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$(Me_3N)Mo(CO)_5$-Catalyzed Reduction of DMF by Disiloxane and Disilane Moieties: Fate of the Silicon-Containing Fragments

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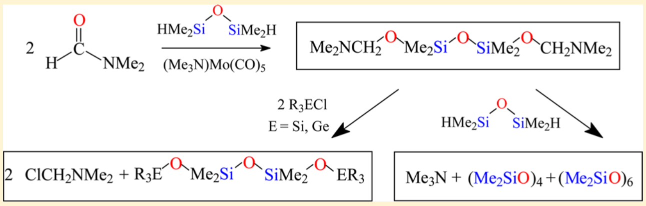
Ⓢ *Supporting Information*



ABSTRACT: The use of $HSiMe_2OSiMe_2H$ (**1**) and various hydrodisilanes, $R_3SiSiMe_2H$ (**2**; R = alkyl, aryl), as reductants for *N,N*-dimethylformamide (DMF) in the presence of $(Me_3N)Mo(CO)_5$ as a catalyst led to the formation of a series of novel and structurally interesting siloxanes as well as trimethylamine. In the case of **1** the cyclic poly(dimethylsiloxanes) $\mathbf{D_4}$ and $\mathbf{D_6}$ are obtained, and for **2** the products are bis(disilyl) ethers, $(R_3SiSiMe_2)_2O$. Siloxymethylamine intermediates resulting from an initial hydrosilylation of DMF, $(Me_2NCH_2OSiMe_2)_2O$ (**3**) and $R_3SiSiMe_2OCH_2NMe_2$ (**4**; R = Me, Ph), from the reactions of **1** and **2**, respectively, can be observed and, in the case of **3**, isolated and purified. In the presence of the respective starting silanes and the catalyst the intermediates readily react to form the appropriate siloxane materials and trimethylamine. Compound **3** was functionalized by reaction with R_3ECl (E = Si, Ge, R = Me, Ph) to provide group 14 containing products $(R_3EOSiMe_2)_2O$ (R = Me, E = Si (**5a**), Ge (**6a**); R = Ph, E = Si (**5b**), Ge (**6b**)). Reactions of $Me_3SiSiMe_2OCH_2NMe_2$ (**4a**) with R_3ECl produced $Me_3SiSiMe_2OER_3$ (R = Me, E = Si (**7**), R = Ph, E = Ge, **8**). The crystal structure of $(Ph_3SiSiMe_2)_2O$ (**9c**) is reported and exhibits an Si−O−Si angle of 165° and the longest Si−Si bond length (2.376(2) Å) for such bis(disilyl) ethers. The new $(Ph_3EOSiMe_2)_2O$ derivatives **5b** and **6b** have been structurally characterized and exhibit distinct conformations about the central SiOSi fragment. In the case of the Ph_3Si compound **5b** the dihedral angle between the two end groups is 180° with completely staggered SiMe groups on the central Si atoms, whereas for the Ge congener it is 55.7° and the structure exhibits eclipsed SiMe groups. The distinction seems to be due to both intra- and intermolecular phenyl group π stacking in **6b** stabilizing this formally higher energy conformation.

■ INTRODUCTION

The metal-catalyzed reduction of amides by hydrosilanes is now a well-established procedure effected by a range of both transition and main-group metals with significant application in the pharmaceutical industry.[1] Although the chemistry was first noted in 1985 for the reduction of DMF along with the formation of disiloxanes,[2] only recently has it developed into a reaction of choice due to its mildness and selectivity in comparison to classical methods.[3] We recently reported the reduction of simple formamides to amines using silanes, germanes, and stannanes with concomitant formation of disiloxanes, digermoxanes, and distannoxanes using $Mo(CO)_6$, $(Me_3N)Mo(CO)_5$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ (FpMe), $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3$ (MpMe), and $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ as catalysts.[4] For the reactions using $Mo(CO)_6$ and $(Me_3N)Mo(CO)_5$ we proposed a stepwise reduction mechanism based upon our first-time observation and isolation of the initial hydrosilylation products, i.e. siloxymethylamines, as intermediates (eq 1).[4b]

$$\mathrm{HC(O)NR'_2} + \mathrm{R_3SiH} \rightarrow \mathrm{R_3SiOCH_2NR'_2} \xrightarrow{\mathrm{R_3SiH}} \mathrm{CH_3NR'_2} + \mathrm{R_3SiOSiR_3} \tag{1}$$

We also reported the related reduction of dimethylthioformamide by silanes to produce Me_3N and disilyl thioethers, $R_3SiSSiR_3$; however, in that case no initial hydrosilylation intermediates were observed.[5a] A related reduction with Et_3SiH also resulting in the formation of bis(triethylsilyl) thioether, using FpMe as catalyst, was more recently reported involving the intermediacy of an interesting iron aminocarbene intermediate.[5b]

The disiloxane 1,1,3,3-tetramethyldisiloxane ($HSiMe_2OSiMe_2H$, **1**) has been reported as a useful amide reductant as well as an alkene hydrosilylation reagent.[6,7] Indeed, it has been suggested that organosilanes bearing two proximate SiH units allow the reduction of tertiary amides to take place under mild conditions, the so-called "dual SiH effect".[6] These reactions employed platinum catalysts and were noted to be amide-specific, and interestingly, there was no reaction when monosilanes bearing a single Si−H bond were used. However, during the use of **1** as an amide reductant no siloxymethylamine intermediates were noted and indeed such

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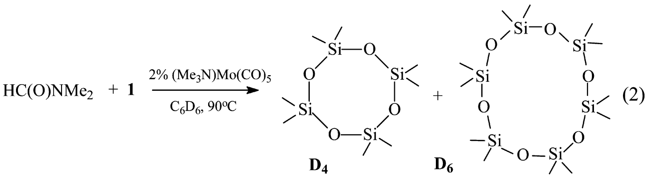
potential transients resulting from an initial hydrosilylation of the amide, e.g. $(\mathrm{Me_2NCH_2OSiMe_2})_2\mathrm{O}$ (**3**), are unknown. Furthermore, in the articles describing the use of **1** as an amide reductant, the ultimate fate of the silicon-containing species was described simply as "silicone waste".[6]

As a continuation of our interest in the reactions of the Si−H bond in the presence of transition metals, we have now explored the reduction of DMF employing **1**, attempting to observe possible siloxymethylamine transients using this reagent. Furthermore, we have extended the range of disilicon compounds useful as reductants by utilizing $\mathrm{R_3SiSiR_2H}$ (**2**; R = aryl, alkyl mixtures) for the metal-catalyzed reduction of DMF, with particular attention to the fate of the Si-containing species. Since the transition-metal-catalyzed activation of the Si−Si bond has been demonstrated, involving rearrangements, Si−Si bond rupture, etc.,[8] the ability to perform amide reduction using disilanes without cleavage of the Si−Si bond in the presence of transition-metal catalysts is an open and interesting question.

RESULTS AND DISCUSSION

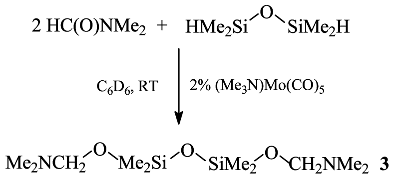
For the DMF reduction experiments we utilized $(\mathrm{Me_3N})\mathrm{Mo(CO)_5}$, 2−3 mol %, as the catalyst under thermal conditions on the basis of our previous studies, which showed its excellent solubility in the solvent of choice for monitoring these reactions, $\mathrm{C_6D_6}$. Thus, all reactions were performed thermally in an oil bath set at 90 °C unless specifically noted otherwise. The disiloxane and disilanes were allowed to react with a 3-fold molar excess of dimethylformamide (DMF) (relative to the active Si−H unit) and the progress of the reactions was monitored by ^{13}C and ^{29}Si NMR spectroscopy.

Use of Tetramethyldisiloxane ($\mathrm{HMe_2SiOSiMe_2H}$, 1). Despite the previous use of **1** as an amide-reducing agent, there is no record of the fate of the Si species subsequent to its use as a reductant other than the claim of "SiO" polymeric materials.[6] Additionally, there has been neither observation nor mention of an initial hydrosilylation product. Using the reaction conditions described above, 90 °C for ~12 h, along with the formation of $\mathrm{Me_3N}$ we observed and isolated the cyclic polysiloxanes octamethylcyclotetrasiloxane ($\mathbf{D_4}$) and dodecamethylcyclohexasiloxane ($\mathbf{D_6}$) in 35 and 16% yields, respectively, as the sole Si-containing materials (eq 2). The identity of these compounds was confirmed unambiguously by mass spectrometry and NMR spectroscopy in comparison to those data for authentic samples.[9] During the monitoring process we noted transient formation of the intermediate material **3**, but under the reaction conditions it could not be isolated.



$$\mathrm{HC(O)NMe_2} + \mathbf{1} \xrightarrow[\mathrm{C_6D_6},\ 90^\circ\mathrm{C}]{2\%\ (\mathrm{Me_3N})\mathrm{Mo(CO)_5}} \mathbf{D_4} + \mathbf{D_6} \qquad (2)$$

However, by performing and monitoring the reaction between **1** and DMF at room temperature, we could observe the high-yield formation of the initial hydrosilylated compound, **3** (eq 3). Optimal conditions for the high-yield preparation of this material involved using the reactant ratio [SiH]:[DMF] = 1:2 in the presence of 1−2 mol % of $(\mathrm{Me_3N})\mathrm{Mo(CO)_5}$ and allowing the mixture to stand at ambient temperatures overnight (12−14 h). Subsequent distillation under reduced pressure provided the product **3** in 72% yield. The new material exhibits three ^{13}C NMR resonances at −0.31 ($\mathrm{SiMe_2}$), 41.5 ($\mathrm{NMe_2}$), and 82.3 ppm ($\mathrm{CH_2}$) and a single ^{29}Si signal at −14.0 ppm, data in accord with those we previously reported for siloxymethylamines.[4]



$$2\,\mathrm{HC(O)NMe_2} + \mathrm{HMe_2Si{-}O{-}SiMe_2H} \xrightarrow[\mathrm{C_6D_6,\ RT}]{2\%\ (\mathrm{Me_3N})\mathrm{Mo(CO)_5}} \mathrm{Me_2NCH_2{-}O{-}Me_2Si{-}O{-}SiMe_2{-}O{-}CH_2NMe_2}\ \mathbf{3} \qquad (3)$$

We have previously shown that, using $(\mathrm{Me_3N})\mathrm{Mo(CO)_5}$ as a catalyst, the siloxymethylamine intermediates formed by initial hydrosilylation of DMF by monosilanes, $\mathrm{R_3SiOCH_2NMe_2}$ (e.g., $\mathrm{R_3}$ = $\mathrm{Et_3}$, $\mathrm{PhMe_2}$ etc.), further react with $\mathrm{R_3SiH}$ in the presence of excess DMF and/or the catalyst to form $\mathrm{R_3SiOSiR_3}$ and $\mathrm{Me_3N}$.[4] In the present case a similar chemistry can also be noted, as shown by the ^{13}C NMR monitoring of the reaction between DMF and **1** (1:3 molar ratio) (Figure 1). Such a sequence clearly denotes the intermediacy (appearance and disappearance) of **3** in the reduction process.

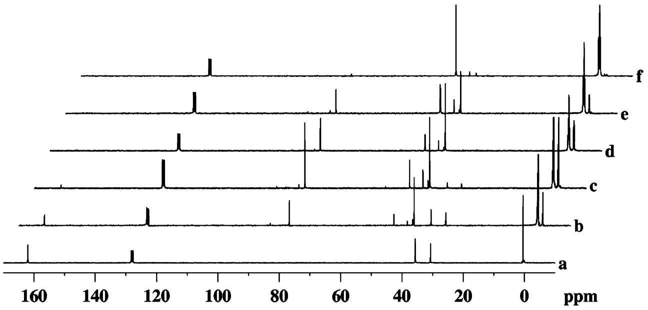
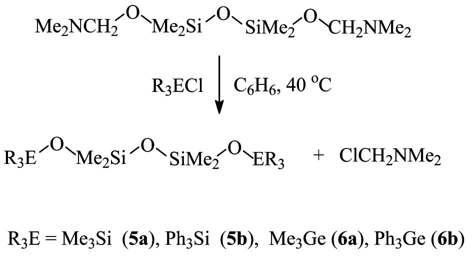


Figure 1. ^{13}C NMR monitoring of the catalyzed reaction between **1** and DMF, exhibiting the intermediacy of **3** with resonances at −0.31, 41.5, and 82.3 ppm and formation of $\mathrm{Me_3N}$ at ~47 ppm: (a) 0 h; (b) 0.5 h; (c) 1 h; (d) 5 h; (e) 16 h; (f) 19 h. For a−c the temperature was 40 °C; for d−f the temperature was raised to 80 °C.

Mironov et al.[10] and ourselves[4] have reported the functionalization of siloxymethylamines, $\mathrm{R_3SiOCH_2NMe_2}$, with $\mathrm{R_3ECl}$ (E = Si,[4,10] Ge,[4] Sn[4]) to form disiloxanes, siloxygermanes, and siloxystannanes, respectively. Siloxanes as materials have a history of a wide range of potential applications,[11] and furthermore the introduction of metal(loid)s to the structure of organosilicone compounds may result in materials with improved thermal, catalytic, and conducting properties; therefore, antimony-,[12a] arsenic-,[12b] boron-,[12c] tin-,[12d] and possibly lead-containing[12e] siloxanes have been investigated in this regard, although not always with success. With the high-yield isolation of compound **3** we have attempted extension of the Si−O−Si chain by reacting it with a variety of $\mathrm{R_3ECl}$ group 14 reagents ($\mathrm{R_3E}$ = $\mathrm{Me_3Si}$, $\mathrm{Ph_3Si}$, $\mathrm{Me_3Ge}$, $\mathrm{Ph_3Ge}$, $\mathrm{Bu_3Sn}$, $\mathrm{Ph_3Sn}$). In the case of the Si and Ge compounds the reaction led to the formation of $(\mathrm{R_3EOSiMe_2})_2\mathrm{O}$ (E = Si, (**5**), Ge (**6**); eq 4). The reactions of **3** with organotin chlorides led to the direct formation of only the cyclic polysiloxanes $\mathbf{D_4}$ and $\mathbf{D_6}$.

The spectroscopic and analytical data for **5** and **6** are in total accord with their proposed structures, and the data are collected in the Experimental Section. Compounds **5a** and **5b** have been reported previously;[13,14] however, no spectroscopic



(4)

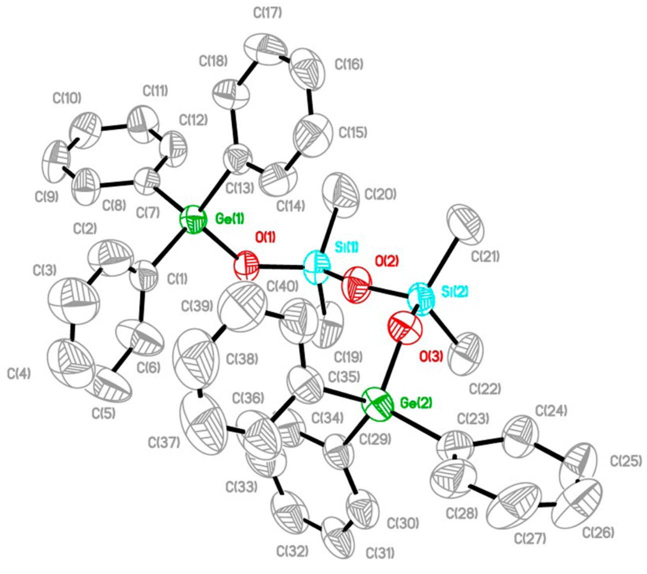


Figure 3. Molecular structure for **6b**. Ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): Ge1−O1 = 1.788(3), Ge2−O3 = 1.777(3), Si1−O1 = 1.619(3), Si2−O3 = 1.622(4), Si1−O2 = 1.624(3), Si2−O2 = 1.617(3); Ge1O1Si1 = 138.5(2), Ge2O3Si2 = 137.6(2), Si1O2Si2 = 155.5(3). The hydrogen atoms are omitted for clarity.

data were reported for **5b**, and the Ge analogues **6** are unreported. Both **5b** and **6b** are solid materials that we were able to crystallize from hexanes, and their structures are illustrated in Figures 2 and 3, respectively.

The bond angles and bond lengths of **5b** and **6b** are unremarkable. The internal Si−O−Si bond angles for **5b** and **6b** are 140 and 155°, respectively. In **5b** the external Si−O−Si angles are wider at 160.5°, whereas in **6b** the corresponding exterior Ge−O−Si angles are significantly reduced at ∼138°. The reduction of the Ge−O−Si bond angle in comparison to the Si−O−Si angle is expected, on the basis of the limited published data.[15] Thus, the 180° Si−O−Si angle in $Ph_3SiOSiPh_3$[15a] is dramatically reduced to 142.5° for the mixed germyl silyl ether $Ph_3GeOSiPh_3$,[15b] and a further reduction to 135.7° has been reported for the all-germanium ether $Ph_3GeOGePh_3$.[15c] These trends can be associated with the lesser ability of the oxygen lone pairs to be delocalized onto the germanium atom.

The dihedral angle X−(SiOSi)−X for **5b** is 180°, similar to that noted in the published structure of the related tetrasiloxane $(Ph_2MeSiOSiMe_2)_2O$.[16] However, for the germanium compound **6b** this angle is dramatically reduced to only 55.7(4)°. In the latter material this small angle results in the phenyl rings forming intramolecular (4.48 Å) and intermolecular (4.55 Å) close contacts. Although these distances are longer than the usually accepted limit for $\pi-\pi$ interactions, they seem important, since such a conformation results in eclipsed methyl groups at the Si atoms for **6b**, as shown in Figure 4. In contrast, **5b** with a dihedral angle of 180°, exhibits completely staggered silicon−methyl groups (Figure 5).

There is an analogue for the structural arrangement of **6b** in the compound 1,7-dihydroxy-1,1,7,7-tetramethyl-3,3,5,5-tetraphenyl-1,3,5,7-tetrasiloxane, $(Ph_2(OH)SiOSiMe_2)_2O$, which also exhibits a similar dihedral angle of 54.4°.[17] However, in this case, the hydroxyl groups play an important role in stabilizing this more energetic structure containing eclipsed Si−methyl groups by an intramolecular hydrogen-bonding interaction. It seems that in the solid state of **6b** even the very long inter- and intramolecular π-stacking phenyl groups have the capacity to provide some stabilization to the eclipsed methyl group conformation.

Attempts to synthesize the tin congeners of **5** and **6** were not successful. Only the cyclic polysiloxanes $\mathbf{D_4}$ and $\mathbf{D_6}$ were obtained, and the fate of the tin materials is unknown; however, in these reactions an insoluble material (SnO?) also was formed. The sole formation of cyclic polysiloxanes is presumably related to the use of such organotins as catalysts

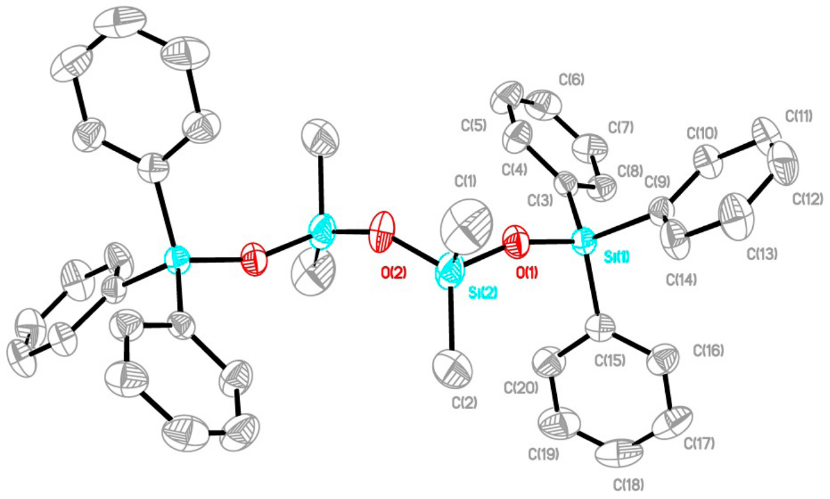


Figure 2. Molecular structure for **5b**. Thermal ellipsoids are drawn at the 35% probability level. Selected bond distances (Å) and angles (deg): Si1−O1 = 1.622(2), Si2−O1 = 1.598(2), Si2−O2 = 1.545(5); Si1O1Si2 = 160.5(2), Si2O2Si2#1 = 140.4(3). The hydrogen atoms are omitted for clarity.

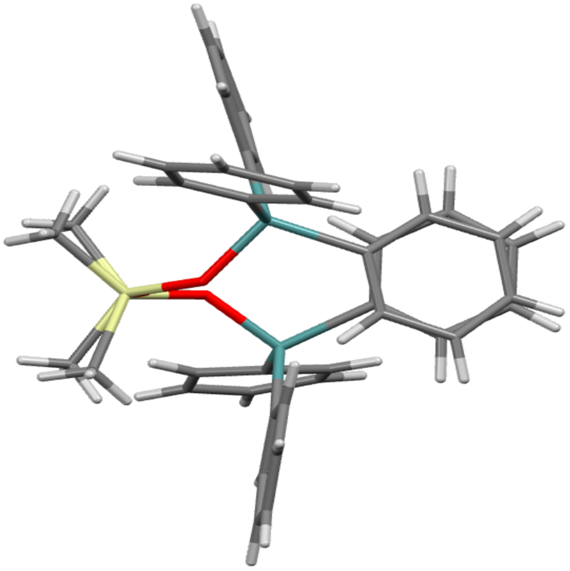


Figure 4. Structure of **6b** showing the eclipsed conformation along the Si–O–Si bond.

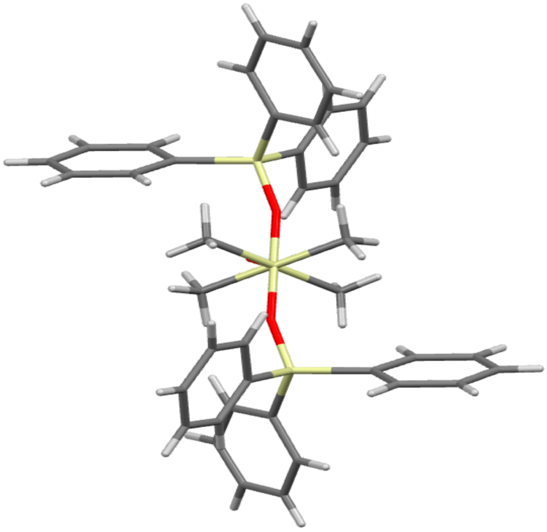


Figure 5. Structure of **5b** showing the staggered conformation along the Si–O–Si bond.

for the condensation of siloxane diols and functional silanes, leading to useful polysiloxanes under mild conditions.[18] Certainly many cyclic stannasiloxanes have been reported and have a thermodynamic and kinetic stability suggesting that under our reaction conditions they should be observed.[19] At present we have not further investigated this aspect of the new chemistry.

Use of Disilanes $R_3SiSiMe_2H$ (R_3 = Me_3 (2a), Ph_2Me (2b), Ph_3 (2c)). Since transition-metal complexes are well-established to facilitate rupture of Si–Si bonds,[8] the use of **2** as an efficient amide reductant was not obvious. However, the reaction between **2** and DMF in the presence of a catalytic amount of $(Me_3N)Mo(CO)_5$ resulted in the efficient formation of Me_3N and transformation of the specific disilane to the corresponding disiloxane **9a–c**, via the appropriate transient disiloxymethylamines **4** (eq 5).

$$
\begin{gathered}
HC(O)NMe_2 + R_3SiSiMe_2H \xrightarrow[5\%\ (Me_3N)MO(CO)_5]{C_6D_6,\ 90\ ^\circ C} \underset{\mathbf{4}}{[R_3SiSiMe_2OCH_2NMe_2]} \\
\mathbf{4} + R_3SiSiMe_2H \rightarrow R_3SiSiMe_2OSiMe_2SiR_3 + NMe_3 \\
R_3 = Me_3\ (\mathbf{9a}),\ Ph_2Me\ (\mathbf{9b}),\ Ph_3\ (\mathbf{9c})
\end{gathered}
\tag{5}
$$

In the case of the reductions using **2a** and **2c** transient siloxymethylamines (**4a** and **4c**) could be noted via NMR spectroscopy, as in the case of the reductions using **1**. However, in the case of **2b** at the "normal" reaction temperature of 90 °C we were unable to observe the intermediacy of the appropriate siloxymethylamine; the reaction was too fast. However, by performing the reaction at room temperature the intermediate **4b** was observed, illustrating the delicate aspects of sterics/electronics at play in this chemistry. In all reactions trimethylamine (Me_3N) was produced, as identified in the ^{13}C NMR as a resonance at ∼47.0 ppm.

Siloxane **9a**, $(Me_3SiMe_2Si)_2O$, is a well-known material[20] and our observed spectral data, recorded in the Experimental Section, are in accord with the proposed structure. Both **9b** and **9c** were characterized by NMR spectral data and HRMS and, in the case of **9c**, by single-crystal X-ray diffraction analysis; its structure is illustrated in Figure 6.

A search of the CCDC revealed only three structures which share the bis(pentaalkyl(aryl)disilyl) ether backbone: 2,2,3,3,5,5,6,6-octamethyl-2,3,5,6-tetrasila-4-oxa-1(1,8)-anthracenacyclohexaphane (INIWEI),[21] 6,7:8,9-dibenzo-3-oxa-1,2,2,4,4,5-hexaphenyl-1,2,4,5-tetrasilabicyclo(3.2.2)-nonadiene–benzene solvate (RURKIY),[22] and 1,5-dihydroxy-1,1,2,2,4,4,5,5-octaphenyl-3-oxa-1,2,4,5-tetrasilapentane–benzene solvate (OFUPIO).[23] Both INIWEI and RURKIY are cyclic siloxanes (Figure 7), and thus the Si–O–Si bond angles (∼153 and 145°, respectively) are significantly smaller than for the acyclic OFUPIO ($(Ph_2Si(OH)SiPh_2)_2O$; average ∼168°) and **9c** (165°) due to ring strain. The Si–Si bond length in **9c** (2.376(2) Å; Table 1) is statistically longer than the others due to the bulky Ph_3Si substituents, and for example, in the other acyclic OFUPIO, the Si–Si bond distance is shorter because one of the Ph groups of **9c** is replaced by a smaller hydroxyl group. The relationships between smaller SiOSi angles and longer Si–O bonds is maintained in this set of molecules.[24] The presence of the hydroxyl groups also has a significant impact upon the Si–Si···Si–Si torsional angle for OFUPIO due to an intramolecular H bond between the two groups, as can be seen in Figures 8 and 9 and Table 1. For the two cyclic molecules the torsional angle is ∼5°, for OFUPIO it averages ∼60°, and for **9c** it is ∼151°.

As noted above, we were able to observe the transient formation of the disiloxymethylamines $R_3SiSiMe_2OCH_2NMe_2$ (**4**) during the reduction reactions; however, attempts to isolate these materials were unsuccessful. They are very sensitive to moisture, and our attempts to distill them from reaction mixtures were unsuccessful. Despite these difficulties, it was possible to use them as transient reagents, and we have treated $Me_3SiSiMe_2OCH_2NMe_2$ (**4a**) with R_3ECl (R = Me, E = Si; R = Ph, E = Ge) to synthesize the corresponding ethers (eq 6).

$$
\begin{gathered}
\mathbf{4a} + R_3ECl \xrightarrow[C_6H_6]{RT} Me_3SiSiMe_2OER_3 + ClCH_2Me_2 \\
R = Me,\ E = Si\ (\mathbf{7});\ R = Ph,\ E = Ge\ (\mathbf{8})
\end{gathered}
\tag{6}
$$

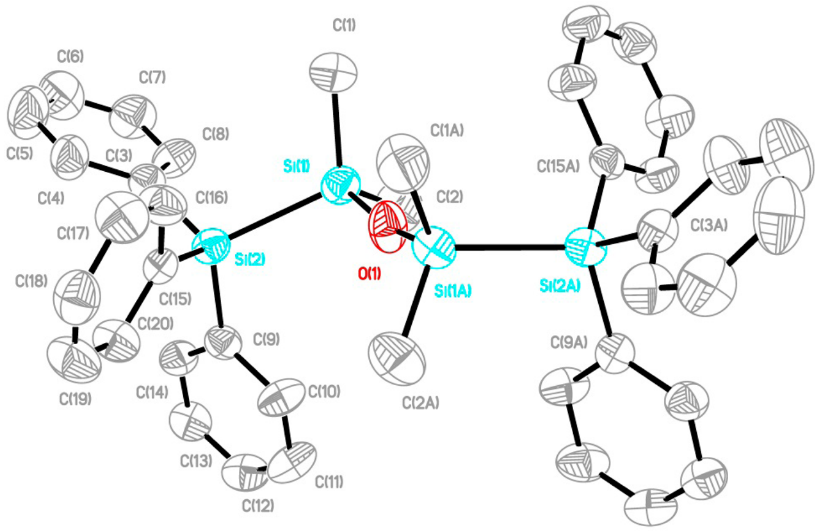
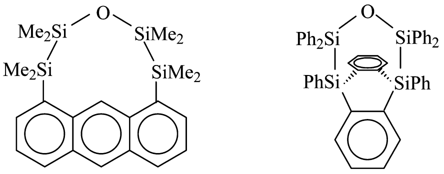


Figure 6. Molecular structure of compound **9c**, with ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Si–O = 1.618(2), Si–Si = 2.376(2); Si–O–Si = 165.2(4). The hydrogen atoms are omitted for clarity.



INIWEI RURKIY

Figure 7. Cyclic structures of bis(disilyl) siloxanes.

Table 1. Selected Structural Data for 9c in Comparison with Published Analogues

	9^{c}	INIWEI[21]	RURKIY[22]	OFUPIO[23]
Si–Si (Å)	2.376(2)	2.351(1), 2.355(1)[a]	2.362(2)	2.352(1), 2.353(1)
Si–O (Å)	1.618(2)	1.637(2), 1.640(2)	1.644(3)	1.628(1), 1.626(1)
Si–O–Si (deg)	165.2(4)	154.3(1), 152.8(1)	144.5(2)	161.5(1), 175.7(1)
Si–Si·Si–Si (deg)[b]	150.9	3.4, 6.8	5.20	82.3, 43.0

[a]When there is more than one isomer in the asymmetric unit, more than one value is listed. [b]The torsion angles are posted as absolute values.

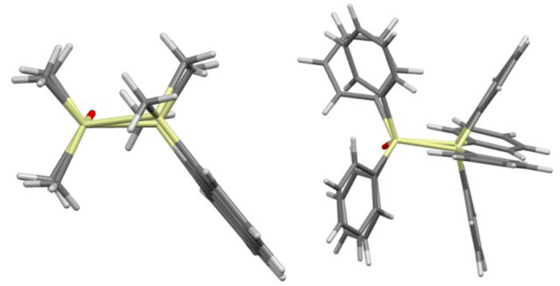


Figure 8. Torsion angle views for cyclic siloxanes INIWEI (left) and RURKIY (right).

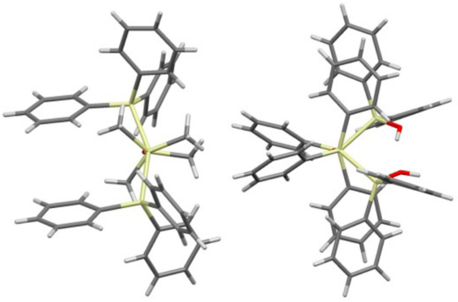


Figure 9. Torsion angle views of **9c** (left) and OFUPIO (right).

Compound **7** mixed with other siloxane materials was previously synthesized from the cross-coupling reaction between $Me_3SiOSiMe_2Cl$ and Me_3SiCl with lithium in a 1:2 molar ratio in THF.[25] Compound **8** is a new material, and we have characterized it by HRMS and NMR, as reported in the Experimental Section. In each case we were unable to remove trace amounts of the corresponding bis(disilyl) ether $(Me_3SiMe_2Si)_2O$ (**9a**).[20]

■ CONCLUSIONS

The widely used transition-metal-catalyzed reduction of amides to amines using silanes (R_3SiH) was first observed by the Voronkov group in a seminal but unrecognized and generally uncited 1985 report.[2] We have now further demonstrated that this reaction leads initially to the hydrosilylation product $R_3SiOCH_2NMe_2$ when $(Me_3N)Mo(CO)_5$ is the catalyst. Using the popular tetramethyldisiloxane $HSiMe_2SiOSiMe_2H$ (**1**) as a reductant, we have observed the corresponding hydrosilylated transient $Me_2NCH_2OSiMe_2OSiMe_2OCH_2NMe_2$ for the first time. Furthermore, we have demonstrated that this intermediate can be isolated and further functionalized in the presence of chlorosilanes and -germanes to form siloxy derivatives of the appropriate group 14 element, $R_3EOSiMe_2OSiMe_2OER_3$. In the absence of such trapping and/or isolation, the ultimate fate is the formation of cyclic dimethylsiloxanes $\mathbf{D_4}$ and $\mathbf{D_6}$. Using disilanes $R_3SiSiMe_2H$ (**2**) as reductants, the ultimate silicon-containing products are the corresponding bis(disilyl) siloxanes $(R_3SiSiMe_2)_2O$.

■ EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out under a nitrogen atmosphere using Schlenk or vacuum line techniques. THF and diethyl ether were distilled under nitrogen from benzophenone ketyl prior to use. Other solvents, hexanes, benzene, and toluene, were dried over sodium metal and distilled prior to use. DMF was distilled over BaO. The complex $(Me_3N)Mo(CO)_5$ was prepared according to the reported method using $Mo(CO)_6$ purchased from Strem Chemicals.[26] Silyl hydrides were purchased either from Aldrich or Gelest; NMR spectra were recorded on a 300 MHz Bruker or 600 MHz JEOL spectrometer in C_6D_6 or $CDCl_3$, and data are singlets unless otherwise stated; HRMS were recorded on a JEOL AccuTOF JMS-T100LC instrument with DART access unit. All column chromatographic separations were performed using silica gel (Aldrich, 700−230 mesh, 60 Å, pore volume 0.75 cm^3/g). The crystal structures of **5b** (CCDC 935196), **6b** (CCDC 935197), and **9c** (CCDC 915315) were determined on a Bruker Apex CCD diffractometer. The crystallographic data and structural refinement details are presented in Table S1 of the Supporting Information, and selected bond lengths and angles of **9c** are given in Table 1.

Large-Scale Preparation of $(Me_2NCH_2OSiMe_2)_2O$ (3). To a mixture of 1,1,3,3-tetramethyl-1,3-disiloxane (**1**; 2.69 g, 20.0 mmol) and *N*,*N*-dimethylformamide (3.20 g, 43.8 mmol) in benzene (12 mL) was added $(Me_3N)Mo(CO)_5$ (0.18 g, 2 mol %) in a Schlenk tube. The resulting solution was degassed, closed, and left standing overnight for approximately 14 h. The solvent was removed in vacuo and the crude liquid product distilled to provide the title compound as a clear, colorless liquid: yield 4.03 g, 72%; bp 70−71 °C/0.5 mmHg. NMR (ppm, C_6D_6): ^{1}H, 0.18 (SiMe), 2.38 (NMe), 4.48 (CH_2); ^{13}C, −0.31 (SiMe), 41.5 (NMe), 82.3 (CH_2); ^{29}Si, −14.0. Anal. Calcd for $C_{10}H_{28}N_2O_3Si_2$: C, 42.82; H, 10.06. Found: C, 41.82; H, 10.38.

Thermal Reaction of 3 with $HSiMe_2OSiMe_2H$ (1) in C_6D_6 with 1 mol % of $(Me_3N)Mo(CO)_5$. A 5 mm Pyrex NMR tube was charged with a solution of $HSiMe_2OSiMe_2H$ (0.095 g, 0.7 mmol) in 0.4 mL of C_6D_6, 0.10 g (0.35 mmol) of **3**, $Me_2NCH_2OSiMe_2OSiMe_2OCH_2NMe_2$, and 1 mol % of the catalyst $(Me_3N)Mo(CO)_5$. The tube was degassed twice using pump−thaw cycles and flame-sealed under vacuum. The tube was immersed in an oil bath maintained at 90 °C. The progress of the reaction was periodically monitored by ^{13}C and ^{29}Si NMR spectroscopy. After 40 h of thermolysis, the NMR analysis indicated the formation of Me_3N, **D_4**, and **D_6** along with traces of other oligomeric siloxanes and starting materials.

Reaction of 3 with Ph_3SiCl To Produce $(Ph_3SiOSiMe_2)_2O$ (5b). A 50 mL Schlenk flask was charged with Ph_3SiCl (0.42 g, 1.42 mmol) in 10 mL of benzene. A benzene solution (8 mL) of **3** (0.2 g, 0.71 mmol) was added via a syringe under an Ar atmosphere at room temperature, and the solution became turbid. The solution was maintained at 40 °C in an oil bath for 20 h. The solution was filtered through Celite to remove white precipitates of $ClCH_2NMe_2$, and the solvent was removed under vacuum. The product, $(Ph_3SiOSiMe_2)_2O$, was twice recrystallized from hexanes: yield 0.22 g (45%); mp 98−99 °C (lit.[14] mp 102−103 °C). NMR (ppm, $CDCl_3$): ^{1}H, −0.03 ($SiCH_3$), 7.31, 7.56−7.58 (m, Ph); ^{13}C, 1.23 ($SiMe_3$), 127.8, 129.8, 135.1, 136.0 (ipso) (Ph); ^{29}Si, −19.3, −21.2.

Reaction of 3 with Me_3SiCl To Produce $(Me_3SiOSiMe_2)_2O$ (5a). Using the above procedure, the reaction of **3** with Me_3SiCl led to the formation of **5a**: yield 86% as a colorless oil; NMR (ppm, C_6D_6): ^{1}H, 0.03 ($SiMe_2$), 0.08 ($SiMe_3$); ^{13}C, 1.8 ($SiMe_2$), 2.3 ($SiMe_3$); ^{29}Si, −21.1 ($OSiMe_2$), 7.6 ($OSiMe_3$). Data are in accord with those reported.[13]

Reaction of 3 with Me_3GeCl To Produce $(Me_3GeOSiMe_2)_2O$ (6a). In a 50 mL Schlenk flask under an Ar atmosphere at room temperature was charged **3** (0.38 g, 1.35 mmol) in 8 mL of benzene and, via syringe, Me_3GeCl (0.415 g, 2.7 mmol) in 10 mL of benzene. The reaction was exothermic, and after the addition of Me_3GeCl the solution became turbid. The solution was heated to 40 °C for 15 h. The solution was filtered through Celite to remove a white precipitate of $ClCH_2NMe_2$, and the solvent was removed under vacuum at 20 mmHg. The product $(Me_3GeOSiMe_2)_2O$ (**6a**) was distilled under vacuum at 88 °C/18 mmHg; yield 0.31 g (57%). NMR (ppm, C_6D_6): ^{1}H, 0.25 ($SiCH_3$), 0.34 ($GeMe_3$); ^{13}C, 2.25 ($SiMe_3$), 2.74 ($GeMe_3$); ^{29}Si, −20.1. HRMS (ESI): calcd 401.0249 $[M + 1]^+$, found 401.0113. Anal. Calcd for $C_{10}H_{30}Ge_2O_3Si_2$: C, 30.05; H, 7.57. Found: C, 29.96; H, 7.60.

Reaction of 3 with Ph_3GeCl To Form $(Ph_3GeOSiMe_2)_2O$ (6b). A 50 mL Schlenk flask was charged with Ph_3GeCl (0.475 g, 1.40 mmol) in 10 mL of benzene, and to this was added 8 mL of a benzene solution of **3** (0.2 g, 0.71 mmol) via syringe under an Ar atmosphere at room temperature. After the addition of Ph_3GeCl the solution became turbid and the solution was maintained at 40 °C in an oil bath for 20 h. The solution was filtered through Celite to remove white precipitates of $ClCH_2NMe_2$, and the solvent was removed under vacuum. The product $(Ph_3GeOSiMe_2)_2O$ (**6b**) was repeatedly recrystallized from hexanes: yield 0.18 g (33%); mp 68−69 °C. NMR (ppm, $CDCl_3$): ^{1}H, −0.21 ($SiCH_3$), 7.26−7.36, 7.51−7.55 (m, Ph); ^{13}C, 1.71 ($SiMe_3$), 128.1, 129.7, 134.2, 136.5 (ipso) (Ph); ^{29}Si, −17.9. Anal. Calcd for $C_{40}H_{42}Ge_2O_3Si_2$: C, 62.22; H, 5.48. Found: C, 62.44; H, 5.18.

Reaction of $Me_3SiSiMe_2H$ (2a) with DMF. In a typical experiment, an NMR tube was charged with $Me_3SiSiMe_2H$ (0.33 g, 0.5 mmol), DMF (0.11 g, 1.5 mmol), 2−5 mol % of $(Me_3N)Mo(CO)_5$, and 0.5 mL of C_6D_6. The tube was sealed under vacuum and heated in an oil bath at 90 °C. When the reaction was complete, as noted by crude ^{13}C and/or ^{29}Si NMR spectroscopic analysis, the volatiles and DMF were removed by flash distillation (into liquid nitrogen cooled receptacles) at ambient temperature (0.5 mm of Hg) to leave the desired product, which was further purified by distillation under vacuum (59−60 °C, 0.5 mmHg) to give 0.39 g (60% yield) of $(Me_3SiSiMe_2)_2O$ (**9a**).[20] NMR (ppm, C_6D_6): ^{1}H, 0.34 ($SiMe_2$), 0.23 ($SiMe_3$); ^{13}C, 2.7 (SiMe), −1.9 (SiMe); ^{29}Si, −23.2 ($SiMe_3$), 5.3 ($SiMe_2O$). HRMS: calcd 279.1374 $[M + 1]^+$, found 279.1369.

Using the same methodology the reactions of $Ph_2MeSiSiMe_2H$ and $Ph_3SiSiMe_2H$ with DMF led to the following products.

$(Ph_2MeSiSiMe_2)_2O$ (9b): purified by column chromatography with hexanes as eluent; 33% yield as an oil. NMR (ppm, C_6D_6): ^{1}H, 0.33 ($SiMe_2$), 0.67 (SiMe), 7.29, 7.68 (ArH); ^{13}C, −4.33 (SiMe), 3.22 (SiMe), 129.6, 134.8, 135.8, 137.6 (ArH); ^{29}Si, −26.1 (Ph_2MeSi), 5.6 ($SiMe_2O$). HRMS: calcd 526.2000, found 526.2010; Anal. Calcd for $C_{30}H_{38}OSi_4$: C, 68.38; H, 7.24. Found: C, 68.00; H, 7.07.

$(Ph_3SiSiMe_2)_2O$ (9c): recrystallized from hexanes; 32% yield; mp 94−95 °C. NMR (ppm, C_6D_6): ^{1}H, 0.33 ($SiMe_2$), 7.68 (m, ArH); ^{13}C, 3.7 (SiMe), 128.5, 129.9, 135.7, 136.8 (Ar); ^{29}Si, −25.1 (Ph_3Si), 5.8 ($SiMe_2O$).

Reaction of $Me_3SiMe_2SiOCH_2NMe_2$ (4a), with Ph_3GeCl. A Schlenk tube was charged with pentamethyldisilane (**2a**; 0.662 g, 5.00 mmol), DMF (0.548 g, 7.50 mmol), and $(Me_3N)Mo(CO)_5$ (0.045, 0.15 mmol) dissolved in benzene (12 mL), and the tube was degassed and allowed to stand overnight at ambient temperature. After this time, with complete loss of the disilane, conversion to the transient siloxymethylamine **4a** was observed to be approximately 90% complete (based on ^{1}H NMR). Characteristic NMR resonances (ppm) for $Me_3SiSiMe_2OCH_2NMe_2$ (**4a**) were observed in situ: ^{13}C, 83.3 (OCH_2N), 41.5 (NMe_2), 2.40 (SiMe), −0.15 (SiMe); ^{29}Si, 11.7 ($SiOCH_2NMe_2$), −22.4 ($SiMe_3$). DMF was removed by flash distillation (into liquid nitrogen cooled receptacles) at ambient temperature (0.5 mmHg). Isolation of the pure **4a** proved difficult, and the reaction mixture with traces of **9a** was used directly and treated with 1 equiv of Ph_3GeCl in benzene (5 mL) in a Schlenk flask maintained at 50 °C for 3 days. A white precipitate of $ClCH_2NMe_2$ was formed and removed by filtration over Celite, and the solvents were evaporated under vacuum. Unreacted Ph_3GeCl was removed by repeated recrystallization from hexanes. The residue showed the formation of **7** with traces of **9a**. The ^{1}H, ^{13}C, and ^{29}Si NMR and HRMS data recorded below are illustrated in the Supporting Information.

$Ph_3GeOSiMe_2SiMe_3$ (8): yield 0.17 g, 20%. NMR (ppm, $CDCl_3$): ^{1}H, 0.15 ($SiMe_3$) 0.25 ($SiMe_2$), 7.59 (m, ArH); ^{13}C, −2.3 (SiMe), 2.7 (SiMe), 128.6, 130.5, 136.2 (Ar); ^{29}Si, −22.7 ($SiMe_2O$), 10.1 ($SiMe_3$). HRMS: calcd 453.1004 $[M + 1]^+$, found 453.1129.

$Me_3SiOSiMe_2SiMe_3$ (7). Using the procedure used in the synthesis of **8**, the reaction of the crude $Me_3SiSiMe_2OCH_2NMe_2$ (**4a**) with 1 equiv of Me_3SiCl in benzene produced $Me_3SiOSiMe_2SiMe_3$ (**7**) in 60% yield. NMR (ppm, C_6D_6): ^{13}C, −2.5 ($SiMe_3$), 1.8 ($OSiMe_2$), 2.01 ($OSiMe_3$); ^{29}Si, −23.1 (Me_3Si), 4.4 (Me_2SiO), 7.3 (M_3SiO). The spectroscopic data are in agreement with the reported data.[25]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving ^1H, ^{13}C, and ^{29}Si NMR spectra for **3**, **8**, **9b**, and **9c** and HRMS spectra for **8**, Table S1 giving crystallographic data and structural refinement details for **5b**, **6b**, and **9c**, and CIF files giving crystallographic data. 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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