Nickel catalysed Coupling of Phenylhydrosilanes

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Activated nickel, prepared by lithium reduction of nickel iodide in tetrahydrofuran, catalyses the dehydrogenative coupling of phenysilanes to form di-, tri- and tetrasilanes.

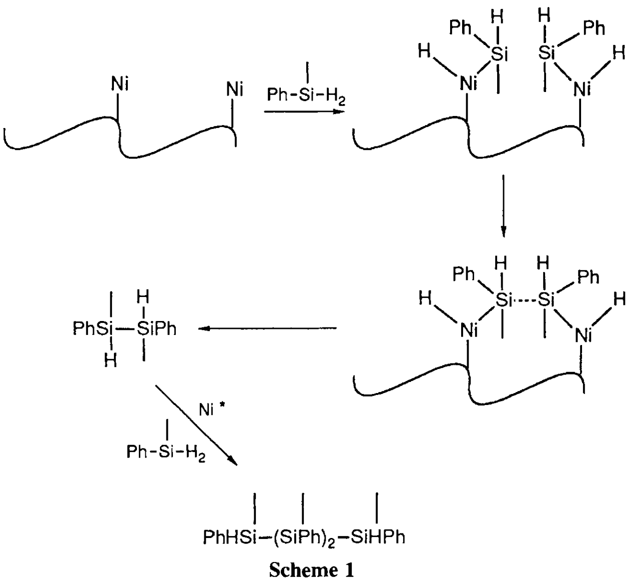
Only recently have catalytic methods of forming silicon–silicon bonds been developed.[1] Herein we report the first example of heterogeneously catalysed dehydrogenative coupling of hydrosilanes.[2]

The rate of generation and the activities of freshly prepared powders can be significantly enhanced when they are produced in an ultrasonic field.[3] We have found that nickel powder, freshly prepared from nickel iodide and lithium dispersion in tetrahydrofuran (THF) in the presence of ultrasonic waves, catalyses the formation of Si–Si bonds from phenyl-substituted hydrosilanes. Diphenylsilane, for example, when treated with one mole percent each of activated nickel and triphenylphosphine at 80 °C gives a 45% yield of *sym*-tetraphenyldisilane in 3–4 h.[4]† However, when phenylmethylsilane is used under the same conditions, a broader distribution of products is obtained (eqn. 1). The reaction does not require triphenylphosphine, although lower yields (15, 25, 7 and 2% respectively) are obtained without it. No higher polysilanes were observed. Commercially available nickel powder gave no coupling products with or without triphenylphosphine.

$$\begin{array}{ll} \mathrm{PhMeSiH_2} \xrightarrow[\mathrm{Ph_3P}]{\mathrm{Ni^*}} & \\ \mathrm{PhMeHSi\text{-}SiHMePh} + \mathrm{PhMeHSi\text{-}SiMePh\text{-}SiHMePh} & \\ \quad 20\% \qquad\qquad\qquad\qquad 40\% & \\ \mathrm{PhMeHSi\text{-}(SiMePh)_2\text{-}SiHMePh} + \mathrm{Ph_2MeSiH} & (1) \\ \quad 25\% \qquad\qquad\qquad\qquad <3\% & \end{array}$$

While it is premature to set down a detailed mechanism, we suggest that oxidative addition of the hydrosilane[4] to nickel followed by reductive elimination of the Si–Si species and H_2 is a reasonable pathway and is consistent with our observations (Scheme 1).

The Raman spectrum of activated nickel exposed to $PhSiH_3$ is presented in Fig. 1*a*. For comparison, the spectrum of trideuteriophenylsilane, $PhSiD_3$, is given in Fig. 1*b*. The



Scheme 1

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† Typically, the silane : solvent mole ratio is 1 : 4. All yields are GC yields using an internal standard and when combined with unreacted starting material the mass balance for silicon is >90%.

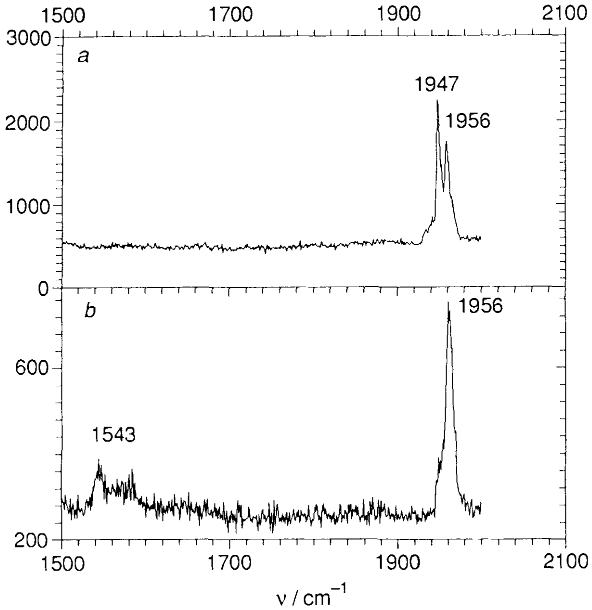

Fig. 1 Raman spectra of activated nickel and phenylsilane in THF suspension: *a* $PhSiH_3$; *b* $PhSiD_3$

important difference between the two spectra is the presence of a strong band at 1947 cm^{-1} in 1*a* and its conspicuous absence and replacement with a less intense absorption at 1543 cm^{-1} in 1*b*. An isotopic shift of this sign and magnitude is consistent with simple replacement of H in a nickel hydride with D.[5] Thus, we assign the band at 1947 cm^{-1} to the Ni–H vibration.[6] To our knowledge this is the first spectroscopic evidence in support of the oxidative addition of silicon hydride to nickel.

Our preliminary studies point to a surface species as the catalytic agent. Rinsing of freshly prepared nickel with solvent followed by extensive pumping on a high vacuum line does not destroy the catalyst. The role of the triphenylphosphine in increasing the yields of coupled products is unclear at this stage. It is reasonable that the donor capabilities of triphenylphosphine enhance the insertion of nickel into the Si–H bond.

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References

1 L. S. Chang and J. Y. Corey, *Organometallics*, 1989, **8**, 1885; C. Aitken, J. F. Harrod and U. S. Gill, *Can. J. Chem.*, 1987, **85**, 1804; W. H. Campbell, T. K. Hilty and L. Yurga, *Organometallics*, 1989, **8**, 2615; K. H. Pannel, S. P. Vincenti and R. C. Scott, III, *Organometallics*, 1987, **6**, 1593; K. A. Brown-Wensley, *Organometallics*, 1987, **6**, 1590; H.-G. Woo and T. D. Tilley, *J. Am. Chem. Soc.*, 1989, **111**, 8043.

2 These results were the subject of a preliminary report: P. Boudjouk, *Abstracts of Papers*, No. A3, XXIII Organosilicon Symposium, Midland, MI, April 1990.

3 P. Boudjouk, D. P. Thompson, W. H. Ohrbom and B.-H. Han, *Organometallics*, 1986, **5**, 1257. For reviews of the effects of ultrasonic waves on heterogeneous reactions see: P. Boudjouk, *Comments Inorg. Chem.*, 1990, **9**, 123 and P. Boudjouk, *High Energy processes in Organometallic Chemistry*; ed. K. S. Suslick, ACS Symposium Series 333, American Chemical Society, Washington, DC, 1987; ch. 13.

4 Oxidative addition of the Si–H bond to metals have been frequently invoked in hydrosilylation reactions see: D. A. Armitage, in *Comprehensive Organometallic Chemistry*; eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Press, Oxford, 1982; vol. 2, ch. 9.

5 H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations*, Academic Press, New York, 1982, ch. 4.

6 G. Longoni, P. Chini and A. Cavlieri, *Inorg. Chem.*, 1976, **12**, 3025.