Reactions of d⁰ alkylidene and amide complexes with silanes*

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Abstract: Reactions of silanes with d⁰ 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 (Me₃SiCH₂)₃Ta(PMe₃)[=CHSiMe₃] (1) with H₂SiR'Ph (R' = Me, Ph) gave (Me₃SiCH₂)₃Ta[=C(SiMe₃)SiHR'Ph] (2a–b). Similar reactions of these two silanes and (H₂PhSi)₂CH₂ with (Me₃SiCH₂)Ta(PMe₃)₂[=CHR] (R = SiMe₃, 3; CMe₃, 4) yielded novel metallasilacyclobutadienes and a metalladisilacyclocyclohexadiene, respectively. In comparison, the reactions between M(NMe₂)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–NR₂ 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 SiO₂ formation [5b]. Reactions of Ti(NR₂)₄ with SiH₄ and NH₃ 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 (Me₃SiCH₂)₃Ta(PMe₃)[=CHSiMe₃], (Me₃SiCH₂)Ta(PMe₃)₂[=CHR] (R = SiMe₃, Bu⁴), and M(NMe₂)₄ (M = Ti, Zr, Hf) with silanes [4e,6–8].

*Lecture presented at the XIXth International Conference on Organometallic Chemistry (XIX ICOMC), Shanghai, China, 23–28 July 2000. Other presentations are published in this issue, pp. 205–376.
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REACTIONS OF Ta ALKYLIDENE COMPLEXES WITH SILANES

(Me₃SiCH₂)₃Ta(PMe₃)[=CHSiMe₃] (1) [9] was found to react with H₂SiR'Ph (R' = Me, Ph) at 23 ºC to give (Me₃SiCH₂)₃Ta(PMe₃)[=C(SiMe₃)SiHR'Ph] (2a–b). Reactions of (Me₃SiCH₂)₂Ta(PMe₃)₂[=CHSiMe₃] (3) [4c,7] with H₂SiR'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 (H₂PhSi)₂CH₂ [10] was found to give 7, which was isolated as the meso-isomer (Scheme 1).

The reaction of 1 with excess D₂SiMePh was found to give (Me₃SiCH₂)₃Ta[=C(SiMe₃)SiDMePh] (5a–d), HDSiMePh, and D₂ as the major gaseous product. Kinetic studies of this reaction suggested a pathway involving the loss of PMe₃, followed by addition of the silane to the Ta=C bond, leading to products. These observations are consistent with the mechanism in Scheme 2.

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

When M(NMe₂)₄ was exposed to excess SiH₄, instantaneous reactions were observed yielding HSi(NMe₂)₃, H₂, and black solids. No HNMe₂ was detected. Analyses of the black solids showed –NMe₂ but no silyl groups. The reaction of the solids with DCI–D₂O yielded H₂, HD, and D₂ as well as DNMe₂, but no HDSiR₂. These results indicated that the black solids contained –NMe₂ and –H ligands. Heating the black solids from the reactions of Ti(NMe₂)₄ with SiH₄ to 297–1100 ºC gave mainly mixtures of TiN and Si₃N₄ [11]. The reaction of Ti(NMe₂)₄ with SiH₄ conducted in a chemical vapor deposition (CVD) reactor at 300–450 ºC was found to give thin films consistent with TiN and Si₃N₄ [11]. Reactions of Zr(NMe₂)₄ or Hf(NMe₂)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].

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$_2$)$_2$. 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].

\[
\begin{align*}
\text{Scheme 3} \\
\end{align*}
\]

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 ºC [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 I 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).

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\begin{align*}
\text{Scheme 4} \\
\end{align*}
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\begin{align*}
\text{Scheme 5} \\
\end{align*}
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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.

ACKNOWLEDGMENTS

We thank the U.S. National Science Foundation [CHE-9904338, CHE-9457368, and Research Experiences for Undergraduates (REU) program], Camille Dreyfus Teacher-Scholar program, DuPont Young Professor program, U.S. Department of Energy under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, and the Research Grant Council of Hong Kong for financial support. We also thank Prof. David C. Joy for help with EDS analysis.

REFERENCES AND NOTES


11. There were also graphitic carbon and TiO₂ as identified by XPS.


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