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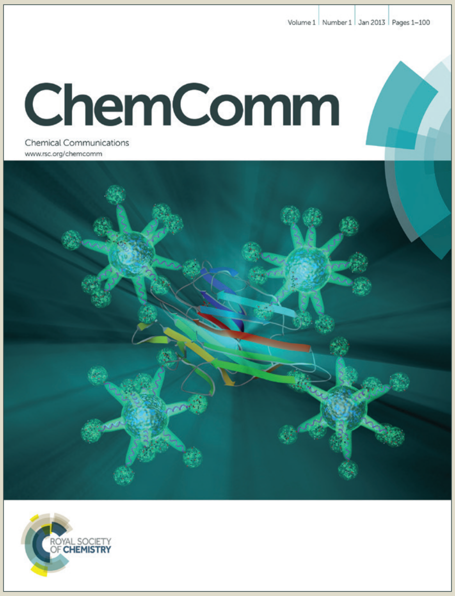

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DOI: 10.1039/C4CC06979J

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Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Tandem-Reduction of DMF with Silanes via Necklace-type Transition over Pt(0) Nanoparticles: Deciphering the Dual Si-H Effect as an Extension of Steric Effects

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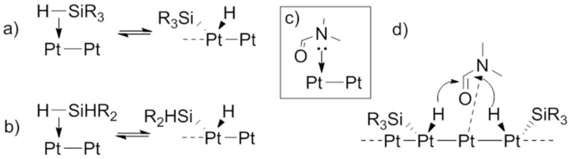
Dimethylformamide (DMF) undergoes "double-reduction" to yield trimethylamine as a result of the concerted activation of DMF by *two* Si-H bonds (from different Si atom) at Pt(0) nanoparticles as catalytic centers. Sterics on the Si atom govern the reaction and are also decisive for the structure of siloxane products due to potential limitations on the concerted activation.

A plethora of homogeneous catalysts has been developed in order to carry out the reduction of amides, a highly thermodynamically stable functional group to amines via hydrosilylation[1-10] although most require elevated temperature[1, 4-7, 10] and produce other N-based side products. Amongst these systems a few[2, 4, 8-10] stand out as they show a unique but unexplained "dual Si-H effect". Ito and co-workers[2] were the first to report such a study in which a dihydrosilane (R_2SiH_2) was found capable of reducing an amide to an amine in the presence of a Rh catalyst. They further noticed that the monohydrosilane analogue (R_3SiH) was ineffective in carrying out such transformation and a disiloxane molecule ($R_2HSiOSiHR_2$) that was a side-product from the original dihydrosilane (R_2SiH_2) reagent was also ineffective in further reducing the amide. Nagashima and co-workers[4, 10] then published somewhat contradicting reports and observed that although the Pt-based catalytic systems they used also did not reduce an amide to an amine in the presence of a monohydrosilane (R_3SiH) such reduction was not viable with dihydrosilanes (R_2SiH_2), too. The only reduction of an amide they observed was with a disiloxane ($(R_2HSi)_2O$) type of molecule and the term "dual Si-H effect" was coined, which essentially implied that with the catalytic systems used, only silane molecules with *two* Si-H moieties within *one* molecule could reduce an amide to the corresponding amine. Later, a plausible mechanism was reported[10] but it fell short as it suggested the formation of a four-membered siloxane ring in the process of abstracting an oxygen atom from the amide by the disiloxane molecule, however, no such product was reported as its formation is energetically disfavored[10, 11]. Pannell's group[8, 9] also contributed to that topic by using DMF as a model molecule to isolate O-silylated hemi-aminals as single-reduction intermediates. Although the "dual Si-H effect" has been cited to explain the results, no study has been able to unambiguously explain such a phenomenon till date. Here, we zero-in on this phenomenon and the compilation of our results shows that the dual Si-H effect is simply an extension of steric effects; most important, the process we explain here is without contradictions and fully accounts for all observed (by-) products and intermediates.

We chose DMF as a model molecule to observe its reduction by silanes at room temperature. Because of its resonance structure, DMF is a very stable molecule ($(CH_3)_2N\text{-}C(H)\text{=}O \leftrightarrow (CH_3)_2N^+\text{=}C(H)\text{-}O^-$). Treatment of DMF with a silane does not result in any reaction. Nonetheless, Si-H bonds can be activated by transition metal complexes.[12] Here, we focused on the reduction of DMF by a simple heterogeneous system consisting of Pt(0) nanoparticles (NPs) immobilized on a monolithic polymeric support, whose synthesis and use in both the reduction of CO_2 and in the continuous hydrosilylation of olefins is explained elsewhere[13-16]. We propose as shown in **Scheme 1** that Pt(0) NPs in the catalytic system can activate DMF and silanes which can lead to a very specific attack of hydrides on the activated DMF molecule.



Scheme 1: Proposed activation of a) a monohydrosilane, b) a dihydrosilane and c) DMF over Pt(0) and d) concerted activation of DMF and Si-H bonds from two different Si atoms over Pt(0) NPs.

Schemes 1a) and **b)** differ only as one of the R groups on the Si atom is replaced by H in case of **b)** thus reducing the sterics around the Si atom. Our first assumption here is that only one hydride attached to a Si atom can be activated by the catalytic system at a

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given instant. **Scheme 1c)** shows the lone pair on the N atom in DMF donated to the Pt atom on the catalytic NP surface which can make the carbonyl carbon more susceptible to nucleophilic attack and finally **d)** shows the concertedly activated DMF molecule and Si-H bonds from two different Si atoms in a close vicinity engaged at a Pt NP although the two hydrides may not attack the carbonyl carbon at the exact same instant and thus this may not be a fully concerted reaction.

In order to better understand the effect of silanes on DMF reduction in presence of the Pt-based catalytic system, the following experiments were designed. First, diethylsilane (Et_2SiH_2) was chosen as it is one of the silanes that carries the least sterics around the Si atom but is also easy to handle. 600 µL of DMF-d_7 were used as reagent, reaction and NMR solvent. To this, 50 µL of Et_2SiH_2 were added. No reaction in the absence of the catalyst was observed thus establishing a negative control. In a parallel experiment, the NMR tube with the above-mentioned contents was charged with 5 mg of Pt immobilized monolith (357 ppm Pt; ~9 nanomol of Pt). The molar ratio of Si-H to Pt in this case was ~85700 ($1.2 \cdot 10^{-3}$ mol-%). This very small amount of catalyst is in stark contrast to earlier studies carried out with homogeneous type catalysts where 2 to 10 mol-% of catalyst were used[1, 3, 5, 6]. It is also important to mention that due to the excess of DMF-d_7 the silane was the limiting reagent and a single-reduction product of DMF-d_7 could also be expected to form. However, due to the concerted activation nature of the double-reduction no single-reduction products were observed. The reaction was monitored by acquiring ^{1}H NMR spectra at defined intervals. **Figure 1** (bottom) shows the ^{1}H NMR acquired immediately (10 minutes) after the addition of the reagents and shows a quintet at δ = 3.62 ppm for Et_2SiH_2 ($^{3}J_{H\text{-}H}$ = 3.56 Hz). The top spectrum is the NMR acquired 3 days after the beginning of the reaction and shows the absence of the original Et_2SiH_2 peak at δ = 3.62 ppm, which clearly demonstrates the activation of the Si-H bond followed by the consumption of the Et_2SiH_2 species shifting the equilibrium in the forward direction in **Scheme 1b)**. The top spectrum in **Figure 1** also reveals the evolution of two new peaks, one at δ = 4.52 ppm and the other at δ = 2.09 ppm (also already observed as tiny peaks after 10 minutes).

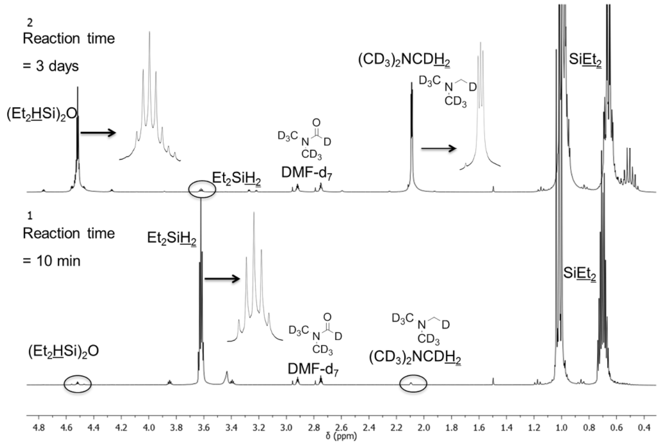
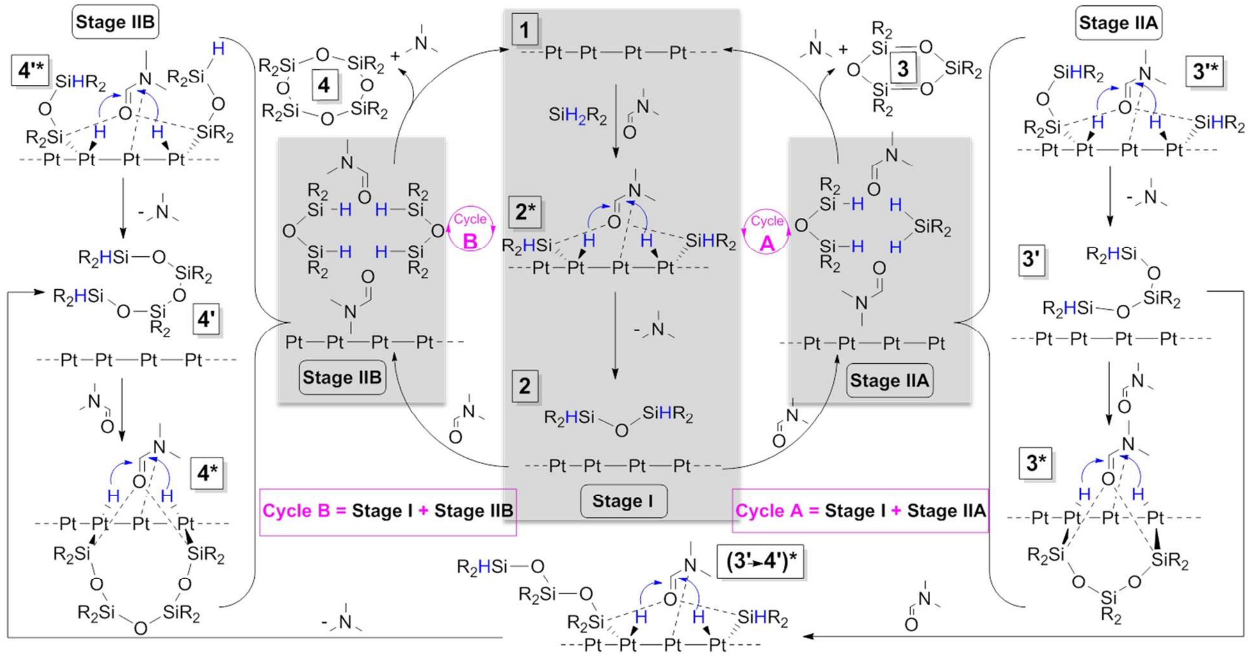


Figure 1: ^{1}H NMR of a reaction mixture containing 600 µL of DMF-d_7, 5 mg of Pt(0)-containing monolith (357 ppm Pt; ~9 nanomole of Pt) and 50 µL of Et_2SiH_2. 1) Bottom spectrum shows the ^{1}H NMR taken after 10 minutes. 2) Top spectrum shows the ^{1}H NMR acquired after 3 days.

The resonance at δ = 4.52 ppm shows a clear quintet similar to the one in Et_2SiH_2 at δ = 3.62 ppm and is thus assigned to the hydride resonance in a **H**-Si(Et_2)-O- species. These observations in combination with the proposed reaction **Scheme 2** imply the formation of a $(Et_2HSi)_2O$ species. This also supports our earlier stated assumption that only one Si-H bond in Et_2SiH_2 is activated at any given instance.



Scheme 2: Details of the reduction of DMF with silanes in presence of the Pt(0) NP-based catalytic system. Reduction was carried out at room temperature.

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This given instance however suggests the abstraction of oxygen from DMF-d_7 and formation of $(CD_3)_2NCDH_2$ (trimethylamine-d_7) for which a newly formed triplet (1:1:1 intensity) at $\delta = 2.09$ ppm is observed. Details of further confirmation, which include a comparison of the NMR and GC-MS data with those of an authentic sample of $(CH_3)_3N$ are provided in the supporting information (**Figure S1** to **Figure S4**; SI). Further it can be said in reference to **Figure 1** ($\delta = 2.09$ ppm and $\delta = 4.52$ ppm) and **Scheme 2** that **Stage I** of the proposed reaction mechanism through which a Et_2SiH_2 molecule goes concludes here.

2* is the key reaction sequence, which leads to the completion of **Stage I** where clearly Si-H bonds from two different molecules of Et_2SiH_2 are activated and jointly attack the activated DMF molecule. We don't have unambiguous proof that the reaction is perfectly concerted as this would imply the simultaneous breaking of a C(sp2)=O bond, formation of two new C(sp3)-H bonds and formation of two new Si-O bonds to form the disiloxane compound **2** (**Scheme 2**). Such a scenario is depicted in **Figure S5(a)** (SI). In fact, studies carried out by Pannell's group[8] suggest that their process first goes through the formation of an O-silylated hemi-aminal, which is then reduced to form trimethylamine and disiloxane. However, in contrast to the Pt-based homogeneous type Karstedt's catalyst used in Pannell's studies, whose use results in a mixture of various reduction products of DMF (**Figure S5(b)** SI), our Pt(0)-based heterogeneous type catalytic system *exclusively* produces trimethylamine as only DMF-reduction product. Therefore, in reference to the **2*** reaction sequence and absence of other DMF-reduction products including O-silylated hemi-aminal we believe that the catalytic system discussed here in fact shows specificity due to its unique concerted activation leading to synergy in double-reduction of DMF.

Every step indicated by an "*****" in **Scheme 2** represents such an event, which involves the above-mentioned concerted activation and results in a double-reduction of DMF to form trimethylamine. After reaching **Stage I** the disiloxane molecule (compound **2**) can either go through **Stage IIA** to follow cycle **A** or through **Stage IIB** to follow cycle **B** as shown in the **Scheme 2**. In case of **Stage IIA** the original Et_2SiH_2 can react with compound **2** in a similar fashion than in step **2***. The detailed **Stage IIA** is on the extreme right of the **Scheme 2** and first goes through step **3'***, which leads to the formation of another siloxane compound **3'**. This siloxane compound can then go through step **3***, which depicts the formation of a "necklace-type" transition due to the activation of two terminal Si-H bonds over Pt resulting in the formation of compound **3** that is a cyclotrisiloxane. Similarly, compound **2** can instead follow cycle **B** and go through **Stage IIB** where two molecules of compound **2** can be activated at the Pt NP surface. The details of **Stage IIB** are depicted at the extreme left of the **Scheme 2** and are similar to **Stage IIA** resulting in the formation of compound **4** that is a cyclotetrasiloxane, again via a "necklace-type" transition, **4***. Another distinction has to be made here in that in case of Et_2SiH_2 the reaction via cycle **A** diminishes as Et_2SiH_2 is consumed (>50% Si-H bonds) within 3 days (**Figure 1**). The reaction later slows down dramatically as it progresses via cycle **B** as the sterics offered by the siloxane molecules (compound **2** and **4'**) are high as compared to those offered by Et_2SiH_2 at the Pt NP. As a result, from day 3 to day 30 the ^1H NMRs show a slow but consistent consumption of hydrides at $\delta = 4.52$ ppm and concomitantly an increase in the trimethylamine-d_7 peak at $\delta = 2.09$ ppm is observed. At the end of day 30 when 99% of the hydrides were consumed the reaction mixture was analysed by GC-MS. The analysis shows the formation of both compound **3** and **4** (R^1=R^2=Et); SI **Figure S6(a) – (e)**.

As shown in **Table 1**, various silanes (50 µL each) were used along with 600 µL of DMF-d_7 and 5 mg of Pt(0) NPs loaded monolith (~9 nanomole of Pt). **Table 1**, entries 2 and 3 show two other dihydrosilanes, namely methylphenlsilane ($MePhSiH_2$) and diphenylsilane (Ph_2SiH_2) that were used in comparison to Et_2SiH_2. Clearly, silane consumption recorded for the first 3 days goes down from almost 99% (>50 % Si-H) in case of Et_2SiH_2 to ~11% in case of $MePhSiH_2$ to ~3% in case of Ph_2SiH_2 distinctly showing that as the sterics on the Si atom increase the reaction dramatically slows down.

Table 1: Reduction of DMF-d_7 with different silanes.

		Silane		Reduction of DMF-d_7[b] (Si-H:Pt)[c]	Silane Consumption[de]	
					mol-%	TON
1	2°	Et_2SiH_2	[a] ↓	yes (85700)	100 (~99)[f]	>42900 (77200)[f]
2		$MePhSiH_2$		yes (80900)	~11	~4500
3		Ph_2SiH_2		yes (60000)	~3	~900
4	3°	$(Me_2HSi)_2O$		yes (62900)	~6	~370
5		$Me_2HSiOSiMe_3$		yes (28500)	~1.3	~400
6		Et_3SiH		yes (34700)	<0.2[f]	<7[f]
7		Me_2PhSiH		no (36200)	0[f]	0[f]

[a] Arrow represents increase in sterics at the Si atom. [b] Reduction of DMF-d_7 to trimethylamine-d_7 as evidenced by the formation of a triplet (1:1:1 intensity) at $\delta = 2.09$ ppm in ^1H NMR for $(CD_3)_2NC\underline{H_2}D$. [c] Molar ratio. [d] With 9 nmol Pt(0) as catalyst. [e] Based on loss of one hydride from each molecule for 3 days. [f] Based on the total amount of Si-H available for the reaction over an extended period of time.

Reaction with these silanes was monitored via ^1H NMR for an extended period of time. Even if more than 90% of $MePhSiH_2$ were consumed *no* formation of compound **3** (R^1=Ph, R^2=Me) was observed (unlike in case of Et_2SiH_2) and GC-MS showed the exclusive formation of compound **4** (**Figures S7(a) - (c)**, SI). This can imply that once the mechanism goes through formation of compound **2** it can still go via cycle **A** or cycle **B** but in case of its journey via cycle **A**, due to the sterics available (R^1=Ph, R^2=Me) on compound **3'** (cycle **A**) it cannot go through "necklace-type" unique step **3*** to form a cyclotrisiloxane but now takes a new route, which involves step **(3'→4')*** (**Scheme 2**) where it prefers cycle **B** over cycle **A** to form compound **4'** and eventually, exclusively compound **4**, a cyclo*tetra*siloxane (**Figures S7(a) - (c)**, SI). It should be noted that the formation of cyclo*tri*siloxanes in case of $MePhSiH_2$ is usually favoured and is also well supported by our earlier studies on the reduction of CO_2 with $MePhSiH_2$ in presence of a Pt NP-based catalytic system[13] (**Figures S8(a) - (c)**, SI). CO_2 shows single-reduction products that is 1st, 2nd and 3rd reduction product of CO_2 to be silylformate, silylacetal and methoxysilane, respectively, accompanied by the exclusive formation of a cyclo*tri*siloxane (R^1=Ph, R^2=Me). This does not require concerted activation of terminal Si-H bonds on the siloxane molecule thus a six-membered

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ring is possible but in case DMF (double) reduction next generation siloxane ring is formed due to ease in wrapping around Pt NP in formation of "necklace-type" transition for concerted activation of terminal Si-H bonds. In case Ph_2SiH_2 is used, silane consumption within three days further drops to ~3% and over an extended period of time a white precipitate is observed to form inside the NMR tube. GC-MS on this reaction mixture after almost 90% of silane consumption revealed that the formation of both compound **3** and compound **4** is not observed implying that because of the high sterics (R^1=R^2=Ph) on the Si atom the compounds are unable to form a "necklace-type" transition and thus form oligomers, which precipitate from the solvent.

Finally, a series of tertiary silanes were used (**Table 1**). Entry 4 shows a disiloxane molecule, $(Me_2HSi)_2O$, which has two hydrides but on two different Si atoms within the molecule. As expected, within 3 days only ~6% of the hydrides were consumed. This explains the drop in reaction rate in case of Et_2SiH_2 after 3 days when all the Et_2SiH_2 is consumed and the hydrides that were available for the reduction of DMF came from $(Et_2HSi)_2O$, again stressing on the effect of sterics on the reduction of DMF. GC-MS analysis of the reaction mixture with $(Me_2HSi)_2O$ shows the exclusive formation of cyclotetrasiloxanes (involvement of two molecules) as compared to a mixture of cyclotetrasiloxanes and cyclododecasiloxanes in case of Pannell's study with a Mo based homogeneous catalyst[11]. This implies that a necklace-type transition results in the formation of the smallest possible cyclosiloxanes as long as the sterics allows wrapping of the siloxane molecules on the Pt NP. Furthermore, this also explains the preferred formation of cyclotrisiloxane with Et_2SiH_2 over cyclotetrasiloxane mentioned earlier. Further, the use of $Me_2HSiOSiMe_3$ (**Table 1**, entry 5) shows that within 3 days only ~1.3% of silane was consumed while using a monohydrosilane, Et_3SiH (analogue of Et_2SiH_2, which is explained in details) shows that the reaction for extended time even resulted in consumption of only 0.2% of silane. Entries 5 and 6 thus provide strong evidence against the "dual Si-H effect" as explained in previous studies; instead it shows that a double reduction of DMF also occurs in the presence of a monohydrosilane but the rate of reaction is extremely slow due to the sterics on the Si atom. Entry 7, **Table 1**, shows that Me_2PhSiH even over an extended period of time does not react at all with DMF, which is consistent with the "sterics effect" theory. The dual Si-H effect can thus be redefined as *the presence of two Si-H bonds at two different Si atoms*, may it be the terminal Si atoms of siloxanes (unlike in the study by Ito[2]) or two molecules of a dihydrosilane (unlike in the study by Nagashima[4, 10]) or two molecules of monohydrosilane (unlike in both studies[2, 4, 10]), and their *concerted activation together with the amide* to form a tertiary amine. The sterics on the silane decides the fate of the reaction. The mechanism proposed here accounts for the formation of an amine by abstraction of the O atom from formamide and also fully accounts for the particular siloxane molecules formed from each specific silane used.

Conclusions

In conclusion, a heterogeneous catalytic system, which contains Pt(0) NPs immobilized on the surface of a monolithic polymeric support in the presence of a dihydrosilane allows for the double-reduction of DMF to produce trimethylamine and cyclosiloxanes. The studies here explain that the "dual Si-H effect" phenomenon mentioned in some earlier studies is a proxy of "sterics effect" and such a reduction is also possible with a monohydrosilane except the reaction is very slow. The reduction step of DMF involves a concerted activation of hydrides from two Si-H bonds and one DMF molecule at the catalytic centre that is the Pt(0) NPs. The reduction is strictly governed by the sterics on the Si atom at the catalytic centre and goes through a "necklace-type" transition prior to formation of the cyclosiloxane.

Notes and references

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† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/c000000x/

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Graphical Abstract + Text

The mechanism of the reduction of dimethylformamide to N(CH$_3$)$_3$ by the action of silanes and a heterogeneous Pt-catalyst is presented.