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Platinum-Catalyzed Reduction of DMF by 1,1,3,3-Tetramethyldisiloxane, $HMeSi_2OSiMe_2H$: New Intermediates $HSiMe_2OSiMe_2OCH_2NMe_2$ and $HSiMe_2(OSiMe_2)_3OCH_2NMe_2$ and Their Further Chemical Reactivity

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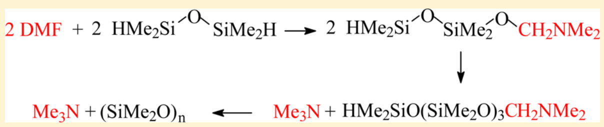
Supporting Information



ABSTRACT: The use of Karstedt's catalyst to study the reduction of Me_2NCHO (DMF) by the popular "dual SiH"-containing tetramethyldisiloxane, $HMe_2SiOSiMe_2H$ (**1**), has revealed that the first step in the process involves an initial single hydrosilylation to form $HSiMe_2OSiMe_2OCH_2NMe_2$ (**3**). This intermediate is readily isolated and purified via distillation. In the continued presence of the catalyst, **3** transforms to the transient tetrasiloxane $HMe_2SiOSiMe_2OSiMe_2OSiMe_2OCH_2NMe_2$ (**4**), along with the formation of Me_3N. The tetrasiloxane **4** itself transforms to Me_3N and $(Me_2SiO)_n$ (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 $SiOCH_2NMe_2$ 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, R_3SiH, could effectively reduce DMF to Me_3N 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, R_3SiH, to reduce DMF as a model amide, we recently demonstrated that such reductions proceed via an initial hydrosilylation reaction to produce siloxymethylamines $R_3SiOCH_2NMe_2$ (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).

$$\begin{tikzcd} Me_2NCHO + R_3SiH \arrow[r] & Me_2NCH_2OSiR_3 \arrow[d, "R_3SiH"] \\ & Me_3N + R_3SiOSiR_3 \end{tikzcd} \qquad (1)$$

A particularly versatile silane for such reductions is 1,1,3,3-tetramethyldisiloxane, $HSiMe_2OSiMe_2H$ (**1**), and using a range of catalysts, including Karstedt's catalyst (bis[1,3-bis(η^2-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 $(Me_3N)Mo(CO)_5$ as catalyst, for the reduction of DMF, a double hydrosilylation occurs to form $Me_2NCH_2OSiMe_2OSiMe_2OCH_2NMe_2$, (**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 ^{29}Si, ^{13}C, and ^1H NMR spectroscopy. Typical monitoring sequences of such a reaction in C_6D_6 at room temperature (~295 K) are presented in Figures 1 (^{29}Si) and 2 (^{13}C). Along with the disappearance of the ^{29}Si 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.

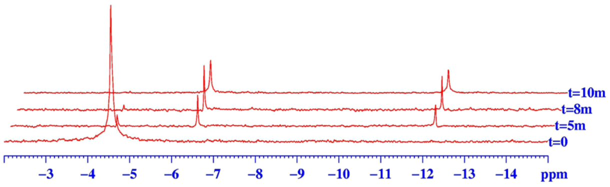


Figure 1. ^{29}Si NMR monitoring of the reaction between $HSiMe_2OSiMe_2H$ (−4.6 ppm) and DMF (1:5 molar ratio) catalyzed by 1 mol % of Karstedt's catalyst, illustrating the formation of **3** (−6.4 and −12.2 ppm).

The related ^{13}C spectral sequence (Figure 2) exhibits the appearance of new resonances at 81.7, 41.0, 0.84, and −0.89 ppm typical of the $SiOCH_2NMe_2$ group and two new Me_2Si units. The new material is the single hydrosilylation product, $Me_2NCH_2OSiMe_2OSiMe_2H$ (**3**; eq 2).

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

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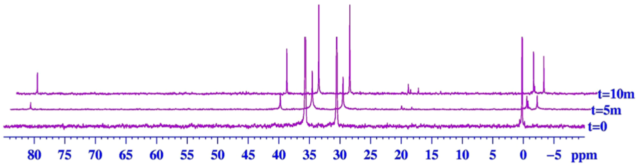
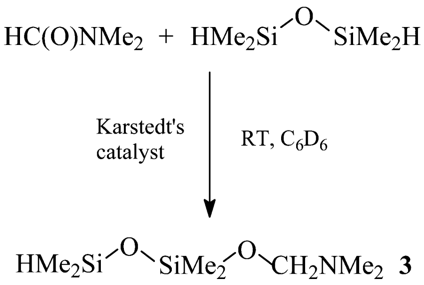


Figure 2. ^{13}C NMR monitoring of the reaction between $HSiMe_2OSiMe_2H$ (0.1 ppm) and DMF (1:5 molar ratio) catalyzed by 1 mol % of Karstedt's catalyst, illustrating the formation of **3** (81.7 (CH_2), 41.0 (NMe_2), 0.84 and −0.89 ppm (SiMe)). Me resonances for DMF appear at 30.6 and 35.2 ppm.



$$\mathrm{HC(O)NMe_2 + HMe_2Si{-}O{-}SiMe_2H} \xrightarrow[\text{RT, } C_6D_6]{\text{Karstedt's catalyst}} \mathrm{HMe_2Si{-}O{-}SiMe_2{-}O{-}CH_2NMe_2} \quad (2)$$

3

able to isolate this material by distillation at 49 °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 $HSiMe_2OSiMe_2OSiMe_2OSiMe_2OCH_2NMe_2$ (**4**). While we have been unable to obtain **4** as an analytically pure material, we have been able to prepare and isolate it in ~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, $(Me_2SiO)_n$ (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.

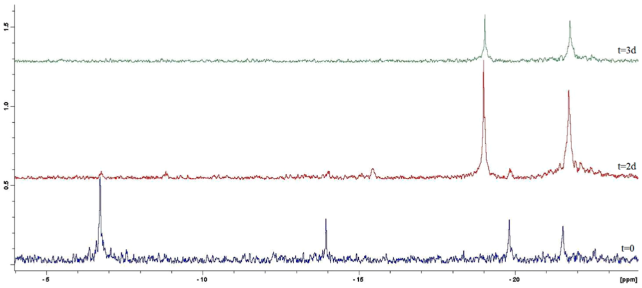


Figure 3. Transformation of **4** (−6.7, −13.9, −19.8, and −21.5 ppm) to predominantly **D4** (−19.1 ppm) and **D6** (−21.6 ppm) monitored by ^{29}Si NMR.

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 $HSiMe_2OSiMe_2OSiMe_2OSiMe_2OSiMe_3$ (**5**), a known compound.[8]

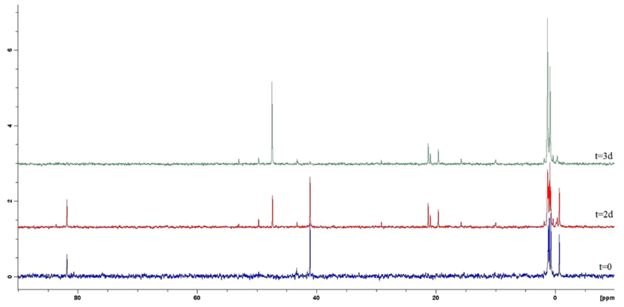
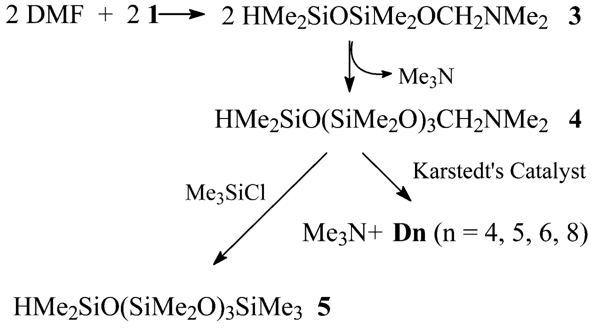


Figure 4. Transformation of **4** (81.8 ppm (CH_2); 41.1 ppm (Me_2N) to Me_3N (47.5 ppm) and **D4−6** monitored by ^{13}C NMR. The minor resonances at ~20 ppm are associated with the xylene solvent of the catalyst solution.

Overall during the reduction of DMF by **1**, the initially formed hydrosilylation product **3** reacts with itself to liberate Me_3N and **4**, which further eliminates Me_3N along with formation of **D*n***, 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 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]

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



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, $DSiMe_2OSiMe_2D$[10] (**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 Me_2NCH_2D 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 $(Me_3N)Mo(CO)_5$ as catalyst for the reduction of DMF by **1** proceeds via a different route, involving the intermediacy of the double-hydrosilylation intermediate $(Me_2NCH_2OSiMe_2)_2O$.[7] We have treated the new intermediate **3** with DMF in the presence of the molybdenum catalyst and observed the rapid formation of $(Me_2NCH_2OSiMe_2)_2O$ (**2**) with no initial Me_3N formation, illustrated in Figure 5. The two catalysts clearly have distinctive properties in this chemistry,

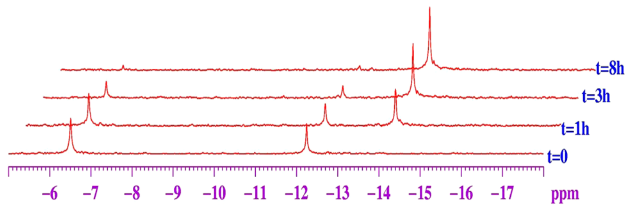
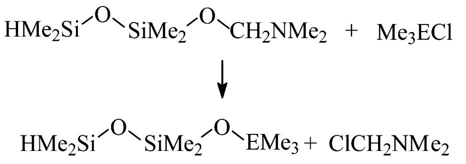


Figure 5. ^{29}Si NMR monitoring of the reaction between DMF and $HSiMe_2OSiMe_2OCH_2NMe_2$ (**3**) catalyzed by 1 mol % of $(Me_3N)Mo(CO)_5$ leading to $Me_2NCH_2OSiMe_2OSiMe_2OCH_2NMe_2$, (**2**) at −13.9 ppm.

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 $SiOCH_2NMe_2$) 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 (E = Si, Ge) led to the high-yield formation of the siloxane chain extension products, resulting in either trisiloxane **6a** or disiloxygermoxane **6b** (eq 5).



$$HMe_2SiOSiMe_2OCH_2NMe_2 + Me_3ECl \longrightarrow HMe_2SiOSiMe_2OEMe_3 + ClCH_2NMe_2 \qquad (5)$$

E = Si (**6a**), Ge (**6b**)

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 $Me_3SiCH{=}CH_2$ 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 regiospecific.

$$\mathbf{3a} \xrightarrow[Me_3SiCH{=}CH_2]{\text{catalyst}} \underset{\mathbf{7}}{Me_3SiCH_2CH_2SiMe_2OSiMe_2OCH_2NMe_2} \qquad (6)$$

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

$$\mathbf{7} \xrightarrow{Me_3SiCl} \underset{\mathbf{8}}{Me_3SiCH_2CH_2SiMe_2OSiMe_2OSiMe_3} \qquad (7)$$

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 $SiOCH_2NMe_2$ 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.

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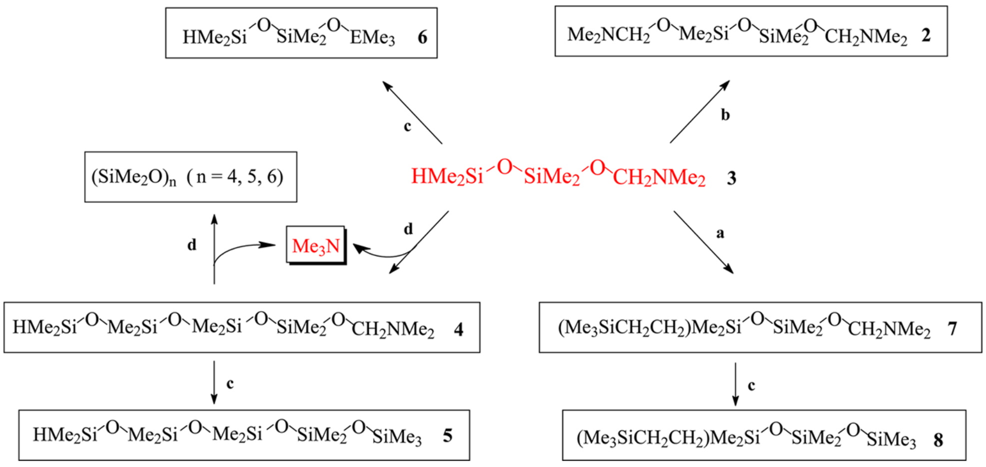
Scheme 2. Reactivity of 3[a]



[a] Legend: (a) $Me_3SiCH{=}CH_2$/Karstedt's catalyst; (b) $(Me_3N)Mo(CO)_5$/DMF; (c) Me_3ECl, E = Si, Ge; (d) Karstedt's catalyst.

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