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Palladium Catalyzed Reactions of Neopentylidenesiliranes

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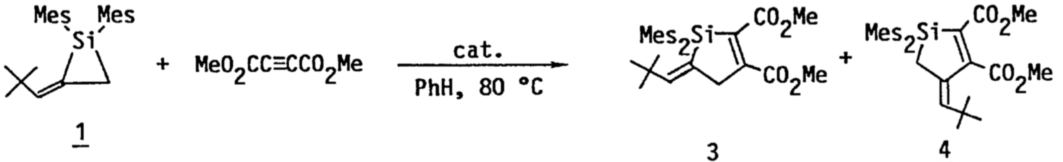
Palladium catalyzed reactions of neopentylidenesiliranes with unsaturated compounds have been studied. Two ring expansion products were obtained from the reaction of 1,1-dimesityl-2-Z-neopentylidenesilirane with dimethyl acetylenedicarboxylate, and their ratio was dependent on the nature of ligands on palladium.

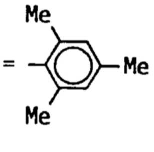
The reaction of methylenecyclopropanes with transition metal complexes was well known as the catalytic σ-π cycloaddition reaction with unsaturated compounds, in which trimethylenemethane complex might exist.$^{1)}$ Recently much interest has focused on the interaction of strained silicon-carbon bond with transition metal complexes.$^{2)}$ In the course of our studies on 1,1-dimesityl-2-Z-neopentylidenesilirane (**1**) and E-isomer (**2**),$^{3)}$ we have observed that palladium catalyzed reactions of **1** and **2** with unsaturated compounds displayed unusual ring expansion reaction modes depending on the nature of the reactant.

To a benzene solution (5 ml) of **1** (72 mg, 0.20 mmol) and $Pd(PPh_3)_4$ (17 mg, 0.015 mmol), dimethyl acetylenedicarboxylate (568 mg, 4.0 mmol) was added under argon atmosphere, and the reaction mixture was stirred at 80 °C for 30 min to give insertion product **3** in 86% yield and a trace amount of **4**, after separation on preparative TLC. The product ratio of **3** and **4** dramatically changed when catalyst was replaced from $Pd(PPh_3)_4$ to Pd(II) complexes whose ligands were varied. Under the reaction conditions, there was insignificant isomerization of **1** and the products were neither isomerized nor destroyed. It should be noted that acetylenedicarboxylate has a high co-ordinaiton ability toward Pd(0) which is thought to be an active catalyst in these reactions. Thus, more stabilized Pd(0) by bulky and π-acceptable ligand and acetylenedicarboxylate might be



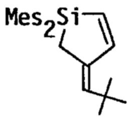
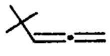
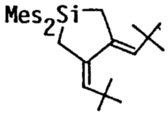
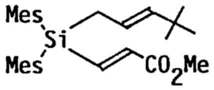
1 3 4

cat., Time/h;		3	4
$Pd(PPh_3)_4$,	0.5	86%	trace
$PdCl_2(PPh_3)_2$,	0.5	60%	25%
$PdCl_2(PEt_3)_2$,	13	35%	55%
$PdCl_2(PhCN)_2$,	0.5	trace	87%

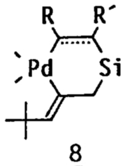
Mes =


preferentially inserted into the Si-C3 bond which is less reactive than the Si-C2 bond, but sterically less hindered. Similarly, acetylene, t-butylallene, and methyl acrylate afforded the corresponding adducts in good yields, as shown in Table 1, and these products were formed via selective insertion at Si-C2 bond that was found to be highly strained by steric repulsion.3) To explain the formation of the adducts **4**-**7**, six membered palladasilacycle such as **8** might exist as an intermediate, and its composed order may be reasonable in consideration of a generation of **7** via β-elimination. Pd(II) complexes were also found to be effective for these reactions. The structures of **3**-**7** were confirmed by ^{1}H-NMR, ^{13}C-NMR, mass spectra, and elemental analysis.4)

Table 1. Pd-Catalyzed Reactions of 1

Entry	Reactant	Catalyst a)	Time/h b)	Products and Yield/%		
1	HC≡CH	Pd(PPh$_3$)$_4$	4 c)		5	quant
2		Pd(PPh$_3$)$_4$	20		6	71
3	"	PdCl$_2$(PEt$_3$)$_2$	47		6	73
4	CH$_2$=CHCO$_2$Me	Pd(PPh$_3$)$_4$	25		7	51
5	"	PdCl$_2$(PPh$_3$)$_2$	40		7	67

a) 5-10% of catalyst was used. b) The reactions were carried out at 80 °C in benzene under argon atmosphere unless otherwise noted. c) In toluene.



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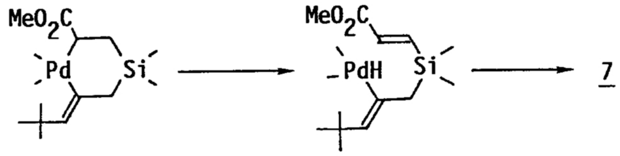
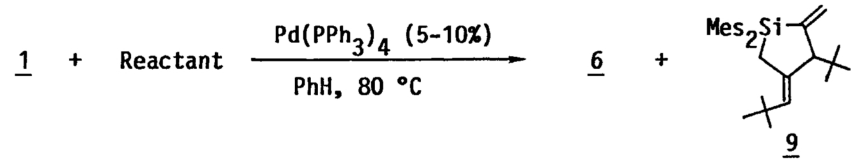
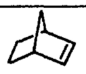
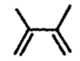
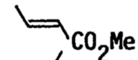
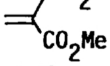
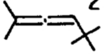


In the reactions of **1** with electron rich olefins or diphenylacetylene, products **6** and **9**, which were adducts of t-butylallene from **1**, were obtained as shown in Table 2, however, no adduct of reactant with **1** or dimesitylsilylene was found. Interestingly, **6** and **9** were formed when a catalytic amount of reactant was used, but not in its absence. These observations strongly indicate that the presence of reactant is essential for the reaction to proceed and an interaction of palladium with reactant might be the first step of the catalytic cycle. The weak interaction of palladium with electron rich reactant followed by oxidative addition of **1** may afford a formation of palladasilacyclobutane intermediate but no cyclization to **8**, then the former decomposes to palladium-silylene complex and

Table 2. Pd-Catalyzed Reactions of 1 with Electron Rich Olefins



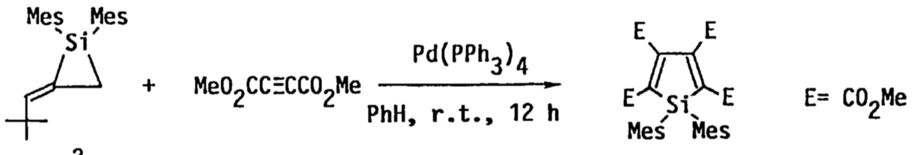
Entry	Reactant	Time/h	Products and Yields/%[a)]	
			6	9
1		40	11	7
2		5	10	13
3		12	9	11
4		10	16	22
5		15	15	10
6	PhC≡CPh	10	25	12

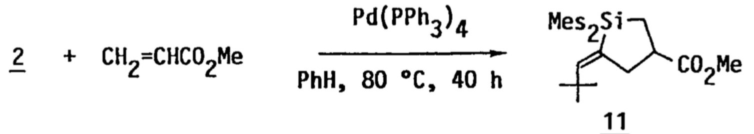
a) Yields were based on Mes_2Si moiety of 1 .

allene which is well known as the reaction of metallacyclobutane.[5)] Product **9** which was not observed in the reaction with t-butylallene might be the result of a reaction of silylene complex with allene.

In these reactions of **1**, it would be suggested that reactant plays a role of activation of catalyst to remove bulky phosphine ligand or to accept the electrons from palladium center.

Comparable results were obtained in palladium catalyzed reactions of **2**. In a reaction with dimethyl acetylenedicarboxylate, silole **10** was isolated in 31% yield from the complex reaction mixture, whose formation could be understood in terms of the reaction of silylene or silirene complex with acetylene as reported.[2b,f,6)] In the reaction with methyl acrylate, cycloaddition product **11** was obtained in 61% yield, and no β-elimination product like **7** was found. When **2** underwent the cycloaddition reaction, insertion occurred on the conventionally strained Si-C bond.





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2) a) H. Sakurai and T. Imai, Chem. Lett., 1975, 891; b) H. Sakurai, Y. Kamiyama, and Y. Nakadaira, J. Am. Chem. Soc., 99, 3879 (1977); c) M. Ishikawa, H. Sugisawa, O. Harata, and M. Kumada, J. Organomet. Chem., 217, 43 (1981); d) M. Ishikawa, S. Matsuzawa, T. Higuchi, S. Kamitori, and K. Hirotsu, Organometallics, 4, 2040 (1985); e) M. Ishikawa, J. Ohshita, Y. Ito, and J. Iyoda, J. Am. Chem. Soc., 108, 7417 (1986); f) D. Seyferth, M. L. Shannon, S. C. Vick, and T. F. O. Lim, Organometallics, 4, 57 (1985).

3) W. Ando and H. Saso, Tetrahedron Lett., 27, 5625 (1986).

4) The following spectral data of **3**, **4**, and **7** are shown as representative.
3: white crystals, mp 152-155 °C, ^{1}H-NMR(CDCl$_3$) δ 0.88(s,9H), 2.22(s,6H), 2.31(s,12H), 3.57(s,3H), 3.65(s,3H), 3.70(d,2H, J= 1.2 Hz), 6.25(t,1H, J= 1.2 Hz), 6.76(s,4H); ^{13}C- NMR(CDCl$_3$) δ 21.1(q), 24.0(q), 29.4(q), 34.6(s), 45.9(t), 51.6(q), 52.0(q), 129.6(d), 130.1(s), 131.2(s), 139.4(s), 143.1(s), 144.6(s), 150.8(s), 155.3(d), 164.9(s), 170.9(s); IR(NaCl) 1710 cm^{-1}; MS m/z 504(M$^+$,27%), 489(9), 447(14), and 384(100); Found: C,73.62; H,8.07% (Calcd for $C_{31}H_{40}O_4Si$ C,73.77; H,7.99%). **4**: white crystals, mp 115-116 °C, ^{1}H-NMR(CCl$_4$) δ 0.97(s,9H), 2.23(s,18H), 2.54(brs,2H), 3.47(s,3H), 3.69(s,3H), 5.50(brs,1H), 6.67(s,4H); ^{13}C- NMR(CDCl$_3$) δ 21.0(q), 24.1(q), 30.5(q), 34.2(s), 37.7(t), 51.6(q), 52.0(q), 129.0(d), 130.1(s), 132.3(s), 139.1(s), 141.2(d), 143.7(s), 149.0(s), 152.5(s), 167.4(s), 169.7(s); IR(NaCl) 1710 cm^{-1}; MS m/z 504(M$^+$,100%), 489(25), and 447(59); Found: C,73.73; H,8.05% (Calcd: see **3**). **7**: colorless oil; ^{1}H-NMR(CDCl$_3$) δ 0.83(s,9H), 2.18(s,12H), 2.23(s,6H), 2.28 (d,2H,J= 6.6 Hz), 3.71(s,3H), 5.02(dt,1H, J= 6.6 and 15.6 Hz), 5.28(d,1H, J= 15.6 Hz), 6.74(s,4H), 6.93(q$_{AB}$,2H, J_{AB}= 18.6 Hz, $\Delta\nu_{AB}$= 108 Hz) These J values indicate trans conformation for two double bonds; ^{13}C-NMR(CDCl$_3$) δ 21.0(q), 24.5(q), 24.7(t), 29.5(q), 32.9(s), 51.6(q), 119.6(d), 129.2(d), 131.0(s), 132.9(d), 138.7(s), 142.5(d), 143.4(s), 149.3(d), 166.6(s); IR(NaCl) 1720 cm^{-1}; MS m/z 448(M$^+$,0.06%), 433(0.1), and 351(100); Found: C,77.37; H,9.21% (Calcd for $C_{29}H_{40}O_2Si$ C,77.62; H,8.99%).
The other products described in this paper gave satisfactory spectral data as well as elemental analyses. The stereochemistry of **3**, **4**, **5**, **9**, and **11** were determined by ^{1}H-NMR NOE observations.

5) A. Miyashita, M. Ohyoshi, H. Shitara, and H. Nohira, J. Organomet. Chem., 338, 103 (1988).

6) H. Okinoshima, K. Yamamoto, and M. Kumada, J. Am. Chem. Soc., 94, 9263 (1972).

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