dergoing rapid ring inversion. The cyclotetrasilane anion radicals with two hindered substituents $(s\text{-Bu}_2\text{Si})_4^{-}\cdot$ and $(i\text{-Pr}_2\text{Si})_4^{-}\cdot$ each have two α-^{13}C hfsc and so appear to be bent and not rapidly interconverting on the ESR time scale. The $(t\text{-BuMeSi})_4^{-}\cdot$ anion radicals appear from their ESR spectra to be bent and rapidly inverting.

It is of interest to compare cyclopolysilane anion radicals with the more familiar aromatic anion radicals. For aromatic hydrocarbons the SOMO is adequately represented by using only carbon $2p_z$ orbitals. According to the model developed in the following paper, the SOMO in cyclopolysilanes may be described in the mixing of Si–Si σ^* orbitals constructed from silicon 3p orbitals, with substituent-to-ring Si–C σ^* orbitals.[13]

The alkylcyclopolysilane σ^* radical anions differ from their aromatic π^* counterparts in two important ways. First, in aromatic π^* anion radicals, spin density is transmitted to carbon and hydrogen substituents by spin polarization, and a McConnell relationship is found between substituent hfsc and odd electron density at the ring carbon atom. For the cyclosilane σ^* anion radicals, spin density arises at carbon substituents directly via odd electron delocalization from the silane ring, and neither the proton nor the α-carbon hfsc is proportional to odd electron density at the silicon atom. Secondly, unlike the aromatic anion radicals, the σ^* alkylcyclopolysilane species can have ground-state conformations which are bent. Our ESR results indicate probable bent conformations for at least several of these anion radicals.

Acknowledgment. Research sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Contract No. F49620-83-C-0044. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation thereon. We thank Corey W. Carlson and Elizabeth M. Kean for technical assistance.

Factors Influencing the Magnitude of α-^{13}C Hyperfine Couplings in Cyclosilane Anion Radicals

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Considerations of hyperfine coupling constants (hfsc) in the ESR spectra of cyclopolysilane anion radicals $(\text{R}_2\text{Si})_n^{-}\cdot$ lead to a representation of the singly occupied molecular orbital (SOMO) as a linear combination of Si–C σ^* and symmetry-adapted Si–Si σ^* hybrid orbitals. The atomic orbital contributions to these hybrid orbitals are believed to be principally silicon $3p_x$, $3p_y$, and $3p_z$ and carbon 2s, $2p_x$, $2p_y$, and $2p_z$. A simple perturbation approach is used to rationalize the values of ^{13}C hfsc measured for substituted cyclopentasilanes $\text{Me}_9\text{Si}_5\text{R}^{-}\cdot$ compared to the value observed for $(\text{Me}_2\text{Si})_5^{-}\cdot$, in terms of altered mixing of the Si–Si σ^* and Si–C σ^* orbitals.

Introduction

Anion radicals of the cyclic silanes $(\text{Me}_2\text{Si})_5$ and $(\text{Me}_2\text{Si})_6$ were first observed by electron spin resonance (ESR) spectroscopy in 1965.[1] In the intervening years we and others have reported many examples of cyclosilane anion radicals.[2] Formation of anion radicals appears to be general for cyclosilanes $(\text{RR}'\text{Si})_4$ and $(\text{RR}'\text{Si})_5$,[3,4] and unsymmetrical (substituted) cyclic anion radicals are also known.[5] From the ESR spectra it is clear that in cyclosilane anion radicals the unpaired electron is fully delocalized over the ring.

The nature of the singly occupied orbital (SOMO) in these species was briefly discussed in earlier publications[6] but has not been well understood. In this paper we consider this question in greater detail, making use of the information which has accumulated from ESR studies to develop a model for the SOMO and for chemical bonding in cyclosilane anion radicals. The model will then be applied to account for the odd-electron distribution in some substituted cyclosilane anions.

Experimental Section

Bi(nonamethylcyclopentasilanyl) was prepared[7] from $\text{Si}_5\text{Me}_9\text{Cl}$ using a slight variation of methods[8] which produce related cyclopolysilanes. The spectral properties of our sample, including the ^{29}Si chemical shifts, agreed with literature values.[9] The UV spectrum shows bands at 210 (sh) (ϵ 51 000), 224 (37 000), 248 (29 000), and 290 nm (br, 6300), with significant tailing out to 325 nm. The first vertical ionization potential is 7.2 eV.[10] The identity of the sample used in the ESR experiment was further confirmed by its mass spectrum showing a parent peak at m/e 550 with a peak match correct to 2 ppm. The anion radical of this compound

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[1] Husk, G. R.; West, R. *J. Am. Chem. Soc.* **1965,** *87,* 3993.

[2] For a review see: West, R. *Pure Appl. Chem.* **1982,** *54,* 1041.

[3] Kira, M.; Bock, H.; Hengge, E. *J. Organomet. Chem.* **1979,** *164,* 277.

[4] Wadsworth, C. L.; West, R.; Nagai, Y.; Watanabe, H.; Muraoka, T. *Organometallics,* preceding paper in this issue.

[5] (a) West, R.; Kean, E. S. *J. Organomet. Chem.* **1975,** *96,* 323. (b) Buchanan, A. C.; West, R. *Ibid.* **1979,** *172,* 273.

[6] (a) West, R.; Carberry, E. *Science (Washington, D. C.)* **1975,** *189,* 179. (b) Carberry, E.; West, R.; Glass, G. E. *J. Am. Chem. Soc.* **1969,** *91,* 5446.

[7] Brough, L. Ph.D. Thesis, University of Wisconsin—Madison, 1979.

[8] (a) Ishikawa, M.; Kumada, M. *Synth. Inorg. Met.-Org. Chem.* **1971,** *1,* 191. (b) Ishikawa, M.; Wakamura, A.; Kumada, M. *J. Organomet. Chem.* **1973,** *59,* C11.

[9] Ishikawa, M.; Watanabe, M.; Iyoda, J.; Ikeda, H.; Kumada, M. *Organometallics* **1982,** *1,* 317.

[10] Obtained in the research group of H. Bock, University of Frankfurt, Frankfurt, West Germany, with a He I lamp, electrostatic sector field 127°.

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Table I. Observed ^{13}C and ^{29}Si Hfsc and Estimated ^{13}C Spin Polarization Hfsc in Cylopolysilane Anion Radicals

	$a(^{13}C)$ obsd, G	$a(\alpha\text{-}^{13}C)$ sp calcd, G	% C 2s total	^{29}Si obsd, G	g	ref
$(Me_2Si)_5$	16.03	−2.2	14	5.18	2.0032	6
$(Et_2Si)_5$	14.10 (α)	−2.2	13	4.46	2.0034	4
	1.9 (β)		1.7			
$[(CH_2)_5Si]_5$	15.71	−2.2	14	5.2	2.0031	4
$(Ph_2Si)_5$	10.1	−2.2	9	3.6	2.0046	3
$(Me_2Si)_4$	21.07	−2.8	15		2.0034	4
$(Et_2Si)_4$	18.40 (α)	−2.8	13	4.70	2.0037	4
	2.47 (β)		1.8			
$[(CH_2)_5Si]_4$	20.80	−2.8	15	5.20	2.0034	4
$(Ph_2Si)_4$	13.1	−2.8	9	4.4	2.0046	3

was generated electrolytically according to standard procedures,[4] in tetrahydrofuran solvent at −95 °C.

Discussion

The ^{13}C and ^{29}Si Hfsc in Cyclosilane Anion Radicals. The hyperfine splitting constants (hfsc, a) observed in ESR spectra can be approximated as the sum of two contributions, such that $a(\text{total}) = a(\text{sp}) + a(\text{dir})$.[11] The direct contribution, a(dir), can be regarded as arising from s orbital participation in ground-state representation of the SOMO. The spin polarization term, a(sp), represents unpaired electron density in s orbitals arising from mixing of suitable excited electronic configurations into the ground state.[12]

The determine if the ^{13}C hfsc arises from direct coupling a knowledge of the maximum ^{13}C hfsc expected to result only from spin polarization would be useful. The maximum spin polarization contribution to the ^{13}C hfsc can be roughly estimated from the Hunter–Symons equation,[13a] as −2.2 G in $(Me_2Si)_5^{-}\cdot$ and −1.7G in $(Me_2Si)_4^{-}\cdot$. The actual absolute values observed for these anion radicals are far greater than these estimates (Table I).[13b] We conclude that the α-^{13}C hfsc in cyclosilane anion radicals results from direct odd-electron delocalization into 2s orbitals on carbon. Furthermore since γ for ^{13}C is positive, the ^{13}C hfsc must also be positive.

Direct coupling indicates that the carbon 2s orbitals contribute to the ground-state representation of the SOMO. The amount of this contribution can be estimated according to eq 1,[14] where c^2_{ns} is the square of the s orbital

$$a(\text{dir}) = c^2_{ns}A^x \qquad (1)$$

coefficient at atom X (n designates the valence level) and A^x is the one-electron isotropic hyperfine splitting constant for X, taken as 1110 G for ^{13}C.[13] The square of the s orbital coefficient is also equal to the odd electron density in the carbon 2s orbital. The amount of odd electron density which has been accounted for can be estimated from the sum of c^2_{ns} taken over all carbon atoms. The sums, listed in Table I, are about 15% for both the four- and five-membered rings. Because the total percentage of odd-electron density in C 2s orbitals is small, there should be some odd-electron density on the silicon atoms, as expected, as well as in the C 2p orbitals.

It is likely that odd-electron density is also delocalized onto β-carbon atoms when these are present. As seen from data in Table I, small β-^{13}C hfsc of ~1.7 G were observed for ethylcyclopolysilane anion radicals.[4] In these species the α-^{13}C hfsc are reduced by about the same amount, 1.5–2 G, compared to the permethylcyclosilane anion radicals. Further branching at the α-carbon leads to additional decreases of ~1.5 G for each β-carbon atom added. The total of α and β hfsc remains nearly constant, suggesting that the amount of odd-electron delocalization onto larger alkyl groups is similar to that onto methyl groups in the $(Me_2Si)_n^{-}\cdot$ series, according to eq 1.

Consider now the ^{29}Si hfsc which are given in Table I for several alkyl-substituted cyclopolysilane anion radicals. Recent ENDOR and triple experiments[15] have shown that the ^{29}Si, ^{13}C, and the two ^{1}H hfsc in $(t\text{-BuMeSi})_4^{-}\cdot$ all have the same sign, so that according to the above assignment of the ^{13}C hfsc as positive, the ^{29}Si hfsc must also be positive. Since λ_{Si} is negative, the hfsc must be determined by spin polarization, and therefore no direct silicon 3s orbital contribution to the SOMO is indicated. The lack of 3s participation in the SOMO probably reflects the low energy of the silicon 3s orbital relative to the SOMO. It seems reasonable that the silicon contribution to the SOMO will be principally 3p, because calculations[16] on Si_2Me_6 show that the highest orbitals with Si–Si bonding character are mainly silicon 3p.[17] However, silicon 3d orbital contribution to the SOMO cannot be excluded.

A Model for the SOMO in Cyclosilanes

Following earlier workers we will employ a linear combination of bond orbitals (LCBO) approach[18,19] which combines equivalent localized Si–Si antibonding orbitals (σ^*) and Si–C antibonding orbitals (σ^*) to produce the appropriate delocalized molecular orbitals. The first step in the LCBO approach is to construct symmetry-adapted linear combinations of these antibonding orbitals. If the Si–Si σ^* and Si–C σ^* orbitals lie at different energies, then the ring orbitals divide naturally into two sets, which will be considered separately at first.

Symmetry-adapted delocalized Si–Si σ^* orbitals are obtained from consideration of their transformations in

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(11) This classification of a(dir) and a(sp) follows that of: Ellinger, Y.; Rassat, A.; Subra, R.; Berthier, G. *J. Am. Chem. Soc.* **1973**, *95*, 2372. And is further discussed in: (b) King, F. W. *Chem. Rev.* **1976**, *76*, 157.

(12) Because the spin density arising from the direct contribution is always positive, a(dir) must have the same sign as the magnetogyric ratio γ for the atom. Spin density arising from spin polarization may be positive or negative, so a(sp) may have either sign with respect to γ.

(13) (a) Hunter, F. T.; Symons, M. C. R. *J. Chem. Soc. A* **1967**, 1770. (b) To estimate the maximum spin-polarization contribution to carbon from spin density in p orbitals on the *carbon* atoms, the benzene anion radical is a suitable model. The total ^{13}C hfsc for benzene, divided by the number of C atoms in the cyclosilane anion radicals, leads to maximum spin polarization values of 2.1 G for $(Me_2Si)_4^{-}\cdot$, and 1.7 G for $(Me_2Si)_5^{-}\cdot$.

(14) Asycough, P. B. "Electron Spin Resonance in Chemistry"; Methuen: London, 1967; p 70.

(15) Kirste, B.; Kurreck, H.; West, R. *J. Am. Chem. Soc.* **1985**, *107*, 3013.

(16) Berkovitch-Yellin, Z.; Ellis, D. E.; Ratner, M. A. *Chem. Phys.* **1981**, *62*, 21.

(17) This expectation is supported by the large energies observed for electronic transitions to 3d states, which do not mix with other optical states. For an extensive review see: Robin, M. D. "Higher Excited States of Polyatomic Molecules"; Academic Press: New York, 1974; Vol. I.

(18) (a) Bock, H.; Ensslin, W. *Angew. Chem., Int. Ed. Eng.* **1971**, *10*, 404. (b) Pitt, C. G. In "Homoatomic Rings, Chains and Macromolecules of Main Group Elements"; Rheingold, A. L., Ed.; Elsevier: New York, 1977; Chapter 8.

(19) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669.

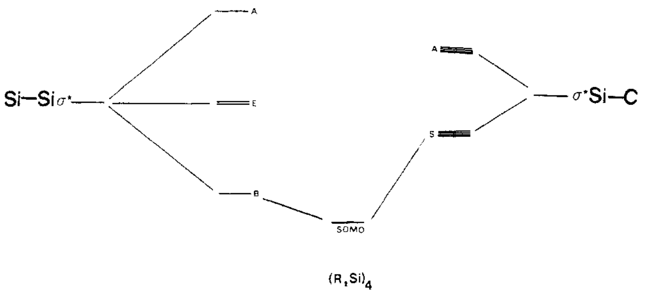

Figure 1. Qualitative antibonding molecular orbital ordering for cyclotetrasilane rings, LCBO model.

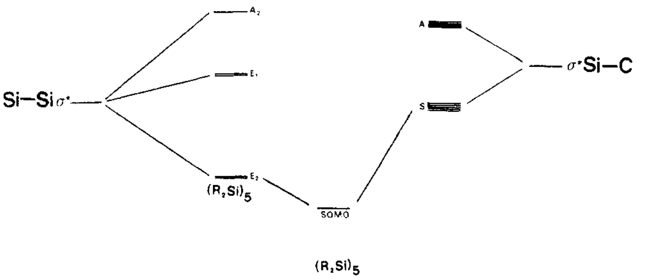

Figure 2. Qualitative antibonding molecular orbital ordering for cyclopentasilane rings, LCBO model.

the cyclic group C*n*, where n is the number of silicon atoms in the ring. The resulting orbitals span E_2, E_1, and A for the five-membered ring and B, E, and A for the four-membered ring. The degeneracy of the orbitals is lifted by geminal (across atom) interactions between the n Si–Si σ^* orbitals. The orbitals are arranged in order of increasing number of nodes with the orbital with the smallest number of nodes lying lowest.

The Si–C σ^* orbitals are combined to give a symmetric (S) and antisymmetric (A) orbital at each silicon atom; according to the number of nodes S lies below A. In the cyclic group C*n*, the S and A combinations span the same representations as the Si–Si σ^* orbitals, but the orbitals belonging to the different representations are degenerate because nongeminal interactions across the Si–Si bond are neglected in this model. The result for the entire molecule is a set of n degenerate orbitals of the S and A type which are free to mix with any of the symmetry-adapted Si–Si σ^* orbitals.

In the final step the only remaining geminal interaction is considered, and the SOMO is formed from mixing between the lowest Si–Si σ^* symmetry-adapted orbital and the S Si–C σ^* orbitals. The steps used to form the SOMO from the sets of equivalent orbitals are diagrammed in Figures 1 and 2 for the four- and five-membered rings, respectively.[20]

Because the lowest symmetry-adapted Si–Si σ^* orbital lies below the S Si–C σ^* orbital (vide infra), increased mixing causes the odd-electron density to be delocalized from the silicon ring to carbon, and, according to eq 1, the ^{13}C hfsc and the total carbon 2s odd-electron density will increase. Therefore in rings of different sizes but with the same alkyl substituents, the total carbon 2s odd-electron density measured by the α-^{13}C hfsc provides a measure of the relative amount of mixing of the Si–Si σ^* and Si–C σ^* orbitals. The values for the permethyl- and perethylcyclosilanes (Table I) show that the relative proportion of Si–C σ^* orbitals in the SOMO is about the same for these four- and five-membered rings.

Anion Radicals of Perphenylcyclosilanes. The ESR spectra for anion radicals of perphenylcyclotetrasilane and -cyclopentasilane have been reported by Bock et al.[3] (Table I). These species each show single ^{29}Si and ^{13}C hfsc, indicating equivalence of the phenyl groups on the ESR time scale, and have *g* values rather larger than for the methyl analogues $(Me_2Si)_4^{-}\cdot$ and $(Me_2Si)_5^{-}\cdot$. The earlier workers suggested that the high *g* value in the perphenyl species resulted from odd-electron density which was highly localized in the silane ring and so influenced by the larger spin–orbit coupling of silicon. However, interpreting the hfsc in terms of the model presented in this paper suggests that considerable odd-electron delocalization onto the phenyl rings takes place.

The α-^{13}C hfsc for $(Ph_2Si)_n$ anion radicals, as for cyclopolysilanes generally, are too large to be produced from spin polarization alone. This immediately indicates that odd-electron delocalization must take place at least onto the α-carbon. Odd-electron delocalization into the π^*-orbitals of the phenyl rings is indicated by the width of the central line found for the perphenyl anion radicals, which must result from unresolved hfsc from the hydrogen atoms on the aromatic ring. From the line width of 1.3 G for $(Ph_2Si)_4^{-}\cdot$,[3] it is estimated that approximately 10% of the odd-electron density is located on the ortho, meta, and para carbon atoms of the eight phenyl rings.[21] Finally, the rather low ^{29}Si hfsc for phenylcyclosilane anion radicals suggests that substantial electron removal from silicon rings toward the phenyl rings takes place.

Substituted Cyclosilane Anion Radicals. In this section a simple perturbation approach will be used with the linear combination model outlined above, to rationalize ESR results for some substituted anion radicals. The species of this type so far studied are all monosubstituted derivatives[5] of $(Me_2Si)_5$, which will serve as a reference compound with which to compare ^{13}C hfsc.

The two principal factors which affect the mixing of Si–Si σ^* and Si–C σ^* orbitals and hence influence the ^{13}C hfsc are (1) the energy differences between the orbital sets and (2) the overlap between the orbitals. Regarding (1), substituents which are more electron attracting toward silicon than methyl will lower the energy of the Si–Si σ^* orbitals compared to those of $(Me_2Si)_5^{-}\cdot$. Such substitution should also stabilize the Si–C σ^* orbital at the site of substitution relative to the other Si–C σ^* orbitals.[22] Regarding (2), introduction of a substituent could change the angle between the silicon–carbon bonds and the mean plane of the ring, which might alter orbital overlap. Evidence from geometrically restricted anion radicals indicates that as this angle increases,[4] odd-electron delocalization onto carbon also increases. This effect is expected to be important only for the carbon(s) bonded to the substituted silicon.

Substitution lifts the degeneracy of the E_2 and E_1 orbitals of $(Me_2Si)_5$. The change in the energy level of each orbital (within the pair) is proportional to the bond orbital coefficient of $(Me_2Si)_5$ at the site of the attachment, which by symmetry must be between bonds three and four (Figure 3). Figure 3 shows the lowest Si–Si σ^* orbitals of $(Me_2Si)_5$, the E_2 orbitals, which we have labeled as A′

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[20] Figures 1 and 2 show one possible dovetailing of the Si–Si σ^* and Si–C σ^* orbitals. We can only show that the relative placement of the lowest lying member of each set in $(SiMe_2)_5^{-}\cdot$ is correct (see text).

[21] Based on the McConnell relationship $a(H) = Q\rho_c$, where $Q = 22.5$ G. The number of hydrogens whose hfsc contribute to the line width is not known, but the total odd-electron density on the remote carbon atoms is not strongly dependent on this number.

[22] The energies of the other Si–C σ^* orbitals should be changed only slightly. For the purposes of this model, it is required only that the Si–C σ^* orbitals at unsubstituted silicon atoms do not become markedly different in energy. Substituents more electron releasing than methyl will lead to the opposite changes in the orbital energies.

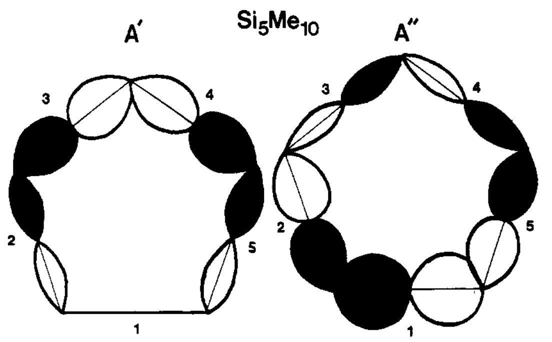

Figure 3. The lowest lying Si-Si σ^* molecular orbitals in cyclopentasilanes, symmetry designation for C_s.

and A″ according to the C_s symmetry designation appropriate for a substituted cyclopentasilane. The coefficients are for A′, $0.372\ \sigma_2^* - 0.602\ \sigma_3^* + 0.602\ \sigma_4^* - 0.372\ \sigma_5^*$, and for A″, $-0.632\ \sigma_1^* + 0.512\ \sigma_2^* - 0.195\ \sigma_3^* - 0.195\ \sigma_4^* + 0.512\ \sigma_5^*$. From these coefficients it is evident that the energy of both orbitals will change with substitution but that the A′ orbital will change more than A″.

The final energy difference between the A′ and A″ orbitals determines how the ^{13}C hfsc in the substituted cyclopentasilane are affected. There are two possible limiting cases.

1. If the A′ - A″ energy difference is sufficiently large that the odd electron resides only (or mainly) in one of these orbitals, the odd-electron density in the silane ring will be polarized. Differences in odd electron density among the silicon atoms would result in differing amounts of odd-electron density being delocalized to the various methyl substituents. The ^{13}C hfsc would change according to eq 1, and five different values would be expected in a planar ring or in one rapidly pseudorotating; otherwise ten values are expected. This case has an analogy in the benzene anion radicals, in which the degeneracy of the A and S orbitals is split upon substitution.[23]

2. If the difference between A′ and A″ is small, so that they are almost equally populated, spin density will remain approximately equal at each silicon atom in the ring. In this case the change in the energy between the S Si-C σ^* orbitals and the unique Si-C σ^* orbital relative to the lowest lying symmetry adapted Si-Si σ^* orbitals is the only factor which influences the ^{13}C hfsc, provided that the ring is planar or rapidly pseudorotating. Two values for the ^{13}C hfsc are expected, one for the eight methyl groups at unsubstituted silicons and one for the unique methyl group. The value of the ^{13}C splitting will increase if this energy difference becomes less, or decrease if it becomes larger. The relative placement of the E_2 Si-Si σ^* orbitals and the S Si-C σ^* orbitals can be established by a substituent known to be more electronegative or more electropositive than a methyl toward silicon since its effect on the symmetry adapted Si-Si σ^* orbitals is predictable (vide supra). An analogy for the case wherein near degeneracy of the A′ and A″ orbitals is preserved is provided by the substituted cyclopentadienyl radicals, as seen from their ESR spectra.[24]

This model will now be used to interpret the ESR spectra of several substituted radicals, beginning with the hydride anion radical $(Si_5Me_9H)^{-}\cdot$.[5a] This spectrum consists of a doublet from splitting due to the unique H atom; each wing of the doublet is split into a multiplet by methyl protons. Consistent with case 2 above, only two ^{13}C hfsc are observed, one for the methyl on Si–H and one for all eight methyl carbons at the unsubstituted silicon atoms. Resolution of the very small (0.51 G) hydrogen hfsc at the unsubstituted methyl groups suggests that these hydrogens experience an odd-electron density which is not significantly polarized, also consistent with case 2.

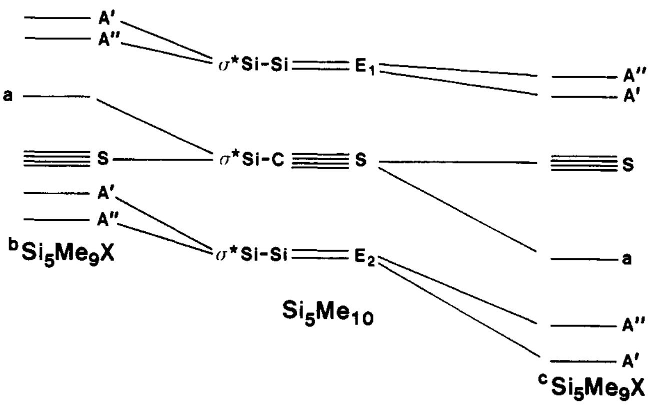

Figure 4. Qualitative antibonding molecular orbital order for substituted cyclopentasilane anion radicals. The Si–X σ^* orbital is not shown. The unique Si–C σ^* orbital is designated a. X-electron releasing compared to methyl is shown as b. X-electron accepting compared to methyl is shown as c.

Table II. ESR Parameters for Substituted Cyclopentasilane Anion Radicals

		a(H), G	$a(^{13}C)$, G	ref
Si_5Me_{10}	$a(SiCH_3)$	0.53	16.03	8
Si_5Me_9H	a(SiH)	14.1		5
	$a(SiCH_3)$	0.51	13.3 (8C)	
	$a(SiCH_3)$	1.02 (unique)	24.4 (1C)	
Si_5Me_9PH	$a(SiCH_3)$	0.51	14.7[a]	5, 6
p-$(CH_3)_3SiC_6H_4Si_5Me_9$		0.46	13.5[a]	6
p-$CH_3OC_6H_4Si_5Me_9$		0.61	19.7[a]	6
p-$CH_3C_6H_4Si_5Me_9$			20.0	6
$Si_5Me_8(SiMe_3)_2$			23.1 (8 C) 17.2[b]	5
(Me_9Si_5)–$Si_5Me_9^{-}\cdot$			14.5 (8 C) 22.9 (1 C)	

[a] To within experimental error the relative intensity was correct for eight or nine carbons. According to the model presented here eight is the expected value, with the unique ^{13}C hfsc not observed. [b] Relative intensity could not be determined.

The ^{13}C hfsc for the unsubstituted methyl carbons in the hydride is 13.3 G, reduced from 16.03 G in $(Me_2Si)_5^{-}\cdot$. The decrease in the hydride indicates that the energy difference between the A′ and A″ orbitals and the S Si–C σ^* orbitals has increased. It is well established that for silicon hydrogen is more electron withdrawing than methyl.[25] According to the above model, we expect that the symmetry-adapted Si–Si σ^* orbitals are stabilized by the hydride substituent. Therefore, the lowest lying symmetry-adapted Si–Si σ^* orbitals (E_2 or A′ and A″) must lie below the S Si–C σ^* orbitals (Figure 2).[26,27] The hy-

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[23] Ayscough, P. B. "Radical Ions"; Kaiser, E. T., Kevan, L., Eds.; Methuen: London, 1967; Chapter 8.

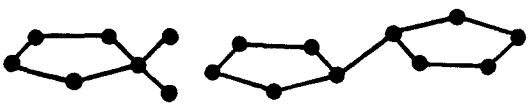
[24] Kira, M.; Watanabe, M.; Sakurai, H. *J. Am. Chem. Soc.* **1977**, *99*, 7780.

[25] (a) Le Fevre, R. J. W.; Rao, D. A. A. S. N. *Aust. J. Chem.* **1954**, 7, 135. (b) Le Fevre, R. J. W.; Rao, D. A. A. S. N. *Ibid.* **1954**, *8*, 39. (c) Altshuller, A. P.; Rosenblum, L. *J. Am. Chem. Soc.* **1955**, *77*, 272. (d) Eaborn, C. "Organosilicon Compounds"; Academic Press: New York, 1960; p 89.

[26] The same order is expected for cyclotetrasilanes, Figure 1. This expectation is supported by similar relative magnitudes of the ^{13}C hfsc found in the four- and five-membered rings (vide infra).

[27] In Figure 2, the n Si–Si σ^* orbitals are placed below the 2n Si–C σ^* orbitals although this is not required. If the gem interaction of the latter was very small compared to the former, then the E2 orbital in $(Me_2Si)_5$ could lie below the S Si–C σ^* orbitals even with 2n Si–C σ^* < n Si–Si σ^*. However, it is unlikely that the gem Si–Si σ^* and the gem Si–C σ^* interactions are sufficiently different to produce this effect.

Chart I



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dride substituent will also stabilize the unique Si–C σ^* orbital, and as expected from the orbital ordering determined above the ^{13}C hfsc for the unique methyl carbon is large (24.4 G). These results are generalized and presented qualitatively for substituted cyclopentasilanes in Figure 4.

Phenyl-substituted cyclopentasilane anion radicals $\mathrm{Si_5Me_9Ar^{-}\cdot}$ have also been investigated in earlier studies.[5] The unpaired electron was found to be mainly associated with the cyclosilane ring rather than the aromatic ring in these species. The ^{13}C hfsc for these anions (Table II) is due to eight equivalent carbon atoms. Therefore, these species are also examples of case 2, with the odd-electron density essentially uniform over the polysilane ring. Phenyl and *p*-(trimethylsilyl)phenyl groups lead to decreased ^{13}C hfsc for these equivalent carbons and are therefore more electron attracting than methyl (Figure 4). However the *p*-tolyl and *p*-methoxyphenyl substituents, which produce increases in ^{13}C hfsc compared to $\mathrm{(Me_2Si)_5^{-}\cdot}$, are therefore more electron releasing than methyl and destabilize the Si–Si σ^* orbitals (Figure 4).[28]

In cyclopolysilane anion radicals bearing exocyclic silicon atoms as substituents (Chart 1), the additional geminal Si–Si interactions may completely alter the orbital arrangement such that our model is no longer appropriate without modification. Nevertheless it is of interest to see if the model can be used to rationalize the ESR spectra of such species. The ESR spectrum of 1,1-bis(trimethylsilyl)octamethylcyclopentasilane[5b] consists of a single broad central line accompanied by two doublet sidebands at 23.1 and 17.2 G. Because the 23.1-G splitting has an intensity corresponding to eight carbons, it is assigned to the ring methyl carbons and the 17.2-G coupling is assigned to the carbons on the exocyclic trimethylsilyl groups. This anion radical behaves as another example in class 2. The very large ^{13}C hfsc for the ring methyl carbons indicates that Si–Si σ^* to Si–C σ^* mixing is greatly increased, consistent with the $\mathrm{Me_3Si}$ substituents acting as strongly electron releasing compared to methyl. However the large hfsc observed for the carbon atoms β to the ring show that the actual situation is not so simple. Odd-electron delocalization onto the exocyclic silicons must be very substantial.

The spectrum of the bi(nonamethylcyclopentasilanyl) anion radical (Chart I and Figure 5) consists of a single broad central line containing unresolved hydrogen hyperfine coupling, accompanied by two doublet sidebands. The ^{13}C hfsc, Table II, are assigned at 14.5 G to eight equivalent carbons and at 22.9 G to one carbon. The pattern of ^{13}C hfsc is consistent with uniform odd-electron density which is *mainly localized in one ring.*

Localization of the odd electron within a single cyclopentasilane ring was unexpected, since Si–Si σ^* mixing should lead to delocalization of the SOMO over both rings.

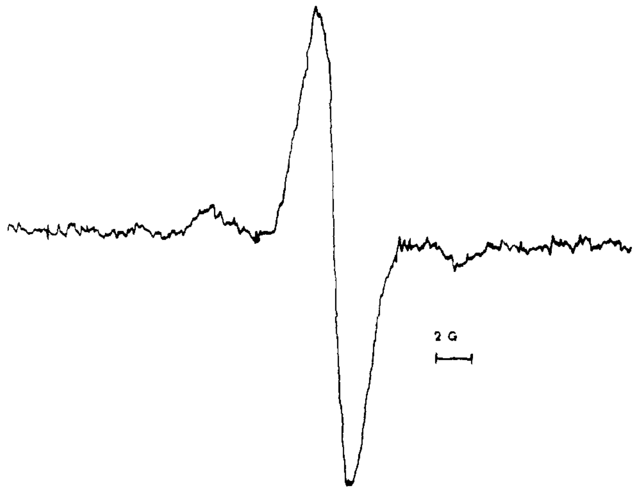

Figure 5. The ESR spectrum of $\mathrm{(Me_9Si_5){-}Si_5Me_9^{-}\cdot}$.

Similar electron localization in a single ring is observed in some bridged diaryl anion radicals and attributed mainly to solvation energy, which is maximized if the odd electron is localized in one ring.[29] The odd electron in $\mathrm{(Me_9Si_5){-}Si_5Me_9^{-}\cdot}$ may similarly be localized in order to maximize the solvation energy between this highly polarizable anion radical and the THF solvent.[30]

In the ESR spectrum for $\mathrm{(Me_9Si_5){-}Si_5Me_9^{-}\cdot}$, the ^{13}C hfsc for the eight methyl carbons on the ring which is reduced is slightly less than that for $\mathrm{(Me_2Si)_5^{-}\cdot}$, indicating a decrease in mixing between the ring Si–Si σ^* and Si–C σ^* orbitals. Within the limits of our model, the cyclo-$\mathrm{Me_9Si_5}$ substituent is behaving as a slightly more electron-attracting group than methyl, but less electron attracting than hydrogen. However, the actual situation is undoubtedly more complex, since some mixing of exocyclic Si–Si σ^* orbitals with ring σ^* orbitals undoubtedly takes place.

It is interesting that no cases of polarized odd-electron density in substituted cyclopentasilanes have yet been observed. Evidently in the anion radicals studied to date, the energy difference between the perturbed A and A′ orbitals does not become sufficiently large so that either orbital is primarily occupied by the odd electron.

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Registry No. $\mathrm{(Me_2Si)_5^{-}\cdot}$, 34469-54-0; $\mathrm{(Et_2Si)_5^{-}\cdot}$, 97486-98-1; $\mathrm{[(CH_2)_5Si]_5^{-}\cdot}$, 97486-99-2; $\mathrm{(Ph_2Si)_5^{-}\cdot}$, 69399-50-4; $\mathrm{(Me_2Si)_4^{-}\cdot}$, 97487-00-8; $\mathrm{(Et_2Si)_4^{-}\cdot}$, 97487-01-9; $\mathrm{[(CH_2)_5Si]_4^{-}\cdot}$, 97487-02-0; $\mathrm{(Ph_2Si)_4^{-}\cdot}$, 69399-49-1; $\mathrm{Si_5Me_9H^{-}\cdot}$, 57171-27-4; $\mathrm{Si_5Me_9Ph^{-}\cdot}$, 57171-30-9; *p*-$\mathrm{(CH_3)_3SiC_6H_4Si_5Me_9^{-}\cdot}$, 71000-68-5; *p*-$\mathrm{CH_3OC_6H_4Si_5Me_9^{-}\cdot}$, 71000-67-4; *p*-$\mathrm{CH_3C_6H_4Si_5Me_9^{-}\cdot}$, 71000-66-3; $\mathrm{Si_5Me_8(SiMe_3)_2^{-}\cdot}$, 57573-05-4; $\mathrm{(Me_9Si_5){-}Si_5Me_9^{-}\cdot}$, 97487-03-1.

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(28) In an earlier investigation,[5b] and ^{13}C hfsc in aryl-substituted cyclopentasilane anion radicals was correlated with the Hammett-type σ constant $\sigma_p{}^n$. Although it is not evident from the ESR of the $\mathrm{Si_5Me_9AnX}$ anion radicals, in all of these species the odd electron must be delocalized to some extent onto the aromatic ring, as it is in the $\mathrm{(Ph_2Si)_n^{-}\cdot}$ anion radicals.

(29) (a) McConnell, H. M. *J. Chem. Phys.* **1961**, *35*, 508. (b) Harriman, J. E.; Maki, A. H. *J. Chem. Phys.* **1963**, *39*, 778.

(30) The proposed mechanism of odd-electron transfer between the rings in bridged diaryl systems is one in which the odd-electron density follows the random solvent motions adiabatically, so that the rate of odd-electron transfer between rings should increase with increasing temperature.[29b] In an effort to observe a fully delocalized spectrum for $\mathrm{(Me_9Si_5){-}Si_5Me_9^{-}\cdot}$ due to rapid electron transfer, the temperature was gradually increased. However, only rapid decay of the anion radical to unidentified diamagnetic products was observed.