

***Supporting Information for:***

**Mo(CO)<sub>6</sub>-Catalyzed Reduction of N,N-Dimethylthioformamide by Silanes, Germanes and Stannanes, R<sub>3</sub>EH, to Produce Trimethylamine and Group 14 Thioethers, R<sub>3</sub>E-S-ER<sub>3</sub>**

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All manipulations were carried out under Argon atmosphere using Schlenk or vacuum line techniques. Thioformamide was distilled under nitrogen over barium oxide prior to use. Other solvents, hexanes, benzene and toluene were dried over sodium metal and distilled before use. Mo(CO)<sub>6</sub> were purchased from Strem Chemicals. Group 14 hydrides, R<sub>3</sub>EH were purchased either from Aldrich or Gelest. The metal complex Mo(CO)<sub>5</sub>(S=CHNMe<sub>2</sub>) and Mo(CO)<sub>5</sub>(NMe<sub>3</sub>) were synthesized by the reported methods.<sup>[1,2]</sup> NMR spectra were recorded on 300 MHz Bruker spectrometer in C<sub>6</sub>D<sub>6</sub>. The 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, 60A° Pore Volume 0.75 cm<sup>3</sup>/g.

**Synthesis of R<sub>3</sub>ESER<sub>3</sub>, E=Si, Ge, Sn using Mo(CO)<sub>6</sub> as catalyst:** In a typical experiment, a Pyrex NMR tube was charged with 1 mmol of R<sub>3</sub>EH, E = Si, R<sub>3</sub> = Me<sub>2</sub>Ph, MePh<sub>2</sub>, Et<sub>3</sub>; E = Ge, R<sub>3</sub> = Et<sub>3</sub>, Bu<sub>3</sub>, Ph<sub>3</sub>; E = Sn, R<sub>3</sub> = Bu<sub>3</sub>, Ph<sub>3</sub> and 3 mmol excess of HC(S)NMe<sub>2</sub>, 5 mol % of Mo(CO)<sub>6</sub> catalyst in 0.5 mL of C<sub>6</sub>D<sub>6</sub>. The tube was degassed and sealed under vacuum and heated at 120 °C in an oil bath. The progress of

the reaction was monitored by  $^{13}\text{C}$ ,  $^{29}\text{Si}$  or  $^{119}\text{Sn}$  NMR spectroscopy. After 1-3 days of heating, the reaction was complete and thiane derivatives  $\text{R}_3\text{ESER}_3$  were purified on silica gel column, eluting with hexanes and were isolated in 53-90 % yield.

**Reaction of  $\text{PhMe}_2\text{SiH}$  with  $\text{N,N}$ -dimethylthioformamide in the presence of  $\text{Mo}(\text{CO})_5(\text{S}=\text{CHNMe}_2)$  (**3c**) catalyst:** A Pyrex NMR tube was charged with 1 mmol of  $\text{PhMe}_2\text{SiH}$  and 3 mmol excess of  $\text{HC}(\text{S})\text{NMe}_2$ , 5 mol % of  $\text{Mo}(\text{CO})_5(\text{S}=\text{CHNMe}_2)$  (**3c**) catalyst in 0.5 mL of  $\text{C}_6\text{D}_6$ . The tube was degassed and sealed under vacuum and heated at  $120^\circ\text{C}$  in an oil bath. The progress of the reaction was monitored by  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectroscopy. After 3h of heating, the reaction was complete and  $(\text{PhMe}_2\text{Si})_2\text{S}$  was isolated in 80 % yield.

**Reaction of  $\text{PhMe}_2\text{SiH}$  with  $\text{N,N}$ -dimethylthioformamide in the presence of  $\text{Mo}(\text{CO})_5(\text{NMe}_3)$  (**3b**) catalyst:** A Pyrex NMR tube was charged with 1 mmol of  $\text{PhMe}_2\text{SiH}$  and 3 mmol excess of  $\text{HC}(\text{S})\text{NMe}_2$  and 5 mol % of  $\text{Mo}(\text{CO})_5(\text{NMe}_3)$  (**3b**) catalyst in 0.5 mL of  $\text{C}_6\text{D}_6$ . The tube was degassed and sealed under vacuum and heated at  $120^\circ\text{C}$  in an oil bath. The progress of the reaction was monitored by  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectroscopy. After 3h of heating, the reaction was complete and  $(\text{PhMe}_2\text{Si})_2\text{S}$  was isolated in 90 % yield.

**$\text{PhMe}_2\text{SiSSiMe}_2\text{Ph}$  <sup>[3]</sup>:** Yield: 87%.  $^1\text{H}$  NMR:  $\delta$  0.42 (s, 12H, Me), 7.3, 7.5, 7.6 (m, 10H, Ph).  $^{13}\text{C}$  NMR:  $\delta$  2.6 (Me), 128.1, 129.8, 133.8, 138.6 (Ph).  $^{29}\text{Si}$  NMR:  $\delta$  7.1; GC/Mass:  $m/z$ : 301( $\text{M}^+-1$ , 1%), 287( $\text{M}^+-\text{Me}$ , 42%), 209( $\text{M}^+-1-\text{MePh}$ , 100%), 135( $\text{PhMe}_2\text{Si}^+$ , 10%),

105(PhSi<sup>+</sup>, 7%).

**Ph<sub>2</sub>MeSiSSiMePh<sub>2</sub>**<sup>[3,4]</sup>: Yield: 63%. <sup>1</sup>H NMR : δ 0.4 (s, 6H, Me), 7.1, 7.2, 7.3 (m, 20H, Ph). <sup>13</sup>C NMR : δ 0.5 (Me), 127.8, 129.8, 134.2, 136.4 (Ph). <sup>29</sup>Si NMR : δ 1.5; GC/Mass: *m/z*: 427(M<sup>+</sup>+1, 1%), 411(M<sup>+</sup>-Me, 37%), 333(M<sup>+</sup>-1-MePh, 100%), 271(M<sup>+</sup>-1-Ph<sub>2</sub>, 9%), 181 (Ph<sub>2</sub>Si<sup>+</sup>-1, 12%).

**Et<sub>3</sub>SiSSiEt<sub>3</sub>**<sup>[5]</sup>: Yield: 62%. <sup>1</sup>H NMR : δ. 0.6 (q, 12H, CH<sub>2</sub>), 0.9 (t, 18H, CH<sub>3</sub>). <sup>13</sup>C NMR : δ 7.3, 8.0 (Et). <sup>29</sup>Si NMR : δ 22.5; GC/Mass: *m/z*: 261(M<sup>+</sup>-1, 1%), 233(M<sup>+</sup>-Et, 58%), 205(M<sup>+</sup>+1-2Et, 100%), 177(M<sup>+</sup>+2-3Et, 75%), 149(Et<sub>3</sub>SiSH<sup>+</sup>+1, 26%), 115(Et<sub>3</sub>Si<sup>+</sup>, 8%), 87(Et<sub>2</sub>Si<sup>+</sup>+1, 10%), 59(EtSi<sup>+</sup> +1, 24%).

**Et<sub>3</sub>GeSGeEt<sub>3</sub>**<sup>[6]</sup>: Yield: 63%. <sup>1</sup>H NMR : δ 0.9 (q, 12H, CH<sub>2</sub>), 1.0 (t, 18H, CH<sub>3</sub>). <sup>13</sup>C NMR : δ 8.7, 10.1(Et); GC/Mass: *m/z*: 354(M<sup>+</sup>, 15%), 325(M<sup>+</sup>-3Et, 90%), 295(M<sup>+</sup>-1-2Et, 100%), 267(M<sup>+</sup>-3Et, 55%), 239(M<sup>+</sup>-1-4Et, 6%), 161(Et<sub>3</sub>Ge<sup>+</sup>, 70%), 133(Et<sub>2</sub>Ge<sup>+</sup>+1, 70%), 103(EtGe<sup>+</sup>, 45%), 75(GeH<sup>+</sup>, 33%).

**Bu<sub>3</sub>GeSGeBu<sub>3</sub>**<sup>[7]</sup>: Yield: 67%. <sup>1</sup>H NMR : δ 0.8, 1.0, 1.3, 1.5(m, 54H, Bu). <sup>13</sup>C NMR : δ 13.6, 18.7, 26.4, 27.3 (Bu); GC/Mass: *m/z*: 521(M<sup>+</sup>-1, 1%), 407(M<sup>+</sup>-1-2Bu, 61%), 351(M<sup>+</sup>-3Bu, 100%), 295(M<sup>+</sup>+1-4Bu, 70%), 189(Bu<sub>2</sub>Ge<sup>+</sup>+1, 25%), 105(GeS<sup>+</sup>-1, 12%), 89 (BuS<sup>+</sup>, 25%).

**Ph<sub>3</sub>GeSGePh<sub>3</sub>**<sup>[8]</sup>: Yield: 53%. <sup>1</sup>H NMR : δ 7.1, 7.2, 7.3. <sup>13</sup>C NMR : δ 128.1, 129.4, 134.7, 136.8. m.pt: 121-123°C. Lit. m.pt: 130°C; HRMS (ESI): Calcd. for C<sub>36</sub>H<sub>31</sub>Ge<sub>2</sub>S: (M<sup>+</sup>+1): 641.05791, Found 641.0670

**Bu<sub>3</sub>SnSSnBu<sub>3</sub>**<sup>[9]</sup>: Yield: 80%. <sup>1</sup>H NMR : δ 0.7, 0.9, 1.2, 1.4 (m, 54H, Bu). <sup>13</sup>C NMR : δ 13.9, 15.9, 27.4, 28.9 (Bu). <sup>119</sup>Sn NMR : δ 80.6; HRMS (ESI): Calcd. for C<sub>24</sub>H<sub>53</sub>Sn<sub>2</sub>S:

(M<sup>+</sup>-1): 611.19061, Found 611.2218.

**Ph<sub>3</sub>SnSSnPh<sub>3</sub>**<sup>[10]</sup>: Yield: 60%. <sup>1</sup>H NMR : δ 7.1, 7.2, 7.3. <sup>13</sup>C NMR : δ 128.5, 129.3, 136.5, 138.9. <sup>119</sup>Sn NMR : δ -53.7. m.pt: 141-143°C. Lit.m.pt: 141-143°C; HRMS (ESI): Calcd. for C<sub>36</sub>H<sub>31</sub>Sn<sub>2</sub>S: (M<sup>+</sup>+1): 733.01846, Found 733.0561.

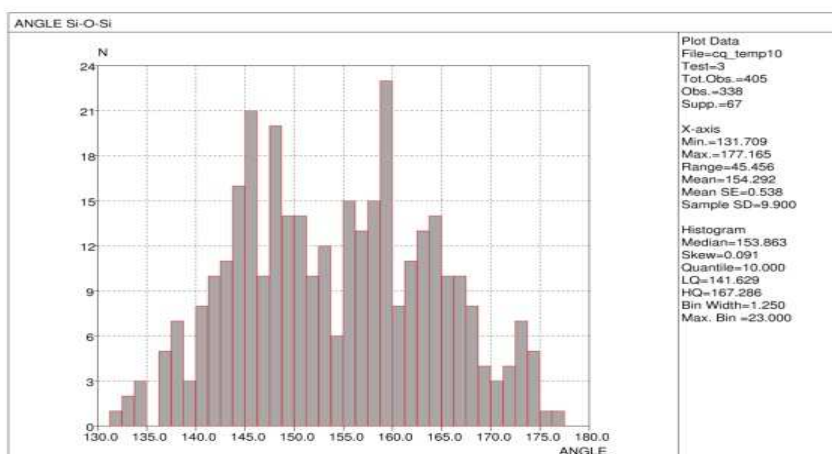
### **X-ray structural analysis of 3c:**

The data was collected on a Bruker APEX CCD diffractometer (Mo Kα) with APEX2 [Bruker AXS, Inc., Madison, WI, USA, 2010]. The program twinabs was used for absorption, incident beam and decay corrections. Cell refinement and data reduction were carried out with SAINT-Plus [Sheldrick, G.M. SAINT-Plus 6.23c Bruker AXS, Inc., Madison, WI, USA, 2000]. The structure was solved by direct methods and refined by full- matrix least-squares techniques in SHELXTL [Sheldrick, G.M. SHELXTL 6.10 Bruker AXS, Inc., Madison, WI, USA, 2000]. Hydrogen atoms were generated in calculated positions and constrained with the use of a riding model. Crystal Data: Mo(CO)5(C<sub>3</sub>H<sub>7</sub>NS) FW= 325.15. SPG P2<sub>1</sub>/c, a = 10.6872(15), b = 12.8629(18), c = 9.7035(14) Å, β= 109.022(7)°. Cell Volume = 1261.1(3) Å<sup>3</sup>, T= 298(2) K, Z = 4, 3797 reflections collected, 2112 unique [R(int) = 0.0302]. Completeness to 2θ = 50°: 95.3%. R1 = 0.0434, wR2 = 0.2031 [I > 2 sigma (I)]. The complete crystal data has been deposited with the Cambridge Crystallographic Data Center, CCDC 833336. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or <http://www.ccdc.cam.ac.uk>)

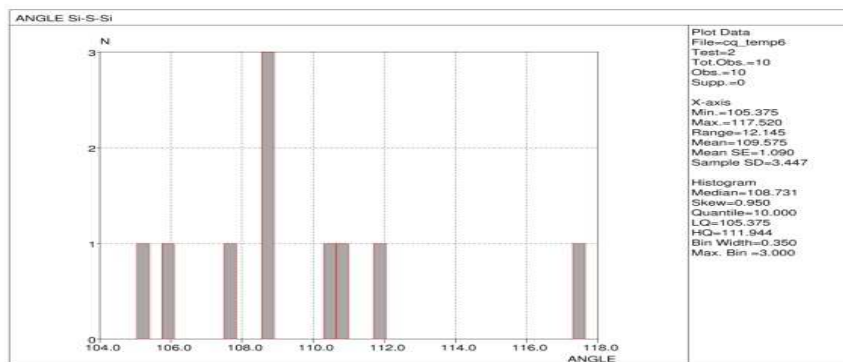
### Comparison of Si-O-Si and Si-O-C with Si-S-Si and Si-S-C Bond Angles:

The data for comparison of Si-O-Si and Si-O-C with Si-S-Si and Si-S-C bond angles and lengths is retrieved from CSD v5.32.

For compounds with Si-O-Si linkage, the bond angle ranges from 130 to 177° with a mean angle of 154° (Figure S-1). In Si-S-Si linkage, mean angle is reduced to 109° (Figure S-2).

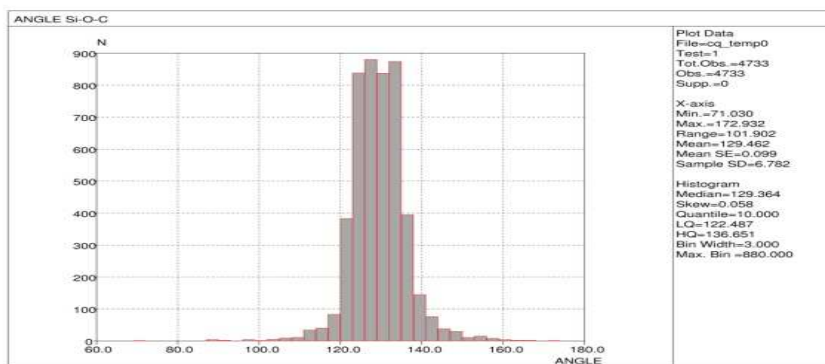


**Figure S- 1: Bond angles for Si-O-Si linkage**



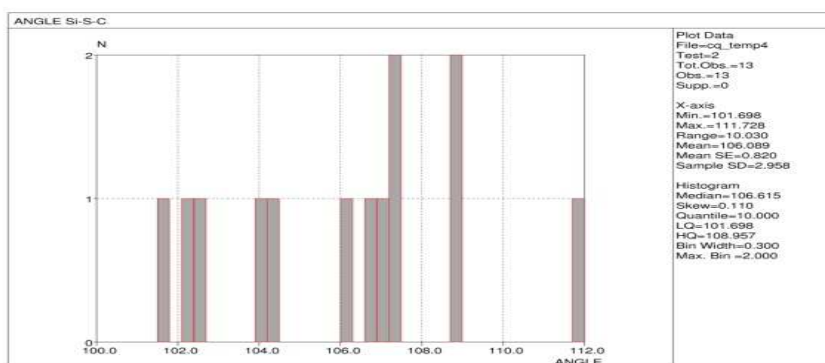
**Figure S- 2: Bond angles for Si-S-Si linkage**

In structures with Si-O-C bond, the mean Si-O-C bond angle is 130° as shown in Figure S-3.



**Figure S- 3: Bond angles for Si-O-C linkage**

In compounds with Si-S-C bond (only 13 structures), mean Si-S-C bond angle is 106° considerably smaller than the Si-O-C bond angle, Figure S-4.



**Figure S- 4: Bond angles for Si-S-C linkage**

## References:

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