Analysis of the compositions of the Ti–Si–N ternary films revealed that they were along the tie line of TiN and  $Si_3N_4$  in the Ti–Si–N phase diagram (Figure 5). In other words, these films prepared from the reactions of  $Ti(NR_2)_4$  with  $SiH_4$  and  $NH_3$  are a mixture of TiN and  $Si_3N_4$ .<sup>51</sup> The probable role of  $NH_3$  in these reactions is that it undergoes transamination with  $Ti-NR_2$ . A key question is why the reactions of  $Ti(NR_2)_4$  with  $SiH_4$  gave TiN and  $Si_3N_4$  in the Ti–Si–N ternary phases. Another issue of current interest is why, in chemical vapor deposition reactions using metal amide complexes as precursors to give microelectronic materials, metal carbides are often formed as an impurity.<sup>52</sup> Recent reports<sup>51</sup> of formation of M–Si–N ternary phases thus prompted us to investigate the nature of the reactions between amide ligands ( $M-NR_2$ ) and silanes ( $H-SiR_3$ ).

Among the first studies we conducted was the reaction of  $Ti(NMe_2)_4$  and  $SiH_4$  both at room temperature and at high temperature in a CVD reactor. The chemical vapor deposition of the thin films was carried out in an ultrahigh-vacuum (UHV) CVD reactor in Dr. David B. Beach's group at Oak Ridge National Laboratory. These studies were designed in part to confirm that, in the absence of  $NH_3$ , this reaction gave TiN and  $Si_3N_4$ .<sup>47</sup>

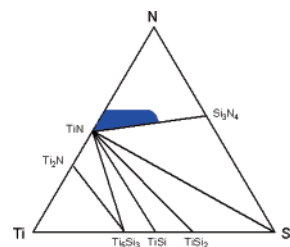
Our studies show that the reaction between  $Ti(NMe_2)_4$  and  $SiH_4$  at 23 °C, followed by heating, likely gave TiN– $Si_3N_4$  ternary powders. This reaction, conducted in a CVD reactor at 448–450 °C, yielded a film of mixtures of TiN– $Si_3N_4$ . In other words, the compositions of the powders and films prepared at room and high temperatures suggest that similar chemistry and mechanistic pathways take place in a large temperature range.

Deuterium-labeling studies and surface analyses of the solid materials produced from this reaction at 23

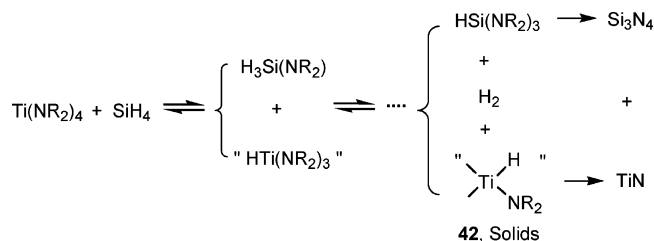
(50) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*, Ellis Horwood: Chichester, U.K., 1980.

(51) (a) Smith, P. M.; Custer, J. S. *Appl. Phys. Lett.* **1997**, *70*, 3116. (b) Custer, J. S.; Smith, P. M.; Fleming, J. G.; Roherty-Osmun, E. In *Inorganic Materials Synthesis*; ACS Symp. Ser. 727; Winter, C. H., Hoffman, D. M., Eds., American Chemical Society: Washington, DC, 1999; p 86.

(52) Fix, R. M.; Gordon, R. G.; Hoffman, D. M. *Chem. Mater.* **1990**, *2*, 235.



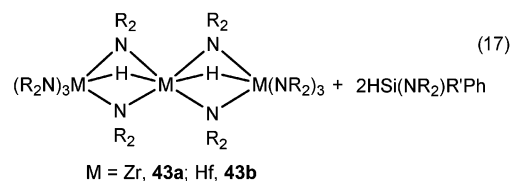
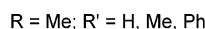
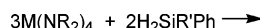
**Figure 5.** Formation of Ti–Si–N ternary films from the reactions of  $Ti(NR_2)_4$  with  $SiH_4$  and  $NH_3$ . The compositions of the materials are in the blue area along the TiN– $Si_3N_4$  tie line.<sup>51</sup>

**Scheme 20**

°C indicate the mechanistic pathway in Scheme 20. H–Si and Ti– $NR_2$  bonds undergo hydride and amide exchanges to give aminosilanes such as  $HSi(NR_2)_3$  and Ti hydride amide solids **42**. These two products containing Si–N and Ti–N bonds then convert to  $Si_3N_4$  and TiN, respectively. The Ti hydride amide solids **42**, which are likely polymeric species with reduced titanium, were not isolated, however, and were identified by the surface analyses.

The reaction in Scheme 20 did not yield isolable complexes. We then studied the reactions of  $M(NMe_2)_4$  ( $M = Zr, Hf$ ) with  $H_2SiR'Ph$  ( $R' = H, Me, Ph$ ). Zr and Hf complexes are less likely to be reduced than Ti complexes, and the hindered silanes may slow the reactions so that intermediates could be isolated.

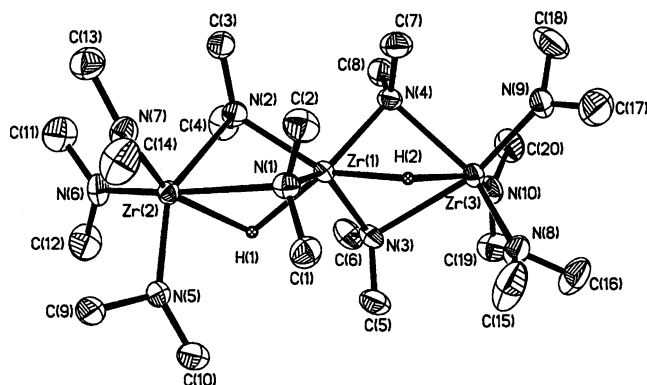
When  $M(NMe_2)_4$  ( $M = Zr, Hf$ ) were reacted with  $H_2SiR'Ph$  ( $R' = H, Me, Ph$ ), aminosilanes and the novel amide complexes  $[(Me_2N)_3M(\mu-H)(\mu-NMe_2)_2]_2M$  ( $M = Zr$  (**43a**),  $Hf$  (**43b**); eq 17, Figure 6) were isolated.<sup>46,47</sup> As



in Scheme 20, exchanges of amide and hydride ligands occurred, and quick isolation of the products gave the isolable intermediates **43a,b**. Such exchanges between silanes and amide complexes are rare,<sup>53</sup> and the hydride complexes **43a,b** are unusual. They are among the few structurally characterized Cp-free group 4 hydrides.<sup>54,55</sup>

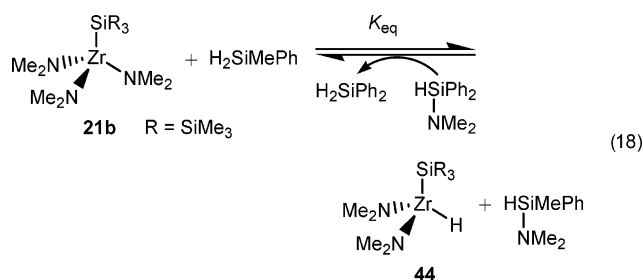
We have also studied the reactions of  $(Me_2N)_3Zr-Si-(SiMe_3)_3$  (**21b**; eq 7) and  $H_2SiR'Ph$  ( $R' = H, Me, Ph$ ). These reactions were found to give the unstable hydride

(53) Holland, P. L.; Andersen, R. A.; Bergman, R. G.; Huang, J.; Nolan, S. P. *J. Am. Chem. Soc.* **1997**, *119*, 12800.



**Figure 6.** Molecular drawing of **43a** from X-ray single-crystal diffraction.<sup>46,47</sup>

complex  $(\text{Me}_2\text{N})_2\text{Zr}(\text{H})[\text{Si}(\text{SiMe}_3)_3]$  (**44**) and  $\text{HSi}(\text{NMe}_2)\text{R}^{\text{Ph}}$ , and the reactions are reversible. In other words, in the reverse reactions, the hydride ligand in **44** reacts with amide  $-\text{NMe}_2$  in  $\text{HSi}(\text{NMe}_2)\text{MePh}$  to give  $\text{Si}-\text{H}$  and  $\text{Zr}-\text{NMe}_2$  bonds. The equilibrium  $\mathbf{21b} + \text{H}_2\text{SiPh}_2 \rightleftharpoons \mathbf{44} + \text{HSi}(\text{NMe}_2)\text{Ph}_2$  favors **21b** and  $\text{H}_2\text{SiPh}_2$  at  $0^\circ\text{C}$ , as shown in the equilibrium constant  $K_{\text{eq}}$  (0.11(0.01)) and  $\Delta G^\circ$  value (1.20(0.05) kcal/mol) at  $0^\circ\text{C}$  (eq 18). The



reactions leading to the hydrides were the first direct observation from transition-metal amides with silanes through unusual equilibria.<sup>53</sup>

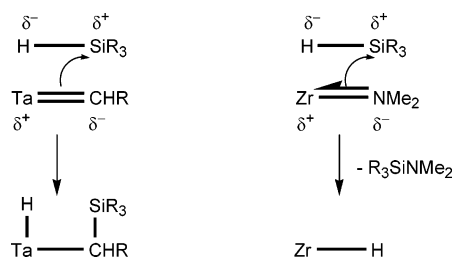
Ab initio quantum-chemical calculations were conducted by the group of Prof. Yun-Dong Wu at the Hong Kong University of Science and Technology to understand the reactions of  $\text{Ti}(\text{NR}_2)_4$  ( $\text{R} = \text{Me}, \text{H}$ ) with  $\text{SiH}_4$ . These theoretical studies indicate that the formation of aminosilanes and  $\text{HTi}(\text{NR}_2)_3$  is favored. These calculations also showed that  $\text{HTi}(\text{NH}_2)_3$  reacted with  $\text{SiH}_4$  or  $\text{H}_3\text{Si}-\text{NH}_2$  in the following step to give  $\text{H}_2\text{Ti}(\text{NH}_2)_2$  and aminosilanes.

It is interesting to note that the reactions of silanes with both amides  $\text{M}(\text{NMe}_2)_4$  ( $\text{M} = \text{Zr}, \text{Hf}$ ) and alkylidene complexes  $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}(\text{PMe}_3)(=\text{CHSiMe}_3)$  (**37**), **7a**, and **7c** proceed through a step involving some degree of nucleophilic attack on the silicon center of the incoming silane molecule by the  $d-\pi$  bonds in the

(54) For group 4 metallocene and heterometallic hydrides, see: (a) Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1. (b) Toogood, G. E.; Wallbridge, M. G. H. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 267. (c) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (d) Labinger, J. A. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; p 361. (e) Etkin, N.; Hoskin, A. J.; Stephan, D. W. *J. Am. Chem. Soc.* **1997**, *119*, 11420. (f) Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *96*, 8115.

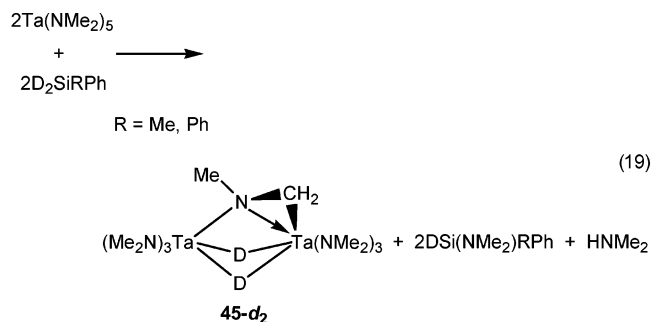
(55) (a) Basch, H.; Musaev, D. G.; Morokuma, K.; Fryzuk, M. D.; Love, J. B.; Seidel, W. W.; Albinati, A.; Koetzle, T. F.; Klooster, W. T.; Mason, S. A.; Eckert, J. *J. Am. Chem. Soc.* **1999**, *121*, 523. (b) Nöth, H.; Schmidt, M. *Organometallics* **1995**, *14*, 4601. (c) Jacoby, D.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1993**, *115*, 3595.

## Scheme 21



$\text{N}-\text{M}$  bonds and the  $\pi$  electron density of the  $\text{Ta}=\text{CHR}$  bonds, leading to the formation of products with new  $\text{N}-\text{Si}$  and  $\text{C}-\text{Si}$  bonds, respectively (Scheme 21). Such nucleophilic attack of the  $\pi$  electron density on the incoming silane may explain the observed preferential reaction of only the amide and alkylidene ligands, but not the alkyl ligands, with silanes.

We further investigated the reactions of  $\text{Ta}(\text{NMe}_2)_5$  with silanes.<sup>48</sup> As expected, the reactions give  $\text{Ta}-\text{H}$  bonds in  $(\text{Me}_2\text{N})_3\text{Ta}(\mu-\text{H})_2[\mu(\text{N})-\eta^2(\text{N}, \text{C})-\text{CH}_2\text{NMe}]_2\text{Ta}(\text{NMe}_2)_3$  (**45**; Figure 7), as in the reactions of  $\text{M}(\text{NMe}_2)_4$  ( $\text{M} = \text{Zr}, \text{Hf}$ ) with silanes. The presence of two hydride ligands was confirmed by neutron diffraction studies of a single crystal of **45**, and **45** is one of the few Ta hydrides<sup>48</sup> to be structurally characterized by neutron diffraction. However, to our surprise, the reactions yield an imine ligand in **45** as well. Reactions with  $\text{D}_2\text{SiRPh}$  ( $\text{R} = \text{Me}, \text{Ph}$ ) give the dideuteride **45-d<sub>2</sub>** and  $\text{HNMe}_2$  (eq 19).

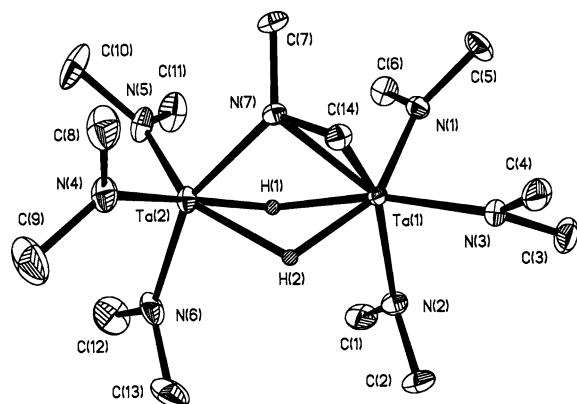


It is thus likely that the formation of the imine ligand in **45** with  $\text{M}-\text{C}$  bonds is through  $\beta$ -H abstraction of an amide ligand by another amide ligand.

The formation of imine complexes from homoleptic  $\text{M}(\text{NR}_2)_n$  is particularly significant to the understanding of mechanistic pathways and the incorporation of metal carbide impurities into metal nitrides in chemical vapor deposition reactions.<sup>52</sup> Initial  $\beta$ -H abstraction between two amide ligands in  $\text{M}(\text{NR}_2)_n$  to give an  $\eta^2$ -imine moiety was postulated as the first step to establish  $\text{M}-\text{C}$  bonds in C incorporation into the metal nitride materials, on the basis of analysis of organic products<sup>56a</sup> and spectroscopic,<sup>56b-d</sup> theoretical,<sup>56e</sup> and kinetic<sup>56f,g</sup> studies. **45** is one of the few structurally characterized  $\eta^2$ -imine complexes from  $\beta$ -H abstraction between amide ligands.<sup>57</sup>

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**Figure 7.** Molecular drawing of **45** from X-ray single-crystal diffraction (reproduced by permission of The Royal Society of Chemistry).<sup>48</sup>

Reducing C incorporation is of intense interest in the formation of the metal nitrides as microelectronic materials.

#### IV. Concluding Remarks

Our studies summarized here demonstrate that there is rich and often unusual basic chemistry in the studies of molecular approaches to advanced materials. The drive to develop advanced materials provides new

opportunities to explore novel chemistry, which in turn may help us better understand the processes that form these materials. The rapid advances in microelectronic materials and computer technologies, as shown by Moore's Law<sup>58</sup>—the doubling of Si-based transistors every couple of years—over the past four decades will continue to offer us opportunities to explore the novel chemistry of silicon and transition metals.

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