Preliminary communication

Evidence for "silylenoid" species in disproportionation of pentamethyldisilane catalyzed by trans-[PtCl₂ ($Et_3 P$)₂]

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Recently we have reported the first examples of platinum complex-catalyzed disproportionation of methylsilicon hydrides^{1,2}, which are of value for preparing homologous series of 1H- and α,ω -di-H-methylpolysilanes.

$$Me_{3}SiSiMe_{2}H \xrightarrow{[Pt]} \Sigma Me(SiMe_{2})_{n}H (n = 1-6)$$

$$HMe_{2}SiSiMe_{2}H \xrightarrow{[Pt]} \Sigma H(SiMe_{2})_{n}H (n = 1-6)$$

$$(1)$$

We now report studies which indicate that these reactions involve an α -elimination to give "dimethylsilylene"³, which then takes part in a series of insertions into Si-H bonds. Evidence in support of this suggestion is provided by the observatior, that treatment of pentamethyldisilane with diphenylacetylene in presence of the platinum complex as catalyst gives a 1,1,4,4-tetramethyl-1,4-disilacyclohexadiene derivative⁴.

Thus a mixture of 0.35 g (2 mmoles) of diphenylacetylene, 0.37 ml (2 mmoles) of pentamethyldisilane and 2 mg of *trans*-[PtCl₂(Et₃P)₂] dissolved in 1.5 ml of cyclohexane was heated in a de-gassed sealed glass tube at 90° for 24 h. Cooling of the clear mixture gave off-white needles, which were filtered off and recrystallized from benzene to yield 25.1 mg (5.3% yield) of 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexadiene (I); mass: m/e 472; IR (KBr): 1435w (δ_{as} (Si-CH₃)), 1250m and 1242m (δ_{s} (Si-CH₃)), and 885s (δ (SiCH₃)); NMR (CH₂Cl₂): τ 9.95 (SiMe₂, 12H), and centered at 2.95 (Ph, 20H). The filtrate was analyzed by GLC, and found to consist of small amounts of trimethylsilane and recovered pentamethyldisilane and diphenylacetylene. None of the higher homologs of methylsilanes were detected, whereas they are readily produced under the conditions used in absence of diphenylacetylene. Thus the formation of the disilahexadiene (I) is the only reaction of "dimethylsilylene", except possibly for its insertion into the trimethylsilane formed at the same time.



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The trapping of "dimethylsilylene" provides convincing evidence that the platinum-catalyzed disproportionation of pentamethyldisilane (Eqn. 1) or tetramethyldisilane (Eqn. 2) probably proceeds via an α -elimination to produce "dimethylsilylene" followed by insertion into the Si-H bond⁵, rather than by a mechanism involving a four-centered transition state of the type shown below or any other mechanism not involving the "dimethylsilylene" intermediate.

 $\begin{array}{c} Me_{3}Si - SiMe_{2}H \\ H - SiMe_{2} - SiMe_{3} \end{array} (complexed with platinum) \end{array}$

The "dimethylsilylene" may arise from an intermediate involving pentamethyldisilane and the platinum complex, which may eliminate trimethylsilane to leave a dimethylsilylene moiety on the platinum atom; thus the silylene species is by no means a free divalent silicon species^{*}, but is complexed with platinum("silylenoid"). It is noteworthy that both diphenylacetylene⁷ and silicon hydrides^{8,9}, which efficiently intercept the dimethylsilylene moiety, can easily add oxidatively to a low valent platinum complex.

Although some of the related platinum complexes bearing dichlorosilylene have been reported^{9,10}, interception of the "silylenoid" species has not previously been reported.

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*Free dimethylsilylene may be formed readily by pyrolysis of sym-dimethoxytetramethyldisilane⁴ or by photolysis of dodecamethylcyclohexasilane⁶.

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