

Metal-Catalyzed Reduction of HCONR'₂, R' = Me (DMF), Et (DEF), by Silanes to Produce R'₂NMe and Disiloxanes: A Mechanism Unraveled

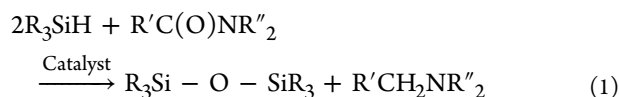
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S Supporting Information

ABSTRACT: We demonstrate that using Mo(CO)₆, Mo(CO)₅NMe₃, and (η⁵-C₅H₅)Mn(CO)₃ as catalysts for the silane, R₃SiH, reduction of *N,N*-dimethylformamide (DMF), and *N,N*-diethylformamide (DEF), we can observe, intercept, and isolate, the important siloxymethylamine intermediates, R₃SiOCH₂NR'₂, R' = Me, Et, for the first time. In the presence of excess DMF such intermediates thermally react with a variety of silanes to form the corresponding disiloxanes in the absence of a metal catalyst. We also show that the germanium hydrides, Et₃GeH and Bu₃GeH, also reduce DMF to form trimethylamine and the corresponding digermoxane but observe no intermediates R₃GeOCH₂NMe₂. Bu₃SnH reduces DMF, but along with the low yields of Bu₃SnOSnBu₃ (but no Bu₃SnOCH₂NMe₂) significant side products are obtained including (Bu₃Sn)₂ and Bu₄Sn. In the absence of DMF the siloxymethylamines can undergo metal-catalyzed reactions with silanes, germanes and stannanes to form disiloxanes, and R₃SiOER₃ E = Ge, Sn, respectively. To date, the most efficient catalyst for this latter process is (η⁵-C₅H₅)Mo(CO)₃CH₃ via a photochemical reaction.

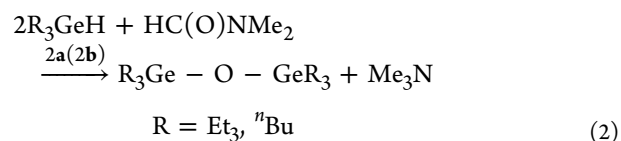
The transition metal-catalyzed reduction of amides by hydrosilanes is an efficient method for amine synthesis along with the appropriate disiloxane,^{1–8} eq 1.



In 1985, the Voronkov group first reported that the reaction of various silanes R₂R'SiH (R₂R' = Cl₂Me, Cl₂Et; Et₂Me and Et₃) with DMF, in the presence of the metal complexes (NO)₂PtCl₆ or [Me₂NH₂]⁺[Rh(CO)₂Cl₂]⁻, led to the formation of the corresponding disiloxanes.¹ More recently both Fe₂(CO)₉ and Fe₃(CO)₁₂ have been used as catalysts for the efficient reduction of *N,N*-dimethylbenzamide with the formation of benzyl dimethylamine² and zinc acetate was shown to catalyze the reduction of aromatic heterocyclic amides.³ In between these reports a number of groups have reported variations on the theme using different metal catalysts; “green” Pt resins;⁴ Ru₃(CO)₁₂^{4a} and related variants;⁵ a range of other metal carbonyl complexes,⁶ and the main group metal salt InBr₃.⁷ A variety of “plausible” mechanisms have been suggested but to date, no process involving possible organo-silicon intermediates and metal catalytic transients has been

reported to back up a general mechanism, even when postulated.⁵

We have reported that (η⁵-C₅H₅)Fe(CO)₂CH₃, (**1a**) is also efficient in the photolytic reduction of *N,N*-dimethylformamide (DMF) by silanes leading to trimethylamine and disiloxane formation,^{9a} an observation that was later corroborated by others.^{9b} Continuation of this research led us to use the molybdenum analogs (η⁵-C₅H₅)Mo(CO)₂(L)CH₃, L = CO (**2a**), PPh₃ (**2b**), and we observe that **2a** is more efficient photochemically than **1a**, Table 1, entries 6 vs 4 and 16 vs 14. Use of the phosphine-substituted complex **2b** to generate the needed 16-electron species thermally, thus removing the need for photochemical equipment, also led to reduction of DMF to Me₃N, Table 1, entries 7 and 17. Using **2a/2b** as catalysts the transformation of germanes to digermoxanes was also performed for the first time, eq 2, Table 1. Whereas only



trace amounts of the digermoxane can be observed from the reactions between R₃GeH (R = Et, Bu) and DMF catalyzed by either **1a** or **1b**, Table 1, entry 22, 27, such reactions are superior when using **2** as catalyst, over long reaction times, Table 1, entries 23, 24, 28 and 29.

We initially suggested that the first step in the silane reduction process was the hydrosilylation of the amides to form siloxymethylamines (R₃SiOCH₂NMe₂) subsequent to DMF activation via coordination with the metal complex.^{9a} We proposed this intermediate could either react directly with excess R₃SiH or via a more complex route involving the key intermediacy of (η⁵-C₅H₅)Fe(CO)₂CH₂NMe₂ to form the observed disiloxane products. We could not observe either of these materials when using the Fe catalysts **1a** or **1b**.

The literature contains reports of DMF acting as a metal ligand, and the work of Dobson and Sheline clearly detailed the formation of Mo(CO)₅(DMF) from the reaction of Mo(CO)₆ and DMF.¹⁰ We decided to investigate the use of Mo(CO)₆ (**3a**) as a catalyst for the reaction of tertiary silanes with DMF. In all cases it is an excellent catalyst, Table 1, entries 1, 8, 18, 21, 25, 30, and 34. Thermal reactions were performed at 90 °C

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Table 1. Synthesis of R₃EOER₃ (E = Si, Ge, Sn) using Fe, Cr, Mo, W and Mn Catalysts with excess of DMF

entry	R ₃	E	cat.	hv/Δ	time (h)	yield ^{a,b} /%
1	Et ₃	Si	3a	hv/Δ	1/3	(100)
2	Et ₃	Si	3b	hv/Δ	1/3	(100)
3	Et ₃	Si	5	hv	28	(90)
4	PhMe ₂	Si	1a	hv	14	(100)
5	PhMe ₂	Si	1b	Δ	48	TR
6	PhMe ₂	Si	2a	hv	3	65(100)
7	PhMe ₂	Si	2b	Δ	6	75(100)
8	PhMe ₂	Si	3a	hv/Δ	2/6	80(100)
9	PhMe ₂	Si	3b	hv/Δ	2/8	80(100)
10	PhMe ₂	Si	5	hv/Δ	18/24	(80) ^c
11	PhMe ₂	Si ^d	5	hv/Δ	12/24	(85) ^c
12	PhMe ₂	Si	6	hv/Δ	4/1	93(100)
13	PhMe ₂	Si	7	hv/Δ	7/7	81(100)
14	Ph ₂ Me	Si	1a	hv	18 h	(100)
15	Ph ₂ Me	Si	1b	hv	2d	TR
16	Ph ₂ Me	Si	2a	hv	3 h	60(100)
17	Ph ₂ Me	Si	2b	Δ	2d	65(100)
18	Ph ₂ Me	Si	3a	Δ	12 h	65(100)
19	Ph ₃	Si	1a,1b,2a	hv/Δ	48	NR
20	Ph ₃	Si	2b	Δ	24	TR
21	Ph ₃	Si	3a	Δ	48	50(100) ^c
22	Et ₃	Ge	1a,1b	hv/Δ	120	TR
23	Et ₃	Ge	2a	hv	24	(30)
24	Et ₃	Ge	2b	Δ	120	55(80)
25	Et ₃	Ge	3a	Δ	72	70(100)
26	Et ₃	Ge	3b	Δ	48	(100)
27	Bu ₃	Ge	1a,1b	hv/Δ	168	TR
28	Bu ₃	Ge	2a	hv	24	(30)
29	Bu ₃	Ge	2b	Δ	168	45(55)
30	Bu ₃	Ge	3a	Δ	120	70(100)
31	Bu ₃	Ge	3a, 3b	hv	120	TR
32	Ph ₃	Ge	1a,1b	hv/Δ	168	NR
33	Ph ₃	Ge	2a,2b	hv/Δ	168	TR
34	Ph ₃	Ge	3a	Δ	168	60(100) ^c
35	Bu ₃	Sn	1a,2a	hv	12	TR
36	Bu ₃	Sn	1b	Δ	48	5(15)

^aIsolated yields. ^bYields based upon ¹H NMR in parentheses. ^cReaction performed at 120 °C. ^dDEF. TR: traces; NR: no reaction. CpFe(CO)₂Me (1a); CpFe(CO)₂(Ph₃P)Me (1b); CpMo(CO)₃Me (2a); CpMo(CO)₂(Ph₃P)Me (2b); Mo(CO)₆ (3a); Mo(CO)₅NMe₃ (3b); CpMn(CO)₃ (5); Cr(CO)₆ (6); W(CO)₆ (7).

and photochemical reactions at ambient temperature. Monitoring the thermal reaction between PhMe₂SiH and DMF ([SiH]/[DMF] = 1:2) catalyzed by 3a in C₆D₆ using ²⁹Si NMR, clearly illustrated the efficient transformation of the silane to the corresponding disiloxane (PhMe₂Si)₂O; however, it is clear that a transient silicon-containing compound is formed with a ²⁹Si NMR resonance at 5.4 ppm, Figure 1. Monitoring of the same reaction by ¹³C NMR also indicated the formation of a transient species with three ¹³C NMR resonances at 82.4 (CH₂), 41.1 (Me₂N) and -1.4 (Me₂Si) ppm, Figure 1. Isolation of this transient by stopping the overall reaction prior to completion permitted us to identify it as PhMe₂SiOCH₂NMe₂ (4a) and, for the first time, observe the initial hydrosilylation product of DMF, illustrating it is an intermediate in the overall DMF reduction process, eq 3.

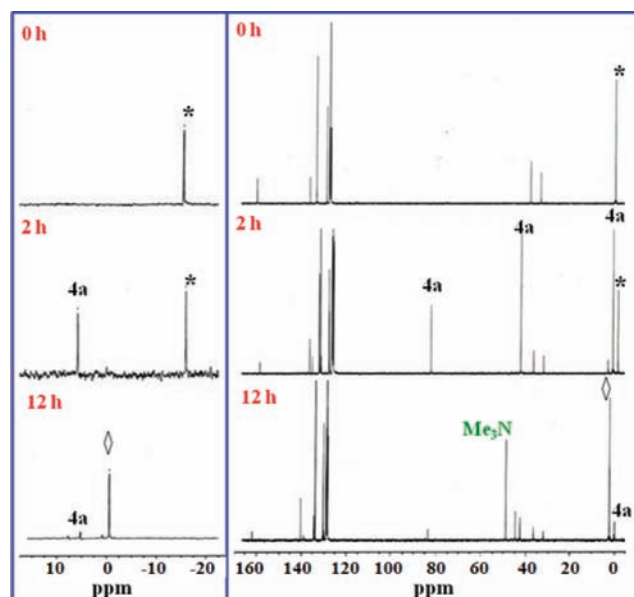
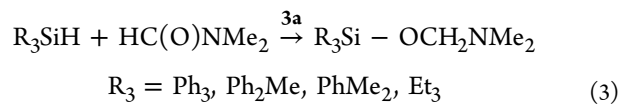


Figure 1. NMR monitoring of the reaction of PhMe₂SiH and DMF catalyzed by Mo(CO)₆, 3a. (Left) ²⁹Si NMR showing the disappearance of PhMe₂SiH, -17.3 ppm (*) and transient formation of 4a (5.4 ppm) en route to (PhMe₂Si)₂O, -0.6 ppm (◇): (Right) ¹³C spectra illustrating transient formation of PhMe₂SiOCH₂NMe₂ (4a).



Full experimental details for the isolation of 4a are provided in the Supporting Information, and we also isolated and characterized Ph₂MeSiOCH₂NMe₂ (4b), Ph₃SiOCH₂NMe₂ (4c) and Et₃SiOCH₂NMe₂ (4d) (Table 2). The ¹³C NMR

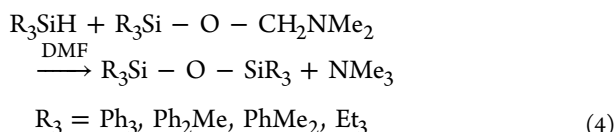
Table 2. Synthesis of R₃SiOCH₂NMe₂ using 3a

R ₃	time/h	yield ^{a,b} /%	NMR data for R ₃ SiOCH ₂ NMe ₂			
			²⁹ Si	¹³ C (CH ₂)	(Me) ₂ N	MeSi
Me ₃			13.8	81.5	40.4	-0.86
Et ₃	2	90(100)	15.3	82.3	41.1	
PhMe ₂	2	25(60)	5.4	82.4	41.1	-1.42
Ph ₂ Me	5	10(25)	-5.1	82.5	40.8	-3.04
Ph ₃	5	(10)	-15.2	82.9	40.9	

^aIsolated yield. ^bYields based upon ¹H NMR in parentheses.

data for 4a-d are almost equivalent to that of Me₃SiOCH₂NMe₂ (4f) the only previously reported member of this family.¹¹

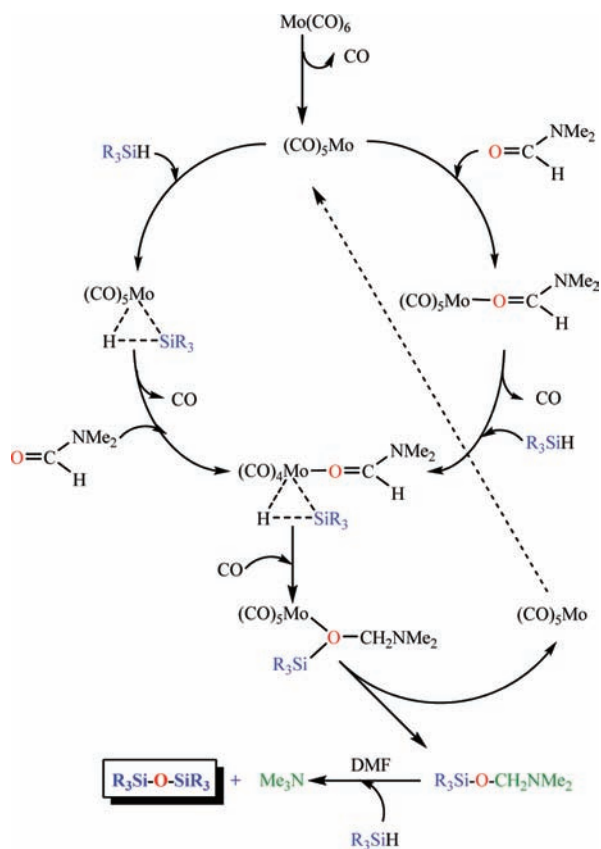
We examined the thermal reactivity of 4 in the presence of various silanes and observed no apparent chemical reaction when the reaction was performed in deuterobenzene, the solvent of choice for monitoring the reaction progress using NMR spectroscopy. However, upon addition of excess DMF to these same C₆D₆ solutions, under the thermal conditions similar to those used for the chemistry observed in Figure 1, but without the metal catalyst, the appropriate disiloxane and Me₃N were formed in high yield, eq 4, see Supporting Information.



This new reaction is reminiscent of similar reactions of silanes with hydroxylic reagents and related systems where activation of the Si–H bond via DMF coordination to form 5- and 6-coordinated transients has been proposed and in some cases observed.¹² The Mironov group has reported that **4f** readily reacts with chlorosilanes to form disiloxanes and $\text{ClCH}_2\text{NMe}_2$.¹³

From these results we now propose the thermal reduction of amides to amines occurs via the cycle noted in Scheme 1 in the

Scheme 1. Proposed Catalytic Cycle for the Formation of Me_3N and $\text{R}_3\text{SiOSiR}_3$ from the Reaction between R_3SiH and Excess DMF Catalyzed by 5 mol % $\text{Mo}(\text{CO})_6$ (3a**)**



case of using **3a** as a catalyst. The initial hydrosilylation can proceed either via initial amide coordination to molybdenum as has been reported,¹⁰ followed by η^2 -silane coordination after further loss of CO, or *vice versa*, initial coordination of the η^2 -SiH, followed by the amide. Molybdenum η^2 -silane σ -complexes, $(\text{CO})_5\text{Mo}(\eta^2\text{-HSiR}_3)$ have been detected by ^1H NMR spectroscopy in the photochemical reaction of group 6 metal carbonyls and the R_3SiH .¹⁴ Migration of R_3Si group to oxygen can lead to the reductive elimination of the siloxy-methyl amines $\text{R}_3\text{SiOCH}_2\text{NMe}_2$, **4**. It is significant that direct hydrosilylation of acetone by $\text{W}(\text{CO})_5(\eta^2\text{-HSiR}_3)$ to yield $\text{R}_3\text{SiOCHMe}_2$ has also been observed previously.^{14d,e} Whether both reagents need to be coordinated to the metal center is an open question since the activation of the hydrogen via the η^2 -

HSiR_3 coordination may be sufficient for initial reduction with the amide $\text{C}=\text{O}$ group. Similarly the electron-deficiency at the amide C atom induced by co-ordination to the metal center may be sufficient for the interaction with the silane. However, we have included the dual coordination step in the mechanism since although we have not observed any Mo-tetracarbonyl transients they have been observed in related chemistry.^{14d}

Interestingly, the use of **2a** as catalyst for photochemical reactions of **4f** with the group 14 hydrides in C_6D_6 solutions, but in the absence of DMF, also led to the formation of the appropriate disiloxane, siloxygermane^{15a} or siloxystannane,^{15b} eq 5, Table 3.

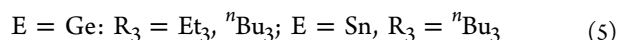
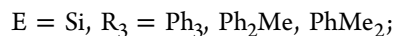
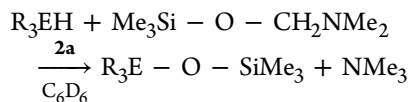


Table 3. Photochemical Synthesis of $\text{Me}_3\text{SiOER}_3$ Catalyzed by **2a, eq 5**

R_3	E	time/h	yield ^a / % (NMR) ^b	NMR data for $\text{R}_3\text{EOSiMe}_3$	
				^{29}Si	^{119}Sn
Ph_3	Si	6	83(100)	11.1	−20.0
Ph_2Me	Si	4	60(100)	10.2	−11.0
PhMe_2	Si	4	70(100)	9.2	−1.6
Ph_3	Ge	12	40(80)	8.3	
Et_3	Ge	18	(100)	6.8	
Bu_3	Sn	2	80(100)	5.6	76.4

^aIsolated yield. ^bYield based upon ^1H NMR in parentheses.

The same reactions occur using **3a** as the catalyst both thermally and photochemically; however, to date, yields are lower and reaction times are longer compared to those when using **2a**. Clearly two distinct mechanisms are occurring, DMF-catalyzed and/or metal-catalyzed for the transformation of $\text{R}_3\text{SiOCH}_2\text{NMe}_2$ to disiloxanes in the presence of R_3SiH . The unsymmetrical disiloxanes, siloxygermanes and siloxystannanes, $\text{R}_3\text{Si} = \text{Me}_3\text{Si}$, were also synthesized independently from the direct thermal reactions of **4f** with R_3ECl following the Mironov procedure.¹³

Regarding the metal-catalyzed reaction between **4f** and R_3EH in an “inert” solvent, we have attempted to form molybdenum complexes of **4f** from reactions with either **2a** or **3a** but these attempts have, to date, proven unsuccessful and led to unrelated chemistry. We suggest that the metal-catalyzed reactions outlined in eq 5 involve the metal-silane transients and our studies are continuing on this aspect of the chemistry.

By careful examination of the ^{13}C NMR data of the reactions between R_3SiH and DMF catalyzed by **3a**, we can observe trace amounts of the $(\text{CO})_5\text{MoNMe}_3$, **3b**. We have independently synthesized **3b**¹⁶ and in a separate experiment shown that it acts as a catalyst for the overall transformation of R_3SiH to $\text{R}_3\text{SiOSiR}_3$ in the presence of DMF, Table 1, entries 9 and 26.

Other metal systems that have been reported to activate R_3SiH , and where DMF coordination can play a role, include $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$, **5**, $\text{Cr}(\text{CO})_6$, **6**, and $\text{W}(\text{CO})_6$, **7**.^{17,18} Use of these materials as catalysts for the silane reduction of DMF

and DEF chemistry was also successful, Table 1, entries 10–13. The intermediacy of organosilicon compounds **4** was also observed for each of these new catalysts.

In the case of the reduction of DMF by germanes and stannanes we have, to date, been unable to observe any $R_3EOCH_2NMe_2$ (E = Ge, Sn) intermediates when using any of the catalysts noted above. It is possible that these group 14-substituted amines react more rapidly under the reaction conditions than their silicon analogs. Alternatively another mechanism may be operative for Ge and Sn hydride reductions. In the case of the Sn chemistry the range of other products suggests a considerable radical participation as noted in other stannane reduction reactions.¹⁹ Also, for the amide reductions catalyzed by **1a**, **1b**, **2a** and **2b** where no $R_3SiOCH_2NMe_2$ intermediates are observed, the overall mechanism may be different to that proposed for the use of **3a**.

■ ASSOCIATED CONTENT

■ Supporting Information

Detailed experimental procedures and characterization of products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) We have synthesized the new materials $R_3SiOCH_2NMe_2$, in good yields for $R_3 = Ph_3, Ph_2Me, PhMe_2, Et_3$ and the procedure can be readily extended to a wide variety of silyl groups. Previously only the Me_3Si compound had been reported by the Mironov group by a

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