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CHEMISTRY OF ORGANOSILICON COMPOUNDS
XCVI. THE Si-Si/Si-Si METATHESIS REACTION CATALYZED BY PALLADIUM COMPLEXES*

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Summary

1,1,2,2-Tetramethyl-1,2-disilacyclopentane undergoes the Si-Si/Si-Si metathesis reaction with vinyl- or ethynyl-substituted disilanes in the presence of a palladium complex.

Introduction

Some years ago [2], we reported thermal Si-Si/Si-Si redistribution reaction of hexaorganodisilanes. The reaction proceeds exceedingly slowly at about 200°C and we suggested a thermally "forbidden" molecular mechanism for the reaction.

$$R^1_3Si{-}SiR^1_3 + R^2_3Si{-}SiR^2_3 \longrightarrow R^1_3Si{-}SiR^2_3 + R^1_3Si{-}SiR^2_3 \qquad (1)$$

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* The result of this research has been published at the 34 Annual meeting of the Chemical Society of Japan [1]. For part XCV see ref. 9.

In view of the recent development of the chemistry of organodisilanes in which we have demonstrated an interesting analogy in the reactivity between silicon-silicon σ and carbon-carbon π bonds as evidenced by the palladium complex-catalyzed intermolecular [σ+π] reactions of hexaorganodisilanes with acetylenes [3] and dienes [4], and by photochemical [σ+π] reactions [5], it seemed very interesting to realize the transition metal-catalyzed metathesis of the Si-Si bond at a moderate condition.

In this paper we report that 1,1,2,2-tetramethyl-1,2-disilacyclopentane (I), one of the most reactive organodisilanes [6,7], reacts with vinyl- or ethynyl-substituted disilanes in the presence of a catalytic amount of palladium complex to give the product of Si-Si/Si-Si redistribution.

Results and Discussion

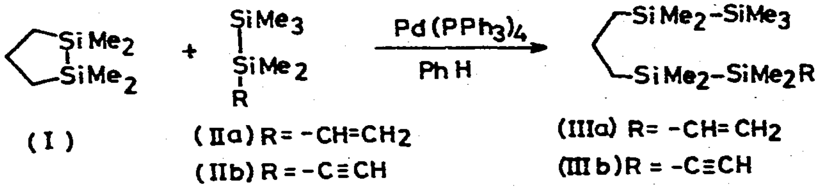
As a typical example, a mixture of (I) and vinylpentamethyldisilane (IIa) dissolved in benzene was heated at reflux for 36h in the presence of a catalytic amount of bis(triphenylphosphine)(maleic anhydride)palladium to yield a homogeneous yellow solution. After usual work-up 3,3,4,4,8,8,9,9-octamethyl-3,4,8,9-tetrasila-1-decene (IIIa) was obtained in 13.0% yield as an oil. We have examined various metal complexes as a possible catalyst of the reaction and have found that nickel and rhodium complexes are also effective to a degree. Table I summarizes the results.

Similarly, the reaction of (I) with pentamethyldisilanylacetylene (IIb) in the presence of tetrakis(triphenylphosphine)palladium gave (IIIb) in 33.4% yield as an oil, the results, also being summarized in Table I.

TABLE I REACTION OF (I) WITH (IIa) AND (IIb)[a]

Reactants	Catalyst	Yield(%)
(I) + (IIa)	$Pd(PPh_3)_2$(maleic anhydride)	13.0
(I) + (IIa)	$PdCl_2(PPh_3)_2$	7.5
(I) + (IIa)	$Ni(COD)_2$	2.4
(I) + (IIa)	$RhCl(CO)(PPh_3)_2$	trace
(I) + (IIb)	$Pd(PPh_3)_4$	33.4
(I) + (IIb)	$PdCl_2(PPh_3)_2$	26.3
(I) + (IIb)	$Ni(COD)_2$	trace
(I) + (IIb)	$RhCl(CO)(PPh_3)_2$	trace

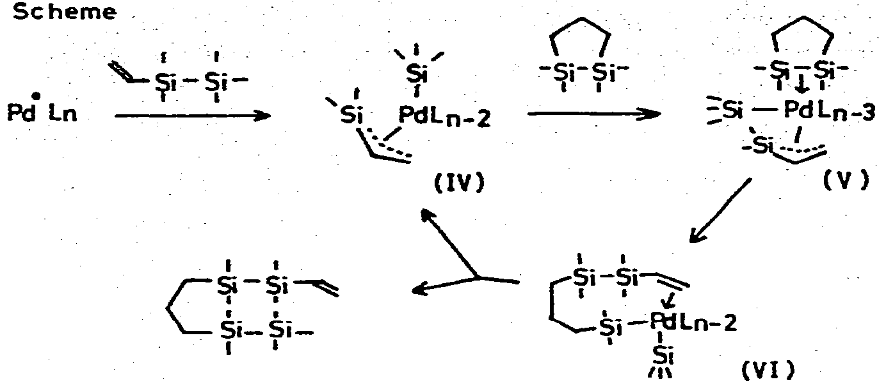
[a] The reaction condition was typically discribed in Experimental.



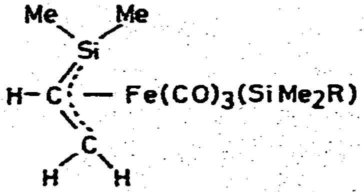
Examination of the reaction mixture by GLC revealed no product other than (III), unreacted starting materials being recovered. Interestingly, the vinyl or ethynyl group was intact after the reaction, but was essential to drive the reaction. Recently, Tamao, Hayashi and Kumada [8] reported palladium complex-catalyzed reactions between (I) and fluorodisilanes. Metathesis of (I) was also reported under a slightly forced condition.

However, under the present reaction condition no metathesis of (I) occurred. Undoubtedly the vinyl or ethynyl group facilitates the reaction considerably. Therefore, the first oxidative addition of the Si-Si bond is seemingly assisted by the vinyl or ethynyl group in the following reaction scheme.

Scheme



Although the scheme is rather speculative, we have recently prepared and characterized the η^3-silapropenyliron complexes such as (VIIa) and (VIIb) which should be a model complex of (IV) in the reaction of (I) with (IIa) [9].



(VII a) R=Me

(VII b) R=-CH=CH$_2$

Experimental

Materials

1,1,2,2-Tetramethyl-1,2-disilacyclopentane (I) [7] vinylpentamethyldisilane (IIa) [10] and pentamethyldisilanylacetylene (IIb) [11] were prepared by standard methods with Grignard reagents.

Transition metal complexes were prepared by standard methods:

$Pd(PPh_3)_2(C_4H_2O_3)$[12], $Pd(PPh_3)_4$[13], $PdCl_2(PPh_3)_2$[14], Ni(COD)$_2$ [15], and RhCl(CO)$(PPh_3)_2$[16].

Reaction of (I) with (IIa) in the presence of bis(triphenylphosphine)(maleic anhydride)palladium

A solution of (I)(1.06mmol), (IIa)(1.05mmol) and bis(triphenylphosphine)(maleic anhydride)palladium (0.01mmol) in benzene (10ml) was heated at reflux for 36h to give a homogeneous yellow solution. After evaporation of the solvent, the mixture was subjected to silica gel TLC to give (IIa) in 13.5% yield as an oil; n_D^{20} 1.4320; MS M^+ 3.6(2.7), *m/e* 73(100); IR (neat) cm^{-1} 2930(m), 1600(w), 1250(s), 830(s), 790(s); NMR (CCl_4) δ (ppm) 0.12(s, 6H, Si-C$\underline{H}_3$), 0.13(s, 6H, Si-C$\underline{H}_3$), 0.15(s, 9H, Si-C$\underline{H}_3$), 0.22(s, 6H, Si-C$\underline{H}_3$), 0.74(m, 4H, Si-C$\underline{H}_2$-), 1.40(m, 2H, Si-CH$_2$-C$\underline{H}_2$), 5.50-6.30(m, 3H, -C$\underline{H}$=C$\underline{H}_2$); UV (n-hexane) λ_{max}(nm) 224.0 (ε=5900). Anal. Found: C, 53.28; H, 11.67. $C_{14}H_{36}Si_4$ calcd.: C, 53.08; 11.46%

Reaction of (I) with (IIb) in the presence of tetrakis(triphenylphosphine)palladium

By a similar procedure, the reaction of (I) (1.02mmol) with (IIb)(1.02mmol) in the presence of tetrakis(triphenylphosphine) palladium (0.01mmol) gave (IIIb) in 33.4% yield as an oil; n_D^{23} 1.4723; MS M^+ 314(1.6), *m/e* 73(100); IR (neat) cm^{-1} 3300(w), 2900(m), 2150(w), 1245(s), 830(s); NMR (CCl_4) δ (ppm) 0.14(s, 6H, Si-C$\underline{H}_3$), 0.17(s, 9H, Si-C$\underline{H}_3$), 0.21(s, 6H, Si-C$\underline{H}_3$), 0.33(s, 6H, Si-C$\underline{H}_3$), 0.88(m, 4H, Si-C$\underline{H}_2$), 1.50(m, 2H, Si-CH$_2$-C$\underline{H}_2$-), 2.40 (s, 1H, C≡C$\underline{H}$). Anal. Found: C, 53.17, H, 10.66. $C_{14}H_{34}Si_4$ calcd.: C, 53.42; H, 10.89%.

Acknowledgment

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