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

Jorge L. Martinez, Hemant K. Sharma, Renzo Arias-Ugarte, and Keith H. Pannell*

Department of Chemistry, The University of Texas at El Paso, El Paso, Texas 79968-0513, United States

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 HMe₂SiOSiMe₂OSiMe₂OSiMe₂OCH₂NMe₂ (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.

Supporting Information

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 siloxymethylamines 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).

Me₂NCHO + R₃SiH → Me₂NCH₂OSiR₃
R₃SiH
Me₃N + R₃SiOSiR₃

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 Me₃NCH₂OSiMe₂OSiMe₂OCH₂NMe₂ (2), which can be isolated and characterized.⁷ As a continuation of our studies in this area 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 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.

![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).](image-url)

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, Me₂NCH₂OSiMe₂OSiMe₂OCH₂NMe₂ (3); eq 2).

2 DMF + 2 HMe₂SiO⁻SiMe₂H → 2 HMe₂SiO⁻SiMe₂OCH₂NMe₂
Me₂N + (SiMe₂-O)ₙ → Me₃N + HMe₂SiO(SiMe₂-O)ₙCH₂NMe₂

This new material is isolated and characterized as a transient tetrasiloxane, HMe₂SiOSiMe₂OSiMe₂OSiMe₂OCH₂NMe₂ (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.
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 $^{29}\text{Si}$ 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 $^{13}\text{C}$ NMR we observe the concurrent formation of Me$_3$N. The new silicon-containing material is the tetrasiloxane HSiMe$_2$OSiMe$_2$OSiMe$_2$OSiMe$_2$OCH$_2$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 ~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$_3$N and a mixture of cyclic dimethylpolysiloxanes, (Me$_2$SiO)$_n$ ($n = 4$, D$_4$; $n = 5$, D$_5$; $n = 6$, D$_6$), as noted by comparison of their $^{29}\text{Si}$ NMR and GC/MS spectra with those of known materials (Figures S-5–S-8, respectively (Supporting Information)). The $^{29}\text{Si}$ and $^{13}\text{C}$ monitoring of this transformation is presented in Figures 3 and 4, respectively.

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

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

The transformation of 4 to Me$_3$N 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 D$_4$ 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$_2$OSiMe$_2$D$_{10}$ (1D). Use of 1D to reduce DMF resulted, as expected, in the formation of Me$_3$NCHD$_2$. However, an equimolar mixture of 1 and 1D resulted predominantly in the formation of Me$_3$NCH$_2$D and Me$_3$N and smaller amounts of Me$_3$NCHD$_2$; i.e., a significant H/D scrambling had occurred (Figure S-4 (Supporting Information)). Separate experiments mixing 1D and Et$_3$SiH resulted in a very rapidly established equilibrium illustrating the metal-catalyzed H/D exchange in hydrosilanes, thus ruling out the mechanistic clarification we sought.

As we previously reported, the use of (Me$_3$N)Mo(CO)$_5$ as catalyst for the reduction of DMF by I proceeds via a different route, involving the intermediacy of the double-hydrosilylation intermediate (Me$_3$NCH$_2$OSiMe$_2$)$_2$O. We have treated the new intermediate 3 with DMF in the presence of the molybdenum catalyst and observed the rapid formation of (Me$_3$NCH$_2$OSiMe$_2$)$_2$O (2) with no initial Me$_3$N formation, illustrated in Figure 5. The two catalysts clearly have distinctive properties in this chemistry.
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 SiOCH₂NMe₂) retain their established chemistry in the presence of each other, even in the presence of metal catalysts. Thus, the reaction of 3 with Me₃ESC (= Si, Ge) led to the high-yield formation of the siloxane chain extension products, resulting in either trisiloxane 6a or disiloxyg germoxane 6b (eq 5).

The trisiloxane 6a is a useful, commercially available reagent, 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 ²⁹Si NMR data for 6a exhibits three resonances at 7.4, −6.9, and −19.4 ppm for the Me₃SiO, HMe₂SiO, and Me₂SiO silicon atoms, respectively. The Ge analogue 6b exhibits ²⁹Si 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 Me₃SiCH=CH₂ 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.

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 SiOCH₂NMe₂ functionality (Scheme 2).

Scheme 2. Reactivity of 3

![Scheme 2. Reactivity of 3](image)

**Legend:** (a) Me₃SiCH=CH₂/Karstedt’s catalyst; (b) (Me₃N)Mo(CO)₅/DMF; (c) Me₃ECl, E = Si, Ge; (d) Karstedt’s catalyst.
REFERENCES

(1) Kopylova, L. I.; Ivanova, N. D.; Voronkov, M. G. Zh. Obshch. Khim. 1985, 55, 1649–1651.
(2) (a) Motoyama, Y.; Mitsui, K.; Ishida, T.; Nagashima, H. J. Am. Chem. Soc. 2005, 127, 13150–13151. (b) Hanada, S.; Motoyama, Y.; Nagashima, H. Tetrahedron Lett. 2006, 47, 6173–6177. (c) Matsubara, K.; Iura, T.; Makí, T.; Nagashima, H. J. Org. Chem. 2002, 67, 4985–4988. (d) Zhou, S.; Junge, K.; Adis, D.; Das, S.; Beller, M. Angew. Chem., Int. Ed. 2009, 48, 9507–9510. (e) Das, S.; Addis, D.; Zhou, S.; Junge, K.; Beller, M. J. Am. Chem. Soc. 2010, 132, 1770–1771. (f) Das, S.; Addis, D.; Junge, K.; Beller, M. Chem. Eur. J. 2011, 17, 12186–12192. (g) Miles, D.; Ward, J.; Foucher, D. A. Macromolecules 2009, 42, 9199–9203. (h) Park, S.; Brookhart, M. J. Am. Chem. Soc. 2012, 134, 640–653. (i) Cheng, C.; Brookhart, M. J. Am. Chem. Soc. 2012, 134, 11304–11307. (j) Li, B.; Sortais, J.-B.; Darcel, C. Chem. Commun. 2013, 49, 3691–3693. (k) Volkov, A.; Buitrago, E.; Adolfsson, H. Eur. J. Org. Chem. 2013, 11, 2066–2070.
(3) Arias-Ugarte, R.; Sharma, H. K.; Morris, A. L. C.; Pannell, K. H. J. Am. Chem. Soc. 2012, 134, 848–851.
(4) Larson, G. L. Chim. Oggi 2013, 31, 36–39.
(5) (a) Hanada, S.; Tsutsumi, E.; Motoyama, Y.; Nagashima, H. J. Am. Chem. Soc. 2009, 131, 15032–15040. (b) Reeves, J. T.; Tan, Z.; Marsini, M. A.; Han, Z. S.; Xu, Y.; Reeves, D. C.; Lee, H.; Lu, B. Z.; Senanayake, C. H. Adv. Synth. Catal. 2013, 1, 47–52. (c) Pisiewicz, S.; Junge, K.; Beller, M. Eur. J. Inorg. Chem. 2014, 2345–2349.
(6) Two recent reviews from an academic and industrial viewpoint: (a) Hydroisilylation: A Comprehensive Review on Recent Advances; Marciniec, B., Ed.; Springer Science: Berlin, 2009. (b) Troegel, D.; Stohrer, J. Coord. Chem. Rev. 2011, 255, 1440–1459.
(7) Sharma, H. K.; Arias-Ugarte, R.; Tomlinson, D.; Gappa, R.; Metta Magna, A.; Ito, H.; Pannell, K. H. Organometallics 2013, 32, 3788–3794.
(8) Chai, M.; Rinaldi, P. L.; Hu, S. In NMR Spectroscopy of Polymers in Solution and in the Solid State; Cheng, H. N., English, A. D., Eds.; American Chemical Society: Washington, DC, 2002; ACS Symposium Series 834, pp 137–146.
(9) Larson, G. L.; Fry, J. L. Organic Reactions; Wiley: Hoboken, NJ, 2008; Vol. 71, Chapter 21.
(10) For the synthesis of DSiMe₂OSiMe₂D, see the Supporting Information.
(11) (a) Janowicz, A. H.; Bergman, R. G. J. Am. Chem. Soc. 1983, 105, 3929. (b) Iluc, V. M.; Fedorov, A.; Grubbs, R. H. Organometallics 2012, 31, 39–41.
(12) Gelest product SIH5844.0.