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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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Supporting Information

ABSTRACT: We demonstrate that using $Mo(CO)_6$, $Mo(CO)_5NMe_3$, and $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ as catalysts for the silane, R_3SiH, reduction of *N*,*N*-dimethylformamide (DMF), and *N*,*N*-diethylformamide (DEF), we can observe, intercept, and isolate, the important siloxymethylamine intermediates, $R_3SiOCH_2NR'_2$, 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, Et_3GeH and Bu_3GeH, also reduce DMF to form trimethylamine and the corresponding digermoxane but observe no intermediates $R_3GeOCH_2NMe_2$. Bu_3SnH reduces DMF, but along with the low yields of $Bu_3SnOSnBu_3$ (but no $Bu_3SnOCH_2NMe_2$) significant side products are obtained including $(Bu_3Sn)_2$ and Bu_4Sn. In the absence of DMF the siloxymethylamines can undergo metal-catalyzed reactions with silanes, germanes and stannanes to form disiloxanes, and R_3SiOER_3 E = Ge, Sn, respectively. To date, the most efficient catalyst for this latter process is $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3$ 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.

$$2R_3SiH + R'C(O)NR''_2 \xrightarrow{\text{Catalyst}} R_3Si - O - SiR_3 + R'CH_2NR''_2 \quad (1)$$

In 1985, the Voronkov group first reported that the reaction of various silanes $R_2R'SiH$ (R_2R' = Cl_2Me, Cl_2Et; Et_2Me and Et_3) with DMF, in the presence of the metal complexes $(NO)_2PtCl_6$ or $[Me_2NH_2]^+[Rh(CO)_2Cl_2]^-$, led to the formation of the corresponding disiloxanes.[1] More recently both $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ have been used as catalysts for the efficient reduction of *N*,*N*-dimethylbenzamide with the formation of benzyldimethylamine[2] 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] $Ru_3(CO)_{12}$[4a] and related variants;[5] a range of other metal carbonyl complexes,[6] and the main group metal salt $InBr_3$.[7] A variety of "plausible" mechanisms have been suggested but to date, no process involving possible organosilicon intermediates and metal catalytic transients has been reported to back up a general mechanism, even when postulated.[5]

We have reported that $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$, (**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 $(\eta^5\text{-}C_5H_5)Mo(CO)_2(L)CH_3$, L = CO (**2a**), PPh_3 (**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 Me_3N, 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

$$2R_3GeH + HC(O)NMe_2 \xrightarrow{\mathbf{2a}(\mathbf{2b})} R_3Ge - O - GeR_3 + Me_3N \quad R = Et_3, {}^nBu \quad (2)$$

trace amounts of the digermoxane can be observed from the reactions between R_3GeH (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 ($R_3SiOCH_2NMe_2$) subsequent to DMF activation via coordination with the metal complex.[9a] We proposed this intermediate could either react directly with excess R_3SiH or via a more complex route involving the key intermediacy of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2NMe_2$ 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 R_3EOER_3 (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_2Me	Si	**1a**	hv	18 h	(100)
15	Ph_2Me	Si	**1b**	hv	2d	TR
16	Ph_2Me	Si	**2a**	hv	3 h	60(100)
17	Ph_2Me	Si	**2b**	Δ	2d	65(100)
18	Ph_2Me	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)

[a]Isolated yields. [b]Yields based upon ^{1}H NMR in parentheses. [c]Reaction performed at 120 °C. [d]DEF. TR: traces; NR: no reaction. $CpFe(CO)_2Me$ (**1a**); $CpFe(CO)_2(Ph_3P)Me$ (**1b**); $CpMo(CO)_3Me$ (**2a**); $CpMo(CO)_2(Ph_3P)Me$ (**2b**); $Mo(CO)_6$ (**3a**); $Mo(CO)_5NMe_3$ (**3b**); $CpMn(CO)_3$ (**5**); $Cr(CO)_6$ (**6**); $W(CO)_6$ (**7**).

and photochemical reactions at ambient temperature. Monitoring the thermal reaction between $PhMe_2SiH$ and DMF ([SiH]/[DMF] = 1:2) catalyzed by **3a** in C_6D_6 using ^{29}Si NMR, clearly illustrated the efficient transformation of the silane to the corresponding disiloxane $(PhMe_2Si)_2O$; however, it is clear that a transient silicon-containing compound is formed with a ^{29}Si NMR resonance at 5.4 ppm, Figure 1. Monitoring of the same reaction by ^{13}C NMR also indicated the formation of a transient species with three ^{13}C NMR resonances at 82.4 (CH_2), 41.1 (Me_2N) and −1.4 (Me_2Si) ppm, Figure 1. Isolation of this transient by stopping the overall reaction prior to completion permitted us to identify it as $PhMe_2SiOCH_2NMe_2$ (**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.

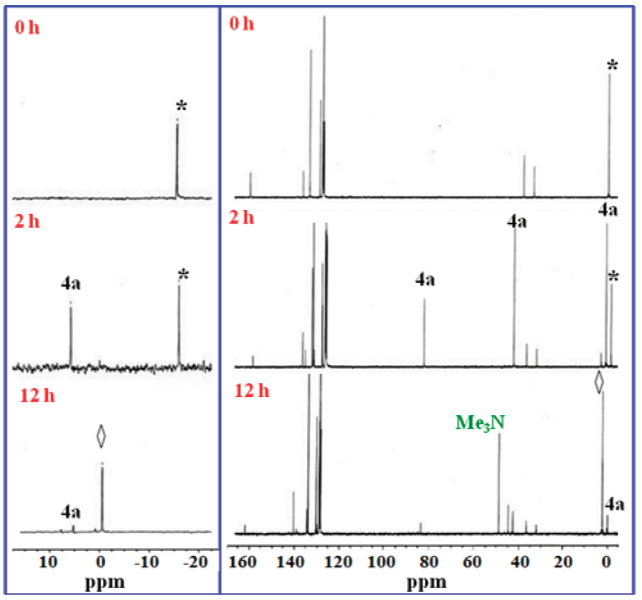

Figure 1. NMR monitoring of the reaction of $PhMe_2SiH$ and DMF catalyzed by $Mo(CO)_6$, **3a**. (Left) ^{29}Si NMR showing the disappearance of $PhMe_2SiH$, −17.3 ppm (*) and transient formation of **4a** (5.4 ppm) en route to $(PhMe_2Si)_2O$, −0.6 ppm (◇): (Right) ^{13}C spectra illustrating transient formation of $PhMe_2SiOCH_2NMe_2$ (**4a**).

$$R_3SiH + HC(O)NMe_2 \xrightarrow{\mathbf{3a}} R_3Si - OCH_2NMe_2$$
$$R_3 = Ph_3,\ Ph_2Me,\ PhMe_2,\ Et_3 \qquad (3)$$

Full experimental details for the isolation of **4a** are provided in the Supporting Information, and we also isolated and characterized $Ph_2MeSiOCH_2NMe_2$ (**4b**), $Ph_3SiOCH_2NMe_2$ (**4c**) and $Et_3SiOCH_2NMe_2$ (**4d**) (Table 2). The ^{13}C NMR

Table 2. Synthesis of $R_3SiOCH_2NMe_2$ using 3a

			NMR data for $R_3SiOCH_2NMe_2$			
R_3	time/h	% yield[a,b](NMR)	^{29}Si	^{13}C (CH_2)	$(Me)_2N$	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_2Me	5	10(25)	−5.1	82.5	40.8	−3.04
Ph_3	5	(10)	−15.2	82.9	40.9	

[a]Isolated yield. [b]Yields based upon ^{1}H NMR in parentheses.

data for **4a-d** are almost equivalent to that of $Me_3SiOCH_2NMe_2$ (**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 C_6D_6 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 Me_3N were formed in high yield, eq 4, see Supporting Information.

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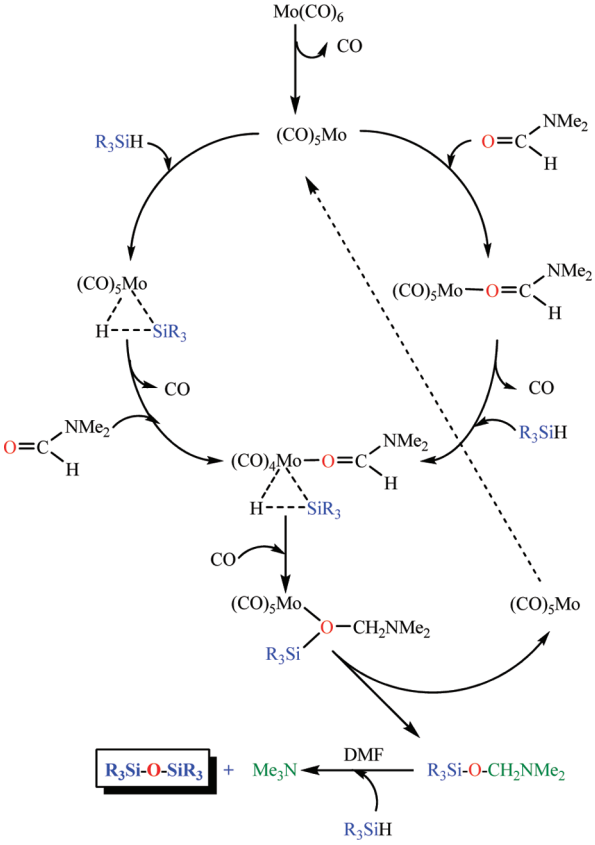
$$R_3SiH + R_3Si - O - CH_2NMe_2 \xrightarrow{DMF} R_3Si - O - SiR_3 + NMe_3$$

$$R_3 = Ph_3,\ Ph_2Me,\ PhMe_2,\ Et_3 \qquad (4)$$

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 $ClCH_2NMe_2$.[13]

From these results we now propose the thermal reduction of amides to amines occurs via the cycle noted in Scheme 1 in the 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, $(CO)_5Mo(\eta^2\text{-}HSiR_3)$ 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 siloxymethyl amines $R_3SiOCH_2NMe_2$, **4**. It is significant that direct hydrosilylation of acetone by $W(CO)_5(\eta^2\text{-}HSiR_3)$ to yield $R_3SiOCHMe_2$ 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 C=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]

Scheme 1. Proposed Catalytic Cycle for the Formation of Me_3N and $R_3SiOSiR_3$ from the Reaction between R_3SiH and Excess DMF Catalyzed by 5 mol % $Mo(CO)_6$ (3a)



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.

$$R_3EH + Me_3Si - O - CH_2NMe_2 \xrightarrow[C_6D_6]{\mathbf{2a}} R_3E - O - SiMe_3 + NMe_3$$

$$E = Si,\ R_3 = Ph_3,\ Ph_2Me,\ PhMe_2;$$

$$E = Ge:\ R_3 = Et_3,\ {}^nBu_3;\ E = Sn,\ R_3 = {}^nBu_3 \qquad (5)$$

Table 3. Photochemical Synthesis of Me_3SiOER_3 Catalyzed by 2a, eq 5

				NMR data for $R_3EOSiMe_3$	
R_3	E	time/h	yield[a]/% (NMR)[b]	^{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

[a]Isolated yield. [b]Yield 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 $R_3SiOCH_2NMe_2$ to disiloxanes in the presence of R_3SiH. The unsymmetrical disiloxanes, siloxygermanes and siloxystannanes, $R_3Si = Me_3Si$, 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 $(CO)_5MoNMe_3$, **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 $R_3SiOSiR_3$ 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 $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, **5**, $Cr(CO)_6$, **6**, and $W(CO)_6$, **7**.[17,18] Use of these materials as catalysts for the silane reduction of DMF

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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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