

# **Catalytic Dehydrogenative Coupling of Secondary Silanes Using Wilkinson's Catalyst**

## **Supplementary Material**

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## Experimental

### Warning

Described below are conditions that minimize the amount of silane substituent redistribution in the presence of Wilkinson's catalyst,  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ , (**1**). However, it should be noted that without due care, redistribution may occur, which may ultimately lead to the formation of  $\text{SiH}_4$ , a pyrophoric gas. Appropriate precautions should be taken when handling silanes in the presence of this catalyst.

### General Comments

All reactions and manipulations were done under an  $\text{N}_2(\text{g})$  atmosphere in an MBraun Unilab 1200/780 glovebox or using conventional Schlenk techniques, unless otherwise noted. Hexanes, ether, and THF were purified by distillation from sodium/benzophenone under argon, toluene was distilled from sodium under argon, and benzene was vacuum transferred from over sodium/benzophenone. Deuterated solvents were purchased from Cambridge Isotopes, degassed and vacuum transferred from over sodium/benzophenone ( $\text{d}_6$ -benzene,  $\text{d}_8$ -toluene) or calcium hydride ( $\text{d}_1$ -chloroform).  $\text{Ph}_2\text{SiCl}_2$ ,  $(n\text{-Hex})_2\text{SiCl}_2$  were purchased from Aldrich.  $\text{Ph}_2\text{SiH}_2$ ,  $\text{MePhSiH}_2$ , and  $\text{Et}_2\text{SiH}_2$  were purchased from Aldrich, refluxed overnight over  $\text{CaH}_2$ , and distilled.  $\text{Ph}_2\text{SiH}_2$  was also prepared using standard literature procedures,<sup>1</sup> as was  $(n\text{-Hex})_2\text{SiH}_2$ . Wilkinson's catalyst,  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ , (**1**)<sup>2</sup> was prepared according to the literature procedure. Florisil columns were constructed as follows: glass columns, either 9" Pasteur pipettes ("narrow bore") or tapered glass columns (20 cm long, 1 cm ID, "wide bore") were plugged with cotton wool and filled to a height of 4-7 cm with 60–100 mesh Florisil, purchased from Acros Chemicals. The columns were heated to 120-140°C in an oven for a minimum of 12h, then cooled under vacuum, overnight, in the glovebox antechamber.

<sup>1</sup> Benkeser, R. A.; Landesman, H.; Foster, D. J. *J. Am. Chem. Soc.* **1952**, 74, 648.

<sup>2</sup> Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1967**, 10, 68.

NMR spectra were obtained on a Bruker AM300 operating at 300.133 MHz for  $^1\text{H}$ , or on a Bruker AMX 500 operating at 500.13 MHz for  $^1\text{H}$ . Chemical shifts are reported (in ppm) for 300K unless otherwise stated.  $^1\text{H}$  chemical shifts are referenced to residual protonated solvent peaks at 7.15 ppm ( $\text{C}_6\text{D}_5\text{H}$ ) and 2.09 ppm ( $\text{PhCD}_2\text{H}$ ), relative to tetramethylsilane.

### Reaction of $\text{Ph}_2\text{SiH}_2$ in toluene

Under a strong flow of nitrogen, a solution of  $\text{Ph}_2\text{SiH}_2$  (258 mg, 1.40 mmol) in toluene (1.6 mL) was added to a flask equipped with a reflux condenser and stir bar and containing solid **1** (13 mg, 0.014 mmol). The formation of bubbles began immediately upon addition of substrate to catalyst. With the system open to the nitrogen manifold and an oil bubbler, the mixture was stirred and heated at  $65^\circ\text{C}$  for 23 h. The solid red catalyst took about ten minutes to dissolve, with the initially clear, colourless substrate solution changing first to yellow and finally to a deep red-brown. The cooled reaction mixture was taken into the glovebox, where its volume was reduced by 1/3 under vacuum. The residue was passed through several narrow bore Florisil columns to remove the catalyst, using a total volume of 35 mL hexanes to elute the product mixture.<sup>3</sup> A small aliquot of the resulting solution was removed for  $^1\text{H}$  NMR spectroscopic analysis, and integration of the Si–H signals for unreacted  $\text{Ph}_2\text{SiH}_2$  (40%), **2** (33%), and  $\text{Ph}_3\text{SiH}$  (13%) indicated the extent of chemoselectivity for coupling over redistribution, with total redistribution estimated at 26% ( $\text{Ph}_3\text{SiH} + \text{PhSiH}_3$ ).

### Small scale reactions of $\text{Ph}_2\text{SiH}_2$ with variation of catalyst concentration:

**Initial procedure** Complex **1** (2–32 mg;  $2 \times 10^{-3}$ – $3 \times 10^{-2}$  mmol), which is relatively stable to oxidation, was weighed outside the glovebox into 1 mL, Accuform<sup>®</sup> microvials. The vials were taken into the glovebox, where  $\text{Ph}_2\text{SiH}_2$  (200 mg, 1.1 mmol) and a flea stir bar were added to

<sup>3</sup> (a) This workup was carried out in the glovebox for all catalytic runs, since the sensitivity of both  $\text{Ph}_2\text{SiH}_2$  and **2** to reaction with water in the presence of **1** is well-documented. (Lukevics, E.; Dzintara, M. *J. Organomet. Chem.* **1985**, 295, 265; Watanabe, H.; Ahkawa, T.; Muraoka, T.; Nagai, Y. *Chem. Lett.* **1981**, 1321.) (b) Corey has also reported the degradation of **2**, in the presence of **1**, to the disiloxane  $\text{Ph}_2\text{Si}(\text{H})\text{OSi}(\text{H})\text{Ph}_2$ , **3**, on silica and Florisil columns under anhydrous conditions. (Chang, L. S.; Corey, J. Y. *Organometallics* **1989**, 8, 1885.) We do see traces of **3** in some of our eluted reaction mixtures.

each. The uncapped reaction vials were immediately placed on a stir plate and the mixtures stirred for about 4-5h at 29°C (the temperature of the stir plate surface was monitored and recorded throughout the runs). The reaction was quenched and the catalyst was removed by hexanes elution (~11 mL) of the reaction mixtures through narrow bore Florisil columns. The solvent was removed from the eluted solutions *in vacuo* to give white crystalline solid and/or clear oil, depending on the relative amounts of disilane present. Product mixtures were analyzed by  $^1\text{H}$  NMR spectroscopy, with yields calculated based on the relative intensities of Si-H resonances. Results are summarized in Fig 1(a). In some cases traces of 1,2-diphenyldisilane (resulting from the coupling of phenylsilane produced in the redistribution reaction) were also observed. This procedure, which gave maximum sample depth in the reaction vial and limited control over the stir rate (due to tapered vial), gave lower conversions and greater relative amounts of redistribution, so was modified as described below.

**Modified procedure** In a typical reaction, **1** (0.5 - 10 mg;  $5 \times 10^{-4}$  -  $11 \times 10^{-3}$  mmol, giving catalyst concentrations in the range 0.2 - 3.2 mol%) was weighed outside the glovebox into a 1-dram (~3.7 mL), flat-bottomed vial. The vial was taken into the glovebox, where  $\text{Ph}_2\text{SiH}_2$  (50 mg, 0.27 mmol) and a flea stir bar were added to it. The uncapped reaction vial was immediately placed on a stir plate and the stirring rate optimized to give maximum mixing and removal of  $\text{H}_2(\text{g})$  without the spattering the mixture on the walls of the vial. After 1h of stirring at 23°C, the reactions were quenched and the catalyst was removed by hexanes elution (30 mL) of the reaction mixture through a narrow bore Florisil column. The solvent was removed from the eluted solutions *in vacuo* and product mixtures were analyzed by  $^1\text{H}$  NMR spectroscopy, as described above. The results are summarized in Fig. 1(b).

Since complex **1** is insoluble in neat silane, for the above reactions the initial mixtures are heterogeneous. The red solid complex begins immediately to react with the clear diphenylsilane, with evolution of bubbles. As **1** reacts, a yellow solution forms, which gradually darkens through a deep golden-orange to a rusty red colour. The mixtures become increasingly viscous

and eventually solidify (time taken varies with reaction conditions). This progression of events is strikingly accelerated at higher catalyst concentrations, and also at higher temperatures.<sup>4</sup>

### Synthesis of 1,1,2,2-tetraphenyldisilane, **2**.

(PPh<sub>3</sub>)<sub>3</sub>RhCl (50mg, 0.054 mmol) was placed in a Schlenk tube (OD 35 mm, ID 31 mm, normal curved bottom) equipped with a gas dispersion tube<sup>5</sup> and a stir bar (14 mm x 8 mm), and connected to an oil bubbler through its side arm. The Schlenk Diphenylsilane (5.02 mL, 5.0 g, 27.1 mmol) was added by syringe, via the gas dispersion tube, through the rubber tubing attaching the tube to the nitrogen manifold, under a strong flow of nitrogen. The reaction mixture was stirred with a strong flow of nitrogen passing through the partially immersed frit of the dispersion tube. After ~1 h, the reaction mixture solidified (activity = 380 mol monomer consumed/mol catalyst/hr, assuming 75% conversion to dimer at this point). Toluene (4 mL) was added to allow stirring to continue. After another 40 minutes, the mixture solidified again. More toluene (4 mL) was added, and the mixture was stirred for a further 20 minutes before the gas dispersion tube was rinsed out with toluene, and the solvent was removed under vacuum from the combined washings and reaction mixture. The <sup>1</sup>H NMR spectrum of the crude product showed 98% **2**. The pink, solid residue was transferred with hexanes to a wide bore Florisil column (filled to 7 cm) and the products eluted with hexanes (~200 mL). After the volume of the resulting colourless solution was reduced by one half under vacuum, a white crystalline solid formed. The product was filtered (3.05 g, 61.4%), and a second crop of 0.83 g (17%) was isolated from the concentrated (30-40 mL) filtrate, for a combined yield of 3.88 g (78.4%), m.p. 82-83°C (lit. 79-80°C<sup>6</sup>). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 7.60-7.57 (m, 8H, Ph), 7.09-7.07 (m, 12H, Ph), 5.48 (s, 2H, Si-H). MS: m/e 366 (M<sup>+</sup>), 259 (Ph<sub>3</sub>Si), 183 (Ph<sub>2</sub>SiH), 105, 78.

<sup>4</sup> Rosenberg, L., unpublished results.

<sup>5</sup> The term "glass dispersion tube" refers to a hollow glass tube (about 1/2 cm OD) with a sintered glass frit (coarse) attached at one end. In the reaction described it sits in a rubber cork in the mouth of the Schlenk flask, with the frit partially immersed in solution, and with rubber tubing attaching the other end to the nitrogen manifold.

<sup>6</sup> This was obtained for **2** prepared by traditional, Wurtz reductive coupling of diphenylchlorosilane, a difficult synthesis to reproduce, and one that often gives significant amounts of siloxane impurities. Steudel, W.; Gilman, H. *J. Am. Chem. Soc.* **1961**, 83, 6129.

### Reaction of 1,1,2,2-tetraphenyldisilane, **2**, with H<sub>2</sub>(g) in the presence of **1**:

Compounds **1** (0.7 mg,  $8 \times 10^{-4}$  mmol) and **2** (35.4 mg,  $966 \times 10^{-4}$  mmol) were placed in a sealable NMR tube. Deuterated solvent (0.5 mL, C<sub>6</sub>D<sub>6</sub> or C<sub>7</sub>D<sub>8</sub>), pre-saturated with hydrogen gas, was added by syringe under a strong flow of hydrogen, and the sample was sealed under slightly less than one atmosphere of hydrogen. The reaction was monitored by <sup>1</sup>H NMR spectroscopy. Signals due to Ph<sub>2</sub>SiH<sub>2</sub> were observed in the first spectrum run (within about 30 minutes of sample preparation), and increased in intensity in subsequent spectra. No signal due to dissolved hydrogen ( $\delta$ 4.51 ppm in C<sub>7</sub>D<sub>8</sub>,  $\delta$ 4.46 ppm in C<sub>6</sub>D<sub>6</sub>) was observed until a week after the sample was prepared. After the appearance of the dissolved hydrogen signal, there were no further changes in spectra of the sealed samples recorded over several weeks. We took this to mean that equilibrium had been established in the system, and calculated an equilibrium constant, K<sub>c</sub>, using the relative intensities of the Si–H signals for Ph<sub>2</sub>SiH<sub>2</sub> and **2**, and the signal due to dissolved H<sub>2</sub>(g). ( $K_c = [\mathbf{2}][\text{H}_2]/[\text{Ph}_2\text{SiH}_2]^2$ ) Some redistribution was also observed in this closed system. Overall yields at equilibrium under these sealed tube conditions were approximately 83% Ph<sub>2</sub>SiH<sub>2</sub>, 5% **2**, and 6% Ph<sub>3</sub>SiH.

### Small scale reactions of other secondary silanes:

These reactions were carried out for MePhSiH<sub>2</sub>, Et<sub>2</sub>SiH<sub>2</sub>, and (*n*-Hex)<sub>2</sub>SiH<sub>2</sub> using 0.2 mol% **1** in the modified procedure described above for reactions of Ph<sub>2</sub>SiH<sub>2</sub>, and the amounts and conditions specified in Table 2, below. In the case of Et<sub>2</sub>SiH<sub>2</sub>, <sup>1</sup>H NMR spectra were run of the crude reaction mixture prior to removal of catalyst. Product distributions and overall catalyst activities for coupling (TOF) are summarized in Table 1.

**Table 2**

silane	amount of silane	amount of <b>1</b>
MePhSiH <sub>2</sub>	59 mg (0.47 mmol)	0.8 mg ( $9 \times 10^{-4}$ mmol)
Et <sub>2</sub> SiH <sub>2</sub>	143 mg (1.62 mmol)	3.0 mg ( $3.2 \times 10^{-3}$ mmol)
( <i>n</i> -Hex) <sub>2</sub> SiH <sub>2</sub>	54 mg (0.27 mmol)	0.5 mg ( $5 \times 10^{-4}$ mmol)

**Variation of method of H<sub>2</sub>(g) removal during reaction of MePhSiH<sub>2</sub>:**

Two reactions were carried out simultaneously as follows: Portions of **1** (15.5 mg; 0.0168 mmol) were placed in two Schlenk tubes equipped with stir bars. MePhSiH<sub>2</sub> (1.0 g; 8.2 mmol), was transferred via syringe into each of the nitrogen-filled Schlenks. The headspace in one of the Schlenks was evacuated and back-filled with nitrogen. The Schlenk was then closed and the reaction mixture was stirred under a static atmosphere of nitrogen. To the second Schlenk, a sparging (dispersion) tube was attached through a septum, such that a strong flow of nitrogen could be directed at the surface of the stirred reaction mixture. The Schlenk was vented to a nujol bubbler, and the reaction mixture was stirred under a stream of nitrogen. The reactions were both quenched after 75 minutes. The workup was similar to that described above. After removal of solvent from the eluted solutions, the crude products were analyzed by <sup>1</sup>H NMR spectroscopy.