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

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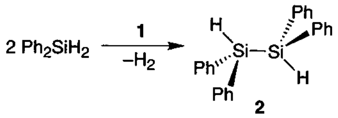
The pursuit of clean, straightforward alternatives to Wurtz coupling reactions for the synthesis of polysilanes has focused attention on dehydrocoupling reactions of silanes catalyzed by transition metals.[1] Among complexes investigated in their capacity to produce these polymers[2] two classes have emerged. One includes group 4 metallocene derivatives, which are considered the most active for catalytic dehydrocoupling, since they are capable of producing oligomers and sometimes polymers from primary silanes. Catalysts in the second class include many late metal complexes, such as Wilkinson's catalyst, $(Ph_3P)_3RhCl$, **1**, and other Rh(I) phosphine complexes;[3] these are considered relatively inactive for dehydrocoupling, since they do not produce long chains, even for primary silane monomers.[4] Complex **1** and other late metal complexes catalyze the coupling of secondary silanes to di- and trisilanes, but their application to the large-scale synthesis of these useful, hydrido-substituted oligosilanes has been discouraged by the known activity of such catalysts for a competing reaction of silanes: redistribution of substituents at silicon.[5] In this communication we describe results indicating that **1** actually exhibits high activity and chemoselectivity for coupling of secondary silanes, under appropriate conditions. We have demonstrated that coupling in this system is extremely fast but is not thermodynamically favored; chemoselectivity is therefore exceedingly sensitive to the presence of hydrogen gas, also a product of the coupling reaction.



**2**

Our interest in preparing 1,2-bis(hydrido)-substituted disilanes on a synthetically useful scale led us to reinvestigate the activity of **1** in the dehydrocoupling of diphenylsilane (eq 1). Since previous reports of this reaction invariably included the observation of considerable amounts of $Ph_3SiH$, arising from redistribution of the phenyl and hydride groups on silicon,[6] we needed to identify conditions that would favor dehydrocoupling over redistribution.

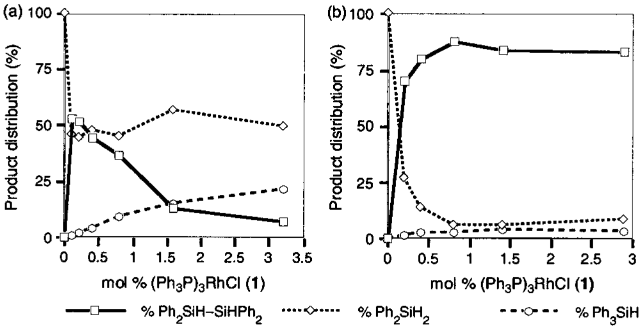


**Figure 1.** Dependence of product distribution on catalyst concentration, observed for small-scale reactions of $Ph_2SiH_2$ where (a) removal of hydrogen was not rigorously controlled and (b) hydrogen was removed efficiently (see text for details).

We therefore investigated the effects of varying both substrate and catalyst concentration on the reactions of diphenylsilane in the presence of **1**. We obtained lower conversions of diphenylsilane, with higher relative amounts of redistribution, when we used solvent in our initial experiments,[7] so carried out subsequent reactions in neat diphenylsilane. Preliminary, small-scale reactions[8] of the neat substrate (e.g. Figure 1a) consistently gave more dehydrocoupling than redistribution[9] but with much greater selectivity for coupling at lower catalyst concentrations. At high catalyst concentrations, an increase in the amount of redistribution was apparently at the expense of coupled product.

However, in these small-scale reactions, the product distributions were surprisingly sensitive to the size of reaction vial relative to the volume of substrate and to the rate and efficacy of stirring. Chemoselectivity was enhanced, and its catalyst concentration dependence became far less pronounced, when these conditions were manipulated to allow more efficient removal of hydrogen gas from the reaction mixtures (Figure 1b).[10] We obtained optimum conversion (75−80%, at which point the mixture solidifies) and minimum redistribution using flat-bottomed vials, wide enough to allow the substrate to be spread thinly, and high stir rates, with stir bars of lengths approaching the inner diameter of the vial. Thus, although redistribution of phenyl groups at silicon can be a major competing reaction for diphenylsilane in the presence of **1**, it can be kept to a minimum with efficient removal of $H_2$(g).[11] Based on the above results, which suggest good catalyst activity and selectivity for coupling at low catalyst concentrations, we prepared **2** on a 5-g scale from neat diphenylsilane using 0.2 mol % **1** as catalyst.[12] The reaction proceeds readily at room temperature and is complete within 2 h, which

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[1] (a) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37. (b) Corey, J. Y. *Adv. Silicon Chem.* **1991**, *1*, 327. (c) Gauvin, F.; Harrod, J. F.; Woo, H. G. *Adv. Organomet. Chem.* **1998**, *42*, 363. (d) Reichl, J. A.; Berry, D. H. *Adv. Organomet. Chem.* **1999**, *43*, 197.

[2] Polysilanes are of interest for their unusual electronic and optical properties, arising from extensive electron delocalization along the all-silicon backbone: (a) West, R. *J. Organomet. Chem.* **1986**, *300*, 327. (b) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. (c) Hamada, T. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 509.

[3] Ojima, I.; Inaba, S.; Kogure, T. *J. Organomet. Chem.* **1973**, *55*, C7. (b) Lappert, M. F.; Maskell, R. K. *J. Organomet. Chem.* **1984**, *264*, 217. (c) Brown-Wensley, K. A. *Organometallics* **1987**, *6*, 1590. (d) Chang, L. S.; Corey, J. Y. *Organometallics* **1989**, *8*, 1885. (e) Rosenberg, L.; Fryzuk, M. D.; Rettig, S. J. *Organometallics* **1999**, *18*, 958.

[4] For exceptions to this classification of late metal catalysts, see: (a) Fontaine, F.-G.; Kadkhodazadeh, T.; Zargarian, D. *Chem. Commun.* **1998**, 1253 (b) Chauhan, B. P. S.; Shimizu, T.; Tanaka, M. *Chem. Lett.* **1997**, 785.

[5] Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213.

[6] Phenylsilane is also produced by this redistribution reaction, but this more volatile product is less often detected.

[7] Product distributions, showing 26% redistribution, were similar to those reported in ref 3d for this reaction.

[8] Reactions were carried out at room temperature in small, open vials in the glovebox. Fixed amounts of substrate (50−200 mg) and reaction times (1−4 h) were used for each series of experiments, with reactions being quenched by hexanes elution through Florisil.

[9] Product distributions were determined from the amounts of **2** and $Ph_3SiH$ observed by $^1H$ NMR spectroscopy.

[10] The apparent dependence on catalyst concentration of chemoselectivity initially observed (Figure 1a) suggests that very different mechanistic pathways exist for these rhodium-mediated dimerization and redistribution reactions. A system exhibiting such concentration dependence presents an attractive opportunity to identify differences in key intermediates in these competing reactions. However, almost complete disappearance of the concentration dependence of this chemoselectivity with efficient removal of hydrogen (Figure 1b) suggests that rhodium intermediates in the two mechanisms may not actually be so different. Neither mechanism has been firmly established for the late transition metals: proposed mechanisms rely on either the intermediacy of transition metal silylene fragments or a series of oxidative addition/reductive elimination steps (refs 1 and 5), and the involvement of dinuclear intermediates has not been ruled out (ref 3e, for example).

[11] The maximum amount of $Ph_2SiH_2$ undergoing redistribution in these experiments was 9%.

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**Scheme 1**

represents an average turnover frequency (TOF) of 240 (moles of monomer consumed/moles of catalyst/hour). This is in marked contrast to a TOF of ∼3 observed for the same reaction mediated at 90 °C by a titanocene-based catalyst system.[13] This activity of **1** for dehydrocoupling of diphenylsilane is also several orders of magnitude higher than is observed for the coupling of $MePhSiH_2$ to di- and trisilanes,[14] and for dehydropolymerization of primary silanes,[15] by group 4 metallocenes.

The differences between a and b in Figure 1 can be explained by the effects of an equilibrium between diphenylsilane and the products of coupling, **2** and $H_2$(g), which lies heavily toward the substrate monomer (Scheme 1). Local concentrations of hydrogen formed in the reaction mixture, if not dispersed by rapid stirring or by other means, will allow this monomer−dimer equilibrium to be established, thus limiting the amount of **2** produced, regardless of the rate of formation (i.e. the forward rate of the coupling reaction). At higher catalyst concentrations, the rates of both coupling and redistribution of diphenylsilane will be greater than at lower catalyst concentrations. Higher local concentrations of hydrogen gas, resulting from fast coupling, will maintain increased monomer concentrations in these runs, which should give higher relative rates of redistribution (i.e. poorer chemoselectivity). At lower catalyst concentrations the hydrogen is produced more slowly and is therefore readily dissipated with "normal" stirring, allowing isolation of **2**, the kinetic product. This situation explains the observed erratic and lower yields of **2** and the steadily increasing yields of $Ph_3SiH$ with increasing catalyst concentration, when the removal of hydrogen (i.e. stir rate and sample depth) is not stringently controlled (Figure 1a). When hydrogen is more efficiently removed (Figure 1b), the relative amounts of **2** and $Ph_3SiH$ observed within a fixed reaction time more accurately reflect chemoselectivity, since the *real* rate of dimerization is in effect in this controlled situation. Clearly redistribution of phenyl and hydrido groups in $Ph_2SiH_2$ proceeds very slowly, relative to dimerization, at *all* catalyst concentrations.

Evidence for the participation and importance of the above equilibrium in these rhodium-catalyzed reactions is provided by experiments in which $H_2$(g)-saturated, $d_6$-benzene or $d_8$-toluene solutions containing **2** and catalytic amounts of **1** are sealed in an NMR tube under an atmosphere of hydrogen. Within minutes a significant amount of $Ph_2SiH_2$ is observed by $^1$H NMR spectroscopy, with equilibrium being attained after 1 week.[16] Integration of the relevant Si−H signals and that due to dissolved hydrogen gives a room-temperature equilibrium constant for the coupling (forward) reaction of $K_c = 2 \times 10^{-4}$, indicating that the equilibrium lies significantly toward monosilane under these conditions.[17]

**Table 1.** Dehydrocoupling of Other Secondary Silanes in the Presence of **1**[a]

| silane | reaction time (h) | product (yield[b]) | total monomer coupled (TOF[c]) |
|---|---|---|---|
| $MePhSiH_2$ | 0.58 | disilane (11%), trisilane (59%), $Me_2PhSiH$ (<1%), $MePh_2SiH$ (<1%) | 70% (600) |
| $Et_2SiH_2$ | 1.0 | disilane (44%), trisilane (9%) | 57% (290) |
| ($n$-Hex)$_2SiH_2$ | 1.5 | disilane (60%), trisilane (13%) | 73% (250) |

[a] Reactions were run at room temperature, without solvent, using 0.2 mol % **1**. [b] Based on integration of $^1$H NMR. [c] Average value, in mol monomer/mol catalyst/h.

Our technique for promoting chemoselectivity for the dehydrocoupling of silanes by **1** is general. Preliminary, small-scale reactions indicate that under the conditions we developed for the reactions of diphenylsilane, similar or improved chemoselectivity is possible for a range of secondary silanes in the presence of **1** (Table 1). Dialkylsilanes react less vigorously than the aryl-substituted silanes, yet for all three substrates we see significant amounts of trisilane, as well as disilane. Group 4 metallocene catalysts are not active for the dehydrocoupling of dialkylsilanes.[18] We consistently observe more phenyl/hydride redistribution than methyl/hydride redistribution for $MePhSiH_2$ in the presence of **1**. Two experiments, one in a sealed reaction vessel, the other open to a nitrogen manifold and being flushed with $N_2$(g), confirm that this is not simply due to reaction conditions that facilitate the departure of $MeSiH_3$(g) preferentially to $PhSiH_3$(l). The preferred redistribution of aryl over alkyl groups is further illustrated by the fact that for the dialkyl substrates $Et_2SiH_2$ and ($n$-Hex)$_2SiH_2$ we see *no* products arising from redistribution in the presence of **1**.

Our results indicate rates of silane dehydrocoupling catalyzed by a late metal complex that are much higher than previously thought, and much higher than those reported for early metal dehydrocoupling catalysts. The barrier to coupling in this system is low enough, relative to that for redistribution, to allow almost complete selectivity for coupling, under appropriate conditions. This work suggests that other late metal complexes that are known to catalyze silane redistribution may actually be extremely active for dehydrocoupling, under conditions that shift the monosilane/disilane equilibrium via highly efficient removal of hydrogen. Work is underway to optimize large-scale syntheses of disilanes and trisilanes (both useful building blocks in organosilicon chemistry) for a range of substrates using **1**, and to probe mechanistic issues through further study of the reactions with silanes of **1** and related Rh systems.

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**Supporting Information Available:** Full experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) To remove hydrogen sufficiently quickly in this larger volume of $Ph_2SiH_2$, $N_2$(g) was passed through a gas dispersion tube immersed in the reaction mixture. Twice, small amounts of toluene were added as the mixture solidified, to allow it to be stirred. This procedure gave >98% (by $^1$H NMR spectroscopy) conversion to disilane, which was isolated by recrystallization from hexanes in 78% yield, after removal of the catalyst on a Florisil column.

(13) Corey, J. Y.; Kraichely, D. M.; Huhmann, J. L.; Braddock-Wilking, J.; Lindeberg, A. *Organometallics* **1995**, *14*, 2704. Calculated TOF is based on the reported isolated yield.

(14) (a) Corey, J. Y.; Zhu, X.-H.; Bedard, T. C.; Lange, L. D. *Organometallics* **1991**, *10*, 924. (b) Imori, T.; Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *Chem. Mater.* **1993**, *5*, 1487.

(15) These estimated TOFs are based on total conversion of monomer to oligomer or polymer in the presence of group 4 catalysts, and thus are not strictly analogous to TOFs for dimerization. Longer chain lengths probably arise from the coupling of additional monosilane with oligomers, but these condensations are likely to be increasingly slower than dimerization (ref b below). Still, given the much faster coupling normally observed for primary versus secondary silanes for any one catalyst, the differences in these TOFs are striking. See, for example: (a) Aitken, C.; Barry, J.-P.; Gauvin, F.; Harrod, J. F.; Malek, A.; Rousseau, D. *Organometallics* **1989**, *8*, 1732. (b) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047. (c) Dioumaev, V. K.; Harrod, J. F. *Organometallics* **1994**, *13*, 1548. (d) Grimmond, B. J.; Corey, J. Y. *Organometallics* **2000**, *19*, 3776.

(16) The absence of any signal due to dissolved $H_2$(g) until this time suggests that hydrogenolysis of **2** occurs as rapidly as the gas dissolves in deuterated solvent. Since diffusion of gases in NMR samples is notoriously slow, the real rate of approach to equilibrium in these reactions is probably much higher.

(17) The disilane/monosilane equilibrium ratio is ∼0.03:1.

(18) The activity of a titanocene-based catalyst for the coupling of ($n$-Pr)$_2SiH_2$ has been reported, but requires the presence of cyclic olefins, which are hydrogenated in tandem with the coupling process. The resulting product mixtures are complex, including hydrosilation products. Corey, J. Y.; Zhu, X.-H. *Organometallics* **1992**, *11*, 672.