$RuCl_2]_2$, (TMT)$RuCl_2(PR_3)$, and (TMT)$RuCl_2(NH_2R)$.[3] The reduced character on the thiophene ring is further suggested by the extremely high-field ^{13}C NMR shifts for one pair of the TMT ring carbons, the assignment being established by long-range ^1H–^{13}C chemical shift correlation spectroscopy. This very high-field ring carbon also features the largest value of $J(^{103}Rh,^{13}C)$.

A crystallographic analysis of a low quality crystal of $[1]^0$ confirms its assignment as $(\eta^5\text{-}C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)$.[10] In each of the three crystallographically independent molecules, the rhodium atom is bound to nine carbon atoms and the sulfur atom is oriented away from the rhodium atom, out of the plane of the carbon atoms in the TMT ring (Scheme I). A full paper will present a detailed comparison of the structures of $[1](OTf)_2$ and $[1]^0$, contingent on the availability of suitable crystals.

The η^4-thiophene ligand in $[1]^0$ desulfurizes upon reaction with $Fe_3(CO)_{12}$ (toluene solution, 110 °C, 18 h) to give a good yield of the bright yellow compound Cp*Rh(C_4Me_4)$Fe(CO)_3$ (**2**). On the basis of spectroscopic and analytical data, this compound[11] is assigned as a symmetrical metallacycle analogous to the ferroles $Fe_2C_4R_4(CO)_6$ isolated from the reaction of $Fe_3(CO)_{12}$ and thiophenes (see Scheme I).[2,12] The conversion $[1]^{2+} \rightarrow [1]^0 \rightarrow 2$ involves a net replacement of a vertex on a nido RhC_4X cluster.

To summarize, we have shown that electron transfer can induce a change in hapticity from η^5- to η^4-thiophene (Scheme I). The metal ion facilitates the buckling (dearomatization?) of the thiophene ring since we found that TMT itself is not reduced in the range 0 to −2 V vs Ag/AgCl. On the basis of these results, η^4-thiophene intermediates should be considered whenever thiophenes encounter reduced metal centers as is frequently the case in the catalytic[1] and stoichiometric[13] desulfurization of thiophenes.

Compound $[1]^0$ is highly reactive and well behaved; it is therefore a likely source of new developments in thiophene coordination chemistry.

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Supplementary Material Available: Experimental conditions for crystallography, tables of atomic coordinates, bond distances, and bond angles, and ORTEP drawings (15 pages); a listing of structure factors (13 pages). Ordering information is given on any current masthead page.

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(10) Crystal data: red transparent crystal, 0.2 × 0.4 × 0.6 mm, orthorhombic $P2_12_12_1$ (D_2^4 – No. 19); $a = 35.513$ (22), $b = 10.411$ (5), $c = 14.053$ (4) Å; $Z = 12$; $\rho_{calcd} = 1.451$ g/cm³. Diffraction data: Enraf-Nonius CAD4 automated diffractometer, Mo radiation (Kα, $\lambda = 0.71073$ Å), graphite monochromator, range $2.0 < 2\theta < 46.0°$ for $-h,-k,+l$ and $2.0 < 2\theta < 8.0°$ for $\pm h,\pm k,\pm l$, 4348 reflections, 4081 unique data, 2315 observed ($I > 2.58\sigma(I)$); corrected for anomalous dispersion, absorption, Lorentz, and polarization effects. Least-squares refinement of 2315 structure factors converged at $R = 0.130$ and $R_w = 0.15$.

(11) Anal. Calcd for $C_{21}H_{27}FeO_3Rh$: C, 51.85; H, 5.60. Found: C, 51.85; H, 5.64. ^1H NMR (benzene-d_6): δ 2.29 (s, 6 H), 1.43 (s, 15 H), 1.31 (s, 6 H). ^{13}C NMR (acetone, $J(^{103}Rh,^{13}C)$ values (Hz) in parentheses): δ 167.62 (C_4Me$_4$, 18.3), 113.16 (C_4Me$_4$), 97.13 (C_5Me$_5$, 7.3), 28.50 (C$_4$$Me_4$), 12.30 (C$_4$$Me_4$), 9.80 ($C_5Me_5$). FDMS: 486 ($M^+$ for ^{56}Fe). IR (hexane, cm^{-1}): 1994, 1939, 1935 (sh). Also isolated were trace amounts of two red compounds formulated as isomers of $[Cp^*Rh]_2FeS(CO)_4$ based on ^1H NMR spectroscopy (isomer A, δ 1.69; isomer B, δ 1.59), IR [isomer A (hexanes), ν_{CO} 2012, 1967, 1954 cm^{-1}; isomer B (CH_2Cl_2), ν_{CO} 1931 (br), 1758, 1751 cm^{-1}], and FDMS (676, M^+ for ^{56}Fe).

(12) Dettlaf, G.; Weiss, E. *J. Organomet. Chem.* **1976**, *108*, 213. Hübener, P.; Weiss, E. *Ibid.* **1977**, *129*, 105.

(13) Raney nickel is widely used for stoichiometric thiophene desulfurization. A recent review emphasizes that this family of alloys are "extremely useful reducing agents": Keefer, L. K.; Lunn, G. *Chem. Rev.* **1989**, *89*, 459.

(14) **Note Added in Proof.** The structure of **2** has been confirmed by X-ray crystallography.

Polymeric Organosilicon Systems. 7. Ring-Opening Polymerization of 1,2,5,6-Tetrasilacycloocta-3,7-diynes

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Summary: Treatment of 1,2,5,6-tetramethyl(tetraphenyl)- and 1,2,5,6-tetraethyl(tetramethyl)-1,2,5,6-tetrasilacycloocta-3,7-diyne with a catalytic amount of *n*-butyllithium in THF at room temperature led to ring-opening polymerization to give the respective poly[(disilanylene)ethynylenes] with high molecular weights. Treatment of the films of these polymers with SbF_5 vapor produced highly conducting films.

Recently, we have demonstrated that the polymers in which the regular alternating arrangement of a disilanyl unit and the π-electron system such as a phenylene,[1,2] ethenylene,[3] and butenyne group[4] is found in the polymer backbone are photoactive and show conducting properties when the polymers are doped by exposure to vapor of SbF_5.

During the course of our studies concerning the synthesis of the disilanylene-containing polymers that can be used as functional material, we have discovered that treatment of 1,2,5,6-tetrasilacycloocta-3,7-diynes[5,6] with a catalytic amount of *n*-butyllithium led to ring opening polymerization to give poly[(disilanylene)ethynylenes] with high molecular weight.

The starting 1,2,5,6-tetramethyl(tetraphenyl)-1,2,5,6-tetrasilacycloocta-3,7-diyne[7] (**2a**) was prepared as follows:

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(1) Ishikawa, M.; Nate, K. *Inorganic and organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington DC, 1988; Chapter 16.

(2) Treatment of the film of poly[*p*-(1,2-dimethyldiphenyldisilanylene)phenylene] with SbF_5 gave a highly conducting film whose conductivity was found to be 1.75 S·cm^{-1}.

(3) Ohshita, J.; Kanaya, D.; Ishikawa, M.; Yamanaka, T. *J. Organomet. Chem.* **1989**, *369*, C18.

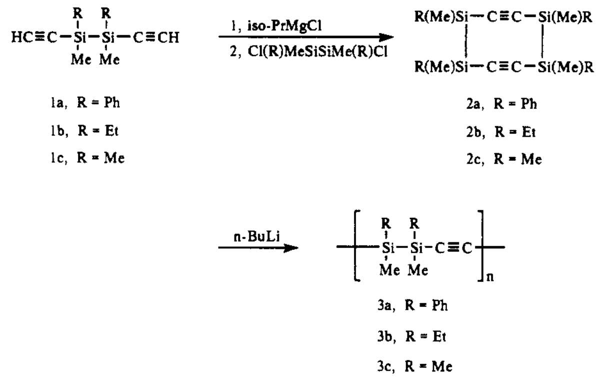
(4) Ohshita, J.; Furumori, K.; Ishikawa, M.; Yamanaka, T. *Organometallics* **1989**, *8*, 2084.

(5) Sakurai, H.; Nakadaira, Y.; Hosomi, A.; Eriyama, Y.; Kabuto, C. *J. Am. Chem. Soc.* **1983**, *105*, 3359.

(6) Iwahara, T.; West, R. *J. Chem. Soc., Chem. Commun.* **1988**, 594.

(7) Compound **2a**: mp 200–202 °C; MS *m/e* 528 (M^+); IR 1428, 1249, 1108 cm^{-1}; UV λ_{max} (log ϵ) 252 nm (4.35); ^1H NMR (δ in $CDCl_3$) 0.40 (12 H, s, MeSi), 7.36–7.74 (20 H, m, phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) −4.4 (MeSi), 119.9 ($C{\equiv}C$), 128.2, 129.5, 133.8, 134.3 (phenyl ring carbons). Anal. Calcd for $C_{32}H_{32}Si_4$: C, 72.61; H, 6.08. Found: C, 72.66; H, 6.10.

Scheme I



the di-Grignard reagent prepared from 1,2-diethynyl-1,2-dimethyldiphenyldisilane (**1a**) and isopropylmagnesium chloride was allowed to react with 1,2-dichloro-1,2-dimethyldiphenyldisilane in THF. The mixture was heated to reflux for 15 h, and then it was hydrolyzed with water. After the solvent was evaporated, the residue was chromatographed on silica gel eluting with benzene. The resulting crystals were recrystallized from benzene to give **2a** in 20% yield as a single isomer. Similar treatment of a di-Grignard reagent of 1,2-diethyl-1,2-diethynyldimethyldisilane (**1b**) with 1,2-dichloro-1,2-diethyldimethyldisilane afforded 1,2,5,6-tetraethyl(tetramethyl)-1,2,5,6-tetrasilacycloocta-3,7-diyne[8] (**2b**) in 47% yield.

The anionic ring-opening polymerization was carried out with the use of *n*-butyllithium as a catalyst in THF at room temperature. Thus, a mixture of 1.37 mmol of 1,2,5,6-tetrasilacycloocta-3,7-diyne (**2a**) with a catalytic amount of *n*-butyllithium (1.7 mol %) in 5 mL of dry THF[9] was stirred at room temperature in a sealed glass tube for 64 h. The mixture was poured into ethanol, and the resulting white-yellow solid was reprecipitated twice from benzene–ethanol to give 0.253 g (35% yield) of poly[(1,2-dimethyldiphenyldisilanylene)ethynylene] (**3a**)[10] (Scheme I). Molecular weight of the polymer **3a** was determined to be $\bar{M}_w = 8.08 \times 10^4$ ($\bar{M}_w/\bar{M}_n = 4.08$), relative to polystyrene standards. The polymer **3a** melts at 60–85 °C without decomposition and is soluble in common organic solvents, such as benzene, ethers, and halocarbons.

The structure of **3a** was verified by IR and ^{1}H and ^{13}C NMR spectroscopic analysis.[11] The ^{13}C NMR spectrum revealed a single resonance at 114.4 ppm, indicating the presence of ethynylene carbons in the polymer chain.

The ring-opening polymerization catalyzed by butyllithium is remarkably general for tetrasilacycloocta-3,7-diynes. In fact, alkyl-substituted tetrasilacycloocta-3,7-diynes readily undergo ring-opening polymerization. Thus, when a solution of 1,2,5,6-tetraethyl(tetramethyl)-1,2,5,6-tetrasilacycloocta-3,7-diyne (**2b**) is stirred in the presence of a catalytic amount of *n*-butyllithium in THF at room temperature for 40 h, poly[(1,2-diethyldimethyldisilanylene)ethynylene][12] (**3b**) was obtained as a white solid in 92% yield. The polymer **3b** melts at 140–145 °C and is soluble in common organic solvents. The molecular weight of **3b** determined by GPC was calculated to be $\bar{M}_w = 1.05 \times 10^5$ ($\bar{M}_w/\bar{M}_n = 3.25$). The ^{13}C NMR spectrum of **3b** reveals a resonance at 114.2 ppm, indicating the presence of the ethynylene group.

Similar reaction of 1,1,2,2,5,5,6,6-octamethyltetrasilacycloocta-3,7-diyne[5] (**2c**) with *n*-butyllithium under the same conditions gave a white polymer, poly[(tetramethyldisilanylene)ethynylene] (**3c**). In contrast to the ring-opening polymerization of **2a** and **2b**, in which no insoluble polymers were formed, in the case of **2c**, the precipitation of the polymers was observed in the early stages of the polymerization. The polymer **3c** thus obtained did not melt but decomposed at 205–210 °C and was scarecely soluble in common organic solvents. Insolubility for this polymer may be ascribed to the high crystallinity.

The polymer **3a** and **3b** can be cast to the film by spin coating of their methylene chloride solution. Characteristic of the polymers **3a** and **3b** is a strong absorption at 242 nm in the ultraviolet region. As expected, **3a** and **3b** are highly photoactive. Thus, irradiation of thin solid films of **3a** and **3b** with a low-pressure mercury lamp in air led to the disappearance of this absorption, indicating that homolytic scission of silicon–silicon bonds in the polymer backbone occurred, as observed in the photolyses of the polymers composed of a disilanylene unit and a π-electron system as a repeating unit.[1,3,4]

Interestingly, when the films of **3a** and **3b** were treated with SbF_5 vapor, the highly conducting films were obtained. The conductivity determined by the four-probe method was found to be 0.41 S·cm^{-1} for **3a** and 1.96 S·cm^{-1} for **3b**, respectively.[13]

Aluminum chloride also acts as a catalyst for ring-opening polymerization of **3a** and **3b**. However, at present, the molecular weights of the resulting polymers were determined to be 2500–4000.

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[8] Compound **2b**: mp 30–32 °C; MS *m/e* 336 (M$^+$); IR 1248, 1008, 955 cm^{-1}; UV λ_{max} (log ϵ) 211.0 (4.04), 248 nm (4.19); ^{1}H NMR (δ in $CDCl_3$) 0.22 (12 H, s, MeSi), 0.57–1.16 (20 H, m, EtSi); ^{13}C NMR (δ in $CDCl_3$) −5.1 (MeSi), 6.1 and 8.1 (EtSi), 119.5 (C≡C). Anal. Calcd for $C_{16}H_{32}Si_4$: C, 57.06; H, 9.58. Found: C, 57.27; H, 9.47.

[9] The solvent THF used for polymerization was dried over sodium–potassium alloy and transferred into a glass tube under reduced pressure.

[10] In this reaction, no insoluble polymers were formed. The evaporation of the solvent used in the reprecipitation of the polymer **3a** gave 0.38 g of yellow liquid.

[11] Polymer **3a**: mp 60–85 °C; IR 1428, 1248, 1108 cm^{-1}; UV λ_{max} (in solid film) 242.0 nm, λ_{max} (in THF) 249.0 nm; ^{1}H NMR (δ in $CDCl_3$) 0.42 and 0.55 (6 H, br s, MeSi), 7.02–7.80 (10 H, m, phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) −3.9 (MeSi), 114.4 (C≡C), 127.8, 129.2, 133.6, 134.5 (phenyl ring carbons).

[12] Polymer **3b**: mp 140–145 °C; IR 1248, 1011, 957 cm^{-1}; UV λ_{max} (in solid film) 242.0, λ_{max} (in THF) 247.0 nm; ^{1}H NMR (δ in $CDCl_3$), 0.21 and 0.20 (6 H, s, MeSi), 0.56–1.16 (10 H, m, EtSi); ^{13}C NMR (δ in $CDCl_3$) −4.9 and −4.8 (MeSi), 6.3, 8.1 (EtSi), 114.2 (C≡C).

[13] For conducting polysilane, see: West, R.; David, L. D.; Djurovich, L.; Stearley, K. L.; Srinivasan, K. V. S.; Yu, H. *J. Am. Chem. Soc.* 1981, *103*, 7352.

1,3-Scrambling of Chlorine in $RhCl(PPh_3)_3$-Catalyzed Decarbonylations of Allylic Acid Chlorides

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Summary: Reactions of $RhCl(PPh_3)_3$ with *trans*-3-pentenoyl chloride (at −20 °C), mixtures of *cis-/trans*-3-pentenoyl chloride (at −20 °C), and 2-methyl-3-butenoyl chloride (at room temperature) in $CDCl_3$ all produced the