Reactions of d^0 alkylidene and amide complexes with silanes*

Jonathan B. Diminnie[1], Xiaozhan Liu[1], Hu Cai[1], Zhongzhi Wu[1],
Jaime R. Blanton[1], Tianniu Chen[1], Albert A. Tuinman[1],
Keith T. Quisenberry[1], Catherine E. Vallet[2], Ray A. Zuhr[3],
David B. Beach[2,†], Zhihui Peng[4], Yun-Dong Wu[4,†],
Thomas E. Concolino[5], Arnold L. Rheingold[5,†], and Ziling Xue[1,†]

[1]Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA;
[2]Chemical and Analytical Sciences Division and [3]Surface Modification and
Characterization (SMAC) Research Center, Oak Ridge National Laboratory,
Oak Ridge, TN 37831, USA; [4]Department of Chemistry, Hong Kong University
of Science and Technology, Hong Kong, China; [5]Department of Chemistry &
Biochemistry, University of Delaware, Newark, DE 19716, USA

Abstract: Reactions of silanes with d^0 Ta alkylidene and Group 4 amide complexes were found to involve the initial attack on silicon atoms in the silanes by nucleophilic alkylidene carbon or amide nitrogen atoms. The reaction of $(Me_3SiCH_2)_3Ta(PMe_3)[=CHSiMe_3]$ (**1**) with $H_2SiR'Ph$ (R' = Me, Ph) gave $(Me_3SiCH_2)_3Ta[=C(SiMe_3)SiHR'Ph]$ (**2a–b**). Similar reactions of these two silanes and $(H_2PhSi)_2CH_2$ with $(Me_3SiCH_2)Ta(PMe_3)_2[=CHR]_2$ (R = SiMe_3, **3**; CMe_3, **4**) yielded novel metallasilacyclobutadienes and a metalladisilacyclohexadiene, respectively. In comparison, the reactions between $M(NMe_2)_4$ (M = Ti, Zr, Hf) and silanes were found to give aminosilanes and metal amide hydride species which were perhaps involved in the formation of titanium–silicon–nitride (Ti–Si–N) ternary materials.

INTRODUCTION

The reactivity of H–Si bonds toward metal complexes is of intense current interest [1]. M=CHR and M–NR$_2$ both have metal–ligand π bonds. Direct reactions of silanes with the M=CHR moiety of Schrock alkylidene complexes, to our knowledge, have not been observed [1,2]. Reactions of nucleophilic amide ligands with silanes are relatively unknown [3]. We are particularly interested in the reactions of cyclopentadienyl (Cp)-free complexes with silanes. The research here is part of our studies of Cp-free silyl or related complexes [4]. We have studied silane reactions with metal–ligand multiple bonds with two-fold interest: (1) mechanistic pathways of these reactions; (2) potential applications of this chemistry in molecular approaches to solid-state materials such as ternary M–Si–N thin films. These materials are of current interest as diffusion barriers in integrated microelectronic circuits [5a] and oxygen diffusion barriers in dynamic random access memory (DRAM) structures to prevent SiO$_2$ formation [5b]. Reactions of Ti(NR$_2$)$_4$ with SiH$_4$ and NH$_3$ were shown to give Ti–Si–N [5a]. The mechanism of such reactions is not yet clear. This paper is a summary of our recent studies of reactions of $(Me_3SiCH_2)_3Ta(PMe_3)[=CHSiMe_3]$, $(Me_3SiCH_2)Ta(PMe_3)_2[=CHR]_2$ (R = SiMe$_3$, Bu^t), and M(NMe$_2$)$_4$ (M = Ti, Zr, Hf) with silanes [4e,6–8].

REACTIONS OF Ta ALKYLIDENE COMPLEXES WITH SILANES

$(Me_3SiCH_2)_3Ta(PMe_3)[=CHSiMe_3]$ (**1**) [9] was found to react with $H_2SiR'Ph$ (R' = Me, Ph) at 23 °C to give $(Me_3SiCH_2)_3Ta(PMe_3)[=C(SiMe_3)(SiHR'Ph)]$ (**2a–b**). Reactions of $(Me_3SiCH_2)Ta(PMe_3)_2[=CHSiMe_3]_2$ (**3**) [4c,7] with $H_2SiR'Ph$ yielded **5a–b**. **5a–b**, to our knowledge, represent the first examples of 1,1-metal-lasilacyclobutadiene complexes and the first metallacyclobutadiene complexes in which both double bonds are localized exclusively on the metal atom. The reaction of **3** with $(H_2PhSi)_2CH_2$ [10] was found to give **7**, which was isolated as the *meso*-isomer (Scheme 1).
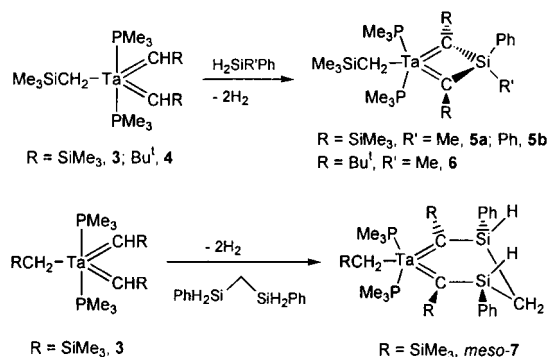
Scheme 1

The reaction of **1** with excess $D_2SiMePh$ was found to give $(Me_3SiCH_2)_3Ta[=C(SiMe_3)SiDMePh]$ (**5a–d_1**), HDSiMePh, and D_2 as the major gaseous product. Kinetic studies of this reaction suggested a pathway involving the loss of PMe_3, followed by addition of the silane to the Ta=C bond, leading to products. These observations are consistent with the mechanism in Scheme 2.
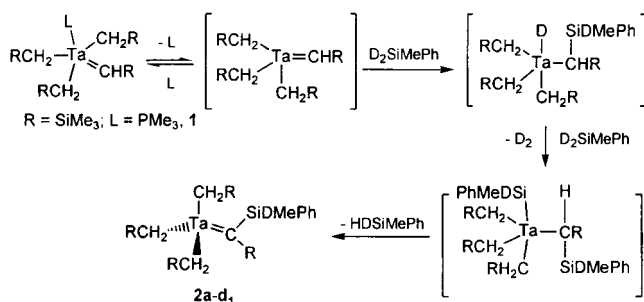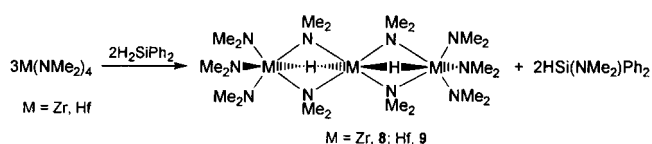

Scheme 2

REACTIONS OF d⁰ AMIDE COMPLEXES M(NMe₂)₄ (M=Ti, Zr, Hf) WITH SILANES

When $M(NMe_2)_4$ was exposed to excess SiH_4, instantaneous reactions were observed yielding $HSi(NMe_2)_3$, H_2, and black solids. No $HNMe_2$ was detected. Analyses of the black solids showed $-NMe_2$ but no silyl groups. The reaction of the solids with $DCl–D_2O$ yielded H_2, HD, and D_2 as well as $DNMe_2$, but no $HDSiR'_2$. These results indicated that the black solids contained $-NMe_2$ and $-H$ ligands. Heating the black solids from the reactions of $Ti(NMe_2)_4$ with SiH_4 to 297–1100 °C gave mainly mixtures of TiN and Si_3N_4 [11]. The reaction of $Ti(NMe_2)_4$ with SiH_4 conducted in a chemical vapor deposition (CVD) reactor at 300–450 °C was found to give thin films consistent with TiN and Si_3N_4 [11]. Reactions of $Zr(NMe_2)_4$ or $Hf(NMe_2)_4$ with less than 1 equiv of phenyl-containing silanes gave **8** and **9** (Scheme 3). These reactions are two of few known examples of such reactions. To our knowl-

edge, the only other reported transition-metal amide reaction to give an isolated amide hydride involves Cp*Ni(PEt$_3$)NHTol [12].

Scheme 3

Smith and coworkers recently reported that the reaction of Ti(NEt$_2$)$_4$ with SiH$_4$ and NH$_3$ in chemical vapor deposition (CVD) gave Ti–Si–N ternary films [5a]. Compositions of the films placed them near or above the TiN–Si$_3$N$_4$ tie line in the Ti–Si–N phase diagram. In other words, these ternary films are mostly mixtures of TiN and Si$_3$N$_4$.

The current studies suggest that the first step in CVD of Ti–Si–N involves the formation of "HTi(NMe$_2$)$_3$" and H$_3$Si(NMe$_2$). In the following steps, similar reactions occur to give black solids containing –H and unreacted –NMe$_2$. Subsequently, the black solids and H$_n$Si(NMe$_2$)$_{4-n}$ perhaps undergo *separate* decompositions to give TiN and Si$_3$N$_4$, respectively (Scheme 4). HSi(NMe$_2$)$_3$ is a known precursor to Si$_3$N$_4$ [13].
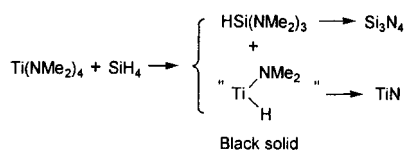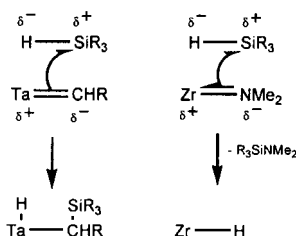

Scheme 4

Transamination is known between Ti(NMe$_2$)$_4$ and NH$_3$ [14]. Such transaminations may occur as well in reactions of Ti(NMe$_2$)$_4$ with NH$_3$ and SiH$_4$. However, SiH$_4$ and NH$_3$, either alone or mixtures thereof, are unreactive at low temperatures. To grow Si$_3$N$_4$ from NH$_3$–SiH$_4$ requires temperatures over 800 °C [15]. Thus, the intermediates formed from the reaction of Ti(NMe$_2$)$_4$ and SiH$_4$ are essential for Si$_3$N$_4$ growth. Further studies involving NH$_3$ are needed to understand the mechanistic pathways in the reactions.

COMPARISON OF ALKYLIDENE AND AMIDE REACTIONS WITH SILANES

It is interesting to compare the reactivities of alkylidene and amide bonds with silanes. The reactions of silanes with **1** perhaps proceed through a step involving nucleophilic attack on the Si center of the incoming silane by the π-bond of the alkylidene. Similar chemistry was observed in reactions of *d-p* π bonds in M(NMe$_2$)$_4$ with silanes to yield amidosilanes and **8–9** (Scheme 5).

Scheme 5

The current research shows unique chemistry of silanes in their reactions with nucleophilic alkylidene and amide ligands. It gives an example that studies of fundamental chemistry could lead to an understanding of the mechanistic pathways in solid-state materials formation and the compositions of these materials.

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