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Synthesis and Polymerization of 5-Silaspiro[4.4]nona-2,7-dienes

Young Tae Park, Stephen Q. Zhou, Georges Manuel, and William P. Weber*

Donald P. and Katherine B. Loker Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661

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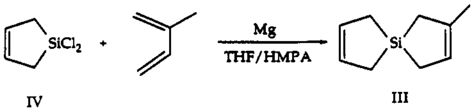
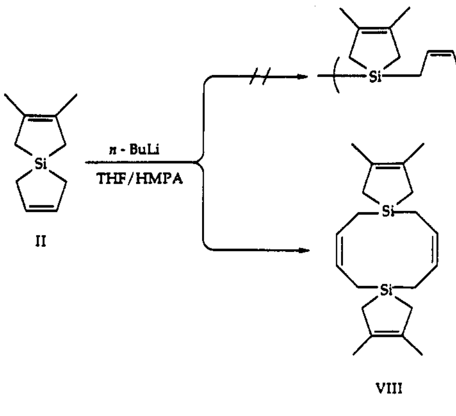
ABSTRACT: Symmetrical and unsymmetrical 5-silaspiro[4.4]nona-2,7-dienes have been prepared. Ring-opening reactions of these dienes catalyzed by alkyllithium reagents and hexamethylphosphoramide (HMPA) in THF lead to dimers, oligomers, and polymers of unusual structure. Thermal degradation of these results in high char yields.

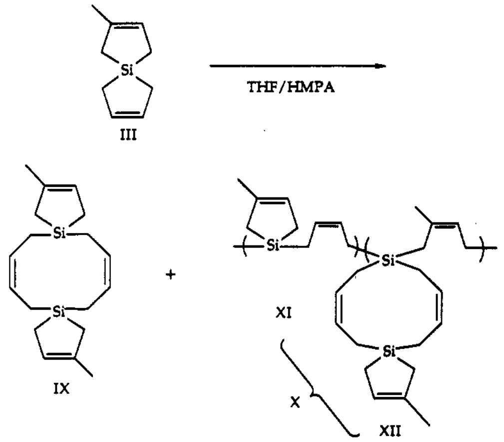
While a few symmetrical 5-silaspiro[4.4]nona-2,7-dienes have been synthesized,[1-3] no unsymmetrically substituted examples of this ring system are known. We have prepared 5-silaspiro[4.4]nona-2,7-diene (I), 2,3-dimethyl-5-silaspiro-[4.4]nona-2,7-diene (II), and 2-methyl-5-silaspiro[4.4]-nona-2,7-diene (III) by the dissolving-metal (Mg) reaction of 1,1-dichlorosilacyclopent-3-ene (IV) with 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, and 2-methyl-1,3-butadiene, respectively. The recently reported preparation of IV from readily available starting materials makes this synthetic route feasible.[4]



We anticipated that treatment of II with catalytic amounts of alkyllithium reagent and HMPA in THF at low temperature would result in a polymer formed by the selective ring opening of the unsubstituted 1-silacyclopent-3-ene ring of II. Such a polymer, poly(3,4-dimethyl-1-silacyclopent-3-en-1-ylidene-*cis*-but-2-en-1,4-ylene), would have 1,4-(cis-but-2-ene) units bonded to the silicon atoms of the 3,4-dimethyl-1-silacyclopent-3-ene rings. This expectation was based on our previous work, which has shown that, while 1,1-dimethyl-1-silacyclopent-3-ene (V) undergoes polymerization under these conditions to yield poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) (VI),[5] 1,1,3,4-tetramethyl-1-silacyclopent-3-ene (VII) does not.[6] In fact, treatment of II under these conditions has been shown to result in almost quantitative formation of a dimer, 2,3,-12,13-tetramethyl-5,10-disiladispiro[4.4.4.4]octadeca-2,7,-12,16-tetraene (VIII).[7]



Similar reaction of III with catalytic amounts of alkyllithium reagents and HMPA led to a mixture of a dimer, 2,12-dimethyl-5,10-disiladispiro[4.4.4.4]octadeca-2,7,12,-16-tetraene (IX), and oligomer (X). The latter is made up of 3-methyl-1-silacyclopent-3-en-1-ylidene-*cis*-but-2-en-1,4-ylene (XI) and 8-methyl-1,6-disilaspiro[4.9]tetradeca-3,8,12-trien-1-ylidene-2-methyl-*cis*-2-en-1,4-ylene (XII) units.



The following product ratio and M_w/M_n were obtained with methyllithium as initiator: III (13%), IX (42%), X (41%), M_w/M_n = 1120/950. On the other hand, when *n*-butyllithium was utilized, IX (36%), X (58%), and M_w/M_n = 3200/1600 were found. The structure of IX is based on its molecular weight, determined by mass spectrometry, as well as comparison of its ^{1}H, ^{13}C, and ^{29}Si NMR spectral data with those observed for VIII. In particular, the ^{1}H NMR signals for the vinyl hydrogens of IX are found at 5.50 and 5.30 ppm in a 1:2 ratio. The former is assigned to the vinyl hydrogens of the 3-methyl-1-silacyclopent-3-ene rings. For comparison, the vinyl hydrogen of 1,1,3-trimethyl-1-silacyclopent-3-ene (XIII) is found at 5.40 ppm.[5] The resonance at 5.30 ppm of IX is assigned to the vinyl hydrogens of the 1,4-(*cis*-but-2-ene) units of the ten-membered 1,6-disiladeca-3,8-diene ring system of IX. This chemical shift is almost identical with that of the vinyl hydrogens of VI, which is found at 5.29 ppm. Likewise, the vinyl and allyl ^{13}C and ^{29}Si resonances of IX can be assigned by comparison with those of XIII, VIII, and VI (see Table I).

The formation of the dimer IX can be rationalized by the following mechanistic proposal. Anionic attack by an alkyllithium reagent on the silyl center of III leads to a pentacoordinate hypervalent silicon species (XIV).[5,6] While both V and XIII undergo polymerization under these conditions to yield respectively VI and poly(1,1,3-trimethyl-1-sila-*cis*-pent-3-ene) (XV), it is apparent that the unsubstituted ring of XIV opens preferentially to form a *cis*-allyl anion intermediate (XVI) which reacts with another molecule of III to form a new hypervalent siliconate species (XVII). This process must occur faster than rotation about the partial carbon-carbon double bonds of the *cis*-allyl anion which would convert it into a *trans*-allyl anion. This is reasonable since energy barriers

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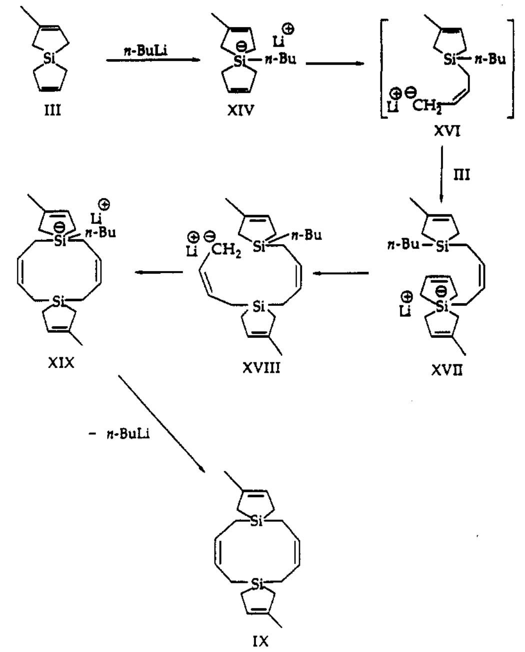
of at least 10 kcal/mol have been observed for this type of isomerization process.[8-10] Ring opening of the unsubstituted five-membered ring of XVII leads to a new *cis*-allyl anion intermediate (XVIII). This may react intramolecularly to establish the central ten-membered ring of IX and form a new hypervalent siliconate species XIX which loses a molecule of alkyllithium to give IX.



Formation of oligomer X results from intermolecular reaction of the *cis*-allyl anion XVIII with either a molecule of III or IX to form new hypervalent siliconate species XX or XXI, respectively. Ring opening of the unsubstituted silacyclopent-3-ene of XX results in a new reactive *cis*-allyl anion and formation of an XI unit of the oligomer product X. On the other hand, ring opening of the 3-methyl-1-silacyclopent-3-ene ring of XXI leads to formation of an XII unit of oligomer X.

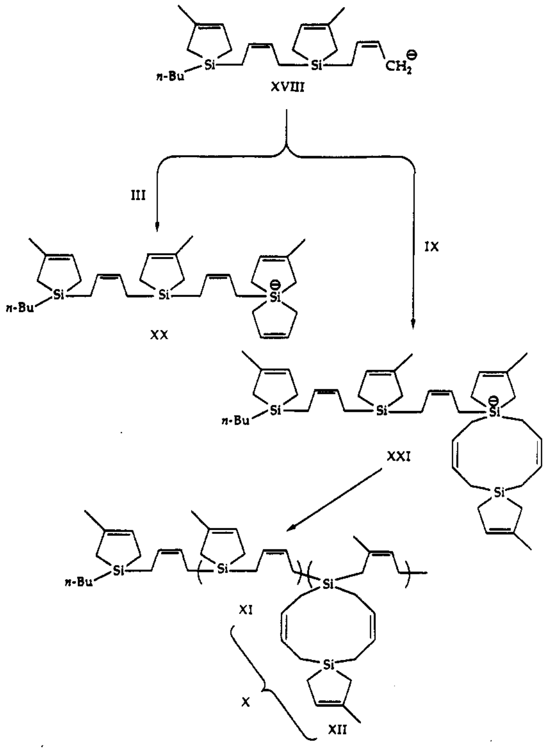
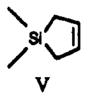
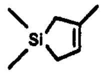
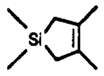
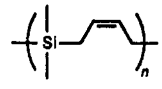
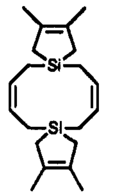
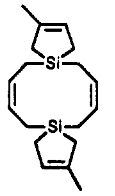


Table I
^{1}H, ^{13}C, and ^{29}Si NMR Chemical Shifts (ppm)

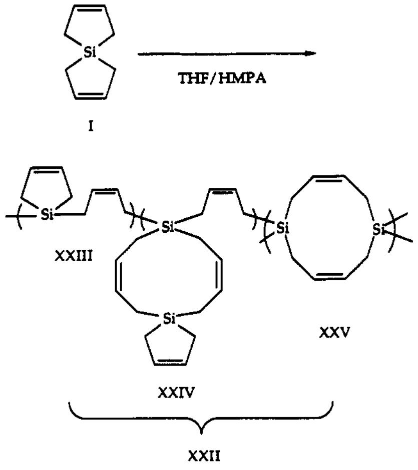
	^{1}H$_{vinyl}$	^{13}C$_{vinyl}$	^{13}C$_{allyl}$	^{13}C$_{methyl}$	^{29}Si
 V	5.73	130.74	17.80	-2.30	16.5
 XIII	5.40	124.74 139.69	18.90 22.47	-1.84 23.09	17.88
 VII		130.56	25.67	-1.89 19.22	9.88
 VI	5.29	123.22	16.47	-3.41	2.17
 VIII	5.30	122.92 130.58	14.06 22.99	19.34	11.87
 IX	5.30 5.50	122.88 124.59 140.01	14.15 16.22 22.64	20.42	20.59

The ^{1}H NMR of oligomer X is consistent with a random copolymer made up of XI and XII units. Four signals due to vinyl hydrogens are observed. A broad singlet at 5.31 ppm is assigned to the vinyl hydrogen of the 1,4-(*cis*-but-2-ene) units present in both XI and XII. For comparison, the vinyl hydrogen resonance for VI is found at 5.29 ppm. A broad singlet at 5.06 ppm is assigned to the vinyl hydrogen of the 1,4-(2-methyl-*cis*-but-2-ene) component of XII. For comparison, the vinyl hydrogen of XV is found at 5.00 ppm. Two vinyl ^{1}H NMR signals are observed that are consistent with the presence of 3-methyl-1-silacyclopent-3-en-1-ylidene rings at 5.45 and 5.51 ppm. For comparison, the vinyl hydrogen signal for XIII is found at 5.40 ppm, while that for the vinyl hydrogen of the 3-methyl-1-silacyclopent-3-ene ring of IX is found at 5.50 ppm.

^{13}C NMR signals of the vinyl carbons can be assigned in the following manner. The resonances found at 139.91, 124.35, and 124.59 ppm result from the vinyl carbons of the 3-methyl-1-silacyclopent-3-en-1-ylidene rings of XI and XII. Four vinyl carbon resonances are predicted for these nonequivalent rings; however, only three are observed. Apparently, two signals are fortuituously coincident at 139.91 ppm. For comparison, the vinyl carbons of XIII are found at 139.69 and 124.74 ppm. The signals at 130.77 and 131.02 ppm as well as those at 117.15 and 117.40 ppm are assigned to the vinyl carbons of the 1,4-(2-methyl-*cis*-but-2-ene) units of XII. For comparison, the vinyl carbons of XV are found at 131.15 and 117.20 ppm. Finally, the ^{13}C NMR signals at 122.61, 122.65, 122.84, 122.88, and 123.12 ppm may be assigned to the vinyl carbons of the 1,4-(*cis*-but-2-ene) units of XI and XII on the basis of a diad analysis. For comparison, the vinyl carbons of VI are found at 123.22 ppm, while the unsubstituted vinyl carbons of VIII are observed at 122.92 ppm. In a similar manner, the ^{13}C NMR resonances due to allylic methylene and methyl groups of XI and XII can be assigned (see Table II).

The ^{29}Si NMR of X is consistent with an oligomer made up of XI and XII units. Specifically, two groups of resonances are observed. The first is centered at 20.45 ppm while the second is found at 3.40 ppm. The first is assigned to silicon atoms of 3-methyl-1-silacyclopent-3-ene rings of XI and XII. For comparison, the ^{29}Si resonance of XIII is found at 17.88 ppm while that for IX is found at 20.59 ppm. The resonances centered at 3.40 ppm are assigned to the 1-silicon atoms of XII, which is part of the polymer backbone. For comparison, the ^{29}Si NMR of XV is found at 2.02 ppm.

Similar reaction of I with a catalytic amount of alkyllithium and HMPA in THF gave no dimeric product (5,-10-disiladispiro[4.4.4.4]octadeca-2,7,12,16-tetraene) analogous to VIII or IX. On the other hand, an excellent yield (93%) of high molecular weight (M_w/M_n = 723000/266000) polymer (XXII) was obtained.



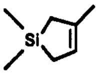
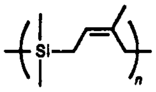
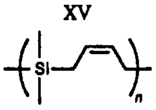
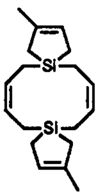
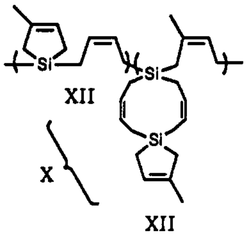
We believe that this polymer is not cross-linked due to its significant solubility in common organic solvents such as THF, CHCl$_3$, and ether. On the basis of ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy it appears that this polymer is made up of 1-silacyclopent-3-en-1-ylidene-*cis*-but-2-en-1,4-ylene (XXIII), 1,6-disilaspiro[4.9]tetradeca-3,8,12-trien-1-ylidene-*cis*-but-2-en-1,4-ylene (XXIV), and finally 1,6-disilacyclodeca-3,8-dien-1,6-diylidene (XXV) ladder-type units.

In the ^{29}Si NMR two groups of three signals are observed. Those centered at 17.5 ppm result from silicon atoms in 1-silacyclopent-3-ene rings of XXIII and XXIV, while those whose resonances are found between 2.99 and 4.64 ppm result from silicon atoms that are part of an open-chain structure or ladder units joined by 1,4-*cis*-but-2-ene units as in XXIV and XXV.

Similarly, two groups of vinyl carbon signals are observed in the ^{13}C NMR. Those at 130.83 and 130.98 ppm result from vinyl carbons of silacyclopent-3-ene rings, while those found at ca. 122.6 ppm arise from the 1,4-(*cis*-but-2-ene) units of XXIV and XXV.

Finally, two groups of vinyl hydrogens are observed in the ^{1}H NMR. The signals at 5.88 and 5.83 ppm result from the vinyl hydrogens of silacyclopent-3-enes of XXIII and XXIV. On the other hand, the ^{1}H NMR resonances at 5.30 and 5.37 ppm are due to the vinyl hydrogens of the 1,4-(*cis*-but-2-ene) units of XXIV and XXV. Comparison of the integrated intensities of the signals at 5.30 and 5.37 ppm to those at 5.83 and 5.88 ppm leads to the conclusion that there are too many 1,4-(*cis*-but-2-ene) units if the polymer were composed only of XXIII and XXIV units. Thus the ratio of these two types of vinyl hydrogens should be 1:1 for XXIII and 3:1 for XXIV units. The excess intensity in the signals at 5.30 and 5.37 ppm result from the existence of ladder microstructure XXV.

Table II
^{1}H, ^{13}C, and ^{29}Si NMR Chemical Shifts (ppm)

	$^{1}\text{H}_{\text{vinyl}}$	$^{13}\text{C}_{\text{vinyl}}$	$^{13}\text{C}_{\text{allyl}}$	$^{13}\text{C}_{\text{methyl}}$	^{29}Si
 XIII	5.40	124.74 139.69	18.90 22.47	−1.84 23.09	17.88
 XV	5.00	117.20 131.15	18.28 21.49	−2.29 26.30	2.02
 XV	5.29	123.22	16.47	−3.41	2.17
 IX	5.30 5.50	122.88 124.59 140.01	14.15 16.22 22.64	20.42	20.59
 XII X XII	5.06 5.31 5.45 5.51	117.15 117.40 122.61 122.65 122.84 122.88 123.12 124.35 124.59 130.77 131.02 139.91	12.15 12.22 12.52 12.65 12.91 13.17 13.24 13.87 13.98 14.11 16.19 17.69	18.81 18.93 19.00 19.20 20.38 22.55 22.62 26.02 26.07 26.14 26.24 26.29	2.52 3.28 3.40 3.72 4.19 19.68 19.89 20.91 21.23

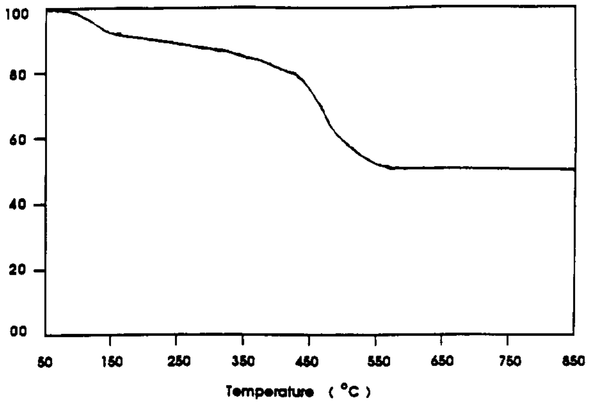


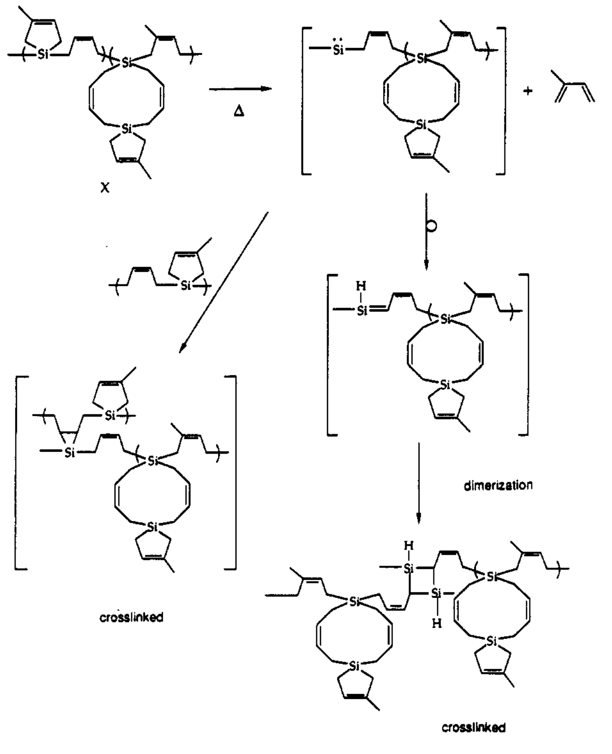
Figure 1. TGA of X in nitrogen.

The thermal stability of oligomer X was determined by TGA in nitrogen, argon, and air. In addition, the residue obtained in nitrogen was subjected to further heating at high temperature in air. In nitrogen, X is thermally stable at 80 °C. It then loses eight at a rate of 2% for every 25 °C increase in temperature between 80 and 160 °C. It loses 4–5% for every 100 °C temperature increase between 160 and 400 °C. Rapid weight loss occurs between 430 and 500 °C. By 580 °C 48% weight loss has occurred. No further weight loss occurs up to 850 °C (Figure 1). A black residue was obtained. Similar results were obtained when purified argon was utilized.

If the above black char is heated at 750 °C in air for 30 min, an additional rapid weight loss of 20% occurs. No further loss is observed at 750 °C over 3 h. The white residue (32%) is composed of silicon and oxygen by energy-dispersive spectroscopy (EDS). The theoretical yield of silicon dioxide from X is 33%.

The TGA of X in air is similar. Thus X is stable in air to 80 °C. Between 80 and 160 °C the sample loses weight at a rate of 1% for each 25 °C increase in temperature. Between 160 and 230 °C virtually no weight loss is observed. Between 260 and 450 °C a 25% weight loss is observed. Between 480 and 590 °C an additional 36% weight loss is observed. No further weight loss is observed above 620 °C. A white residue, composed of silicon and oxygen by EDS, amounting to 35% of the initial sample is obtained (Figure 2).

The observed thermal stability of X is quite unusual. For comparison, high molecular weight $M_w/M_n = 1180000/744000$ poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) is thermally stable in nitrogen to 380 °C. Between 400 and 450 °C it undergoes complete catastrophic degradation. No residue is found. Considering the low molecular weight of X, the formation of a high char yield is unexpected. We believe that the thermal stability of X is due to its ability to undergo cross-linking reaction. It is well-known that silylenes will react with 1,3-butadiene to yield 1-silacyclopent-3-enes.[11] The microscopic reverse of this reaction with loss of 2-methyl-1,3-butadiene may occur on pyrolysis of X. This would result in the formation of a reactive silylene center. Cross-linking may result from reaction of this silylene with carbon–carbon double bonds on adjacent oligomer chains.[12] Alkyl-substituted silylenes are also known to undergo 1,2-hydrogen migration to yield silenes.[13] Thus, alternatively, cross-linking may involve dimerization of reactive silenes to form 1,3-disilacyclobutanes which serve to cross-link adjacent oligomer chains.



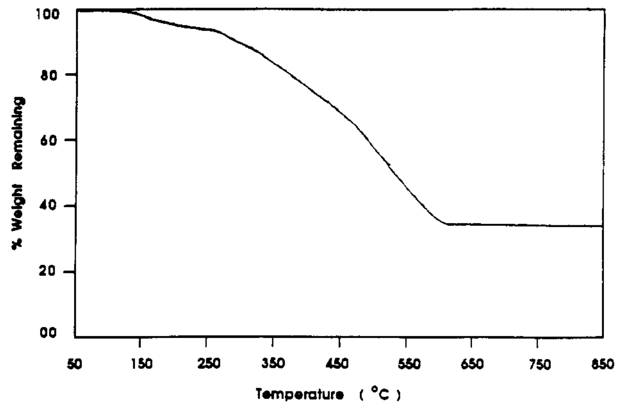


Figure 2. TGA of X in air.

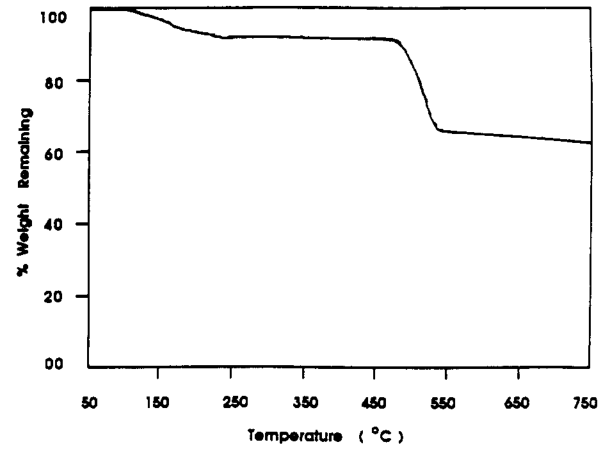


Figure 3. TGA of XXII in nitrogen.

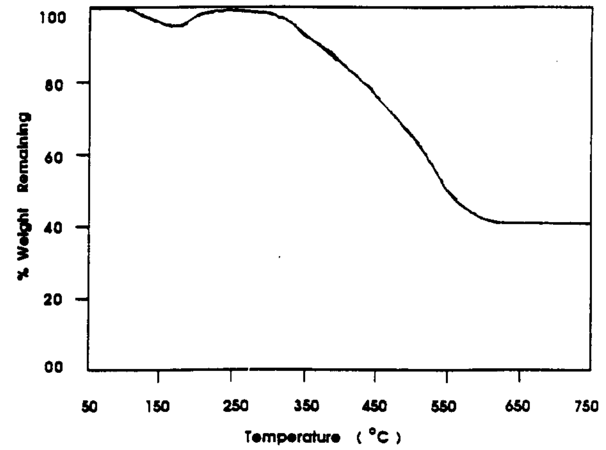


Figure 4. TGA of XXII in air.

The thermal stability of XXII in a nitrogen atmosphere was determined by TGA. It was stable to 130 °C. Between 150 and 250 °C the sample loses 10% of its initial weight. Between 250 and 480 °C an additional loss of 3% is observed. Rapid weight loss of 26% of the initial sample weight occurs between 480 and 560 °C. Between 560 and 750 °C an additional 4% weight loss occurs (Figure 3). A black residue amounting to 57% of the initial sample weight is obtained.

Heating this black char in air at 750 °C results in a rapid weight loss (over 20 min) of 27%. A white residue, which was composed of silicon and oxygen by EDS, amounting to 30% has been found. No further change occurs on heating this material in air at 750 °C for 2 h. The theoretical yield of silicon dioxide from polymer XXII is 36%. The TGA of XXII in air (Figure 4) results in a 40% yield of a white residue composed of silicon and oxygen by EDS.

Experimental Section

^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on an IBM-Bruker 270-SY or Bruker AM-360 spectrometer operating in the Fourier transform mode. ^{13}C NMR spectra were run with broadband proton decoupling. A DEPT pulse sequence was used to obtain ^{29}Si NMR spectra. This was effective since all the silicon atoms have at least one methylene group bonded to them.[14] Identical ^{29}Si NMR spectra could be obtained by use of a heteronuclear gated decoupling pulse sequence (NONOE) with a pulse delay of 30 s.[15] Ten of fifteen percent solutions in chloroform-*d* were used to obtain ^{13}C and ^{29}Si NMR spectra. Five percent solutions were used to obtain ^{1}H NMR spectra. Chloroform was utilized as an internal standard for ^{1}H and ^{13}C NMR spectra. ^{29}Si NMR spectra were externally referenced to TMS.

IR spectra were recorded on a Perkin-Elmer PE-281 spectrometer. Spectra of oils were taken as neat films on NaCl plates. IR spectra of solids were taken on KBr pellets.

Low-resolution mass spectra were obtained on a Finnigan Mat Incos 50 GCMS instrument at an ionizing voltage of 70 eV. A 0.25 mm × 30 m fused-silica DB-5 capillary column was used in the gas chromatographic inlet of the mass spectrometer. High-resolution mass spectra were obtained at the University of California Riverside Mass Spectrometry Facility on a VG-7070 EHF mass spectrometer at an ionizing voltage of 20 eV. Exact masses were determined by peak matching against known masses of perfluorokerosene.

The molecular weight distribution of oligomers and polymers was determined by gel permeation chromatography on a Waters system. This was comprised of a U6K injector, a 510 HPLC solvent delivery system, an R401 differential refractometer, and a Maxima 820 control system. A Waters 7.8 mm × 30 cm Ultrastyragel linear column packed with <10-μm particles of mixed pore size cross-linked styrene–divinylbenzene copolymer was maintained at 20 °C. The eluting solvent was HPLC-grade THF at a flow rate of 0.6 mL/min. Retention times were calibrated against known monodisperse polystyrene standards: 929 000, 170 900, 110 000, 20 400, 4800, and 1350 whose M_w/M_n values are <1.09.

Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGS-2. The temperature program for the analysis was 50 °C for 10 min followed by an increase of 4 °C/min to 750 or 850 °C. These runs were conducted with a nitrogen, argon, or air flow rate of 40 cm^3/min. Chars from the inert-atmosphere runs were then heated in an atmosphere of air at a flow rate of 40 cm^3/min at 750 °C.

Energy-dispersive spectra (EDS) were run on a Link AN-10,000 at the University of Southern California Electron Microanalysis Center. Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

Tetrahydrofuran (THF) was distilled immediately prior to use from a deep blue solution of sodium benzophenone ketyl. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride and was stored over activated 4-Å molecular sieves. 2,3-Dimethyl-1,3-butadiene, 2-methyl-1,3-butadiene, and active magnesium powder were purchased from Aldrich Chemical Co. 1,3-Butadiene was purchased from Matheson Gas Products.

All glassware was dried overnight in an oven at 120 °C. It was assembled and flame dried under at atmosphere of purified argon. All reactions and transfers were conducted under an atmosphere of purified argon. 1,1-Dichlorosilacyclopent-3-ene (IV) was prepared from trichlorosilane and *cis*-1,4-dichloro-2-butene. It had properties in agreement with literature values.[4]

2,3-Dimethyl-5-silaspiro[4.4]nona-2,7-diene (II). In a 500-mL, three-neck, round-bottom flask equipped with a reflux condenser, a pressure-equalizing addition funnel, and a Teflon-covered magnetic stirring bar were placed magnesium powder (2.48 g, 0.1 mol), 2,3-dimethyl-1,3-butadiene (8.4 g, 0.1 mol), THF (63 mL), and HMPA (17 mL).[16] The flask and its contents were cooled to 0 °C. IV (10.4 g, 68 mmol)[4] and THF (20 mL) were placed in the addition funnel. This solution was added dropwise to the vigorously stirred suspension of magnesium powder over 1 h. The reaction mixture was allowed to warm to room temperature and was stirred for 72 h. Pentane (100 mL) was added. Saturated aqueous ammonium chloride (100 mL) was then added dropwise with vigorous stirring. The organic layer was separated, washed with water, dried over anhydrous magnesium sulfate, and filtered. The organic solvents were removed by fractional distillation through a 15-cm vacuum-jacketed Vigreux column. The residue was transferred to a smaller flask, and the distillation was continued under reduced pressure. A fraction, bp 108–110 °C/11 mm, 4.4 g, 40% yield, was obtained. It had the following properties. ^{1}H NMR: δ 1.45 (d, 4 H, J = 1.0 Hz), 1.51 (d, 4 H, J = 1.1 Hz), 1.72 (t, 6 H, J = 1.0 Hz), 5.91 (t, 2 H, J = 1.0 Hz). ^{13}C NMR: δ 16.54, 19.18, 24.13, 130.87, 131.16. ^{29}Si NMR: δ 25.54. IR: ν 3020, 2970, 2890, 2880, 1605, 1440, 1395, 1205, 1175, 1090, 940, 820, 760, 725, 615 cm^{-1}. GC/MS: *m/e* (rel intensity) 166 (3.5), 165 (12.9), 164 (82.4) $M^{\bullet+}$, 149 (4.0) $(M-15)^+$, 112 (3.7), 111 (12.6), 110 (100.0) $(M-C_4H_6)^{\bullet+}$, 97 (4.0), 96 (9.8), 95 (83.2) $(M-C_4H_6-15)^+$, 84 (2.1), 82 (25.6) $(M-C_6H_{10})^{\bullet+}$. High-resolution MS: *m/e* calcd for $C_{10}H_{16}Si$ ($M^{\bullet+}$) 164.1021; found 164.1023. Anal. Calcd for $C_{10}H_{16}Si$: C, 73.09; H, 9.82. Found: C, 72.59; H, 10.20.

2-Methyl-5-silaspiro[4.4]nona-2,7-diene (III). The reaction between magnesium powder, 2-methyl-1,3-butadiene, and IV was carried out on the same scale as above. A fraction, bp 76–77 °C/7.8 mm, 4.5 g, 45% yield, was obtained. It had the following properties. ^{1}H NMR: δ 1.41 (s, 2 H), 1.47 (d, 6 H, J = 1.0 Hz), 1.78 (m, 3 H), 5.53 (m, 1 H), 5.90 (d, 2 H, J = 1.0 Hz). ^{13}C NMR: δ 16.72, 17.44, 21.39, 22.56, 124.84, 131.06, 140.13. ^{29}Si NMR: δ 34.27. IR: ν 3020, 2960, 2920, 2900, 2880, 1640, 1610, 1450, 1430, 1390, 1370, 1215, 1205, 1155, 1100, 1020, 1010, 940, 860, 800, 740, 720, 630 cm^{-1}. GC/MS: *m/e* (rel intensity) 152 (3.2), 151 (10.9), 150 (71.1) $M^{\bullet+}$, 137 (0.2), 136 (0.4), 135 (4.6) $(M-15)^+$, 124 (0.7), 123 (2.2), 122 (18.8) $(M-28)^+$, 110 (1.2), 109 (5.4), 108 (13.1), 98 (4.2), 96 (100.0) $(M-C_4H_6)^{\bullet+}$, 95 (34.5), 84 (1.4), 83 (6.9), 82 (44.4) $(M-C_5H_8)^{\bullet+}$, 81 (25.3), 70 (7.9), 69 (15.0), 68 (26.7), 67 (37.4), 57 (4.9), 56 (9.1), 55 (54.2), 54 (27.6), 53 (49.9). High-resolution MS: *m/e* calcd for $C_9H_{14}Si$ ($M^{\bullet+}$) 150.0865; found 150.0873. Anal. Calcd for $C_9H_{14}Si$: C, 71.92; H, 9.38. Found: C, 69.96; H, 9.18.

5-Silaspiro[4.4]nona-2,7-diene (I). The reaction between magnesium powder, 1,3-butadiene, and IV was carried out on the same scale as above, except that the reflux condenser was replaced by a cold finger condenser filled with dry ice–acetone. A fraction, bp 62–63 °C/7.0 mm (lit.[3] bp 65–68 °C/13 mm), 1.7 g, 19% yield, was obtained. ^{1}H NMR: δ 1.47 (d, 8 H, J = 0.70 Hz), 5.91 (t, 4 H, J = 0.64 Hz). ^{13}C NMR: δ 16.41, 131.04. ^{29}Si NMR: δ 31.79. IR: ν 3020, 2886, 2780, 1605, 1398, 1205, 1171, 1101, 944, 839, 749, 650 cm^{-1}. GC/MS: *m/e* (rel intensity) 138 (1.7), 137 (5.7), 136 (42.1) ($M^{\bullet+}$), 123 (0.1), 122 (0.3), 121 (2.2), 110 (0.7), 109 (2.7), 108 (15.4), 96 (0.9), 95 (2.7), 94 (4.2), 84 (3.6), 83 (10.5), 82 (100.0), $(M-C_4H_6)^{\bullet+}$, 81 (12.8), 69 (1.9), 68 (2.7), 67 (23.4), 58 (4.0), 57 (3.3), 56 (8.8), 55 (31.4), 54 (26.6), 53 (30.9). The ^{1}H NMR and IR spectra are in agreement with previously reported spectra.[3]

Reaction of III with Methyllithium. In a flame-dried 100-mL Schlenk flask equipped with a Teflon-covered magnetic stirring bar were placed III (0.91 g, 6.0 mmol), THF (20 mL), and 5 drops of HMPA. The flask and its contents were cooled to −78 °C. To the well-stirred reaction mixture was slowly added methyllithium (1.4 M, 0.5 mL) via a syringe. The mixture was stirred at −78 °C for 4 h. The reaction was then quenched at −78 °C by the addition of saturated aqueous ammonium chloride. Ether (50 mL) was added, the organic layer was washed with water, dried over anhydrous magnesium sulfate, and filtered, and the volatile solvents were removed by evaporation under reduced pressure. The residue was dissolved in a minimum amount of THF. The polymer was purified by precipitation from methanol. In this way, 0.37 g, 41% yield of X (M_w/M_n = 1119/950), was obtained. With *n*-butyllithium (1.6 M, 0.2 mL) as initiator no starting material was recovered. A 58% yield of X was obtained (M_w/M_n = 3200/1600). ^{1}H, ^{13}C, and ^{29}Si NMR (Table II). IR: ν 3002, 2958, 2924, 2872, 1687, 1639, 1435, 1407, 1375, 1350, 1215, 1159, 1103, 1023, 940, 856, 824, 679, 641 cm^{-1}. Anal. Calcd for $C_9H_{14}Si$: C, 71.92; H, 9.39. Found: C, 69.38; H, 9.46.

Volatile solvents were removed from the supernatant solution by evaporation under reduced pressure. In this way, starting material (0.12 g, 13%) and 0.38 g (42% yield) of IX were obtained from the methyllithium reaction. In a similar manner with *n*-butyllithium as initiator no starting material was recovered. In this case, a 36% yield of IX was obtained. It had the following spectral properties. ^{1}H NMR: δ 1.28 (s, 4 H), 1.35 (s, 4 H), 1.58 (d, 8 H, J = 6.5 Hz), 1.76 (s, 6 H), 5.30 (t, 4 H, J = 5.8 Hz), 5.50 (s, 2 H). ^{13}C NMR: δ 14.15, 16.22, 20.42, 22.64, 122.88, 124.59, 140.01. ^{29}Si NMR: δ 20.59. IR: ν 2999, 2960, 2928, 2874, 1699, 1634, 1434, 1406, 1375, 1261, 1214, 1162, 1102, 1023, 941, 828, 795, 683, 638 cm^{-1}. GC/MS: *m/e* (rel intensity) 302 (3.6), 301 (9.3), 300 (30.5) $M^{\bullet+}$, 247 (0.8), 246 (2.6) $(M - C_4H_6)^{\bullet+}$, 245 (5.5), 233 (1.2), 232 (3.9), 231 (5.8) $(M - C_4H_6 - 15)^+$, 230 (3.1), 153 (0.9), 152 (2.9), 151 (11.9), 150 (40.6) $(M - 150)^{\bullet+}$, 138 (0.8), 137 (2.9), 136 (4.0), 135 (5.7), 124 (4.2), 123 (16.4), 122 (22.9), 121 (8.3), 111 (2.6), 110 (4.1), 109 (18.7), 108 (16.8), 107 (9.3), 99 (1.8), 98 (5.4), 97 (21.1), 96 (100.0) $(M - 150 - 54)^{\bullet+}$, 95 (38.6), 84 (2.5), 83 (10.0), 82 (22.9), 81 (21.0), 69 (15.3), 68 (15.5), 67 (16.0), 58 (3.1), 57 (4.2), 56 (4.2), 55 (26.9), 54 (7.0), 53 (12.3). High-resolution MS *m/e* calcd for $C_{18}H_{28}Si_2$ $(M^{\bullet+})$ 300.1729, found 300.1725.

Reaction of I with *n*-Butyllithium. In a flame-dried 100-mL Schlenk flask equipped with a Teflon-covered magnetic stirring bar were placed I (0.41 g, 3.0 mmol), THF (20 mL), and three drops of HMPA. The flask and its contents were cooled to −78 °C. To the well-stirred reaction mixture was slowly added *n*-butyllithium (2.5 M, 100 μL, 0.25 mmol) via a syringe. The reaction mixture became yellow and was stirred at −78 °C for 3 h. The reaction was quenched at −78 °C by addition of saturated ammonium chloride solution. Ether (50 mL) was added, the solution was washed with water, dried over anhydrous magnesium sulfate, and filtered, and the volatile solvent was removed by evaporation under reduced pressure. The residue was dissolved in a minimum amount of THF, and the product polymer was precipitated from methanol. This process was repeated. In this way, 0.38 g (93% yield) of polymer was obtained. It had the following properties. $M_w/M_n = 722950/265690$. ^1H NMR: δ 1.29–1.34 (br s, 7.48 H), 1.53–1.58 (br s, 23.35 H), 5.30 (br s, 7.81 H), 5.37 (br s, 4.28 H), 5.83 (s, 1.22 H), 5.88 (s, 2.07 H). ^{13}C NMR: δ 12.54, 12.62, 12.68, 12.90, 13.18, 13.32, 13.61, 13.82, 14.01, 14.32, 14.80, 15.37, 122.22, 122.32, 122.46, 122.75, 122.94, 123.12, 130.83, 130.98. ^{29}Si NMR: δ 2.99, 3.82, 4.64, 17.39, 17.50, 17.77. IR: ν 3003, 2923, 2871, 2776, 1637, 1607, 1406, 1375, 1204, 1154, 1097, 1023, 943, 910, 824, 733, 688, 627, 536 cm^{-1}. Anal. Calcd for $C_8H_{12}Si$: C, 70.51; H, 8.88. Found: C, 65.49; H, 8.54.

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Registry No. I, 52856-32-3; II, 129571-34-2; III, 133401-85-1; IV, 872-46-8; IX, 133401-86-2; X (homopolymer), 133401-87-3; XXII (homopolymer), 133401-88-4; $H_2C{=}C(CH_3)C(CH_3){=}CH_2$, 513-81-5; $H_2C{=}C(CH_3)CH{=}CH_2$, 78-79-5; $H_2C{=}CHCH{=}CH_2$, 106-99-0.