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COMMUNICATION

Dehydrogenative condensation of monohydrosilanes yielding disilanes in the presence of platinum complex catalysts

Masato Tanaka,* Toshi-aki Kobayashi, Teruyuki Hayashi and Toshiyasu Sakakura
National Chemical Laboratory for Industry, Yatabe, Tsukuba, Ibaraki 305, Japan

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Dimethylphenylsilane was catalytically dehydrogenated and condensed in the presence of platinum complexes to give 1,1,2,2-tetramethyl-1,2-diphenyldisilane.

Keywords: Catalysis, dehydrogenation, hydrosilane, disilane, platinum complex

INTRODUCTION

Recently, silicon chemicals and materials have attracted increasing attention. In particular, polysilanes have been found to be versatile functional materials as exemplified by their use as precursors for silicon carbide ceramics, oxygen-RIE resistant photoresists, photo-initiators for vinyl polymerization, and dopable semiconductors.[1,2] However, the only synthetic method presently available for polysilanes is the Wurtz-type condensation of dichlorosilanes with alkali metals, so that alternative methods are highly desirable. Among possible methods, dehydrogenative condensation of hydrosilanes seems to be promising in view of hydrogen being a tractable adjunct product. There are a number of transition-metal complexes which are active as hydrosilylation catalysts. Activation of silicon–hydrogen bonds yielding silyl–metal intermediates is the key step in the hydrosilylation reaction. If a second hydrosilane molecule attacks the silyl–metal intermediate, then disilane formation may be anticipated. As a matter of fact, a few papers have disclosed that dehydrogenative condensation of di- and tri-hydrosilanes are promoted by some transition-metal complex catalysts.[3–9] However, monohydrosilanes are usually inert in this reaction. To rationalize the lack of dehydrogenative condensation of monohydrosilanes, Ojima *et al.*[3] have proposed an alternative mechanism for the reaction of dihydrosilanes which involves silenoid intermediates. Very recently, Brown-Wensley has also reported that several transition-metal complexes successfully catalyse the reaction of dihydrosilanes, but that monohydrosilanes are inert.[10] The paper prompted us to report our preliminary results which give details of dehydrogenative condensation of a monohydrosilane.

The reaction was carried out by heating a mixture of dimethylphenylsilane (3.26 mmol) and a complex catalyst (0.02 mmol) in a sealed Pyrex ampoule at 150°C for 12 h. The resulting mixtures were analysed by GC and GC MS.

Firstly, the performance of several hydrosilylation catalysts was evaluated for the purpose of dehydrogenative condensation. These included $Fe_2(CO)_9$, $Ru_3(CO)_{12}$, $Co_2(CO)_8$, $RhCl(PPh_3)_3$, $IrCl(CO)(PPh_3)_2$, $NiCl_2(PPh_3)_2$, $PdCl(PPh_3)_2$, and $PtCl_2(PPh_3)_2$. Only the platinum complex afforded a small amount of the disilane (1,1,2,2-tetramethyl-1,2-diphenyldisilane) (Eqn. [1]). The ruthenium and iridium complexes extensively promoted the redistribution reaction as evidenced by the formation of a large amount of methyldiphenylsilane. The others did not promote the dehydrogenative condensation at all, nor did they efficiently catalyse the redistribution reaction.

$$2\,Me_2PhSiH \xrightarrow{\text{Pt catalyst}} (Me_2PhSi)_2 + H_2 \qquad [1]$$

A number of platinum catalysts were then checked for the possibility of catalytic reaction. The presence of phosphines ligated on the metal seems to be a requisite for the reaction; platinum

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*Author to whom correspondence should be addressed.

compounds without phosphine ligands such as PtO_2, $H_2PtCl_6 \cdot 6H_2O$, $PtCl_2(PhCN)_2$ and platinum black were totally inactive. On the other hand, phosphine complexes exhibited variant activities, providing what we believe to be the first experimental demonstration of genuinely catalytic dehydrogenative condensation of the monohydrosilane. Selected examples are summarized in Table 1. Even though the catalytic activity is low as yet, it is recognizable that the performance of the ligand decreases in the order $PMe_3 > PMe_2Ph > PMePh_2 > PPh_3$ among the dichlorobis(phosphine)platinum(II) series. The trend was also observed with tetrakis(phosphine)-platinum(0) complexes, and almost 50% of the consumed monohydrosilane was transformed to the corresponding disilane by the use of $Pt(PMe_2Ph)_4$. The performance of the ligands seems to be associated with their steric rather than electronic nature. Accordingly, PEt_3, which is more sterically congested and more electron-donating than PMe_3, showed an inferior performance.

Table 1 Dehydrogenative condensation of Me_2PhSiH in the presence of platinum complex catalysts

Catalyst	Recovery of Me_2PhSiH (%)	Yield of $(Me_2PhSi)_2$ (%)[a] (1)	(2)
$PtCl_2(PPh_3)_2$	91.0	0.3	3.3
$PtCl_2(PMePh_2)_2$	89.6	2.4	23.1
$PtCl_2(PMe_2Ph)_2$	83.3	4.8	28.7
$PtCl_2(PMe_3)_2$	77.0	7.0	30.4
$PtCl_2(PEt_3)_2$	81.5	1.7	9.2
$Pt(PPh_3)_4$	92.8	1.6	22.2
$Pt(PMe_2Ph)_4$	85.8	6.8	47.9

[a] (1) Based on Me_2PhSiH starting material used; (2) based on Me_2PhSiH actually consumed.

Diphenylmethylsilane, albeit in a lower yield, also underwent dehydrogenative condensation under identical conditions.

Exploration to achieve more efficient catalysis and extension to di- and tri-hydrosilanes are in progress.

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