Preliminary communication

FLUORINATED POLYSILANES. PALLADIUM-CATALYZED DISILANE METATHESIS, DOUBLE SILYLATION OF ACETYLENES, AND THE STEREOCHEMICAL COURSE

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(Received April 21st, 1976)

Summary

Fluorinated and angle-strained Si—Si compounds undergo palladium-catalyzed disilane metathesis and double silylation of acetylenes, the latter being stereo-specific at silicon atoms.

Pronounced differences in physical properties and chemical reactivities between organofluoro compounds and their non-fluorinated counterparts have long been recognized. We recently reported that the Si—Si bond of fluorinated disilanes is readily air-oxidized, while that of the permethylated analogs is not, and also pointed out that the reactivities of open-chain organofluorodisilanes are formally analogous to those of the angle-strained Si—Si compounds and even those of tetrafluoroethylene [1]. We now report two types of novel reactions of fluorinated disilanes catalyzed by palladium complexes: (1) disilane metathesis of fluorinated and angle-strained disilanes, bearing a formal resemblance to the olefin metathesis [2], and (2) double silylation of acetylenes, with discussion of the stereo-chemical course determined by a catalytic asymmetric reaction.

$$
\begin{array}{c}
\text{Si}^1 \\
| \\
\text{Si}^2
\end{array}
+
\begin{array}{c}
\text{Si}^3 \\
| \\
\text{Si}^4
\end{array}
\xrightleftharpoons{[\text{Pd}]}
\begin{array}{c}
\text{Si}^1\!-\!\text{Si}^3 \\
+ \\
\text{Si}^2\!-\!\text{Si}^4
\end{array}
\tag{1}
$$

$$
\begin{array}{c}
\text{Si} \\
| \\
\text{Si}
\end{array}
+
\begin{array}{c}
| \\
\text{C} \\
\mathrel{|||} \\
\text{C} \\
|
\end{array}
\xrightarrow{[\text{Pd}]}
\begin{array}{c}
\text{Si}\diagdown \quad \diagup \text{C}\diagup \\
\qquad \text{C} \\
\diagup \text{C}\diagdown \\
\text{Si}
\end{array}
\tag{2}
$$

Disilane metathesis occurred between fluorinated disilanes I [1b, 3] and the five-membered ring compounds IIa [4] containing an angle-strained Si—Si bond

TABLE 1

DISILANE METATHESIS BETWEEN FLUORODISILANES I AND IIa CATALYZED BY VIIIa[a]

Fluorodisilane	Products (yield %)	
	IV	V
Ia[b]	a, 85	0
Ib	b, 61	4.5
Ic	c, 27	6.0
Id	d, 0	14
none	—	39

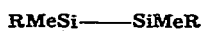[a]Heated at 100°C for 15 h in a degassed, sealed tube, unless otherwise noted. I/IIa/VIIIa = 2 : 1 : 10^{-2}.
[b]At 100°C for 3 h.

at 100°C in the presence of VIIIa as a catalyst. Results summarized in Table 1 contain several notable features. The strained Si—Si compound IIa underwent homo metathesis to form a cyclic dimer V*. In contrast, highly selective cross-metathesis occurred between tetrafluorodimethyldisilane (Ia) and IIa to give IVa to the complete exclusion of V. Difluorodisilanes Ib and Ic also underwent the cross-metathesis with IIa, but the reactions were accompanied by the homo metathesis of IIa. Monofluorodisilane Id did not react with IIa. No reaction was observed between Ia and hexamethyldisilane (Ie) and between IIa and 1,2-dichloro-

$F_mMe_{3-m}SiSiMe_{3-n}F_n$

(I)

a, $m = n = 2$
b, $m = n = 1$
c, $m = 2, n = 0$
d, $m = 1, n = 0$
e, $m = n = 0$

RMeSi———SiMeR
$\lfloor$(CH$_2$)$_n\rfloor$

(II)

a, $n = 3$, R = Me
b, $n = 4$, R = F

RC≡CR′

(III)

a, R = R′ = Ph
b, R = Ph, R′ = H
c, R = R′ = Et

Me$_2$
Si——SiMe$_{3-m}$F$_m$

Si——SiMe$_{3-n}$F$_n$
Me$_2$

(IV)

a, $m = n = 2$
b, $m = n = 1$
c, $m = 2, n = 0$
d, $m = 1, n = 0$

Me$_2$ Me$_2$
Si——Si

Si——Si
Me$_2$ Me$_2$

(V)

R   R′
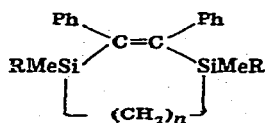 C=C
F_mMe_{3-m}Si   SiMe$_{3-n}$F$_n$
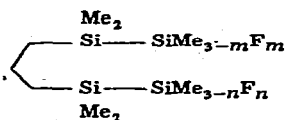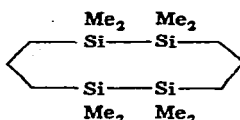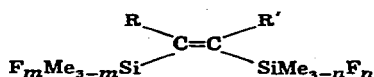
(VI)

a, R = R′ = Ph, $m = n = 2$
b, R = R′ = Ph, $m = n = 1$
c, R = R′ = Ph, $m = 2, n = 0$
d, R = R′ = Ph, $m = 1, n = 0$
e, R = Ph, R′ = H, $m = n = 1$
f, R = R′ = Et, $m = n = 1$

Ph   Ph
  C=C
RMeSi   SiMeR
$\lfloor$ (CH$_2$)$_n\rfloor$

(VII)

a, $n = 3$, R = Me
b, $n = 4$, R = F

[PdL$_2$Cl$_2$]

(VIII)

a, L = PPh$_3$
b, L = (R)-(+)-(PhCH$_2$)MePhP

*All new compounds obtained here gave satisfactory analytical and spectral data.

tetramethyldisilane under the same conditions. The reversibility of the metathesis was observed in one case of IVa which gave several per cent of IIa under the same conditions. With 1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane (IIb) [1a], consecutive metathesis occurred under similar conditions to form non-volatile polymers, since the products continue to have the reactive 1,2-difluorodisilane systems.

The foregoing results reveal that the reactivity of the fluorodisilanes toward the palladium complex decreases in the order (alkyl groups are omitted): $F_2SiSiF_2 > FSiSiF > F_2SiSi \gg FSiSi$.

Double silylation of acetylenes was observed between fluorodisilanes I and acetylenes III in the presence of VIIIa or $[Pd(PPh_3)_4]$ as a catalyst at 100°C within 3 h to form Z-disilylolefins VI in 60—95% isolated yields, excepting VId and VIf whose yields were less than 50%. Interestingly, the double silylation of aryl acetylenes proceeded more readily than the above disilane metathesis; monofluorodisilane (Id) also reacted with IIIa but slowly. Hexamethyldisilane (Ie) did not react at all. Diethylacetylene (IIIc) was less reactive than the aryl acetylenes. The strained Si—Si compound IIa was also found to react with IIIa at 100°C to form VIIa in 78% yield[*]. Here again, we observed the analogy in reactivities between the fluorinated and the strained Si—Si bond.

The Z-configuration of VI was unambiguously determined by conversion to the known permethylated compounds [6]. The double silylation was found to be stereospecific at silicon atoms. Thus, reactions of cis- and trans-IIb [1] with IIIa catalyzed by VIIIa (100°C, 10 min) proceeded in a highly stereospecific fashion to give (Si)-cis- and (Si)-trans-VIIb[**], respectively. The stereochemistry of VIIb could be determined unequivocally by catalytic asymmetric reaction using a chiral phosphine-palladium complex as a catalyst. In principle, since the (Si)-trans isomer is a resolvable dl mixture, while the (Si)-cis isomer a non-resolvable meso form, a successful asymmetric reaction should give one isomer as an optically active form and the other as an inactive one, and then the former is trans and the latter cis. Actually, in the presence of VIIIb [7][***] as a catalyst reactions of IIb with IIIa (mole ratio ca. 1.7:1) went to completion within 30 min at 100°C, and the stereoisomer of VIIb obtained from trans-IIb was indeed optically active, $[\alpha]_D^{25}$ —6.85° (c 3.27, benzene), while the other isomer of VIIb from cis-IIb was optically inactive, $[\alpha]_D^{25}$ 0° (c 1.55, benzene). Therefore, the reactions proceeded stereospecifically, most probably, with retention of configuration of both the silicon atoms.

cis-IIb + IIIa $\xrightarrow{\text{VIIIb}}$ optically inactive VIIb

trans-IIb + IIIa $\xrightarrow{\text{VIIIb}}$ optically active VIIb

The present asymmetric reaction turned out to be a catalytic kinetic resolution of dl-trans-IIb. While it has been well established that reactions involving the oxidative addition of hydrosilanes to transition metal complexes proceed with retention of configuration of the silicon center [8], the present result demon-

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[*]Palladium-catalyzed reaction of IIa with acetylenes has recently been reported by Sakurai et al., who observed no reaction between IIa and IIIa at 80°C in benzene [5].

[**]Notations (Si)-cis and (Si)-trans are introduced to denote the stereochemistry at silicon atoms.

[***]The optical purity of the phosphine ligand used was 81% ($[\alpha]_D^{20}$ +92.8° (c 0.50, toluene)).

strates for the first time that both of the reacting sites proceed with the same stereochemical course.

Of particular interest is that both the strain-free but electron-deficient Si—Si bond and the strained, electron-rich one can equally be activated by palladium complexes. In this respect, it seems worthy of note that the reactivity order of the Si—Si bond is in parallel with the increased stability observed in fluorinated- and strained-olefin complexes of low valent transition metals [9].

Although the mechanism of the present reactions has not yet been fully clarified, the observed electronic and stereochemical aspects may be visualized by a mechanism involving the direct oxidative addition of the Si—Si bond to a low valent palladium—phosphine complex to form a disilylpalladium(II) species, followed by the reaction with another molecule of disilane to give the disilane metathesis product, or followed by the attack of an acetylene to give the double-silylation product. The observed selective cross-metathesis may be attributable to the successive reactions of an electron-deficient disilane and an electron-rich one on palladium or vice versa.

While there have been several types of cleavage reaction of the Si—Si bond by transition metal complexes [5, 10]*, the present novel features may shed light on modes of catalytic activation of σ-bonds other than the Si—Si bond.

Acknowledgements

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