Redistribution of Bis- and Tris(silyl)methanes Catalyzed by Red-Al

Hee-Gweon Woo*, Sun-Jung Song, Eun Jeong Cho†, and Il Nam Jung†

Department of Chemistry, Chonnam National University, Kwangju 500-757, Korea
†Organometallic Chemistry Laboratory, Korea Institute of Science & Technology, P.O. Box 131 Cheongryang, Seoul 130-650, Korea

Received November 15, 1995

Red-Al (or Vitride; sodium bis(2-methoxyethoxy)aluminum hydride) is known to catalyze the polymerization of lactams and olefins and the trimerization of isocyanates.1 Corriu and coworkers reported the exchange reactions of di- and trihydrosilanes2 (eq 1) and the oligomerization of disilanes3 (eq. 2), catalyzed by inorganic hydrides (e.g., NaH, KH, etc.). They suggested a mechanism via the intermediacy of a pentacoordinated hydrosilyl anion,4 which is formed by addition of hydride (H−) on the silanes.

\[ 3 \text{RSiH}_3 \xrightarrow{H^-} \text{RSiH}_2 \xrightarrow{H^-} \text{RSiH} \] (1)

Red-Al(SiMe3)3 + H− → RSiH+ (Me3Si)k + Me3Si(SiMe3)kH (2)

Riviere et al. described the preparation of oligogermaine (PhHGe), by redistribution of PhH2GeH2Ph with PhH2GeLi.3 The Lewis acid AlC3 is well known to catalyze the redistribution reaction of hydroarylsilane to afford quaternary arylsilane and SiH4.4 We recently reported the dehydropolymerization of bis(silyl)alkylbenzenes catalyzed by group 4 metalloocene complexes, generated in situ from Cp2MCl3/Red-Al, to produce highly cross-linked polysilanes.5 During the study we found an intriguing redistribution of bis- and tris(silyl) methanes, catalyzed by Red-Al.

2-Phenyl-1,3-disilapropene 1,1-phenyl-3,5-disilapentane 2, and 1-phenyl-4-silyl-3,5-disilapentane 3 were prepared by reaction of corresponding chlorosilanes with LiAlH4. In a typical experiment, 1 (0.18 g, 1.18 mmol) was slowly added to a Schlenk flask charged with Red-Al (17 μL, 0.058 mmol; 3.4 M solution in toluene) and toluene (5 mL). (Warning! In the absence of toluene solvent, rapid addition of 1 to Red-Al resulted in a violent explosion with fire due to the drastic production of SiH4, which is an explosive gas upon contact with air. Therefore, the reaction should be performed in the dilute condition with suitable precaution. We recommend you not to exceed the reaction scale employed here.) The reaction started immediately, as monitored by the immediate release of SiH4 gas. After being stirred for 1 h, GC/MS analysis and 29Si NMR spectroscopy showed that 1 was quantitatively converted to benzylsilane as major and as yet uncharacterized high-boiling oligomers as minor. The starting silane 1 was completely disappeared. However, it was difficult to assign the exact composition and yields of the products because the minor product could be a mixture of high-boiling oligomers, and the amount of evolved gases is difficult to measure. Similarly, the bis(silyl)methane 2 was quantitati-
vely transformed to methylphenethylsilane and phenethylsilane (7:3 ratio, identified by GC/MS analysis) as major and as yet uncharacterized high-boiling oligomers as minor with SiH₄ and MeSiH₂ gases. The tris(silyl)methane 3 was quantitatively changed to 2, methylphenethylsilane, and phenethylsilane (3:12:4 ratio, identified by GC/MS analysis) as major and as yet uncharacterized high-boiling oligomers as minor with SiH₄, MeSiH₂, and CH₃SiH₃ gases (eq. 3).

\[
\begin{align*}
\text{PhCH(SiH)₂} & \xrightarrow{\text{Red-Al}} \text{PhCH₂SiH₃ + SiH₄ + oligomers} \\
\text{Ph(CH₃)₂SiH₂CH₃SiH₃} & \xrightarrow{\text{Red-Al}} \\
2. & \quad \text{Ph(CH₃)₂SiH₂CH₃ + Ph(CH₃)₂SiH₃ + SiH₄ + CH₃SiH₃ + oligomers} \\
\text{Ph(CH₃)₂SiH₃CH(SiH)₃} & \xrightarrow{\text{Red-Al}} 2 + \text{Ph(CH₃)₂SiH₂CH₃ + Ph(CH₃)₂SiH₃ + SiH₄ + CH₃SiH₃ + oligomers} \\
3. & \quad \text{Ph(CH₃)₂SiH₃CH(SiH)₃} + \text{Ph(CH₃)₂SiH₂} + \text{SiH₄ + CH₃SiH₃ + oligomers}
\end{align*}
\]

The benzylsilane seemed not to undergo appreciably a further redistribution in the redistribution reaction of 1. The methylphenethylsilane can be obtained via Si-C bond cleavage of 2, giving off SiH₄ gas in the redistribution reaction of 2. However, the phenethylsilane cannot be obtained via the direct Si-C bond cleavage of methylphenethylsilane, but via the direct Si-C bond cleavage of 2 with CH₃SiH₃ gas evolution. These facts were confirmed by the control experiments: the independently prepared benzylsilane, methylphenethylsilane and phenethylsilane were apparently inert toward Red-Al catalyzed redistribution (1 h, room temperature). The methylphenethylsilane was obtained in higher yield than the phenethylsilane, implying that SiH₄ formation is easier than CH₃SiH₃ formation due to different steric hindrance in the addition of hydride on the silanes. On the other hand, the methylphenethylsilane can be formed via consecutive Si-C bond scissions of 3, discharging SiH₄ gas in the redistribution reaction of 3. However, the phenethylsilane cannot be obtained by the direct Si-C bond cleavage of methylphenethylsilane, but either by the direct Si-C bond cleavage of 2 with CH₃SiH₃ gas release or by the direct Si-C bond cleavage of 3 with CH₃SiH₃ gas evolution. The yield for methylphenethylsilane was higher than for phenethylsilane, suggesting that SiH₄ formation is easier than CH₃SiH₃ formation due to their different steric hindrance in the addition of hydride on the silane. The as yet uncharacterized high-boiling oligomers are believed to be obtained only during the redistribution because the reaction of benzylsilane, methylphenethylsilane, and phenethylsilane with Red-Al did not yield the oligomeric mixture of silanes.

It is known that methylene bridges between two silicon atoms are more readily deprotonated by strong organometallic bases than are methyl groups bonded to a single silicon atom, but cleavage of the Si-C bond occurs normally under extremely vigorous conditions. No appreciable redistribution of 1-3 with AlCl₃ for 24 h at ambient temperature was observed. Experiments for trapping silylene or silene using 2,3-dimethyl-1,3-butadiene, cyclohexene, and trimethylmethoxysilane were unsuccessful due probably to the hydroxsilane species possessing active Si-H bonds existed in the reaction mixture. It is apparently essential to occur the rapid Si-C bond cleavage at room temperature that a silane should have at least one Si-C-Si connection. The more Si-C-Si connection apparently accelerates the redistribution reaction (judged by 'H NMR spectroscopy and GC analyses).

Although enough experimental data are not currently available, some comments on the redistribution mechanism seem appropriate. We propose a mechanism involving the preferential attack of the hydride on the less hindered silicon with formation of a pentacoordinated anionic species which collapses to give an α-silyl carbamion intermediate and a silane gas. The α-silyl carbamion may then pick up a hydrogen from the hydrogen source (e.g., silane or solvent) to yield a silane, may lose a hydride to produce a silene associating to produce some oligo(carbosilanes), or may be isomerized to a silyl anion. The silyl anion may lose a hydride to give an unstable silylene which will add to silane or associate, producing some cyclic or linear oligosilanes. The regenerated hydride may participate again in the catalytic cycle (Scheme 1).

We tentatively assign the as yet uncharacterized high-boiling oligomers as a mixture of oligo(carbosilanes) and oligosilane. We are making our effort to elucidate the structure of the oligomeric mixture with ²⁹Si NMR, GPC, and TGA analytical techniques.

The silanes 1-3 might be used along with Red-Al as a potent α-silyl carbamion synthon in the organic synthesis. The redistribution reaction might be further employed for modifying polycarbosilanes (SiH₃R-CH₃ₙ) with Red-Al. The detailed studies on the full characterization of the oligosilanes and on the application of these redistribution reactions are in progress and will be reported in the near future.

In conclusion, the redistribution of bis- and tris(silyl)methanes with Si-C-Si connection, catalyzed by Red-Al, produces new silanes via cleavage of the Si-C bonds, which could be attributed to the stability of resulting α-silyl carbamion intermediate.

Acknowledgment. This research was supported by the Non-directed Research Fund, Korea Research Foundation.
References


Soonheum Park

Department of Chemistry, College of Natural Science, Dongguk University, Kyong-Ju 780-714, Korea

Received November 15, 1995

Although ammine complexes of transition metals have been known since the early history in the classical coordination chemistry, such complexes containing tertiary phosphines or organic moieties are relatively rare.\(^1\) Recently there has been an increasing interest in the amido complexes of transition metals because of their potential applications for catalysis.\(^2\) One class in this category is such complexes of late transition metals having unsubstituted amide ligand NH\(_2\).\(^3\) Ammine complexes having tertiary phosphines are useful synthetic precursors for unsubstituted amido complexes in which the coordinated tertiary phosphines can stabilize electronically and sterically with a variety of substituents.\(^4\) Ammonia is a very weak acid (\(pK_a = 33\)) and the N-H bond dissociation energy in ammonia is very high (107 kcal/mol).\(^5\) Ammonia upon coordination to cationic metal centers, however, becomes considerably acidic to be deprotonated by appropriate base.

Reported here is the synthesis and characterization of a novel dicaticonic palladium(II) diamine complex containing 1,2-bis(diphenylphosphino)ethane as a supporting ligand. Our initial attempt to synthesize dicaticonic diamine complex having monodentated bis-triphenylphosphine has been proven not successful. When gaseous ammonia was added to a THF solution of \([\text{Pd}(\text{Ph}_3\text{P})_2(\text{THF})_2]\)\((\text{ClO}_4)_2\) prepared in situ by the reaction of \(\text{PdCl}_2(\text{Ph}_3\text{P})_2\) and 2 equivalents of AgClO\(_4\), dicaticoon tetraamine complex \([\text{Pd}(\text{NH}_2)_4]\)(\text{ClO}_4)_2\) (I) was obtained (eq. 1). The formation of I can be explained by a sequence of reactions involving the initial formation of \([\text{Pd}(\text{PPh}_3)_2(\text{NH}_2)_2]\)(\text{ClO}_4)_2\) and then further substitution of coordinated triphenylphosphines with excess ammonia. We can not observe the intermediate complex \([\text{Pd}(\text{PPh}_3)_2(\text{NH}_2)_2]\)(\text{ClO}_4)_2\). The formulation of I has been confirmed by its independent synthesis from the reaction of aqueous THF solution of \([\text{PdCl}_2]^2-\), 4 equivalents of AgClO\(_4\) and ammonia (eq. 2).\(^6\)

\[
\begin{align*}
\text{Pd}(\text{PPh}_3)_2\text{Cl}_2 + 2 \text{AgClO}_4/\text{MeOH} & \overset{2\text{AgCl/THF}}{\longrightarrow} \text{[Pd}(\text{PPh}_3)_2(\text{THF})_2]\text{[ClO}_4\text{]}_2 + \text{NH}_3 \\
\text{[Pd}(\text{NH}_2)_4]\text{[ClO}_4\text{]}_2 & + 2 \text{PPh}_3 \\
\text{I} & \\
\text{Na}_3\text{PdCl}_4 & \overset{\text{i}}{\underset{\text{THF/H}_2\text{O}}{\longrightarrow}} \overset{\text{ii}}{\underset{\text{THF/H}_2\text{O}}{\longrightarrow}} \text{Pd}(\text{NH}_2)_4\text{[ClO}_4\text{]}_2 \\
\text{I}
\end{align*}
\]

Targetting diamine complex of bis-phosphine palladium (II) has been successfully prepared by employing 1,2-bis(diphenylphosphino)ethane as chelating ligand in the displace-