Novel Skeletal Rearrangement Reaction of Tetrasilanes with Aryl Isocyanides

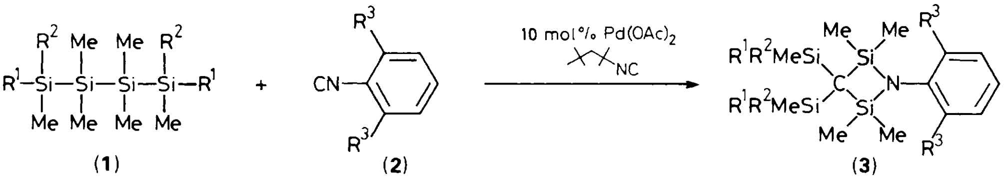
Yoshihiko Ito,*[a] Michinori Suginome,[a] Masahiro Murakami,[a] and Motoo Shiro[b]

[a] *Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan*
[b] *Shionogi Research Laboratories, Fukushima-ku, Osaka 553, Japan*

A novel skeletal rearrangement of tetrasilanes in the palladium catalysed reaction with aryl isocyanides gives 3,3-disilyl-2,4-disila-1-azacyclobutane derivatives, the structure of one example of which has been determined by *X*-ray crystallography.

Organopolysilanes are known to undergo skeletal rearrangements catalysed by Lewis acids as well as transition metal complexes.[1] We now report a novel skeletal rearrangement of tetrasilanes (**1**) in the palladium catalysed reaction with aryl isocyanides (**2**) to give 3,3-disilyl-2,4-disila-1-azacyclobutane derivatives (**3**). The rearrangement is unique and interesting in that the product (**3**) is completely reconstituted from the four fragments of tetrasilane (**1**) and two fragments of isocyanide (**2**).

This novel rearrangement reaction was found in the course of our recent study[2] on the palladium catalysed insertion of isocyanide into the silicon–silicon linkage of polysilanes; *i.e.*, the reaction of polysilanes with an excess of aryl isocyanides was catalysed by a palladium complex to afford the corres-



(**1**)
a; $R^1 = R^2 = Me$
b; $R^1 = Ph, R^2 = Me$
c; $R^1 = R^2 = Ph$

(**2**)
a; $R^3 = Me$
b; $R^3 = Pr^i$

(**3**)
a; $R^1 = R^2 = Me, R^3 = Me$ 40%
b; $R^1 = R^2 = Me, R^3 = Pr^i$ 45%
c; $R^1 = Ph, R^2 = Me, R^3 = Me$ 31%
d; $R^1 = Ph, R^2 = Me, R^3 = Pr^i$ 62%
e; $R^1 = R^2 = Ph, R^3 = Me$ 28%
f; $R^1 = R^2 = Ph, R^3 = Pr^i$ 48%

Scheme 1

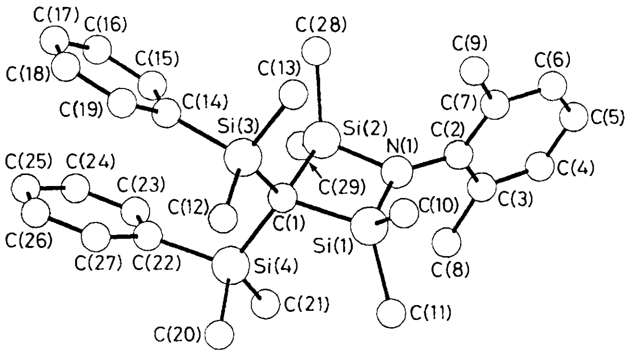


Figure 1. Molecular structure of (**3c**). Selected bond lengths (Å) and angles (°): C(1)–Si(1) 1.925(3), C(1)–Si(2) 1.913(3), N(1)–Si(1) 1.733(3), N(1)–Si(2) 1.746(3), N(1)–C(2) 1.436(4), Si(1)–C(1)–Si(2) 84.9(1), Si(1)–N(1)–Si(2) 96.2(1), C(1)–Si(1)–N(1) 89.4(1), C(1)–Si(2)–N(1) 89.5(1), Si(1)–N(1)–C(2) 135.5(2), Si(2)–N(1)–C(2) 128.2(2).

ponding poly[sila(*N*-aryl)imine]. However, the palladium catalysed reaction of tetrasilane (**1**) with 1.5 equivalents of aryl isocyanide (**2**) in the presence of 1,1,3,3-tetramethylbutyl isocyanide† gave unexpectedly (**3**) in moderate yields.‡ The rearrangement of tetrasilanes occurred in the reaction with aryl isocyanides, but not with alkyl isocyanides. The use of sterically bulky 2,6-di-isopropylphenyl isocyanide gave better yields of the corresponding rearranged products (**3**) than 2,6-xylyl isocyanide.

The reactions were carried out by heating a mixture of tetrasilane (**1**) (0.26 mmol), aryl isocyanide (**2**) (0.39 mmol), 1,1,3,3-tetramethylbutyl isocyanide (0.26 mmol), and $Pd(OAc)_2$ (0.026 mmol) in toluene (1 ml) at reflux for 6 h under a nitrogen atmosphere and (**3**) was isolated by preparative t.l.c. (Scheme 1). The 3,3-disilyl-2,4-disila-1-azacyclobutane (**3**) thus formed was stable and the Si–N bond of (**3**) was not cleaved even on treatment with aqueous acid. The structure of (**3**) was in accord with the n.m.r.,§ i.r., and mass spectra, and established by *X*-ray crystal structure analysis. The crystal structure of (**3c**) is shown in Figure 1, together with selected bond lengths and angles.¶ Puckering of the four-membered ring is slight: the two half-rings are folded along the Si(1)–Si(2) diagonal, forming a dihedral angle of 2.2(2)°. The 2,6-xylyl ring is perpendicular [89.7(1)°] to the mean plane of the four-membered ring.

Intermediacy of a palladium–silylene complex might be involved in the present skeleton rearrangement of tetrasilanes, but this still remains to be clarified.

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References

1 M. Kumada, *J. Organomet. Chem.*, 1975, **100**, 127.

2 Y. Ito, T. Matsuura, and M. Murakami, *J. Am. Chem. Soc.*, 1988, **110**, 3692.

3 P. Main, MULTAN87, 'Program for the Automatic Solution of Crystal Structures from *X*-Ray Diffraction Data by Multiple Starting Point Tangent Formula and XMY,' University of York, 1987.

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† 1,1,3,3-Tetramethylbutyl isocyanide was not incorporated in the product. In the absence of 1,1,3,3-tetramethylbutyl isocyanide, (**3**) was also obtained but in lower yield.

‡ Under similar conditions [Ar–NC (1.8 mmol), $Pd(OAc)_2$ (0.15 mmol) in toluene (5 ml) at reflux for 6 h], trisilanes [RMe_2Si–($SiMe_2$)–$SiMe_2R$] (1.5 mmol) gave the corresponding mono-insertion products [RMe_2Si–(C=N–Ar)–($SiMe_2$)–$SiMe_2R$].

§ ^1H N.m.r. for (**3c**) ($CDCl_3$, 200 MHz): δ 0.21 (12 H, s), 0.59 (12 H, s), 2.37 (6 H, s), 6.86—7.08 (3 H, m), 7.23—7.41 (10 H, m).

¶ *Crystal data* for (**3c**): $C_{29}H_{43}NSi_4$, $M = 518.0$, monoclinic, space group $P2_1/c$, $a = 9.344(1)$, $b = 12.233(1)$, $c = 26.197(3)$ Å, $\beta = 90.34(1)°$, $Z = 4$, $U = 2994.4(5)$ Å^3, $D_c = 1.149$ g cm^{-3}, radiation, Cu-K_α ($\lambda = 1.54178$ Å), $\mu = 18.9$ cm^{-1}, crystal size 0.4 × 0.3 × 0.2 mm, 4455 unique reflections measured ($2\theta_{max} = 120°$). The structure was solved using the program MULTAN87[3] and refined by the block-diagonal least-squares method to $R = 0.040$, $R_w = 0.061$ and $S = 1.020$ for 3973 reflections. All H atoms were located on a difference electron density map. The thermal parameter of each H atom was assumed to be isotropic and equal to B_{eq} of the bonded atom. Weights were taken as $w = [\sigma^2(F_o) + 0.00290|F_o|^2]^{-1}$ for the reflections with $w^{1/2}|F_o|>3$ and $w^{1/2}|\Delta F|<4$, and $w = 0$ otherwise. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.