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Highly Efficient Palladium Catalyst System for Insertion of Acetylenes into Si-Si Bonds. A New Method for Modification of Silicon-containing Polymers

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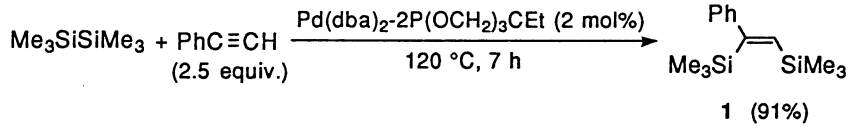
The Pd(dba)$_2$-2P(OCH$_2$)$_3$CEt (dba = dibenzylideneacetone) system exhibited highly efficient catalysis in the insertion of acetylenes into Si-Si bonds of hexamethyldisilane, octamethyltrisilane, poly[(disilanylene)phenylene], poly[(disilanylene)-ethylene], and poly(dimethylsilylene).

Synthesis of silicon-containing polymers is a subject of vigorous growth owing to the unique physicochemical properties, and new methodologies to polymerize silicon compounds have been extensively explored.$^{1)}$ However, little attention has been paid to the transformation of the backbone of silicon polymers leading to new polymers. In this context, double silylation seems to be of great potential which, in principle, transforms a Si-Si linkage in the backbone. However, the conventional catalysts for double silylation, in particular with acetylenes, are not effective for those Si-Si bonds which are not activated by electronegative substituents such as halogen atoms or alkoxy groups.$^{2)}$ Now we report that Pd(dba)$_2$-2P(OCH$_2$)$_3$CEt catalytst system is highly active for the insertion of acetylenes into Si-Si bonds of non-activated disilane or trisilane, and can be successfully applied to the modification of Si-Si bond-containing polycarbosilanes and poly(dimethylsilylene).

When a mixture of hexamethyldisilane (0.4 mmol), phenylacetylene (1.0 mmol) was heated in the presence of Pd(dba)$_2$ (0.008 mmol) and P(OCH$_2$)$_3$CEt (0.016 mmol) in a sealed tube at 120 °C for 7 h, (Z)-1,2-bis(trimethylsilyl)-1-phenylethene (**1**)$^{3)}$ was obtained in 91.0% GC yield, Eq. 1. Under the same conditions, the use of conventional catalysts such as PdCl$_2$(PPh$_3$)$_2$ and Pd(PPh$_3$)$_4$ resulted in very low yields (7.3% and 11.6%, respectively). Likewise, the insertion of phenylacetylene (1.2 mmol) into each Si-Si bond of octamethyltrisilane (0.4 mmol) easily occurred in benzene (0.1 cm^3) in the presence of Pd(dba)$_2$ (0.008 mmol) and P(OCH$_2$)$_3$CEt (0.016 mmol) to selectively afford the product **2** in 90.7% GC yield, Eq. 2. In a separate threefold scale reaction, **2** was isolated in 81% yield by silica gel chromatography (hexane) and subsequent



(1)

1 (91%)

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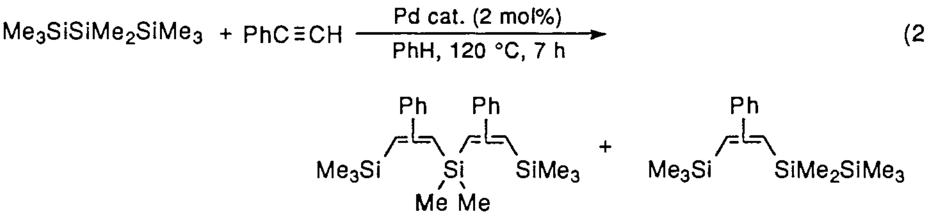
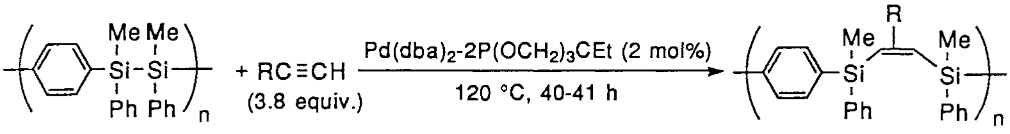
Kugelrohr distillation.4) The single insertion product **3** was not detected at all in these reactions. Here again, the result obtained with $PdCl_2(PPh_3)_2$ or $Pd(PPh_3)_4$ was much inferior; the yields of **2** and **3** were only 3.2% and 6.9% for the former, and 0% and 1.9% for the latter, respectively. The yields were somewhat improved by the use of PMe_3 which is sterically less demanding than PPh_3. Likewise, $P(OMe)_3$ gave better result than sterically bulky $P(OPh)_3$ or $P(O^iPr)_3$. Accordingly, the high performance of $P(OCH_2)_3CEt$ seems to be mainly associated with the steric factor of the ligand.6)



(2)

Pd cat.	**2**	**3**
	Yield / %	
$Pd(PPh_3)_4$	0	1.9
$PdCl_2(PPh_3)_2$	3.2	6.9
$PdCl_2(PMe_3)_2$	6.8	20.3
$Pd(dba)_2 + 2PPh_3$	0	2.0
$Pd(dba)_2 + 2P(OPh)_3$	0.4	8.1
$Pd(dba)_2 + 2P(O^iPr)_3$	9.4	23.3
$Pd(dba)_2 + 2P(OMe)_3$	19.3	38.3 5)
$Pd(dba)_2 + 2P(OCH_2)_3CEt$	90.7	0

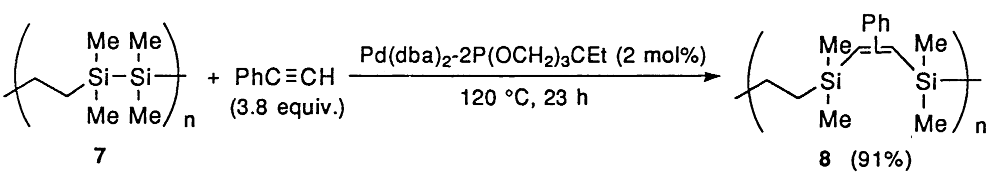
The present catalytic system could be successfully applied to the modification of the backbone of poly[p-(disilanylene)phenylene] ($\overline{Mw}$ = 2.3 x 10^4) (**4**).7) Thus, when **4** (0.4 mmol monomer unit) was treated with phenylacetylene (1.5 mmol) in the presence of $Pd(dba)_2$-$2P(OCH_2)_3CEt$ (0.008 mmol Pd) at 120 °C for 40 h in a sealed tube, the insertion of phenylacetylene into each Si-Si bond was found by ^1H NMR to have quantitatively occurred to give poly[p-(2- or 3-phenyl-1,4-disila-2-butenylene)phenylene] (**5**), Eq. 3. After purification by reprecipitation from THF-^{i}PrOH, pale yellow solid polymer was obtained in 95% yield.8) The shape of the GPC curve of **5** in the reaction mixture was almost same as that of the starting polymer **4**, and $\overline{Mw}$ was estimated at 2.9 x 10^4 (theoretical value = 3.0 x 10^4). Accordingly, the insertion of phenylacetylene into every Si-Si bond of **4** seems to have proceeded without degradation. ^1H NMR of **5** showed Si-Me proton signals at 0.06, 0.13, 0.32, and 0.38 ppm. The appearance of the four signals is probably due to the regioisomeric insertion of phenylacetylene into the neighboring Si-Si bond triads. The intensity of the four signals was almost equal to each other, indicating that the direction of the insertion was almost random. Similarly, the reaction of **4** with 1-octyne and the reaction of poly[(disilanylene)ethylene] ($\overline{Mw}$ = 2.5 x 10^5) (**7**)2) with phenylacetylene also proceeded quantitatively (^1H NMR), and poly[p-(2- or 3-hexyl-1,4-disila-2-butenylene)phenylene] (**6**)9) and poly[p-(2- or 3-phenyl-1,4-disila-2-butenylene)ethylene] (**8**)10) were obtained, respectively, Eqs. 3, 4.



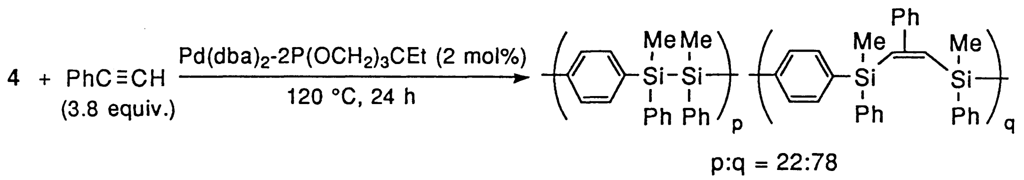
(3)

4

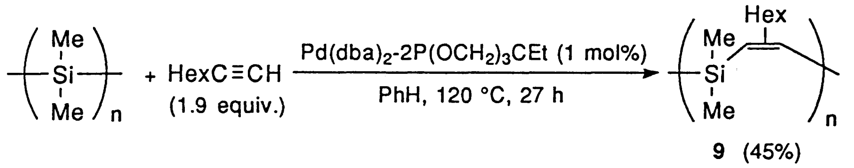
R = Ph **5** (95%)
R = Hex **6** (53%)


(4)

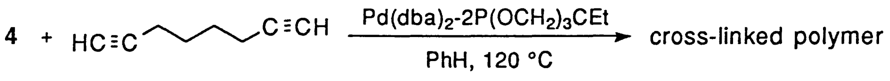
Partial modification of polymer backbones was also possible by controlling the reaction conditions. Thus, the reaction of **4** with phenylacetylene was discontinued at 24 h reaction time. ^{1}H NMR spectra of the resulting polymer revealed that 22% of the total Si-Si bonds of **4** remained intact, Eq. 5.


(5)

Interestingly, even in the case of poly(dimethylsilylene) (0.8 mmol monomer unit),[11] which is well-known as an insoluble and somewhat intractable polymer, the present catalyst did promote the insertion of 1-octyne (1.5 mmol) in benzene (0.2 cm^3) without extensive decrease of molecular weight, Eq. 6.[12]


(6)

Finally, the present catalyst has proved to be effective for cross-linking of Si-Si bond-containing polymers. For instance, the treatment of **4** (0.2 mmol monomer unit) with 1,7-octadiyne (0.005 mmol) in benzene (0.1 cm^3) at 120 °C for 33 h afforded a polymer with increased $\overline{Mw}$ (4.0×10^4) as compared with that of **4** (2.3×10^4), Eq. 7. Use of an increased amount of 1,7-octadiyne resulted in highly cross-linked insoluble polymer.


(7)

In conclusion, $Pd(dba)_2$-$P(OCH_2)_3CEt$ system has been demonstrated to be an excellent catalyst for insertion of acetylenes into Si-Si bonds, which has been successfully applied to the direct reconstruction of backbones of polysilanes as well as polycarbosilanes. Investigations on the physical properties of the reconstructed polymers as well as further extensions of the present procedure to other double silylation reations are under way.

References

1) a) "Inorganic and Organometallic Polymers," ed by M. Zeldin, K. J. Wynne, and H. R. Allcock, ACS Symposium Series **360**, American Chemical Society, Washington, DC (1988); b) "Silicon-Based Polymer Science," ed by J. M. Zeigler and F. W. G. Fearon, Advances in Chemistry Series **224**, American Chemical Society, Washington, DC (1990); c) "Synthesis and Applications of Organosilicon Polymers," ed by H.

Sakurai, CMC, Tokyo (1989); d) R. West, *J. Organomet. Chem.*, **300**, 327 (1986); e) R. D. Miller and J. Michl, *Chem. Rev.*, **89**, 1359 (1989).

2) T. Hayashi, T. -a. Kobayashi, A. M. Kawamoto, H. Yamashita, and M. Tanaka, *Organometallics*, **9**, 280 (1990), and references cited therein.

3) H. Watanabe, M. Kobayashi, K. Higuchi, and Y. Nagai, *J. Organomet. Chem.*, **186**, 51 (1980).

4) **2**: Bp 185-190 °C/0.6 Torr. Anal. Found: C, 70.50%; H, 8.93%. Calcd for $C_{24}H_{36}Si_3$: C, 70.51%; H, 8.88%. GC and NMR analyses revealed that **2** was a mixture of three regio isomers (**2a**, **b**, **c**) (60 : 33 : 7), probably with respect to the location of the phenyl groups. Based on the similarity between the ^1H NMR chemical shift values of MeSi groups of (**2**'s) and those of (Z)-bis(methylsilyl)ethene compounds,$^{3)}$ these three isomers seems to have (Z, Z) geometry. ^1H NMR ($CDCl_3$, TMS): δ **2a** 0.14 (s, 18H, $(H_3C)_3Si$), 0.43 (s, 6H, $(H_3C)_2Si$), 6.39 (s, 2H, =CH), 6.83-7.30 (m, 10H, C_6H_5); **2b** 0.10 (s, 9H, $(H_3C)_3Si$), 0.18 (s, 9H, $(H_3C)_3Si$), 0.36 (s, 6H, $(H_3C)_2Si$), 6.48 (s, 1H, =CH), 6.58 (s, 1H, =CH), 6.83-7.30 (m, 10H, C_6H_5); **2c** 0.15 (s, 18H, $(H_3C)_3Si$), 0.38 (s, 6H, $(H_3C)_2Si$), 6.57 (s, 2H, =CH), 7.01-7.33 (m, 10H, C_6H_5).

5) The compound **3** was obtained as a mixture of two regio isomers (**3a**, **b**) (20 : 80) which seem to have (Z) geometry on the basis of their ^1H NMR; see Ref. 3. ^1H NMR ($CDCl_3$, TMS): δ **3a** 0.11 (s, 9H, $SiSi(CH_3)_3$), 0.13 (s, 9H, $(H_3C)_3Si$), 0.26 (s, 6H, $(H_3C)_2Si$), 6.40 (s, 1H, =CH), 6.96-7.29 (m, 5H,C_6H_5); **3b** -0.03 (s, 9H, $SiSi(CH_3)_3$), 0.20 (s, 9H, $(H_3C)_3Si$), 0.23 (s, 6H, $(H_3C)_2Si$), 6.44 (s, 1H, =CH), 6.96-7.29 (m, 5H, C_6H_5).

6) Recently Yoshihiko Ito et al. reported that a Pd catalyst combined with a large amount of *tert*-isocyanides could promote the insertion of acetylenes into Si-Si bonds. Presented at the 37th Symposium on Organometallic Chemistry, Osaka, 1990, Abstr., No. B110.

7) K. Nate, M. Ishikawa, H. Ni, H. Watanabe, and Y. Saheki, *Organometallics*, **6**, 1673 (1987).

8) **5**: Softening temperature 150-190 °C; $\overline{Mw} = 2.9 \times 10^4$; ^1H NMR ($CDCl_3$, TMS) δ 0.06, 0.13 0.32, 0.38 (each s, 6H, $Si\text{-}CH_3$), 6.85-7.60 (m, 20H, C_6H_4, C_6H_5, and =CH); IR (KBr): 1594 w, 1488 w, 1430 m, 1380 w, 1254 m, 1130 m, 1110 m, 864 m, 786 s, 738 m, 698 s, 604 w, 542 m, 514 m cm^{-1}.

9) **6**: Softening temperature 70-110 °C; $\overline{Mw} = 2.7 \times 10^4$; ^1H NMR ($CDCl_3$, TMS) δ 0.12, 0.18, 0.40, 0.42 (each s, 6H, $Si\text{-}CH_3$), 0.77 (t, 3H, $C\text{-}CH_3$), 0.85-1.35 (m, 8H, CH_2), 2.01-2.28 (m, 2H, $=C\text{-}CH_2$), 6.95 (brs, 1H, =CH), 7.10-7.50 (m, 14H, C_6H_4 and C_6H_5); IR (KBr): 1426 s, 1250 m, 1128 s, 1106 s, 778 s, 734 s, 696 s, 542 m, 510 s cm^{-1}.

10) **8**: Softening temperature 60-80 °C; $\overline{Mw} = 2.8 \times 10^5$; ^1H NMR($CDCl_3$, TMS) δ 0.01, 0.03, 0.07, 0.08, 0.10, 0.11, 0.15, 0.16 (each s, 12H, $Si\text{-}CH_3$), 0.37, 0.47, 0.56 (1:2:1) (each brs, 4H, CH_2), 6.30, 6.32, 6.38, 6.41 (each s, 1H, =CH), 6.84-7.40 (m, 5H, C_6H_5); IR (KBr): 1600 m, 1492 s, 1444 m, 1408 s, 1250 s, 1134 s, 1058 s, 1034 m, 922 m, 810 s, 700 s, 620 m, 540 m, 480 m cm^{-1}.

11) Dimethylpolysilane is commercially available from Nippon Soda Co. Ltd. The $\overline{Mw}$ of the polymer has been estimated at about 4.7×10^3; see T. Ohnaka, Ref. 1c, p. 99.

12) Purification of **9** was performed by short-path silica gel chromatography (hexane) and subsequent washing with ethanol. **9**: Colorless viscous oil; $\overline{Mw} = 5.8 \times 10^3$; ^1H NMR ($CDCl_3$, TMS): δ 0.01-0.48 (m, 6H, $Si\text{-}CH_3$), 0.75-1.05 (m, 3H, $C\text{-}CH_3$), 1.24-1.50 (m, 8H, $(CH_2)_4$), 2.03-2.35 (m, 2H, $CH_2\text{-}C=C$), 6.30-6.56 (m, 1H, =CH); IR (neat): 1546 w, 1460 m, 1378 w, 1246 s, 842 s, 674 m, 502 w cm^{-1}.

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