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Accounts

Transition Metal-Catalyzed Synthesis of Silicon Polymers

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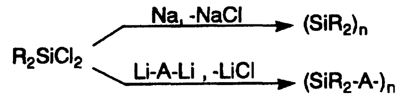
Si–H and Si–Si bonds are efficiently transformed by early and late transition metal catalyses that involve possible key elemental steps, such as σ-bond metathesis, the oxidative addition of Si–H and Si–Si bonds, insertion of unsaturated compounds into silylmetals, the reductive elimination of Si–Si and Si–C bonds, and silylene generation via α-substituent migration in silylmetal species. These catalyses have enabled us to develop a dehydrogenative poly/oligosilane formation from hydrosilanes, oligosilane formation via a redistribution of hydrodisilanes, silylene-phenylene polymer synthesis via a redistribution of bis(trihydrosilyl)benzene, and (step-)ladder polycarbosilane synthesis by a dehydrogenative double silylation of diynes with a tetrakis(hydrosilyl)benzene. Insertion of unsaturated compounds (acetylenes, quinones, etc.) into Si–Si bonds of polymer backbones provides a new methodology for the modification/synthesis of silicon polymers. Cyclooligosilanes and cyclic disilanes undergo ring-opening copolymerization with *p*-quinones to give silylene and arylenedioxy unit-containing polymers. Other relevant processes as well as some chemical and physicochemical properties (ceramization, electric conductivity, thermal stability, etc.) of the resulting polymers are also described.

Polysiloxanes represented by the so-called silicones possess unique properties that have not been realized by ordinary organic polymers and have been widely used industrially in the past decades. On the other hand, new generation silicon polymers, such as polysilanes and some polycabosilanes, exhibit intriguing physicochemical properties, which may lead to the development of future electric, optoelectric, photoreactive, or structural materials and/or efficient non-oxide ceramic precursors.[1] However, the practical methods associated with the preparation of these new polymers have been limited in principle to some reactions involving Si–Cl bonds, such as Wurtz-type coupling using alkali metals and coupling with organoalkali metals or Grignard reagents, as shown in Eq. 1. These conventional methods have some drawbacks in the control of the polymer structures and molecular-weight distributions, the introduction of functional groups, and/or the creation of new polymer frameworks. Meanwhile, transition metal catalyses have been extensively studied and widely used in the synthesis of organic polymers, particularly in the industrial manufacture of polyolefins. In organosilane chemistry, Si–E (E=Cl, OR, H, Si) compounds are relatively easily accessible starting materials. Although the transition metal-catalyzed conversion of Si–Cl and Si–OR bonds seems to have several difficulties to be overcome, efficient transformations of Si–H and Si–Si bonds have been achieved by transition metal catalyses. Herein are described some of the catalyses, mainly those derived from our studies, for silicon polymer synthesis.



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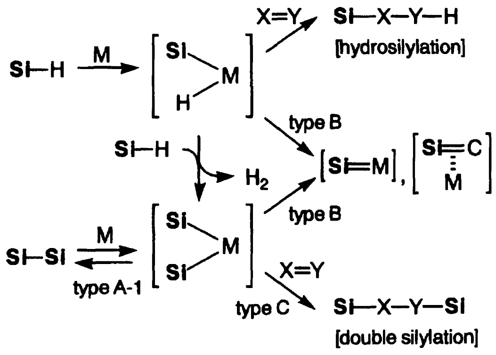
1. Possible Key Elemental Reactions behind Catalyses

The oxidative addition of Si–H bonds to late transition metals forming hydro(silyl)metal species has been well documented for various metal complexes (Scheme 1).[2] The interaction of the hydro(silyl)metal species with unsaturated compounds (X=Y) can form Si–X–Y–H compounds, via either the hydrometalation or silylmetalation route, which is postulated as a key elemental step in widely exploited hydrosilylation reactions,[3] while α-substituent (α-hydrido, silyl, etc.) migration or β-hydride elimination generates silylenemetal[4] or (silene)metal[4a,5] (silene=methylenesilane) species, respectively. On the other hand, group 10 metal complexes occasionally react with two Si–H bonds, presumably via hydro(silyl)metal

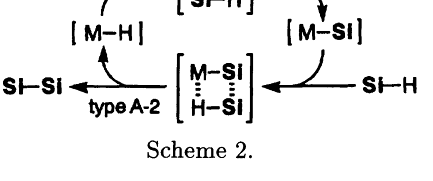


Scheme 1.

species, to generate bis(silyl)metal complexes with H_2 evolution.[6a—i] The same type bis(silyl)metal species are alternatively formed from Si–Si bonds and low valent metal complexes.[4g,4h,6d,6e,7a—d] Investigations of the reactivities of the group 10 bis(silyl)metal complexes have revealed several key features, such as: (a) the reductive elimination of Si–Si bonds,[6h,8a] (b) the generation of silylenemetal or silylene species via α-substituent migration,[4f—h,6d,8a] and (c) the formation of Si–X–Y–Si compounds via insertion of unsaturated compounds (X=Y; acetylene, olefin, etc.) into the silicon–metal bonds.[7a—d,9a,9b] These basic reactivities can in principle be applied not only to group 10 metal complexes, but also to other late transition metal (mainly groups 8[6i,8b,9c,9d] and 9[6i—l,7e,8c]) complexes.

On the other hand, early transition metal complexes (mainly of groups 3 and 4) readily undergo σ-bond metathesis between an M–H species and a Si–H bond to give H_2 and M–Si species, the latter of which then reacts with a second Si–H bond to form a Si–Si bond along with a regeneration of the M–H species (Scheme 2).[10a] Accordingly, in the overall reaction, two equivalents of Si–H compounds are converted into a Si–Si bonded compound and H_2.

The possible key elemental reactions in Schemes 1 and 2 permit new catalyses that are categorized in the following sections into (A) Si–Si bond formation by (A-1) reductive elimination or (A-2) σ-bond metathesis of Si–H bonds with M–Si species, (B) Si–X (X=Si, C, O, etc.) bond formation via (silylene)metal or silylene intermediates, and (C) Si–X–Y–Si linkage formation from (C-1) Si–H (two equivalents) and X=Y compounds or (C-2) Si–Si and X=Y compounds.[11]



Scheme 2.

2. Catalytic Polymer Synthesis via Transformation of Si–H Bonds

2-1. Poly/oligosilane Formation by Dehydrocoupling of Hydrosilanes (Type A-1, 2). There have been quite a few papers on the formation of Si–Si bonds starting with Si–H compounds since the first example using the $RhCl(PPh_3)_3$ catalyst, Eq. 2.[12] Late transition metal complexes that are active for hydrosilylation are generally capable of catalyzing the reaction.[13] Thus, a Pt complex, $Pt(CH_2{=}CH_2)(PPh_3)_2$, is effective for dehydrocoupling of R_2SiH_2 (R_2=PhMe, Et_2), although it is inactive for monohydrosilanes, Eq. 3. The $Pt(PMe_2Ph)_4$ complex appears to be more active, and even a monohydrosilane R_3SiH (R_3=$PhMe_2$, Ph_2Me) can undergo dimerization, albeit at much lower reaction rates, Eq. 4.[14] These results suggest the possibility of polysilane synthesis from di- and/or trihydrosilane. However, in late transition metal catalyses, the selectivity for long polysilane chains is still low. Meanwhile, Harrod et al. discovered that $Cp_2TiR'_2$ (R′=Me, $PhCH_2$) effectively catalyzed the dehydrocoupling of $RSiH_3$ (R=Ph, Hex) to give low molecular weight polysilanes (degree of polymerization≈10), Eq. 5.[15a] These findings triggered studies of early transition metal (mainly Ti and Zr) catalyses, aiming at the synthesis of polysilanes with higher molecular weights.[10a] Lanthanoid metal complexes are also known to be effective for the reaction.[16,17]

$$R_2SiH_2 \xrightarrow[70\text{-}80\,^{\circ}C,\ -H_2]{RhCl(PPh_3)_3\ \text{cat.}} H(SiR_2)_nH + R_mSiH_{4-m} \qquad (2)$$

R_2 = PhMe, Et_2, PhH, etc. 44% (R_2 = PhMe, n = 2, 3)

$$R_2SiH_2 \xrightarrow[-20\,^{\circ}C,\ -H_2]{Pt(CH_2{=}CH_2)(PPh_3)_2\ \text{cat.}} H(SiR_2)_2H \qquad (3)$$

R_2 = PhMe, Et_2 27-95%

$$PhMe_2SiH \xrightarrow[150\,^{\circ}C,\ -H_2]{Pt(PMe_2Ph)_4\ \text{cat.}} (PhMe_2Si)_2 \qquad (4)$$

7% (48% based on the consumed silane)

$$RSiH_3 \xrightarrow[r.t.,\ -H_2]{Cp_2TiR'_2\ \text{cat.}} (SiRH)_n \quad R = Ph, Hex \quad R' = Me, PhCH_2 \qquad (5)$$

n∼10

A neodymium catalyst, Cp^*_2NdR ($Cp^*=\eta^5$-C_5Me_5; R=$CH(SiMe_3)_2$), promotes dehydrocoupling of $PhSiH_3$ in a glass autoclave at 80 °C to give a polysilane, $(SiPhH)_n$, with M_w=780, Eq. 6 (Table 1).[16a] Active species seem to be Nd–H and Nd–Si complexes, as suggested in the group 3[18] or 4[10a] metal catalyses. A neodymium chloride, $(Cp^*_2NdCl_2)Li(Et_2O)_2$, is inactive under comparable conditions, indicating that the conversion of the Nd–Cl species into an active species is much more difficult than that of Nd–C species. The values of M_w are less than 10^3 at reaction temperatures lower than 100 °C. However, a polysilane with a

Table 1. Dehydrocoupling of Silanes $RSiH_3$[a)]

Run	R	Nd cat.[b)] (/mol%)	Temp	Time	M_w (M_w/M_n)[c)]
1[d)]	Ph	NdR(0.12)	Room temp	15d	520(1.3)
2[d)]	Ph	NdR(0.12)	80 °C	2d	780(1.4)
3	Ph	NdCl(0.12)	80 °C	2d	No reaction
4[d)]	Ph	NdR(0.12)	130 °C	2d	1600(1.9)
			→160 °C[e)]	→7d[e)]	→4830(3.1)[e)]
5[d)]	Hex	NdR(0.16)	80 °C	2d	530(—)
6[d)]	Hex	NdR(0.16)	160 °C	13d	950(1.3)
7[f)]	Me	NdR(0.23)	Room temp	3.5d	540(1.3)
8[g)]	Me	NdR(0.23)	70 °C	2d	530(1.6)
9[h)]	Me	NdR(0.23)	90 °C	2d	7340(5.0)
10[i)]	Me	NdR(0.23)	100 °C	2d	—[j)]

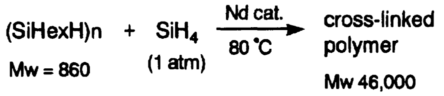
a) Silane (1.0 ml), cat. (0.01 mmol) for Runs 1—6; Silane (ca. 1010 mg, ca. 22 mmol), cat. (0.05 mmol), benzene (2 ml) for Runs 7—9. b) NdR = $Cp^*_2NdCH(SiMe_3)_2$; NdCl = $(Cp^*_2NdCl_2)Li(Et_2O)_2$. c) Estimated by GPC with reference to polystyrene standards. d) Conversion of the silane was ca. 100%. e) The reaction mixture (130 °C, 2 d) was further heated at 160 °C for 7 d. f) Polymer (281 mg), H_2 (5.7 mmol), CH_4 (<0.1 mmol). g) Polymer (317 mg), H_2 (5.5 mmol), CH_4 (<0.1 mmol). h) Polymer (662 mg), H_2 (13.5 mmol), CH_4 (1.6 mmol). i) Polymer (>604 mg), H_2 (15.0 mmol), CH_4 (2.0 mmol). j) Not measured because of low solubility.

relatively high molecular weight ($M_w=1600$) has been obtained as a white solid at an elevated reaction temperature of 130 °C. Noteworthy is the high thermal stability of the Nd catalyst; it is still active after the reaction, and further heating at 160 °C gives a polymer with an appreciably high M_w (4830). The reactivity of $HexSiH_3$ is much lower, and the molecular weight of the polymer is only 950, even for a reaction at 160 °C. The structures of these polymers have not yet been fully characterized. However, in the ^1H NMR of $(SiPhH)_n$ ($M_w=780$), the integral ratio of the SiC_6H_5 to the SiH protons is close to five, indicating that the major components of the polymer are cyclic. On the other hand, the FD (field desorption)-MS spectra of $(SiRH)_n$ (R=Ph, Hex) show that polysilanes that are longer than pentamer are cyclic, while oligosilanes ranging from dimer to pentamer are linear; molecular ion peaks of the components in a polymer of $HexSiH_3$ (Table 1, Run 6) correspond to $Si_n(Hex)_nH_n$ for $6\leq n$ and $Si_n(Hex)_nH_{n+2}$ for $2\leq n\leq 5$.

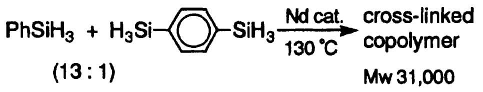
$$RSiH_3 \xrightarrow[\text{r.t.–160 °C, -}H_2]{Cp^*_2NdCH(SiMe_3)_2\text{ cat.}} (SiRH)_n \qquad (6)$$

$$R = Ph, Hex, Me$$

The polymers obtained by this method still have reactive Si–H bonds, and undergo cross-linking with silane (SiH_4) gas in the presence of the Nd catalyst to form polysilanes with increased molecular weights; the treatment of $(SiHexH)_n$ ($M_w=860$) with SiH_4 (1 atm) in the presence of the Nd catalyst at 80 °C yields a cross-linked polysilane with a significantly increased M_w (46000), Eq. 7.[16c)] Copolymerization of $PhSiH_3$ with a small amount of *p*-disilylbenzene, *p*-$(H_3Si)_2C_6H_4$, (1/13 equiv) also smoothly proceeds at 130 °C to give a copolymer with a rather high molecular weight, M_w $(M_w/M_n)=31000$ (14), Eq. 8. The relatively large value of M_w/M_n indicates any cross-linking having taken place during the reaction.[19)]

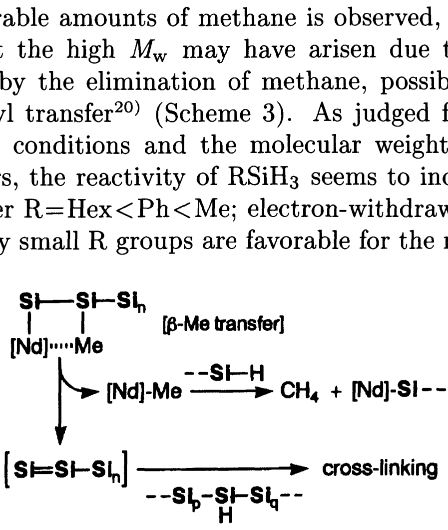


$$\underset{Mw = 860}{(SiHexH)n} + \underset{(1\text{ atm})}{SiH_4} \xrightarrow[80\text{ °C}]{\text{Nd cat.}} \underset{Mw\ 46,000}{\text{cross-linked polymer}} \qquad (7)$$



(8)

Poly(methylsilylene), $(SiMeH)_n$, appears to be an ideal SiC precursor because of the correct Si/C ratio. By applying the Nd catalysis to $MeSiH_3$, a polysilane with an appreciably high molecular weight ($M_w=7340$, $M_w/M_n=5$) is obtained in the reaction at 90 °C (Table 1).[16b)] A higher reaction temperature (e.g. 100 °C) gives a higher molecular weight polymer with a very low solubility. In reactions at ≥90 °C, the formation of considerable amounts of methane is observed, suggesting that the high M_w may have arisen due to cross-linking by the elimination of methane, possibly via a *β*-methyl transfer[20)] (Scheme 3). As judged from the reaction conditions and the molecular weights of the polymers, the reactivity of $RSiH_3$ seems to increase in the order R=Hex<Ph<Me; electron-withdrawing and sterically small R groups are favorable for the reaction.



Scheme 3.

Similar trends have been observed for Ti[15b)] and Zr[21b)] catalysts.

Pyrolysis (under He, up to 900 °C) of the $(SiMeH)_n$ polymers obtained by reactions at ≥ 90 °C generates $MeSiH_3$ (mainly at 200—400 °C), CH_4 (at 400—600 °C), and H_2 (mainly at 400—800 °C) to give black powders in ceramic yields higher than 70%.[16b)] The yield obtained with a polymer prepared at 70 °C is only about 10%, suggesting that cross-linking is beneficial to achieve high ceramic yields. Further heating of the black powders up to 1400 °C promotes crystallization to exhibit XRD patterns assignable to β-SiC and metallic Si, Eq. 9.[22)] When a carbon rich polysilane $(SiPhH)_n$ ($M_w = 1600$) is blended (22 weight%), pyrolysis of the mixture forms β-SiC without metallic Si (by XRD, 58% ceramic yield), Eq. 10.

$$(SiMeH)_n \xrightarrow[\to 900\,^\circ C]{-MeSiH_3,\ -CH_4,\ -H_2} \xrightarrow[\to 1400\,^\circ C]{} \beta\text{-SiC} + Si \quad (9)$$

$$\underset{(w/w = 78/22)}{(SiMeH)_n + (SiPhH)_n} \xrightarrow[\to 1400\,^\circ C]{} \beta\text{-SiC} \quad (10)$$

In relation to lanthanoid metal catalysts, $(Cp^*_2MH)_2$, the activity in the reaction of $PhSiH_3$ has recently been reported to increase in the order M=La<Nd<Sm<Y<Lu, presumably reflecting the effective eight-coordinate ionic radius; metals with a smaller ionic radius are more active.[18)] Based on kinetic studies with early transition metals, σ-bond metathesis via a four center interaction is the key elemental step involved in the catalysis.[10a,18)] Major efforts are now being focused on the formation of a higher molecular weight polymer with a higher linear selectivity. A considerable improvement has been achieved by using $CpCp^*Zr[Si(SiMe_3)_3]Me$ under so-called dynamic vacuum conditions (M_w for $(SiPhH)_n = 5300$, linear/cyclic = 86/14).[10a)] A very recent paper by Harrod et al. has disclosed highly efficient cationic Zr catalyst systems, $LL'ZrCl_2/2BuLi/B(C_6F_5)_3$ ($LL' = CpCp^*$, $[C_5H_4(SiMe_3)]_2$), which catalyze the reaction of $PhSiH_3$ at room temperature to give polysilanes with higher molecular weights ($M_w = 11000$—14000) and higher linear selectivities (linear/cyclic$\geq$90/10), Eq. 11.[15e)] Although tacticity control remains to be studied, the use of the 1,2-di(1-indenyl)ethane ligand in the Zr-catalyzed reaction of $PhSiH_3$ appears to lead to a higher stereoselectivity than that of the parent Cp or indenyl ligand.[15c,21a)] The dehydrocoupling is applicable to functionalized silanes $RSiH_3$ with R=p-BrC_6H_4- and $(OC)_3Cr$-η^6-C_6H_5-, Eq. 12.[10c)] In addition, the treatment of a polymer $(SiPhH)_n$ with CX_4 (X=Cl, Br) converts the Si–H bonds into more reactive Si–X bonds, which can be easily transformed into methoxy and methyl substituents, Eq. 13.[21c)] Accordingly, it seems that dehydrocoupling is becoming a promising general method for polysilane synthesis.

$$PhSiH_3 \xrightarrow[r.t.,\ -H_2]{CpCp^*ZrCl_2/2BuLi/B(C_6F_5)_3\ cat.} \underset{Mw \sim 14{,}000}{(SiPhH)_n} \quad (11)$$

$$RSiH_3 \xrightarrow[r.t.,\ -H_2]{CpCp^*ZrH_2\ cat.} \underset{Mw\ 1{,}100\text{-}1{,}700}{(SiRH)_n} \quad (12)$$

$$R = p\text{-}BrC_6H_4\text{-},\ (OC)_3Cr\text{-}\eta^6\text{-}C_6H_5\text{-}$$

$$(SiPhH)_n \xrightarrow[r.t.]{CX_4} (SiPhX)_n \xrightarrow{Nu^-} (SiPhNu)_p(SiPhX)_q \quad (13)$$

$$X = Cl,\ Br;\ Nu^- = MeO^-,\ Me^-$$

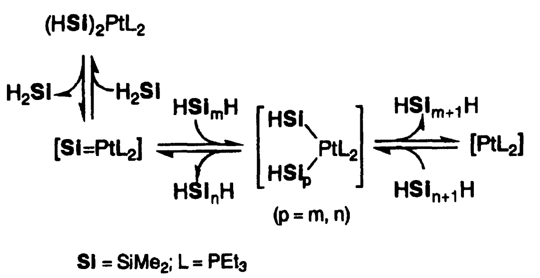
2-2. Oligosilane Formation by Redistribution of Hydrodisilanes (Type B).

$H(SiMe_2)_2H$ is known to undergo a redistribution in the presence of the $PtCl_2(PEt_3)_2$ catalyst at 90 °C to provide a mixture of $H(SiMe_2)_nH$ ($1 \leq n \leq 6$), Eq. 14.[23)] On the other hand, we have found that $H(SiMe_2)_2H$ reacts with a coordinatively unsaturated Pt(0) complex, $Pt(PEt_3)_3$, at −20 °C to give cis-$(HMe_2Si)_2Pt(PEt_3)_2$ in a quantitative yield, Eq. 15,[4h)] probably via α-silyl migration in the HMe_2SiMe_2Si–Pt–H intermediate.[6d)] Accordingly, the bis(hydrosilyl)platinum species is likely to participate in the catalysis. Indeed, cis-$(HMe_2Si)_2Pt(PEt_3)_2$ (1 mol%) is able to catalyze the redistribution of $H(SiMe_2)_2H$ even at room temperature to give oligosilanes with a maximum of $n = 7$ (GC), Eq. 16. The catalysis seems to involve a silyleneplatinum species that is generated from the bis(hydrosilyl)platinum via α-hydrido migration (Scheme 4). A supportive result is obtained in the thermolysis of cis-$(HMe_2Si)_2Pt(PEt_3)_2$; heating a toluene-d_8 solution at 60 °C yields Me_2SiH_2 as a major volatile product, indicative of the co-production of the $[Me_2Si{=}Pt]$ species. In the presence of $Pt(PEt_3)_3$, $Me(SiMe_2)_2H$ and $Me_3SiSiMeH_2$ also undergo facile redistributions at room temperature to give oligosilanes with a maximum of $n = 7$ (GC), Eqs. 17 and 18. $Me_3SiSiMeH_2$ gives three types of oligosilanes: $Si_pMe_{2p+1}H$ ($1 \leq p \leq 3$), $Si_qMe_{2q}H_2$ ($2 \leq q \leq 6$), and $Si_rMe_{2r-1}H_3$ ($3 \leq r \leq 7$). Their formation is explained by two kinds of silyleneplatinum species, HMeSi=Pt and $(Me_3Si)MeSi{=}Pt$, participating in the chain propagation step. These silylene species are also generated by α-silyl and hydrido migration in the $(Me_3Si)HMeSi$–Pt–H species that is formed by the oxidative addition of the $(Me_3Si)HMeSi$–H bond.

$$H(SiMe_2)_2H \xrightarrow[90\,^\circ C]{PtCl_2(PEt_3)_2\ cat.} \underset{1 \leq n \leq 6}{H(SiMe_2)_nH} \quad (14)$$

$$\underset{L = PEt_3}{H(SiMe_2)_2H + PtL_3} \xrightarrow[-20\,^\circ C]{} \underset{\sim 100\%}{cis\text{-}(HMe_2Si)_2PtL_2} \quad (15)$$

$$H(SiMe_2)_2H \xrightarrow[r.t.]{cis\text{-}(HMe_2Si)_2Pt(PEt_3)_2\ cat.} \underset{1 \leq n \leq 7}{H(SiMe_2)_nH} \quad (16)$$



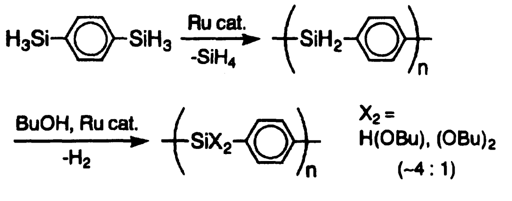
Scheme 4.

$$Me(SiMe_2)_2H \xrightarrow[r.t.]{Pt(PEt_3)_3} \underset{1 \le n \le 7}{Me(SiMe_2)_nH} \qquad (17)$$

$$Me_3SiSiMeH_2 \xrightarrow[r.t.]{Pt(PEt_3)_3}$$
$$\underset{1 \le p \le 3}{Si_pMe_{2p+1}H} + \underset{2 \le q \le 6}{Si_qMe_{2q}H_2} + \underset{3 \le r \le 7}{Si_rMe_{2r-1}H_3} \qquad (18)$$

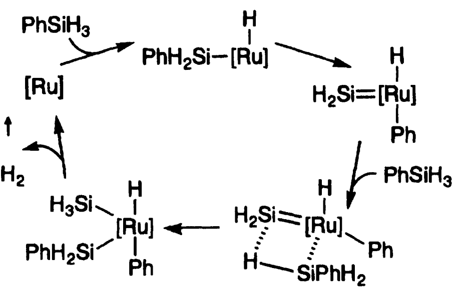
2-3. Polycarbosilane Formation by Desilanative Condensation of Disilylbenzene (Type B). Late transition metal complexes are known to promote the redistribution (disproportionation) of organic silanes.[24] When Ru catalysts are used, $PhSiH_3$ has been found to give Ph_2SiH_2 in good yields ($\geq$80%) along with its co-product, SiH_4, Eq. 19.[25] The activity increases in the order $[Cp^*RuCl_2]_2 < Ru_3(CO)_{12} < Ru(cod)(cot) < RuCl_2(PAr_3)_3$, showing that phosphine ligands are effective for the reaction. The reaction may involve silyleneruthenium species, like $H_2Si{=}RuPhHL_n$, formed by the oxidative addition of the $PhH_2Si{-}H$ bond and subsequent α-phenyl migration (Scheme 5).[26] The catalysis is applicable to the synthesis of a new polycarbosilane. When *p*-disilylbenzene is added to a benzene solution of the $RuCl_2[P(p\text{-tolyl})_3]_3$ catalyst, a smooth reaction proceeds at room temperature along with the evolution of SiH_4 to form a polymer consisting of alternating silylene (SiH_2) and *p*-phenylene units, Eq. 20. Although the polymer is insoluble in benzene, treatment of the reaction mixture with an alcohol, *n*-BuOH, in the presence of the Ru catalyst causes a partial transformation of the Si–H bonds (ca. 60%) into Si–OBu bonds to give a soluble polymer with M_w $(M_w/M_n)=6800$ (2.4).

$$PhSiH_3 \xrightarrow[r.t.]{RuCl_2[P(p\text{-Tol})_3]_3\ cat.} Ph_2SiH_2 + SiH_4 \qquad (19)$$

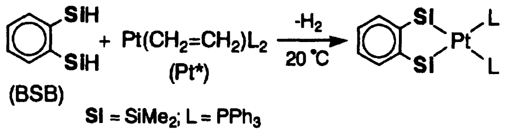


(20)

2-4. Polycarbosilane Formation by Dehydrogenative Double Silylation (Type C-1). When *o*-bis(dimethylsilyl)benzene (BSB) is treated with $Pt(CH_2{=}CH_2)(PPh_3)_2$, a five-membered bis(silyl)platinum complex is formed nearly quantitatively, Eq. 21.[6b,6i] Bis(silyl)platinum complexes usually exhibit a high reactivity toward C≡C bonds to give Si–C=C–Si linkages.[7a,9a] The cyclic bis(silyl)platinum species also smoothly reacts with phenylacetylene (2.5 equiv) at 30 °C to form a 1,4dihydro-1,4-disilanaphthalene ring system quantitatively, Eq. 22.[27a,27b] The reactions of BSB with various acetylenes proceed catalytically in the presence of $Pt(CH_2{=}CH_2)(PPh_3)_2$ (2 mol%) to give 1,4-disilacyclic compounds in excellent yields, Eq. 23.[27a,27b] Previously Tamao, Kumada et al. reported on the dehydrogenative double silylation of acetylenes with hydrochlorosilanes, RCl_2SiH (R = Cl, Me), forming Si–C=C–Si compounds.[28] However, the reaction required the use of less reactive aliphatic internal acetylenes, such as EtC≡CEt and BuC≡CBu, to minimize unfavorable simple hydrosilylation. In contrast, the present catalysis is applicable to aliphatic/aromatic internal acetylenes (vide infra). Similar dehydrogenative double silylation readily takes place as well with other unsaturated compounds, such as olefins,[27a,27c] dienes,[27a,27c] aldehydes,[27d] and α,β-unsaturated ketone,[27d] a ketene,[27d] nitriles,[27e] and an azirine,[27e] some of which are reluctant to undergo double silylation with disilanes (Scheme 6).



Scheme 5.



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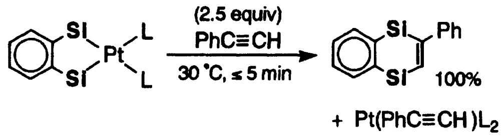

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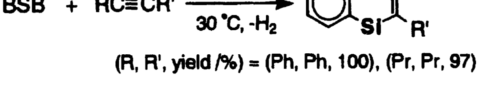


(23)

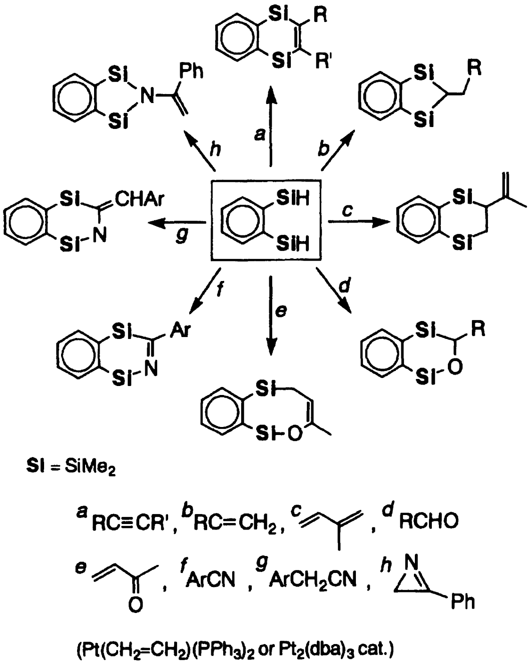
(R, R', yield/%) = (Ph, Ph, 100), (Pr, Pr, 97)

The dehydrogenative double silylation cleanly proceeds between BSB and diynes and between 1,2,4,5-tetrakis(dimethylsilyl)benzene (TSB) and diphenylacetylene, Eqs. 24 and 25.[29a] Accordingly, the catalysis is successfully utilizable for the synthesis of new polycarbosilanes with step-ladder structures. Thus, *p*-di(1-octynyl)benzene smoothly reacts with TSB (1

Table 2. Dehydrogenative Double Silylation of Diynes RC≡C–A–C≡CR with TSB[a)]

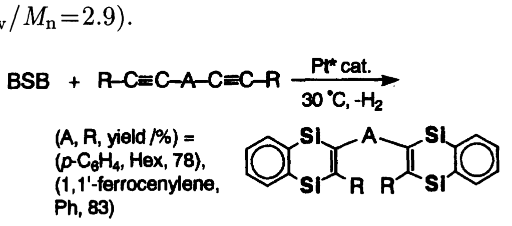
Run	A	R	Yield[b)] %	M_w (M_w/M_n)[c)]	$T_5^{d)}$ °C	Conductivity[e)] S cm^{-1}
1	p-C_6H_4	Hex	72[f)]	12000(2.1)	—	—
			25[g)]	21000(2.8)	424	1×10^{-4}
2	p-C_6H_4	Ph	91	Insoluble	496	6×10^{-4}
3	1,1′-Ferrocenylene	Ph	94	23000(2.9)[h)]	454	7×10^{-3}

a) Diyne (0.25 mmol), TSB (0.25 mmol), $Pt(CH_2{=}CH_2)(PPh_3)_2$ (0.01 mmol), benzene (6 ml), 30 °C, 15—18 h. b) Yield after purification by precipitation from benzene-methanol. c) Estimated by GPC with reference to polystyrene standards. d) Temperature of 5% weight loss in TGA under He (10 °C min^{-1} heating rate). e) Conductivity of pellets doped with $FeCl_3$. f) Benzene-soluble fraction. g) Benzene-insoluble fraction. h) In vapor pressure osmometry the M_n was estimated at 6500.



Scheme 6.

equiv) in the presence of $Pt(CH_2{=}CH_2)(PPh_3)_2$ at 30 °C to give a step-ladder silicon polymer, Eq. 26 (Table 2). The molecular weights (M_w) of benzene-soluble and insoluble fractions have been respectively estimated at 12000 ($M_w/M_n=2.1$) and 21000 (2.8) by GPC with reference to polystyrene standards. Likewise, the reaction of p-bis(phenylethynyl)benzene proceeds under similar conditions to give the corresponding step-ladder polymer, although it is insoluble in common organic solvents. The use of a more flexible ferrocenylene ring in place of the phenylene ring improves the solubility; 1,1′-bis(phenylethynyl)ferrocene reacts with TSB to give a soluble step-ladder polymer with $M_w=23000$ ($M_w/M_n=2.9$).



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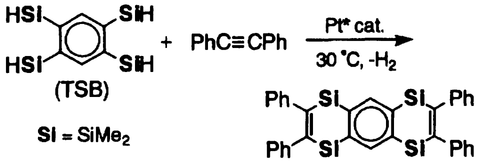

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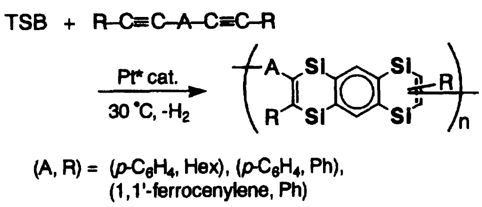
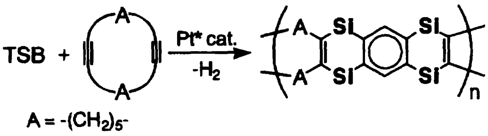


(26)

By applying the same procedure, full-ladder silicon polymers can be synthesized as well, starting with TSB and cyclic diynes, Eq. 27.[29c)] The catalysis also enables unprecedented ladder-type cross-linking of poly[1, 3-butadiynylene(methylphenylsilylene)], Eq. 28.[29b,30)]



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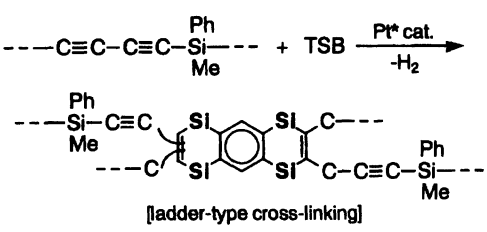


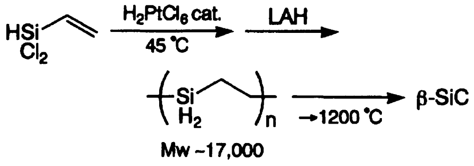
(28)

DSC measurements of the step-ladder polymers show no distinct endothermic peak up to 450 °C, indicative of their backbone being considerably rigid, as anticipated from their structures. In TGA, 5% weight loss temperatures under He (10 °C min^{-1} heating rate) are 424—496 °C (Table 2), revealing significantly high thermal stability. These results suggest their applicability to heat-resistant structural materials. On the other hand, the electric conductivity of the step-ladder polymers upon doping with $FeCl_3$ ranges from 10^{-4} to 10^{-3} S cm^{-1}

2-5. Miscellaneous Polymerization Reactions

with Hydrosilanes. Besides the above-mentioned catalyses, there have been considerably many reactions of hydrosilanes, in which hydro(silyl)metal intermediates are postulated. Among them following catalyses seem to merit consideration for silicon polymer synthesis:

(a) Hydrosilylation of Olefins and Acetylenes. Hydrosilylation is a most exploited reaction in the silicon-containing polymer synthesis. A wide variety of polycarbosilanes have been obtained by the reactions of (a) vinylhydrosilanes,[31a)] (b) bis(hydrosilyl) or dihydrosilane compounds with divinyl or diethynyl compounds,[31b,31c)] and (c) ethynylhydrosilanes,[31d)] as respectively exemplified in Eqs. 29, 30, and 31. Although the reaction (a) is not so suitable to prepare high molecular weight polymers, partly because of the occurrence of cyclization,[31a)] the reaction (c) gives polymers with considerably high molecular weights (M_w= 30000—110000).[31d)] The silylene (SiH_2) or vinylene unit-containing polymers prepared respectively from vinyl- or ethynyl(hydro)silanes are readily converted into β-SiC upon pyrolysis. In most of the hydrosilylative polymerization, the conventional Speier's catalyst, H_2PtCl_6, exhibits high performance. However, hydrosilylation with silane (SiH_4) gas appears to be rather tricky, due to catalyst deterioration. We are finding that a Nd catalyst is stable under hydrosilylation conditions with SiH_4 and that the new method is applicable to polymer synthesis starting with a diene and SiH_4.[32)] 1,7-Octadiene reacts with SiH_4 to form a polymer consisting of octamethylene and silylene units ($M_w \geq 2400$), Eq. 32.[16c)]



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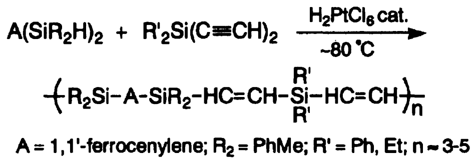

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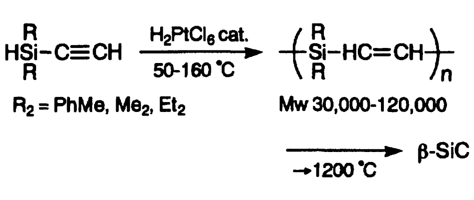

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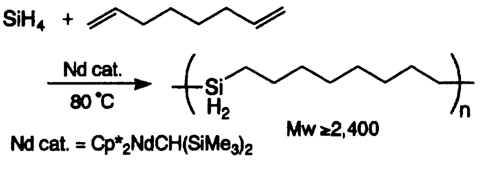
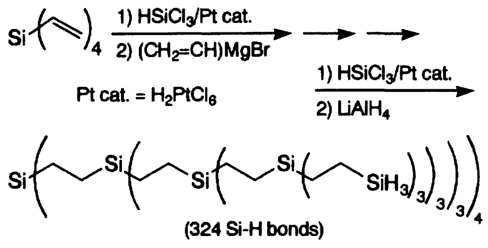


(32)

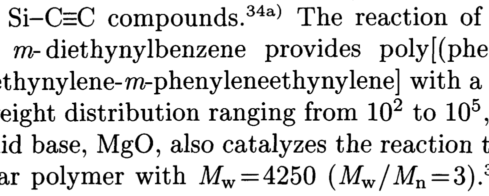
Some organosilicon dendrimers are readily synthesized by applying Pt-catalyzed hydrosilylation, as shown in Eq. 33.[33)]



(33)

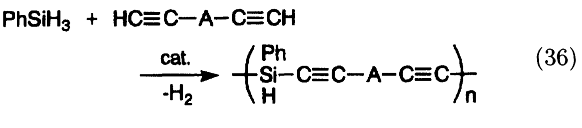
(b) Generation of Silene Species from Me_3SiH. β-Hydride elimination in (methylsilyl)metal species is supposed to generate (silene)metal intermediates, which may extrude silene species that polymerize to give polycarbosilanes. Although such examples of silene generation have been rather rare, pyrolysis of Me_3Si–IrHI-$(PPr^i_3)_2$ at 120 °C forms the corresponding hydride complex, H–IrHI$(PPr^i_3)_2$, indicating a dimethylsilene unit having been extruded in the reaction, Eq. 34.[5c)] In addition, Berry et al. have disclosed in the H/D exchange study between the α-hydrogens of R_3SiH ($R_3 = Me_3$, Me_2Et, Et_3) and C_6D_6 that β-hydride elimination in H–C–Si–M (M = Os, Ru) species takes place to give (silene)metal intermediates.[5e)] Furthermore, they have found that Me_3SiH produces oligomers with $-(SiMe_2CH_2)_n-$ ($n \leq 8$) linkages in the presence of the $RuH_3(SiMe_3)(PMe_3)_3$ catalyst, suggesting (silene)-ruthenium species being involved in the catalysis, Eq. 35.[5d)]

(34)



(35)

(c) Dehydrogenative Silylation of Terminal Acetylenes. Dehydrocoupling between Si–H and H–C≡C bonds proceeds with CuCl/amine catalysts to from Si–C≡C compounds.[34a)] The reaction of $PhSiH_3$ with *m*-diethynylbenzene provides poly[(phenylsilylene)ethynylene-*m*-phenyleneethynylene] with a molecular-weight distribution ranging from 10^2 to 10^5, Eq. 36. A solid base, MgO, also catalyzes the reaction to give a similar polymer with M_w=4250 (M_w/M_n=3).[34b)] The polymer exhibits remarkably high thermal stability in TGA; the weight loss after heating up to 900 °C under Ar is only ca. 5%.



$$\mathrm{PhSiH_3 + HC{\equiv}C{-}A{-}C{\equiv}CH \xrightarrow[-H_2]{cat.} \left(\overset{Ph}{\underset{H}{Si}}{-}C{\equiv}C{-}A{-}C{\equiv}C\right)_n} \qquad (36)$$

A = m-C_6H_4, SiPhMe; cat. = CuCl/amine, MgO

(d) Dehydrogenative Si–N Bond Formation. Catalytic dehydrocoupling between Si–H and N–H bonds has not been extensively studied, compared with that between Si-H and O-H bonds.[35a)] $Ru_3(CO)_{12}$-catalyzed reactions of hydrosilanes with NH_3 give polymers with M_n ranging from 1000 to 7000, Eq. 37.[35b)] An oligosilazane, $MeHN(SiH_2NMe)_nH$ ($M_n \approx 700$), undergoes polymerization/cross-linking to provide higher molecular weight polymers ($M_n \approx 1600$) with favorable viscoelastic properties for Si_3N_4 precursors. Cp_2TiMe_2 also promotes dehydrocoupling of $RSiH_3$ (R=Ph, Me) with NH_3, but forms unexpected polymers, mainly consisting of aminosilylene, $-SiR(NH_2)-$, units, Eq. 38.[35c)] Upon pyrolysis of the polymer (R=Me), a ceramic material comprising Si_3N_4, SiC, and C is obtained in 77% yield.

$$\mathrm{PhSiH_3 + NH_3 \xrightarrow[60\,^{\circ}C,\,-H_2]{Ru_3(CO)_{12}\ cat.} H\text{-}(SiPhH\text{-}NH)_n\text{-}H} \qquad (37)$$

Mn ~1,000

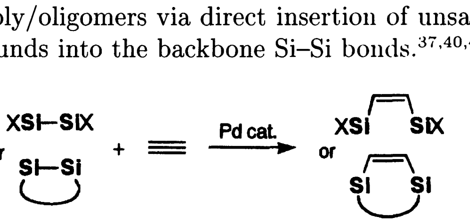
$$\mathrm{RSiH_3 + NH_3 \xrightarrow[70\text{-}95\,^{\circ}C]{Cp_2TiMe_2\ cat.} \text{-}SiR(NH_2)\text{-}\ polymer}$$

Mn = 3,400 (R = Ph) (38)

$$\mathrm{\xrightarrow[\to 1400\,^{\circ}C]{(R\,=\,Me)} \alpha\text{-}Si_3N_4 + \alpha\text{-}SiC + C}$$

3. Catalytic Polymer Synthesis via Transformation of Si–Si Bonds

The addition of Si–Si bonds to unsaturated compounds (acetylenes, dienes, allenes, olefins, etc.) has been rather well studied. However, as far as the conventional catalysts, like Pd/PPh_3 systems, are used, the reaction proceeds nicely only when the Si–Si bonds are activated by electronegative groups or ring strain, Eq. 39.[36)] To overcome this drawback, several new catalyst systems have been devised for the reactions of acetylenes,[37—39)] dienes,[39)] and dicarbonyl compounds[40,41)] with nonactivated Si–Si bonds. Some of the new systems are applicable to modification or synthesis of silicon poly/oligomers via direct insertion of unsaturated compounds into the backbone Si–Si bonds.[37,40,42)]

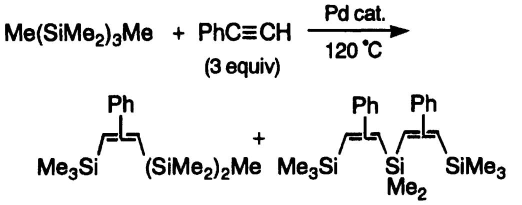


(39)

X = F, Cl, OR; Pd cat. = Pd/PPh_3

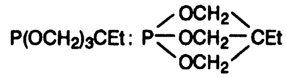
3-1. Backbone Reconstruction of Silicon Poly/oligomers (Type C-2). (a) Insertion of Acetylenes.

A survey of catalysts for phenylacetylene insertion into octamethyltrisilane has revealed that the palladium catalyst system in situ generated with $Pd(dba)_2$ (dba=dibenzylideneacetone) and two equivalents of $P(OCH_2)_3CEt$ that is a sterically smaller and electronically less donating phosphite ligand is highly efficient over the other catalysts examined, Eq. 40. The $Pd/P(OCH_2)_3CEt$ system is effective for the reactions of nonactivated disilanes $(Ph_nMe_{3-n}Si)_2$ (n=0—2) with acetylenes RC≡CH (R=Ph, Hex) as well (≥90% yields).[43)] The ratio of P/Pd is also an important factor, and the use of P/Pd=2 is most favorable activity-wise; in the reaction of hexamethyldisilane (120 °C, 2 h), the yields (the ratios of P/Pd) are 6% (1), 62% (1.5), 73% (2), and 55% (4). In this respect, the $Pd/P(OCH_2)_3CEt$ system is much superior to the Pd/tertiary alkyl isocyanide system[38)] that requires an unusually high ligand to palladium ratio, as high as ca. 15.



A B (40)

Pd cat.	Yield/% A	Yield/% B
$Pd(PPh_3)_4$	1.9	0
$PdCl_2(PPh_3)_2$	6.9	3.2
$PdCl_2(PMe_3)_2$	20.3	6.8
$Pd(dba)_2/2PPh_3$	2.0	0
$Pd(dba)_2/2P(OPh)_3$	8.1	0.4
$Pd(dba)_2/2P(OPr^i)_3$	23.3	9.4
$Pd(dba)_2/2P(OMe)_3$	38.3	19.3
$Pd(dba)_2/2P(OCH_2)_3CEt$ (= Pd*)	0	90.7



(cat. 2 mol%, PhH, 7 h)

By using the new catalyst system, phenylacetylene smoothly inserts into the Si–Si bonds of a disilanylene unit-containing polymer, poly[p-phenylene(1,2-dimethyl-1,2-diphenyldisilanylene)] (PPDS, M_w=48000, M_w/M_n=2.7), to form a new polycarbosilane (M_w=58000, M_w/M_n=2.4) with phenylvinylene moieties being incorporated in almost every Si–Si bond, Eq. 41. Similar reactions between 1-octyne and PPDS and between phenylacetylene and poly[ethylene(tetramethyldisilanylene)] (PEDS) also proceed to give exhaustively reconstructed polymers.

Table 3. Modification of PPDS with Functionalized Acetylenes RC≡CH[a)]

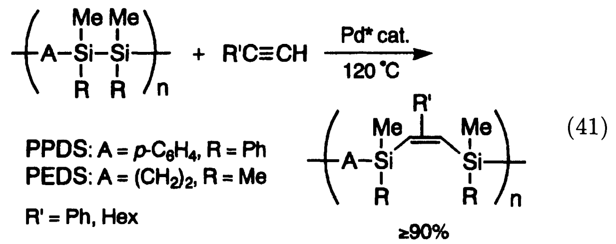
Run	R	RC≡CH equiv	Yield[b)] %	$p:q$	M_w (M_w/M_n)[c)]
1	4-$Me_2NC_6H_4$	0.05	77	16 : 84	44000 (2.7)
2	4-$Me_2NC_6H_4$	0.10	79	35 : 64	39000 (2.8)
3	4-Pyridyl	0.05	88	10 : 90	42000 (2.8)
4	4-Pyridyl	0.10	86	19 : 81	42000 (3.0)
5[d)]	Me_3SiOCH_2	0.10	90	4 : 96	36000 (2.8)
6[d)]	Me_3SiOCH_2	0.80	57	62 : 38	37000 (2.3)

a) PPDS (M_w=48000, M_w/M_n=2.7, 0.20 mmol monomer unit), RC≡CH (0.05—0.80 equiv/Si–Si bond), $Pd(dba)_2$ (0.004 mmol), $P(OCH_2)_3CEt$ (2 equiv/Pd), benzene (0.1 ml), 120 °C, 13.5 h. b) Yield after purification by precipitation from benzene (THF)–2-propanol. c) Estimated by GPC with reference to polystyrene standards. d) 15.5 h.

Table 4. Modification of Polysilanes with Acetylenes[a)]

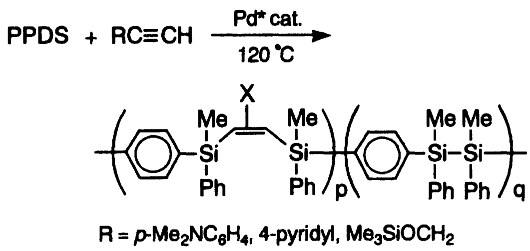
Run	Polysilane[b)]	Acetylene (equiv)	Time h	Yield[c)] %	$p:q$	M_w (M_w/M_n)[d)]
1[e)]	$(SiMe_2)_n$	HexC≡CH (1.9)	27	45	ca. 100 : 0	4400 (1.8)
2	$(SiMePr)_n$	HexC≡CH (2.5)	20	33	ca. 100 : 0	8900 (1.6)
3	$(SiMePr)_n$	PhC≡CH (2.5)	3	60	5 : 95	49000 (4.0)
4	$(SiMePr)_n$	4-$Me_2NC_6H_4$C≡CH (0.5)	3	54	20 : 80	9800 (3.0)

a) Polysilane (0.40—0.80 mmol monomer unit), acetylene (0.5—2.5 equiv/Si–Si bond), $Pd(dba)_2$ (1—2 mol%/Si–Si bond), $P(OCH_2)_3CEt$ (2 equiv/Pd), benzene or toluene (0.1—0.2 ml), 100 °C. b) $(SiMe_2)_n$: M_w=4700, M_w/M_n=1.8 (T. Ohnaka, "Synthesis and Applications of Organosilicon Polymers," ed by H. Sakurai, CMC, Tokyo (1989), p. 99); $(SiMePr)_n$: M_w=64000, M_w/M_n=3.1. c) Yield after purification by short-path column chromatography (silica gel, hexane) or precipitation from benzene–2-propanol (ethanol). d) Estimated by GPC with reference to polystyrene standards. e) 120 °C.



(41)

The use of functionalized terminal acetylenes with 4-(dimethylamino)phenyl, 4-pyridyl, and trimethylsiloxymethyl substituents allows functionalization of a disilanylene polymer, PPDS (M_w=48000), Eq. 42 (Table 3).[37b)] The M_w of the polymers obtained in the reactions ranges from 36000 to 44000, indicating that no extensive degradation has taken place. The extent of functionalization is readily controlled by the quantity of acetylenes to be charged; doubling the quantity of 4-(dimethylamino)phenylacetylene or 4-pyridylacetylene provides a polymer with an almost doubled extent of functionalization. The use of diynes causes cross-linking to give polymers with higher M_w.[37a,37c)] When PPDS (M_w=48000) is treated with 1,7-octadiyne (1/40 equiv), a cross-linked polymer (M_w=160000) is obtained nearly quantitatively, Eq. 43. Increased amounts of the diyne give highly cross-linked insoluble polymers. *p*-Diethynylbenzene (1/160 equiv) is also effective for the cross-linking (M_w=190000).



(42)

$$\mathrm{PPDS} + \underset{(1/160\text{–}1/40\ \mathrm{equiv})}{\mathrm{HC{\equiv}C{-}A{-}C{\equiv}CH}} \xrightarrow[120\,^{\circ}\mathrm{C}]{\mathrm{Pd^{*}\ cat.}} \text{cross-linked polymer} \qquad (43)$$

A = $(CH_2)_4$, *p*-C_6H_4 Mw 48,000 → 130,000~190,000

Besides disilanylene polymers, polysilanes undergo the reaction as well. Thus, poly(dimethylsilylene) (M_w≈4700), which is known as an intractable insoluble polymer, does react with 1-octyne in the presence of the Pd/$P(OCH_2)_3CEt$ catalyst to give a soluble polymer consisting of alternating dimethylsilylene and hexylvinylene units (M_w=4400), Eq. 44 (Table 4). Likewise, the reaction of poly(methylpropylsilylene) (M_w=64000) with 1-octyne provides a new silylene–vinylene polymer, albeit with a substantial decrease in the molecular weight (M_w=8900).[44)] Partially modified polymers of poly(methylpropylsilylene) are also obtained by insertion of arylacetylenes RC≡CH (R=Ph, 4-$Me_2NC_6H_4$). The UV spectrum of a partially (20%) modified polymer with 4-(dimethylamino)phenylvinylene groups shows an

Table 5. Conductivity of Modified Polymers $[p\text{-}C_6H_4(\mathbf{Si}\text{-}A\text{-}\mathbf{Si})]_p[p\text{-}C_6H_4(\mathbf{Si}\text{-}\mathbf{Si})]_q$ ($\mathbf{Si}$=SiPhMe, A=RC=CH or HC=CR)

Run	R	$p:q$	M_w (M_w/M_n)	Conductivity[a)] S cm^{-1}
1	—	0 : 100	48000 (2.7)	3×10^{-4}
2	Ph	ca. 100 : 0	58000 (2.4)	5×10^{-5}
3[b)]	$(CH_2)_4$–	—	160000 (ca. 8)	4×10^{-4}
4[c)]	p-C_6H_4–	—	190000 (ca. 10)	5×10^{-4}
5	4-Pyridyl	19 : 81	42000 (3.0)	4×10^{-4}
6	4-$Me_2NC_6H_4$	16 : 84	44000 (2.7)	1×10^{-3}

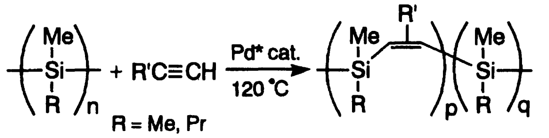
a) Conductivity of thin films (125—153 nm) doped with I_2 for 2.5—7 h. b) A cross-linked polymer obtained by the reaction of PPDS (Run 1) with 1,7-octadiyne (1/40 equiv/Si–Si bond). c) A cross-linked polymer obtained by the reaction of PPDS (Run 1) with p-diethynylbenzene (1/160 equiv/Si–Si bond).

Table 6. Modification of Si–Si Bond-Containing Polymers with Quinones[a)]

Run	Starting polymer[b)]	Quinone (equiv)	Time min	Yield[c)] %	$p:q$	M_w (M_w/M_n)[d)]
1	PPDS	PQ (1.05)	180	90	ca. 100 : 0	58000 (3.0)
2[e)]	PPDS	PQ (0.30)	180	86	29 : 71	52000 (2.9)
3	PEDS	PQ (1.05)	60	84	ca. 100 : 0	50000 (2.5)
4	PDSO[f)]	PQ (0.30)	40	ca. 100[g)]	20 : 80	18000 (2.4)
5[h)]	PEDS	BQ (1.05)	180	83	ca. 100 : 0	19000 (2.4)
6[h)]	PDSO[f)]	BQ (0.30)	180	66[g)]	21 : 79	110000 (2.4)

a) Polymer (0.20 mmol monomer unit), quinone (1.05 or 0.30 equiv/Si–Si bond), $Pd(dba)_2$ (ca. 2 mol%/quinone), $P(OCH_2)_3CEt$ (2 equiv/Pd), benzene (0.1 ml), 120 °C. b) PPDS: M_w=46000, M_w/M_n=2.6; PEDS: M_w=250000, M_w/M_n=2.3; PDSO: M_w=190000, M_w/M_n=2.3. c) Yield after purification by precipitation from benzene–2-propanol. d) Estimated by GPC with reference to polystyrene standards. e) Pd cat. (4 mol%/PQ). f) 0.50 mmol monomer unit. g) Purified by short-path Florisil column chromatography. h) $PdCl_2(PEt_3)_2$ cat.

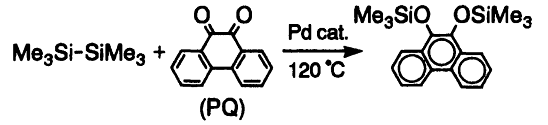
absorption band (λ_{max}=304 nm) in a region similar to that of the original polymer (λ_{max}=306 nm), indicative of the polymer still possessing polysilane properties attributed to σ-conjugation through the backbone.



(44)

The new process appears to have a great potential to control such properties as the electric conductivity (Table 5). An exhaustively modified polymer with phenylvinylene moieties incorporated in almost all Si–Si bonds of PPDS shows, upon doping with I_2, about a one tenth lower conductivity than that of the parent polymer. Cross-linking by 1,7-octadiyne or p-diethynylbenzene does not improve the conductivity. On the other hand, a partially modified polymer that contains basic dimethylamino groups and may interact favorably with Lewis acidic I_2 exhibits about a three-times higher conductivity (1×10^{-3} S cm^{-1}) than that of the original polymer.

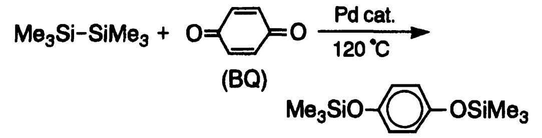
(b) Insertion of Dicarbonyl Compounds. Model experiments using hexamethyldisilane have disclosed that $Pd(dba)_2/2P(OCH_2)_3CEt$ or $PdCl_2(PEt_3)_2$ is respectively the catalyst of choice for insertion of 9,10-phenanthraquinone (PQ) or p-benzoquinone (BQ) into the Si–Si bond, Eqs. 45 and 46.[40,45)] By using the former catalyst, PQ (1.05 equiv) smoothly inserts into the Si–Si bonds of PPDS to give a new polymer with 9,10-phenanthrenedioxy groups incorporated in almost every Si–Si bond, Eq. 47 (Table 6). Since the reaction proceeds nearly quantitatively, the extent of the modification can be readily controlled by the quantity of PQ to be charged; the use of 0.30 equiv PQ gives a polymer with 29% of the Si–Si bonds being transformed under the same conditions. Other disilanylene polymers, PEDS and poly(tetramethyldisiloxane) (PDSO), also undergo the reaction with PQ to provide exhaustively or partially modified polymers. Likewise, backbone reconstruction with BQ proceeds in high yields by using the $PdCl_2(PEt_3)_2$ catalyst. The treatment of PEDS with BQ (1.05 equiv) forms an exhaustively reconstructed polymer with p-phenylenedioxy moieties incorporated in the backbone. Similarly, a facile reaction of PDSO with BQ (0.30 equiv) forms a partially reconstructed polymer with the degree of modification being 21%. Even a polysilane, poly(dimethylsilylene), also reacts with BQ (1.1 equiv) cleanly to give a silyleneoxy-p-phenyleneoxy polymer, Eq. 48.



(45)

Pd cat.	Yield /%
$PdCl_2(PPh_3)_2$	78
$PdCl_2(PEt_3)_2$	99
$Pd(dba)_2/2P(OCH_2)_3CEt$	~100

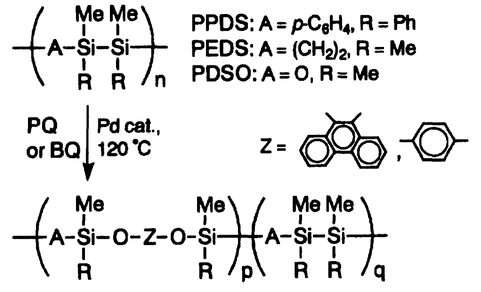
(cat. 2 mol%, PhH, 120 °C, 1 h)



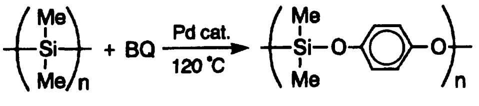
(46)

Pd cat.	Yield /%
$PdCl_2(PPh_3)_2$	10 (~100[a])
$PdCl_2(PMe_3)_2$	17
$PdCl_2(PEt_3)_2$	~100
$Pd(dba)_2/2P(OCH_2)_3CEt$	40[a]

(cat. 1 mol%, PhH, 5 min; a) cat. 2 mol%, 1 h)



(47)

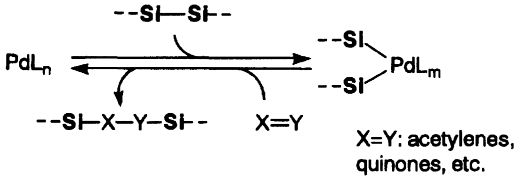


(48)

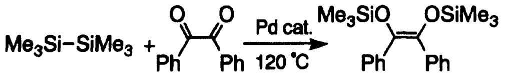
Pd cat. = $PdCl_2(PEt_3)_2$ Mw = 15,000, 85% yield

Modified polymers obtained by insertion of PQ into PPDS exhibit, as anticipated, photochemical and thermal properties different from those of the parent polymer.[46] Under UV irradiation of a benzene solution (8×10^{-3} M) with a low-pressure mercury lamp, the parent polymer continues to be degraded via photochemical bond scission. On the other hand, a partially (29%) modified polymer discontinues an extensive decrease in the molecular weight after about 40 min; the values of M_w at 0, 40, and 100 min are respectively 52000, 31000, and 29000 for the modified polymer, while they are 46000, 29000, and 16000 for the parent one. TGA at 10 °C min^{-1} heating rate under He reveals that the modification with PQ improves the thermal stability; the temperatures of 5 and 10% weight loss (extent of modification, %) are respectively 455 and 466 °C (0), 470 and 485 °C (29), and 480 and 513 °C (ca. 100).

For insertion of an α-diketone, benzil, into hexamethyldisilane $PdCl_2(PMe_3)_2$ is the catalyst of choice, Eq. 49.[41] With the Pd catalyst, partial insertion of benzil (0.30 equiv) into PPDS smoothly proceeds to give a modified polymer with 1,2-vinylenedioxy groups ($E/Z=10/90$) incorporated in 27% of the backbone Si–Si bonds, Eq. 50



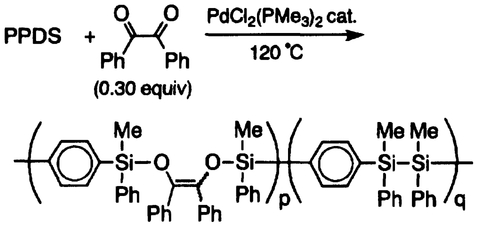
Scheme 7.



(49)

Pd cat.	yield (%)
$PdCl_2(PPh_3)_2$	1.0
$Pd(dba)_2/2P(OCH_2)_3CEt$	4.2
$PdCl_2(PEt_3)_2$	91
$PdCl_2(PMe_3)_2$	93 (99 [2 h])

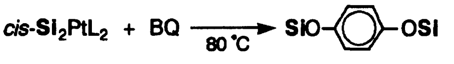
(cat. 2 mol%, PhH, 1 h)



(50)

p : q = 27 : 73, E/Z = 10/90, Mw = 31,000, 88% yield

The mechanism of inserting dicarbonyl compounds is rather ambiguous at the moment. However, a bis(silyl)platinum complex has been shown to react with BQ to form a p-bis(siloxy)benzene (≥60% yield), Eq. 51, as in the reactions of group 10 bis(silyl)metals with acetylenes yielding 1,2-bis(silyl)ethenes, Eq. 52.[7a—d,9a,9d] Accordingly, the reaction of dicarbonyl compounds, as well as that of acetylenes, is likely to involve bis(silyl)palladium intermediates (Scheme 7). The effect of phosphorus ligands on elemental steps of double silylation has not yet been clarified. However, sterically small ligands seem to facilitate access of both unsaturated compounds and sterically rather demanding Si–Si bonds to the palladium center, resulting in high activities, as observed in the reactions of acetylenes and dicarbonyl compounds.



(51)

Si = $PhMe_2Si$; L = PMe_2Ph

$$(R_3Si)_2ML_n + R'C\equiv CR'' \longrightarrow (R_3Si)R'C=CR''(SiR_3) \quad (52)$$

M = Pt, Pd, Ni

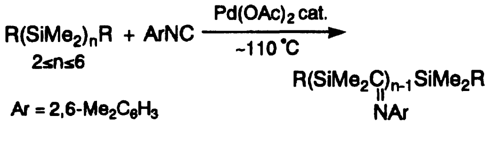
(c) Insertion of Isocyanides. Ito et al. have

Table 7. Ring-Opening Copolymerization of Silacycles with *p*-Quinones[a)]

Run	Silacycle	Quinone	Yield[b)]/%	M_w (M_w/M_n)[c)]
1	$(SiMe_2)_6$	NQ	60	6400 (2.1)
2	$(SiMe_2)_6$	BQ	68	21000 (5.8)
3	$(SiPh_2)_4$	NQ	76	3900 (2.2)
4	$(SiPh_2)_4$	BQ	41[d)]	17000 (5.1)[e)]
			30[f)]	82000 (11)
5[g)]	$(SiMe_2)_2(CH_2)_4$	BQ	65	19000 (3.9)
6[g)]	$(SiMe_2)_2(CPh{=}CPh)_2$	BQ	71	49000 (3.6)
7[h)]	$[(SiMe_2)_2O]_2$	BQ	ca. 100[i)]	9500 (3.2)

a) Silacycle (0.10 mmol), *p*-quinone (1.1 equiv/Si–Si bond), $PdCl_2(PEt_3)_2$ (2 mol%/Si–Si bond), benzene (0.1 mol), 120 °C, 12—14 h. b) Yield after purification by precipitation from benzene–2-propanol. c) Estimated by GPC with reference to polystyrene standards. d) Benzene-soluble fraction. e) A bimodal molecular-weight distribution: A ($M_w = 32000$, $M_w/M_n = 1.8$) and B ($M_w = 2700$, $M_w/M_n = 1.6$), GPC area ratio of A/B=0.8. f) Benzene-insoluble fraction. g) Silacycle (0.40 mmol), 20 h. h) $PdCl_2(PPh_3)_2$ (2 mol%/Si–Si bond), 1 h. i) By ^{1}H NMR.

found that isocyanides RNC (R=2,6-xylyl, 2,6-diisopropylphenyl) insert into the Si–Si bond of hexamethyldisilane in the presence of a $Pd(OAc)_2$ catalyst to give the corresponding bis(silyl)imines.[42)] Partial or exhaustive insertion of 2,6-xyryl isocyanide into methyl- and/or phenyl-substituted oligosilanes ($n \leq 6$) gives silylene-iminomethylene linkage-containing products, Eq. 53. Sterically more demanding 2,6-diisopropylphenyl isocyanide (3.5 equiv) reacts with decamethyltetrasilane only at the terminal Si–Si bonds and the internal Si–Si bond remains intact.

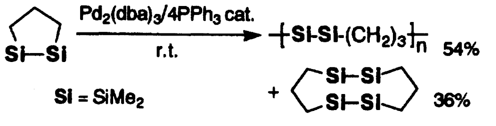


$$R(SiMe_2)_nR + ArNC \xrightarrow[\sim 110\,^{\circ}C]{Pd(OAc)_2\ cat.} R(SiMe_2\underset{\underset{NAr}{\|}}{C})_{n-1}SiMe_2R \quad (2 \leq n \leq 6;\ Ar = 2,6\text{-}Me_2C_6H_3)$$

(53)

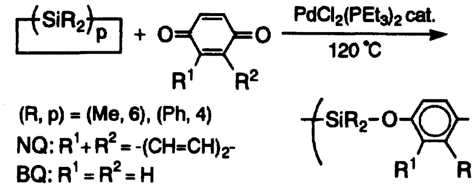
3-2. Polymer Synthesis with Silacyclic Compounds.

(a) Ring-Opening Polymerization of Silacycles. High valent transition metal-catalyzed ring-opening polymerization has been long known for strained cyclocarbosilanes, such as silacyclobutane and 1,3-disilacyclobutane derivatives. Groups 9 and 10 transition metal compounds are effective catalysts and provide rather high molecular weight polymers with $M_w \geq 10^5$.[47)] On the other hand, low valent metal-catalyzed reactions are still rare. Suzuki and Saegusa et al. reported only recently that 1,1,2,2-tetramethyl-1,2-disilacyclopentane underwent Pd(0)- catalyzed polymerization (molecular weight ≥500000, 54% yield), although a considerable amount of a dimerization product (36%) was also formed as a by-product, Eq. 54.[48)] Transition metal-catalyzed polymerization of cyclooligosilanes appears to be even harder (vide infra), although a cyclotetrasilane[49a)] and a cyclopentasilane[49b)] readily polymerize in the presence of anion catalysts.



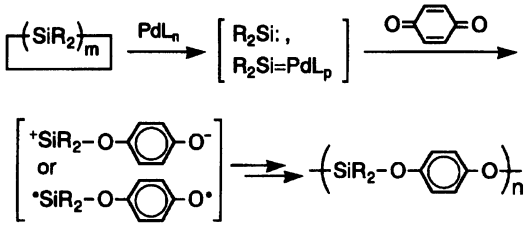
(54)

(b) Ring-Opening Copolymerization of Silacycles with *p*-Quinones (Type B, C-2). The insertion of a *p*-quinone into a Si–Si bond in a small ring system, if it occurs at all, is expected to end up with ring-opening because of a considerable strain that arises by introducing a non-flexible *p*-arylenedioxy moiety. Indeed, cyclooligosilanes react with *p*-quinones in the presence of Pd catalysts to provide silicon polymers containing silylene and arylenedioxy units.[50)] Heating a mixture of dodecamethylcyclohexasilane, 1,4-naphthoquinone (NQ, 1.1 equiv/Si–Si bond), $PdCl_2(PEt_3)_2$ (2 mol%/Si–Si), and benzene in a sealed tube at 120 °C gives a new polymer consisting of alternating dimethylsilylene and 1,4-naphthylenedioxy units (M_w= 6400, M_w/M_n=2.1, 60% yield), Eq. 55 (Table 7). The overall reaction is formally a combination of insertion of the quinone into every Si–Si bond of the hexasilane and ring-opening polymerization. Similarly, the cyclohexasilane reacts with *p*-benzoquinone (BQ) to give poly[(dimethylsilylene)oxy-*p*-phenyleneoxy] (M_w= 21000, M_w/M_n=5.8). Ring-opening copolymerization of somewhat congested octaphenylcyclotetrasilane with NQ and BQ also proceeds to give the corresponding copolymers. The polymers obtained from BQ have higher molecular weights than those from NQ. This may be due to the higher reactivity of BQ, that is sterically less demanding than NQ. The polymers containing diphenylsilylene units show a rather high thermal stability; in TGA the weight loss under He has been less than 5% up to 400 °C (10 °C min^{-1} heating rate).



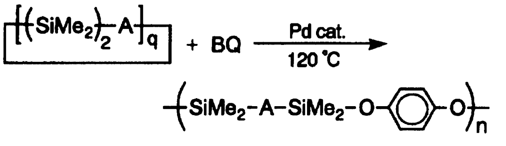
(55)

When the procedure is applied to cyclic disilanes, ring-opening 1 : 1 copolymerization cleanly proceeds. Thus, the reaction between 1,1,2,2-tetramethyl-1,2-



Scheme 8.

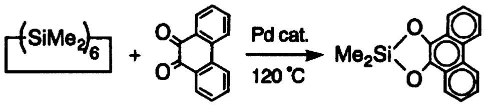
disilacyclohexane, $(SiMe_2)_2(CH_2)_4$, and BQ gives a new polymer consisting of alternating 1,6-disilahexane-1,6-diyl and *p*-phenylenedioxy units, Eq. 56 (Table 7).[51] Likewise, 1,1,2,2-tetramethyl-3,4,5,6-tetraphenyl-1,2-disilacyclohexa-3,5-diene, $(SiMe_2)_2(CPh{=}CPh)_2$, smoothly reacts with BQ to yield the corresponding copolymer. Octamethyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane, $[(SiMe_2)_2O]_2$, undergoes facile ring-opening 1 : 2 copolymerization with BQ to provide a new siloxane polymer.



(56)

(A, q) = (-(CH$_2$)$_4$-, 1), (-(CPh=CPh)$_2$-, 1), (O, 2)

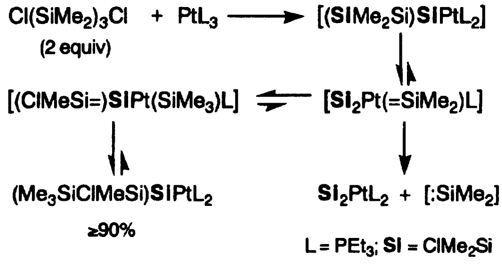
Ring-opening polymerization of silacycles, such as $(SiMe_2)_6$, $(SiPh_2)_4$, and $(SiMe_2)_2(CH_2)_4$, hardly proceeds in the absence of *p*-quinones ($PdCl_2L_2$ ($L{=}PEt_3$, PPh_3) or $Pd(dba)_2/2P(OCH_2)_3CEt$ cat., 120 °C).[52] Accordingly, the copolymers appear unlikely to be formed by initial ring-opening polymerization of the silacycles followed by insertion of *p*-quinones into the Si–Si bonds. On the other hand, a possible involvement of silylene species in the reaction of cyclooligosilanes is supported by the reaction of $(SiMe_2)_6$ with 9,10-phenathraquinone affording a silylene adduct, Eq. 57. Silylene species are expected to somehow interact with *p*-quinones to give the copolymers (Scheme 8), as has been proposed for the reaction of a stable germylene with *p*-quinones forming 1 : 1 alternating copolymers.[53]



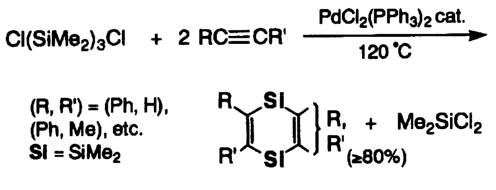
(57)

Pd cat. = $PdCl_2(PEt_3)_2$

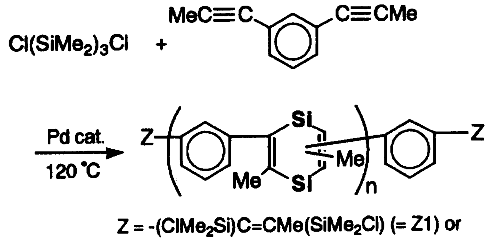
3-3. Polycarbosilane Formation from $Cl(SiMe_2)_3Cl$ and Diynes. In the course of the studies on the reactivities of Si–Si bonds toward metal complexes, $Cl(SiMe_2)_3Cl$ has been found to react with $Pt(PEt_3)_3$ to form *cis*-$(ClMe_2Si)(Me_3SiMeClSi)Pt(PEt_3)_2$, presumably via silyleneplatinum intermediates (Scheme 9).[4g] The silyl(disilanyl)platinum readily extrudes a dimethylsilylene unit upon removal of the liberated phosphine in vacuo to form *cis*-$(ClMe_2Si)_2Pt(PEt_3)_2$. The results have led to the development of a new catalysis in which $Cl(SiMe_2)_3Cl$ reacts with two equivalents of an acetylene in the presence of the $PdCl_2(PPh_3)_2$ catalyst to form a 1,4-disilacyclohexa-2,5-diene and Me_2SiCl_2 as the major products, Eq. 58.[4g] The reaction is applicable to the synthesis of 1,4-disilacyclohexa-2,5-diene ring-containing polymers, Eq. 59. Thus, $Cl(SiMe_2)_3Cl$ reacts with *m*-di(1-propynyl)benzene to give a new polymer consisting of alternating 1,4-disilacyclohexa-2,5-dienediyl and *m*-phenylene units. *p*- or *m*-Diethynylbenzene also yields a new silicon polymer that contains 1,4-disilacyclohexa-2,5-diene rings in the backbone; $Cl(SiMe_2)_3Cl$ reacts with *p*-diethynylbenzene to give an insoluble polymer, whereas the reaction with a 9 : 2 mixture of *m*-diethynylbenzene and phenylacetylene forms a soluble polymer with $M_w{=}28000$.



Scheme 9.



(58)

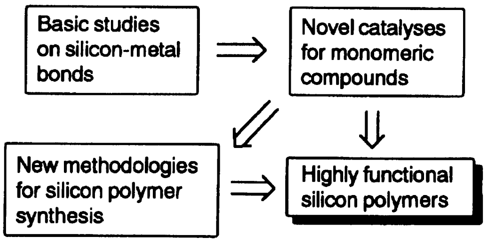


(59)

Z = -(ClMe$_2$Si)C=CMe(SiMe$_2$Cl) (= Z1) or -C≡CMe (= Z2) (Z1/Z2 ≥ 9/1), n ≈ 4

Conclusion

We hope to have produced convincing evidence that transition metal-catalyzed reactions are powerful tools to synthesize silicon-containing polymers, as exemplified in the dehydrocoupling of hydrosilanes, the redistribution of hydrodisilanes, dehydrogenative double silylation with an *o*-bis(hydrosilyl)benzene, the insertion of acetylenes and dicarbonyl compounds into polymeric Si–Si bonds, 1,4-disilacyclohexa-2,5-diene formation from a 1,3-dichlorotrisilane, etc. However, to find further opportunities, the variety and understanding of the reactions are still too poor. Intensive studies on the mechanism, particularly the generation and reactivity



Scheme 10.

of silylmetal species, and an extensive search for new catalyses and new catalysts are highly encouraged to promise a bright future of new silicon polymers with superior physicochemical properties that are hard to be achieved by conventional organic polymers (Scheme 10).

We wish to thank all our colleagues for the fruitful works herein described and suggestive discussions during the course of these studies: in particular, Drs. Teruyuki Hayashi, Toshiaki Kobayashi, and Toshiyasu Sakakura, Ms. Yuko Uchimaru, and Drs. N. Prabhakar Reddy and Shigeru Shimada.

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23) K. Yamamoto, H. Okinoshima, and M. Kumada, *J. Organomet. Chem.*, **23**, C7 (1970).

24) For a review of redistribution of organosilanes: M. D. Curtis and P. S. Epstein, *Adv. Organomet. Chem.*, **19**, 213 (1981).

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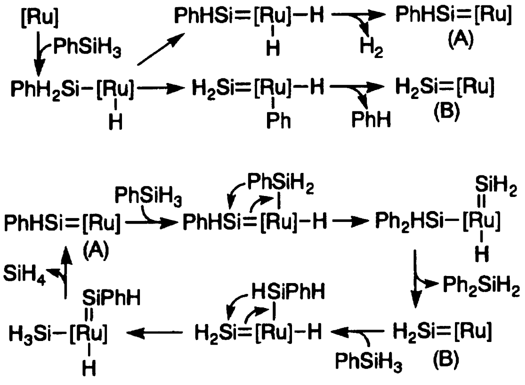

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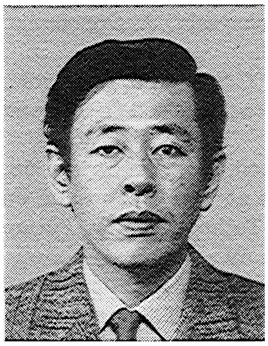

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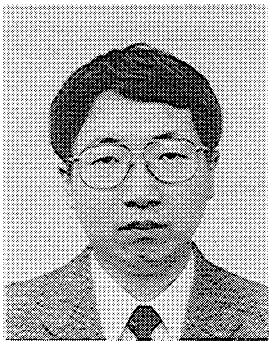

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