refinement.[29] No hydrogen atoms were located in the structure, but their contributions were included in the refinements. Scattering factors were taken from ref 30. Supplementary material is available.[31]

Acknowledgment. This work was financially supported by the Robert A. Welch Foundation, the National Science Foundation, and the ARO (Grant No. DAAL 03-89-K-0164). We thank Dr. Kristi Allan and Professor Alan Campion for the recording of our XPS data.

Supplementary Material Available: For 1, complete listings of positional and thermal parameters (2 pages); a table of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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[29] *P* is used in calculation of $\sigma(I)$ to downweight intense reflections in the least-squares refinement. The function minimized was $\sum w(|F_o|-|F_c|)^2$, where $w = 4(F_o)^2/[\sum(F_o)^2]^2$, $[\sum(F_o)^2]^2 = [S^2(C + R^2B) + (P(F_o)^2)^2]/Lp^2$, and *S* is the scan rate, *C* is the total integrated peak count, *R* is the ratio of scan time to background counting time, *B* is the total background count, and *Lp* is the Lorentz–polarization factor.

[30] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

[31] See paragraph at the end of paper regarding supplementary material.

Synthesis and NMR Spectroscopy of Permethylpolysilane Oligomers $\mathrm{Me(SiMe_2)_{10}Me}$, $\mathrm{Me(SiMe_2)_{16}Me}$, and $\mathrm{Me(Me_2Si)_{22}Me}$

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Compounds $\mathrm{Me(SiMe_2)_{10}Me}$ (Si10), $\mathrm{Me(SiMe_2)_{16}Me}$ (Si16), and $\mathrm{Me(Me_2Si)_{22}Me}$ (Si22) were synthesized by coupling a toluene solution of $\mathrm{Me_3SiSiMe_2Cl}$ and $\mathrm{Cl(SiMe_2)_6Cl}$ with sodium–potassisum alloy. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of Si10 were fully assigned by 2D ^{1}H–^{13}C and ^{1}H–^{29}Si NMR spectroscopy; the latter method is useful for obtaining Si–Si as well as Si–H connectivities. Si–Si coupling constants for Si10 were determined with use of INEPT-INADEQUATE NMR spectroscopy.

Introduction

The linear permethylpolysilane oligomers $\mathrm{Me(SiMe_2)_nMe}$ (n = 2–12) were prepared in the 1960s by Kumada and his students,[1] but polysilane oligomers with longer chains are almost unknown. The only exceptions are the compounds $\mathrm{Me(SiMe_2)_{18}Me}$ and $\mathrm{Me(SiMe_2)_{24}Me}$, which were reported by Boberski and Allred from the coupling reaction of eq 1.[2] Oligomeric polysilanes of this type can serve as model compounds for the polysilane polymers, which have now acquired considerable interest.[3]

$$\mathrm{Me(SiMe_2)_6Cl + Cl(SiMe_2)_6Cl \xrightarrow[toluene]{Na/K} Me(SiMe_2)_{6n}Me} \quad n = 2\text{–}4 \qquad (1)$$

$$\mathrm{Me_3SiSiMe_2Cl + Cl(SiMe_2)_6Cl \xrightarrow[toluene]{Na/K} Me(SiMe_2)_nMe} \quad \begin{array}{l} n = 10,\ \mathrm{Si10} \\ n = 16,\ \mathrm{Si16} \\ n = 22,\ \mathrm{Si22} \end{array} \qquad (2)$$

We have synthesized permethylsilane oligomers Si10, Si16, and Si22 according to eq 2 and studied these molecules by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy. The NMR spectra of Si10 were reported earlier[4,5] but could not be decisively assigned. This has now been accomplished with use of two-dimensional NMR methods. One-, two-, and three-bond coupling constants between silicon atoms in Si10 were determined with use of INEPT-INADEQUATE NMR spectroscopy,[6] modified for ^{29}Si.[7,8] The coupling constants may be important for understanding the electron delocalization in polysilanes.[3]

Experimental Section

NMR Spectroscopy. NMR spectra were recorded on a Bruker AM-500 spectrometer at 125.3 MHz for ^{13}C and 99.36 MHz for ^{29}Si. Silicon-29 NMR spectra were recorded with use of the proton-decoupled INEPT pulse sequence D1 = 3.0 s, D2 = 37 ms, and D3 = 12 ms. 2D NMR spectra were acquired with the XHCORR microprogram D1 = 3.0 s, D3 = 74 ms, and D4 = 24 ms. The COLOC microprogram gave similar results. Experimental times were 2.5 h.

The INEPT-INADEQUATE pulse sequence was used for ^{29}Si–^{29}Si couplings with repetition delay 3.0 s, τ_1 = 37 ms, τ_2 = 10 ms, and $\tau_3 = \tau_4$ = 7.2 ms. The notation corresponds to that in Figure 1. Acquisition time was 12 h. Experimental manipulations were carried out in oven-dried glassware under a nitrogen atmosphere.

1,6-Dichlorohexasilane (1). Dodecamethylcyclohexasilane, $\mathrm{(Me_2Si)_6}$ (30 g, 0.082 mol), synthesized from $\mathrm{Me_2SiCl_2}$ by a standard procedure,[9] was treated with $\mathrm{Cl_2}$ in $\mathrm{CCl_4}$ at 0 °C to give 1 and smaller chlorinated permethylsilanes.[10] After Kugelrohr distillation of the mixture, 6.3 g (18%) of 1 was isolated pure.

Pentamethylchlorodisilane (2). $\mathrm{Me_2PhSiCl}$ (17 g, 0.10 mol) was added to 1.75 g (0.25 mol) of Li wire in 150 mL of THF to

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[1] Kumada, M. *Adv. Organomet. Chem.* **1969**, *6*, 19.

[2] Boberski, W. G.; Allred, A. L. *J. Organomet. Chem.* **1968**, *6*, 80.

[3] For reviews see: West, R. *J. Organomet. Chem.* **1986**, 300, 327. West, R. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 19, pp 1207–1240. Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.

[4] Ishikawa, M.; Iyoda, J.; Ikeda, H.; Kotake, K.; Hashimoto, T.; Kumada, M. *J. Am. Chem. Soc.* **1981**, *103*, 4845.

[5] Stanislawski, D. A.; West, R. *J. Organomet. Chem.* **1981**, *204*, 295.

[6] Sørensen, O. W.; Freeman, R.; Frenkiel, T.; Mareci, T. H.; Schuck, R. *J. Magn. Reson.* **1982**, *46*, 180.

[7] Yokelson, H. B.; Millevolte, A. J.; Adams, B. R.; West, R. *J. Am. Chem. Soc.* **1987**, *109*, 4116.

[8] Maxka, J.; Adams, B. R.; West, R. *J. Am. Chem. Soc.* **1989**, *111*, 3447.

[9] Chen, S.-M.; Katti, A.; Blinka, T. A.; West, R. *Synthesis* **1985**, 684.

[10] Wojnowski, W.; Hurt, C. J.; West, R. *J. Organomet. Chem.* **1977**, *124*, 271.

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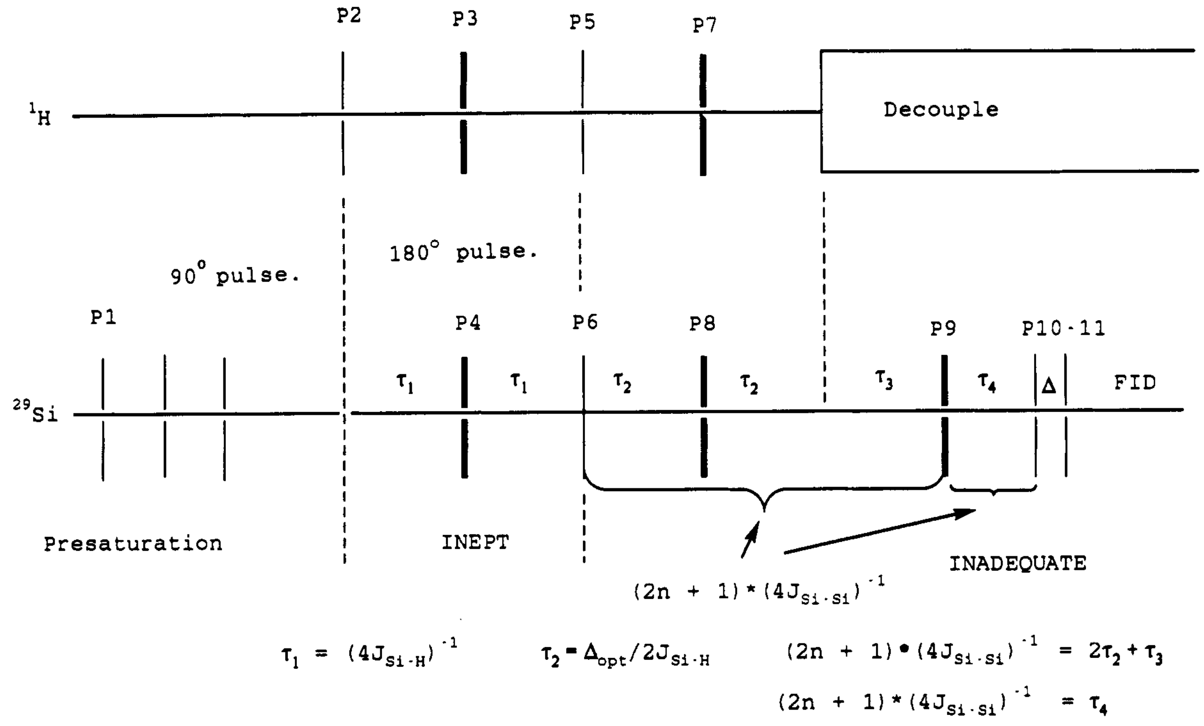


Figure 1. INEPT-INADEQUATE pulse sequence, as adapted for ^{29}Si from the sequence of Sørensen for ^{13}C.[6]

give $Me_2PhSiLi$. The resulting solution was added to a solution of 13 g (0.12 mol) of Me_3SiCl in 100 mL of THF, yielding $Me_3SiSiMe_2Ph$. After 24 h the THF was removed under reduced pressure and 90 mL of benzene was added along with 0.05 g of $AlCl_3$. Gaseous HCl was added to the solution until GC analysis indicated the disappearance of starting material. $AlCl_3$ was deactivated by addition of acetone, and the benzene was removed by distillation. Compound **2**, 9.5 g (60%), was distilled at 134 °C (lit.[11] bp 134 °C).

Me(SiMe$_2$)$_n$Me. Sodium (0.46 g, 0.02 mol) and potassium (1.56 g, 0.04 mol) were added to 150 mL of toluene and stirred to form an alloy. The toluene solution was heated to reflux, and a mixture of 6.3 g (0.015 mol) of **1** and 8.1 g (0.048 mol) of **2** was slowly added. After the solution was heated for 48 h, the reaction was quenched with ethanol, and water was added to dissolve the salts. The water was discarded, and an insoluble fraction was filtered from the toluene. The toluene was stripped off, leaving a viscous oil that was distilled at 245 °C/14 Torr, yielding Si10 (2.3 g, 25%), having properties identical with those reported earlier:[4,5,12] mp 115 °C; ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 9 H), 0.11 (s, 6 H), 0.16 (s, 6 H), 0.18 (s, 6 H), 0.19 (s, 6 H); HRMS calcd 610.2857 (M^+), found 610.2856. Crystallization of the residual solid from 1:1 cyclohexane–ethanol gave Si16 (0.6 g, 8%), a new compound:[13] mp 198–200 °C; ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 9 H), 0.11 (s, 6 H), 0.16 (s, 6 H), 0.18 (s, 6 H), 0.19 (br s, 24 H); ^{13}C NMR (cyclohexane-d_{12}, 70 °C) δ −1.08, −5.32, −3.90, −3.60, −3.54, −3.51, −3.50 (2); ^{29}Si NMR (cyclohexane 70 °C) δ −14.900, −42.661, −38.481, −37.170, −36.932, −36.878, −36.787, −36.775; UV (λ_{max}, nm (ϵ); 3-MP) 293 (5.6×10^4), 224 sh (3.5×10^4); HRMS calcd 958.4290 (M^+), found 958.4292 (10.4%). Anal. Calcd for $C_{34}H_{102}Si_{16}$: C, 42.52; H, 10.70. Found: C, 42.69; H, 10.66.

The fraction of the product insosluble in cyclohexane–ethanol was extracted twice with boiling octane. Removal of the solvent gave 0.4 g (6%) of Si22: mp 216–218 °C; ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 9 H), 0.11 (s, 6 H), 0.16 (s, 6 H), 0.19 (br s, 48 H); UV (λ_{max}, nm; 2-MeTHF) 292, 241; LRMS calcd 1308 (M^+), found 1308 (5.6%). Anal. Calcd for $C_{46}H_{138}Si_{22}$: C, 42.19; H, 10.62. Found: C, 42.09; H, 10.76.

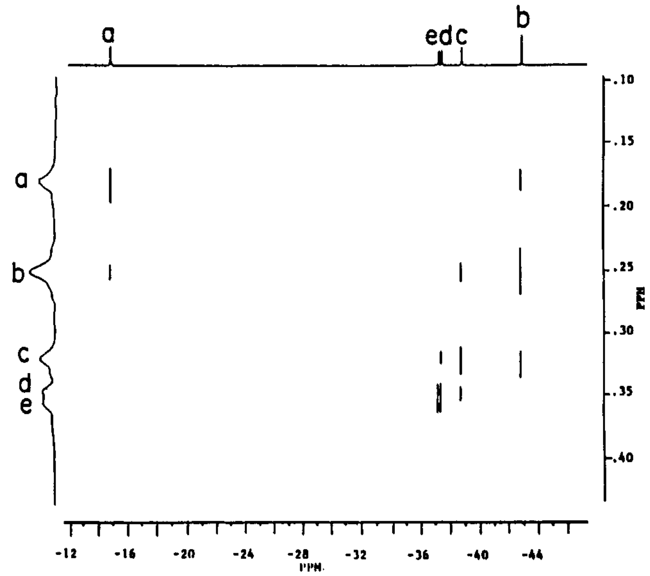
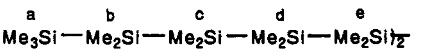


Figure 2. 2D ^{1}H–^{29}Si correlated NMR spectrum of Si10. The ^{29}Si NMR spectrum is projected horizontally and the ^{1}H NMR spectrum vertically.

Chart I. Designations of Si, C, and H Atoms in Spectra of Si10



$$(\overset{a}{\mathrm{Me_3Si}}-\overset{b}{\mathrm{Me_2Si}}-\overset{c}{\mathrm{Me_2Si}}-\overset{d}{\mathrm{Me_2Si}}-\overset{e}{\mathrm{Me_2Si}})_2$$

Results and Discussion

2D NMR Spectroscopy of Si10. The peak assignments and proton–silicon connectivities for Si10 were established in a straightforward manner from the 2D ^{1}H–^{29}Si NMR spectrum, shown in Figure 2.[14] In this and other spectra, atoms are designated by letters as shown in Chart I. Analysis of the spectrum is greatly aided by the fact

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(11) Ishikawa, M.; Kumada, M.; Sakurai, H. *J. Organomet. Chem.* **1970**, *23*, 63.

(12) Kumada, M.; Ishikawa, M.; Maeda, S. *J. Organomet. Chem.* **1966**, *5*, 120.

(13) Properties of Si16 are rather similar to those reported for Me(SiMe$_2$)$_{18}$Me in ref 2.

(14) For an earlier application of 2D ^{1}H–^{29}Si NMR spectroscopy using a somewhat different technique, see: Liepinsh, E.; Sekacis, I.; Lukevics, E. *Magn. Reson. Chem.* **1985**, *23*, 10.

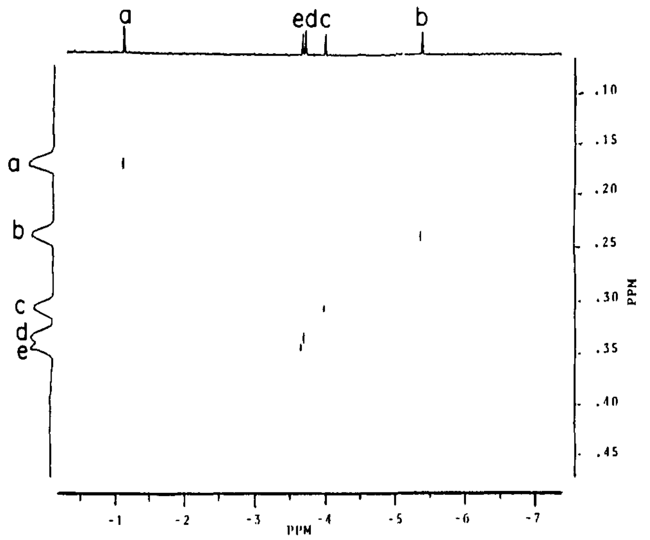

Figure 3. 2D ^1H–^{13}C correlated NMR spectrum of Si10. The ^{13}C NMR spectrum is projected horizontally and the ^1H NMR spectrum vertically.

that both $^2J_{Si-H}$ (~7 Hz) and $^3J_{Si-H}$ (~3.5 Hz) are observable in the 2D spectrum and can be distinguished because of the difference in their magnitudes. It is therefore possible to determine not only the Si–H but also the Si–Si connectivities from this experiment, as explained below.

Peak a, corresponding to the terminal unit in the ^1H spectrum, can be positively identified since it is the only one with nine protons. In the ^{29}Si dimension, the silicon directly related (two bonds away) to a can be found by locating the long line, corresponding to the larger coupling, in the same row as proton a. The silicon represented by the peak in this column must be silicon a. By finding the shorter line (corresponding to the three-bond coupling) in the column under silicon a, and following the row back to the left side where the proton projection is displayed, we find the methyl proton that must correspond to the penultimate Me_2Si unit, proton b. Tracking the row corresponding to proton b leads to the longer vertical line that identifies this column as silicon b. Since silicon b would be indirectly bonded (three-bond) to both a and the methyl proton in the antepenultimate Me_2Si unit c, tracking the column for the new shorter line will identify the row on the proton projection that corresponds to proton c. Likewise, the long line on the row projected from proton c gives the column for silicon c. Silicon c will also have a peak corresponding to methyl protons on the Me_2Si unit d. In the column projected from silicon d, no other short line that would point to the methyl proton relating to the innermost Me_2Si unit e is observed, because in the proton dimension there is not sufficient resolution to prevent the two lines from overlapping. Similarly, the column under silicon e has only one observable line, which is actually composed of a long line on the row projected to e and a short line projected to d.[15]

A simple ^1H–^{13}C 2D correlation provides assignments for the ^{13}C peaks. That spectrum (Figure 3) shows only one line in each column and row, as expected for the ^{13}C–^1H relationship since $^1J_{C-H} \gg {}^{2,3}J_{C-H}$.

It is generally observed that ^{29}Si resonances are shifted upfield when additional Si atoms are attached. Thus, the outermost a silicon in Si10 has a peak at δ −14.9 ppm, while the next atom in the chain, b, shows a peak at δ −44.2 ppm. However, moving from silicon b to c, d, and e, the ^{29}Si chemical shifts appear progressively downfield by 4.2, 1.3, and 0.4 ppm.

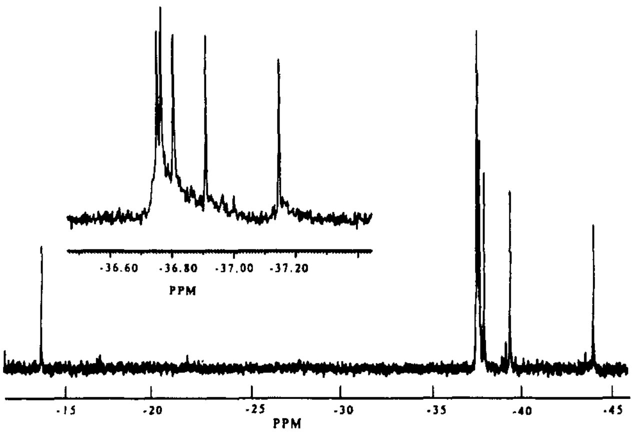

Figure 4. ^{29}Si NMR spectrum of Si16. The expansion covers the five resonances between −38 and −36 ppm.

In Figure 4 the ^{29}Si NMR spectrum for Si16 is displayed. The resonances fall too close together to allow a full 2D analysis, but the spectrum can be interpreted by analogy to that of Si10; the peak at −14.9 ppm is assigned to the terminal silicon, and the peaks from −42.661 to −36.775 ppm are assigned to internal Si atoms, with the innermost atoms giving the most downfield shift. Similar trends are found for the ^{13}C chemical shifts, both for Si10 and Si16.

INEPT-INADEQUATE ^{29}Si NMR Spectroscopy of Si10. Double quantum coherence (INADEQUATE) NMR spectroscopy was first applied to ^{29}Si in 1987[7] and has since been employed by several groups to determine Si–Si connectivities and coupling constants.[16,17] In the INADEQUATE experiment the normally observed ^{29}Si resonances are suppressed and the peaks that arise from coupling to other silicon nuclei, usually observed as satellites buried in the base line noise, are enhanced.

The INEPT-INADEQUATE spectrum for Si10 is displayed in Figure 5. The one-bond coupling constants are detected as up–down antiphased doubles, while the two-bond and three-bond coupling constants give a characteristic down–up pattern.

Analysis of the patterns for silicons a and b (Figure 5A) is straightforward because the chemical shift difference is much greater than the coupling constant. For silicons c–e, the patterns are much more complex because the coupling constants are similar in magnitude to the chemical shift differences. The spectrum for silicon c (right side of Figure 5B) shows two one-bond couplings. The inner up–down doublet, with lines equidistant from the chemical shift for silicon c, is assigned as $^1J_{cb}$. The outer two lines form one wing of an AB quartet, representing the coupling of silicon c to d. The other part of that quartet is indicated as $^1J_{dc}$ on the left-hand side of the figure. Resonance c has two two-bond couplings, $^1J_{ca}$ and $^2J_{ce}$, which cannot be completely resolved.[18]

Because the resonances for silicons d and e are only separated by 19.56 Hz, their coupling patterns overlap (Figure 5B). The outermost lines in the cluster around silicons d and e can be identified as part of the quartet belonging to $^1J_{cd}$. The residual single quantum resonances

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[15] In spite of this apparent confusion silicons d and e can easily be identified because c only shows correlation to d.

[16] Kuroda, M.; Kabe, Y.; Hashimoto, M.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1727.

[17] Hengge, E.; Schenk, F. *J. Organomet. Chem.* **1989**, *362*, 11.

[18] In Chart I, the values are taken from measuring these couplings at resonances a and e, where there is only one two-bond coupling.

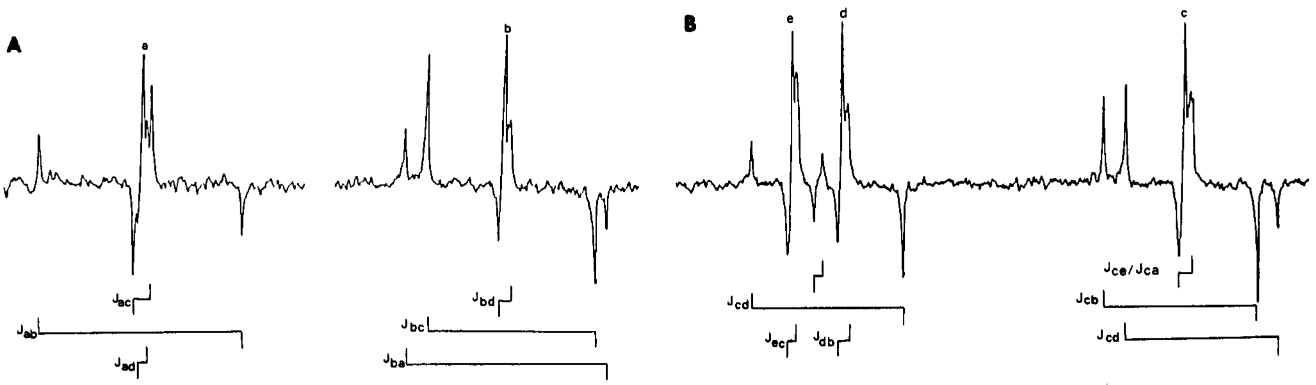

Figure 5. (A) INEPT-INADEQUATE ^{29}Si NMR spectrum of the a (on the left) and b (on the right) resonances of Si10. The residual single-quantum peaks also appear in the spectrum and are indicated. For resonance a, a three-bond coupling is clearly resolved. (B) INEPT-INADEQUATE ^{29}Si NMR spectrum of the c, d, and e resonances in Si10. This spectrum contains two "AB" patterns, c–d and d–e. Both wings of the quartet for c–d are observable, but for d–e only the central two lines of the quartet can be seen. Residual single-quantum peaks are indicated.

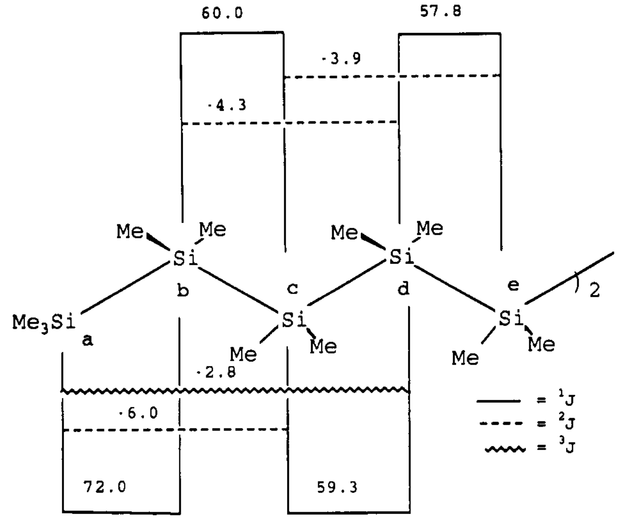

Figure 6. ^{29}Si–^{29}Si coupling constants for Si10, in Hz. Estimated errors are ±0.2 Hz.

for silicons d and e are each surrounded by intense, equidistant down–up doublets, assigned as $^2{}_{\rm jdb}$ and $^2J_{ec}$. Finally, two lines phased up–down appear between d and e; these are the center lines of a quartet representing $^1J_{de}$. Although the outer lines of the quartet cannot be resolved, the coupling constant can be calculated from a standard equation.[19]

The ^{29}Si coupling constants measured for Si10 are displayed in Figure 6. The one-bond coupling is greatest for the terminal Si–Si bond (72 Hz); the interior Si–Si bonds all show ^1J values near 60 Hz, but these decrease slightly toward the center of the molecule. The decrease in $^1J_{\rm Si-Si}$ from the terminal to the internal Si–Si bonds can be explained by hybridization changes reflecting the electronegativity of silicon being lower than that of carbon. Terminal silicon a, bonded to three carbons and one silicon, can direct much of its s character to silicon atom b, leading to a high value for the terminal coupling constant. Because the internal silicons are each bonded to two other silicon atoms, the s orbital contribution to each of their Si–Si bonds is smaller, resulting in lower $^1J_{\rm Si-Si}$ values. Similar decreases in $^1J_{\rm Si-Si}$ with increasing numbers of bonded Si atoms have been noted previously in the series $(Me_2Si)_2SiMe_2$ (73.2 Hz), $(Me_3Si)_3SiCH_3$ (62 Hz), and $(Me_3Si)_4Si$ (52.5 Hz)[20] and in a linear tetrasilane studied recently.[17]

The two-bond Si–Si coupling constants are much smaller and are expected to be opposite in sign.[21] They also decrease somewhat as one goes toward the center of the chain. One three-bond coupling, $J_{ad} = -2.8$ Hz, was observed in the signal for silicon a. In the signal for silicon d, J_{ad} overlaps J_{bd} and so was not resolved.

Conclusions. Si–Si connectivities can be established by INADEQUATE (double quantum coherence) ^{29}Si NMR spectroscopy as seen from these results and as shown by us and by other workers earlier.[7,8,16,17,22] However, the 2D ^{1}H–^{29}Si NMR spectrum provides a much easier means to obtain the same connectivity information. This method is uniquely applicable to alkylpolysilanes, because of the fortuitous circumstance that both $^2J_{\rm Si-H}$ and $^3J_{\rm Si-H}$ appear in the 2D spectrum and can be separately identified. The INEPT-INADEQUATE ^{29}Si NMR method, of course, allows determination of ^{29}Si–^{29}Si coupling constants as well as connectivities.

Acknowledgment. Research was sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Contract Nos. F49620-86-0010 and AFOSR-89-0004 and a grant from the 3M Co.

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[19] See: Wiberg, K. B.; Nist, B. J. *The Interpretation of NMR Specta*; W. A. Benjamin: New York, 1962; p 3. The intensity ratio of the outer to the inner lines is given by the formula $[(\Delta^2 + J^2) - J]/[(\Delta^2 + J^2) + J]$. With use of the values $\Delta = 19.56$ and $J = 57.8$, the outer lines are predicted to have an intensity of only 3% of the inner ones.

[20] Sharp, K. G.; Sutor, P. A.; Williams, E. A.; Cargioli, J. D.; Farrar, T. C.; Ishibitsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 1977.

[21] Marsmann, H. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Ed.; Springer: New York, 1981; Vol. 17, p 128.

[22] Gillette, G. R.; Maxka, J.; West, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 54.