Conclusion

Alkylation of glycolate-*O,O* derivatives of metal oxides is a better, more direct way to organometal oxides, especially when the metal is in the correct oxidation state (Scheme II). As we show in other cases,[1] a glycolate ligand is replaced by two alkyl groups much more selectively than an oxo group. This rule should be kept in mind with attempts to synthesize other organometal oxides, a class of compounds that is still missing for most transition metals. We have recently also been successful with this general procedure in organorhenium chemistry.[32] Further work with these and other metals is in progress.

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Synthesis and Structure of a Highly Branched Polycarbosilane Derived from (Chloromethyl)trichlorosilane

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A highly branched hydridopolycarbosilane has been prepared by Grignard coupling of (chloromethyl)trichlorosilane, followed by reduction with lithium aluminum hydride. Trapping studies show that the initial step in the polymerization is a nearly quantitative formation of the Grignard compound Cl_3SiCH_2MgCl. This Grignard compound undergoes head-to-tail (Si–C) coupling almost exclusively, and due to its trifunctional $SiCl_3$ "tail", a complicated, branched, polycarbosilane polymer results, which contains the following structural units: $SiCl_3CH_2–$, $–SiCl_2CH_2–$, $>SiClCH_2–$, and $>SiCH_2–$. The chloropolycarbosilane undergoes side reactions with ether, leading to incorporation of small amounts of ethyl and ethoxy functionality. During the reduction step the ethoxy groups are eliminated, yielding a polymer with the approximate formula $[SiH_{1.85}Et_{0.15}CH_2]_n$, which has been characterized by ^1H, ^{13}C, and ^{29}Si NMR, IR, GPC, and elemental analysis. This polymer is of interest as a precursor to near-stoichiometric silicon carbide.

Introduction

Highly branched silicon-containing polymers have been previously reported in conjunction with studies on silicon carbide precursors. Schilling et al.[1] have investigated several systems in which various mixtures of Me_3SiCl, Me_2SiCl_2, and $H_2C{=}CHSi(Me)Cl_2$ were treated with potassium, resulting in the formation of complicated, branched polysilanes. The branching was induced by reaction of the vinyl groups with potassium, leading to formation of $SiCH_2CHSi_2$ units in the polymer. Baney[2] has prepared polymers composed of complicated arrangements of fused polysilane rings. These polymers are prepared by treating mixtures of partially chlorinated disilanes of the general formula $Me_{6-x}Cl_xSi_2$ (x = 2–4) with Bu_4PCl at elevated temperatures. Kriner[3] reported the formation of polymeric byproducts during the "reverse Grignard" reaction of (chloromethyl)dichloromethylsilane employed to prepare various cyclic carbosilane compounds. These byproducts were presumably branched polycarbosilanes but were not investigated in any detail.

We report herein the characterization of a novel polycarbosilane with a highly branched structure. Due to the complex nature of this polymer, precise naming is difficult. The polymer isolated from the initial Grignard coupling reaction and its $LiAlH_4$-reduced analogue will be referred to as chloropolycarbosilane and hydridopolycarbosilane, respectively. The theoretical "average" formulas for these polymers would be $[SiCl_2CH_2]_n$ and $[SiH_2CH_2]_n$; however, due to their highly branched nature and side reactions with the ether solvent, the actual structures are much more complicated. The hydridopolycarbosilane is potentially useful as a precursor to silicon carbide ceramics, as it has nearly at 1:1 Si:C ratio and undergoes facile thermal cross-linking reactions leading to high ceramic yields.

Experimental Section

General Procedures. All manipulations involving air-sensitive materials were carried out in oven-dried glassware by using standard inert-atmosphere techniques.[4] Solvents were distilled under nitrogen from appropriate drying agents.[5] Magnesium powder (No. 50 mesh) was reground by using a modified pepper

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grinder, under nitrogen, before use. Other commercially available reagents were used as received, unless otherwise specified. ^1H, ^{13}C, and ^{29}Si NMR spectra were run on a Varian XL-200 spectrometer using benzene-d_6 or toluene-d_8 as solvents. Spectra were referenced to residual protons in the solvent, as TMS often interfered with sample peaks. IR spectra were taken, as neat films, between salt plates on a Perkin-Elmer 298 spectrometer. GC analyses were performed on a Shimadzu GC-9A gas chromatograph equipped with a Shimadzu C-R3A recorder–integrator unit. Unless otherwise specified, samples separated satisfactorily by using the following parameters: 6-ft SE-30 column, 100–250 °C at 15 °C/min, INJ and TCD at 275 °C, He at 45 cm^3/min. Elemental analyses were carried out by either Schwarzkopf Microanalytical Laboratory, Galbraith Laboratories Inc., or LECO Corp.

Preparation of Chloropolycarbosilane. Dry ether (1 L) and 30 g of magnesium powder (1.25 mol) were added to a 2-L, three-neck flask equipped with a reflux condenser, mechanical stirrer, and a nitrogen inlet. The reaction was started by addition of 5–10 mL of (chloromethyl)trichlorosilane to the flask, followed by intermittent heating with a heat-gun without stirring. Once the reaction was started, a 50 °C water bath was employed.[6] The remainder of the Cl_3SiCH_2Cl (126 mL, 1.0 mole total) was added over about 8 h by using a syringe. After the addition was complete, a highly air-sensitive, dark brown solution, containing small amounts of magnesium chloride and excess magnesium was obtained. This solution was heated under reflux for 3–5 days, causing a gradual color change to brownish yellow as large amounts of $MgCl_2$ precipitated. Due to the large volume of solid which formed, addition of more ether was required to maintain a sufficiently fluid consistency. The ether solution of the product was removed by using a cannula fitted with a gas diffuser frit to prevent clogging. The resulting solution of chloropolycarbosilane was stripped of ether under vacuum with the aid of the 50 °C water bath. A yellow-brown, moisture-sensitive, highly viscous oil was obtained in 45–50% yield (based on an assumed "average" formula $[SiCl_2CH_2]_n$). IR (cm^{-1}): 2980 (s), 2930 (m), 2900 (m), 1440 (m), 1385 (m), 1345 (m), 1290 (w), 1260 (m), 1160 (m), 1100–1030 (vs, b), 965 (s), 815–755 (vs. b). All NMR peaks are complex multiplets or broad [ppm (relative integral)]: ^1H 0.2–1.5 (25), 1.9–2.3 (1.0), 3.6–4.1 (3.6); $^{13}C\{^1H\}$ 8–24 (major portion, several multiplets), 29–33, 56–61; $^{29}Si\{^1H\}$ −20 to −12.5; −6 to +2 (both minor), 2–10, 13–28 (both major). Anal. Calcd for $[SiCl_2CH_2]_n$: C, 10.63; H, 1.77; Si, 24.80; Cl, 62.80. Calcd for $[SiCl_{1.7}Et_{0.15}OEt_{0.15}CH_2]_n$ (the best approximation based on NMR integration): C, 16.94; H, 2.09; Si, 24.7; Cl, 53.16; O, 2.1. Calcd for $[SiCl_{1.1}Et_{0.15}OEt_{0.35}CH_2]_n$ (the best approximation based on the observed elemental analyses): C, 34.7; H, 4.45; Si, 27.7; Cl, 38.57; O, 5.54. Found: C, 21.90; H, 4.14; Si, 22.30; Cl, 37.34.

Reduction of Chloropolycarbosilane. Typically, about 0.5 mol (56 g) of chloropolycarbosilane in 500 mL of ether was transferred to a 1-L, three-neck flask equipped with a reflux condenser, magnetic stirrer and nitrogen inlet and cooled to 10 °C by using an ice/water bath. $LiAlH_4$, 12.3 g (0.33 mol, 30% excess) suspended in 200 mL of ether was added over 30 min, via cannula or syringe, with rapid stirring. The resulting light gray suspension was refluxed overnight under nitrogen. The large excess of $LiAlH_4$ was employed due to uncertainty in the amount of Si–Cl in the polymer.

Aqueous Workup of Crude Hydridopolycarbosilane. Initially, dilute HCl (about 3 M) was added dropwise to the rapidly stirred $LiAlH_4$/polymer slurry under nitrogen. An oil bubbler allowed the byproduct gases to escape. After the reaction became sluggish, the remainder of about 1 L of the acid was poured in, resulting in the dissolution of the lithium and aluminum salts. (If large amounts of unreacted $LIAlH_4$ are present, this process can be expedited by allowing the slurry to settle and transferring the liquid portion to another flask for hydrolysis.) The ether layer was separated and again washed with dilute HCl, and the ether was stripped off to yield a cloudy, yellow oil. This oil was redissolved in pentane to drive out small amounts of emulsified water and residual aluminum complexes. After settling, the pentane solution was easily separated from the residue, dried, and passed through a 0.5-μm syringe filter, and the solvent was stripped off, under vacuum, with warming to 60 °C. A viscous, transparent, pale yellow oil was obtained in about 85% yield (or 40% overall, from Cl_3SiCH_2Cl) on the basis of the assumed "average" formula $[SiH_2CH_2]_n$ for the hydridopolycarbosilane. This polymer is not pyrophoric, and appears to be reasonably air-stable.[7] IR (cm^{-1}): 2950 (m), 2920 (m), 2870 (m), 2140 (vs), 1450 (w), 1350 (m), 1250 (w), 1040 (s), 1040 (s), 930 (vs), 830 (s), 760 (vs). All NMR peaks are complex multiplets or broad [ppm (relative integral)]: ^1H −0.4 to −0.05, −0.05 to +0.3 [16 (total)], 0.85–1.15 (3), 1.55–1.8 (1), 3.55–3.85, 3.85–4.1, 4.1–4.3 [13.3 (total)]; $^{13}C\{^1H\}$ −12 to +9 (major portion), 12.5–16, 23–26; $^{29}Si\{^1H\}$ −66 to −53 (4 large singlets and small multiplets), −39 to −26, −14 to −8, 0.0–5 (all complicated multiplets); $^{29}Si(^1H$ coupled) −73 to −45 [several overlapping quartets, J_{Si-H} about 200 Hz (other multiplets became more complicated)]; $^{29}Si\{^1H\}$ (DEPT, multiplicity = 1.5) −66 to −53, −14 to −8 (positive); −39 to −26 (negative). Anal. Calcd for SiH_2CH_2 (the theoretical "average" formula): C, 27.27; H, 9.09; Si, 63.63. Calcd for $[SiH_{1.85}Et_{0.15}CH_2]_n$ (the best approximation from NMR integration): C, 32.3; H, 9.54; Si, 58.1. Calcd for $[SiH_{1.1}Et_{0.025}CH_2]_n$ (the best approximation from C and H analyses): C, 28.07; H, 7.36; Si, 63.9. Found: C, 28.26; H, 7.36; Si, 48.71; Cl, 1.63; O, 0.02.

Gel Permeation Chromatography (GPC) Analysis of Hydridopolycarbosilane. GPC of the reduced polymer was performed on a Waters 600 solvent delivery system, 410 RI detector, and 745 data-processing unit. Waters Ultrastyragel columns of 100-, 500-, and 10 000-Å porosity were kept at 40 °C. Helium-sparged HPLC grade toluene at a flow rate of 0.6 mL/min was used as the eluant. Molecular weights were obtained from a 15-point calibration curve by using polystyrene standards from 200 to 470 000 amu. A wide MW distribution of 300 to about 50 000 amu, with the majority of the polymer falling between 300 and 3000 amu was observed. The M_n (750), M_w (5200), and polydispersity of 6.9 reflect the broad MW distribution of this polymer.

Nonaqueous Workup of Hydridopolycarbosilane. The crude, reduced mixture was stripped of as much ether as possible under vacuum with heating to 50 °C. The resulting solids were extracted with pentane and allowed to settle, and the clear, yellow pentane solution was transferred by cannula to remove the polymer from the lithium and aluminum salts. The solution remained clear yellow during removal of the solvent under vacuum; only a gradual increase in viscosity was observed. Finally, an extremely viscous, yellowish, air-sensitive polymer was recovered in about 85% yield. The IR spectrum of this material was identical with that from the aqueous workup, except for two additional peaks: 1930 (w), 670 (w) cm^{-1}, respectively. ^1H NMR (ppm): C–H peaks −0.6 to +1.2 (broad, complex); Si–H peaks

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(6) The onset of the reaction is signaled by the formation of a blackish coating on the Mg; the addition of more than 10% of the Cl_3SiCH_2Cl prior to the initiation of a self-sustaining reaction with the Mg should be avoided, as a violent exotherm can result.

(7) The hydridopolycarbosilane, when left exposed to air as a film between salt plates about 2 h, showed no significant changes on rerunning the IR spectrum.

(8) Petrarch Systems Catalog S-7 (Silicon Compounds Register and Review) 1987, p 176.

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(11) Subjecting a 1:2 mixture of Me_3SiCH_2Cl and Me_3SiCl to Grignard coupling conditions showed that the Grignard reagent prefers to couple with the Si–Cl group rather than the $SiCH_2Cl$ group. The compounds $Me_3SiCH_2SiMe_3$ and $Me_3SiCH_2CH_2SiMe_3$ were formed in a ratio of 33:1 confirmed by GC and ^1H NMR spectroscopy. Due to the large amount of $-SiCl_3$ groups present, the probability for head–head coupling should be even less in the chloropolycarbosilane. In addition, no Si–Si bonded compounds were observed.

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3.6–3.9, 3.9–4.1, 4.1–4.3 (3 separate regions); 2.8:1 integration ratio for the C–H vs Si–H regions. Anal. Calcd for SiH_2CH_2: C, 27.27; H, 9.09; Si, 63.63. Found: C, 20.88; H, 5.82; Si, 34.51; Al, 6.64.

Preparation of Deuteriopolycarbosilane. Chloropolycarbosilane (5.02 g, 0.0444 mol as $[SiCl_2CH_2]_n$) was reduced with 1.165 g of $LiAlD_4$ (0.0277 mol) by using a scaled-down version of the procedure employed for preparation of hydridopolycarbosilane. Reduction was followed by aqueous/HCl workup as described previously. The product was a pale yellow, viscous liquid similar to hydridopolycarbosilane. IR (cm^{-1}): 2960 (m), 2920 (m), 2870 (m), 2840 (m), 2120 (vw), 1540 (vs), 1450 (w), 1350 (m), 1250 (m), 1035 (s), 940 (w), 890 (w), 750–850 (s, b), 675 (vs). ^1H NMR (ppm, all peaks relatively broad singlets): 1.7, 1.05, –0.4 to +0.6.

Preparation of Chloro- and Hydridopolycarbosilane in Ether-d_{10}. Chloropolycarbosilane was prepared as previously described but on a smaller scale, with the substitution of magnetic stirring due to the small quantities of reactants used. Cl_3SiCH_2Cl (3 mL) was added dropwise by syringe over about 1 h to 5 g of ether-d_{10} and 1.05 g of Mg powder. Gentle heating was required to initiate the reaction. When addition was complete the resulting brownish solution was refluxed for 3 days to complete the polymerization. The ether was removed under vacuum, and the resulting solids were extracted with about 20 mL of dry pentane. On evaporation, the chloropolycarbosilane was recovered as a nearly clear, viscous, moisture-sensitive liquid. If the formula $[SiCl_2CH_2]_n$ is assumed for this polymer, a 46.7% yield was obtained. Hydridopolycarbosilane was prepared from this chloropolycarbosilane by $LiAlH_4$ reduction followed by the aqueous workup procedure as previously described. A nearly clear, viscous oil was obtained in 87% yield, assuming the formula $[SiH_2CH_2]_n$. Chloropolycarbosilane (ether-d_{10}): IR (cm^{-1}) 2960 (m), 2930 (m), 2875 (w), 2210 (m), 2095 (w), 1450 (w), 1400 (w), 1350 (m), 1265 (m), 1185 (m), 1110 (sh), 1075 (s), 1045 (sh), 945 (m), 795 (vs); ^1H NMR (ppm) –0.1 to +1.8 (complex multiplet); ^2D NMR (ppm) 1.1 (asymetric singlet), 2.0, 3.6 (all broad). Hydridopolycarbosilane (ether-d_{10}): IR (cm^{-1}) 2950 (w), 2920 (m), 2890 (w), 2205 (m), 2140 (vs), 1350 (m), 1250 (w), 1115 (w), 1050 (vs), 940 (vs), 850 (vs), 765 (vs); ^1H NMR (ppm) 0.0 (broad), 3.7, 4.1 (broad), minor peaks at 0.9, 1.35, 4.65, 4.9; ^2D NMR (ppm) 0.60, 1.1 (2:3 ratio).

Reduction of Solid Residue from Chloropolycarbosilane Preparation. The residual solids from the chloropolycarbosilane preparation, after two ether extractions, were suspended in about 1 L of dry ether. The amount of reducible material remaining in the residue was unknown, so $LiAlH_4$ was added until the yellowish slurry assumed a light gray color, suggesting excess $LiAlH_4$ was present. This slurry was allowed to reflux overnight. The "aqueous workup" was performed in the same manner as that for the soluble fraction of polymer. Vigorous foaming during the initial dropwise addition of 3 M HCl to the crude product showed that an excess of $LiAlH_4$ was present. This process recovered variable amounts of additional hydridopolycarbosilane corresponding to 10–25% of the theoretical yield. The IR and NMR of this product was similar to that from the soluble fractions of the chloropolycarbosilane. GPC was also quite similar; the majority of the polymer falling between 400 and 3400 amu, with M_n = 681.

Trapping of Chlorocarbosilane Oligomers as Methoxy Derivatives. (Chloromethyl)trichlorosilane (0.5 mol, 63 mL) was added to Mg powder as in the preparation of chloropolycarbosilane, except that the resulting brown solution was refluxed for only $^1/_2$ h before transferring, by cannula, to well-stirred cooled excess methanol. After the resulting white solids settled, a pale yellow solution was separated. Removal of the excess methanol gave a liquid/solid mixture, which was extracted with hexane and distilled under N_2. The major components were identified as $[MeO]_3SiMe$ and $[MeO]_3SiCH_2Si[OMe]_2CH_2Cl$ by boiling point and/or NMR data. A yellow, oily liquid, a mixture of higher weight oligomers, accounting for about 25% of the crude mixture, remained behind. $[MeO]_3SiMe$: 105–110 °C (lit. 103 °C).[8] $[MeO]_3SiCH_2Si[OMe]_2CH_2Cl$: 150–160 °C. ^1H NMR (all singlets) [ppm (number of protons)]: $[MeO]_3SiMe$ –0.28 (3) ($SiCH_3$), 3.37 (9) (OCH_3); $[MeO]_3SiCH_2Si[OMe]_2CH_2Cl$ 0.103 (2) ($SiCH_2Si$), 2.6 (2) (CH_2Cl), 3.42 (15) (OCH_3).

Preparation of Hydridopolycarbosilane Oligomers. Using 0.25 mol of Cl_3SiCH_2Cl (31.5 mL) the initial brown solution was prepared as before and allowed to reflux for 1 h. The solution was reduced by addition of 30% excess $LiAlH_4$ as a suspension in ether and allowed to stir overnight. After aqueous/HCl workup and solvent removal, about 8 mL of light yellow liquid was recovered. Distillation of this product under N_2 yielded only about 0.25 mL of liquid before undergoing a rapid exothermic cross-linking reaction, with much gas evolution, to form a white foamlike glassy solid. The fraction obtained was found by GC to be 80% one component, identified by NMR as $H_3SiCH_2Si[H]_2CH_2Cl$. The remaining 20% consisted of several related compounds in quantities too small to separate and characterize in detail. $H_3SiCH_2Si[H]_2CH_2Cl$: 75–85 °C; ^1H NMR [ppm (number of protons)]: –0.4 (2) ($SiCH_2Si$), sextet; 2.46 (2) ($-CH_2Cl$), triplet; 3.6 (3) ($-SiH_3$), triplet; 3.87 (2) ($-SiH_2-$), overlapping triplet of triplets (nearly a quintet).

Results and Discussion

Part I: Chloropolycarbosilane. Investigations of the chloropolycarbosilane by NMR spectroscopy were performed in order to identify the functional units present. In the ^1H NMR spectrum (Figure 1A) a broad, complex peak is seen near 1 ppm. This peak is consistent with an assignment to the protons of methylene units between many slightly different $SiCl_x$ functionalities, which are a result of the extensive branching of the polymer. The corresponding carbons for these methylene groups are believed to be the origin of the several complex peaks observed between 8 and 25 ppm in the $^{13}C\{^1H\}$ NMR spectrum (Figure 2). Several groups of overlapping peaks are seen in the range 2–28 ppm in the ^{29}Si NMR spectrum (Figure 3). These groups are attributed to $>SiCH_2-$, $>SiClCH_2-$, $-SiCl_2CH_2-$, and $SiCl_3CH_2-$ units in the polymer.[9] Additional peaks are observed in the NMR spectra of this polymer, indicating that other functional groups are present as well. The ^1H NMR spectrum (Figure 1A) shows a smaller, broad peak at 3.8 ppm, which is assigned to the $-OCH_2-$ protons of ethoxy groups. The peaks due to the methyl protons for these ethoxy groups would lie near 1 ppm and presumably are buried under the carbosilane methylene peak. ^1H NMR analysis of a sample of the chloropolycarbosilane prepared in ether-d_{10} (Figure 1B) did not exhibit the peak at 3.8 ppm, and the peak near 1 ppm showed distinct changes. In addition, ^2D NMR of the same sample (Figure 4A) exhibits the missing peaks, demonstrating that the ether was the source of these ethoxy groups. The asymmetric shape of the peak at 1 ppm in Figure 4A is attributed to Si–Et groups, also introduced by the reaction with the ether solvent. This will be discussed in more detail later, as the ethyl groups are more easily seen in the hydridopolycarbosilane where interference in the ^1H NMR spectrum due to $-CH_3$ portion of the –OEt groups is no longer present. The carbons from the $-OCH_2-$ of ethoxy groups presumably give rise to the peaks between 56 and 61 ppm seen in the ^{13}C NMR spectrum of the chloropolycarbosilane. The corresponding methyl carbon peaks would be buried under those due to $Si-CH_2-Si$ in the polymer chain. The ^{29}Si NMR spectrum (Figure 3) shows smaller upfield multiplets from +2 to –6 and –17.5 to –20 ppm, strongly suggestive that oxygen, in addition to chlorine, is bound to silicon.[9] In addition to Si–OEt, these upfield peaks could result from the presence of Si–Si bonding in the polymer. Small peaks from 1.9 to 2.3 and 29 to 33 ppm in the ^1H and ^{13}C NMR spectra, respectively, have been assigned to unreacted chloromethyl end groups in this polymer. The infrared spectrum of this polymer shows medium-intensity bands at 1385 and 1160 cm^{-1}, which are consistent with CH_2Cl groups on silicon.[10]

The IR data (Figure 5A) also support the conclusion that ethoxy substitution has occurred during the preparation

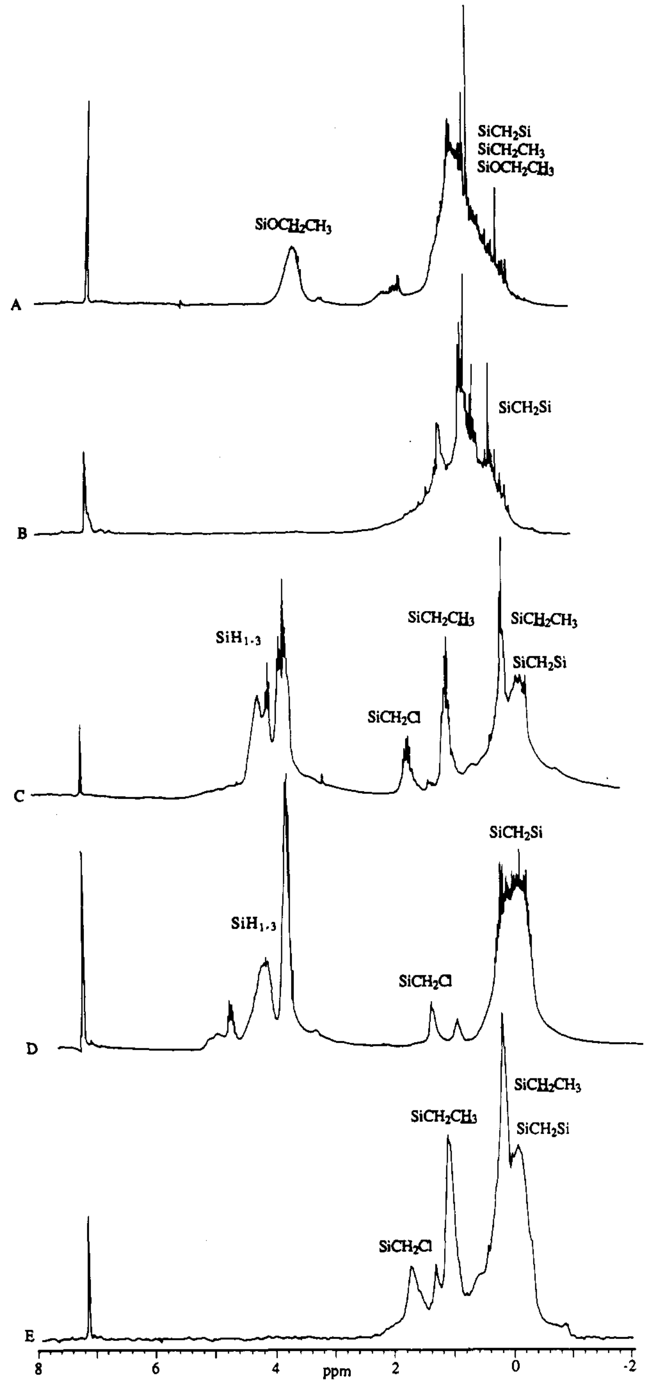
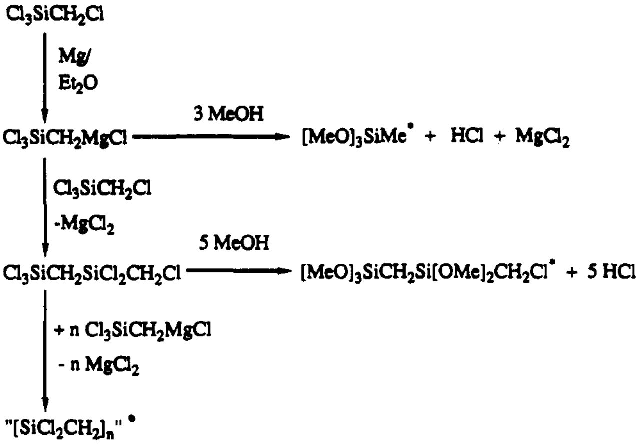


Figure 1. Proton NMR spectra of polycarbosilanes: chloropolycarbosilane prepared in ether (A) and in ether-d_{10} (B); hydridopolycarbosilane prepared in ether (C), in ether-d_{10} (D), and in ether but reduced with $LiAlD_4$ (E). The singlets near 7 ppm are protons in C_6D_6 solvent. The fine structure in some samples is attributed to the presence of oligomers.

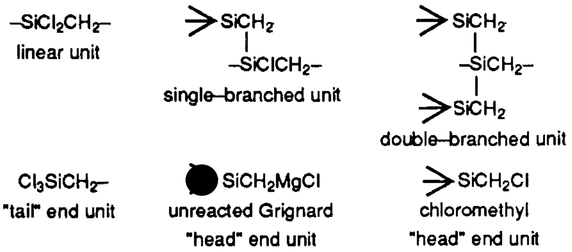
of the chloropolycarbosilane. Peaks of medium intensity at 965 and 1160 cm^{-1} are consistent with the presence of SiOEt groups.[10] The strong, broad band between 1000 and 1120 cm^{-1} also can result from Si–OR functionality in addition to the expected Si–CH_2–Si carbosilane "backbone" units of the polymer.[10] The major differences found in the IR spectrum of the chloropolycarbosilane prepared in ether-d_{10} (Figure 5B) were changes in, or disappearance of certain peaks in the C–H region and the appearance of new C–D peaks at 2090 and 2210 cm^{-1}. These changes are consistent with the presence of deuterated –OEt and –Et groups in the polymer.

Scheme I. Proposed Routes for Formation of Products Based on Methanol Trapping Experiments[a]



[a] Asterisks indicate those compounds that were actually observed.

The IR, NMR, and other experimental results indicate that the chloropolycarbosilane consists of the following "units" randomly assembled:



In addition, chlorine (on silicon) in any of these groups can be replaced with either –OEt or –Et.

The experimental results suggest that the formation of the chloropolycarbosilane proceeds in the following manner. Due to the complexity of the system, the side reactions will be discussed separately.

Slow addition of Cl_3SiCH_2Cl to refluxing Mg/ether was found to initially yield a dark, air-sensitive solution which, on extended reflux, gradually produced large amounts of $MgCl_2$ and a brownish yellow, viscous, moisture-sensitive polymer. The initial dark solution was suspected to contain the Grignard reagent, Cl_3SiCH_2MgCl, and was further investigated by quenching a freshly made batch with excess methanol before significant polymerization had occurred. On distillation, the principal compound obtained (about 80% of the volatiles) was $[MeO]_3SiMe$, the expected product from reaction of Cl_3SiCH_2MgCl with excess MeOH. Smaller amounts (about 17%) of $[MeO]_3SiCH_2Si[OMe]_2CH_2Cl$ were recovered. Compounds suggestive of head to head coupling, such as $[MeO]_3SiCH_2CH_2Si[OMe]_3$, were not observed. No $[MeO]_3SiCH_2Cl$ (from unreacted Cl_3SiCH_2Cl) was recovered, suggesting that the reactant was either converted to the Grignard reagent, or coupled with it to form $Cl_3SiCH_2SiCl_2CH_2Cl$ before the methanol was added. Proposed pathways explaining the formation of the observed compounds are outlined in Scheme I.

These results suggest that most of the Cl_3SiCH_2Cl is quickly converted to the corresponding Grignard reagent. Some of this Grignard reagent couples with Si–Cl of unreacted Cl_3SiCH_2Cl to form the dimeric intermediate compund $Cl_3SiCH_2SiCl_2CH_2Cl$. The corresponding reduced compound, $H_3SiCH_2SiH_2CH_2Cl$, was recovered from the $LiAlH_4$ "quench" of a batch of the Cl_3SiCH_2MgCl that

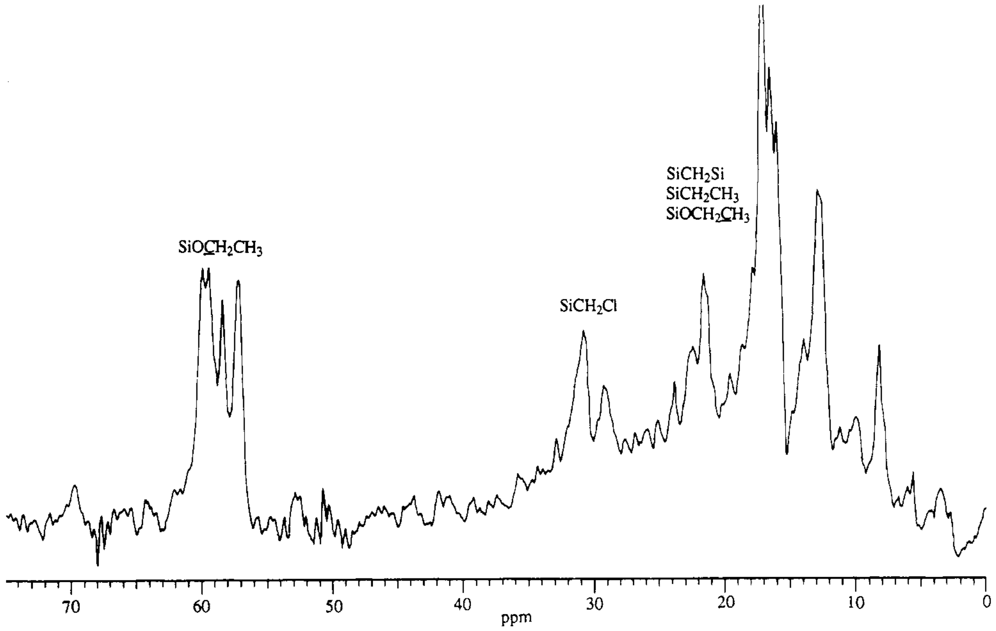


Figure 2. $^{13}C\{^1H\}$ NMR spectrum of chloropolycarbosilane.

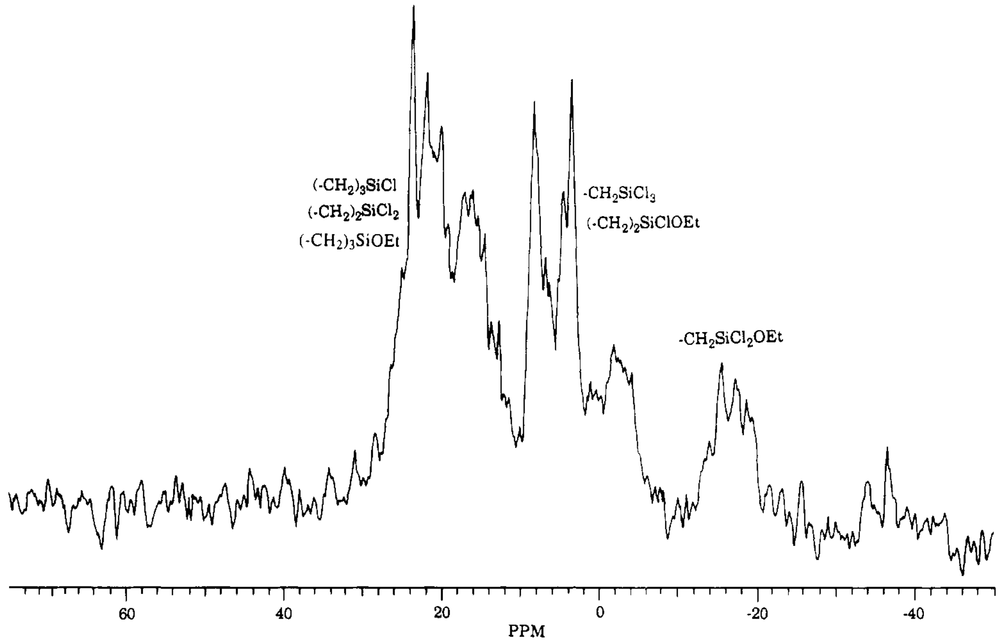


Figure 3. $^{29}Si\{^1H\}$ NMR spectrum of chloropolycarbosilane.

had been allowed to reflux for about 1 h (the chloromethyl group does not reduce as easily as SiCl). Any H_3SiCH_2Cl or H_3SiMe (from Cl_3SiCH_2Cl or Cl_3SiCH_2MgCl, respectively) would have escaped as gases along with the hydrogen formed during the aqueous workup step. The head-to-tail self-coupling of the Grignard reagent (Cl_3SiCH_2MgCl) appears to be relatively sluggish, as most of it could be trapped with methanol to give $[MeO]_3SiMe$. In fact, the initial Grignard solution must be refluxed for a considerable time before visible amounts of $MgCl_2$ are formed.

The trifunctional $SiCl_3$ "tail", monofunctional $-CH_2MgCl$ "head", and strong bias toward head-to-tail coupling[11] give this polymer system several interesting features. Up to three Grignard head-end groups can couple to each $SiCl_3$ site on the growing polymer. With the addition of each new monomer, another $SiCl_3$ site is formed. Continuation of this process results in a polymer exhibiting extensive branching, limited only by steric effects. Due to the branching, this polymer is characterized by a relatively large number of $SiCl_3$ "tail" functionalities. Only one "CH_2" end group exists for each polymer molecule, as all others are employed in linking the carbosilane polymer together. If no side reactions occur, the extent of branching does not affect the theoretical 2:1 Cl:Si ratio for this polymer. This theoretical Cl:Si ratio can be justified in that the monomer contains three chlorine sites on each silicon ($-SiCl_3$) and one CH_2Cl group (which becomes the Grignard functionality). If all of the Grignard reagent couples with Si–Cl groups, there will be 2 equiv of Si–Cl remaining regardless of the extent of branching. Branching of this polymer can be described by the relationships: $X = T + L + S + D$ and $T = 2D + S + 1$ (where X = total units, T = "tail" units (Cl_3SiCH_2-), L = "linear" units ($-SiCl_2CH_2-$), S = "single-branched" units ($>SiClCH_2-$), and D = "double-branched" units ($>SiCH_2-$). An example

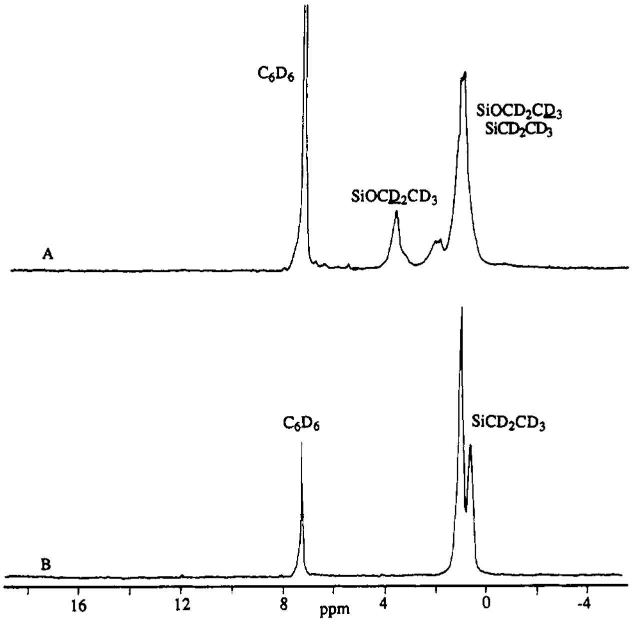


Figure 4. ^{2}D NMR spectra of polycarbosilanes prepared in ether-d_{10}: chloropolycarbosilane (A) and hydridopolycarbosilane (B). A small amount of C_6D_6 was added to the benzene solvent as an internal reference.

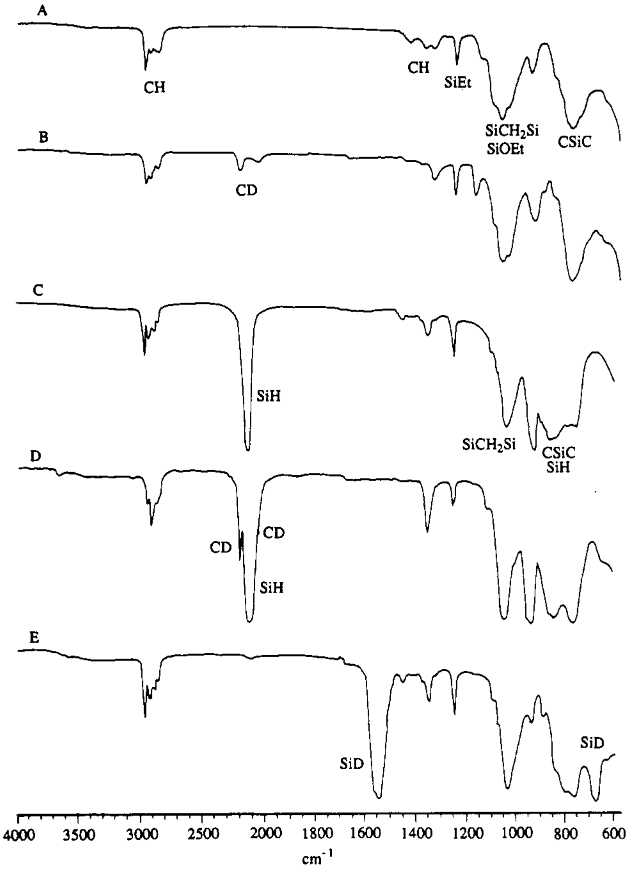
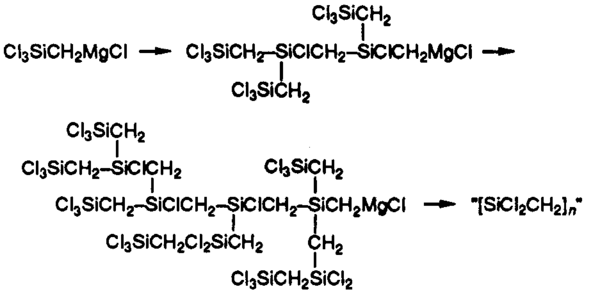


Figure 5. IR spectra of polycarbosilanes: chloropolycarbosilane prepared in ether (A) and in ether-d_{10} (B); hydridopolycarbosilane prepared in ether (C), in ether-d_{10} (D), and in ether but reduced with $LiAlD_4$ (E).

of how the highly branched structure of chloropolycarbosilane develops is given in eq 1. It is important to note that this head–tail coupling process does not cause cross-linking of the branched polymer. For this system, cross-linking would require species with two head-end groups. Cross-linking by direct formation of Si–Si bonding



$$\mathrm{Cl_3SiCH_2MgCl} \rightarrow \mathrm{Cl_3SiCH_2{-}}\underset{\mathrm{Cl_3SiCH_2}}{\mathrm{Si}}\mathrm{ClCH_2{-}}\overset{\mathrm{Cl_3SiCH_2}}{\mathrm{Si}}\mathrm{ClCH_2MgCl} \rightarrow$$

$$\mathrm{Cl_3SiCH_2{-}}\overset{\overset{\mathrm{Cl_3SiCH_2}}{\mathrm{Cl_3SiCH_2{-}SiClCH_2}}}{\mathrm{Si}}\mathrm{ClCH_2{-}}\underset{\mathrm{Cl_3SiCH_2Cl_2SiCH_2}}{\mathrm{Si}}\mathrm{ClCH_2{-}}\overset{\mathrm{Cl_3SiCH_2}}{\underset{\underset{\mathrm{Cl_3SiCH_2SiCl_2}}{\mathrm{CH_2}}}{\mathrm{Si}}}\mathrm{CH_2MgCl} \rightarrow \text{"}[\mathrm{SiCl_2CH_2}]_n\text{"} \qquad (1)$$

by magnesium dechlorination has not been observed, except in the case of phenyl- or aryl-substituted silanes.[12]

The actual chloropolycarbosilane system is found to be considerably more complex, as side reactions are found to occur. In addition to the previously described groups, NMR and IR data indicate that both Si–OEt and Si–Et functionalities are present. Elemental analysis of chloropolycarbosilane shows both a low chlorine and high carbon and hydrogen content for the expected "$[SiCl_2CH_2]_n$" average formula. This is consistent with ^{1}H, ^{13}C and ^{29}Si NMR and IR results, which suggest, in addition to $SiCl_x$, there are significant amounts of Si–OEt and Si–Et functionalities in the chloropolycarbosilane. Precedent for the cleavage of ethers by halosilanes to form alkoxysilanes is well established, having been known for over 100 years.[13] For iodosilanes the reaction is often quantitative.[14] Chlorosilanes are less active, but react similarly,[15] moreover, the extended reflux employed to effect coupling of the Grignard reagent would be expected to increase the extent of ether cleavage.

The formation of the Si–Et functionality is less obvious, it appears to originate from magnesium reacting with EtCl, a product of the side reactions,[15] to form ethyl magnesium chloride, which couples with the Si–Cl functionality to form SiEt groups. These ethyl groups were shown to originate from the diethyl ether used as solvent. When chloropolycarbosilane is prepared by using Et_2O-d_{10} during the Grignard coupling step, the incorporation of SiEt-d_5, (and OEt-d_5) groups occurs. When the polymer is reduced, the usual "ethyl" peaks are not seen in the proton in the proton NMR spectra. These ethyl groups can be seen in the ^{2}D NMR of the same sample, confirming the previous observation. These side reactions are outlined in eqs 2–4.

$$\mathrm{Si{-}Cl} + \mathrm{Et_2O} \rightarrow \mathrm{Si{-}OEt} + \mathrm{Et{-}Cl} \qquad (2)$$

$$\mathrm{Et{-}Cl} + \mathrm{Mg/Et_2O} \rightarrow \mathrm{Et{-}MgCl/Et_2O} \qquad (3)$$

$$\mathrm{Et{-}MgCl/Et_2O} + \mathrm{Si{-}Cl} \rightarrow \mathrm{Si{-}Et} + \mathrm{MgCl_2} \qquad (4)$$

It is difficult to propose an exact formula for the chloropolycarbosilane due to its complexity. Factors such as the rate of addition of Cl_3SiCH_2Cl, concentration, temperature, and length of reflux may have significant effects on the degree of branching, molecular weight, and stochiometry of this polymer. However, the "average" formula appears to be $[SiCl_{1.7}OEt_{0.15}Et_{0.15}CH_2]_n$. This formula represents the best agreement between ^{1}H, ^{13}C and ^{29}Si NMR and IR spectra and literature precedent. If the elemental analysis data are given priority, a considerably different formula, corresponding approximately to $[SiCl_{1.1}Et_{0.15}OEt_{0.35}CH_2]_n$, is obtained. In order to estimate this formula for the chloropolycarbosilane, it was presumed

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(13) Friedel, C. *Ber. Dtch. Chem. Ges.* **1872**, *5*, 327.

(14) (a) Jung, M. E.; Lyster, M. A. *J. Org. Chem.* **1977**, *42*, 3761. (b) Keinan, E.; Perez, D. *J. Org. Chem.* **1987**, *52*, 4846.

(15) (a) Kipping, F. S.; Murray, A. G. *J. Chem. Soc.* **1927**, 2735. (b) Schwartz, R.; Kuchen, W. *Chem. Ber.* **1956**, *89*, 12. (c) Kibbel, H. U.; Schott, G. *Z. Anorg. Allg. Chem.* **1968**, *362*, 81.

Table I. ^1H, ^{13}C, and ^{29}Si NMR Chemical Shift Values (ppm) for the Series $[Me_3SiCH_2]_xSiH_{4-x}$ (x = 1–4)[17e]

	compd (R = Me_3SiCH_2–)			
	$RSiH_3$	R_2SiH_2	R_3SiH	R_4Si
		^1H NMR		
$SiCH_2Si$	−0.40	−0.26	−0.19	−0.11
Si–Me	0.02	0.07	0.10	0.14
Si–H	3.70	4.05	4.29	-
		^{13}C NMR		
$SiCH_2Si$	−8.86	−1.25	3.39	8.58
Si–Me	−0.235	0.906	1.15	1.65
		^{29}Si NMR		
Si–H	−65.1	−38.7	−17.3	14.5
Si–Me	1.81	1.13	0.66	−0.54

that the C, H, and Cl analyses were reasonably accurate. The silicon analysis was not employed for this estimation as it was found to be very low for all of the compounds studied.[16] The formula obtained from elemental analysis is considered to be less reliable in that it suggests a large amount of Si–Si bonding, which in not supported by literature precedent.[12] It also assumes that the C, H, and Cl analyses of the carbosilane are accurate, which is not justified by prior observations on analogous systems.[16]

The molecular weight of the chloropolycarbosilane was not determined by GPC, as even traces of water in the solvent required would cause cross-linking, seriously affecting the results. The MW of this polymer can be indirectly estimated from the GPC of the hydridopolycarbosilane, which is not highly moisture-sensitive. This value was found to be about 15.4 units (vide infra), corresponding to a molecular weight of about 1700 amu, if the "average" repeat unit, $[SiCl_{1.7}OEt_{0.15}Et_{0.15}CH_2]$, for the chloropolycarbosilane is accurate.

Part II: Hydridopolycarbosilane (from Aqueous Workup). The IR spectrum of the hydridopolycarbosilane (Figure 5C) is consistent with the proposed highly branched structure: $[SiH_xCH_2]_n$ (where x = 0–3). Strong peaks at 2140, 930, 830, and 760 cm^{-1} confirm the presence of SiH, SiH_2, and SiH_3 groups.[10] The disappearance of the peaks at 1160 and 960 cm^{-1} and the narrowing of the band near 1060 cm^{-1} are consistent with the reduction of Si–OR groups to Si–H. The absence of the characteristic peak for $SiCH_2CH_2Si$ between 1120 and 1180 cm^{-1} indicates that little or no head-to-head coupling has occurred.[10]

The ^1H NMR spectrum of the hydridopolycarbosilane (Figure 1C) consists of complex multiplets and broad peaks, as expected on the basis of its highly branched structure. The two groups of peaks centered at −0.2 and 0.15 ppm are attributed to the various $SiCH_2Si$ environments and the $SiCH_2$– (of the Si–Et) functionality.[10b,17] Any Si–Me functionality in the polymer from reduced CH_2Cl end groups would also appear in this region. The peak near 1 ppm is consistent with the "–CH_3" protons of ethyl groups on silicon. Residual chloromethyl functionalities not reduced by $LiAlH_4$ treatment appear as a peak of 1.65 ppm. This peak underwent a small upfield shift when the polymer was reduced, as would be expected for the replacement of the electron-withdrawing chlorine atoms on silicon by hydrogen. The three groups of peaks at 3.7, 3.95, and 4.2 ppm closely match the values for the SiH_3, SiH_2, and SiH groups, respectively, in the series of compounds $[Me_3SiCH_2]_xSiH_{4-x}$ (x = 1–3)[17e] (Table I).

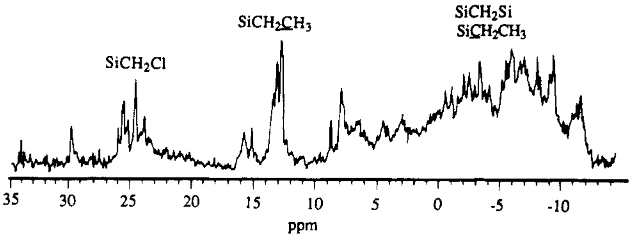

Figure 6. $^{13}C\{^1H\}$ NMR spectrum of hydridopolycarbosilane.

It is difficult to verify by proton NMR spectroscopy that all the Si–OEt functionalities in the chloropolycarbosilane are eliminated during reduction, as the resonances in the ^1H NMR spectrum due to Si–H and Si–OCH_2– tend to overlap. The interference due to the Si–H protons was eliminated by performing the reduction using $LiAlD_4$. The ^1H NMR spectrum of the resulting deuteriopolycarbosilane (Figure 1E) shows no peaks in the 3–5 ppm region, indicating that reduction of the Si–OEt functionality in the polymer is complete. The peaks near 0.2 and 1.0 ppm, for the CH_2 and CH_3 of Si–Et, respectively, and the peak for residual CH_2Cl were not affected. The infrared spectrum of the deuteriopolycarbosilane (Figure 5E) is similar to that for the corresponding hydrido polymer except for those peaks due to Si–H groups. The Si–H stretching peak normally found at 2130 cm^{-1} moved to 1540; the Si–H bending bands at 940 and 820 moved to 675 and below 600 cm^{-1}, respectively.

The peaks seen in the proton NMR spectrum of the hydridopolycarbosilane at 0.15 and 1.0 ppm were suspected to be due to ethyl groups from ether solvent being incorporated into the polymer during the Grignard coupling procedure. Proton NMR analysis of a sample of the chloropolycarbosilane prepared in ether-d_{10} and then reduced with $LiAlH_4$ (Figure 1D) showed that these peaks nearly disappeared.[18] ^2D NMR analysis of this same polymer sample (Figure 4B) shows these ethyl peaks as the only deuterated functionality present. The infrared spectrum of this polymer (Figure 5D) showed distinct changes in the C–H stretching region that were consistent with the proton NMR results. The Et-d_5-substituted polymer shows new peaks at 2205 and 2070 cm^{-1} (due to the C–D functionality) with corresponding decreases in the C–H peaks at 2950 and 2850 cm^{-1}. Some of the weaker peaks in the C–H bending region near 1400 cm^{-1} disappeared, presumably shifting to lower frequency, where they are obscured by the strong Si–CH_2–Si deformation or Si–H bands.

The data from the ^{13}C NMR spectrum of the reduced polymer (Figure 6) are consistent with assignments from the ^1H spectra. Due to the numerous Si–CH_2–Si environments, the major feature is a broad, complicated multiplet extending from −12 to +8 ppm. These NMR chemical shift values are comparable to those for the "model" compounds given in Table I. A small group of peaks at 25 ppm is attributed to residual $SiCH_2Cl$ functionality not completely reduced by the $LiAlH_4$. A second small group of peaks, near 13 ppm is assigned to the "–CH_3" carbon of ethyl groups on silicon. The "CH_2" carbons

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(16) (a) Bacqué, E.; Pillot, I. P.; Birot, M.; Dunoguès, J. *Macromolecules* **1988**, *21*, 30. Patai, S., Rappoport, Z., Eds. *The Chemistry of Organic Silicon Compounds*; Wiley: New York, 1989; Chapter 6. (c) Wu, H. J.; Interrante, L. V. *Chem. Mater.* **1989**, *1*, 564.

(17) (a) Fritz, G.; Maas, J.; Hornung, A. *Z. Anorg. Allg. Chem.* **1980**, *460*, 115. (b) Fritz, G.; Götz, N. *Z. Anorg. Allg. Chem.* **1970**, *370*, 171. (c) Fritz, G.; Grobe, J.; Kummer, D. *Adv. Inorg. Chem. Radiochem.* **1965**, *7*, 349. (d) Fritz, G.; Buhl, H. J.; Kummer, D. *Z. Anorg. Allg. Chem.* **1964**, *327*, 165. (e) Interrante, L. V.; Whitmarsh, C. K., submitted for publication in *J. Organomet. Chem.*

(18) Slight changes in the SiH region of this NMR spectrum are most likely due to differences in the degree of branching compared with other batches rather than any exchange reaction, as no peaks were seen in the Si–H region in the ^2D NMR spectrum.

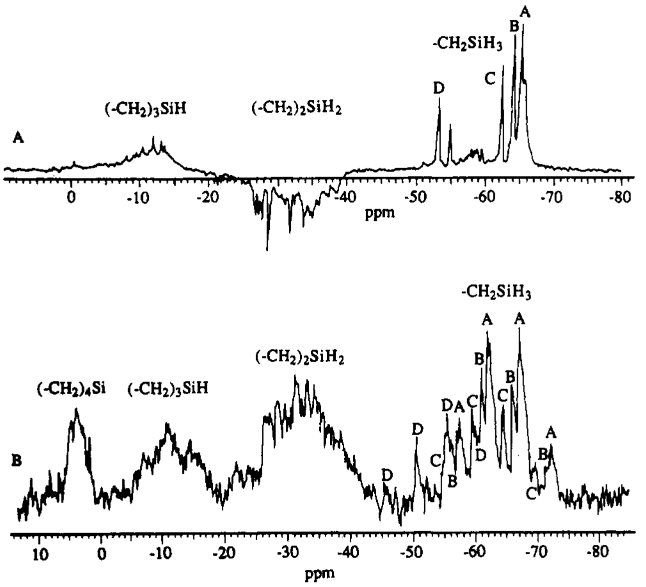

Figure 7. $^{29}Si\{^1H\}$ NMR spectra of hydridopolycarbosilane: (A) DEPT (multiplicity = 1.5); (B) proton coupled. Letters indicate sets of quartets ($^1J_{Si-H} \approx 200$ Hz) arising from SiH_3 end groups.

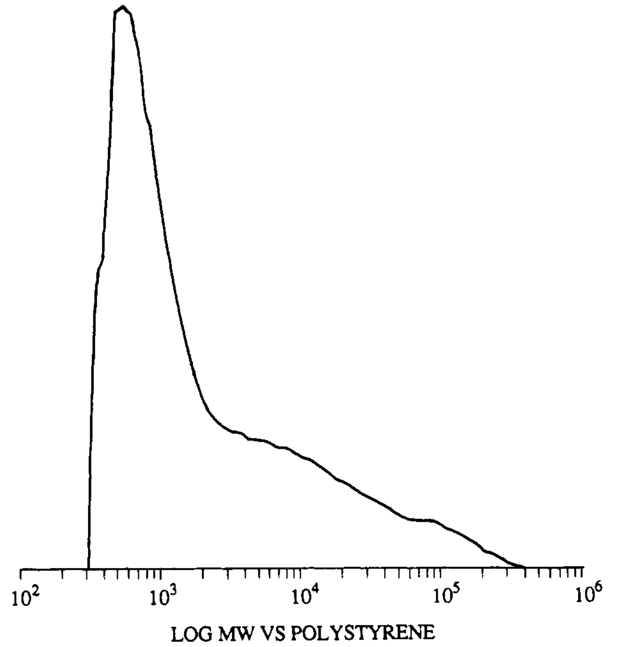

Figure 8. GPC of hydridopolycarbosilane, $M_n = 747$, $M_w = 5200$ vs polystyrene.

of the Si–Et groups are presumably buried under the Si–CH_2–Si multiplet. Peaks observed near 60 ppm in the ^{13}C NMR spectrum of the chloropolycarbosilane (assigned to the $-OCH_2-$ carbons of SiOEt groups) are not seen in the reduced polymer, again suggesting that the ethoxy groups are eliminated during reduction.

The decoupled ^{29}Si DEPT NMR spectrum (multiplicity of 1.5) of the hydridopolycarbosilane (Figure 7A) shows that the groups of peaks between −8 and −14 ppm and several resolved singlets ranging from −53 to −66 ppm have odd numbers of hydrogens, whereas those between −26 and −39 have an even number. This is consistent with assignments as $>SiHCH_2-$, SiH_3CH_2-, and $-SiH_2CH_2-$ polymer functionalities, respectively, using information from the NMR spectra of the model compounds[17e] (Table I). The complexity of these NMR spectra reflects the branched structure of the polymer. The $>SiCH_2-$ units do not appear on this NMR spectrum, as only silicons bearing hydrogens respond under these conditions. The coupled ^{29}Si NMR spectrum (Figure 7B) shows several clearly discernible, overlapping quartets with typical Si–H coupling constants of about 200 Hz. The coupled ^{29}Si NMR spectrum gives little information about the other Si–H functionalities because the peaks are so complicated.

The molecular weight distribution by GPC of the hydridopolycarbosilane (Figure 8) shows a very broad MW distribution, with most of the polymer falling between 450 and 3000 amu, but tailing off up to 50 000 amu to give a large polydispersity value of 6.95. The M_w for this polymer is 745, corresponding to about 15.4 repeat units as $SiH_{1.85}Et_{0.15}CH_2$, the approximate formula suggested by NMR and IR spectroscopy. The actual MW distribution could be considerably different from this, as this polymer is not very similar to the polystyrene standards employed.

NMR integration values show the actual "average" formula for the reduced polymer to be approximately $[SiH_{1.85}Et_{0.15}CH_2]_n$, about one ethyl group for every seven repeat units. As with the chloropolycarbosilane, the elemental analyses disagree; suggesting a formula closer to $[SiH_{1.1}Et_{0.025}CH_2]_n$. Due to the problems in obtaining good elemental analyses on preceramic compounds,[16] this disagreement is not surprising. Low hydrogen content for this type of polymer could also result from several causes, such as Si–Cl, Si–Et, or Si–OEt substitution, in addition to Si–Si or Si–O–Si bonding. The presence of residual Si–Cl groups in the reduced polymer is unlikely, due to the reduction and aqueous workup procedure. Indeed, analysis of the hydridopolycarbosilane found only 1.63% chlorine, which appears to exist as residual chloromethyl groups seen in the proton NMR of the polymer. From the M_w of this polymer and approximate repeat unit weight, the chloromethyl end groups would result in about 2.6% chlorine content. The analysis of 1.63% seems reasonable, as partial reduction of these groups is achieved. The presence of oxygen-containing groups, such as Si–OEt or Si–O–Si, in this polymer is rendered unlikely by the results of oxygen analyses, which indicated only about 0.2% oxygen.[19] In addition, proton and deuterium NMR studies indicated complete reduction of the SiOEt functionality. This is consistent with previous observations that alkoxy groups on silicon, even when surrounded by bulky groups, as in the case of $[1\text{-naphthyl}]_3Si\text{-}OEt$, are converted to the corresponding silanes by $LiAlH_4$ in high yield.[20] Alkyl-substituted alkoxysilanes react similarly.[21] It is difficult to detect any Si–O–Si in the polymer by ^{29}Si NMR spectroscopy as peaks due to SiH interfere. In addition, the strong Si–CH_2–Si deformation band obscures the Si–O–Si region in the IR spectrum of this polymer.

There is little evidence to suggest Si–Si bonding in the hydridopolycarbosilane. There is no precedent for magnesium-induced Si–Si bond formation, except for phenyl- (or aryl-) substituted chlorosilanes.[12] Previous work by others[22] showed that $Cl_3Si\text{-}SiCl_3$ gave silane gas on reduction with excess $LiAlH_4$. This suggests that if any Si–Si bonding is present in the chloropolycarbosilane, it could also undergo reduction to Si–H. The high solubility of the reduced polymer in pentane suggests that either Si–Si bonding does not form, or that it is eliminated during reduction, since formation of Si–Si bonding during the coupling reaction would lead to cross-linking. The pres-

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(19) Oxygen analysis for this compound was performed by LECO; values ranged from 0.01 to 0.02% for three trials.

(20) Gilman, H.; Brannen, C. G. *J. Am. Chem. Soc.* **1951**, *73*, 4640.

(21) Emeléus, H. J.; Smythe, L. E. *J. Chem. Soc.* **1958**, 609.

(22) (a) Gutowski, H. S.; Stejskal, E. O. *J. Chem. Phys.* **1954**, *22*, 939. (b) Finholt, A. E.; Bond, A. C. Jr.,; Wilzbach, K. E.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1947**, *69*, 2692.

ence of Si–Si bonding in the hydridopolycarbosilane is difficult to confirm by ^{29}Si NMR spectroscopy, as the Si–Si regions overlap with Si–H regions.

The formation of Si–Si bonding in the reduced polymer (with loss of hydrogen) after isolation, but prior to the sample analysis, could account for the low hydrogen content by elemental analysis. Samples of the reduced polymer have been observed to gradually increase in viscosity, eventually becoming rubbery and insoluble, and develop pressure when stored in sealed containers exposed to light. This is consistent with cross-linking through Si–Si bond formation and hydrogen loss.

The ethyl groups, as expected, are not affected by the reduction and remain in the hydridopolycarbosilane. Residual Grignard end groups in the chloropolycarbosilane, if any, would be converted to a magnesium aluminum hydride complex during the reduction.[23] Subsequent aqueous acid workup would result in the corresponding hydrocarbon end group, as shown in reactions 5 and 6.

$$>SiCH_2MgCl + LiAlH_4/Et_2O \rightarrow >SiCH_2MgAlH_4 + LiCl \quad (5)$$

$$>SiCH_2MgAlH_4 \xrightarrow{\text{excess } HCl/H_2O} >SiMe + MgCl_2 + H_2 + Al^{3+} + Cl^- \quad (6)$$

Part III: Hydridopolycarbosilane (from Nonaqueous Workup). The polymeric products from the nonaqueous workup are tacky, yellow solids which, unlike those prepared by aqueous workup, rapidly develop a whitish coating on exposure to air. The IR spectrum of this polymer is similar to that from the aqueous workup, except for two additional peaks at 1930 and 670 cm^{-1}. These peaks, in addition to elemental analysis showing 6.64% aluminum, suggest that residual $Al-H_x$ functionality is present.[24] $LiAlH_4$ itself is insoluble in the pentane used to extract the polymer from the residue and therefore not likely to be a contaminant. Furthermore, the polymer had a transparent yellow color with no sign of suspended solid.[25]

The ^1H NMR spectrum of this polymer contains a broad, complex peak between −0.6 and +1.5 ppm, on which is superimposed a narrower peak between 0.8 and 1.1 ppm. The Si–H peaks are similar to those of the polymer derived from the aqueous workup, appearing at 3.6–3.9, 3.9–4.1, and 4.1–4.3 ppm. Their integration ratio with respect to the $Si-CH_2Si$ protons is considerably below the approximately 1:1 ratio seen for the polymer derived from the aqueous workup. Difficulty in separating byproducts of $LiAlH_4$ reductions of polymeric halosilanes by nonaqueous methods has been previously observed.[16a]

Acknowledgment. We thank Dr. Todd Trout and Dr. Corrina Czekaj for helpful discussions and assistance during the course of this work. This work was supported by grants from the Air Force Office of Scientific Research (AFOSR-89-0439) and a DARPA/ONR (URI Program on High-Temperature Advanced Structural Composites).

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(23) Gaylord, N. G. *Reduction With Complex Metal Hydrides*; Interscience: New York, 1956; p 70.

(24) These peaks are observed when the IR spectrum of $LiAlH_4$ was run in Nujol.

(25) The possibility of a colloidal suspension of the $LiAlH_4$ in the polymer cannot be excluded.

Structure and Bonding in the Unsymmetrically Hydrido-Bridged Heterobimetallic Complex $(\eta^5\text{-}C_5H_5)_2Mo(\mu\text{-}H)(\mu\text{-}CO)Co(CO)_3$

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Long-term reaction of $Cp_2Mo(\eta^2\text{-}CO_2)$ ($Cp = \eta^5\text{-}C_5H_5$) with $HCo(CO)_4$ produces the novel hydride-bridged heterobimetallic complex $Cp_2Mo(\mu\text{-}H)(\mu\text{-}CO)Co(CO)_3$ (1) whose X-ray structure and bonding are described in detail. Complex 1 features a deficient electron count, a rare "reverse" unsymmetrical hydride bridge placing the hydride closer to the larger Mo atom [1.64 (3) Å vs 1.88 (3) Å to Co], and a close Mo–Co contact (2.8449 (4) Å). Analysis of 1 using extended Hückel calculations reveals that the metals bond to the hydride and carbonyl bridges in a four-center, four-electron bond. Despite the relatively short Mo–Co distance in 1, there is only a weak metal–metal bonding interaction.

Introduction

Molecules containing an early and a late transition metal in close proximity are being actively studied to search for new catalytic behavior derived from bifunctional activation of substrates[1] and, more fundamentally, to enhance our understanding of the varying bonding and reactivity features of different transition-metal centers. Already, these "early–late heterobimetallics" have shown the ability to incorporate hydrogen,[2] to bind CO in novel ways,[2] and thus to promise a rich reduction chemistry for CO[3] and potentially for CO_2.[4,5]

As part of our studies of the chemistry of coordinated carbon dioxide, we recently reported on the reactions of

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