

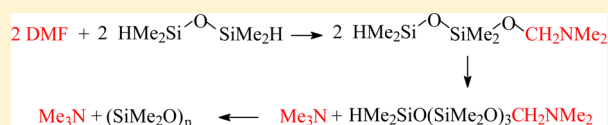
Platinum-Catalyzed Reduction of DMF by 1,1,3,3-Tetramethyldisiloxane, HMeSi₂OSiMe₂H: New Intermediates HSiMe₂OSiMe₂OCH₂NMe₂ and HSiMe₂(OSiMe₂)₃OCH₂NMe₂ and Their Further Chemical Reactivity

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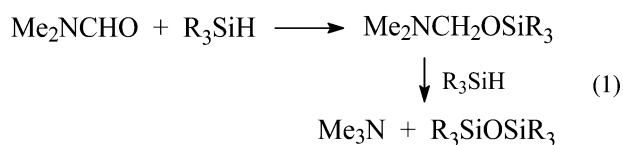
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S Supporting Information

ABSTRACT: The use of Karstedt's catalyst to study the reduction of Me₂NCHO (DMF) by the popular "dual SiH"-containing tetramethyldisiloxane, HMe₂SiOSiMe₂H (**1**), has revealed that the first step in the process involves an initial single hydrosilylation to form HSiMe₂OSiMe₂OCH₂NMe₂ (**3**). This intermediate is readily isolated and purified via distillation. In the continued presence of the catalyst, **3** transforms to the transient tetrasiloxane HMe₂SiOSiMe₂OSiMe₂OCH₂NMe₂ (**4**), along with the formation of Me₃N. The tetrasiloxane **4** itself transforms to Me₃N and (Me₂SiO)_n (*n* = 4–6). Despite the demonstrated reactivity of **3**, it can also be used to perform the expected metal-catalyzed hydrosilylation chemistry of the SiH group as well as reactions of the SiOCH₂NMe₂ functionality involving siloxane chain extension and is thus an important new reagent for siloxane chemistry.



Since the initial, and generally uncited, report by the Voronkov group that silanes, R₃SiH, could effectively reduce DMF to Me₃N with concomitant formation of disiloxanes,¹ their use as reducing agents to transform amides to amines has been well-studied and widely used due to the generally mild reaction conditions employed.² Using monosilanes, R₃SiH, to reduce DMF as a model amide, we recently demonstrated that such reductions proceed via an initial hydrosilylation reaction to produce siloxy-methylamines R₃SiOCH₂NMe₂ (O-silylated hemi-aminals).³ This class of compounds can further react with silanes in the presence of catalysts, and also in excess DMF, to form the amine and appropriate disiloxane (eq 1).



A particularly versatile silane for such reductions is 1,1,3,3-tetramethyldisiloxane, HSiMe₂OSiMe₂H (**1**), and using a range of catalysts, including Karstedt's catalyst (bis[1,3-bis(η²-ethenyl)-1,1,3,3-tetramethyldisiloxane]platinum), this reagent possesses some unique reduction characteristics.^{4–6} For example, it has been demonstrated that **1** can effectively reduce amides under conditions where other silanes are ineffective and this special property has been associated with a "dual SiH effect".^{5a} Furthermore, the same disiloxane has been noted as a poor reagent for other reactions.^{5c} We have previously reported that using **1** in the presence of (Me₃N)Mo(CO)₅ as catalyst, for the reduction of DMF, a double hydrosilylation occurs to form Me₂NCH₂OSiMe₂OSiMe₂OCH₂NMe₂ (**2**), which can be isolated and characterized.⁷ As a continuation of our studies in

this arena we have now used Karstedt's catalyst to study the reaction of **1** with DMF, monitoring the reaction with ²⁹Si, ¹³C, and ¹H NMR spectroscopy. Typical monitoring sequences of such a reaction in C₆D₆ at room temperature (~295 K) are presented in Figures 1 (²⁹Si) and 2 (¹³C). Along with the

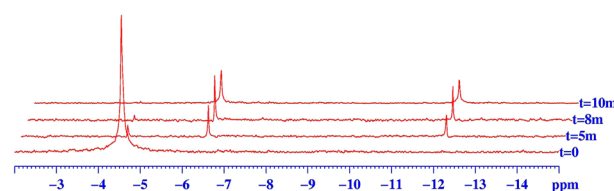


Figure 1. ²⁹Si NMR monitoring of the reaction between HSiMe₂OSiMe₂H (−4.6 ppm) and DMF (1:5 molar ratio) catalyzed by 1 mol % of Karstedt's catalyst, illustrating the formation of **3** (−6.4 and −12.2 ppm).

disappearance of the ²⁹Si resonance at −4.6 ppm due to **1**, there is a growth of two resonances at −6.4 and −12.2 ppm, and under the reaction conditions used, no further significant chemistry takes place.

The related ¹³C spectral sequence (Figure 2) exhibits the appearance of new resonances at 81.7, 41.0, 0.84, and −0.89 ppm typical of the SiOCH₂NMe₂ group and two new Me₂Si units. The new material is the single hydrosilylation product, Me₂NCH₂OSiMe₂OSiMe₂H (**3**; eq 2).

The same chemistry takes place on a larger preparative scale using either hexane or benzene as solvent, and we have been

Received: April 26, 2014

Published: June 11, 2014

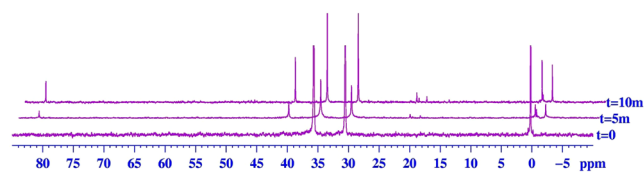
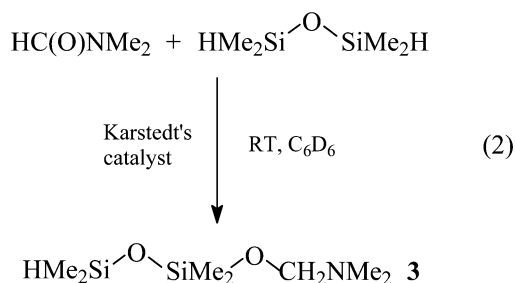


Figure 2. ^{13}C NMR monitoring of the reaction between $\text{HSiMe}_2\text{OSiMe}_2\text{H}$ (0.1 ppm) and DMF (1:5 molar ratio) catalyzed by 1 mol % of Karstedt's catalyst, illustrating the formation of **3** (81.7 (CH_2), 41.0 (NMe_2), 0.84 and -0.89 ppm (SiMe)). Me resonances for DMF appear at 30.6 and 35.2 ppm.



able to isolate this material by distillation at $49^\circ\text{C}/15$ mmHg in excellent yield. Compound **3** is relatively stable at room temperature; however, when it is subjected to the presence of Karstedt's catalyst the ^{29}Si resonances at -6.4 and -12.2 ppm transform to four new signals at -6.7 , -13.9 , -19.8 , and -21.5 ppm and via ^{13}C NMR we observe the concurrent formation of Me_3N . The new silicon-containing material is the tetrasiloxane $\text{HSiMe}_2\text{OSiMe}_2\text{OSiMe}_2\text{OSiMe}_2\text{OCH}_2\text{NMe}_2$ (**4**). While we have been unable to obtain **4** as an analytically pure material, we have been able to prepare and isolate it in $\sim 95\%$ purity and study its further chemistry, as described in the Supporting Information. Continued exposure of **4** to the catalytic conditions results in formation of more Me_3N and a mixture of cyclic dimethylpolysiloxanes, $(\text{Me}_2\text{SiO})_n$ ($n = 4$, **D4**; $n = 5$, **D5**; $n = 6$, **D6**), as noted by comparison of their ^{29}Si NMR and GC/MS spectra with those of known materials (Figures S-5–S-8, respectively (Supporting Information)). The ^{29}Si and ^{13}C monitoring of this transformation is presented in Figures 3 and 4, respectively.

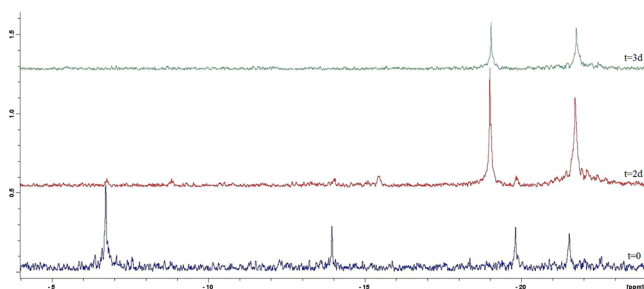


Figure 3. Transformation of **4** (-6.7 , -13.9 , -19.8 , and -21.5 ppm) to predominantly **D4** (-19.1 ppm) and **D6** (-21.6 ppm) monitored by ^{29}Si NMR.

To prove the structure and formulation, we have reacted **4** with Me_3SiCl . This procedure results in the formation and high-yield isolation of the expected pentasiloxane $\text{HSiMe}_2\text{OSiMe}_2\text{OSiMe}_2\text{OSiMe}_2\text{OSiMe}_3$ (**5**), a known compound.⁸

Overall during the reduction of DMF by **1**, the initially formed hydrosilylation product **3** reacts with itself to liberate

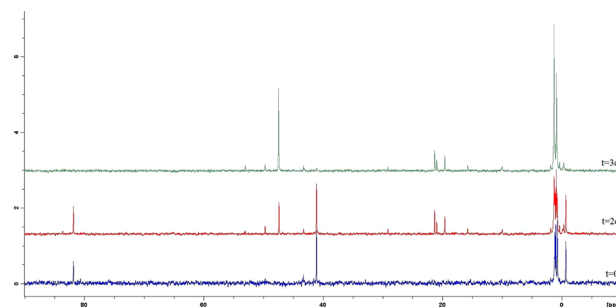
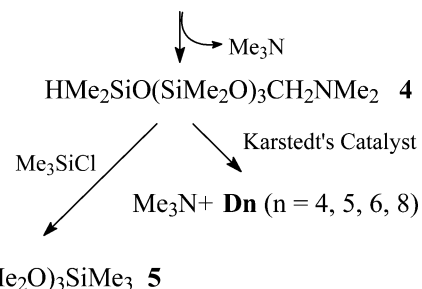


Figure 4. Transformation of **4** (81.8 ppm (CH_2); 41.1 ppm (NMe_2)) to Me_3N (47.5 ppm) and **D4–6** monitored by ^{13}C NMR. The minor resonances at ~ 20 ppm are associated with the xylene solvent of the catalyst solution.

Me_3N and **4**, which further eliminates Me_3N along with formation of **Dn**, both reactions demonstrating the reactivity of the siloxymethylamines with SiH species involving formation of Me_3N and siloxanes (Scheme 1).³ This is a further illustration

Scheme 1. Sequence of Reactions Leading to Production of Me_3N and **Dn**



of the capacity of hydrosilanes to reduce siloxymethylamines (O-silylated hemi-aminals), as illustrated in eq 1, and the more general capacity to reduce aminals.⁹

The transformation of **4** to Me_3N poses the question as to whether this is an intramolecular elimination reaction or involves a bimolecular reaction with a second SiH functionality. Since the silicon-containing compound formed is predominantly **D4** and we see no significant amounts of long-chain polysiloxanes, we favor the intramolecular amine elimination. We attempted to answer that question by D-labeling experiments using deuteriotetramethyldisiloxane, $\text{DSiMe}_2\text{OSiMe}_2\text{D}$ (**1D**). Use of **1D** to reduce DMF resulted, as expected, in the formation of Me_2NCHD_2 . However, using an equimolar mixture of **1** and **1D** resulted predominantly in the formation of $\text{Me}_2\text{NCH}_2\text{D}$ and Me_3N and smaller amounts of Me_2NCHD_2 ; i.e., a significant H/D scrambling had occurred (Figure S-4 (Supporting Information)). Separate experiments mixing **1D** and Et_3SiH resulted in a very rapidly established equilibrium illustrating the metal-catalyzed H/D exchange in hydrosilanes,¹¹ thus ruling out the mechanistic clarification we sought.

As we previously reported, the use of $(\text{Me}_3\text{N})\text{Mo}(\text{CO})_5$ as catalyst for the reduction of DMF by **1** proceeds via a different route, involving the intermediacy of the double-hydrosilylation intermediate $(\text{Me}_2\text{NCH}_2\text{OSiMe}_2)_2\text{O}$.⁷ We have treated the new intermediate **3** with DMF in the presence of the molybdenum catalyst and observed the rapid formation of $(\text{Me}_2\text{NCH}_2\text{OSiMe}_2)_2\text{O}$ (**2**) with no initial Me_3N formation, illustrated in Figure 5. The two catalysts clearly have distinctive properties in this chemistry,

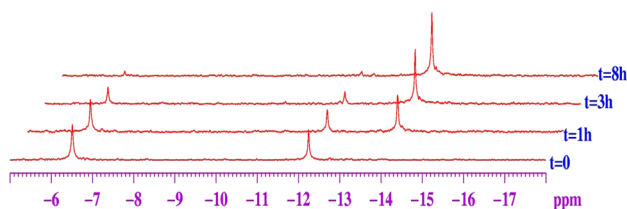
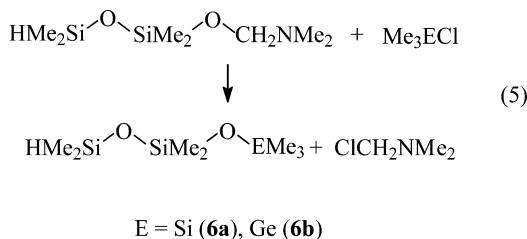


Figure 5. ^{29}Si NMR monitoring of the reaction between DMF and $\text{HSiMe}_2\text{OSiMe}_2\text{OCH}_2\text{NMe}_2$ (**3**) catalyzed by 1 mol % of $(\text{Me}_3\text{N})\text{-Mo}(\text{CO})_5$ leading to $\text{Me}_2\text{NCH}_2\text{OSiMe}_2\text{OSiMe}_2\text{OCH}_2\text{NMe}_2$ (**2**) at -13.9 ppm.

and studies to tease out these distinctions, along with those of other catalysts, are in progress.

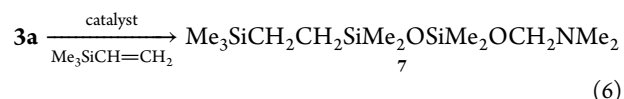
Treatment of **3** under varying conditions of the functional group reactivity was performed to illustrate that the two terminal silyl groups (SiH and $\text{SiOCH}_2\text{NMe}_2$) retain their established chemistry in the presence of each other, even in the presence of metal catalysts. Thus, the reaction of **3** with Me_3ECl ($\text{E} = \text{Si}, \text{Ge}$) led to the high-yield formation of the siloxane chain extension products, resulting in either trisiloxane **6a** or disiloxgermoxane **6b** (eq 5).



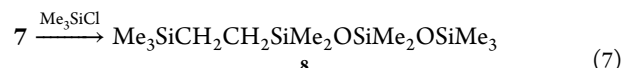
The trisiloxane **6a** is a useful, commercially available reagent,¹² whereas the germanium analogue is unreported. All analytical and spectroscopic data are in accord with either the published data or those expected. For example, the ^{29}Si NMR data for **6a** exhibits three resonances at 7.4, -6.9 , and -19.4 ppm for the Me_3SiO , HMe_2SiO , and Me_2SiO silicon atoms, respectively. The Ge analogue **6b** exhibits ^{29}Si resonances at -8.2 and -17.6 ppm, in accord with expectation.

The chemistry of the SiH functionality of **3** was initially expected to be complicated, since the hydrosilylation reaction normally needs a catalytic species similar to that required for

the amine elimination/amide reduction product (eq 2). Hence, a competition between hydrosilylation and amine elimination was anticipated. However, in a test hydrosilylation reaction we treated **3** with $\text{Me}_3\text{SiCH}=\text{CH}_2$ in the presence of Karstedt's catalyst and obtained a high yield of the "expected" hydrosilylation product **7** (eq 6). No amine elimination chemistry was observed and the hydrosilylation appears to be regioselective.



Compound **7** can be readily reacted with chlorosilanes for further siloxane chain extension (eq 7).



Thus, the newly observed and isolated material **3** has three distinct and very useful modes of chemistry: elimination of the reduced amide as the amine, hydrosilylation using the SiH group, and siloxane chain extension using the $\text{SiOCH}_2\text{NMe}_2$ functionality (Scheme 2).

■ ASSOCIATED CONTENT

📄 Supporting Information

Text and figures giving experimental details and spectroscopic/analytical data for all compounds prepared in this paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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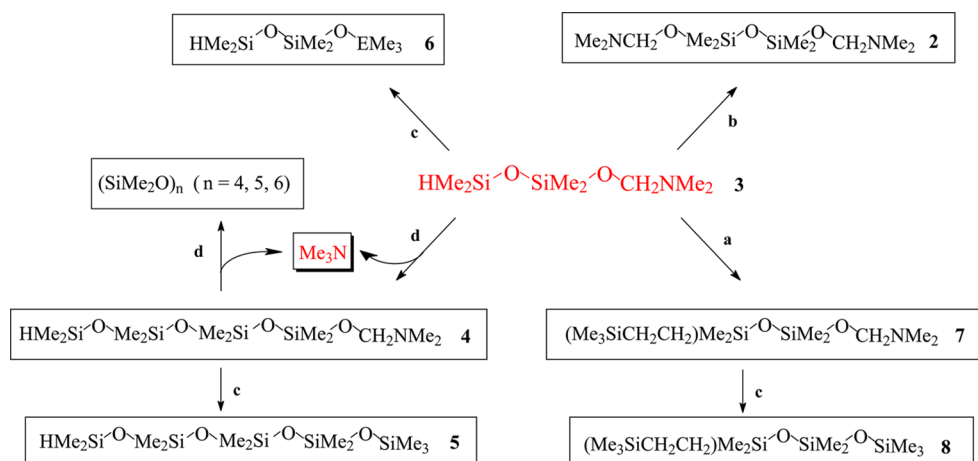
Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Welch Foundation (Grant No. AH-0546) and the NIH-MARC program (Grant No. 2T34GM008048) for support of this research.

Scheme 2. Reactivity of **3**^a



^aLegend: (a) $\text{Me}_3\text{SiCH}=\text{CH}_2$ /Karstedt's catalyst; (b) $(\text{Me}_3\text{N})\text{Mo}(\text{CO})_5$ /DMF; (c) Me_3ECl , $\text{E} = \text{Si}, \text{Ge}$; (d) Karstedt's catalyst.

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