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ELECTRON SPIN RESONANCE STUDIES OF ARYL-SUBSTITUTED CYCLOPOLYSILANE ANION-RADICALS

A.C. BUCHANAN, III and ROBERT WEST *

Department of Chemistry, University of Wisconsin, Madison, WI 53706 (U.S.A.)

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Summary

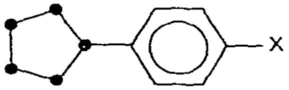
Several aryl-substituted cyclopolysilanes have been reduced to anion-radicals and have been studied by ESR spectroscopy. Compounds investigated were Si_5Me_9X (X = phenyl, biphenyl, p-$Me_3SiC_6H_4$, p-$MeOC_6H_4$, and p-MeC_6H_4) and $Si_5Me_9SiMe_2X$ (X = phenyl, p-$Me_3SiC_6H_4$ and p-$Me_2NC_6H_4$). The species have ESR spectra typical of delocalized cyclopentasilane anion-radicals except for biphenylnonamethylcyclopentasilane, which gives an ESR pattern indicating that the unpaired electron is mainly associated with the biphenyl ring system. An analysis of ^1H and ^{13}C hyperfine coupling constants for $Si_5Me_9X^{-\cdot}$ suggests that the principal effect of the aryl substituents is inductive. The anion-radicals of $Si_5Me_9SiMe_2X$ decay to $Si_5Me_9H^{-\cdot}$, and the electronic nature of the aryl substituent has no major effect on the stability of the parent radical.

Introduction

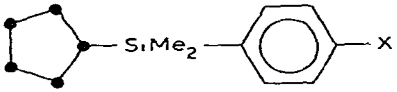
The permethylcyclopolysilanes, $(Me_2Si)_n$, where $n = 4,5$ [1] and 6 [2] undergo reduction to anion-radicals, $(Me_2Si)_n^{-\cdot}$. Electron spin resonance (ESR) spectroscopy shows that the unpaired electron contacts each methyl group equally, and is therefore delocalized over the entire silicon ring system. The ^{29}Si hyperfine splitting (hfs) of 6.13 G for $(Me_2Si)_5^{-\cdot}$ can be accounted for by a spin polarization mechanism, suggesting that the singly occupied orbital has little or no atomic *s* character, and may be of π symmetry [2].

Recently, a series of substituted five- and six-membered cyclopolysilane anion-radicals, $Si_5Me_9X^{-\cdot}$ and $Si_6Me_{11}X^{-\cdot}$ (X = hydrogen, phenyl, benzyl and trimethylsilyl), were examined by ESR [3]. In compounds which contain an aryl ring, the unpaired electron might be mainly associated either with the cyclosilane or with the benzenoid ring. The kinds of ESR patterns obtained are quite different so that the two possibilities can easily be distinguished. Results showed that the electron spin distribution differed greatly, depending on the size of the cyclosilane ring. In the cyclopentasilane derivatives $Si_5Me_9Ph^{-\cdot}$ and $Si_5Me_9Ch_2Ph^{-\cdot}$ the unpaired electron is distributed mainly over the polysilane ring, whereas in the substituted cyclohexasilanes $Si_6Me_{11}Ph^{-\cdot}$ and $Si_6Me_{11}CH_2Ph^{-\cdot}$, the odd electron is mainly on the benzene ring. These observations are consistent with the order of relative reducibility found for the unsubstituted species, $(Me_2Si)_5$ > benzene > $(Me_2Si)_6$ [2].

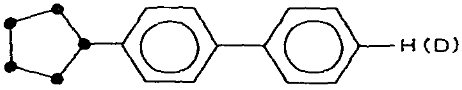
We have now prepared several substituted aryl derivatives of $(Me_2Si)_5$ of three different classes: (a) arylnonamethylcyclopentasilanes (I—IV), (b) aryldimethylsilylnonamethylcyclopentasilanes (V—VIII), and (c) biphenylnonamethylcyclopentasilanes (VIII). These compounds were all reduced to their anion-radicals, which were investigated by ESR spectroscopy. Our interest was in determining how the nature of the substituent group X would alter the electron-density distribution in these anion-radicals.



(I, X = H ; II, X = $SiMe_3$; III, X = OMe ; IV, X = Me)



(V, X = H ; VI X = $SiMe_3$; VII, X = NMe_2)



(VIII, X = H (D))

(Dots represent silicon atoms with attached methyl groups)

Experimental

All compounds, except VIII-D, were synthesized by Brough [4]. The identity of the samples was confirmed by NMR spectroscopy and mass spectrometry. ESR experiments were conducted on samples freshly purified by gas chromatography on a column containing Dexsil 300 on 60/80 mesh Chromosorb W.

Preparation of VIII-D. In an argon atmosphere, 5.0 g (0.016 mol) 4,4′-dibromobiphenyl in 70 ml THF was added dropwise to 0.43 g (0.018 mol) Mg turnings in 30 ml THF. The yellow reaction mixture was refluxed for 12 h. Following the addition of 1.0 ml (0.055 mol) D_2O, the solution was refluxed for an additional 2 h. The organic layer was separated by an ether/water work-up, and the solvent removed on a Rotovap to yield 3.3 g of yellow solid containing about 60% (by GLC) 4-bromo-4′-deuteriobiphenyl.

Similarly, 1.13 g (4.82 mmol) 4-bromo-4′-deuteriobiphenyl in 30 ml THF was added to 0.130 g (5.23 mmol) Mg in 10 ml THF and the resulting mixture was refluxed for 2.5 h. Chlorononamethylcyclopentasilane (1.25 g, 4.02 mmol) in 15 ml THF was added over a 30 min period, and the resulting solution was refluxed for 7 h. A saturated ammonium chloride solution was added, and the layers were separated and washed. The solvent was removed on a Rotovap, and the Kügelrohr fraction of 90—120°C (0.03 Torr) yielded 0.9 g (52%) of VIII-D as a colorless oil. The mass spectrum (12 eV) gave the parent ion at *m/e* 429 with approximately 93% isotopic purity.

Electrolytic reduction. Electrolytic reductions were carried out in cells constructed of 3 mm glass tubing with platinum wire electrodes [2]. The solvent was highly purified THF, and the supporting electrolyte was tetra-n-butylammonium perchlorate. The concentrations were approximately 0.01 *M* in cyclopolysilane and 0.2 *M* in $n\text{-Bu}_4N^+ ClO_4^-$. After several freeze-pump-thaw cycles, electrolysis was carried out in situ at —95°C at the lowest current (generally 1.0 μA) which produced an observable ESR spectrum. The cyclopentasilane anion-radicals had a characteristic deep blue color.

Reduction of VIII-D. Greatly enhanced resolution in the ESR spectrum of VIII-D was obtained when the electron transfer reagent, trimethylsilylpotassium, was employed. Me_3SiK was prepared in THF according to published procedures [5]. To produce the anion-radical, 2 mg of VIII-D and a 0.5 ml aliquot of a 0.83 *M* Me_3SiK stock solution were transferred under Ar to a 3 mm glass tube. The tube was sealed after several degassing cycles on a vacuum line.

Attempted generation of $p\text{-}CF_3C_6H_4Si_5Me_9^{-\bullet}$. The *p*-trifluoromethylphenyl group would provide a strong electron-withdrawing substituent. However, electrolytic reduction of $p\text{-}CF_3C_6H_4Si_5Me_9$ gave an uncharacteristic orange solution at the cathode, and no ESR signal was observed. Presumably, loss of fluoride ion takes place too rapidly for the anion-radical to be observed [3].

ESR spectra. ESR spectra were obtained on a Varian V-4502-13 X-band spectrometer using 100 kc modulation and a Varian V-4557 variable temperature accessory. The microwave frequency was measured with a Hewlett—Packard 5245L counter and a 5256A frequency converter. To enhance resolution, line sharpened spectra were obtained by including third-derivative character in the first-derivative signal according to the method reported by Glarum [6]. The *g*-factor and hyperfine splitting constants were measured in a dual cavity relative to an aqueous solution of peroxylamine disulfonate anion (Fremy's salt). Proton and carbon-13 hyperfine coupling constants are believed to be accurate to at least ±0.03 G and ±0.3 G respectively, and *g*-values were reproducible to ±0.0001.

Molecular orbital calculations. Hückel molecular orbital calculations with the McLachlan modification were performed on $VIII^{-\bullet}$, treating the Me_9Si_5 group as a heteroatom possessing a vacant orbital which interacts with the π-system. The parameters describing the heteroatom, M, are the Coulomb integral, α_M, and the resonance integral, β_{CM}, which are scaled in terms of the resonance integral of an ordinary aromatic carbon—carbon bond [7]:

$$\alpha_M = \alpha_O + h_M\beta_O\ ; \quad \beta_{CM} = k_{CM}\beta_O$$

The inductive effect of the metal substituent on the contiguous ring carbon was incorporated in the calculation by use of the auxiliary inductive parameter, δ: $\alpha_{CM} = \alpha_O + \delta h_M\beta_O$.

In the Hückel model, the spin density on atom i is the probability amplitude of the odd electron on that atom, $\rho_i = (C_{ij})^2$ where C_{ij} is the coefficient for atom i in the molecular orbital to which the unpaired electron is assigned. Generally, however, McLachlan spin densities give better agreement with experimental spin densities. The McLachlan method corrects the Hückel spin densities for configuration interaction by including an additional parameter λ [8]. In the calculations, the standard values for $\delta(0.10)$ and $\lambda(1.2)$ were taken [9,10, 11]. The heteroatom parameters h_{Si} and k_{CSi} were adjusted to obtain the best agreement between the calculated and the experimental spin densities. The optimum values were $h_{Si} = -1.09$ and $k_{CSi} = 0.337$.

Results and discussion

The hyperfine splitting constants obtained from the electron spin resonance measurements are given in Tables 1 and 2 and representative spectra for each of three classes of compounds are shown in Figs. 1, 4, and 5. Reduction of compounds I—VII all produce blue solutions giving ESR spectra typical of those for substituted cyclopentasilane anion-radicals (Figs. 1, 4). In all of these cases it is clear that the unpaired electron is associated with the cyclosilane ring rather than with the benzene ring. Just the opposite is found for the biphenyl derivative VIII, which gives a green anion-radical solution with a completely different ESR pattern indicating that the unpaired electron is associated with the biphenyl ring system (Fig. 5). The latter result is consistent with competitive reduction experiments on unsubstituted compounds, which show that biphenyl is reduced more easily than $(Me_2Si)_5$, but that $(Me_2Si)_5$ is reduced in preference to benzene.

For a cyclopolysilane anion-radical such as $(Me_2Si)_5^{-\bullet}$, the ESR spectrum is a symmetric multiplet resulting from the equivalent interaction of the unpaired electron with all of the methyl hydrogens. In monosubstituted cyclopolysilanes the symmetry is broken and the methyl groups are no longer equivalent. Different hfs by nonequivalent methyl groups should give rise to overlapping patterns and result in an unresolved broad band ESR spectrum. This is what was observed earlier for $Si_5Me_9SiMe_3^{-\bullet}$ [3], and in this study for the related anions $V^{-\bullet}$, $VI^{-\bullet}$ and $VII^{-\bullet}$.

However, certain substituents alter the spin density distribution in the cyclosilane ring very little, so that the hfs from methyl protons are nearly equivalent.

TABLE 1

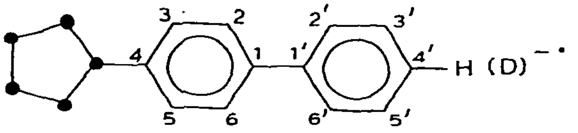
ESR PARAMETERS FOR $Si_5Me_9X^{-\bullet}$

X	$a(^1H)$ (G)	$a(^{13}C)$ (G)	g-value
p-$CH_3C_6H_4$	[a]	20.0	2.0043
p-$CH_3OC_6H_4$	0.61 [b]	19.7	2.0042
CH_3 [c]	0.53	16.03	2.0032
C_6H_5	0.51	14.7	2.0034
p-$(CH_3)_3SiC_6H_4$	0.46	13.5	2.0045

[a] Unresolved, probably >0.6 G. [b] Measured peak-to-peak. [c] From ref. 2.

TABLE 2

COUPLING CONSTANTS AND CALCULATED AND EXPERIMENTAL SPIN DENSITIES FOR



Atom	$a_i(^1H)$, G	ρ_i(obsd.) [a]	ρ_i(calcd.)	
			McLachlan	Hückel
4'	4.75 [b]	0.170	0.167	0.134
3', 5'	0.65	0.023	—0.023	0.015
2', 6'	2.69	0.096	0.096	0.079
2, 6	2.23	0.080	0.088	0.076
3, 5	<0.35 [c]	<0.012	—0.005	0.027

[a] For $Q = -28$ gauss. [b] $a(D) = 0.73$ G for VIII-$D^{-\cdot}$. [c] Value quoted is ESR linewidth for VIII-$D^{-\cdot}$.

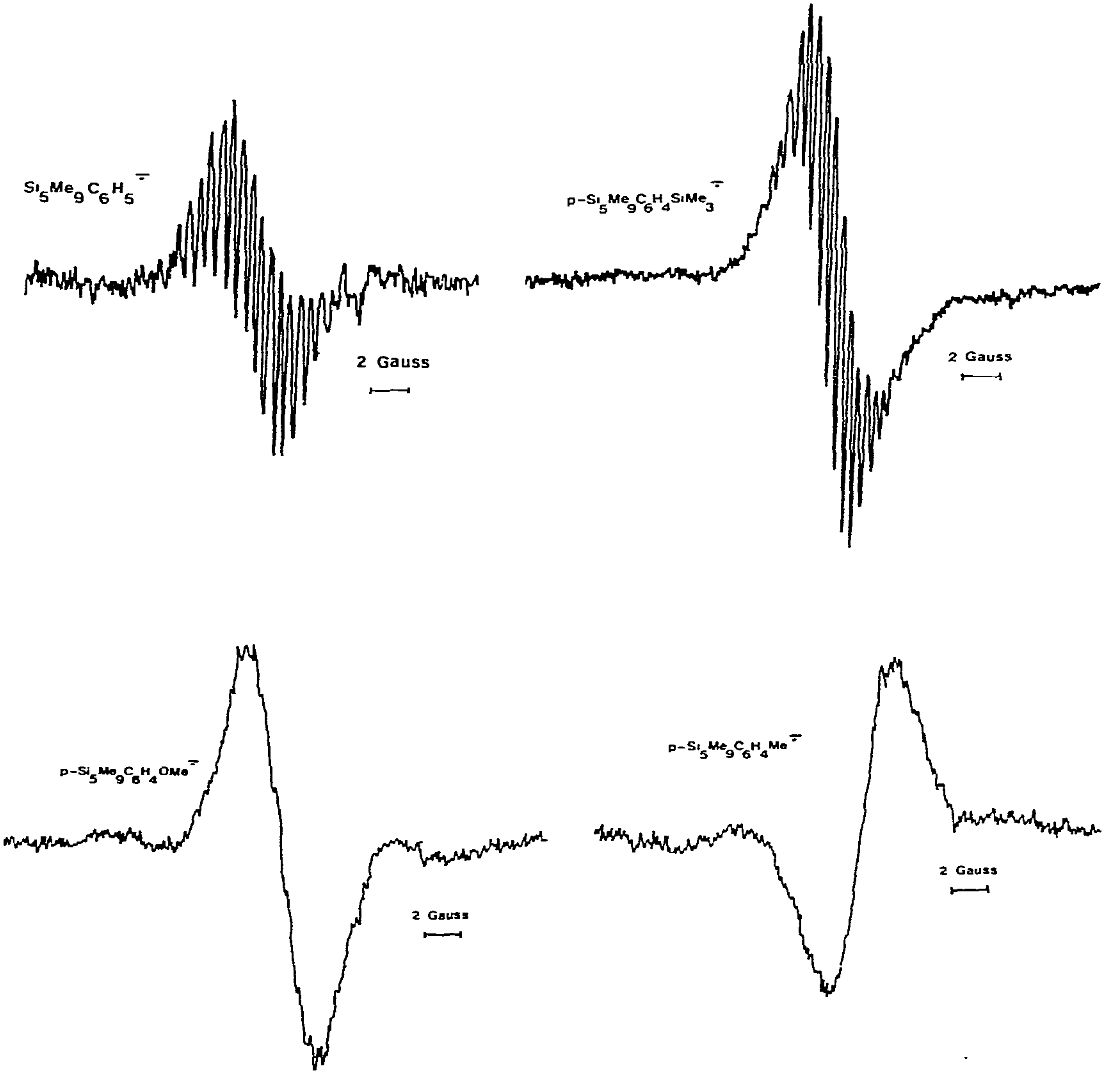


Fig. 1. ESR spectra of anion-radicals of compounds I—IV.

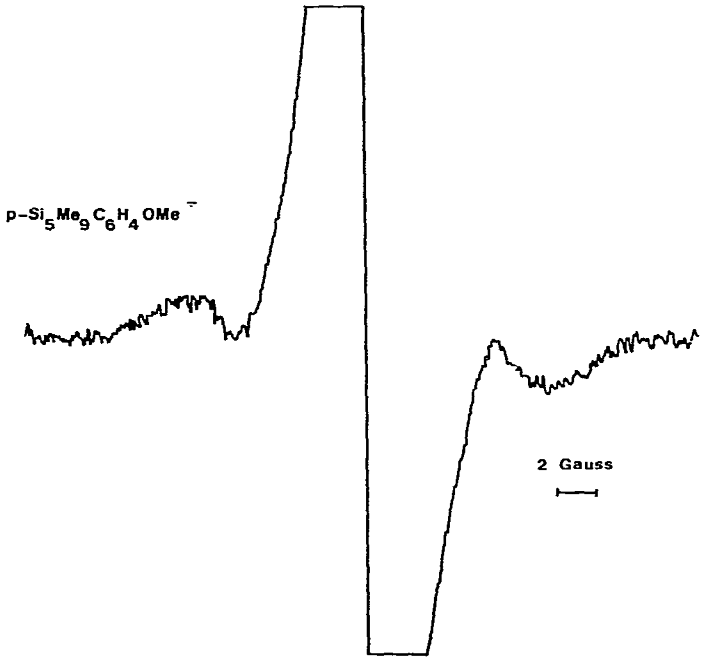


Fig. 2. ESR spectrum of anion-radical $III^{-\bullet}$ at high gain, showing ^{13}C satellites.

An example is $Si_5Me_9CH_2Ph^{-\bullet}$, which has an ESR spectrum almost identical with that for $(Me_2Si)_5^{-\bullet}$ [3]. We find that the aryl substituents in anion-radicals of I—IV also have relatively small effect on spin densities in the silane ring, with the result that average values of the hfs for protons and ^{13}C can be determined (Table 1).

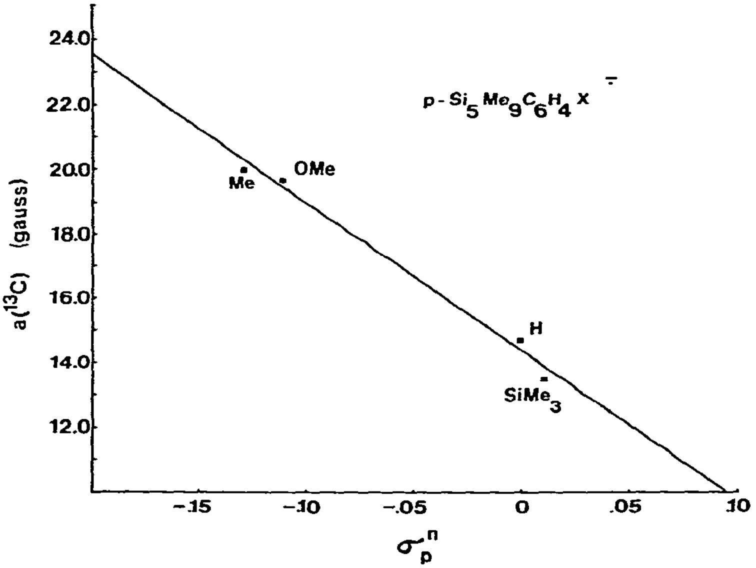


Fig. 3. Plot of $a(^{13}C)$ vs. $\sigma_p{}^n$ for anion-radicals of I—IV.

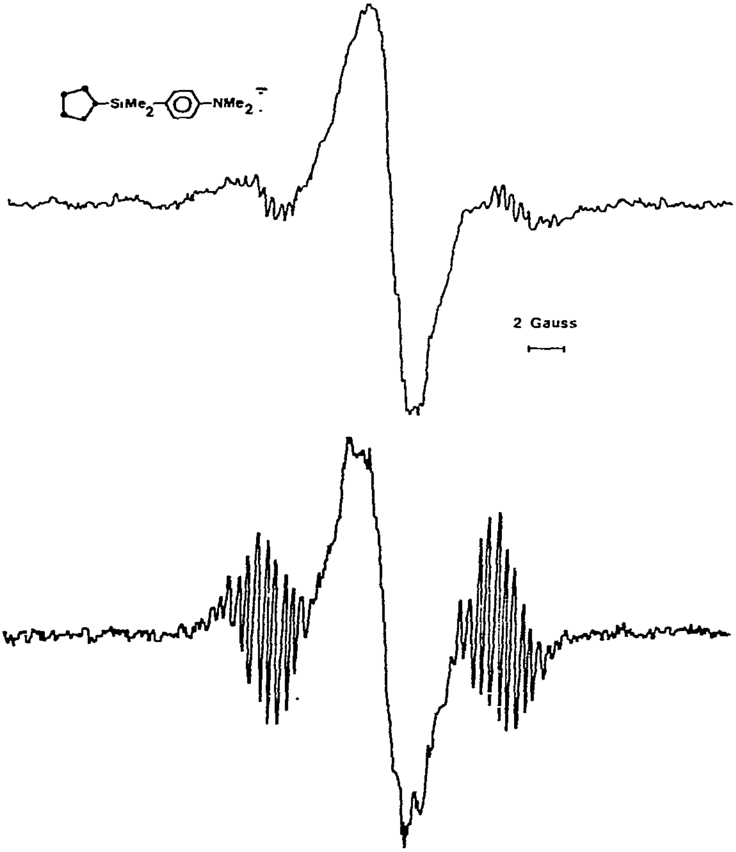


Fig. 4. ESR spectra observed for anion-radical of VII. Above, immediately after preparation; below, after 25 min, showing decay to $Si_5Me_9H^{-\bullet}$.

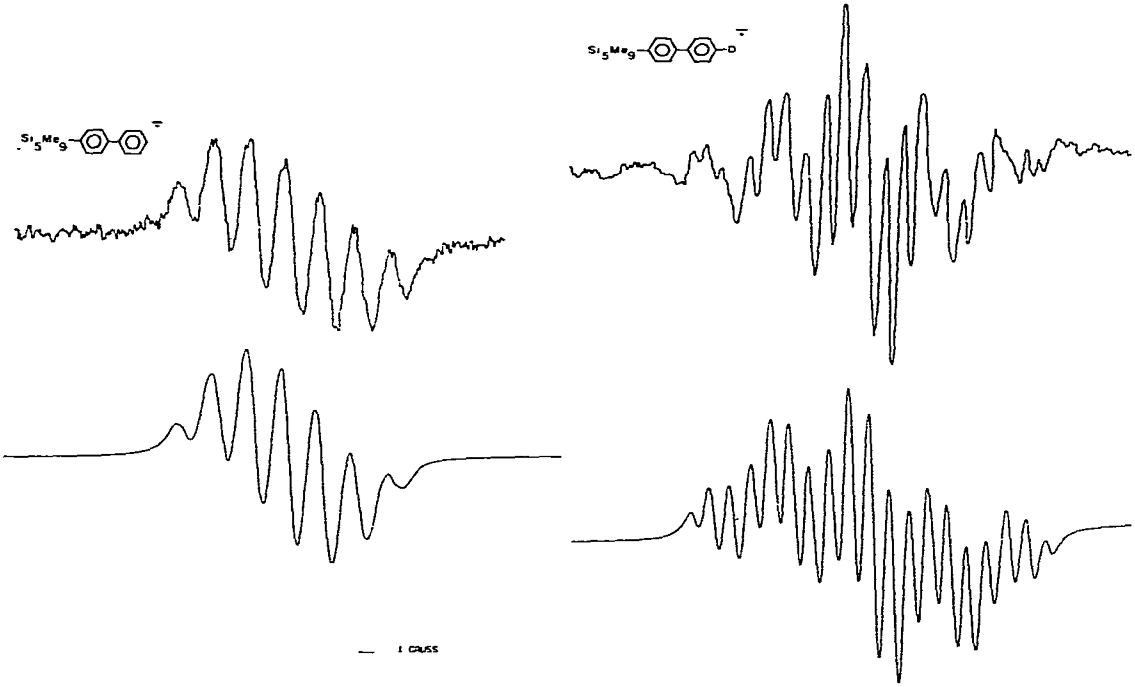


Fig. 5. ESR spectrum of VIII-$H^{-\bullet}$ (left) and VIII-$D^{-\bullet}$ (right). Above experimental; below, computer simulations.

Anion-Radicals of I—IV. The ESR spectrum of $I^{-\cdot}$ is shown in Fig. 1. The hyperfine splitting constants for protons and carbon-13 in $I^{-\cdot}$ are slightly smaller than those for $(Me_2Si)_5^{-\cdot}$ (Table 1), showing that the phenyl group on the cyclopentasilane ring is weakly electron-withdrawing compared with methyl. However, because the difference is slight, the unpaired electron density on each of the five silicon atoms remains nearly equivalent. As a result the proton hfs for various methyl groups are nearly the same so that the spectrum is well-resolved (Fig. 1) *.

The hfs for $II^{-\cdot}$ are further reduced from $(Me_2Si)_5^{-\cdot}$, consistent with the fact that *p*-trimethylsilylphenyl is more electron-attracting than phenyl [13]. Nevertheless the ESR spectrum for $II^{-\cdot}$ is fairly well resolved, showing that the hfs of the various methyl protons must not be very different **. Therefore for this species also, the spin densities must be only slightly altered around the ring.

Anion-radicals $III^{-\cdot}$ and $IV^{-\cdot}$ give hfs larger than for $(Me_2Si)_5^{-\cdot}$, indicating that the *p*-anisyl and *p*-tolyl groups are electron-releasing compared to methyl in this series. Proton hfs in the ESR spectrum of $III^{-\cdot}$ are poorly resolved, and in $IV^{-\cdot}$ the proton hfs is lost altogether (Fig. 1). Apparently these substituents polarize the Si_5Me_9 ring such that the electron densities on various silicon atoms are no longer so nearly equal.

Average values for the ^{13}C hfs were determined for all of the four anion-radicals. Typical ^{13}C satellite spectra are shown in Fig. 2 for the anion-radical of III. The intensities of the ^{13}C satellites relative to the central spectrum could not be accurately measured, but were in the range calculated for VIII (4.44%) or IX (5.00%) carbons. The data, given in Table 1, show the interesting result that *p*-tolyl is more electron-releasing than *p*-anisyl toward the polysilane ring. This indicates lack of conjugation between the benzenoid and the polysilane ring, for in aromatic compounds where direct conjugation with the reaction center is possible, *p*-methoxy is far more electron-donating than *p*-methyl. The ^{13}C hfs for $I^{-\cdot}$—$IV^{-\cdot}$ correlate well with σ_p^n, a σ constant for substituents which do not conjugate to the reaction center [15]; a plot of σ_p^n vs. ^{13}C hfs is shown in Fig. 3. The correlation coefficient r is 0.994, and a similarly good correspondence is found between the ^1H coupling constant and σ_p^n. These results suggest that the principal effect of the aryl substituents is an inductive one, polarizing the spin density in the polysilane ring either toward or away from the aryl group ***.

In π-type organic radicals, the proton hfs are proportional to the π-spin density on the carbon atom adjacent to the proton [18,19]. If it is assumed that

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* The following discussions assume that the magnitude of the proton hfs is proportional to the amount of spin density on the silicon atom to which the methyl group is bonded. This type of correspondence is observed between the methyl proton hfs and the π-spin densities on the contiguous ring carbon for the anion-radicals of methyl substituted benzenes and methyl substituted trimethylsilylbenzenes [11,12].

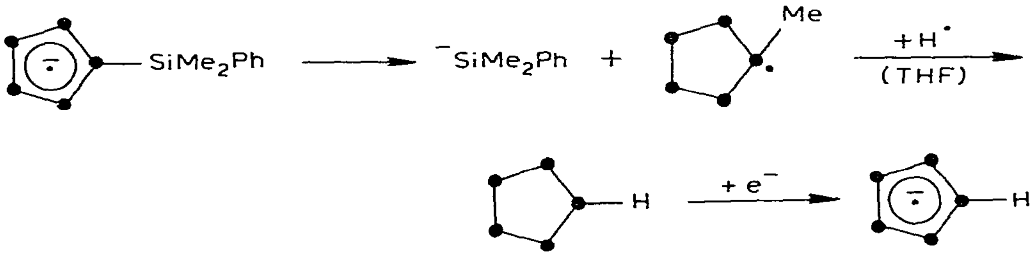
** This conclusion is supported by a computer simulation study of the effect of methyl proton hfs variations on the ESR spectral resolution [14].

*** If this conclusion is correct, a question arises as to why there is so little conjugative (resonance) interaction between the aromatic and cyclosilane rings. The lack of resonance could result from poor energy matching, or unfavorable conformation of the two rings in the radical. It would also be consistent with the singly occupied polysilane orbital being of σ^* type, as suggested by others [16] rather than π type, but we do not favor this explanation.

the ^{13}C hfs in $III^{-\cdot}$ and $IV^{-\cdot}$ are related to the spin density on the adjacent silicon atom by a McConnell-type relationship, the results for the electron-releasing *p*-tolyl and *p*-anisyl substituents suggest that there is very little spin density on the substituted silicon atom. The sum of ^{13}C splitting constants for $(Me_2Si)_5^{-\cdot}$, $\Sigma_c\, a(^{13}C)$, is $10 \times 16.03 = 160.3$. For the *p*-tolyl radical $IV^{-\cdot}$, assuming that the measured ^{13}C hfs is an average for all carbons except on the substituted silicon atom, $\Sigma_c\, a(^{13}C)$ is $8 \times 20.0 = 160$, numerically the same. A similar analysis holds approximately for the ^{13}C splitting in $III^{-\cdot}$. The analysis suggests that the spin density on the substituted silicon atom is near zero in these species. If this is so, the polysilane ring is exceptionally susceptible to polarization by these electron-releasing substituents.

A similar McConnell analysis can be applied to $I^{-\cdot}$ and $II^{-\cdot}$. As explained above, the well-resolved proton hfs in the ESR spectra show that the spin density must be rather evenly distributed over the ring. The ratios between the ^{13}C hfs for $I^{-\cdot}$ and $(Me_2Si)_5^{-\cdot}$, and for $II^{-\cdot}$ and $(Me_2Si)_5^{-\cdot}$, should then give the total spin density population on the polysilane ring in the substituted anion-radicals. These ratios are 0.92 for $I^{-\cdot}$, and 0.84 for $II^{-\cdot}$. These results indicate partial delocalization of spin density onto the aryl ring with greater delocalization onto *p*-trimethylsilylphenyl than phenyl, as expected.

Anion-radicals of V, VI and VII. Reduction of V at —95° C was found earlier to give a single broad line ESR spectrum which, upon continued electrolysis, decayed to the ESR spectrum of $Si_5Me_9H^{-\cdot}$ [3]. The formation of $Si_5Me_9H^{-\cdot}$ was rationalized by the mechanism shown in eq. 1, involving decomposition of the parent anion-radical to a silyl anion and a cyclopolysilanyl radical, followed



(1)

by hydrogen abstraction from the solvent and addition of an electron to give the observed anion-radical product.

Compounds VI and VII were investigated to see whether the stability of the parent anion-radical would be affected by an electron-withdrawing ($X = SiMe_3$) or -donating ($X = NMe_2$) substituent attached to the phenyl ring. However, reduction of either VI or VII similarly produced a broad line, unresolved ESR pattern which gradually decayed with the production of the ESR spectrum of $Si_5Me_9H^{-\cdot}$ (Fig. 4). The spectrum of $Si_5Me_9H^{-\cdot}$ is characterized by a major doublet (14.1 G) due to the unique proton on silicon, and further split into a multiplet (0.51 G) by the methyl protons.

Therefore, it appears that the electronic nature of the substituent has no major effect on the stability of these aryldimethylsilylnonamethylcyclopentasilane anion-radicals, and that their decomposition to $Si_5Me_9H^{-\cdot}$ is probably general.

VIII-H(D). Reduction of biphenylnonamethylcyclopentasilane (VIII-H) produced a dark green anion-radical ($g = 2.0036$) with an ESR pattern consisting of 7 lines separated by 2.5 ± 0.3 G (Fig. 5). This spectrum is consistent with the unpaired electron being primarily in the aromatic ring system rather than in the polysilane ring.

In order to identify the coupling constants for VIII-H$^{-\cdot}$, VIII-D was also synthesized. Reduction of VIII-D gave an ESR spectrum (Fig. 5) consisting of 19 lines separated by 0.68 ± 0.05 G. The 0.68 G spacing was employed as an estimate of the deuterium hfs. This can be related to the proton coupling constant in VIII-H$^{-\cdot}$ by the proton to deuterium gyromagnetic ratios [17]:

$$\begin{aligned} a_{4'}(\text{H}) &= a_{4'}(\text{D}) \times \gamma_\text{H}/\gamma_\text{D} \\ &= 0.68 \text{ G} \times 6.51 = 4.43 \text{ G} \end{aligned}$$

Using this value as a probe, Hückel and McLachlan calculations were performed (see experimental) on VIII-H(D) to give a set of coupling constants as a starting point for computer simulation of the ESR spectra. The best simulations of the experimental spectra, also shown in Fig. 5, were obtained using the coupling constants listed in Table 2. The proton coupling constants may then be related to the spin densities on the corresponding carbon atoms (Table 2) in the π-system by the relation [18,19] $a_i = Q\rho_i$ where a_i is the observed coupling constant, ρ_i is the spin density, and Q is a constant. The value of Q is taken to be —28 G and is that generally employed for substituted biphenyls [9].

The spin density distribution in VIII$^{-\cdot}$ was also obtained using Hückel—McLachlan calculations, and the results are given in Table 2. Reasonable agreement was obtained between the experimental spin densities and the McLachlan spin densities employing the heteroatom parameters, $h_\text{Si} = -1.09$ and $k_\text{CSi} = 0.337$.

The value of $h_\text{Si} = -1.09$ is significant when compared to $h_\text{Si} = -1.20$ employed by Curtis and Allred [9] for trimethylsilylbiphenyl anion-radical. Because the Coulomb integral, α, is a measure of the core potential of an atom, it has been suggested that α is proportional to the electronegativity of that atom, $h_m \propto (X_m - X_c)$ [7]. Since α and β are negative quantities, a relatively more positive value of h_m implies a greater core potential for the heteroatom [7]. The result that $h_\text{Si}(\text{Si}_5\text{Me}_9) > h_\text{Si}(\text{SiMe}_3)$ therefore implies that the cyclopentasilyl group is a stronger electron-withdrawing substituent than the trimethylsilyl group in these anion-radicals.

This conclusion is supported by a comparison of the hyperfine splitting constants for the corresponding anion-radicals [14]. The values in Gauss of a_H for the protons at the 4′ positions, which have the largest spin densities, are 5.4 for biphenyl, 5.08 for 4-trimethylgermylbiphenyl, 4.96 for 4-trimethylsilylbiphenyl, 4.75 for VIII-H, and less than 1.5 for 4-nitrobiphenyl [20].

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