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## Preliminary communication

# The action of tris(triphenylphosphine)chlororhodium on polyhydromonosilanes

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Several metal derivatives are known to catalyse disproportionation reactions of silicon compounds, and hydrosilanes have been shown to undergo disproportionation very readily in the presence of these and other catalysts[1]. The complex $(Ph_3P)_3RhCl$ is known to react readily with hydrosilanes[2], and we wish now to report a novel generation of "silenoid" species from polyhydrosilanes by the action of the rhodium complex.

Typically, heating 2.42 mmoles of phenylmethylsilane in the presence of 0.1 mole% of $(Ph_3P)_3RhCl$ at 70° for 1 h gave 0.73 mmoles (30%) of diphenylmethylsilane containing trace of triphenylmethylsilane, together with 0.17 mmoles (14%) of 1,2-dimethyl-1,2-diphenyldisilane and 0.23 mmoles (30%) of 1,2,3-trimethyl-1,2,3-triphenyltrisilane. Similar treatment of diphenylsilane at 80° gave 45% of the unchanged silane, 8% of triphenylsilane, traces of phenylsilane and tetraphenylsilane and 38% of 1,1,2,2-tetraphenyldisilane. Similarly, phenylsilane gave polysilanes such as 1,2-diphenyldisilane, 1,1,2-triphenyldisilane and 1,2,3-triphenyltrisilane, whereas diethylsilane yielded 1,1,2,2-tetraethyldisilane and 1,1,2,2,3,3-hexaethyltrisilane; in both cases the usual disproportionation products and some higher polysilanes were also formed. Structures of all the isolated polysilanes were confirmed by means of their elemental analyses, and spectral characteristics after purification by preparative GLC. It is thus obvious that disproportionation is of relatively minor importance in these systems, the formation of polysilanes predominating.

This finding led us to postulate "silene" or "silenoid" intermediates which can insert into Si–H bonds, and so reactions were carried out in the presence of triethylsilane which is regarded as an effective trapping agent for silenes*. Thus, a 1/10 mixture of diphenylsilane and triethylsilane was heated in the presence of a catalytic amount of the

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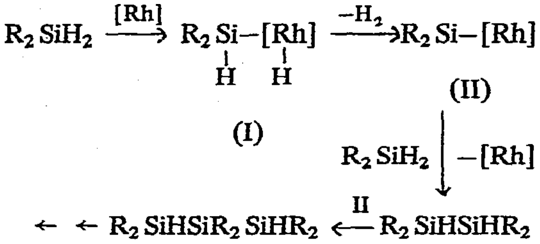
*As for the insertion of "silene" species into silicon–hydrogen bonds, see ref. 3.

rhodium catalyst at 80° for several hours, and the expected "silene" insertion product, 1,1,1-triethyl-2,2-diphenyldisilane, was obtained in 8% yield. The structure of the insertion product was confirmed by its NMR, IR, and mass spectra.

Since there is another possible mechanism for the disilane-forming reactions, involving dehydrogenative condensation between the silyl derivative of the rhodium

$$Ph_2SiH_2 \xrightarrow[\text{in } Et_3SiH]{(Ph_3P)_3RhCl} Ph_2SiHSiEt_3 + Ph_2SiHSiHPh_2 + Ph_3SiH + \text{etc.}$$

complex and a hydrosilane, we have examined the reaction of triethylsilane with the rhodium catalyst under similar conditions, and the only reaction was found to be the formation of a silyl derivative of the rhodium complex, $(Ph_3P)_2RhH(SiEt_3)Cl$[2d,4]. The results strongly indicate participation by "silenoid" intermediates, (II), which may be formed through β-elimination of molecular hydrogen from complex (I) which is produced in the initial oxidative addition; this route is depicted below:



$$\begin{tikzcd}
R_2SiH_2 \arrow[r, "{[Rh]}"] & R_2\underset{H}{Si}-\underset{H}{[Rh]}\ \text{(I)} \arrow[r, "-H_2"] & R_2Si-[Rh]\ \text{(II)} \arrow[d, "R_2SiH_2"', "-[Rh]"] \\
\leftarrow \leftarrow R_2SiHSiR_2SiHR_2 & & R_2SiHSiHR_2 \arrow[ll, "II"']
\end{tikzcd}$$

## REFERENCES

1 C. Eaborn and R.W. Bott, in A.G. MacDiarmid (Ed.), *Organometallic Compounds of the Group IV Elements, Vol. 1, Part 1*, Dekker, New York, 1968, pp. 332, 350.

2 For example, (a) J.A. Osborn, F.H. Jardine, J.F. Young and G. Wilkinson, *J. Chem. Soc. (A)*, (1966) 1711; (b) W.S. Knowles, M.J. Sabacky and B.D. Vineyard, *Chem. Commun.*, (1972) 10; (c) R.N. Haszeldine, R.V. Parish and D.J. Parry, *J. Organometal. Chem.*, 9 (1967) P13; (d) I. Ojima, M. Nihonyanagi and Y. Nagai, *Chem. Commun.*, (1972) 938; (e) I. Ojima, T. Kogure, M. Nihonyanagi and Y. Nagai, *Bull. Chem. Soc. Japan*, 45 (1972) 3506; (f) R.J.P. Corriu and J.J.E. Moreau, *Chem. Commun.*, (1973) 38.

3 K. Yamamoto, H. Okinoshima and M. Kumada, *J. Organometal. Chem.*, 27 (1971) C31; H. Sakurai and M. Murakami, *J. Amer. Chem. Soc.*, 94 (1972) 5080.

4 R.N. Haszeldine, R.V. Parish and D.J. Parry, *J. Chem. Soc., (A)*, (1969) 683.