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THE CHEMISTRY OF OCTAMETHYL-1,2-DISILACYCLOBUTANE. SOME Si–Si CLEAVAGE AND INSERTION REACTIONS *

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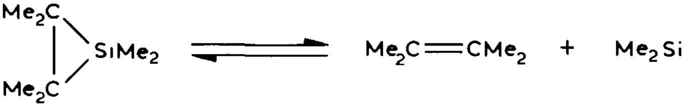
Summary

Octamethyl-1,2-disilacyclobutane is very air-sensitive. Its Si–Si bond is readily cleaved by water, HCl, CF_3CO_2H, Cl_2, Br_2 and organolithium reagents. In the presence of $(Ph_3P)_2PdCl_2$, various acetylenes, conjugated dienes and allene insert into the Si–Si bond of the disilacyclobutane. The stoichiometric reaction of the disilacyclobutane and $(Ph_3P)_2PdCl_2$ gave $ClMe_2SiCMe_2CMe_2SiMe_2Cl$ and the 1,1-bis(triphenylphosphine)-2,2,3,3,4,4,5,5-octamethyl-1-pallada-2,5-disilacyclopentane. The latter reacted with phenylacetylene to give the same product which was obtained in the catalyzed reaction. This suggests that the catalyzed process involves initial reduction of $(Ph_3P)_2PdCl_2$ to $(Ph_3P)_2Pd$ and insertion of the latter into the Si–Si bond of the disilacyclobutane.

Introduction

When hexamethylsilirane is decomposed thermally at ~ 70°C in the absence of an external silylenophile, the dimethylsilylene which is extruded inserts into the SiC_2 ring of as yet undecomposed silirane (eq. 1, 2) [1]. The octamethyl-1,2-disilacyclobutane, **1**, which is produced is a volatile white, crystalline solid, m.p. 71–71.5°C. It is quite air sensitive, being easily oxidized to **2**, and is thermally quite stable. Its pyrolysis has been studied in detail [2]. The thermal decomposition of octamethyl-



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* Dedicated to Professor Makoto Kumada, the Grand Master of the Si–Si bond.

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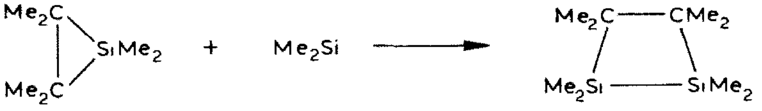

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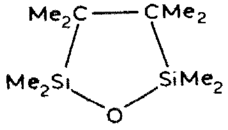
1,2-disilacyclobutane proceeds via homolytic C–C bond rupture to give $Me_2CHSiMe_2SiMe_2C(Me){=}CH_2$.

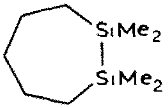


(**2**)

Octamethyl-1,2-disilacyclobutane, at the time of its discovery in 1976, was only the second 1,2-disilacyclobutane to be prepared. The first, 1,1,2,2-tetrafluoro-1,2-disilacyclobutane, a product of the reaction of ethylene with the species generated in the high temperature reaction of SiF_4 with elemental silicon [3], was unstable at room temperature and hence was not amenable to study of its chemistry. After the present study was well underway, Gusel'nikov et al. [4] reported the synthesis of 1,1,2,2-tetramethyl-1,2-disilacyclobutane by the reaction of $ClSiMe_2CH_2CH_2SiMe_2Cl$ with Na/K vapor. The C-unsubstituted 1,2-disilacyclobutane was found to polymerize at room temperature and to autoxidize very readily to give the 1-oxa-2,5-disilacyclopentane.

The eight methyl substituents of **1** should serve to stabilize the 1,2-disilacyclobutane ring with respect to the cleavage/polymerization processes encountered in the C-unsubstituted ring [4]. However, they will also have a damping effect on the reactivity of the Si_2C_2 ring. Nevertheless, one might hope that, as in the case of hexamethylsilirane, the permethyl substitution will still leave us with a very reactive system to study. Accordingly, we embarked upon a survey of the reactivity of octamethyl-1,2-disilacyclobutane.

Before a discussion of our results, it is worthwhile to summarize briefly what is known about the lower cyclic disilanes. Kumada and coworkers [5] have prepared cyclic disilanes **3**, **4** and **5** and showed that their Si–Si bonds are more reactive than the Si–Si bond of hexamethyldisilane. Other workers have shown that the charge transfer energy of these compounds decreases as *n* becomes smaller, indicating that the Si–Si bond becomes relatively more electron-rich as the ring size decreases [6]. Also, the rate of oxidation with *m*-chloroperbenzoic acid of the Si–Si bonds of **3**, **4**



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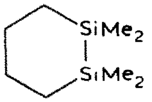

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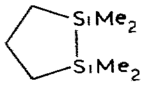


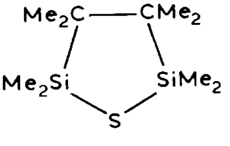
(**5**)

and **5** increases as the ring size decreases. The rate of oxidation of 1,1,2,2-tetramethyl-1,2-disilacyclopentane is 10^3 times faster than that of hexamethyldisilane [6]. In fact, the silacyclopentane undergoes air oxidation readily, giving 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane. It is thus clear that the 1,2-disilacyclobutane ring should be highly reactive unless steric factors operate to give a measure of kinetic protection.

Results and discussion

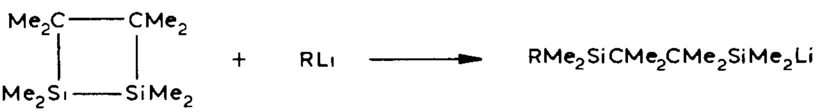
Some simple, uncatalyzed ring cleavage reactions of octamethyl-1,2-disilacyclobutane

In order to obtain a rough measure of the reactivity of the Si–Si bond of octamethyl-1,2-disilacyclobutane we first studied its reactions with some simple reagents. Its hydrolysis with deoxygenated water was exothermic at room temperature, giving the cyclic siloxane **2** in 96% yield. The expected product is $HOSiMe_2CMe_2CMe_2SiMe_2H$, but contact of this material with the metal parts of the GC unit at high temperature could have induced its intramolecular condensation to **2** since it was isolated by gas chromatography. The Si–Si bond of the disilacyclobutane was readily cleaved at room temperature or below by acids such as HCl and CF_3CO_2H, and $ClSiMe_2CMe_2CMe_2SiMe_2H$ and $CF_3CO_2SiMe_2CMe_2CMe_2SiMe_2H$, respectively, were obtained in essentially quantitative yield. Chlorination and bromination of the disilacyclobutane was readily effected. The product halosilanes, $ClSiMe_2CMe_2CMe_2SiMe_2Cl$ and $BrSiMe_2CMe_2CMe_2SiMe_2Br$, respectively, were obtained in nearly quantitative yield. Octamethyl-1,2-disilacyclobutane also reacted rapidly with elemental sulfur in benzene at 60°C to give **6**, the sulfur analog of **2**.



(6)

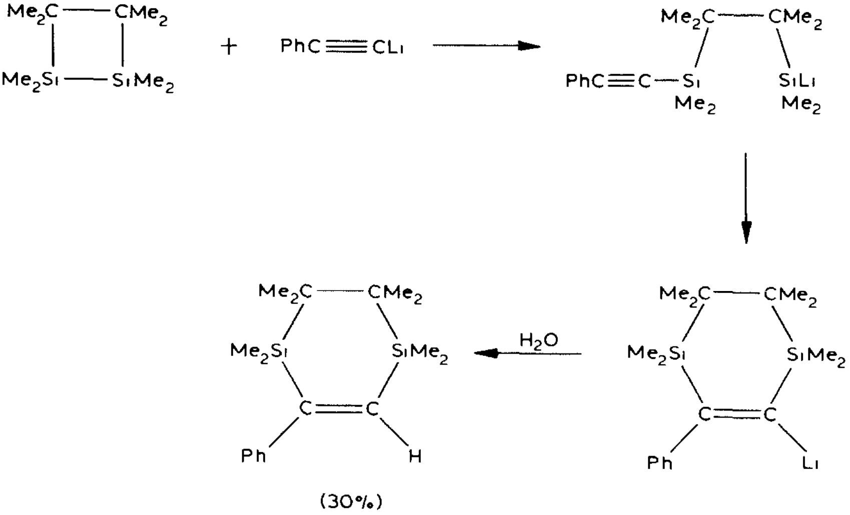
Of particular interest were the reactions of the disilacyclobutane with organolithium reagents (eq. 3) since a reactive silyllithium reagent was formed. When methyllithium was the reagent used, treatment of the reaction mixture with Me_3SiCl



(3)

gave the trisilane $Me_3SiCMe_2CMe_2SiMe_2SiMe_3$ (90%), while hydrolysis gave $Me_3SiCMe_2CMe_2SiMe_2H$ (96%). Phenyllithium also reacted; after hydrolysis of the reaction mixture $PhMe_2SiCMe_2CMe_2SiMe_2H$ was obtained in 80% yield. The reaction of $PhC{\equiv}CLi$ with the disilacyclobutane did not stop with the Si–Si cleavage; an intramolecular addition of the silyllithium species to the phenylethynyl group followed (eq. 4). The addition of trialkylsilyllithium reagents to unsaturated systems is a known reaction [7], so this closure to a favorable six-membered ring is not surprising.

This brief survey showed the C_2Si_2 ring of octamethyl-1,2-disilacyclobutane to be quite reactive and encouraged us to investigate other aspects of its reactivity.



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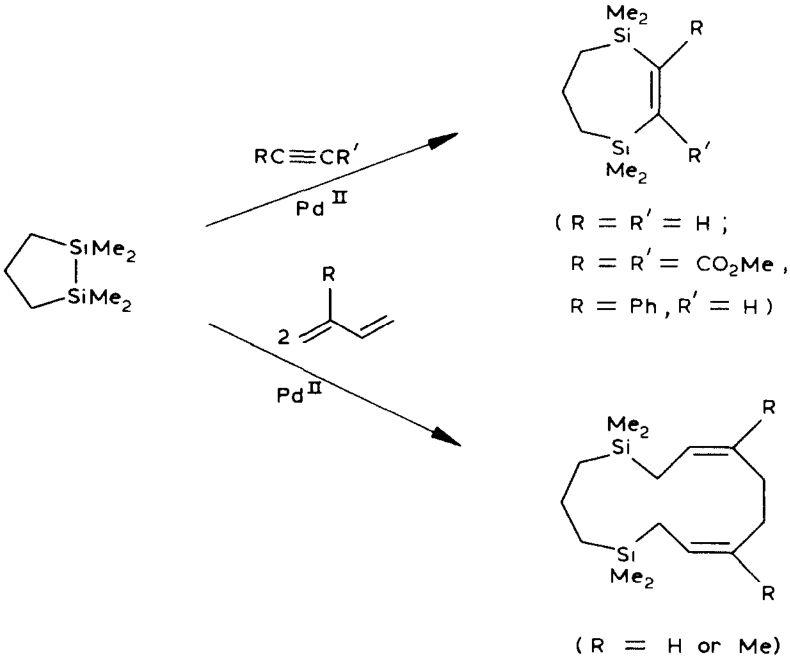
Palladium-catalyzed reactions of octamethyl-1,2-disilacyclobutane with unsaturated hydrocarbons

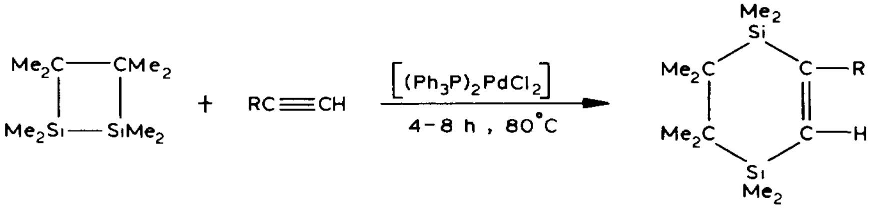
One of the more interesting reactions of the Si–Si bond of the more reactive disilanes is the transition metal-catalyzed insertion of unsaturated hydrocarbons. Scheme 1 shows such reactions of 1,1,2,2-tetramethyl-1,2-disilacyclopentane which have been reported by Sakurai et al. [8]. The catalyst used was $(Ph_3P)_2PdCl_2$.



SCHEME 1

Similar reactions have been reported by other workers for other cyclic and acyclic disilanes [9].

Octamethyl-1,2-disilacyclobutane reacted with terminal acetylenes in refluxing benzene in the presence of 1 mole percent of $(Ph_3P)_2PdCl_2$ to give the respective 1,4-disilacyclohexene, **7**, generally in high yield (eq. 5). Products of type **7** were not formed in the absence of the palladium(II) catalyst. Internal acetylenes bearing alkyl, aryl or trimethylsilyl substituents did not react with the disilacyclobutane in the presence of the palladium(II) catalyst, even at temperatures as high as 140°C. However, two activated internal acetylenes, $MeO_2CC{\equiv}CCO_2Me$ and $MeC(O)C{\equiv}CMe$, did react very readily. All successful reactions which gave products of general type **8** are listed in Table 1. A similar reactivity had been noted with 1,1,2,2-tetramethyl-1,2-disilacyclopentane: insertion into the Si–Si bond by



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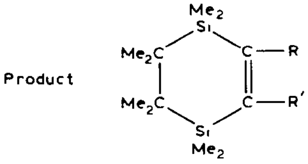


(8)

TABLE 1

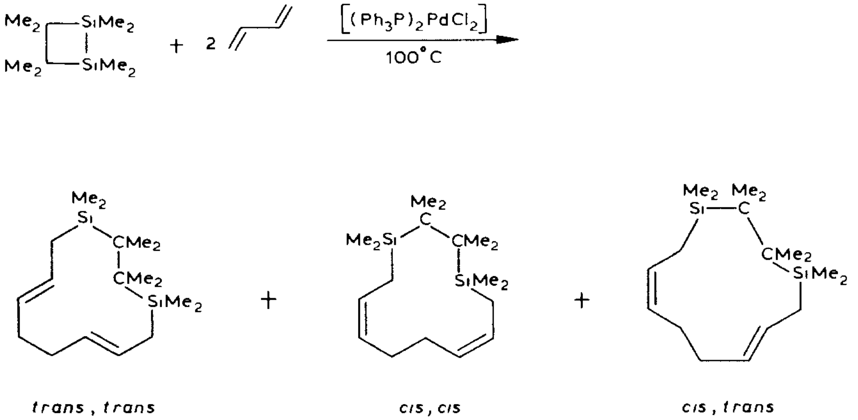
$(Ph_3P)_2PdCl_2$-CATALYZED INSERTION OF ACETYLENES INTO THE Si–Si BOND OF OCTAMETHYL-1,2-DISILACYCLOBUTANE

Acetylene	R,R′ in **8**	Yield (%)
$PhC{\equiv}CH$	Ph, H	73
$HC{\equiv}CH$	H, H	57
$HC{\equiv}CCO_2Me$	H, CO_2Me	92
$HC{\equiv}CC(O)Me$	H, C(O)Me	83
$n\text{-}C_5H_{11}C{\equiv}CH$	$n\text{-}C_5H_{11}$, H	83
$Me_3C{\equiv}CH$	Me_3C, H	96
$MeC{\equiv}CH$	Me, H	91
$CH_2{=}\underset{Me}{\underset{\vert}{C}}{-}C{\equiv}CH$	$CH_2{=}\underset{Me}{\underset{\vert}{C}}$, H	81
$MeO_2CC{\equiv}CCO_2Me$	MeO_2C, MeO_2C	99 [a]
$MeC{\equiv}CC(O)Me$	Me, C(O)Me	100

[a] Yield of crude product, m.p. 75–80°C. 72% Yield of recrystallized product, m.p. 81.5–83°C.

$MeO_2CC{\equiv}CCO_2Me$, $PhC{\equiv}CH$ and $HC{\equiv}CH$ but not by $PhC{\equiv}CPh$ and $Me_3SiC{\equiv}CSiMe_3$ [8].

In the presence of $(Ph_3P)_2PdCl_2$, octamethyl-1,2-disilacyclobutane reacted very rapidly with gaseous dienes in refluxing toluene. For instance, when gaseous 1,3-butadiene was bubbled for a few minutes at atmospheric pressure into a refluxing toluene solution of octamethyl-1,2-disilacyclobutane which contained the palladium(II) catalyst, a 2/1 diene/disilacyclobutane adduct, a white, volatile, crystalline solid, m.p. 82–84°C, was obtained in 92% yield. The 2/1 stoichiometry was demonstrated by combustion analysis and mass spectroscopy. GLC showed only one peak but the proton NMR spectrum showed three $SiMe_2$ signals (δ −0.02, 0.08, 0.11 ppm) and two CMe_2 signals (δ 0.89, 1.23 ppm). As eq. 6 shows, three isomeric 2/1 butadiene/disilacyclobutane adducts are possible, and it is clear that at least two, if not all three, have been formed. A similar reaction of gaseous isoprene with the disilacyclobutane in refluxing toluene gave a high yield of a liquid product whose analysis and mass spectrum were consistent with a 2/1 isoprene/disilacyclobutane adduct. The proton NMR spectrum of this product showed two $SiMe_2$ and two CMe_2 signals, again suggesting the presence of more than one isomer (eq.



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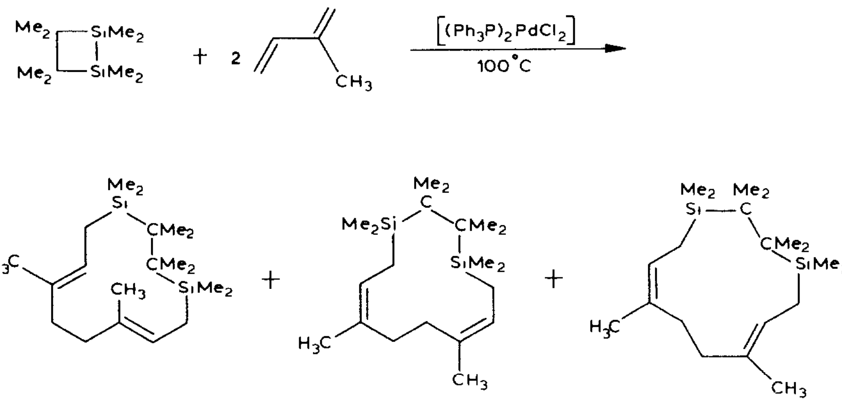
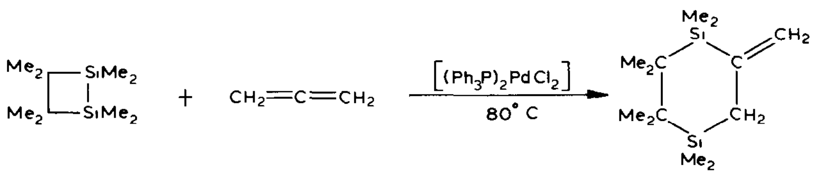


(7)

+ other possible isomers from head-to-tail dimerization

7). In contrast, similar $(Ph_3P)_2PdCl_2$-catalyzed 1,3-diene insertion into the Si–Si bond of 1,1,2,2-tetramethyl-1,2-disilacyclopentane appeared to give only the *cis,cis* isomer shown in Scheme 1.

Under the same reaction conditions used in the 1,3-diene reactions, allene reacted with octamethyl-1,2-disilacyclobutane to give **9** in 91% yield (eq. 8).



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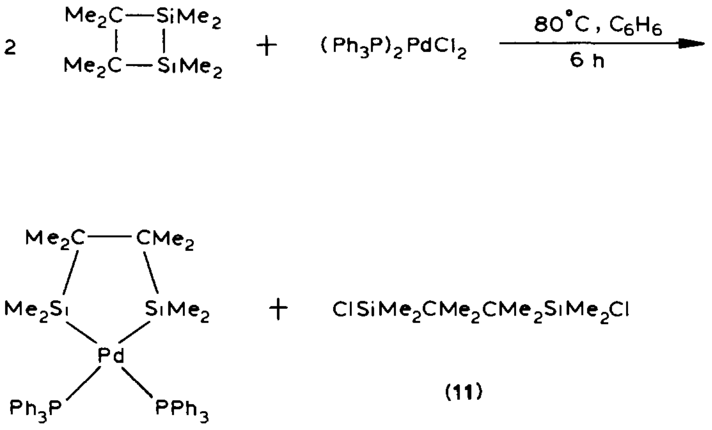
(9)

The mechanism of the palladium(II) catalyzed insertions of acetylenes and dienes into the Si–Si bond of octamethyl-1,2-disilacyclobutane was of some interest. It was found that tetrakis(triphenylphosphine)palladium(0) catalyzed the insertion of phenylacetylene into the Si–Si bond of the disilacyclobutane equally well, giving the adduct, **7** (R = Ph) in 90% yield. This raised the possibility that the $(Ph_3P)_2PdCl_2$ which was being used to catalyze the insertions had to be reduced to a palladium(0) species before catalysis could occur. An experiment in which octamethyl-1,2-disilacyclobutane was treated with a stoichiometric amount of $(Ph_3P)_2PdCl_2$ confirmed that this was the case. The reaction produced two products (eq. 10). The palladium-containing product, **10**, a bright yellow solid which is insoluble in common inorganic solvents was obtained in 73% yield. Its constitution was shown by analysis, but the structure shown is tentative since its insolubility precluded NMR studies. The chlorosilane product **11** was obtained in 80% yield. It would

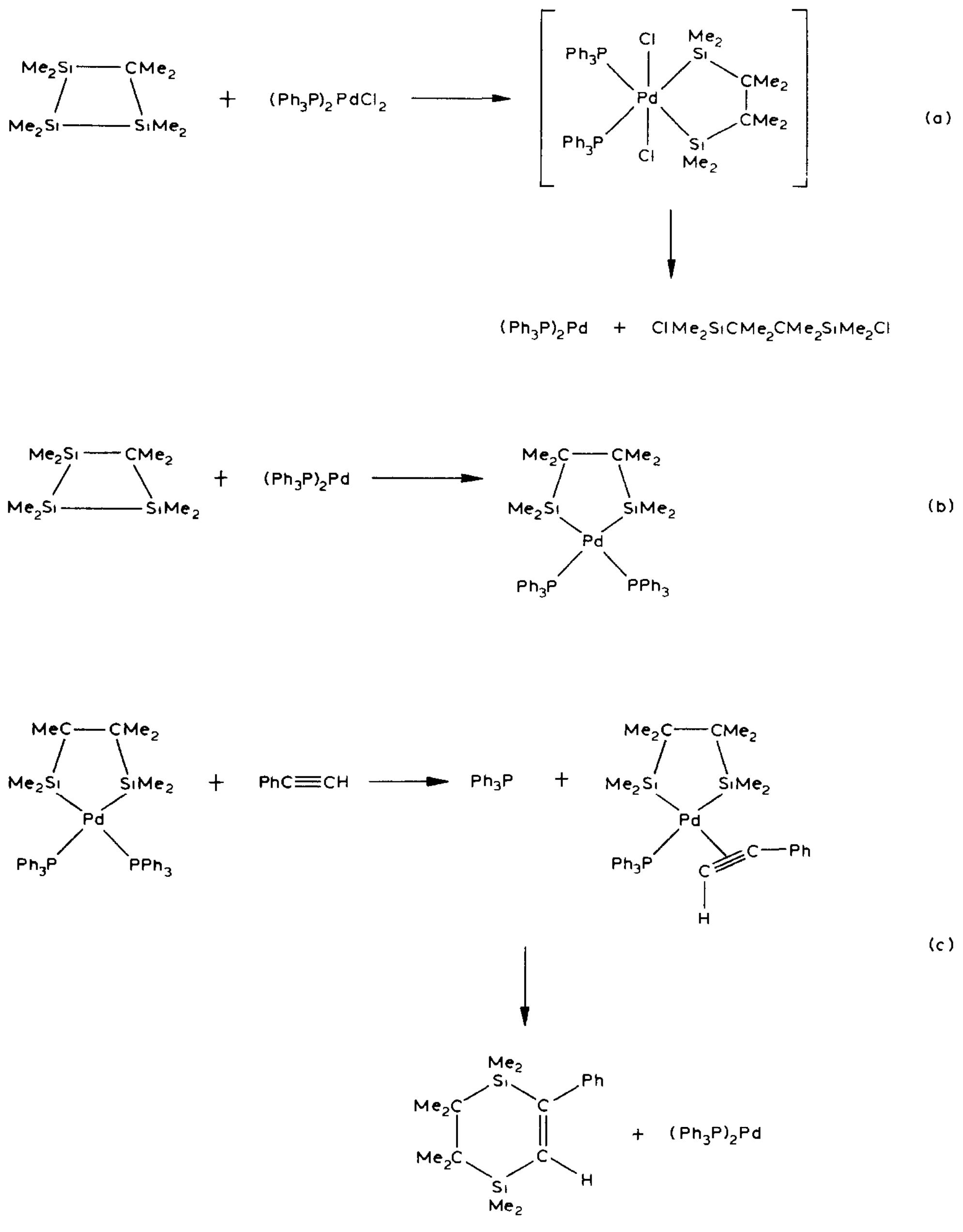


(10)

(11)

(10)

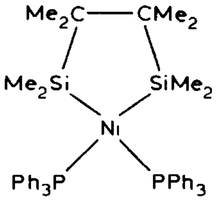
appear that an initial reaction of the disilacyclobutane with $(Ph_3P)_2PdCl_2$ reduces the latter to $(Ph_3P)_2Pd^0$ and forms **11**. Possibly an oxidative addition-reductive elimination sequence is involved. The coordinatively unsaturated $(Ph_3P)_2Pd^0$ then inserts into the Si–Si Bond of the disilacyclobutane. In another experiment, it was shown that **10** reacts rapidly with phenylacetylene in refluxing benzene in a



Then return to reaction (b), etc

SCHEME 2

stoichiometric process to give **7** (R = Ph) in 80% yield. This is recognized as the product which was obtained in the catalytic reaction. The catalytic process may then be summarized as shown in Scheme 2. Bis(triphenylphosphine)dicarbonylnickel(0) also was found to catalyze the octamethyl-1,2-disilacyclobutane/phenylacetylene reaction which suggests the intervention of the nickel analog of **10**, complex **12**, as a



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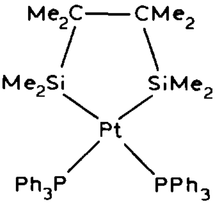

(13)

catalyst. Also, the stoichiometric reaction of octamethyl-1,2-disilacyclobutane with bis(triphenylphosphine)ethyleneplatinum(0) gave the platinum analog of **9**, complex **13**, as a yellow powder, in 95% yield. Here also, the product was insoluble, so that the structure shown must be regarded as tentative.

This study has shown that in all cases it is the Si–Si bond which reacts with the various types of reagents examined. Thus, although it is the C–C which is broken when octamethyl-1,2-disilacyclobutane is pyrolyzed [2], it is the Si–Si bond which is kinetically more labile than the C–C and Si–C bonds in the 1,2-disilacyclobutane ring.

Experimental

General comments

Infrared spectra were recorded using a Perkin–Elmer Model 457A infrared spectrophotometer, proton magnetic resonance spectra using either a Varian Associates T60, a Perkin–Elmer R20 or R22 spectrometer. Chemical shifts are reported in δ units, ppm downfield from internal tetramethylsilane. Chloroform and dichloromethane often were used as alternative internal standards. ^{13}C NMR spectra were obtained with a Jeol FNM HFX-90Q spectrometer, Gas-liquid chromatography (GLC) was used routinely for isolation of pure samples, determination of purity of distilled samples and for yield determinations by the internal standard method. All columns were packed on acid-washed, dimethyldichlorosilane-treated Chromosorb W.

All solvents used were rigorously dried. All reactions were carried out under an atmosphere of prepurified nitrogen or argon. All glassware was flame-dried under a stream of nitrogen before use. Reactive reagents were transferred by syringe or cannula.

In a previous article [1] the preparations of hexamethylsilirane and its precursors are described in detail, as are the methods used for the determination of the yield of hexamethylsilirane, for the preparation of solutions of hexamethylsilirane in solvents other than THF and for the handling of hexamethylsilirane and its solutions. We stress again the high reactivity of hexamethylsilirane towards atmospheric oxygen and moisture and the absolute need to perform all operations involving this compound with complete exclusion of air in rigorously dried glassware using rigorously dried and degassed solvents. Octamethyl-1,2-disilacyclobutane is somewhat less reactive but since it is very sensitive to atmospheric oxygen, the same precautions must be taken when it is prepared, handled and used.

The hydrocarbons used were commercial samples: acetylene (Airco), allene (Matheson), 1,3-butadiene (Matheson), propyne (Matheson), isoprene (Aldrich), 4-octyne,1-heptyne, t-butylacetylene and isopropenylacetylene (Farchan). Bis(triphenylphosphine)dicarbonyl-nickel (0) was purchased from Strem Chemical Co. The other transition metal complexes, $(Ph_3P)_2PdCl_2$ [10], $(Ph_3P)_4Pd$ [11], $(Ph_3P)_2Pt(C_2H_4)$ [12], $(Ph_3P)_2NiBr_2$ [13], and $(Ph_2PCH_2CH_2PPh_2)NiCl_2$ [14], were prepared by literature procedures.

The IR spectra of all and the mass spectra of many of the new compounds prepared in this study were measured, but they are not given here. The spectral data can be found in the M.I.T. Ph.D. thesis (1983) of E.W.G.

Preparation of octamethyl-1,2-disilacyclobutane

A 50 ml Schlenk flask equipped with a magnetic stir-bar and a no-air stopper was flame-dried and purged with nitrogen. It then was charged with 27.2 g of 90% pure (by ^{1}H NMR) hexamethylsilirane (THF concentrate) (0.17 mmol) and 15 ml of dry toluene. While maintaining an atmosphere of nitrogen, the no-air stopper was replaced by a 4″ vacuum-jacketed Vigreux column topped with a distillation head. The flask was heated in an oil bath at 65°C for 18 h. Then the temperature of the oil bath was increased to 100°C and tetramethylethylene was distilled. Upon completion of the reaction, the reaction mixture was trap-to-trap distilled at 60°C/0.03 mmHg into a receiver at −196°C. The distillate was distilled to remove solvents, leaving 9.6 g of wet solid. GLC analysis (6 ft SE-30 at 200°C) showed it to contain 90% octamethyl-1,2-disilacyclobutane and 10% toluene. GLC showed that octamethyl-1-oxa-2,5-disilacyclopentane was absent. A pure sample of the disilacyclobutane was collected by GLC and its m.p. and proton NMR spectrum were compared with those of authentic material as reported earlier [1].

Since the decomposition of hexamethylsilirane is reversible [1], the tetramethylethylene must be removed as described above in order to obtain a high yield of octamethyl-1,2-disilacyclobutane.

Uncatalyzed reactions of octamethyl-1,2-disilacyclobutane

(1) With water. An oven-dried 50 ml one-necked, round-bottomed flask was equipped with a magnetic stir-bar and a no-air stopper, purged with nitrogen and charged with 0.2135 g of 90% octamethyl-1,2-disilacyclobutane. Deaerated THF (2 ml) and water (0.15 ml, 8.33 mmol) were added by syringe. An exothermic reaction was noted. After it had been stirred at room temperature for 1 h, the reaction mixture was dried ($MgSO_4$). Solvent removal at reduced pressure left a clear, colorless oil. GLC showed the presence of a single product. A pure sample was collected by GLC (2 ft SE-30, 150°C) and identified as 2,2,3,3,4,4,5,5-octamethyl-1-oxa-2,5-disilacyclopentane (96% yield by GLC) by means of its ^{1}H NMR spectrum and n_D^{20} 1.4552 (lit. [1] n_D^{25} 1.4526).

(2) With hydrogen chloride. A 100 ml, 2-necked, round-bottomed flash equipped with a magnetic stir-bar, a gas inlet tube and a no-air stopper was charged with 0.265 g of a 54.5% solution of the disilacyclobutane (0.72 mmol) in benzene. Pentane (4 ml) was added and then the reaction flask was cooled to −78°C. Hydrogen chloride was bubbled into the solution through a stainless steel needle for 15 min. The HCl stream was continued while the mixture was allowed to warm to room temperature and for another 15 min. Unreacted HCl was purged from the solution with a stream of dry nitrogen. Solvents were removed at reduced pressure, leaving a liquid residue. Analysis by GLC (6 ft SE-30, 200°C) showed the presence of

$Me_2HSiCMe_2CMe_2SiMe_2Cl$ (96%), n_D^{20} 1.4799. Anal. Found: C, 50.93; H, 10.68. $C_{10}H_{25}ClSi_2$ calcd.: C, 50.69; H, 10.64%. The IR spectrum (CCl_4) showed ν(Si–H) at 2104 cm^{-1}. NMR ($CDCl_3$): δ 0.088 (d, J 3.34 Hz, 6H, Me_2HSi), 0.467 (s, 6H, Me_2ClSi), 1.066 (s, 6H, Me_2C), 1.110 (s, 6H, Me_2C) and 3.79–4.01 (septet, J 3.34 Hz, 1H, SiH).

(3) With trifluoroacetic acid. To a concentrated toluene solution containing 1.05 mmol of the disilacyclobutane (under nitrogen) was added 2 ml of diethyl ether and then 80 μl of distilled trifluoroacetic acid. The reaction mixture was stirred for 2 h at room temperature. Removal of solvent left a clear, viscous liquid which GLC showed to contain one major product, $Me_2HSiCMe_2CMe_2SiMe_2O_2CCF_3$, n_D^{20} 1.4327, in quantitative yield. Anal. Found: C, 46.03; H, 8.16. $C_{12}H_{25}O_2F_3Si_2$ calcd.: C, 45.83; H, 8.01%. The IR spectrum (thin film) showed ν(Si–H) at 2105, ν(C=O) at 1769 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.086 (d, J 3.7 Hz, 6H, Me_2HSi, 0.462 (s, 6H, $Me_2Si_2CCF_3$), 1.025 (s, 6H, Me_2C), 1.079 (s, 6H, Me_2C) and 3.91 (septet, J 3.7 Hz, 1H, SiH).

(4) With chlorine. A 200 ml three-necked flask equipped with a mechanical stirrer, a low temperature thermometer and a Claisen adapter which was fitted with a nitrogen inlet tube and a no-air stopper holding a syringe needle (which was connected to a chlorine gas cylinder) was charged with 1.51 mmol of the disilacyclobutane (toluene concentrate) and 150 ml of pentane. The mixture was cooled to −100°C. Chlorine then was bubbled into the solution for 5 min, until the mixture was light yellow-green in color. The mixture was warmed to room temperature, purged with nitrogen and the solvents then were removed in vacuum. GLC analysis of the residue showed the presence of one product, $ClMe_2SiCMe_2CMe_2SiMe_2Cl$ (78% yield), a solid which melts at room temperature. Anal. Found: C, 44.53; H, 9.02. $C_{10}H_{24}Cl_2Si_2$ calcd.: C, 44.26; H, 8.91%. ^1H NMR ($CHCl_3$): δ 0.50 (s, $SiMe_2$) and 1.22 (s, CMe_2).

(5) With bromine. To a solution of 1.85 mmol of the disilacyclobutane in 5 ml of carbon tetrachloride was added dropwise at room temperature under nitrogen a solution of 1.94 mmol of bromine in 1 ml of CCl_4. The bromine color was discharged immediately upon the addition. The resulting pale orange solution was treated with solid Na_2SO_3, filtered and evaporated in vacuum to leave a solid. The latter was crystallized from pentane at −30°C to give white needles, m.p. 58–61°C in 85% yield. Another recrystallization from pentane gave pure material, m.p. 62–63°C (evacuated capillary), $BrMe_2SiCMe_2CMe_2SiMe_2Br$. Anal. Found: C, 33.79; H, 6.80; Br, 44.35. $C_{10}H_{24}Br_2Si_2$ calcd.: C, 33.34; H, 6.71; Br, 44.36%. ^1H NMR (CCl_4): δ 0.68 (s, Me_2Si) and 1.29 (s, Me_2C).

(6) With elemental sulfur. A solution of 2.05 mmol of the disilacyclobutane and 0.1 g (0.31 mmol S) of S_8 in benzene was stirred and heated at 60°C under nitrogen for 1 h, until most of the sulfur had been consumed. Removal of solvent at reduced pressure left a liquid residue which was purified by GLC (2 ft SE-30 at 115°C). The low melting (m.p. 34–35°C) solid which was obtained was identified as 2,2,3,3,4,4,5,5-octamethyl-1-thia-2,5-disilacyclopentane, **6** (88% yield). Anal. Found: C, 51.61; H, 10.17%. $C_{10}H_{24}SSi_2$ calcd.: C, 51.65; H, 10.40. ^1H NMR (C_6H_6): δ 0.30 (s, Me_2Si) and 0.82 (s, CMe_2).

(7) With methyllithium. A solution of 0.41 g (2.05 mmol) of the disilacyclobutane in 0.51 g of benzene was cooled to −70°C and then 2.5 mmol of methyllithium in 3.5 ml of diethyl ether was added slowly by syringe. The resulting mixture was

stirred and allowed to warm to room temperature. After the deep yellow solution had been stirred for another 2 h it was hydrolyzed with water. The organic components were extracted with Et_2O. The ether solution was dried and concentrated at reduced pressure. The residue was examined by GLC. The single product was identified as $Me_3SiCMe_2CMe_2SiMe_2H$, n_D^{20} 1.4710 (84% yield). Anal. Found: C, 61.11; H, 12.92. $C_{11}H_{28}Si_2$ calcd.: C, 61.02; H, 13.04%. The IR spectrum (thin film) showed ν(Si–H) at 2125 cm^{-1}. ^1H NMR (C_6H_6): δ 0.07 (s, 9H, Me_3Si), 0.08 (d, J 4.0 Hz, 6H, Me_2HSi), 1.02 (s, 12H, Me_2C) and 4.27 (septet, 1H, SiH).

In another such reaction the disilacyclobutane/MeLi reaction mixture was treated with 3.5 ml (an excess) of trimethylchlorosilane and stirred at room temperature for 2 h. The cloudy white reaction mixture was filtered and the filtrate was trap-to-trap distilled (60°C/0.07 mmHg). The distillate was concentrated at reduced pressure. GLC analysis of the residue showed the presence of one product, $Me_3SiCMe_2CMe_2SiMe_2SiMe_3$, n_D^{20} 1.4919 (90% yield). Anal. Found: C, 58.42; H, 12.63. $C_{14}H_{36}Si_3$ calcd.: C, 58.25; H, 12.57%. ^1H NMR ($CDCl_3$): δ 0.019, 0.052, 0.079 (s, 24H, $SiCH_3$) and 0.984, 1.027 (s, 12H, CCH_3).

(8) With phenyllithium. The same procedure was used in the reaction of 0.84 mmol of the disilacyclobutane with 0.85 mmol of phenyllithium in Et_2O/THF medium. After the reaction mixture had been stirred for 1 h at room temperature, the resulting red solution was treated with water. Extraction with pentane was followed by drying and concentration of the pentane extracts. GLC analysis of the oil which remained showed the presence of $PhMe_2SiCMe_2CMe_2SiMe_2H$ in 80% yield. Anal. Found: C, 69.20; H, 10.55. $C_{16}H_{30}Si_2$ calcd.: C, 68.98; H, 10.85%. The IR spectrum showed ν(Si–H) at 2105 cm^{-1}. ^1H NMR (acetone-d_6): δ 0.67(d, J 4.0 Hz, 6H, Me_2HSi), 0.89 (s, 6H, $SiMe_2$), 0.99 (s, 6H, CMe_2), 1.10 (s, 6H, CMe_2), 3.90 (septet, 1H, SiH) and 7.48 (m, 5H, Ph).

(9) With phenylethynyllithium. Phenylethynyllithium was prepared by reaction of 0.64 mmol of phenylacetylene in THF with an equimolar quantity of n-butyllithium at room temperature. This solution was added, at −78°C under nitrogen, to 0.6 mmol of the disilacyclobutane in 5 ml of THF. A 2 h reaction period at room temperature was followed by hydrolytic work-up of the reaction mixture. The residue obtained upon removal of solvents was examined by GLC. One volatile product was present in 30% yield which proved to be identical (IR and NMR) to 1,1,4,4,5,5,6,6-octamethyl-2-phenyl-1,4-disilacyclohex-2-ene(**8**, R = Ph, R′ = H). Full details of the characterization of this compound will be given in a later experiment.

Transition metal-catalyzed insertion reactions of octamethyl-1,2-disilacyclobutane

(1) With acetylenes. The reaction with phenylacetylene is typical of the procedure used.

A dry 50 ml two-necked flask equipped with a magnetic stir-bar a reflux condenser topped with a nitrogen inlet and a no-air stopper was charged with 0.84 mmol of the disilacyclobutane (toluene concentrate) and 20 ml of benzene. Phenylacetylene (0.5 ml, 4.54 mmol) and 0.5 ml of a 0.02 *M* solution of $(Ph_3P)_2PdCl_2$ in benzene (0.01 mmol) were added by syringe. After the reaction mixture had been stirred and heated at reflux for 8 h, it was red in color. Cooling to room temperature was followed by treatment with gaseous oxygen for 5 min. The volatile components then were trap-to-trap distilled (60°C/0.1 mmHg) into a receiver at −78°C. The orange, oily residue (0.29 g) was column chromatographed (8 in. silica gel column, pentane eluant) to give a clear, colorless oil, **8** (R = Ph, R′ = H), n_D^{20} 1.5502 in 73% yield. Anal. Found: C, 71.50; H, 10.01. $C_{18}H_{30}Si_2$ calcd.: C, 71.44; H, 9.99%. ^1H NMR (acetone-d_6): δ 0.149, 0.171 (s, 12H, Me_2Si), 1.075 (s, 12H, Me_2C), 6.562 (s, 1H, HC=) and 7.271 (s, 5H, Ph).

Similar procedures were used in reactions of the other acetylenes listed in Table 1 with octamethyl-1,2-disilacyclobutane. In those cases where pentane alone did not elute the product from the column, pentane/dichloromethane mixtures were used. The following compounds were prepared (for yields, see Table 1).

(a) **8**, R = O_2CMe, R′ = H, an oil, n_D^{20} 1.5082. Anal. Found: C, 59.38; H, 10.00. $C_{14}H_{28}O_2Si_2$ calcd.: C, 59.10; H, 9.92%. The IR spectrum (CCl_4) showed ν(C=O) at 1715(sh), 1700(s) cm^{-1}. ^1H NMR ($CDCl_3$): δ −0.389, −0.312 (s, 12H, Me_2Si), 0.439 (s, 12H, Me_2C), 3.251 (s, 3H, OMe) and 6.771 (s, 1H, HC=).

(b) **8**, R = C(O)Me, R′ = H, oil, n_D^{20} 1.5127. Anal. Found: C, 62.63; H, 10.54. $C_{14}H_{28}OSi_2$ calcd.: C, 62.62; H, 10.51%. The IR spectrum (CCl_4) showed ν(C=O) at 1659 cm^{-1}. ^1H NMR ($CDCl_3$): δ −0.13, 0.030 (s, 12H, Me_2Si), 0.793 (s, 12H, Me_2C), 2.150 (s, 3H, C(O)Me) and 7.131 (s, 1H, HC=).

(c) **8**, R = n-C_5H_{11}, R′ = H, oil n_D^{20} 1.4969. Anal. Found: C, 69.14; H, 12.22. $C_{17}H_{36}Si_2$ calcd.: C, 68.83; H, 12.23%. ^1H NMR ($CDCl_3$): δ −0.008, 0.033 (s, 12H, Me_3Si), 0.886, 0.897 (s, 12H, Me_2C), 1.188–1.412 (m, 9H), 3.471 (t, J 6.84 Hz, 2H, allyl H), 6.204 (s, 1H, HC=).

(d) **8**, R = Me_3C, R′ = H, oil, n_D^{20} 1.5019. Anal. Found: C, 68.05; H, 12.12. $C_{16}H_{33}Si_2$ calcd.: C, 68.24; H, 11.81%. ^1H NMR ($CDCl_3$): δ 0.01, 0.17 (s, 12H, Me_2Si), 0.87, 0.89 (s, 12H, Me_2C), 1.06 (s, 9H, Me_3C) and 6.34 (s, 1H, HC=).

(e) **8**, R = CH_3, R′ = H, oil, n_D^{20} 1.5010 (the gaseous propyne was bubbled into a refluxing benzene solution containing the 1,2-disilacyclobutane and the palladium(II) catalyst). Anal. Found: C, 65.23; H, 11.79. $C_{13}H_{28}Si_2$ calcd.: C, 64.91; H, 11.73%. ^1H NMR ($CDCl_3$): δ 0.003, 0.041 (s, 12H, Me_2Si), 0.902 (s, 12H, Me_2C), 1.867 (s, 3H, MeC=) and 6.787 (s, 1H, HC=).

(f) **8**, R = R′ = H, oil, n_D^{20} 1.4968 (gaseous acetylene was bubbled into a refluxing benzene solution of the disilacyclobutane and the palladium(II) catalyst). Anal. Found: C, 63.61; H, 11.61. $C_{12}H_{26}Si_2$ calcd.: C, 63.63; H, 11.57%. ^1H NMR (CCl_4): δ 0.14 (s, 12H, Me_2Si), 1.03 (s, 12H, Me_2C) and 6.69 (s, 2H, HC=).

(g) **8**, R = CH_2=C(Me), R′ = H, oil, n_D^{20} 1.5168. Anal. Found: C, 67.59; 11.29. $C_{15}H_{30}Si_2$ calcd.: C, 67.59; H, 11.34%. ^1H NMR ($CDCl_3$): δ 0.17, 0.31 (s, 12H, Me_2Si), 1.01, 1.02 (s, 12H, Me_2C), 1.93 (s, 3H, MeC=), 5.02–5.08 (m, 2H, =CH_2) and 6.63 (s, 1H, HC=).

In this reaction there was a second product in 10% yield, $C_{20}H_{36}Si_3$, if the largest ion in its mass spectrum, m/z = 322, is M^+. ^1H NMR ($CDCl_3$): δ 0.07, 0.09, 0.11, 0.16 (s, 12H total, Me_2Si), 0.85, 0.89, 0.94 (s, 12H total, Me_2C), 1.09 (s, 2H), 1.14 (s, 3H, CH_3), 1.56 (s, 3H, MeC=) and 1.56–2.30 (m, 6H).

(h) **8**, R = R′ = CO_2Me, white needles, m.p. 81.5–83°C (from pentane at −30°C). Anal. Found: C, 55.97; H, 8.76. $C_{16}H_{30}O_4Si_2$ calcd.: C, 56.10; H, 8.83%. The IR spectrum (CCl_4) showed ν(C=O) at 1720(sh), 1715(s) cm^{-1}. ^1H NMR (CCl_4): δ 0.08 (s, 12H, Me_2Si), 0.89 (s, 12H, Me_2C) and 3.58 (s, 6H, OMe).

(i) **8**, R = Me, R′ = C(O)Me, colorless solid, m.p. 50–52°C (from pentane). Anal. Found: C, 63.80; H, 10.73. $C_{15}H_{30}Si_2$Calcd.: C, 63.76; H, 10.70%. The IR spectrum (CCl_4) showed ν(C=O) at 1680 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.074, 0.085 (s, 12H, Me_2Si), 0.935 (s, 12H, Me_2C), 1.758 (s, 3H, MeC=) and 2.183 (s, 3H, C(O)Me).

A similar procedure was used in attempted reactions of octamethyl-1,2-disilacyclobutane with PhC≡CPh (also in refluxing xylene), 4-octyne, $Me_3SiC≡CH$ and $Me_3SiC≡CSiMe_3$. No insertion took place. The oxygen treatment converted the disilacyclobutane to **2** and this was the only new product present.

(2) With dienes

(a) Allene. The reaction with allene illustrates the procedure used.

A dry 50 ml two-necked flask equipped with a magnetic stir-bar, a reflux condenser topped with a nitrogen inlet tube and a no-air stopper holding a long syringe needle connected to an allene lecture bottle was charged with 1.69 mmol of the disilacyclobutane (toluene concentrate), 2 ml of 0.01 *M* $(Ph_3P)_2PdCl_2$ in benzene and another 15 ml of benzene. The solution was heated to reflux and then a slow stream of allene was bubbled through for 5 min. After an additional 30 min at reflux, the solvent was removed at reduced pressure and the residue was column chromatographed (silica gel, 1/1 pentane/diethyl ether). The product, **9**, was a solid, m.p. 76–78°C. Anal. Found: C, 64.71; H, 11.67. $C_{13}H_{28}Si_2$ calcd.: C, 64.91; H, 11.73%. ^1H NMR ($CDCl_3$): δ −0.02, 0.07 (s, 12H, Me_2Si), 0.88 (s, 12H, Me_2C), 1.83 (s, 2H, CH_2) and 5.06–5.38 (m, 2H, $=CH_2$).

(b) A similar procedure was used in the reaction of gaseous 1,3-butadiene with the disilacyclobutane in the presence of the palladium(II) catalyst. The gaseous diene was bubbled through the refluxing benzene solution of the disilacyclobutane and the catalyst for 3 min and then the reaction mixture was worked-up as in the allene reaction, except that pentane was used as eluting solvent. The product, a white solid, m.p. 82–84°C, was obtained in 92% yield. GLC examination of this solid (6 ft 15% SE-30 at 250°C) showed only one GC peak, but, as mentioned in the Discussion, probably two (or more) isomers were present. Anal. Found: C, 69.92; H, 11.70. $C_{18}H_{36}Si_2$ calcd.: C, 70.05; H, 11.76%. The EI mass spectrum (70 eV) showed the molecular ion at m/z = 309. ^1H NMR ($CDCl_3$): δ −0.02, 0.08, 0.11 (s, Me_2Si), 0.89, 1.23 (s, Me_2C), 1.70–2.20 (m, allylic H) and 5.08–5.61 (m, vinyl H).

(c) Isoprene. One ml (~ 10 mmol) of the diene was added to a refluxung benzene solution of the disilacyclobutane and the palladium(II) catalyst. After a 3 min reflux period, the reaction mixture was worked-up as above. The oil which was obtained in 85% yield was examined by GLC. Only one GC peak was observed. Anal. Found: C, 71.13; H, 11.88. $C_{20}H_{40}Si_2$ calcd.: C, 71.34; H, 11.97%. The EI mass spectrum (70 eV) showed the molecular ion at m/z = 337. ^1H NMR ($CDCl_3$): δ 0.03, 0.12 (s, Me_2Si), 0.94, 1.21 (s, Me_2C), 1.21 (s, MeC=), 1.7–2.3 (m, allylic H) and 5.3 (m, vinyl H).

Reaction of octamethyl-1,2-disilacyclobutane with phenylacetylene: other catalysts

(a) Tetrakis(triphenylphosphine)palladium(0). The usual procedure was used in a reaction (6 h) of 0.53 mmol of the disilacyclobutane with 4.54 mmol of phenylacetylene in 15 ml of refluxing benzene in the presence of 0.0329 g (0.0285 mmol) of the catalyst. Column chromatography (silica gel/pentane) gave a 90% yield of **8** (R = Ph, R′ = H).

(b) Bis(triphenylphosphine)dicarbonylnickel. The usual procedure was used in a reaction of 0.56 mmol of the disilacyclobutane with 4.54 mmol of phenylacetylene in 15 ml of benzene in the presence of 0.0643 g of $(Ph_3P)_2Ni(CO)_2$ (0.1 mmol) (6 h at

reflux). The usual work-up procedure was followed: **8** (R = Ph, R′ = H) was obtained in 70% yield.

Similar reactions in which $(Ph_3P)_2NiBr_2$ and $(Ph_2PCH_2CH_2PPh_2)NiCl_2$ were evaluated as potential catalysts gave this product in yields of less than 5%.

Reaction of octamethyl-1,2-disilacyclobutane with ethylenebis(triphenylphosphine)platinum(0)

A 100 ml Schlenk flask equipped with a magnetic stir-bar and a no-air stopper was charged with 0.3946 g (0.53 mmol) of $(Ph_3P)_2Pt(C_2H_4)$ and a solution of 0.39 mmol of the disilacyclobutane in 10 ml of benzene. A clear yellow solution resulted and, after 5 min, a yellow solid began to precipitate. The reaction mixture was stirred at room temperature under nitrogen for 8 h and then was filtered. The yellow solid was washed with pentane, dichloromethane, methanol, acetone and THF to afford 0.34 g (95%) of a yellow powder, m.p. 165°C (dec) (evacuated capillary). Anal. Found: C, 59.65; H, 5.87. $C_{46}H_{54}P_2Si_2Pt$ calcd.: C, 60.05; H, 5.92%.

Reaction of octamethyl-1,2-disilacyclobutane with bis(triphenylphosphine)palladium dichloride

A solution of 0.80 g (1.14 mmol) of $(Ph_3P)_2PdCl_2$ and 2.93 mmol of the disilacyclobutane in 20 ml of benzene in a Schlenk tube was stirred and heated at reflux under nitrogen for 6 h. The yellow precipitate which formed was filtered under nitrogen and washed with 100 ml portions of pentane and benzene to give 0.69 g (73%) of yellow powder, m.p. 185–190°C (dec.) (evacuated capillary). Anal. Found: C, 66.29; H, 6.56. $C_{46}H_{54}P_2Si_2Pd$ calcd.: C, 66.45; H, 6.55%.

In another such experiment (0.54 mol of the disilacyclobutane and 0.24 mmol of the palladium complex) the filtrate was retained and trap-to-trap distilled (60°C/0.03 mmHg). GLC analysis of the distillate showed the presence of $ClMe_2SiCMe_2CMe_2SiMe_2Cl$ in 80% yield. This product was identified by comparison of its GLC retention time and its NMR spectrum with those of an authentic sample prepared by chlorination of the disilacyclobutane.

*Reaction of 1,1-bis(triphenylphosphine)-2,2,3,3,4,4,5,5-octamethyl-1-pallada-2,5-disilacyclopentane, **10**, with phenylacetylene*

A 25 ml Schlenk flask equipped with a magnetic stir-bar and a no-air stopper was charged with 0.2327 g (0.28 mmol) of **10**, 0.91 mmol of phenylacetylene and 10 ml of benzene. The reaction mixture was stirred and heated at reflux under nitrogen for 15 min. The resulting dark red mixture was evaporated under reduced pressure. The residue was chromatographed twice (silicic acid, pentane eluant) to give a yellow oil. GLC examination (6 ft 15% SE-30, 150–250°C at 10°C/min) demonstrated the presence of **8** (R = Ph, R′ = H) in 80% yield. The product was identified by comparison of its GLC retention time and NMR spectrum with those of an authentic sample.

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