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Transition Metal Catalyzed Reaction of Peralkylated 3,4-Bis(alkylidene)-1,2-disilacyclobutane

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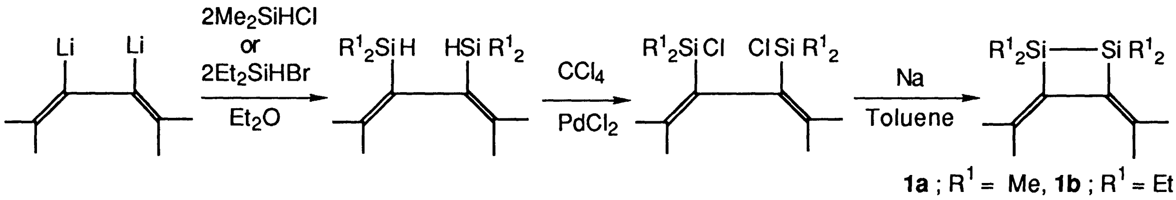
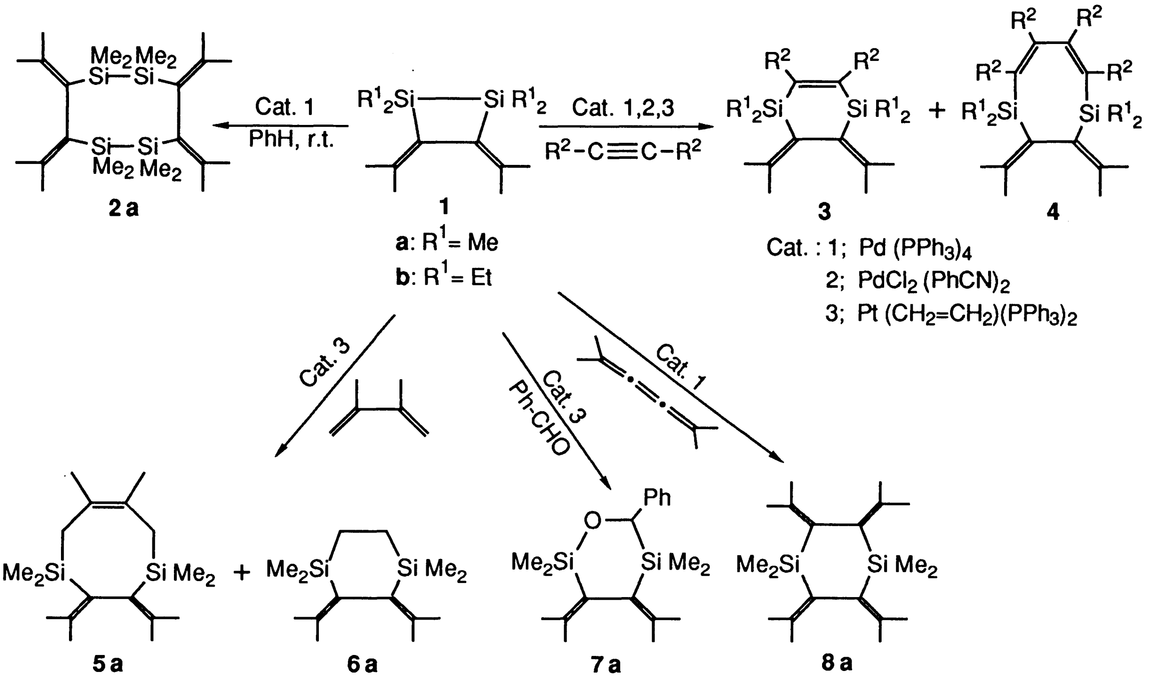
Peralkylated 3,4-bis(alkylidene)-1,2-disilacyclobutanes prepared by convenient synthetic route were quantitatively converted to 3,4,7,8-tetrakis(alkylidene)-1,2,5,6-tetrasilacyclooctane (twist and chair 1:1 mixture) by Pd-catalyzed reaction. In the presence of unsaturated compounds, this disilane metathesis reaction was inhibited to give double silylation products. The reaction pathways are highly dependent upon electronic factors of unsaturated compounds and the catalyst.

Small ring organosilacyclic compounds bearing exocyclic π-bond such as alkylidenesilacyclopropane and bis(alkylidene)silacyclopropane are of much interest because of their intrinsic strains.1) Ishikawa and co-workers have reported first 3,4-bis(alkylidene)-1,2-disilacyclobutane2) and alkylidene disilacyclopropane stabilized by aromatic groups of disilane moiety. Nevertheless, peralkyl substitution of disilane in these rings attracted us as a very reactive system to study. On the other hand, cyclic disilane and disilane with electron-withdrawing substituents on silicon were known to undergo double silylation reaction of alkynes, alkenes and dienes catalyzed by transition metals.3) Kumada and Sakurai's groups3a,c) reported that double silylation of 1,1,2,2-tetramethyl-1,2-disilacyclopentane accompanied disilane metathesis reaction in the presence of Pd catalyst. More recently, Pt-catalyzed dehydrogenative4) and Pd-catalyzed intramolecular variations of double silylation5) were developed by Tanaka and Ito's groups respectively. Now, we report that peralkylated 3,4-bis(alkylidene)-1,2-disilacyclobutane is readily susceptible to transition metal catalyzed disilane metathesis versus double silylation of a variety of unsaturated compounds.

Reactions of dimethylchlorosilane and diethylbromosilane with 3,4-dilithio-2,5-dimethyl-2,4-hexadiene, prepared from metallation of tetramethyl butatriene, led to the formation of 3,4-bis(dimethylsilyl)- and 3,4-bis(diethylsilyl)-2,5-dimethyl-2,4-hexadiene. After chlorination with $PdCl_2$ / CCl_4, the resulting chlorosilanes were reductively cyclized with sodium in toluene to provide 3,4-bis(alkylidene)-1,1,2,2-tetramethyl (tetraethyl) disilacyclobutane (**1a** and **1b**) in 25% and 12% yields.6) Compounds **1a** and **1b**, however, are gradually oxidized in air at room temperature to give corresponding siloxanes.



1a ; R^1 = Me, **1b** ; R^1 = Et



When a solution of disilacyclobutane (0.89 mmol) (**1a**) and tetrakis(triphenylphosphine)palladium (0.09 mmol) in 10 ml benzene was stirred at room temperature for 30 min under an argon atmosphere, a clear yellow solution was obtained. After evaporation of the solvent, the residue was subjected to preparative TLC (silica gel, n-hexane) or GPC (toluene) to give 3,4,7,8-tetrakis(alkylidene)-1,2,5,6-tetrasilacyclooctane (**2a**) as a colorless crystal in 93% yield.[6] The tetrasilacyclooctane (**2a**) exists as 1:1 twist and chair stable conformational isomers, which could not be separated. On one occasion, isomerically pure crystals were successfully grown and X-ray structure of chair conformer was determined and is depicted in Fig. 1. The tetraethyldisilacyclobutane (**1b**) did not afford the corresponding disilane metathesis product.

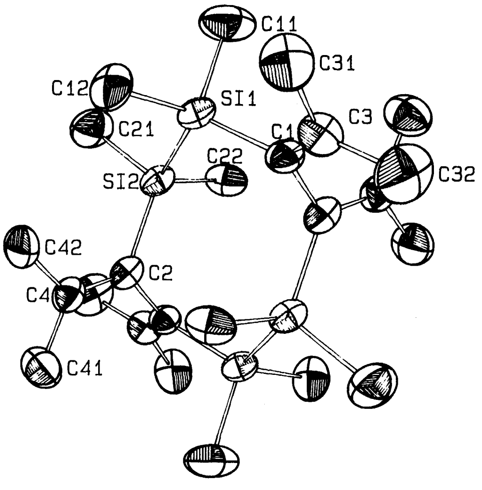


Fig. 1 A view of the structure of **2a** .

With regard to palladium and platinum complex catalyzed double silylation of alkynes with the disilacyclobutanes, the results are summarized in Table 1.[6] It is seen that, while the Pd-catalyzed double silylation of **1a** with alkynes produced monoadduct **3a** and diadduct **4a** along with **2a**, Pt-catalyzed reaction only produced monoadduct **3a**. In the case of **1b**, both Pd- and Pt-catalyzed reaction afforded monoadducts **3a**. Although Pd-catalyzed reaction of **1a** failed with benzaldehyde and 2,3-dimethylbutadiene, Pt-catalyzed reaction gave the products **5a** (41%), **6a** (10%), and **7a** (60%) respectively. Ethylene ligand of Pt-catalyst (10 mol% for **1a**) might be incorporated in the compound **6a**. Of special interest, Pd-catalyzed double silylation of **1a** with tetramethylbutatriene gave 2,3,4,5-tetrakis(alkylidene)-1,1,4,4-tetramethyldisilacyclohexane (**8a**). This com-

Table 1. Transition metal complexes catalyzed double silylation of **1**[a)]

Run	Substrate	Reactant[f)]	Catalyst	Products and Yield / %[b)] **2**	 **3**	 **4**
1	**1a**	A	$Pd(PPh_3)_4$		68	18
2	**1a**	A	$PdCl_2(PhCN)_2$		30	47
3[c)]	**1b**	A	$Pd(PPh_3)_4$		77	
4[d)]	**1a**	A	$Pt(CH_2{=}CH_2)(PPh_3)_2$		71	
5	**1a**	B	$Pd(PPh_3)_4$	61	31	
6	**1a**	B	$PdCl_2(PhCN)_2$	24	51	
7[c)]	**1b**	B	$Pd(PPh_3)_4$		87	
8[e)]	**1a**	B	$Pt(CH_2{=}CH_2)(PPh_3)_2$		82	
9	**1a**	C	$Pd(PPh_3)_4$		80	
10	**1a**	C	$PdCl_2(PhCN)_2$	18	59	

a) Condition: **1**(0.89 mmol), reactant (4.4 mmol), catalyst (0.09 mmol), benzene (10 ml), room temperature, 30 min.
b) Isolated yield and see Ref. 6. c) R.t., 10 h. d) Reflux 12 h. e) Reflux 3 h.
f) Reactant; A: dimethyl acetylenedicarboxylate, B: diphenylacetylene, C: phenylacetylene.

pound (**8a**) has the structure of 3:1 twist and chair conformers, the latter structure having been confirmed by X-ray analysis.[7)]

In summary, in the presence of Pd-catalyst, the disilane metathesis reaction predominated over double silylation, while the disilane metathesis was not observed in the presence of Pt-catalyst. Introduction of alkylidene group on 1,2-disilacyclobutane ring enhanced its reactivity towards disilane metathesis reaction as compared to similar reaction carried out earlier by Sakurai and co-workers.[3d)] In this respect, application of this efficient disilane metathesis reaction is interesting to synthesize Si-Si containing compounds and ladder-type silicon containing polymers.

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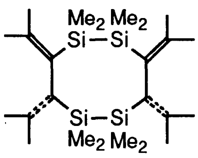
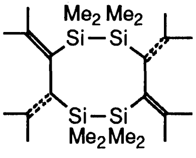
6) **1a:** colorless oil; ^{1}H NMR (C_6D_6) δ = 0.37 (s,12H), 1.62 (s,6H), 1.80 (s,6H); ^{13}C NMR (C_6D_6) δ = -2.8 (q), 23.4 (q), 25.9 (q), 137.5 (s), 143.9 (s); ^{29}Si NMR (C_6D_6) δ = -16.5; HRMS Found: 224.1395. Calcd for $C_{12}H_{24}Si_2$: 224.1417. **1b:** Colorless oil; ^{1}H NMR (C_6D_6) δ = 0.8-1.3 (m20H), 1.64 (s,6H), 1.81 (s,6H); ^{13}C NMR (C_6D_6) δ = 5.7 (t), 9.6 (q), 23.2 (q), 26.3 (q), 137.2 (s), 142.9 (s); ^{29}Si NMR (C_6D_6) δ -4.5; HRMS Found: 280.2045. Calcd for $C_{16}H_{32}Si_2$: 280.2043. **2a** (Twist and chair 1:1 mixture); Chair isomer: mp 215-216 °C; ^{1}H NMR (C_6D_6) δ = 0.23 (s,12H), 0.46 (s,12H), 1.59 (s,12H), 1.84 (s,12H); ^{13}C NMR (C_6D_6) δ = -0.8 (q), 1.3 (q), 23.2 (q), 24.9 (q), 139.3 (s), 140.5 (s); ^{29}Si NMR (C_6D_6) δ = -26.5; HRMS Found: 448.2846. Calcd for $C_{24}H_{48}Si_4$: 448.2833. Twist isomer: ^{1}H NMR (C_6D_6) δ = 0.32 (s,12H), 0.39 (s,12H), 1.59 (s,12H), 1.79 (s,12H); ^{13}C NMR (C_6D_6) δ = -0.03 (q), 0.1 (q), 23.0 (q), 24.7 (q), 139.4 (s), 139.7 (s); ^{29}Si NMR (C_6D_6) δ -27.4. All new compounds obtained from double silylation gave satisfactory spectral data.

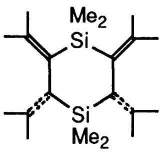
7) 2,3,5,6-Tetrakis(alkylidene)-1,4-dimethyldisilacyclohexane is also reported to exist as stable twist and chair conformational isomers, which can not interconvert to each other at room temperature. A. Maercker, F. Brauers, and W. Brieden, *J. Organomet. Chem.*, **377**, C45 (1989); A. Maercker, W. Brieden, F. Kastner, and A. Mannschreck, *Chem. Ber.*, **124**, 2033 (1991). According to this precedent, and X-ray analysis, **2a** and **8a** were assigned to chair and twist conformational isomers as follows.



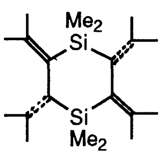
2a-chair



2a-twist



8a-chair



8a-twist

Crystal data for **2a**-chair: $C_{24}H_{48}Si_4$, M = 448.99, triclinic with a = 8.438(4)Å, b = 9.731(3)Å, c = 10.188(4)Å, α = 99.11(3)°, β = 110.60(3)°, γ = 106.75(3)°,V = 717.7Å^3, space group P-1, Z = 1, μ = 2.1 cm^{-1}, ρ = 1.04 g/cm^3. Crystal data for **8a**-twist: $C_{20}H_{36}Si_2$, M = 332.68, triclinic with a = 7.813(1)Å, b = 8.694(1)Å, c = 8.755(1)Å, α = 107.74(1)°, β = 90.90(1)°, γ = 103.97(1)°,V = 5 47.1Å^3, space group P1, Z = 1, μ = 1.5 cm^{-1}, ρ = 1.01 g/cm^3. The 2514 and 2077 independent reflections [$2\theta<50°, |Fo^2|>3\sigma|Fo^2|$] for **2a**-chair and **8a**-twist were measured on Enraf-Nonius CAD4 diffractometer using Mokα irradiation and ω-2θ scan. The structure was solved by direct methods. For **2a**, all non-hydrogen atoms were refined anisotoropically and hydrogen atoms refined with fixed thermal parameters to R = 0.049 (Rw = 0.054). For **8a**, all non-hydrogen atoms were refined anisotropically without hydrogen to R = 0.073 (Rw = 0.089).

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