Disiloxanes

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The Photochemical Irradiation of R_3SiH in the Presence of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3]$ in DMF Leads to Disiloxanes not Disilanes[**]

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We recently reported that the photochemical irradiation of $t\mathrm{Bu}_2\mathrm{SnH}_2$ in the presence of a catalytic amount of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3]$ ([FpMe]) led to the efficient synthesis of the distannane $\mathrm{H}t\mathrm{Bu}_2\mathrm{SnSn}t\mathrm{Bu}_2\mathrm{H}$ in hydrocarbon solutions [Eq. (1)].[1]

$$2\,t\mathrm{Bu}_2\mathrm{SnH}_2 \xrightarrow[\text{[FpMe]},C_6D_6]{h\nu} \mathrm{H}t\mathrm{Bu}_2\mathrm{Sn{-}Sn}t\mathrm{Bu}_2\mathrm{H} + \mathrm{H}_2 \tag{1}$$

It was also recently noted that a similar irradiation of the tertiary silanes R_3SiH with the same catalyst [FpMe] led to the high-yield formation of the corresponding disilane R_3SiSiR_3, but only in the presence of *N*,*N*-dimethylformamide (DMF) as solvent [Eq. (2)].[2]

$$2\,R_3SiH \xrightarrow[\text{[FpMe]},\mathrm{DMF}]{h\nu} R_3Si{-}SiR_3 + H_2 \tag{2}$$

The ability of DMF to react with the hydrogen formed in this dehydrocoupling process to produce Me_3N was used to rationalize such interesting chemistry.

In our hands, the irradiation of the tertiary silanes R_3SiH reported in reference [2] (e.g. Ph_2MeSiH (**1**), $PhMe_2SiH$ (**2**), Et_3SiH (**3**)) in the presence of the catalyst [FpMe] in DMF solution results in the high-yield formation of the corresponding disiloxanes $R_3Si\text{-}O\text{-}SiR_3$ and no apparent formation of the disilane.

In our experiments, 130 mg samples of the tertiary silanes (Gelest) were irradiated in dry DMF (Aldrich) with 5 mol% of the catalyst [FpMe] in sealed NMR tubes at a distance of 3 cm from a 400 W low-pressure mercury lamp. The reactions were monitored by ^{29}Si NMR spectroscopy. The reactions with **1**, **2**, and **3** behaved similarly, with the disappearance of the resonance of the starting silane ($\delta = -17.5$ ppm (**1**) in 48 h; $\delta = -17.2$ ppm (**2**) in 1.5 h; $\delta = 0.5$ ppm (**3**) in 10 h) along with the appearance of a single resonance associated with the formation of the corresponding disiloxane $R_3SiOSiR_3$ ($\delta = -9.1$, 0.6, and 8.4 ppm for the reactions of **1**, **2**, and **3**, respectively). No resonances associated with the corresponding disilanes were observed, for example $(Ph_2MeSi)_2$ at $\delta = -22.6$ ppm[3] or $(PhMe_2Si)_2$ at $\delta = -21.5$ ppm.[3] Figure 1 illustrates this clean process for silane **1**.

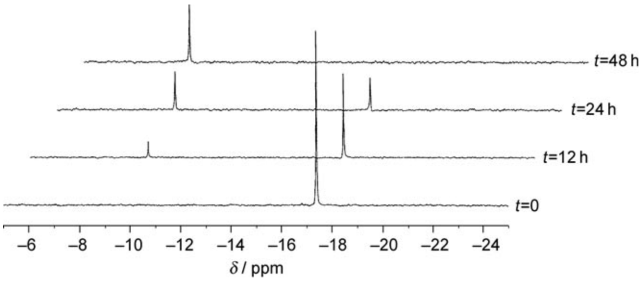

Figure 1. ^{29}Si NMR spectroscopic monitoring showing the disappearance of silane **1** in the presence a 5 mol% [FpMe] catalyst in DMF.

The GC–MS analysis of the product of this reaction also confirmed the formation of the disiloxane and the absence of any disilanes. We illustrate the gas chromatograph of $PhMe_2SiOSiMe_2Ph$ along with that of a commercial product (Gelest) in Figure 2. The equivalence is clear, with retention times of 10.14 and 10.16 min, respectively. The small amount of material at a retention time of 11.28 min is the trisiloxane $PhMe_2SiOSiMe_2OSiMe_2Ph$, which curiously is present both in the commercial material and the material synthesized in our experiments.

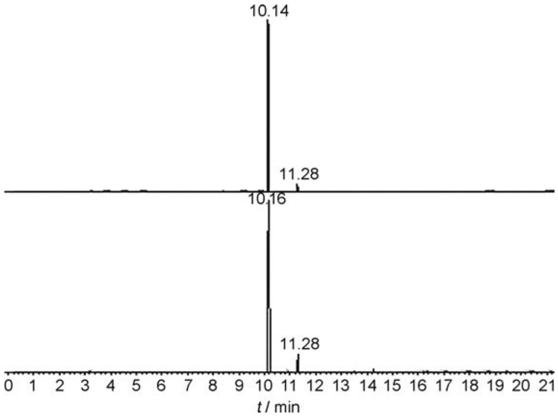

Figure 2. GC retention time data for $PhMe_2SiOSiMe_2Ph$, synthesized herein (top) and an authentic sample (Gelest; bottom).

The mass spectral portion of the GC–MS analysis of the three siloxane materials formed in our studies are illustrated in Figure 3. The inverted mass spectrum on the bottom of each part of Figure 3 is that derived from the standard library of materials and demonstrates absolute equivalence of the

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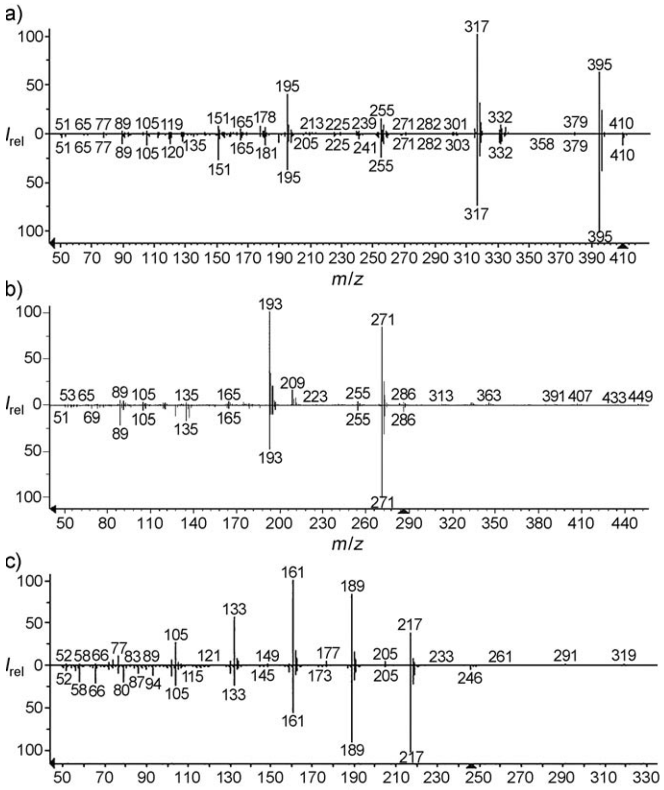


Figure 3. Mass spectra of a) $Ph_2MeSiOSiMePh_2$, b) $PhMe_2SiOSiMe_2Ph$, and c) $Et_3SiOSiEt_3$ formed in the reactions presented (top) and the literature spectra (bottom).

product to the reported standards.[4] No remaining R_3SiH, nor any disilane R_3SiSiR_3, was detected. In the report on the formation of disilanes,[2] neither structural nor spectroscopic evidence of the disilanes was reported, only GC analyses. In our hands, the use of GC to distinguish the disilane from the disiloxane product resulted in retention times of 10.14 min for $PhMe_2SiOSiMe_2Ph$ and 10.35 min for $PhMe_2SiSiMe_2Ph$ (Gelest) under our instrumental conditions. We note that in the supporting information associated with reference [2], the reported elemental analyses correspond more closely to disiloxane products than disilanes. Furthermore, the chemical shift in the ^{29}Si NMR spectrum presented for poly[(tetramethyldisilanylene)ferrocenylene] $[\{(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4\text{-}SiMe_2SiMe_2)\}_n]$ was $\delta = 0.78$ ppm, close to that of the model disiloxane complex $[\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)\}_2SiMe_2OSiMe_2]$, which we reported at $\delta = 0.48$ ppm.[5] In contrast, we also reported a model disilane complex of this type, that is, $[\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)\}_2SiMe_2SiMe_2]$, and noted that its ^{29}Si NMR spectrum contained a single resonance at $\delta = -22.4$ ppm.[6] Thus we have clearly demonstrated that only disiloxane formation takes place under the photochemical conditions reported above.[2]

We performed a series of experiments to determine whether any variation of the reaction conditions could account for our observations. For example, reactions with either dry or wet DMF yielded the same results. We also exposed the appropriate disilane to the same photochemical conditions, in the same solvent, either dry or used "as received", and detected no disiloxane production [Eq. (3)].

$$PhMe_2Si{-}SiMe_2Ph \xrightarrow[{[FpMe],DMF}]{h\nu} \text{no reaction} \qquad (3)$$

This result rules out initial formation of the disilanes and subsequent oxidation. At present we are unable to identify the specific features of our experimental setup that could result in the production of the siloxanes as opposed to disilanes.

The ability of DMF to remove the hydrogen produced to form Me_3N was suggested as a crucial feature for the solvent-specific process; however, this provokes the question as to the fate of the oxygen atom. In 1985 Voronkov and co-workers reported that treatment of various silanes $R_2R'SiH$ ($R_2R' = Cl_2Me$, Cl_2Et, Et_2Me, and Et_3) with DMF in the presence of metal species $(NO)_2PtCl_6$ or $[Me_2NH_2][Rh(CO)_2Cl_2]$ led to the formation of the corresponding disiloxanes.[7] In that study, and from the product yield/time relationship of the recent "disilane" synthesis, it was concluded that electron-withdrawing groups slowed down the process. We can confirm the same relationship using **1**, **2**, and Ph_3SiH. Indeed, in our hands the photolysis of Ph_3SiH with [FpMe] failed to yield a significant amount of $Ph_3SiOSiPh_3$, contrary to the reportedly slow reaction but high recovered yield of $Ph_3SiSiPh_3$.[2]

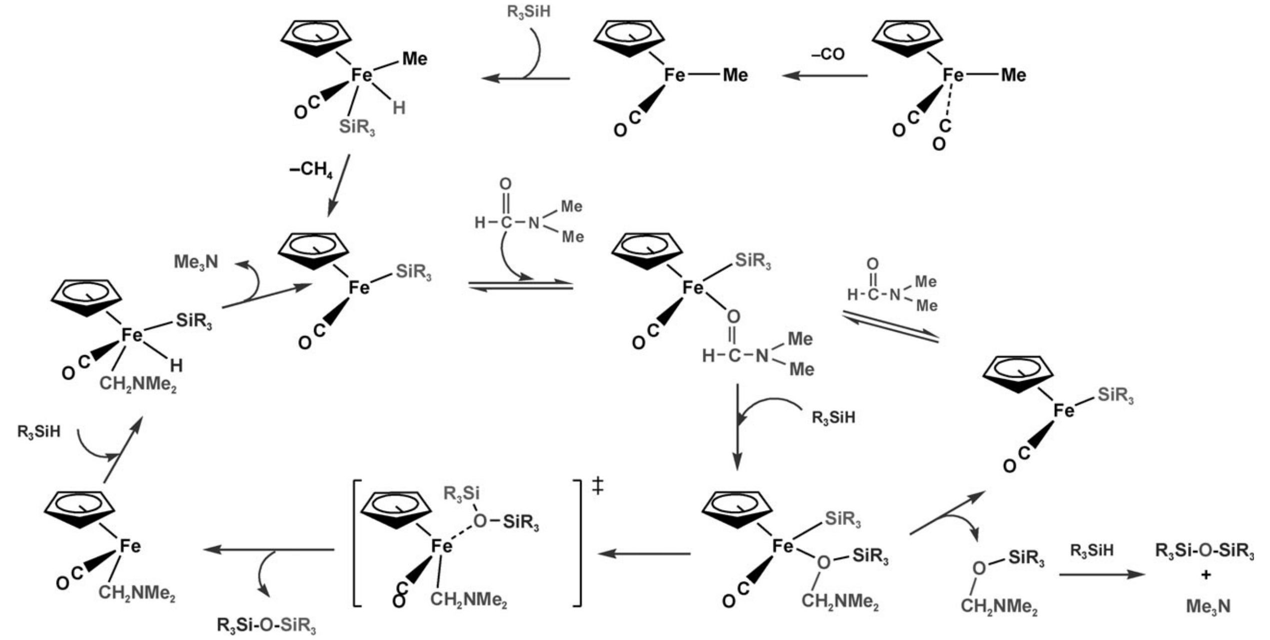
As to a mechanism for this interesting new chemistry, there are several possibilities. One certainly involves the formation of a bis(silyl) iron complex originally proposed for the formation of the disilanes.[2] However, the fact that disiloxane formation was noted by Voronkov using metal complexes of Pt and Rh, for which bis(silyl) complexes are less obviously accessible leads us to suggest the mechanism outlined in Scheme 1.

The key feature of this mechanism involves formation of the DMF metal complex and a subsequent hydrosilylation–reductive elimination process. There is significant precedent for the photochemical formation of DMF metal carbonyl complexes,[8] in which the electron-deficient ketone carbon atom is activated towards hydrosilylation chemistry.[9]

As noted in Scheme 1, it is possible that the hydrosilylated product $R_3SiOCH_2NMe_2$ could be eliminated and itself react with R_3SiH to form the disiloxane and Me_3N. This suggestion comes from a related precedent from Mironov and co-workers involving disiloxane elimination reactions of this product with chlorosilanes and related species [Eq. (4), X = Cl, NR_2 etc.].[10]

$$Me_3SiOCH_2NMe_2 + Me_3SiX \rightarrow Me_3SiOSiMe_3 + XCH_2NMe_2 \qquad (4)$$

We are continuing a detailed mechanistic study of this system, including studies of $R_3SiOCH_2NMe_2$ compounds. Regardless of the exact process, this catalytic process may be very general, as exchanging [FpMe] for $[(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3]$ and other related complexes accomplishes the same transformation of silane to disiloxane.[11] A recent discussion on the role of DMF in activating the



Scheme 1. Proposed catalytic mechanism for transformation of R_3SiH to $R_3SiOSiR_3$.

dehydrocoupling of silanes with hydroxylic reagents illustrates the complexity of the DMF–silane interactions.[12]

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[1] a) K. H. Pannell, H. K. Sharma, R. Arias, Abstracts of Papers, 235th ACS National Meeting, New Orleans, LA, United States, April 6–10, 2008, INOR-015; b) H. K. Sharma, R. Arias-Ugarte, A. J. Metta-Magana, K. H. Pannell, *Angew. Chem.* **2009**, *121*, 6427; *Angew. Chem. Int. Ed.* **2009**, *48*, 6309.

[2] a) M. Itazaki, K. Ueda, H. Nakazawa, *Angew. Chem.* **2009**, *121*, 3363; *Angew. Chem. Int. Ed.* **2009**, *48*, 3313; b) “Disilane bond-containing polymers and preparation thereof”: H. Nakazawa, M. Itazaki, Jpn. Kokai Tokkyo Koho, **2009**; c) “Preparation of Si–Si bond-bearing compounds”: H. Nakazawa, M. Itazaki, U.S. Pat. Appl. Publ., **2009**.

[3] ^{29}Si chemical shift in the NMR spectra of a commercial sample (Gelest) of $PhMe_2Si{-}SiMe_2Ph$ in DMF (without lock) is observed at $\delta = -21.8$ ppm and in C_6D_6 at $\delta = -21.48$ ppm. ^{29}Si chemical shift of the disilane $Ph_2MeSi{-}SiMePh_2$ synthesized from equimolar amounts of $Ph_2MeSiLi$ and $Ph_2MeSiCl$ in THF is observed at $\delta = -22.56$ ppm in C_6D_6.

[4] GC–MS analysis was performed using a trace GC connected to a Polaris Q mass spectrometer (Thermo Fisher Scientific). The library search algorithm used was the NIST MS Search 2.0, which comes in Xcalibur 1.4 SR1 (Thermo Fisher Scientific) package.

[5] K. H. Pannell, H. K. Sharma, *Organometallics* **1997**, *16*, 3077.

[6] K. H. Pannell, H. Sharma, *Organometallics* **1991**, *10*, 954.

[7] L. I. Kopylova, N. D. Ivanova, M. G. Voronkov, *Zhur. Obshch. Khim.* **1985**, *55*, 1649.

[8] I. W. Stolz, G. R. Dobson, R. K. Sheline, *Inorg. Chem.* **1963**, *2*, 323.

[9] a) S. Diez-González, S. P. Nolan, *Organic Preparations and Procedures International* **2007**, *39*, 523; b) R. H. Morris, *Chem. Soc. Rev.* **2009**, *38*, 2282.

[10] V. P. Kozyukov, V. P. Kozyukov, V. F. Mironov, *Zh. Obshch. Khim.* **1983**, *53*, 119.

[11] R. Arias, unpublished results.

[12] J. J. Chruściel, *Can. J. Chem.* **2005**, *83*, 508.