Supporting Information on

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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Table of Contents

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Synthesis of Digermoxanes using CpMo(CO) ₂ (PPh ₃)Me, 2b, as a catalyst	2
Synthesis of Digermoxanes using $Mo(CO)_6$ as a catalyst	2
Isolation of Siloxymethylamines, R ₃ SiOCH ₂ NMe ₂ , (4a-d) from the catalytic cycle	3
Spectroscopic data for R ₃ SiOCH ₂ NMe ₂ , (4a – 4d)	3-5
Isolation of Phenyldimethylsiloxymethyldiethylamine, $PhMe_2SiOCH_2NEt_2$	5
The reaction of PhMe ₂ SiOCH ₂ NMe ₂ with PhMe ₂ SiH using Mo(CO) ₆ as a catalyst	5
Table S-1: Synthesis of $R_3SiOSiR_3$ from the reaction of $R_3SiOCH_2NR'_2$ and R_3SiH	6
Synthesis of unsymmetrical disiloxanes, and mixed siloxygermanes and siloxystannanes	6-9
Photochemical reaction of $Mo(CO)_6$ with Et_3SiH followed by addition of DMF	9-11
The reaction of Et ₃ SiOCH ₂ NMe ₂ and PhMe ₂ SiH in excess DMF without a metal catalyst	11
Synthesis of PhMe ₂ SiOSiMe ₂ Ph from a catalytic cycle using $M(CO)_6$, (M = Cr (6), W (7))	11
References	12

Page

All manipulations were carried out under Argon atmosphere using Schlenk or vacuum line techniques. THF was distilled under nitrogen from benzophenone ketyl prior to use. Other solvents, hexanes, benzene and toluene were dried over sodium metal and distilled before use. DMF was distilled over BaO. Iron dimer $[(\eta^5-C_5H_5)Fe(CO)_2]_2$, Mo dimer, $[(\eta^5-C_5H_5)Mo(CO)_3]_2$ and Mo(CO)₆ were purchased from Strem Chemicals. Group 14 hydrides, R₃EH were purchased either from Aldrich or Gelest. The metal complexes $(\eta^5-C_5H_5)M(CO)_nCH_3$ [1] and $(\eta^5-C_5H_5)M(CO)_{n-1}(PPh_3)-CH_3$ [2,3] (M = Fe, n = 2; M = Mo, n = 3) were synthesized by the reported method. NMR spectra were recorded on 300 MHz Bruker spectrometer in C₆D₆. GC/MS were recorded on Thermo Fisher Scientific GC/mass spectrometer. All column chromatography was performed on small columns (5 x 60 mm) of Silica Gel (Aldrich), 700-230 mesh, 60Å, Pore Volume 0.75 cm³/g.

Synthesis of Digermoxanes using CpMo(CO)₂(PPh₃)Me, 2b, as a catalyst: In a typical experiment, a Pyrex NMR tube was charged with 1 mmol of R₃GeH (R = Et, Bu), 3 mmol of DMF, 5 mol % of CpMo(CO)₂Ph₃PMe and 0.5 mL of C₆D₆. The tube was sealed under vacuum and heated at 90 °C in an oil bath. The reaction was monitored by ¹H and ¹³C NMR spectroscopy. The reaction was 90% complete in 5-8 days to yield digermoxanes which were purified by column chromatography eluting with hexanes.

Synthesis of Digermoxanes using $Mo(CO)_6$ as a catalyst: In a typical experiment a Pyrex NMR tube was charged with 1 mmol of R₃GeH (R = Et, Bu, Ph), 3 mmol of DMF, 5 mol % of $Mo(CO)_6$ and 0.5 mL of C₆D₆. The tube was sealed under vacuum and heated at 90 °C in an oil bath. The reaction was monitored by ¹H and ¹³C NMR spectroscopy. The reaction was complete

in 3-7 days to yield the corresponding digermoxanes. No germoxymethylamines, $R_3GeOCH_2NMe_2$, were observed in the reaction mixture. The ¹³C NMR spectra of the reaction mixture showed a small resonance at 58 ppm which is assigned to the Mo(CO)₅NMe₃ complex. The digermoxanes were purified by column chromatography eluting with hexanes. The yields of digermoxanes were relatively higher than using **2b** as catalyst.

Isolation of Siloxymethylamines, $R_3SiOCH_2NMe_2$, (4a-d) from the catalytic cycle: In a typical experiment, a Pyrex NMR tube was charged with 1 mmol of R_3SiH ($R_3 = PhMe_2$, Ph_2Me , Ph_3 , Et_3), 2 mmol of DMF, 5 mol % of Mo(CO)₆ and 0.5 mL of C₆D₆. The tube was sealed under vacuum and heated at 90 °C in an oil bath under which conditions the catalyst completely dissolved. The reaction was monitored by ²⁹Si and ¹³C NMR spectroscopy and after 2-5 h of heating, the concentration of siloxymethylamines reached a maximum with only a trace of the disiloxane present. The reaction was stopped at this stage and the NMR tube was opened and the solution was filtered through an acrodisc filter to remove the catalyst that had precipitated upon cooling. The volatiles and DMF were removed by flash distillation (into liquid nitrogen cooled receptacles) at ambient temperature (0.5mm of Hg) to leave the siloxymethylamines as colorless liquids which were further purified by distillation under vacuum.

Et₃SiOCH₂NMe₂: b.pt. 70-72 °C at 20mm of Hg. Yield: 90%. ¹H NMR: δ 0.55 (q, 6 H, CH₂), 0.97(t, 9H, CH₃), 2.31, (s, 6 H, Me-N), 4.28 (s, 2 H, CH₂). ¹³C NMR: δ 5.03, 7.15 (Et), 41.1 ((CH₃)₂N), 82.3 (CH₂). ²⁹Si NMR: δ 15.3; HRMS(ESI): Calcd. for C₉H₂₂SiNO: (M⁺-1): 188.1470, Found 188.1445. Anal. Calcd. for C₉H₂₃NOSi: C, 57.1; H, 12.2. Found: C, 55.9; H, 12.2.

PhMe₂SiOCH₂NMe₂: b.pt. 60-62 °C at 0.07 mm of Hg. Yield: 30%. ¹H NMR: δ 0.7 (s, 6 H, Me), 2.6, (s, 6 H, Me-N), 4.6 (s, 2 H, CH₂), 7.6, 7.9 (m, 5H, Ph). ¹³C NMR: δ -1.4 (SiMe), 41.1 ((CH₃)₂N), 82.4 (CH₂), 128.1, 129.7, 133.7, 138.5 (Ph). ²⁹Si NMR: δ 5.4, HRMS(ESI): Calcd. for $C_{11}H_{20}NOSi:$ (M⁺+1): 210.1314, Found 210.1314. Anal. Calcd. for $C_{11}H_{19}NOSi:$ C, 63.11; H, 9.15. Found: C, 63.6; H, 9.42.

Ph₂MeSiOCH₂NMe₂: b.pt. 110-112 °C at 0.07 mm of Hg. Yield: 20%. ¹H NMR δ 0.5 (s, 3 H, MeSi), 2.2 (s, 6 H, Me-N), 4.3 (s, 2 H, CH₂), 7.1, 7.5 (m, 10 H, Ph). ¹³C NMR: δ -3.0 (SiMe), 40.8 (N(CH₃)₂), 82.5 (CH₂), 128.1, 129.9, 134.6, 136.9 (Ph). ²⁹Si NMR δ -5.1; HRMS(ESI): Calcd. for C₁₆H₂₂NOSi: (M⁺+1): 272.1470, Found 272.1417.

Ph₃SiOCH₂NMe₂: Oily semi-solid, Yield: 10%. ¹H NMR: δ 2.28 (s, 6H, Me-N), 4.38 (s, 2 H, CH₂), 7.41, 7.46, 7.65 (m, 15 H, Ph). ¹³C NMR: δ 40.87 (N(CH₃)₂), 81.8 (CH₂), 128.0, 130.2, 135.5, 135.6(Ph). ²⁹Si NMR: δ -14.8; HRMS(ESI): Calcd. for C₂₁H₂₄NOSi: 334.1627:(M⁺+1): Found: 334.1479.

Isolation of Phenyldimethylsiloxymethyldiethylamine, PhMe₂SiOCH₂NEt₂, from a catalytic reaction: In a typical experiment, a Pyrex NMR tube was charged with 1 mmol of R₃SiH (R₃= PhMe₂), 1.5 mmol of DEF and 5 mol % of CpMn(CO)₃ in 0.5 mL of C₆D₆ and was sealed under vacuum. Sealed tube was irradiated 4 cm from a 400 W medium-pressure mercury lamp and the reaction was monitored by ²⁹Si and ¹³C NMR spectroscopy. After 16 h of irradiation, the concentration of siloxymethylamine was reached to maximum and only traces of

siloxane was observed. The reaction was stopped at this stage and NMR tube was opened and the solvents were removed under reduced pressure and PhMe₂SiOCH₂NEt₂ was obtained in 95% yield.

PhMe₂SiOCH₂NEt₂: Yield: 95%. ¹H NMR : δ 0.39(s, 6 H, (Me)), 1.10(t, 6 H, (Me)CH₂N), 2.74(q, 4 H, (CH₂)NMe), 4.55(s, 2 H, (CH₂)NEt₂); 7.31, 7.66(m, 5 H, Ph). ¹³C NMR : δ -1.64 (Me), 13.30, 44.80 (Et)₂N, 76.56 (CH₂)N. ²⁹Si NMR : δ . 3.64. HRMS(ESI): Calcd. for C₁₃H₂₃NOSi: (M⁺): 237.1540, Found 237.1463.

The reaction of PhMe₂SiOCH₂NMe₂ with PhMe₂SiH using Mo(CO)₆ as a catalyst: In a typical experiment, a Pyrex NMR tube was charged with 1 mmol of R₃EH (E = Si, R₃ = PhMe₂), 1.5 mmol of PhMe₂SiOCH₂NMe₂, 5 mol % of Mo(CO)₆ and 0.5 mL of C₆D₆. The tube was sealed under vacuum and heated at 90 °C in an oil bath. The reaction was monitored by ²⁹Si and ¹³C NMR spectroscopy and shown to be complete in 1 day to yield (PhMe₂Si)₂O and NMe₃ (¹³C 47 ppm) and Mo(CO)₅NMe₃ (¹³C 58 ppm). The disiloxane, (PhMe₂Si)₂O was purified by column chromatography eluting with hexanes and was isolated in 80% yield.

In a similar manner a series of symmetrical disiloxanes were synthesized from the reactions of $R_3SiOCH_2NR'_2$ and R_3SiH using $Mo(CO)_6$, $CpMn(CO)_3$ and $CpMo(CO)_3Me$ as catalysts, Table S-1.

Table S-1: Synthesis of R₃SiOSiR₃ from the reaction of R₃SiOCH₂NR'₂ and R₃SiH using CpMo(CO)₃Me (2a), Mo(CO)₆ (3a) and CpMn(CO)₃ (5) as catalyst.

R ₃	R' ₂	Cat	hv/∆	Time	Yield
				_	(NMR) ^b

Et_3	Me ₂	2a	hv	12 h	(100)
Et_3	Me ₂	2a	Δ	12 h	(100)
Et_3	Me ₂	3a	Δ	2d	TR
Et₃	Me ₂	3a	Δ	2d	(80) ^c
Et_3	Me ₂	3a	hv	4d	(20)
PhMe₂	Et_2	5	Δ	5 h	(100) ^c

^bYields based upon ¹H NMR; ^c reaction performed at 120 ^oC. CpMo(CO)₃Me (**2a**); Mo(CO)₆ (**3a**); CpMn(CO)₃ (**5**).

Synthesis of unsymmetrical disiloxanes, and mixed siloxygermanes and siloxystannanes from the reaction of R₃EH and Me₃SiOCH₂NMe₂ using CpMo(CO)₃Me (2a) as a catalyst: In a typical experiment, a Pyrex NMR tube was charged with 1 mmol of R₃EH (E = Si, R₃ = Ph, Ph₂Me, PhMe₂; E = Ge, R₃ = Ph, Et; E = Sn, R₃ = Bu), 1.2 mmol of Me₃SiOCH₂NMe₂, 5 mol % of CpMo(CO)₃Me and 0.5 mL of C₆D₆ and sealed under vacuum. The tube was irradiated with a 450 W medium pressure mercury lamp. The progress of the reactions was monitored by ¹³C, ²⁹Si and ¹¹⁹Sn NMR spectroscopy where appropriate. After 2-18 h of irradiation, the siloxyproducts were maximized and the reaction was stopped. The volatiles were removed by flash distillation, ambient temperature 0.5 mm Hg, and the disiloxanes, siloxygermanes or siloxystannanes were purified by column chromatography eluting with hexanes and isolated in 60-83 % yield.

The same materials were synthesized by the direct reaction of Me₃SiOCH₂NMe₂ and the appropriate chloro-silane, -germane or -stannane by the Mironov technique.[5] In a typical experiment, a Pyrex NMR tube was charged with 1 mmol of R₃ECl (E = Si, R₃ = Ph, Ph₂Me, PhMe₂; E = Ge, R₃ = Ph, Me₃; E = Sn, R₃ = Bu, Ph), 1.2 mmol of Me₃SiOCH₂NMe₂ and 0.5 mL of C₆D₆ and the tube was sealed under vacuum. The tube was heated from 20 to 80 °C depending upon the R₃ECl in an oil bath. The progress of the reaction was monitored by ¹³C,

²⁹Si or ¹¹⁹Sn NMR spectroscopy. After 1-12 h of heating, the reaction was stopped and the volatiles were removed by flash distillation and the disiloxanes, siloxygermanes, siloxystannanes were purified by column chromatography eluting with hexanes and were isolated in 58-90 % yield.

Ph₃SiOSiMe₃: Yield: 83%. ¹H NMR: δ 0.20 (s, 9 H, Me), 7.26, 7.44, 782 (m, 15 H, Ph). ¹³C NMR: δ 2.08 Me, 128.1, 130.1, 135.4, 136.6 Ph. ²⁹Si NMR δ -20.2 Si(Ph), 11.1 Si(Me). GC/Mass: *m/z*: 348 (M⁺, 10%); 333(M⁺-Me, 54%); 255(M⁺-1-PhMe,100%);193(M⁺-1-Ph₂,45%) 179(M⁺-Ph₂Me, 45%).

Ph₂MeSiOSiMe₃: Yield: 60%. ¹H NMR : δ 0.2 (s, 9 H, Me), 0.7 (s, 3H, Me), 7.2, 7.3, 7.8 (m, 12 H, Ph). ¹³C NMR : δ -0.3 Me, 2.0 Me, 128.1, 129.9, 134.4, 138.4 Ph). ²⁹Si NMR : δ -11.2 Si(Ph), 10.2 Si(Me); GC/Mass: *m/z*: 286(M⁺, 1%); 271(M⁺-Me, 63%); 193 (M⁺-1-PhMe, 100%); 179(M⁺-PhMe₂, 1%).

PhMe₂SiOSiMe₃: Yield: 70%. ¹H NMR : δ 0.2 (s, 9 H, Me), 0.4 (s,6 H, Me), 7.2, 7.3, 7.6 (m, 5 H, Ph). ¹³C NMR : δ 0.9 Me, 2.0 Me, 128.0, 129.6, 133.3, 140.1 (Ph). ²⁹Si NMR : δ -1.6 Si(Ph), 9.2 Si(Me). GC/Mass: *m/z*: 224 (M⁺, 1%); 209 (M⁺-Me, 100%); 193(M⁺-1-Me₂, 50%), 179 (M⁺-Me₃, 4%); 135(PhMe₂Si⁺, 4%); 107(M⁺-SiOSiMe₃, 2%).

Ph₃GeOSiMe₃: Yield: 91%. ¹H NMR : δ 0.3 (s, 9 H, Me), 7.2, 7.3, 7.8 (m, 15 H, Ph). ¹³C NMR : δ 2.9 (Me), 128.6, 130.1, 134.5, 137.1 Ge(Ph). ²⁹Si NMR : δ 8.3 GC/Mass: *m/z*: 394 (M⁺); 379.0(M⁺-Me, 100%); 318(M⁺+1-Ph, 33%); 301(M⁺-1-PhMe, 75%); 241(M⁺+1-Ph₂, 7%).

Et₃GeOSiMe₃: Yield: 75 %. ¹H NMR : δ 0.1 (s, 9H, (Me)₃Si), 0.7 (q, 6H, CH₂), 0.9 (t, 9 H, (Me)Ge). ¹³C NMR : δ 2.9 (Me)₃Si, 7.9, 8.6 (Et)₃Ge. ²⁹Si NMR : δ 6.8. HRMS (DART), Calcd.

For C₉H₂₄OSiGe, M+1, 251.0887, Found 251.0844).

Me₃GeOSiMe₃: Yield: 50%. ¹H NMR : δ 0.2 (s, 9 H, Si(Me)₃), 0.3 (s, 9 H, Me). ¹³C NMR : δ 2.8 Si(Me), 2.9 Ge(Me). ²⁹Si NMR : δ 7.9 GC/Mass: *m/z*: 207 (M⁺-1, 4%); 193(M⁺-Me, 25%), 119 (Me₃Ge⁺, 100%); 89(MeGe⁺, 20%); 74(Ge⁺ 1%).

PhMe₂GeOSiMe₃: Yield: 90%. ¹H NMR : δ 0.2 (s, 9 H, SiMe), 0.6 (s, 6 H, GeMe), 7.2, 7.3, 7.7 (m, 5H, Ph). ¹³C NMR : δ 1.1 SiMe 2.88 GeMe, 128.4, 129.6, 132.8, 141.5 (Ph). ²⁹Si NMR : δ 5.9 GC/Mass: *m/z*: 272(M⁺+2, 5%); 255(M⁺-Me,100%); 239(M⁺-1-Me₂,30%); 181(PhMe₂Ge⁺, 66%); 151(PhGe⁺,8%); 73(SiMe₃⁺1,3%).

Bu₃SnOSiMe₃: Yield: 80%. ¹H NMR: δ 0.3 (s, 9 H, Me), 0.9, 1.1, 1.4, 1.7 (m,27H, ⁿBu). ¹³C NMR: δ 3.7 Me, 13.8, 16.2, 27.4, 28.2 Bu. ²⁹Si NMR: δ 5.6, (²J^{119/117}Sn-O-²⁹Si = 37.0 Hz). ¹¹⁹Sn NMR 76.44 HRMS(ESI): Calcd. for C₁₅H₃₆OSiSn: 381.1635 (M⁺+1), Found: 381.1550.

Ph₃SnOSiMe₃: Yield: 84%. ¹H NMR : δ 0.30 (s, 9 H, Me), 7.24, 7.25, 7.75 (m,15H, Ph). ¹³C NMR: δ 3.62 Si(CH₃)₃, 129.15, 130.19, 136.65, 139.32 Sn(Ph)₃. ²⁹Si NMR: δ 11.04, (²J^{119/117}Sn-O-²⁹Si = 32 Hz). ¹¹⁹Sn NMR : -107.5 HRMS(ESI): Calcd. for C₂₁H₂₅OSiSn: 441.0700 (M⁺+1), Found: 441.2524.

Bu₃GeOGeBu₃: Yield: 70%. ¹H NMR : δ 0.8, 0.9, 1.3, 1.5 (m, 54H, ⁿBu). ¹³C NMR : δ 14.1, 18.2, 26.8, 27.0, Ge(ⁿBu). GC/Mass: *m/z*: 506(M⁺, 1%); 447(M⁺-2-Bu, 15%); 391 (M⁺-1-2Bu, 83%); 335.0(M⁺-3Bu,100%); 277(M⁺-1-4Bu,42%); 221(M⁺-5Bu,15%); 163(M⁺-1-6Bu,4%); 75(Ge⁺,1%).

Et₃GeOGeEt₃: Yield: 70%. ¹H NMR: δ 0.8, 1.0 (m, 30H, Et). ¹³C NMR: δ 8.3, 9.3, Et.

GC/Mass: *m/z*: 338(M⁺, 1%); 309(M⁺-Et,100%); 280(M⁺,-2Et,49%); 252(M⁺-1-3Et, 57%); 222(M⁺-4Et, 53%); 195(M⁺+2-5Et, 50%); 75(Ge⁺, 9%).

Ph₃GeOGePh₃: Yield: 60%. Found: ¹³C NMR: δ 128.5, 129.9, 134.4, 137.6 (Ph). Reported in CDCl₃: ¹³C NMR: δ 128.0, 129.3, 134.3, 137.4 (Ph). M. pt found: 184-185°C. Mp: Reported: 184°C [4].

PhMe₂SiOSiMe₃: Yield: 30%. ¹H NMR : δ 0.2 (s, 9 H, Me), 0.4 (s,6 H, Me), 7.2, 7.3, 7.6 (m, 5 H, Ph). ¹³C NMR : δ 0.9 Me, 2.0 Me, 128.0, 129.6, 133.3, 140.1 (Ph). ²⁹Si NMR : δ -1.6 Si(Ph), 9.2 Si(Me).

Photochemical reaction of $Mo(CO)_6$ with Et_3SiH followed by addition of DMF: A Pyrex NMR tube was charged with 0.15 g (1.3 mmol) of Et_3SiH , 0.06 g (0.22 mmol) of $Mo(CO)_6$ and 0.4 mL of C_6D_6 and sealed under vacuum. The tube was irradiated with a 450 W medium pressure mercury lamp. After 20 minutes of photolysis, the color of the solution turned yellow and in the ¹HNMR spectrum a resonance appeared at -8.4 ppm due to the formation of $(CO)_5Mo(\eta^2-H-SiEt_3)$ complex [6]. At this time 0.4 mL DMF was added and the NMR tube was resealed after two freeze-pump-thaw cycles and ¹HNMR spectrum was recorded immediately which exhibited that the resonance at -8.4 ppm is decreasing and a new resonance at 4.28 ppm is appearing which is assigned to the CH₂ group of the Et₃SiOCH₂NMe₂. The NMR tube was left at room temperature for 48 h, the ¹H, ¹³C and ²⁹Si NMR spectra showed that the Et₃SiH is completely consumed and reacted with DMF to form Et₃SiOCH₂NMe₂.

The reaction of Et₃SiOCH₂NMe₂ and PhMe₂SiH in excess DMF without a metal catalyst: In a typical experiment, a Pyrex NMR tube was charged with 1.5 mmol of PhMe₂SiH, 1 mmol of Et₃SiOCH₂NMe₂ and 5 mmol of DMF in C₆D₆ and sealed under vacuum. The tube was heated at 90°C. The progress of the reaction was monitored by ¹³C and ²⁹Si NMR spectroscopy. After 3 h of heating, the ¹³C resonance at 47 ppm due to the formation of Me₃N reached a maximum, and the reaction was stopped and the volatiles removed. Unsymmetrical disiloxane Et₃SiOSiPhMe₂ was formed in 90 % yield along with trace amount of symmetrical disiloxane, PhMe₂SiOSiMe₂Ph.

The same reaction between Et_3SiH and $Et_3SiOCH_2NMe_2$ yielded essentially quantitative yields of $Et_3SiOSiEt_3$. If the reaction is left at ambient temperature in a sealed NMR tube the reaction proceeds slowly over a period of several days.

Et₃SiOSiPhMe₂: Yield: 90%. ¹H NMR : δ 0.35 (s, 3 H, (Me)PhSi), 0.55 (q, 6 H, (CH₂)Si), 0.98 (t, 9 H, (Me)Si), 7.24, 7.62 (m, 5 H, Ph). ¹³C NMR : δ 1.00 (Me), 6.66, 7.03 (Et), 128.33, 129.56, 133.27, 140.30 (Ph). ²⁹Si NMR : δ 10.90 (Si)Et₃, -3.21 (Si)PhMe₂. HRMS(ESI): Calcd. for C₁₄H₂₆Si₂O: (M⁺+1): 267.1600, Found 267.1573.

Table S-2: Synthesis of R₃SiOSiR₃: Reaction of R₃SiOCH₂NR'₂ and R₃SiH using excess of DMF/DEF without a catalyst

R ₃	R'2	T°C	Time	Yield
				(NMR) ^b
Et₃	Me ₂	90	3 h	(100)
Et₃	Me ₂	35	1d	(100)
PhMe ₂	Et ₂	120	5 h	(100) ^b

^a Yields based upon ¹H, ¹³C NMR spectroscopy; ^b DEF



Figure S-1: ¹³C NMR spectra monitoring of a thermal reaction between $Et_3SiOCH_2NMe_2$ (Δ) and Et_3SiH (*) at 90 °C using excess of DMF <u>without a catalyst</u> showing the formation of $Et_3SiOSiEt_3(\Diamond)$ and Me_3N .

Synthesis of PhMe₂SiOSiMe₂Ph from a catalytic cycle using $M(CO)_6$, (M = Cr (6), W (7)) catalysts: In a typical experiment, a Pyrex NMR tube was charged with 1 mmol of PhMe₂SiH, 8 mmol of DMF and 5 mol % of $M(CO)_6$ in 0.5 mL of C₆D₆ and sealed under

vacuum and either heated at 90 °C in an oil bath or photochemically irradiated. The reaction was monitored by ²⁹Si and ¹³C NMR spectroscopy. After 1-6 h of heating or irradiation the silane was consumed to form the disiloxane, PhMe₂SiOSiPhMe₂, and NMe₃. The reaction was stopped at this stage and the NMR tube was opened and the solution was filtered with acrodisc filter to remove the traces of the catalyst, $M(CO)_6$. The volatiles were removed under high vacuum and the disiloxane obtained was passed through a small silica gel column (0.4cm x 2 cm) eluting with hexanes to yield 70-90% of disiloxane, PhMe₂SiOSiPhMe₂.

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