

Novel Skeletal Rearrangement Reaction of Tetrasilanes with Aryl Isocyanides

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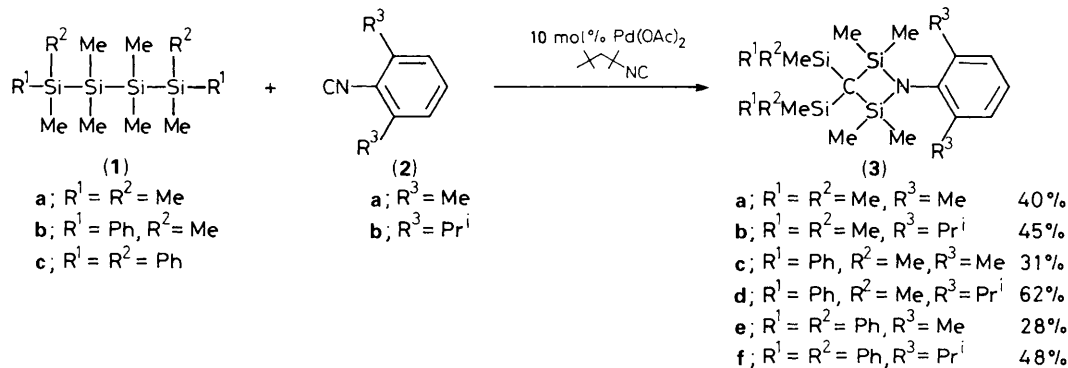
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A novel skeletal rearrangement of tetrasilanes in the palladium catalysed reaction with aryl isocyanides gives 3,3-disilyl-2,4-disila-1-azacyclobutane derivatives, the structure of one example of which has been determined by X-ray crystallography.

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 study² 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-



Scheme 1

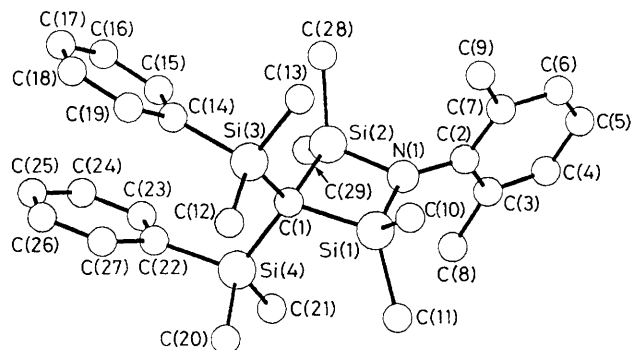


Figure 1. Molecular structure of (**3c**). Selected bond lengths (Å) and angles (°): C(1)–Si(1) 1.925(3), C(1)–Si(2) 1.913(3), N(1)–Si(1) 1.733(3), N(1)–Si(2) 1.746(3), N(1)–C(2) 1.436(4), Si(1)–C(1)–Si(2) 84.9(1), Si(1)–N(1)–Si(2) 96.2(1), C(1)–Si(1)–N(1) 89.4(1), C(1)–Si(2)–N(1) 89.5(1), Si(1)–N(1)–C(2)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

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§ ¹H N.m.r. for (3c) (CDCl₃, 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):* C₂₉H₄₃NSi₄, *M* = 518.0, monoclinic, space group *P*₂₁/*c*, *a* = 9.344(1), *b* = 12.233(1), *c* = 26.197(3) Å, β = 90.34(1)°, *Z* = 4, *U* = 2994.4(5) Å³, *D*_c = 1.149 g cm^{−3}, radiation, Cu-Kα (λ = 1.54178 Å), μ = 18.9 cm^{−1}, crystal size 0.4 × 0.3 × 0.2 mm, 4455 unique reflections measured (2θ_{max} = 120°). The structure was solved using the program MULTAN87³ 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* = [σ²(*F*_o) + 0.00290|*F*₀|²]^{−1} for the reflections with *w*^{1/2}|*F*_o| > 3 and *w*^{1/2}|Δ*F*| < 4, and *w* = 0 otherwise. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

† 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 [RMe₂Si-(SiMe₂)₂-SiMe₂R] (1.5 mmol) gave the corresponding mono-insertion products [RMe₂Si-(C=N-Ar)-(SiMe₂)₂-SiMe₂R].