2D HMQC/HOHAHA, and to Dr. Wälchli of Japan Bruker for NMR measurements. We thank Drs. H. Naoki of Suntory Institute, K. Tanaka of JEOL Co. for measuring mass spectra, and Prof. P. J. Scheuer, University of Hawaii, for discussions. The work was supported in part by a grant-in-aid from the Ministry of Education, Science, and Culture, Japan, and by the Naito Foundation.

Supplementary Material Available: ^{1}H–^{1}H COSY, ^{1}H–^{1}H HOHAHA, NOESY, and ^{1}H–^{13}C HOHAHA spectra of MTX and ^{1}H–^{1}H COSY spectrum of fragment A (5 pages). FABMS and ^{13}C NMR spectra have been published previously.[6] Ordering information is given on any current masthead page.

Palladium-Catalyzed Ring-Opening Copolymerization of Cyclopolysilanes and Cyclic Disilanes with *p*-Quinones

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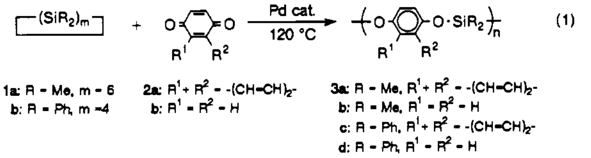
Organosilicon polymers such as polysiloxanes, polycarbosilanes, polysilazanes, and polysilanes have attracted increasing attention for their current and future engineering applications.[1] In this sense, new and efficient methods for their preparation have been highly desired. However, ring-opening polymerization is still very rare except for the reaction of cyclic siloxanes, and only a few examples of strained cyclic disilanes[2] and cyclotetrasilanes[3] have been reported for Si–Si bond-containing polycarbosilanes and polysilanes. We report herein an entirely new and rather unusual copolymerization of cyclopolysilanes and cyclic disilanes with *p*-quinones to afford regular polymers consisting of *p*-(arylenedioxy)silylene linkages.

A mixture of dodecamethylcyclohexasilane (**1a**, 0.10 mmol), 1,4-naphthoquinone (**2a**, 0.66 mmol), $PdCl_2(PEt_3)_2$ (0.008 mmol), and benzene (0.10 mL) was heated at 120 °C for 14 h in a sealed tube under nitrogen. ^{1}H NMR spectroscopy showed clean conversion of the Me signal at 0.07 ppm arising from **1a** into a new rather broad signal at 0.08–0.66 ppm. The resulting mixture was dissolved in benzene (5 mL) and filtered. Concentration of the filtrate to about 1/5 followed by addition of 2-propanol gave a pale gray solid of poly[1,4-naphthylenedioxy)dimethylsilylene] (**3a**)[4a] (eq 1) in 60% yield. The molecular weight (M_w) of **3a** was determined (by GPC with polystyrene standards) to be 6.4×10^3 ($M_w/M_n = 2.1$) (Table I). ^{1}H and ^{13}C NMR spectra[4a] of **3a** are well conformed to the given structure, indicating a highly regular polymer consisting of alternating 1,4-naphthylenedioxy and dimethylsilylene units. Thus, the overall reaction involves ring opening of **1a**, insertion of **2a** into every Si–Si bond, and polymerization.

Table I. Ring-Opening Copolymerization of 1,2-Disilacycles with *p*-Quinones[a]

1,2-disilacycle	quinone	product	M_w (M_w/M_n)[b]	yield, %[c]
1a	**2a**	**3a**	6.4×10^3 (2.1)	60
1a	**2b**	**3b**	2.1×10^4 (5.8)	68
1b	**2a**	**3c**	3.9×10^3 (2.2)	76
1b	**2b**	**3d**	1.7×10^4 (5.1)[d]	41
			8.2×10^4 (11)[e]	30[e]
1c[f]	**2b**	**3e**	1.9×10^4 (3.9)	65
1d[f]	**2b**	**3f**[g]	4.9×10^4 (3.6)	71

[a] Reaction conditions: 1,2-disilacycle, 0.10 mmol; *p*-quinone, 1.10 equiv/Si–Si; $PdCl_2(PEt_3)_2$, 0.008 mmol; benzene, 0.10 mL; 120 °C; 12–14 h. [b] Determined by GPC with polystyrene standards using THF as eluent at 40 °C. [c] Yield after purification by reprecipitation with benzene–2-propanol. [d] Bimodal peaks.[5] [e] Benzene-insoluble fraction. M_w and M_w/M_n were measured by high-temperature GPC using *o*-dichlorobenzene as eluent at 135 °C. [f] 0.4 mmol, 20 h. [g] Not purified.[4f]



Similarly, **1a** reacted with *p*-benzoquinone (**2b**) to give poly[(*p*-phenylenedioxy)dimethylsilylene] (**3b**).[4b] Copolymerization of the somewhat congested octaphenylcyclotetrasilane (**1b**) with **2a** and **2b** also proceeded to give poly[(1,4-arylenedioxy)diphenylsilylene] polymers **3c**[4c] and **3d**,[4d,5,6] respectively. The polymers **3b** and **3d** obtained from **2b** have higher molecular weights than **3a** and **3c** obtained from **2a**. This may be because **2b** is sterically less demanding and thus more reactive than **2a**. Other catalyst systems such as $PdCl_2(PPh_3)_2$ and $Pd(dba)_2$-$2P(OCH_2)_3CEt$ (dba = dibenzylideneacetone) were also effective, although $PdCl_2(PEt_3)_2$ seemed to be beneficial for obtaining polymers with high molecular weight; in the reaction of **1b** with **2b**, $PdCl_2(PPh_3)_2$ and $Pd(dba)_2$-$2P(OCH_2)_3CEt$ afforded only benzene-soluble polymers with M_w's (M_w/M_n) of 2.0×10^4 (3.9) and 4.7×10^4 (5.1), respectively, while $PdCl_2(PEt_3)_2$ gave a polymer that was partly insoluble in benzene (benzene-insoluble fraction; $M_w = 8.2 \times 10^4$, $M_w/M_n = 11$) (Table I).

The present reaction is applicable to cyclic disilanes as well. Thus, 1,1,2,2-tetramethyl-1,2-disilacyclohexane (**1c**) and 1,1,2,2-tetramethyl-3,4,5,6-tetraphenyl-1,2-disila-3,5-cyclohexadiene (**1d**) underwent 1/1 copolymerization with **2b** to give phenylenedioxy unit containing regular polymers **3e**[4e] and **3f**,[4f] respectively (eq 2, Table I).

A mechanism that involves neat ring-opening polymerization of the cyclic monomers and subsequent insertion of quinones into the Si–Si bonds in the backbone[7] appears conceivable. However, the neat polymerization of **1a–c** did not take place ($PdCl_2(PEt_3)_2$ catalyst, 120 °C, 14 h). On the other hand, the reaction of **1a** with phenanthraquinone gave a silylene adduct (**5**) in 46% yield

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(4) Selected physical and spectral data of **3a–f** are as follows (mp, uncorrected; NMR $CDCl_3$, δ). (a) **3a**: mp 88–92 °C; ^{1}H NMR 0.08–0.66 (br m, 6 H, $SiCH_3$) 6.76–7.19 (br m, 2 H, 2,3-ring H of $OC_{10}H_6O$), 7.41 (br s, 2 H, 5,8-ring H of $OC_{10}H_6O$), 8.09 (br s, 2 H, 6,7-ring H of $OC_{10}H_6O$). (b) **3b**: mp 115–120 °C; ^{1}H NMR 0.30 (s, 6 H, $SiCH_3$), 6.78 (s, 4 H, OC_6H_4O). (c) **3c**: mp 127–132 °C; ^{1}H NMR 6.60–6.85 (br m, 2 H, 2,3-ring H of $OC_{10}H_6O$), 6.92–7.52 (br m, 6 H, *m,p*-H of SiC_6H_5), 7.62–7.89 (br m, 4 H, *o*-H of SiC_6H_5), 7.92–8.38 (br m, 4 H, 5,6,7,8-ring H of $OC_{10}H_6O$). (d) **3d** (benzene-soluble fraction): mp 84–90 °C; ^{1}H NMR 6.50–6.83 (br m, 4 H, OC_6H_4O), 7.12–7.50 (br s, 6 H, *m,p*-H of SiC_6H_5), 7.53–7.82 (br m, 4 H, *o*-H of SiC_6H_5). **3d** (benzene-insoluble fraction): mp >300 °C. (e) **3e**: mp 43–46 °C; ^{1}H NMR 0.18 (s, 12 H, $SiCH_3$), 0.69 (t, $J = 7.6$, 4 H, $SiCH_2$), 1.29–1.49 (m, 4 H, $SiCH_2CH_2$), 6.66 (s, 4 H, OC_6H_4O). (f) **3f**: mp 110–120 °C; ^{1}H NMR −0.40 (br s, 12 H, $SiCH_3$), 6.11–6.33 (m, 4 H, OC_6H_4O), 6.48–6.71 (br m, 4 H of CC_6H_5), 6.85–7.19 (br m, 16 H of CC_6H_5).

(5) The GPC curve of **3d** (benzene-soluble part) was bimodal: the area ratio of the higher fraction ($M_w = 3.2 \times 10^4$, $M_w/M_n = 1.8$) to the lower one ($M_w = 2.7 \times 10^3$, $M_w/M_n = 1.6$) was 0.8, suggesting the participation of at least two different copolymerization processes.

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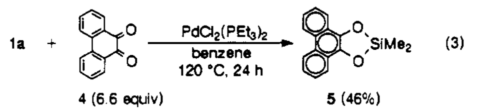
(eq 3). This may suggest silylene species are involved in the polymerization of *p*-quinones, similar to the polymerization of stable germylenes with quinones.[8] However, the silylene mechanism cannot be applied to cyclic disilanes. Further studies are awaited to propose the mechanism.



Since aromatic rings and Si–O bonds are thermally stable, the polymers obtained herein are expected to possess high heat resistance. In fact, thermogravimetric analyses (10 °C/min raising rate, 50 mL/min He stream) showed that the temperatures at 5% and 10% weight loss (T_5 and T_{10}) are 400 and 485 °C for **3c**, 380 and 480 °C for **3d** (soluble part), 250 and 400 °C for **3e**, and 390 and 410 °C for **3f**, respectively.

Supplementary Material Available: Physical, spectral, and analytical data of **3a–f** and **5** (2 pages). Ordering information is given on any current masthead page.

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Nucleophilic Attack at the Central Carbon of a Cationic (η^3-Propargyl)rhenium Complex

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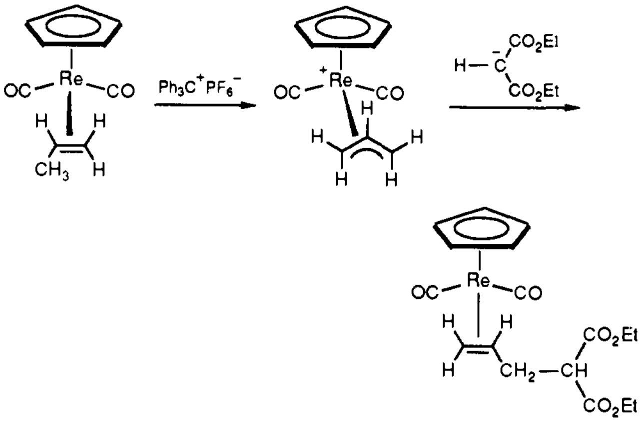
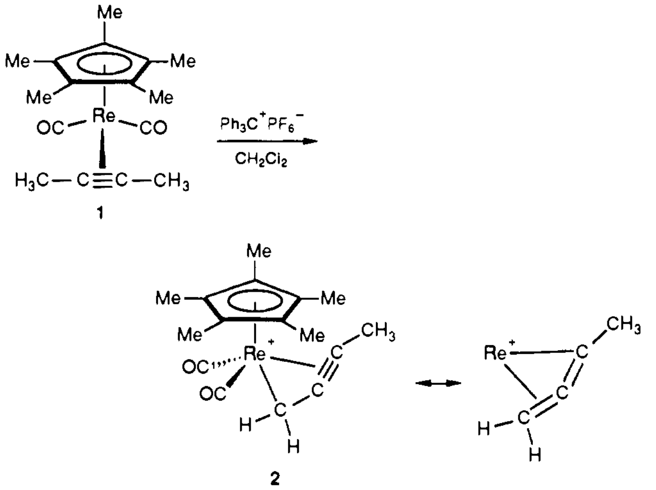
We recently reported an efficient synthesis of the cationic (η^3-allyl)rhenium complex $C_5H_5(CO)_2Re(\eta^3\text{-}CH_2CHCH_2)^+PF_6^-$ by hydride abstraction from the rhenium–propene complex $C_5H_5(CO)_2Re(CH_2{=}CHCH_3)$ with $Ph_3C^+PF_6^-$. The resulting cationic (η^3-allyl)rhenium complex reacted with carbon nucleophiles to produce elaborated rhenium–alkene complexes.[1] We have begun to explore the extension of this hydride abstraction process to rhenium–alkyne complexes. Here we report the synthesis of a cationic (η^3-propargyl)rhenium complex by hydride abstraction from a rhenium–alkyne complex and its reactions with nucleophiles at the central carbon of the propargyl unit to produce metallacyclobutene complexes.



The reaction of $C_5Me_5(CO)_2Re(THF)$[2] with a 5-fold excess of 2-butyne in THF at room temperature for 12 h gave an 85% yield of $C_5Me_5(CO)_2Re(CH_3C{\equiv}CCH_3)$ (**1**),[3] which was isolated as a yellow solid after column chromatography (silica gel, 3:1 hexane/Et_2O).



Hydride abstraction from the rhenium-2-butyne complex **1** produced the η^3-propargyl complex $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2C{\equiv}CCH_3)^+PF_6^-$ (**2**). Reaction of $Ph_3C^+PF_6^-$ (145 mg, 0.371 mmol) with **1** (160 mg, 0.371 mmol) in 10 mL of CH_2Cl_2 at room temperature for 1 h produced a dark brown solution. The solution was concentrated to ~5 mL, and diethyl ether was added. The resulting precipitate was filtered and washed with diethyl ether (3 × 10 mL) to give the pure cationic (η^3-propargyl)rhenium complex $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2C{\equiv}CCH_3)^+PF_6^-$ (**2**) (185 mg, 87%) as a pale brown solid.[4] The ^1H NMR spectrum of **2** in CD_2Cl_2 exhibited a downfield-shifted Cp* signal at δ 2.11, a methyl resonance at δ 2.58 (t, $J = 2.7$ Hz), and two doublets of quartets at δ 4.38 and 3.32, which were assigned to the inequivalent propargyl hydrogens coupled to each other ($J_{gem} = 10.1$ Hz) and to the methyl group ($^5J = 2.7$ Hz). In the coupled ^{13}C NMR spectrum of **2**, two singlets at δ 76.6 and 56.7 were assigned to the quarternary propargyl carbons and a triplet ($J = 170.0$ Hz) at δ 29.0 was assigned to the terminal propargyl CH_2. The propargyl carbon chemical shifts of **2** were similar to those previously reported for η^3-propargyl complexes.[5] In the IR spectrum of **2**, two strong CO bands were observed at 1974 and 1904 cm^{-1}.

η^3-Propargyl complexes are rare. Werner[5] reported the first η^3-propargyl complex, $(Me_3P)_4Os(\eta^3\text{-}PhC{\equiv}CC{=}CHPh)^+PF_6^-$. Related Ru,[6,7] W,[8] and Fe[9] complexes which also have a =CHR group attached to the propargyl terminus have been reported. The

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(3) See supplementary material for full characterization data.

(4) For $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2C{\equiv}CCH_3)^+PF_6^-$ (**2**): ^1H NMR (CD_2Cl_2, 500 MHz) δ 4.38 (dq, $J = 10.1, 2.7$ Hz, ReC*H*H), 3.32 (dq, $J = 10.1, 2.7$ Hz, ReCH*H*), 2.58 (t, $J = 2.7$ Hz, $\equiv CCH_3$), 2.11 (s, C_5Me_5); ^{13}C NMR (CD_2Cl_2, 126 MHz) δ 198.0 and 195.3 (s, CO's), 106.2 (s, C_5Me_5), 76.6 (s, $\equiv \mathit{C}CH_3$), 56.7 (s, $\mathit{C}{\equiv}CCH_3$), 29.0 (t, $J = 170.0$ Hz, CH_2), 10.1 (q, $J = 129.7$ Hz, $C_5\mathit{Me}_5$), 8.2 (q, $J = 134.1$ Hz, $\equiv C\mathit{C}H_3$); IR (Nujol) 2028 (s), 1954 (s), 838 (s), 722 (w) cm^{-1}; IR (THF) 1974 (s), 1904 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{20}O_2RePF_6$: C, 33.39; H, 3.50. Found: C, 33.24; H, 3.61.

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