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# CYCLIC POLYSILANES

## IX*. ANION-RADICALS OF SUBSTITUTED PERMETHYLCYCLOPOLYSILANES

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### Summary

Several substituted permethylcyclopolysilanes were reduced to anion-radicals and studied by ESR spectroscopy. Compounds investigated were $Si_5Me_9X$ (X = hydrogen, phenyl, benzyl, trimethylsilyl, phenyldimethylsilyl), $Si_6Me_{11}X$ (X = hydrogen, phenyl, benzyl, trimethylsilyl) and 1,1-$(Me_3Si)_2Si_5Me_8$. All of the compounds form anion-radicals in which the unpaired electron appears to be delocalized over the polysilane ring, except for $Si_6Me_{11}Ph^{\overline{\cdot}}$ (and possibly $Si_6Me_{11}CH_2Ph^{\overline{\cdot}}$), where the odd electron is located mainly in the aromatic ring. The six-membered ring cyclosilane anion-radicals are all unstable decomposing in most cases to $Si_5Me_{10}^{\overline{\cdot}}$, whereas $Si_5Me_9SiMe_2R^{\overline{\cdot}}$ (R = methyl or phenyl) decompose to $Si_5Me_9H^{\overline{\cdot}}$.

The permethylcyclopolysilanes, $(Me_2Si)_n$ where $n$ = 4-6, undergo reduction to anion-radicals $(Me_2Si)_n^{\overline{\cdot}}$ [2]. Electron spin resonance (ESR) spectroscopy of these anion-radicals shows that the unpaired electron interacts with each of the methyl protons equally, and therefore, is completely delocalized over the ring. The observed hyperfine splitting constants for $(Me_2Si)_5^{\overline{\cdot}}$ indicate that the half-occupied orbital has little or no atomic *s* orbital character and suggest that the orbital in question is "$\pi^*$-like". Similar electron delocalized anion-radicals have been reported for $(MeEtSi)_6$ and $(Et_2Si)_6$ [3].

We have now examined a series of substituted five- and six-membered cyclopermethylpolysilanes with hydrogen, trimethylsilyl, phenyl, benzyl or phenyldimethylsilyl in place of one (or two) of the methyl groups in $(Me_2Si)_5$ or $(Me_2Si)_6$. Our objectives were to find out, first, whether reduction to anion-

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* For part VIII see ref. 1.

radicals was general for cyclic methylpolysilanes, and second, how delocalization would be affected by the changed symmetry of the rings resulting from substitution.

## Experimental

The compounds studied were all provided by Drs. M. Kumada and M. Ishikawa of Kyoto University, Kyoto, Japan [4], and included the following: $Si_5Me_9X$, where X = H, phenyl, benzyl, trimethylsilyl and phenyldimethylsilyl; $Si_6Me_{11}X$, where X = hydrogen, phenyl, benzyl, trimethylsilyl, chlorine and fluorine; and the doubly substituted compound $Si_5Me_8(SiMe_3)_2$, 1,1-bis(trimethylsilyl)octamethylcyclopentasilane. The purity and identity of the samples were confirmed by gas chromatography as well as proton magnetic resonance and mass spectroscopy. ESR experiments were generally carried out on samples freshly purified by gas chromatography, using an SE 30 silicone column on 40/60 mesh Chromosorb W. This precaution was especially necessary for $Si_5Me_9H$, which undergoes fairly rapid oxidation in air.

Anion-radicals were generated by electrolytic reduction, using cells constructed of 4 mm Pyrex tubing with platinum wire electrodes [5]. A plug of glass wool was used to separate the electrode compartments and minimize diffusion. The solvent, generally highly purified tetrahydrofuran, was distilled into the cell containing the cyclosilane and supporting electrolyte (tetra-n-butylammonium perchlorate) and the cell was degassed several times. Final concentrations were approximately 0.01 *M* in cyclosilane and 0.2 *M* in $n\text{-}Bu_4N^+ClO_4^-$. Electrolysis was carried out at the lowest voltage which would give satisfactory current (0.2-0.4 $\mu$A).

Reduction was first attempted at —90 to —95°C in THF as solvent. If a well-resolved spectrum was obtained, the temperature was slowly increased noting any changes until decomposition occurred. The five-membered ring anion-radicals were all stable from —110° up to —70 or —60°C and were cycled over this range to search for temperature effects.

Samples that produced no ESR signal or that showed no proton hyperfine splitting at —95°C in THF were also investigated in 3/1 dimethyl ether/1,2-dimethoxyethane at lower temperatures, down to —140°C. In general, resolution was not improved at temperatures lower than —95°C.

In addition to the compounds listed in Table 1, attempts were made to reduce $Si_6Me_{11}Cl$ and $Si_6Me_{11}F$ to anion-radicals, but no ESR signal was ever observed, even at —140°C. Presumably, loss of halide ion takes place too rapidly for anion-radicals to be observed for these species.

ESR spectra were determined using a Varian V4502 X-band spectrometer with 100 KHz field modulation and V-4557 variable temperature attachment. A dual cavity was used for the determination of *g*-values, which were measured against peroxylamine disulfonate anion in water, recorded simultaneously. To enhance resolution of the spectra, line sharpening by admixture of third and fifth derivative signals with the first derivative signal was used, following the procedure of Glarum [6]. This procedure distorts linewidth but leaves the position and amplitude of the lines unchanged. For further details of the reduction procedure and ESR measurement, see ref. 3.

TABLE 1

ESR PARAMETERS [a] FOR SUBSTITUTED CYCLOPOLYSILANE ANION-RADICALS

| Compound | $g$ | Color of soln. | $a$(H) G | $a$($^{13}$C) G |
|---|---|---|---|---|
| $Si_5Me_{10}^{\cdot -}$ | 2.0032 | Blue | $a$($SiCH_3$) 0.53 | 16.03 (5.6) [b] |
| $Si_5Me_9H^{\cdot -}$ | 2.0029 | Blue | $a$(Si-H) 14.1<br>$a$($SiCH_3$) 0.51, 1.02 | 13.3 (2.3) [b]<br>24.4 (0.7) [b] |
| $Si_5Me_9SiMe_3^{\cdot -}$ | 2.0049 | Blue | $a$(Si—$CH_3$) 0.56 | |
| $Si_5Me_9SiMe_2Ph^{\cdot -}$ | 2.0036 | Blue | Not resolved | |
| $Si_5Me_8(SiMe_3)_2^{\cdot -}$ | 2.0042 | Blue | Not resolved | 23.1 (4.5) [b]<br>17.2 [c] |
| $Si_5Me_9Ph^{\cdot -}$ | 2.0034 | Blue | $a$($SiCH_3$) 0.51 (—90°C)<br>$a$($SiCH_3$) 0.54 (—60°C) | 14.7 at —90°C<br>17.0 at —60°C |
| $Si_5Me_9CH_2Ph^{\cdot -}$ | 2.0032 | Blue | $a$($SiCH_3$) 0.54 | 16.1 (5.6) [b] |
| $Si_6Me_{12}^{\cdot -}$ | 2.0028 | Yellow | $a$($SiCH_3$) 0.49 | 14.60 |
| $Si_6Me_{11}H^{\cdot -}$ | | Yellow | $a$(Si—H) 13.4 (—110°C)<br>$a$($SiCH_3$) Not resolved | |
| $Si_6Me_{11}SiMe_3^{\cdot -}$ | 2.0030 | Yellow | Not resolved | |
| $Si_6Me_{11}Ph^{\cdot -}$ | 2.0049 | Brown | $a$(H, *para*) 7.65<br>$a$(H, *ortho*) 2.65 | |
| $Si_6Me_{11}CH_2Ph^{\cdot -}$ | | Yellow | not resolved | |

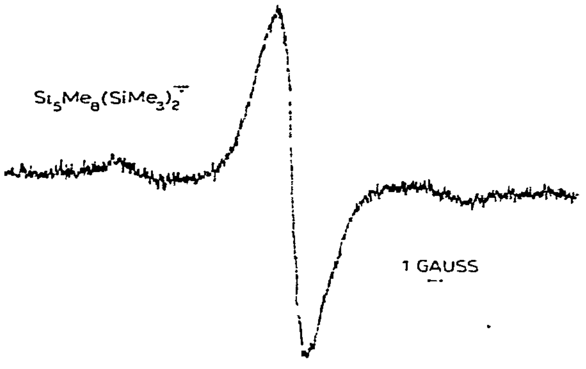
[a] Spectra recorded in THF solution at —95°C except as noted. [b] Intensities of lines relative to the center line are given in parentheses; calculated intensities in % for $^{13}$C sidebands are as follows: 0.56 (1C); 1.11 (2C); 1.68 (3C); 2.22 (4C); 2.80 (5C); 3.33 (6C); 3.92 (7C); 4.44 (8C); 5.04 (9C); 5.55 (10C); 6.06 (11C); 6.66 (12C). [c] Intensity of sideband could not be accurately determined.

## Discussion

The results of the electrolytic reductions are summarized in Table 1. Except for $Si_6Me_{11}Cl$ and $Si_6Me_{11}F$, the compounds studied all gave anion-radicals upon electrolytic reduction. Solutions of the five-membered ring anion-radicals were all blue in color, whereas those of the six-membered ring species were yellow ($Si_6Me_{11}Ph^{\cdot -}$ was brown). These observations are consistent with the colors observed for $(Me_2Si)_5^{\cdot -}$ (blue) and $(Me_2Si)_6^{\cdot -}$ (yellow) whose visible spectra have been investigated previously [3]. The finding that permethylcyclopolysilanes form delocalized anion-radicals can therefore be generalized to include substituted compounds also.

For permethylcyclopolysilane anion-radicals such as $(Me_2Si)_5^{\cdot -}$, the ESR spectrum is a multiplet reflecting the hyperfine interaction of the unpaired electron with all of the equivalent $CH_3$ protons on the methyl groups. In the substituted compounds the symmetry is broken and the methyl groups necessarily become non-equivalent. Different hyperfine splitting by non-equivalent methyl protons should give rise to overlapping patterns and, ultimately, to an unresolved broad line spectrum. A single broad line was in fact observed for $Si_6Me_{11}SiMe_3^{\cdot -}$, $Si_5Me_9SiMe_2Ph^{\cdot -}$, and $Si_5Me_8(SiMe_3)_2^{\cdot -}$; two broad lines (split by Si—H interaction) were found for $Si_6Me_{11}H^{\cdot -}$, in agreement with expectation (Table 1, Fig. 1). However, for $Si_5Me_9H^{\cdot -}$, $Si_5Me_9Ph^{\cdot -}$ and $Si_5Me_9CH_2Ph^{\cdot -}$, proton hyperfine splitting was resolved. Partial resolution of proton splitting was observed also for $Si_5Me_9SiMe_3^{\cdot -}$ (Fig. 2).

Resolution of proton hyperfine splitting could result, if the substituents



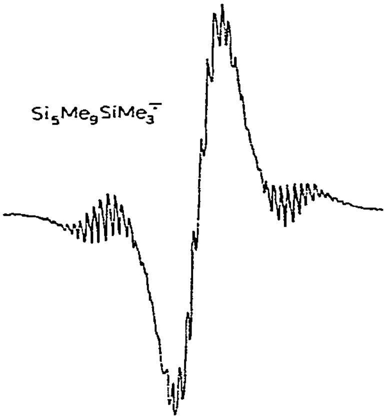


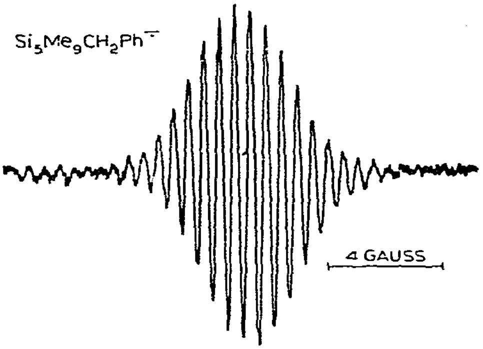
Fig. 1. ESR spectrum of 1,1-$(Me_3Si)_2Si_5Me_8$ anion-radical, —95°C in THF.

Fig. 2. ESR spectrum of $Si_5Me_9SiMe_3$ anion-radical, —95°C in THF showing partial resolution of proton hyperfine splitting Multiplet sidebands are due to the decomposition product $Si_5Me_9H^{\overline{\cdot}}$.

alter the unpaired spin density at various silicon atoms so slightly that the proton splitting constants remain nearly equivalent. This is almost certainly the explanation for the proton splittings in $Si_5Me_9CH_2Ph^{\overline{\cdot}}$ (Fig. 3). This radical shows a multiplet pattern with proton and $^{13}C$ coupling constants almost identical to those for $(SiMe_2)_5^{\overline{\cdot}}$ (Table 1). Moreover the $^{13}C$ sidebands have an intensity correct for 10 equivalent carbons. Likewise, equivalence of proton splitting constants probably accounts for the multiplet for $Si_5Me_9Ph^{\overline{\cdot}}$. This anion-radical shows a temperature dependent ESR spectrum (see below), but generally the pattern and hyperfine splitting constants are similar to those for $(SiMe_2)_5^{\overline{\cdot}}$.

Such a small effect of substituents on the electron distribution in the half-filled orbital was unexpected. By analogy with delocalized anion-radicals of aromatic systems, one might have expected these substituents to cause large changes in spin densities and ESR spectra. But although the cyclopolysilanes show electron delocalization in their anion-radicals as do aromatics, the two classes of compounds are very different. Simple Hückel MO theory allows prediction of how spin densities in aryl systems should vary with various substituents [7]. No such predictions are possible yet for cyclopolysilanes as we lack sufficient knowledge of the molecular orbitals in these systems. Whatever the actual character of these molecular orbitals, it appears that substitution of phenyl and benzyl groups for methyl in cyclopentasilane anion-radicals perturbs the LUMO only very slightly.

Proton hyperfine splitting could also be observed if the proton coupling constants were different but fortuitously related in some simple way. Such a coincidence may account for the well-resolved spectrum of $Si_5Me_9H^{\overline{\cdot}}$. The spectrum is a principal doublet due to hyperfine splitting by the silane proton. As expected, the splitting constant for the silane proton, 14.1 G, is rather higher than that observed for Si—H protons in aromatic anion-radicals with exocyclic $R_2SiH$ groups, which show splittings of 1-8 G. Hyperfine splitting by methyl protons is observed within each wing of the doublet. This spectrum cannot be simulated well if it is assumed that all 27 methyl protons couple equally, but



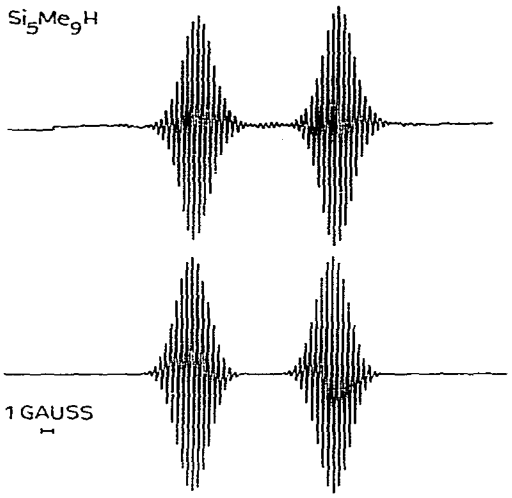


Fig. 3. ESR spectrum of $Si_5Me_9CH_2Ph$ anion-radical, −95°C in THF showing well-resolved proton hyperfine splitting.

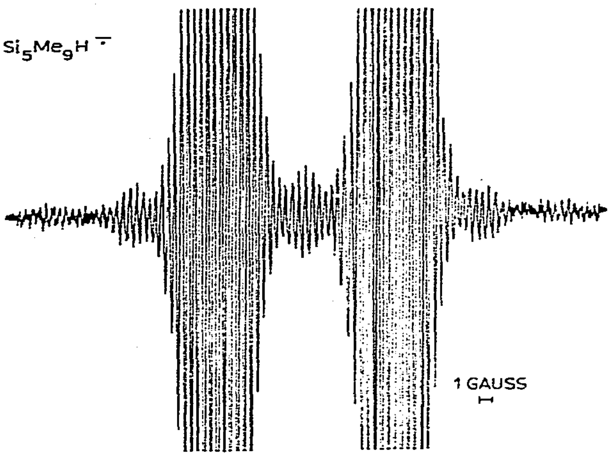
Fig. 4. (Above) ESR spectrum of $Si_5Me_9H$ anion-radical, −90°C in THF. (Below) Computer simulated spectrum assuming $a$(SiH) 14.6 G, $a(CH_3)$ 1.04 G for protons in the unique methyl group, and $a(CH_3)$ 0.52 G for all other methyl protons.

as shown in Fig. 4, a good match is obtained if 24 methyl protons are assigned a hyperfine splitting constant of 0.51 G and three protons (on the methyl group *gem* to the silane hydrogen) a splitting constant of 1.02 G. If the proton hyperfine splittings reflect spin density according to a McConnell type relationship, it appears that spin density is twice as high at the silicon bearing the hydrogen as at the other four silicon atoms.

Some support for this interpretation is obtained from the sideband splitting pattern. Sidebands due to $^{13}C$ splitting are found at 13.3 G for four equivalent carbons and at almost twice this value (24.4 G) for one carbon (Fig. 5). This again suggests that spin density is roughly half as great at the unique carbon atom as at some of the ring carbons. However the other four carbons must also give rise to one or more $^{13}C$ sidebands which were not observed. The eight carbons need not give degenerate splitting even though their attached hydrogens do [8, 9].

In the substituted polysilanes containing aromatic groups, the unpaired electron could be associated with either the polysilane ring or the aromatic ring. Fortunately the types of spectra produced are quite different and therefore a clear distinction can be made. The five-membered ring anion-radicals $Si_5Me_9Ph^{\cdot-}$ and $Si_5Me_9CH_2Ph^{\cdot-}$ show typical multiplet spectra characteristic of methyl cyclopolysilane anion-radicals (Figs. 3, 7); there is no doubt that in these compounds the unpaired electron is associated with the polysilane rather than with the aromatic ring. Although the multiplet structure was not resolved, the same seems to be true for $Si_5Me_9SiMe_2Ph^{\cdot-}$.

The opposite case is illustrated by $Si_6Me_{11}Ph^{\cdot-}$, which has an entirely dif-



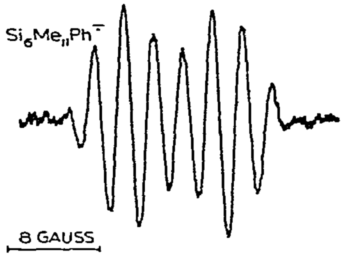


Fig. 5. ESR spectrum of $Si_5Me_9H$ at high gain showing $^{13}C$ sideband multiplets.

Fig. 6. ESR spectrum of $Si_6Me_{11}Ph^{\overline{\cdot}}$ anion-radical, —100°C in THF. The pattern, a doublet of triplets, indicates that the unpaired electron is associated with the benzene ring and not with the polysilane ring.

ferent ESR spectrum, shown in Fig. 6. The pattern is a doublet due to splitting by a single (*para*) proton, further split by interaction with two equivalent protons, probably *ortho* to the silicon. This type of spectrum is characteristic for an anion-radical of a benzene ring substituted by an electron-withdrawing group, and is very similar to that for $Me_3SiPh^{\overline{\cdot}}$ [8, 10]. Hence the unpaired electron is clearly associated with the aromatic rather than the polysilane ring in $Si_6Me_{11}Ph^{\overline{\cdot}}$. These results are consistent with our earlier finding that ease of reduction decreases in the order $(Me_2Si)_5 >$ benzene $> (Me_2Si)_6$ [2].

Reduction of the aromatic rather than the polysilane ring might similarly be expected for $Si_6Me_{11}CH_2Ph^{\overline{\cdot}}$, but because of its instability, proton hyperfine splitting was not observed for this anion-radical; therefore, no conclusion can be drawn as to which ring was reduced.

*Decomposition reactions*

In several instances the anion-radical produced in the initial reduction decomposed into another anion-radical that could be identified by ESR spectroscopy. The mode of decomposition of $Si_5Me_9SiMe_3^{\overline{\cdot}}$ and $Si_5Me_9SiMe_2Ph^{\overline{\cdot}}$ was especially interesting: both decomposed to $Si_5Me_9H^{\overline{\cdot}}$. Reduction of $Si_5Me_9SiMe_3$ at —90°C gives initially a broad partially-resolved line, but even at this temperature sidebands are observed due to $Si_5Me_9H^{\overline{\cdot}}$ (Fig. 2). At —70°C, the original spectrum decays rapidly, and with continued electrolysis only $Si_5Me_9H^{\overline{\cdot}}$ is observed. Similarly, for $Si_5Me_9SiMe_2Ph$ initial reduction at —95°C gives a single broad line, but continued electrolysis at this temperature produced ultimately only $Si_5Me_9H^{\overline{\cdot}}$. The formation of the silane anion-radical could be accounted for by decomposition of the initial anion-radical to a silyl anion and a cyclosilane radical, followed by hydrogen abstraction from the solvent and addition of an electron (Scheme 1).

SCHEME 1

R = Me, Ph

The six-membered ring anion-radicals $Si_6Me_{11}Ph^{\overline{\cdot}}$ and $Si_6Me_{11}SiMe_3^{\overline{\cdot}}$ both underwent decomposition forming $(SiMe_2)_5^{\overline{\cdot}}$ above —70°C. This mode of decomposition is also known for $(SiMe_2)_6^{\overline{\cdot}}$ [2]. Apparently, ring opening and reclosing can take place to give the more stable cyclopentasilane anion-radicals. $Si_6Me_{11}CH_2Ph^{\overline{\cdot}}$ was even less stable, decomposing rapidly even at —100°C and below to $(SiMe_2)_5^{\overline{\cdot}}$. $Si_6Me_{11}H^{\overline{\cdot}}$ was exceptionally unstable, producing no ESR signal at —90°C, and only a fleeting spectrum at —110 to —140°C, consisting of a doublet due to Si—H splitting but otherwise unresolved. This spectrum decayed to the base line, indicating that decomposition takes place to diamagnetic products.

It should be mentioned however that the decomposition reactions observed for the anion-radicals may not be major pathways for decomposition of reduced polysilanes. Using ESR spectroscopy, only that part of the decomposition giving rise to anion-radicals is observable; other decomposition reactions leading to inactive products may be taking place simultaneously.

### *Temperature dependence*

To search for temperature-dependent effects on the ESR spectra, all of the anion-radicals were examined at various temperatures in the region in which they were stable. Noticeable differences were found only for $Si_5Me_9Ph^{\overline{\cdot}}$. At —100°C, the ESR spectra of this anion-radical was a multiplet containing at

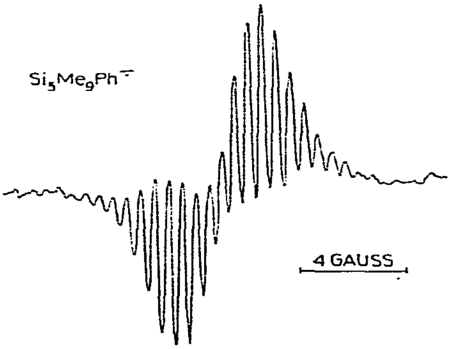


Fig. 7. ESR spectrum of $Si_5Me_9Ph$ anion-radical, —100°C in THF.

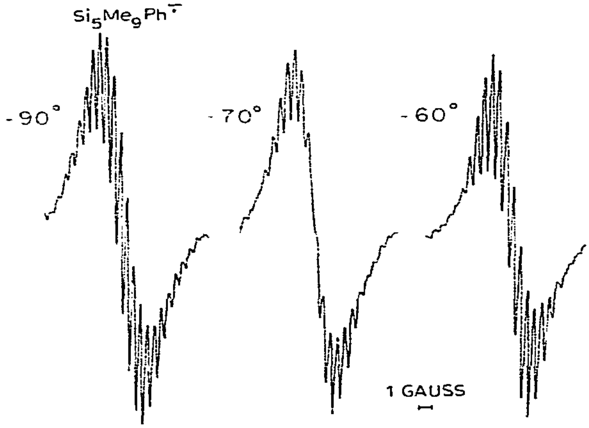


Fig. 8. ESR spectrum for $Si_5Me_9Ph^{\overline{\cdot}}$ showing reversible changes with temperature from —90 to —60°C.

least 21 lines (Fig. 7). As the temperature was increased to —60°C, both $a$(Si—CH$_3$) and $a$($^{13}$C) increased, and the spectrum became an apparent 14 line pattern (Fig. 8). The changes were fully reversible when the temperature was lowered.

The reason for this unusual temperature dependence is not known. The fact that no such effects were found for any other cyclopolysilane anion-radicals suggests that changes in solvent viscosity are not responsible. Rotation of the phenyl ring with respect to the polysilane ring might be restricted at lower temperatures, but the most stable orientation at low temperature is probably one with the phenyl ring nearly perpendicular to the polysilane ring, and if this is true the opposite temperature effect would be observed. Near degeneracy of the polysilane and phenyl ring unfilled orbitals, with partial delocalization onto the phenyl ring increasing at lower temperatures, is another possible explanation of the observed effect.

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