

Preliminary communication

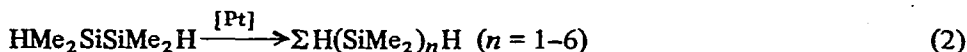
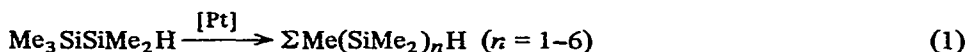
Evidence for "silylenoid" species in disproportionation of pentamethyldisilane catalyzed by *trans*-[PtCl₂(Et₃P)₂]

KEIJI YAMAMOTO, HIROSHIGE OKINOSHIMA and MAKOTO KUMADA

Department of Synthetic Chemistry, Kyoto University, Kyoto (Japan)

(Received January 12th, 1971)

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.



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 observation 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 ($\delta_{\text{as}}(\text{Si}-\text{CH}_3)$), 1250m and 1242m ($\delta_{\text{s}}(\text{Si}-\text{CH}_3)$), and 885s ($\delta(\text{SiCH}_3)$); 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 disilacyclohexadiene (I) is the only reaction of "dimethylsilylene", except possibly for its insertion into the trimethylsilane formed at the same time.

