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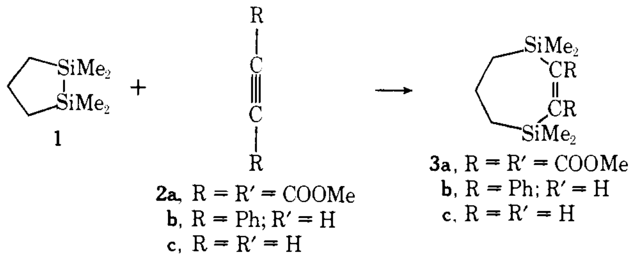
Received June 13, 1974

Novel [$\sigma + \pi$] Reactions of Hexaorganodisilanes with Acetylenes Catalyzed by Palladium Complexes[1]

Sir:

Recently Traven and West[2] and we[3] reported the donor properties of the silicon-silicon σ bond as evidenced by charge-transfer complexation between organopolysilanes and tetracyanoethylene. More recently, we have described that the level of the highest occupied molecular orbital of 1,2-disilacycloalkanes is raised with decreasing ring size, and, as a result, the donor property of the silicon-silicon bond is enhanced, for example, in1,1,2,2-tetramethyl-1,2-disilacyclopentane (**1**).[4] In this context, **1** is a convenient compound for an investigation of reactions in which the silicon-silicon bond may act as a donor. We report here a novel cycloaddition reaction of organodisilanes with some unsaturated compounds such as acetylenes[5] catalyzed by palladium complexes. The reaction afforded mainly *cis*-1,2-disilylethylenes and hence the mode of the reaction is formally analyzed as a thermally forbidden [$_\sigma 2_s + _\pi 2_s$] process.[6] This type of reaction for the carbon-carbon bond can be seen only for a highly strained molecule such as bicyclo[2.1.0]pentane,[7] but we are not aware of any precedented example for the silicon-silicon bond.

When a solution of **1** (1 mmol), dimethyl acetylenedicarboxylate (**2a**) (1 mmol), and bis(triphenylphosphine)palladium dichloride (0.01 mmol) in benzene (10 ml) was heated at reflux for 3 hr under a nitrogen atmosphere, crystalline dimethyl 1,1,4,4-tetramethyl-1,4-disilacyclohept-2-ene-2,3-dicarboxylate (**3a**) was obtained in 83.4% yield.[8,9]



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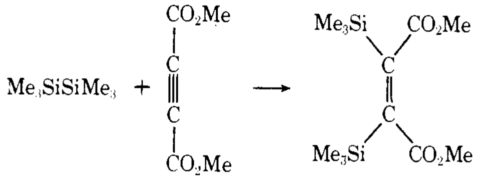
2a, R = R′ = COOMe
b, R = Ph; R′ = H
c, R = R′ = H

3a, R = R′ = COOMe
b, R = Ph; R′ = H
c, R = R′ = H

The reaction of **1** with phenylacetylene (**2b**) under similar conditions (reflux for 9.5 hr) gave the corresponding addition compound, **3b**, in 84.8% yield.[10] Unsubstituted acetylene (**2c**) also reacted with **1**, when **2c** was bubbled into a refluxing benzene solution of **1** in the presence of the catalyst, to give **3c** in 53.3% yield.[11] However, diphenylacetylene and bis(trimethylsilyl)acetylene failed to react with **1** under similar conditions, only the starting materials being recovered.

Hexamethyldisilane (**4**), an example of the unstrained hexaorganodisilane, similarly undergoes the reaction but slowly. Thus, with **2a**, **4** gave dimethyl 1,2-bis(trimethylsilyl)maleate (**5**) in 3.4% yield after refluxing for 23 hr in benzene.[12] The cis stereochemistry of **5** was tentatively assigned by comparison of the uv spectrum with **3a.**



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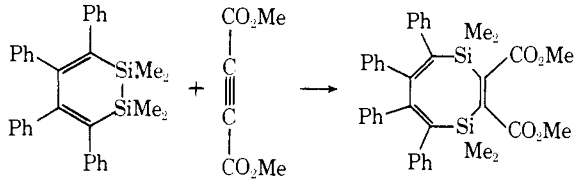
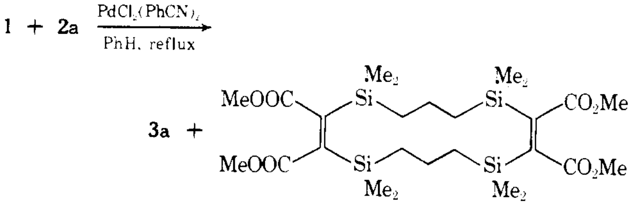
1,1,2,2-Tetramethyl-3,4,5,6-tetraphenyl-1,2-disilane (**6**)[13] gave an interesting new ring system, **7**, by the reaction with **2a** under similar conditions in 72.7% yield.[14]



6 **7**

We have examined various metal complexes as a possible catalyst of the reaction and have found that the palladium complexes such as $PdCl_2(PhCN)_2$, [(π-allyl)PdCl]$_2$, $PdCl_2(PEt_3)_2$, and $Pd(PPh_3)_4$ are also effective. With these palladium complexes, the reaction proceeds similarly, but the details of the reaction such as the rate of the reaction, yields of the products, and the nature of the by-products are different slightly with respect to each catalyst. Thus, for ex-



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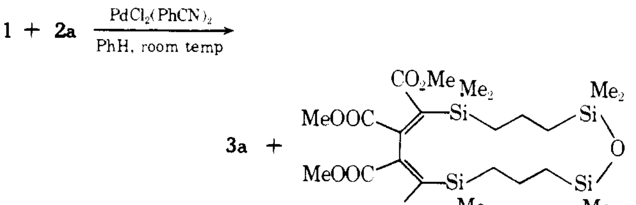

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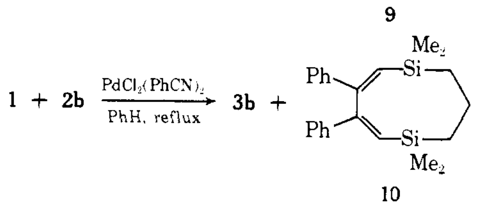

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ample, with $PdCl_2(PhCN)_2$, the reaction of **1** and **2a** gave **8**[15] (11.9%) in addition to **3a** (40.0%) by refluxing in benzene for 3 hr. At room temperature, however, the reaction of **1** with **2a** catalyzed by $PdCl_2(PhCN)_2$ gave **3a** (27.5%) and **9**[16] (8.5%) after 3 days. Similarly with $PdCl_2(PhCN)_2$, the reaction of **1** with **2b** gave both **3b** (19.3%) and **10** (14.5%).[17]

We are actively exploring the related reactions and the details will be reported in a forthcoming paper.

Acknowledgment. We thank Toshiba Silicones Co., Ltd., for gifts of chlorosilanes.

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(5) The reaction of disilanes with dienes will be reported separately.

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(8) All new compounds gave correct elemental analyses. Yields described in this paper are those after isolation with TLC on silica gel.

(9) Compound **3a:** mp 68.0–69.0; M^+ 300 (2) *m/e* 89 (100); NMR δ (CCl_4) 0.30 (12 H, s, Si–CH_3), 1.04 (4 H, t, J = 7 Hz, Si–CH_2–CH_2), 1.91 (2 H, q, J = 7 Hz, $SiCH_2$–CH_2), 3.70 (6 H, s, COOCH_3); ir (cm^{-1}) (KBr) 1725, 1715, 1250; λ_{max} (MeOH) 210.0 (10,000) 262.0 (1,500).

(10) Compound **3b:** an oil; n^{23}D 1.5365; M^+ 260 (64.3) *m/e* 135 (100); NMR δ (CCl_4) 0.12 (6 H, s, SiCH_3), 0.16 (6 H, s, SiCH_3), 0.92 (2 H, t, J = 6 Hz, *Si*–CH_2–), 0.94 (2 H, t, J = 6 Hz, Si–CH_2–), 1.88 (2 H, q, J = 6 Hz, $SiCH_2$–CH_2–), 6.44 (1 H, s, =—H), 7.10 (5 H, m, Ph); ir (cm^{-1}) (neat) 1250; λ_{max} (*n*-hexane) 211.3 (18,100), 249.0 (10,000).

(11) Compound **3c:** an oil n^{23}D 1.4725; M^+ 184 (15) *m/e* 141 (100); NMR δ (CCl_4) 0.08 (12 H, s, Si–CH_3), 0.80 (4 H, t, J = 7 Hz, Si–CH_2–), 1.80 (2 H, q, J = 7 Hz, $SICH_2$–CH_2–), 6.72 (2 H, s, =—H); ir (cm^{-1}) (neat) 1255, 690, λ_{max} (*n*-hexane) <210.0.

(12) Compound **5:** mp 640–65.0°; M^+ 288 (4) *m/e* 125 (100); NMR δ (CCl_4) 0.33 (18 H, s, Si–CH_3), 3.69 (6 H, s, COOCH_3); ir (cm^{-1}) (KBr) 1720, 1250, 850; λ_{max} (MeOH) 209.0 (10,000) 260.0 (1000).

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(14) Compound **7:** mp 243.0–244.0°; NMR δ ($CDCl_3$) −0.18 (6 H, s, Si–CH_3), 0.75 (6 H, s Si–CH_3), 3.64 (6 H, s, COOCH_3), 7.10 (20 H, M, Ph); ir (cm^{-1}) (KBr) 1720, 1250; λ_{max} (MeOH) 252.0 (23,700).

(15) Compound **8:** mp 146.0–147.0°; M^+ 600 (0.2) *m/e* 89 (100); NMR δ (CCl_4) 0.29 (24 H, s, Si–CH_3), 0.93 (8 H, t, J = 8 Hz, Si–CH_2–), 1.56 (4 H, m, Si–CH_2–CH_2–), 3.70 (12 H, s, COOCH_3); ir (cm^{-1}) (KBr) 1710, 1230; λ_{max} (MeOH) <210.0, 260.0 (3000).

(16) Compound **9:** an oil; n^{23}D 1.4850; M^+ 616 (1.5) *m/e* 375 (100); NMR δ (CCl_4) 0.14 (12 H, s, Si–CH_3), 0.27 (12 H, s, Si–CH_3), 0.76 (8 H, m, Si–CH_2–), 1.50 (4 H, m, $SiCH_2$–CH_2–), 3.74 (6 H, s, COOCH_3), 3.81 (6 H, s, COOCH_3); ir (cm^{-1}) (neat) 1720, 1250, 1050; λ_{max} (MeOH) <210.

(17) Compound **10:** mp 91.5–92.5°; M^+ 362 (19) *m/e* 78 (100); NMR δ (CCl_4) −0.18 (6 H, s, SiCH_3), 0.24 (6 H, s, Si–CH_3), 0.72 (2 H, t of d, J = 4 Hz, 15 Hz, Si–CH_2–), 1.20 (2 H, t of d, J = 7 Hz, 15 Hz, Si–CH_2–), 1.88 (2 H, t of t, J = 4, 7 Hz, Si–CH_2–CH_2–), 6.64 (2 H, s, =—H), 7.28 (10 H, m, Ph); NOE 7% between peaks at δ 6.64 and 0.24; ir (cm^{-1}) (KBr) 1250; λ_{max} (*n*-hexane) 212.0 (26,100), 260.5 (27,700).

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Received September 3, 1974

Inversion of Configuration in a Bimolecular Homolytic Substitution at Saturated Carbon

Sir:

Despite the many studies of reactions of both organic and inorganic free radicals with organic compounds, it is only recently that apparent bimolecular homolytic substitution reactions at saturated carbon have been reported[1-3] (eq 1 and 2).

$$\mathrm{MeCo(chelate\text{-}1) + Co(chelate\text{-}2) \rightleftharpoons MeCo(chelate\text{-}2) + Co(chelate\text{-}1)} \quad (1)^4$$

$$\mathrm{Cr^{2+}(aq) + RCo(dmgH)_2(aq) \longrightarrow RCr^{2+}(aq) + Co(dmgH)_2(aq)} \quad (2)^5$$

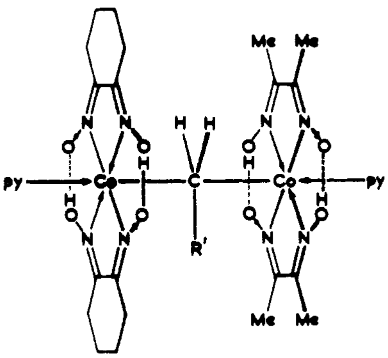

Figure 1. Transition state for bimolecular alkyl transfer reaction.

We now report kinetic and stereochemical studies of one such homolytic substitution (eq 3) which indicate that it involves effectively complete inversion of configuration at the saturated carbon center through a highly restricted transition state. Thus, under anaerobic conditions at 0°, a solution of bis(dimethylglyoximato)pyridinecobalt(II) (I, 10^{-2} *M*) in methanol reacts with an equal concentration of methylbis(cyclohexanedionedioximato)pyridinecobalt(III) (IIa) to give, within a few seconds, a mixture containing the corresponding methylbis(dimethylglyoximato)pyridinecobalt(III) (IIIa) and bis(cyclohexanedionedioximato)pyridinecobalt(II) (IV), such that at equilibrium the concentrations of I–IV are the same (eq 3);[6] i.e., $k_3 = k_{-3}$.

$$\underset{\mathrm{I}}{\mathrm{Co(dmgH)_2py}} + \underset{\mathrm{II}}{\mathrm{RCo(chgH)_2py}} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{\mathrm{III}}{\mathrm{RCo(dmgH)_2py}} + \underset{\mathrm{IV}}{\mathrm{Co(chgH)_2py}} \quad (3)^5$$

IIa, R = Me
b, R = *n*-Pr
c, R = *n*-Oct
d, R = *threo*-PhCHDCHD
e, R = *erythro*-PhCHDCHD
f, R = $PhCH_2CH_2$

IIIa, R = Me
b, R = *n*-Pr
c, R = *n*-Oct
g, R = *t*-BuCHDCHD
h, R = $CH_2{:}CH(CH_2)_4$
i, R = c-$C_5H_9CH_2$
j, R = c-C_6H_{11}

The rates of exchange of alkyl groups in the corresponding reactions of a series of alkylbis(dioximato)pyridinecobalt(III) complexes were determined[9,10] from the rate of increase of III in the total organocobalt(III) complex (II + III) isolated at intervals prior to the establishment of equilibrium, in the manner well documented for isotopic exchange reactions.[12,13] The observed rate of exchange (*R*) in the case of IIb was shown to be first order in the initial concentrations both of the organocobalt(III) complex (II) and in the inorganic cobalt(II) complex (I),[14] and a second-order rate coefficient k_3 (Table I) for the forward path of reaction 3 was derived from *R*.

The variation of k_3 for several different alkyl substituents, shown in Table I, strongly supports a mechanism involving bimolecular displacement at the saturated α-carbon, though it does not distinguish between retention and inversion of configuration at the carbon center.[15,16] The appreciable steric compression in the transition state is evident from the large characteristic influence of both α- and β-substituents on the rate of the reaction.

That an inversion of configuration is involved (Figure 1) was demonstrated by the formation of a mixture of IId ($J_{1,2}$ = 5.3 Hz)[17] and IIe ($J_{1,2}$ = 12.6 Hz)[17,18] in the reaction of the latter with the cobalt(II) species IV (eq 6). The presence of the single diastereoisomer in the reagent and of the