

Preliminary communication

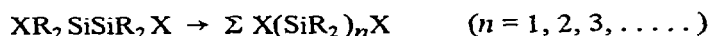
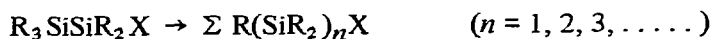
Disproportionation of pentamethyldisilane and *sym*-tetramethyldisilane catalysed by platinum complexes

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Considerable interest has been focused recently on the disproportionation of substituted disilanes:



where $X = H^1, Cl^{2,3}, CN^4, MeO^{5,6}, Ph_3Si^7$, or $PhMe_2Si^8$, and $R = Me, Cl$, etc. Most of the work previously reported concerns base-catalyzed or thermally induced disproportionation, and we now describe the first examples of transition metal complex catalyzed disproportionation of methyldisilicon hydrides.



(I)



(II)

Pentamethyldisilane (I, $n = 2$) was heated with a catalytic amount of *trans*-(Et_3P)₂PtCl₂ in a sealed glass tube at 90° for 18 h. A clear solution resulted which was found to consist of several lower members of the homologous series of (I), $n = 1-6$, and a small amount of higher homologs. Similarly, from *sym*-tetramethyldisilane (II, $n = 2$) was obtained a mixture of lower members of the homologous series of (II), $n = 1-6$. Relative amounts of the volatile products for the two series, determined by VPC, are given in Table I. Each product was isolated by preparative VPC and characterized by comparison of its IR and UV^{1,9} spectra with those of an authentic sample.

Urenovitch and West¹⁰ have reported that pentamethyldisilane (I, $n = 2$) does not enter satisfactory into platinum-catalyzed addition to an olefin. We previously observed that the addition of this disilane to vinyltrimethylsilane could be effected by using *trans*-(C_2H_4)(C_5H_5N)PtCl₂ as catalyst in benzene¹¹, but this seems to be a rather special case, because with other platinum complex catalysts, such as *trans*-(Et_3P)₂PtCl₂ and (Ph_3P)₃Pt, which are quite effective catalysts for hydrosilation of α -olefins with monosilicon hydrides¹², pentamethyldisilane scarcely adds to olefins. The reluctance of

this disilane to the platinum-catalyzed hydrosilation reactions may at least in part be explained by its tendency to undergo disproportionation under the reaction conditions.

In the light of current views of the mechanism of platinum-catalyzed hydrosilation¹³, an intermediate involving the pentamethyldisilane (or tetramethyldisilane) and the platinum complex can be postulated for the disproportionation described above.

TABLE 1

RELATIVE AMOUNTS OF DISPROPORTIONATION PRODUCTS,
Me(SiMe₂)_nH (I) AND H(SiMe₂)_nH (II)

Starting substance	Relative amounts of products ^a					
	<i>n</i> = 1	<i>n</i> = 2	<i>n</i> = 3	<i>n</i> = 4	<i>n</i> = 5	<i>n</i> = 6
(I, <i>n</i> = 2)	<i>b</i>	1.0	1.3	1.5	0.9	0.2
(II, <i>n</i> = 2)	<i>b</i>	1.0	1.5	1.7	1.1	0.2

^aBased on VPC peak area. ^bNot determined quantitatively.

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