methylene protons of the three 1-phenyl-substituted metallacycles **3a**, **4a**, and **5a** appear as a pair of well-resolved doublets in the room-temperature ^{1}H NMR. No significant broadening of the signal occurs on warming to 90 °C. In contrast, the diastereotopic methylene protons of the 1-halo-substituted metallacycles **3b**,**c**, **4b**,**c**, and **5b**,**c** undergo a concentration-dependent exchange reaction. In sufficiently dilute solution ($M \leq 0.015$), the diastereotopic protons of these compounds appear as well-resolved doublets at room temperature; the spectra are virtually identical in the methylene region with the spectra of the phenyl-substituted metallacycles. We attribute the fluxional behavior exhibited by the halometallacycles to a reversible halide exchange reaction. This conclusion is supported by crossover experiments between **4c** and **5b** which indicate that a rapid halide exchange is occurring in solution.[14]

Investigations of the properties and reactivity of these and related main-group metallacycles are in progress.

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Supplementary Material Available: An experimental section containing the preparation and spectroscopic characterization of compounds, crystallographic data and procedures, ORTEP diagrams of **4a** and **5c**, tables of bond distances and angles, tables of final positional and thermal parameters, and tables of least-squares planes (37 pages); listings of structure factors (20 pages). Ordering information is given on any current masthead page.

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(14) A full analysis of the fluxional behavior and reactivity of these compounds will be reported in a full paper.

Polymeric Organosilicon Systems. 5. Synthesis of Poly[(disilanylene)butenyne-1,4-diyls] with Highly Conducting Properties

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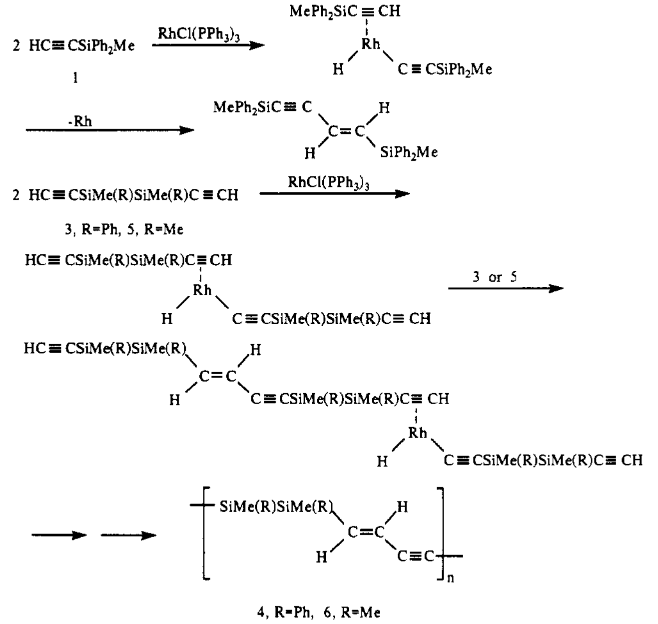
Summary: The reaction of 1,2-diethynyl-1,2-dimethyl-1,2-diphenyl- and 1,2-diethynyltetramethyldisilane with a catalytic amount of $RhCl(PPh_3)_3$ in toluene at room temperature afforded the respective poly[(disilanylene)butenyne-1,4-diyls]. Treatment of the films of these polymers with SbF_5 vapor gave the conducting films.

During the course of our investigation on the C-H bond activation of ethynylsilanes by a transition metal complex,[1-3] we have found that treatment of 1,2-diethynyldisilanes with a catalytic amount of $RhCl(PPh_3)_3$ readily affords a new type of polymers, poly[(disilanylene)butenyne-1,4-diyls], in which the alternate arrangement of a disilanylene unit and an enyne group is found regularly in the polymer backbone. The advantage of this route is that no alkali-metal condensation is involved in all processes.

Scheme I



First, we investigated the reaction of an ethynyl-substituted monosilane with a rhodium catalyst. Thus, when a mixture of ethynylmethyldiphenylsilane (**1**) and a 5 mol % of $RhCl(PPh_3)_3$ in toluene was stirred at room temperature for 24 h, (*E*)-1,4-bis(methyldiphenylsilyl)-1-buten-3-yne (**2**) was obtained in 94% yield (Scheme I). No regio- and stereoisomers were detected in the reaction mixture by either GLC or spectrometric analysis. All spectral data obtained for **2** were identical with those of an authentic sample reported previously.[1]

Interestingly, the reaction of 1,2-diethynyl-1,2-dimethyldiphenyldisilane[4] (**3**) with a rhodium catalyst gave poly[(1,2-dimethyldiphenyldisilanylene)butenyne-1,4-diyl] (**4**) with high molecular weight.[5] The diethynyldisilane **3** used as the starting monomer could readily be obtained by the reaction of ethynylmagnesium bromide prepared from acetylene and ethylmagnesium bromide, with 1,2-dichloro-1,2-dimethyldiphenyldisilane in THF. When a mixture of 2.051 g (7.1 mmol) of **3** and 2 mol % of $RhCl(PPh_3)_3$ in 10 mL of toluene was stirred under an argon atmosphere at room temperature for 2 days, a viscous brown solution that has no insoluble substances was obtained. The solution was poured into ethanol, and the

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(1) Ishikawa, M.; Ohshita, J.; Ito, Y.; Minato, A. *J. Organomet. Chem.* **1988**, *349*, C58.

(2) Ishikawa, M.; Ohshita, J.; Ito, Y. *Organometallics* **1986**, *5*, 1518.

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(4) Compound **3**: bp 138–140 °C (1.0 mmHg); mp 34–36 °C; IR $\nu_{C\equiv C-H}$ 3280, $\nu_{C\equiv C}$ 2040 cm^{-1}; ^{1}H NMR (δ in CCl_4) 0.48, 0.54 (6 H, s, MeSi), 2.56 (2 H, s, HC≡C), 7.2–7.8 (10 H, m, phenyl ring protons). Anal. Calcd for $C_{18}H_{18}Si_2$: C, 74.42; H, 6.24. Found: C, 74.35; H, 6.10.

(5) Compound **4**: mp 90–95 °C; ^{1}H NMR (δ in CCl_4) 0.47 (6 H, br s, MeSi), 5.93 (1 H, d, J = 19 Hz, olefinic proton), 6.66 (1 H, d, J = 19 Hz, olefinic proton), 6.87–7.91 (10 H, m, phenyl ring protons); ^{13}C NMR ($CDCl_3$) δ −5.7, −5.4, −3.9, −3.8 (MeSi), 91.2, 91.3, 91.5, 91.6, 109.81, 109.84, 109.9 (C≡C), 125.8, 125.9 (C=C), 127.86, 127.93, 127.97, 128.1, 129.3, 134.4, 134.5, 134.6, 134.7, 134.8, 134.9 (phenyl ring carbons), 142.5, 142.8 (C=C); IR $\nu_{C\equiv C}$ 2146 cm^{-1}; UV (film) λ_{max} 294 nm.

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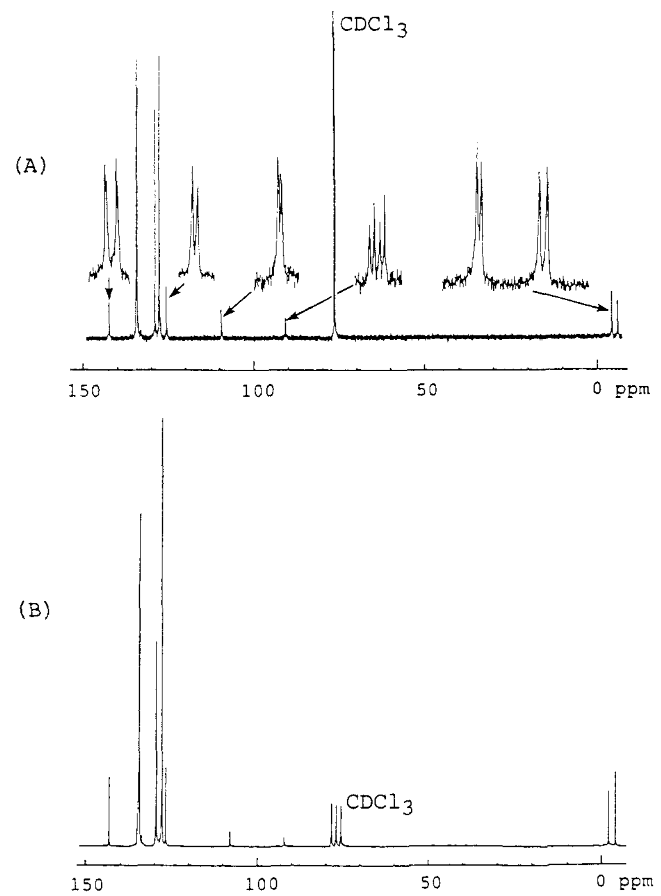

Figure 1. Decoupled ^{13}C NMR spectra: (A) poly[(1,2-dimethyldiphenyldisilanylene)butenyne-1,4-diyl] (**4**) (125 MHz); (B) (*E*)-1,4-bis(methyldiphenylsilyl)-1-buten-3-yne (**2**) (22.5 MHz).

resulting substance was reprecipitated twice from benzene-ethanol to give a light yellow polymer in 73% yield. The polymer thus obtained is soluble in common organic solvents such as benzene, toluene, chlorocarbons, and ethers and melts at 90–95 °C without decomposition. Molecular weight of **4** was determined to be $\overline{M}_w = 117000$ relative to polystyrene standards ($\overline{M}_w/\overline{M}_n = 6.1$). The presence of the (disilanylene)butenyne structure in the polymer backbone was confirmed by its ^{13}C NMR spectrum. Thus, the ^{13}C NMR spectrum of **4** shows resonances at 91.2, 91.3, 91.5, 91.6, 109.81, 109.84, 109.9 ppm and 125.8, 125.9, 142.5, 142.8 ppm, due to ethynylic and ethylenic carbons, respectively. These chemical shifts are consistent with those of product **2** as shown in Figure 1. The existence of four nonequivalent resonances for methylsilyl carbons of **4** indicates that the C–H bond activation by a rhodium complex occurs in the ethynyl group of the starting monomer and of the polymeric systems.

Recently, it has been reported that the reaction of α,ω-bis(ethynyldimethylsilyl)-substituted compounds involving 1,2-diethynyltetramethyldisilane[6] with a tungsten chloride catalyst resulted in formation of polyenes arising from cyclopolymerization.[7] In the present case, however, 1,2-diethynyltetramethyldisilane (**5**) reacted with a rhodium catalyst at room temperature to give poly[(tetramethyldisilanylene)butenyne-1,4-diyl] (**6**) whose molecular weight was calculated to be $\overline{M}_w = 28000$ by GPC ($\overline{M}_w/\overline{M}_n = 13.0$).

Polymers **4** and **6** can be cast to a thin film by spin coating of their methylene chloride solution. The polymers exhibit strong absorption at near 290 nm and are photoactive in the ultraviolet. Irradiation of thin solid films of **4** and **6** with a low-pressure mercury lamp in air led to the disappearence of the absorption at near 290 nm indicating that homolytic scission of silicon–silicon bonds in the polymer backbone occurred, as observed in the photolysis of poly[*p*-(disilanylene)phenylene].[9]

To our surprise, when the films of **4** and **6** were doped by exposure to vapor of SbF_5, the conducting films were obtained. The conductivity determined by the four-probe method showed to be 1.09 S·cm^{-1} for **4** and 0.02 S·cm^{-1} for **6**, respectively.[10]

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(8) Compound **6**: mp >300 °C; ^{1}H NMR (δ in $CDCl_3$) 0.13 (3 H, s, MeSi), 0.23 (3 H, s, MeSi), 0.22 (3 H, s, MeSi), 0.29 (3 H, s, MeSi), 5.90 (1 H, d, J = 19 Hz, olefinic proton), 5.96 (1 H, d, J = 19 Hz, olefinic proton); ^{13}C NMR (δ in $CDCl_3$) −4.6, −4.5, −3.0, −2.9 (MeSi), 92.8, 93.0, 108.0 ($C{\equiv}C$), 123.9, 124.1, 144.7, 145.0 ($C{=}C$); IR $\nu_{C\equiv C}$ 2149 cm^{-1}; UV (film) λ_{max} 293 nm.

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Iodinolysis of the Co–C Bond in *trans*-Bis(dimethylglyoximato)alkyl(4-cyanopyridine)cobalt(III) Complexes: Evidence for a Bimolecular Oxidative Mechanism

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Summary: The iodinolysis of $4CNpyCo(DH)_2R$ (4CNpy = 4-cyanopyridine; R = CH_3, CH_2CH_3, $CH_2CH_2CH_3$, $CH(CH_3)_2$, $CH_2C_6H_5$, CH_2CF_3) in benzene solution is first-order with respect to both the concentration of organocobalt(III) complex and iodine. The appearance of a transient EPR signal due to an organocobalt(IV) intermediate and the strong correlation of the logarithm of the pseudo-first-order rate constants for iodinolysis with reversible oxidation potentials along with other pertinent observations strongly suggest that the rate-limiting step of the reaction is oxidation of the six-coordinate organocobalt(III) complex by iodine.

The mechanism of the cleavage of cobalt–carbon (Co–C) bonds in vitamin B_{12} model compounds by molecular halogens has been the object of intense study[1,2] ever since it was demonstrated that iodinolysis of the Co–C bond in coenzyme B_{12} and $[CH_3Co(CN)_5]^{3-}$ gives 5′-iodo-5′-deoxy-

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