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Palladium-Catalyzed Skeletal Rearrangement of (Alkoxy)oligosilanes via Silylene Transfer

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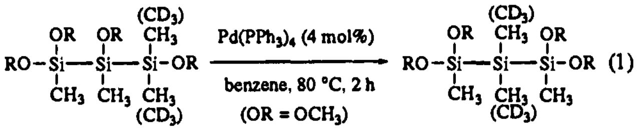
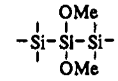
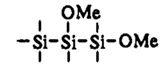
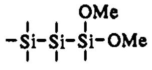
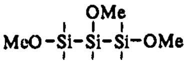
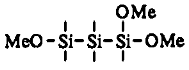
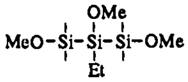
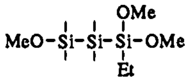
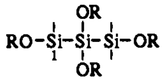
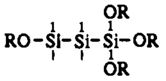
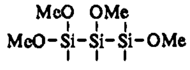
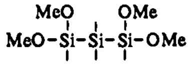
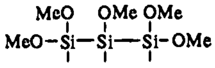
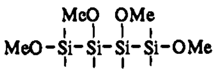
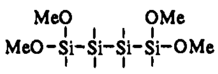
Polysilanes have attracted much attention due to their unique chemical and physical properties.[1] Special interest has recently been paid to the chemistry of functionalized polysilanes that contain functional groups on silicon with the aim of modification of properties.[2] Little has been studied, however, on the reactivity of the functionalized polysilane backbone. We have been engaged in the study of the structure/reactivity correlation using structurally well-defined functionalized oligosilanes as models for functionalized polysilanes.[3] We now report a novel skeletal rearrangement of (alkoxy)oligosilanes catalyzed by a palladium complex via silylene transfer.

Representative results are summarized in Table 1.[4] Typically, 1,1,2,3-(MeO)$_4$Me$_4$Si$_3$ (**14**) was converted into the 1,1,3,3-isomer **15** quantitatively (^{1}H NMR) by heating in benzene under reflux for 2 h in the presence of a catalytic amount of Pd(PPh$_3$)$_4$ (4 mol %), as shown in eq 1. Simple bulb-to-bulb distillation gave the pure product in roughly 90% yield.[5] In a deuterium-labeled experiment, also shown in eq 1, the 3,3-(CD$_3$)$_2$-isomer[4] **14**-d_6 gave the 2,2-(CD$_3$)$_2$-isomer **15**-d_6 exclusively under similar conditions.[5] No CD$_3$/CH$_3$ random scrambling was observed at all. The results strongly suggest a silylene-transfer mechanism for the highly selective skeletal rearrangement.



14 or **14**-d_6 100% yield (^{1}H NMR) **15** or **15**-d_6

Table 1. Palladium-Catalyzed Skeletal Rearrangement of (Alkoxy)oligosilanes[a]

entry	starting material	temp.(°C), time (h)[b]	product[c]
1	 $-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\underset{\underset{\mathrm{OMe}}{\vert}}{\overset{\overset{\mathrm{OMe}}{\vert}}{\mathrm{Si}}}-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-$ **1**	80, 11	no reaction
2	 $-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\underset{\vert}{\overset{\overset{\mathrm{OMe}}{\vert}}{\mathrm{Si}}}-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\mathrm{OMe}$ **2**	110, 170	 $-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\underset{\vert}{\overset{\overset{\mathrm{OMe}}{\vert}}{\mathrm{Si}}}-\mathrm{OMe}$ **3**
3	 $\mathrm{MeO}-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\underset{\vert}{\overset{\overset{\mathrm{OMe}}{\vert}}{\mathrm{Si}}}-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\mathrm{OMe}$ **4**	80, 2	 $\mathrm{MeO}-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\underset{\vert}{\overset{\overset{\mathrm{OMe}}{\vert}}{\mathrm{Si}}}-\mathrm{OMe}$ **5**
4	 $\mathrm{MeO}-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\underset{\underset{\mathrm{Et}}{\vert}}{\overset{\overset{\mathrm{OMe}}{\vert}}{\mathrm{Si}}}-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\mathrm{OMe}$ **6**	80, 50	 $\mathrm{MeO}-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\underset{\underset{\mathrm{Et}}{\vert}}{\overset{\overset{\mathrm{OMe}}{\vert}}{\mathrm{Si}}}-\mathrm{OMe}$ **7**
	 $\mathrm{RO}-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\underset{\underset{\mathrm{OR}}{\vert}}{\overset{\overset{\mathrm{OR}}{\vert}}{\mathrm{Si}}}-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\mathrm{OR}$		 $\mathrm{RO}-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\underset{\underset{\mathrm{OR}}{\vert}}{\overset{\overset{\mathrm{OR}}{\vert}}{\mathrm{Si}}}-\mathrm{OR}$
5	**8** RO = MeO	80, 1	**9** RO = MeO
6	**10** RO = EtO	110, 4.5	**11** RO = EtO
7	**12** RO = *i*-PrO	140, 43	**13** RO = *i*-PrO
8	 $\mathrm{MeO}-\underset{\vert}{\overset{\overset{\mathrm{MeO}}{\vert}}{\mathrm{Si}}}-\underset{\vert}{\overset{\overset{\mathrm{OMe}}{\vert}}{\mathrm{Si}}}-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\mathrm{OMe}$ **14**	80, 2	 $\mathrm{MeO}-\underset{\vert}{\overset{\overset{\mathrm{MeO}}{\vert}}{\mathrm{Si}}}-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\underset{\vert}{\overset{\overset{\mathrm{OMe}}{\vert}}{\mathrm{Si}}}-\mathrm{OMe}$ **15**
9	 $\mathrm{MeO}-\underset{\vert}{\overset{\overset{\mathrm{MeO}}{\vert}}{\mathrm{Si}}}-\underset{\vert}{\overset{\overset{\mathrm{OMe}}{\vert}}{\mathrm{Si}}}-\underset{\vert}{\overset{\overset{\mathrm{OMe}}{\vert}}{\mathrm{Si}}}-\mathrm{OMe}$ **16**	80, 16	"no reaction"
10	 $\mathrm{MeO}-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\underset{\vert}{\overset{\overset{\mathrm{MeO}}{\vert}}{\mathrm{Si}}}-\underset{\vert}{\overset{\overset{\mathrm{OMe}}{\vert}}{\mathrm{Si}}}-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\mathrm{OMe}$ **17**	110, 20	 $\mathrm{MeO}-\underset{\vert}{\overset{\overset{\mathrm{MeO}}{\vert}}{\mathrm{Si}}}-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\underset{\vert}{\overset{\vert}{\mathrm{Si}}}-\underset{\vert}{\overset{\overset{\mathrm{OMe}}{\vert}}{\mathrm{Si}}}-\mathrm{OMe}$ **18**

[a] Methyl groups on silicons are omitted for clarity. Reactions were usually carried out on a 1 mmol scale in benzene (for 80 °C reaction), toluene (for 110 °C reaction), or xylene (for 140 °C reaction) in the presence of 4 mol % of Pd(PPh$_3$)$_4$ as catalyst. [b] Reaction times are rough estimates for the complete conversion monitored by ^{1}H NMR, except for entries 1 and 9. [c] Yields were quantitative by ^{1}H NMR analysis for entries 2−8 and 10.

There are several significant features to be noted: methyl groups on silicon atoms are omitted in most cases for clarity throughout this paper. (1) The reactivity order of methoxytrisilanes is roughly as follows: 1,2,2,3-(MeO)$_4$ (**8**) $\sim$ 1,1,2,3-(MeO)$_4$ (**14**) $\sim$ 1,2,3-(MeO)$_3$ (**4**) $\gg$ 1,2-(MeO)$_2$ (**2**) $\gg$ 2,2-(MeO)$_2$ (**1**) (no reaction). The results indicate that a 1,2-dialkoxytrisilane skeleton is the smallest structural unit for rearrangement. It should be mentioned that the reactivity of the Si−Si bond toward a Pd(0) species has been known to be enhanced by the introduction of electronegative groups on silicon.[6] (2) The rearrangement is highly regioselective in such a fashion that the alkoxysilylene moiety is transferred from the internal to the terminal position. All products thus contain the Me$_2$Si moiety at the internal position, having no 1,2-dialkoxy skeleton requisite for rearrangement. As a result, the rearrange-

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(5) ^{1}H NMR (200 or 270 MHz, C$_6$D$_6$), δ ppm: **14**, 0.361 (s, 3H), 0.417 (s, 6H), 0.595 (s, 3H), 3.427 (s, 3H), 3.465 (s, 3H), 3.487 (s, 3H), 3.498 (s, 3H); **15**, 0.365 (s, 6H), 0.405 (s, 6H), 3.486 (s, 12H). **14**-d_6 and **15**-d_6 lack the singlet at δ 0.417 (6H) and 0.405 (6H), respectively. All other new compounds also exhibited satisfactory spectral and analytical data.

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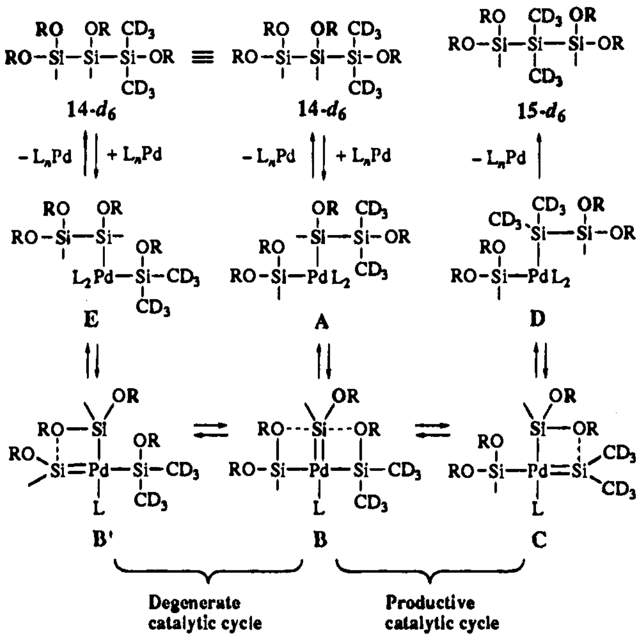
Scheme 1



ment proceeds in one direction under the reaction conditions, neither a reverse reaction nor an equilibrium mixture being observed. (3) There are further clear-cut examples consonant with the silylene-transfer mechanism. If an RO/Me random exchange mechanism were operative, two regioisomers of tetramethoxytrisilanes **8** and **14** would form a common, thermodynamically controlled product; however, different regioisomeric products **9** and **15** were actually formed, respectively (entries 5 and 8). The heat of formation has been estimated by PM3 calculations on four regioisomers of trimethoxytrisilanes $(MeO)_3Me_5Si_3$, decreasing in the order 1,2,3- (−294.6 kcal mol^{-1}) > 1,2,2- (−295.7) > 1,1,3- (−296.8) > 1,1,1- (−300.1). Experimentally, the 1,2,3-isomer gave not the 1,1,1-isomer but the 1,1,3-isomer selectively (entries 3 and 4). The present rearrangement thus seems not to be under thermodynamic control. (4) A tetrasilane also undergoes a similar rearrangement (entry 10). Thus, 1,2,3,4-$(MeO)_4Me_6Si_4$ (**17**) gave 1,1,4,4-isomer **18** rather slowly but cleanly as the sole product. No branched isomer was formed at all: this is different from the thermodynamically controlled rearrangement of Fe−oligosilanes reported by Pannell.[7] (5) No disproportionation reaction was observed: in other words, no lower and higher oligomeric isomers were formed, in contrast to the known metal-catalyzed disproportionation reactions of hydro- and peralkyloligosilanes.[8] Thus, in the present system, no silylene species is extruded, suggesting a mechanism involving special stabilization of the silicon−palladium intermediates by alkoxy groups.[9]

All results are mechanistically reminiscent of the alkoxy-bridged bis(silylene)−Fe and bis(silylene)−Ru complexes reported by Tobita and Ogino[10] and the square-planar (alkylthio)-substituted silylene−Pt(II) complexes prepared recently by Tilley and his co-workers.[11]

A plausible mechanism is illustrated for conversion of the deuterated 1,1,2,3-$(MeO)_4$-3,3-$(CD_3)_2Si_3$ **14-*d*₆** into 1,1,3,3-$(MeO)_4$-2,2-$(CD_3)_2$-isomer **15-*d*₆** (Scheme 1). In the first step, the Si−Si bond with more alkoxy groups[6] in **14-*d*₆** undergoes oxidative addition to a Pd(0) complex to form bis(silyl)−Pd(II) complex **A**.[12] The β-(alkoxy)disilanyl−Pd moiety in **A** undergoes α-elimination to form a key intermediate, $(alkoxysilyl)_2$-(silylene)−Pd(II) complex **B**: The silylene complex may be stabilized by intramolecular coordination by the alkoxy group(s) on the silyl group(s). The bridged alkoxy group can be transferred to the silylene to form a new silylene complex **C**. Subsequent migratory insertion of the silylene into the Pd−Si σ bond forms a new bis(silyl)−Pd(II) complex, **D**, which undergoes reductive elimination to give the observed **15-*d*₆**. Alternatively, intermediate **B** can undergo a similar alkoxy exchange with the other dialkoxysilyl group. The resulting intermediate **B'**, however, contains totally the same silylene and silyl groups on palladium and, hence, eventually goes back to the starting material **14-*d*₆** via bis-silyl intermediate **E**; the process via **A**, **B**, **B'**, and **E** is thus a nonproductive degenerate catalytic cycle. Consequently, the process via **A**, **B**, **C**, and **D** is only one productive catalytic cycle in this route, resulting in the formation of **15-*d*₆** cleanly. The reaction may also start from the less-alkoxy-substituted Si−Si bond of **14-*d*₆** to form **15-*d*₆** via **E**, **B'**, **B**, **C**, and **D**. Since **15-*d*₆** is not converted back into **14-*d*₆**, at least the final step, **D** to **15-*d*₆**, should be irreversible due to the lower reactivity of the Si−Si bonds in **15-*d*₆** than those in **14-*d*₆**.

"No reaction" of 1,1,2,3,3-$(MeO)_5Me_3Si_3$ (**16**) (entry 9), which is expected to be highly reactive, can now be explained by the degenerate silylene-transfer mechanism. Thus, the transfer of the central (MeO)MeSi moiety to either of the terminal positions must give the starting material. It is likely that the rearrangement might have occurred very fast, but simply could not be detected spectroscopically.

The novel skeletal rearrangement of (alkoxy)oligosilanes reported herein must be useful for the structural modification of polyfunctionalized polysilanes.

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(9) We have observed no reaction with 1,2,3-$(Et_2N)_3Me_5Si_3$ and a complex reaction with 1,2,3-$F_3Me_5Si_3$, indicative of the clean skeletal rearrangement being characteristic of (alkoxy)oligosilanes.

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