Supplementary Information: Catalytic behavior of hexaphenyldisiloxane in the synthesis of pyrite FeS$_2$

Paul K. Todd, Andrew J. Martinolich, and James R. Neilson*

Colorado State University, Department of Chemistry, Fort Collins, Colorado 80523-1872, United States

E-mail: james.neilson@colostate.edu

Materials and Methods

All reagents were prepared and stored in an argon-filled glovebox with O$_2$(g) and H$_2$O(g) levels less than 0.1 ppm. Anhydrous FeCl$_2$ was purchased from Sigma-Aldrich (>98% purity), hexaphenyldisiloxane from Santa Cruz Biotechnology (Lot No. A0417, 99.6%), triphenylsilylchloride from TCI (>95%), triphenylsilanol from Alfa Aesar (99%), triphenylphosphine from Alfa Aesar (99+%), triphenylamine from Sigma Aldrich (98%), trityl chloride (97%), and eicosane (C$_{20}$H$_{42}$) from Acros Organics (99%). Triphenylphosphine sulfide was synthesized by heating triphenylphosphine and elemental sulfur in an evacuated silica ampule for 24 h at 150°C and confirmed by ^{31}P NMR spectroscopy.[1]

Na$_2$S$_2$ was prepared through a vapor transport reaction between elemental sodium and sulfur.[2] First, elemental sulfur was purified via vapor transport over a temperature gradient from 400 °C to 550 °C in a sealed silica ampoule under vacuum (<10 mTorr). Sulfur was placed on the high temperature end of the gradient and transported via vapor across the gradient where the purified product condensed and recrystallized. Solid sodium metal was stored in the glovebox under argon. Before use of the sodium metal, a razor blade was used to remove surface oxidation. Using the

proper stoichiometry for Na_2S_2, the elements were weighed and placed in separate alumina crucibles with sulfur on the top to avoid a highly exothermic reaction. The contents were sealed under vacuum in a silica ampoule and heated in a box furnace at 200 °C at a ramp rate of 1 °C/min where the reaction dwelled for 24 h. This initial reaction allowed sulfur vapor to corrode the sodium metal to produce an inhomogeneous solution of Na_2S_2 and Na_2S and unreacted sulfur. The reaction was readmitted to the glovebox and ground to a homogenous powder, pelleted, and sealed in a silica ampoule. An additional annealing step at 300 °C at a ramp rate of 1 °C/min produced a pure product. Air-free PXRD using a polyimide tape covering the powder sample revealed pure crystalline Na_2S_2.

All metathesis reactions were prepared in an argon-filled glovebox. Reagents were weighed on an analytical balance, ground into a homogeneous mixture (2x, 5 min), and pelleted. The pellet was carefully transferred to a closed system sealing station and sealed in a silica ampoule under vacuum (<10 mTorr). Reactions were heated at 150 °C and dwelled for 24 h. Reactions were placed in a hot convection furnace with no designated ramp rate. Reactions that are deemed Air-Exposed (AE) refer to the grinding of the reaction mixture in an agate mortar and pestle under ambient atmosphere for 5 min after the heating step. Thus, the only exposure to ambient air and moisture was *ex post facto* grinding and characterization. The Air-Free (AF) reactions were prepared, reacted, processed, and characterized under argon. Neat reactions refer to the reactions performed with no molecular additive.

Synchrotron X-ray diffraction experiments were performed at beamline 17-BM-B ($\lambda = 0.2415$ Å) at the Advanced Photon Source (APS) at Argonne National Laboratory using a Perkin Elmer plate detector at a distance of 700 mm. Homogenized metathesis precursors were packed into a quartz capillary (1.1mm OD) at Colorado State University in an argon-filled glovebox. Then, capillaries were sealed under vacuum (< 20 mTorr) using a methane-oxygen torch. All capillaries were loaded into a flow-cell apparatus[3] equipped with resistive heating elements and heated at various heating rates depending on the reaction to 300 °C. While heating the samples were continuously rocked at ± 5° around the axis of the capillary. Diffraction patterns were collected every

two seconds and summed every 10 s for experiments performed with heating rates < 160 °C/min. For experiments heated at 160 °C/min, the diffraction patterns were not summed and taken every two seconds. Plate detector images were integrated using GSAS-II and calibrated using a LaB_6 standard.

Powder X-Ray Diffraction (PXRD) was performed on a Bruker D8 DaVinci with CuK_α radiation. All samples were spread on a zero-background disc and covered with a polyimide film to protect the samples from the environment. Rietveld analysis was performed using EXPGUI/GSAS or TOPAS.[4,5] ^{1}H NMR was performed on an Agilent (Varian) 400 MHz NMR spectrometer using deuterated methylene chloride as the solvent (CD_2Cl_2; CIL Inc. 99.96%). All ^{1}H NMR samples were prepared in a glovebox under nitrogen. NMR tubes were sealed with Parafilm® wax to avoid air exposure during transport and characterization. Differential Scanning Calorimetry (DSC) experiments were performed on a TA Instruments 2500 Discovery DSC. Experiments were prepared by hermetically sealing the homogenized metathesis precursors in an aluminum pan. DSC experiments were performed by heating each experiment at 10 °C/min to 300 °C

Properties of organosilicon molecules

Table S1: Properties of select organosilicon molecules

| Name	Formula	Physical Properties	Chemical Properties
Hexaphenyldisiloxane	$(C_6H_5)_6Si_2O$	MP: 224°C Density: 1.20g/cm^3	Weak Lewis Base[6,7] Cleavage of Si$-$O$-$Si functional group[8,9] Ferrosiloxane formation (($R_3SiO)_3$Fe)[10]
Triphenylsilanol	$(C_6H_5)_3SiOH$	MP: 150-153°C	Weak Lewis Acid[11] Precursor to silicone polymers[12] Potential for hydrogen bonding[13]
Triphenylsilyl chloride	$(C_6H_5)_3SiCl$	MP: 91-94°C	Nucleophilic substitution at silicon[14] Precursor for thiosilanes[6,15] Readily hydrolyzes to form silanols[11,13]

Organosilicon control reactions
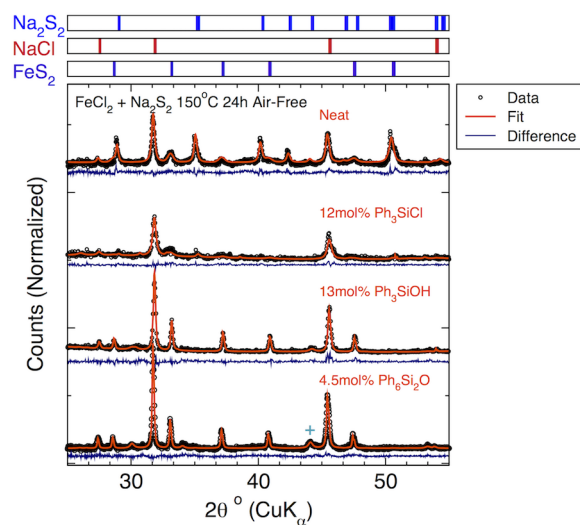
Figure S1: PXRD results with Rietveld refinements from metathesis reactions of $FeCl_2 + Na_2S_2$ at 150 °C for 24h under Argon: Top to Bottom: Neat reaction, 12 mol% Ph_3SiCl, 13 mol% Ph_3SiOH, 4.5 mol% $(C_6H_5)_6Si_2O$. + denotes (206) reflection of Fe_7S_8
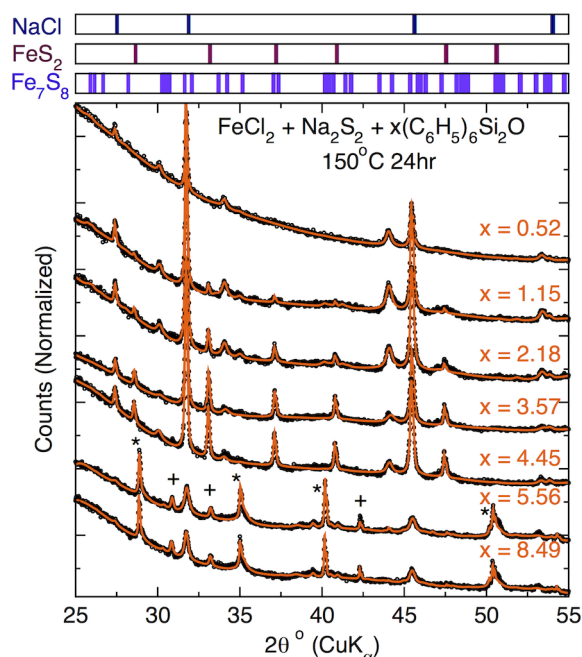
Figure S2: PXRD results with Rietveld refinements from metathesis reactions of $FeCl_2$ and Na_2S_2 at 150 °C for 24h under Argon: varying mol% $(C_6H_5)_6Si_2O$; (+) denote Na_2S_4 (*) denote Na_2S_2.

Table S2: Phase Fraction of Metathesis Products at Various mol% $(C_6H_5)_6Si_2O$ loading as determined by Rietveld analysis of PXRD data.

mol% $(C_6H_5)_6Si_2O$	NaCl	Fe_7S_8	FeS_2	Na_2S_2	Na_2S_4	$FeCl_2$
0.5	96(2)	3.6(1)	–	–	–	–
1.2	93(1)	2.95(8)	3.4(2)	–	–	–
2.2	86(1)	2.58(8)	11.4(4)	–	–	–
3.6	79(1)	0.98(6)	19.9(4)	–	–	–
4.5	78(1)	1.14(7)	20.6(4)	–	–	–
5.6	38(1)	–	–	34(1)	9.4(2)	16.0(3)
8.5	39(2)	–	–	30(1)	11.8(2)	19.0(3)

Triphenylsilyl chloride

^{1}H NMR spectroscopy reveals two unique phenyl environments in washed products from metathesis reactions *and* from reactions between $(C_6H_5)_3SiCl$ and Na_2S_2. Interestingly, the molecule remains unchanged upon heating and in control reactions between $(C_6H_5)_3SiCl$ and $FeCl_2$. Organosilylchlorides are common precursors for producing various organothiosilane molecules and thiosil-

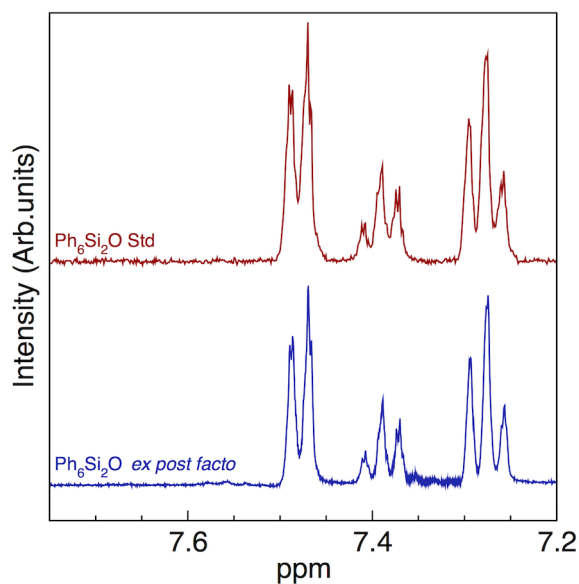Figure S3: ^{1}H NMR spectra of the phenyl region in the $(C_6H_5)_6Si_2O$ standard and the molecular species washed from the metathesis reaction $Na_2S_2 + FeCl_2$ with 4.5 mol% $(C_6H_5)_6Si_2O$. Deuterated methylene chloride (CD_2Cl_2) was used as the solvent.

icone polymers.[16]

Triphenylsilanol

^{1}H NMR studies of the reaction products in deuterated methylene chloride, reveal that the $(C_6H_5)_3SiOH$ polymerizes/decomposes upon heating (Fig. S5(a)). Physically, the reaction product mixture becomes difficult to mix, as it contains a viscous silicone-like polymer, even when prepared in the glovebox. ^{1}H NMR spectra of the 13mol% $(C_6H_5)_3SiOH$ assisted metathesis reaction support the polymerization of the $(C_6H_5)_3SiOH$, as there is a sharp benzene signal at 7.36 ppm and multiple unique phenyl environments (Fig. S5(a)).[17] This polymerization reaction can be described in the
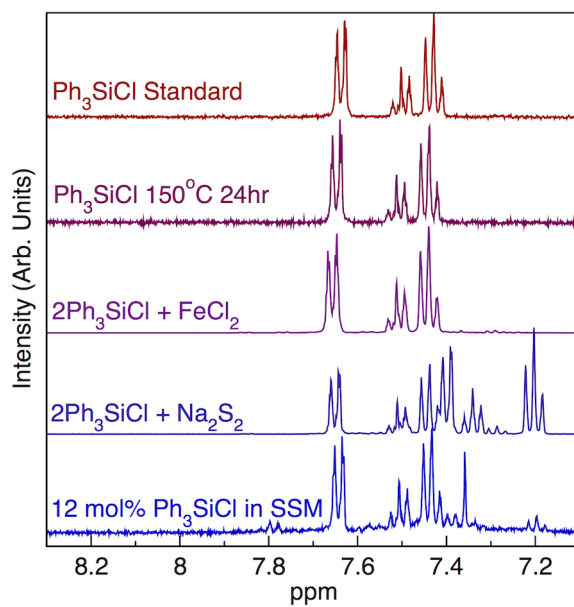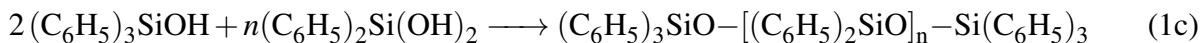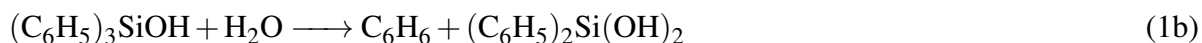
Figure S4: ^{1}H NMR spectra of relevant $(C_6H_5)_3SiCl$ control reactions. All reactions were heated at 150°C for 24hr. From TOP to BOTTOM: $(C_6H_5)_3SiCl$ standard, $(C_6H_5)_3SiCl$ after heating, $(C_6H_5)_3SiCl$ after reaction with $FeCl_2$, $(C_6H_5)_3SiCl$ after reaction with Na_2S_2, $(C_6H_5)_3SiCl$ after reaction with $FeCl_2 + Na_2S_2$. New phenyl environments are observed in reactions with Na_2S_2 attributed to thiosilane species.

following condensation reaction:

$$2\,(C_6H_5)_3SiOH \longrightarrow H_2O + (C_6H_5)_6Si_2O \tag{1a}$$

$$(C_6H_5)_3SiOH + H_2O \longrightarrow C_6H_6 + (C_6H_5)_2Si(OH)_2 \tag{1b}$$

$$2\,(C_6H_5)_3SiOH + n(C_6H_5)_2Si(OH)_2 \longrightarrow (C_6H_5)_3SiO-[(C_6H_5)_2SiO]_n-Si(C_6H_5)_3 \tag{1c}$$

where the water produced in the self-condensation reaction acts as a nucleophile and proton donor to form the diphenylsilanediol and benzene. In Eqn. 1c, $(C_6H_5)_2Si(OH)_2$ is highly unstable and will ultimately react to form higher order siloxanes and silicone polymers as observed previously.[18,19] Self-heating of the $(C_6H_5)_3SiOH$ at 150°C for 24hr reveals a similar result, as the reaction produces a viscous liquid upon cooling and the ^{1}H NMR spectrum shows the presence of benzene and multiple phenyl environments (Fig. S5(a)). Interestingly, if the $(C_6H_5)_3SiOH$ is
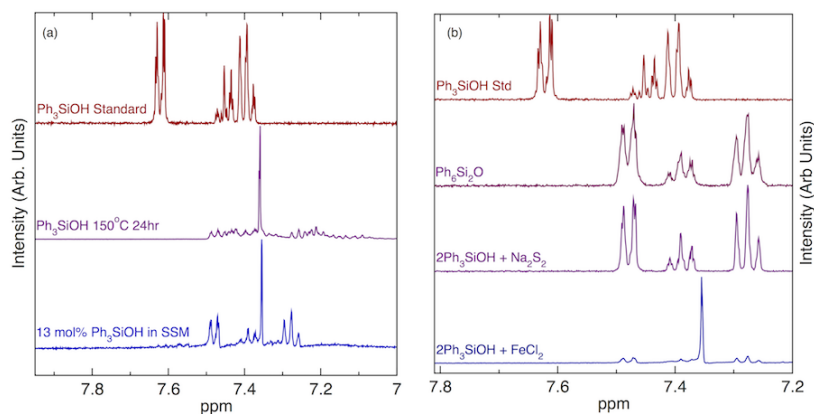
S7

Figure S5: ^{1}H NMR spectra of relevant $(C_6H_5)_3SiOH$ control reactions. All reactions were heated at 150°C for 24hr. (a) $(C_6H_5)_3SiOH$ standard, $(C_6H_5)_3SiOH$ decomposition after heating, $(C_6H_5)_3SiOH$ washes from the reaction $Na_2S_2 + FeCl_2$. (b): $(C_6H_5)_3SiOH$ and $(C_6H_5)_6Si_2O$ standards as compared to $(C_6H_5)_3SiOH$ reactions with each reaction precursor.

stoichiometrically mixed and pelleted with Na_2S_2, a downfield shift of the phenyl protons occurs (Fig. S5(b)) that matches $(C_6H_5)_6Si_2O$. Na_2S_2 is unstable under ambient conditions, as the salt is hygroscopic, so intuition suggests that the Na_2S_2 acts as a water scavenger after the $(C_6H_5)_3SiOH$ has dimerized, thus preventing the nucleophilic attack of water on silicon in the polymerization step (Eqn. 1c). Interestingly, $FeCl_2$ does not prevent polymerization (Fig. S5(b)), although small intensity peaks are present of some $(C_6H_5)_6Si_2O$. On the other hand, when using $(C_6H_5)_6Si_2O$ in the metathesis reaction, the molecule retains the same phenyl environment as a $(C_6H_5)_6Si_2O$ standard (Fig. S3). In order for the $(C_6H_5)_3SiOH$ to polymerize, there has to be H_2O present in the reaction mixture, so the self-condensation reaction (Eqn. 1a) must occur first. Thus, both reactions support the hypothesis that pyrite formation is dependent on the identity of the molecule hexaphenyldisiloxane.

To test the hypothesis that water is influencing the reaction pathway, a vapor transport reaction was performed where the self-condensation reaction of $(C_6H_5)_3SiOH$ was separated from the metathesis precursors physically (e.g., separate crucibles). The results and experimental set-up are shown in Figure S6, where the presence of water vapor does not result in FeS_2. While direct contact with the water may influence the pathway more, the results with pure $(C_6H_5)_6Si_2O$ suggest a

pathway more dependent on the Si−O functional group.
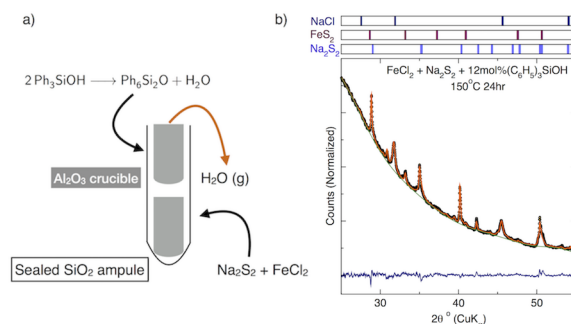

Figure S6: Vapor transport reaction to test the effect of water vapor from the decomposition/polymerization of $(C_6H_5)_3SiOH$ on the metathesis reaction: $Na_2S_2 + FeCl_2 \longrightarrow FeS_2 + 2NaCl$. a) Experimental set-up showing the separation of each reaction physically in a sealed ampule. b) PXRD pattern of reaction products performed under polyimide tape.

References

(1) Martinolich, A. J.; Higgins, R. F.; Shores, M. P.; Neilson, J. R. Lewis Base Mediated Polymorph Selectivity of Pyrite $CuSe_2$ through Atom Transfer in Solid-State Metathesis. *Chem. Mater.* **2016**, *28*, 1854–1860.

(2) Martinolich, A. J.; Neilson, J. R. Pyrite Formation via Kinetic Intermediates through Low-Temperature Solid-State Metathesis. *J. Am. Chem. Soc.* **2014**, *136*, 15654–9.

(3) Chupas, P. J.; Chapman, K. W.; Kurtz, C.; Hanson, J. C.; Lee, P. L.; Grey, C. P. A versatile sample-environment cell for non-ambient X-ray scattering experiments. *J. Appl. Crystallogr.* **2008**, *41*, 822–824.

(4) Toby, B. H. EXPGUI , a graphical user interface for GSAS. *J. Appl. Crystallogr.* **2001**, *34*, 210–213.

(5) Larson, A. C.; Von Dreele, R. B. *General Structure Analysis System (GSAS)*; 2004; pp 1–221.

(6) Eaborn, C. 601. Organosilicon compounds. Part II. A conversion series for organosilicon halides, pseudohalides, and sulphides. *J. Chem. Soc.* **1950**, 3077–3089.

(7) Eaborn, C. 537. Organosilicon compounds. Part III. Some sterically hindered compounds. *J. Chem. Soc.* **1952**, 2840.

(8) Gilman, H.; Benedict, H. N.; Hartzfeld, H. The preparation and cleavage of some hexasubstituted disiloxanes. *J. Org. Chem.* **1954**, *19*, 419–427.

(9) Anderson, H. H.; Fischer, H. Methylsilicon esters. Esters in an organosilicon "conversion series". *J. Org. Chem.* **1954**, *19*, 1296–1299.

(10) Schmidbaur, H.; Schmidt, M. Ferrosiloxanes and Ferrosiliconate Anions. *J. Am. Chem. Soc.* **1962**, *84*, 3600–3601.

(11) Chandrasekhar, V.; Boomishankar, R.; Nagendran, S. Recent Developments in the Synthesis and Structure of Organosilanols. *Chem. Rev.* **2004**, *104*, 5847–5910.

(12) Sieckhaus, J.; Scott, R.; Larcher, T. Siloxane Vulcanizates and a Method for the Preparation Thereof. 1975.

(13) Lickiss, P. D. *Adv. Inorg. Chem.*; Elsevier Masson SAS, 1995; Vol. 42; pp 147–262.

(14) Allen, A. D.; Lavery, S. J. Nucleophilic substitution at silicon: the reaction of triphenylsilyl chloride with 2-propanol in CCl₄. *Can. J. Chem.* **1969**, *47*, 1263–1267.

(15) Jenkins, L.; Willey, G. Hexamethyldisiloxane and Hexamethyldisilathiane: Reactions with Covalent Metal Halides. *J. Chem. Soc. Dalt.* **1979**, 1697–1700.

(16) Backer, H. J.; Stienstra, F. Chlorotrithioorthosilicoformiate et Chlorotrithioorthogermanioformiate de Butyle Tertiaire (Observations sur L'empêchement St érique). *Recueil des Travaux Chimiques des Pays-Bas* **1935**, *54*, 38–46.

(17) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR chemical shifts of trace impurities: Common laboratory solvents, organics, and gases in deuterated solvents relevant to the organometallic chemist. *Organometallics* **2010**, *29*, 2176–2179.

(18) Delaval, J.; Guinet, P.; Morel, J. Process for the Preparation of Linear Organopolysiloxanes. **1969**, 1–10.

(19) Kantor, S. W.; Grubb, W. T.; Osthoff, R. C. The Mechanism of the Acid- and Base-catalyzed Equilibration of Siloxanes. *J. Am. Chem. Soc.* **1954**, *76*, 5190–5197.