conserve the center of symmetry of the molecule. As a consequence, a molecule approximating to an η^4:η^4 bis(arene)iron(0) configuration would result. We may suggest therefore that the observation of a "η^4:η^4" species for toluene I probably arises from formation of a η^6:η^6 species which then distorts to the η^4:η^4. As a result of this argument, the most stable η^6:η^4 species (benzene, tetralin, toluene II) must be produced via a different reaction path possibly involving a concerted bending of one arene on coordination of the second ring.

Passing to the naphthalene case, the existence of a bis(η^6-naphthalene)iron(0) constitutes a rare example of a room-temperature-stable, 20-electron (arene)$_2$M species [others being (η^6-C_6Me_6)$_2$M for M = Fe and Co$^+$].[12,31] However while one may assume that the absence of a Jahn–Teller distortion for arene = C_6Me_6 must result from the excited singlet states being sufficiently destabilized relative to the $^3A_{2g}$ state, the picture is simpler for naphthalene. We have recently suggested that the electronic spectra of (η^6-$C_{10}H_8$)$_2$M (M = Ti, V, Cr) complexes may best be understood based on an assumed C_{2h} or C_{2v} symmetry.[4] For M = Fe, the highest occupied molecular orbital is therefore a nondegenerate level, thereby eliminating the possibility of a distortion as well as implying diamagnetism for the complex. Hence, we must invoke that the observation of a highly unstable η^4:η^4 species for naphthalene and 1-methylnaphthalene arises *not* from a Jahn–Teller distortion but through the ability of naphthalene to bind η^4 to a metal.

Finally, it is interesting to note that the prior macroscale metal vapor reactions between iron atoms and arenes[7] may be understood reasonably in the light of these matrix studies. Under the reaction conditions employed, addition of stabilizing ligands to the low-temperature species was carried out in a temperature range (>77 K)[32] in which the η^6:η^4 species is the major (or sole) product. Hence the isolated products reflect displacement of the η^4-arene, resulting in a (η^6-arene)FeL$_n$ complex.

Acknowledgment. We wish to acknowledge support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. (η^6-C_6Me_6)$_2$Fe, 55280-55-2; (η^6-C_6H_5Me)Fe(η^4-C_6H_5Me), 97487-60-0; (η^6-C_6H_6)Fe(η^4-C_6H_6), 97487-61-1; (η^6-$C_{10}H_{12}$)Fe(η^4-$C_{10}H_{12}$), 97487-62-2; (η^4-C_6H_8)$_2$Fe, 97487-63-3; (η^4-C_7H_8)$_2$Fe, 97487-64-4; (η^4-$C_{10}H(CH_3)_2$Fe, 97521-38-5; (η^4-$C_{10}H_8$)$_2$Fe, 97487-65-5; (η^6-$C_{10}H_8$)$_2$Fe, 97487-66-6; C_6Me_6, 87-85-4; $C_6H_5CH_3$, 108-88-3; C_6H_6, 71-43-2; C_6H_8, 592-57-4; $C_{10}H_7CH_3$, 90-12-0; $C_{10}H_8$, 91-20-3; Fe, 7439-89-6; tetralin, 119-64-2; cyclohexene, 110-83-8; 2,6-diisopropylnaphthalene, 24157-81-1.

---

[31] Fischer, E. O.; Lindner, H. H. *J. Organomet. Chem.* **1964**, *1*, 307. Thompson, M. R.; Day, C. S.; Day, V. W.; Mink, R. I.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 2979.

[32] It is reasonable to assume that the temperature of the matrix in a macroscale metal atom preparation is >77 K, due to radiant heating from the source.

ESR Spectra for Anion Radicals of Alkylcyclotetrasilanes and -cyclopentasilanes

Cynthia L. Wadsworth and Robert West*

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Yoichiro Nagai, Hamao Watanabe, and Tsutomu Muraoka

Department of Chemistry, Gunma University, Kiryu, Gunma 376, Japan

Received October 11, 1984

ESR spectra are reported for anion radicals formed by reduction of the cyclosilanes $(Me_2Si)_4$, $(Et_2Si)_4$, $(Et_2Si)_5$, $[(CH_2)_4Si]_5$, $[(CH_2)_5Si]_4$, $[(CH_2)_5Si]_5$, (i-$Pr_2Si)_4$, (i-$Bu_2Si)_4$, (s-$Bu_2Si)_4$, two isomers of (t-BuMeSi)$_4$, (n-$Pr_2Si)_5$, (n-$Bu_2Si)_5$, (n-PrMeSi)$_5$, and (i-BuMeSi)$_5$. All produce anion radicals in which the unpaired electron is delocalized over the cyclosilane ring. Most give single line spectra, but proton hyperfine splittings are resolved for $(Me_2Si)_4^{-}\cdot$, $[(CH_2)_4Si]_5^{-}\cdot$, and $[(CH_2)_5Si]_5^{-}\cdot$. Splitting constants for α-^{13}C decrease with increasing bulk of the alkyl substituents. For (i-$Pr_2Si)_4^{-}\cdot$ and (s-$Bu_2Si)_4^{-}\cdot$ two equally intense α-^{13}C hyperfine splitting constants (hfsc) are observed, consistent with a bent structure for these anion radicals.

Cyclopolysilanes, especially those containing four- and five-membered rings of silicon atoms, undergo reduction to anion radicals in which the unpaired electron is delocalized over the ring.[1] Systems studied earlier by electron spin resonance (ESR) spectroscopy include permethyl-[2] and perphenylcyclosilanes,[3] *tert*-butylmethylcyclotetrasilane,[4] and a number of substituted methylcyclosilanes $Si_5Me_9X^{-}\cdot$ and $Si_6Me_{11}X^{-}\cdot$.[5] In this paper, we report the ESR spectra of anion radicals of $(Me_2Si)_4$,[6] the perethylcyclosilanes $(Et_2Si)_n$,[7] organosilicon rotanes containing cyclotetramethylenesilane or cyclopentamethylenesilane groups,[8] and several peralkylcyclotetrasilanes and -pen-

---

[1] West, R. *Pure Appl. Chem.* **1982**, *54*, 1041.

[2] Carberry, E.; West, R.; Glass, G. E. *J. Am. Chem. Soc.* **1969**, *91*, 5446.

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

[4] Helmer, B. J.; West, R. *Organometallics* **1982**, *1*, 1458.

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

[6] Prepared according to: Ishikawa, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1970**, 612; *J. Organomet. Chem.* **1972**, *42*, 325.

[7] Carlson, C. W.; West, R. *Organometallics* **1983**, 2, 1792.

0276-7333/85/2304-1659$01.50/0

tasilanes containing bulky alkyl groups.[9]

Experimental Section

Starting compounds, prepared as described in the literature,[6-9] were purified by GLC prior to use. The two isomers of (t-BuMeSi)$_4$ were separated by fractional crystallization.[4] Most of the cyclopolysilanes are stable indefinitely in air in which case they were added directly to the lower portion of the ESR cells. The standard electrochemical cell has been described elsewhere.[10] The chemical cells were made of borosilicate glass and tapered to a 3-mm outer diameter. To the upper portion was joined a 2-cm side arm into which the active metal was initially placed. Compounds (Me$_2$Si)$_4$, (Et$_2$Si)$_4$, [(CH$_2$)$_5$Si]$_4$, and [(CH$_2$)$_4$Si]$_5$ required special handling as they oxidize in air. On the high vacuum line, the extremely air-sensitive (Me$_2$Si)$_4$ was sublimed directly from its storage vessel into the electrochemical ESR cell. In a nitrogen-filled glovebag oily (Et$_2$Si)$_4$ was transferred from a flame-sealed GLC collection tube into the electrochemical cell by placing the portion of the glass tubing containing the compound into the cell. The cell was protected from air during rapid transfer to the high vacuum line where solvent transfer and degassing were carried out; this process washed the (Et$_2$Si)$_4$ into the ESR cell. Compounds [(CH$_2$)$_4$Si]$_5$ and [(CH$_2$)$_5$Si]$_4$, which are crystalline, were stored in an inert atmosphere. They were quickly transferred into the ESR cell which was immediately attached to the high vacuum line.

Solvent transfer and degassing were performed on the vacuum line. After being degassed, electrochemical cells were filled with argon to suppress bubble formation during the electrolysis (bubbles cause loss of current and premature decay of the radical anion spectrum). Chemical cells were flame sealed.

All compounds except (Et$_2$Si)$_6$ and (Et$_2$Si)$_7$ were initially reduced at -90 °C by using highly purified THF stored over LAH as a solvent. Previous research[1,2] on methylcyclosilanes indicated that six- and seven-membered rings required lower initial reduction temperatures of −110 °C. For these a 3:1 mixture of 2-MeTHF stored over LAH and DME stored over the dianion of sodium benzophenone was used as a solvent.

Anion radicals were generated by using either electrochemical or chemical means. For electrochemical generation, the cell was placed in the ESR cavity and maintained at the desired temperature while a small current, 1–20 μA, was passed through solutions approximately 0.01 M in cyclopolysilane and 0.2 M in tetra-n-butylammonium perchlorate. Chemical generation of the anion radicals was accomplished outside of the ESR cavity. The solution (approximately 0.01 M in cyclopolysilane) was maintained at -90 °C and allowed to contact the potoassium mirror or Na/K alloy by inverting the cell. After several minutes it was reinverted and placed in the precooled ESR cavity.

ESR spectra were obtained by using a Varian E-15 X-band spectrometer using 100-kHz modulation and a Varian V-4557 variable-temperature accessory. The g values were determined relative to a pitch sample using a Hewlett-Packard 5254L electronic frequency counter and were reproducible to ±0.0001. Line sharpening was achieved by using a PET 2001 series computer which had been programmed to add small amounts of third and fifth derivative spectra to the main spectrum, after the method of Glarum.[11]

Unresolved hydrogen hyperfine coupling was estimated as follows: the full extent of the ESR line in gauss, taken as twice the peak to peak width ΔH_{pp}, was divided by the number of unresolved lines according to the binomial distribution. Only those lines with intensity >1% of the central peak were counted. Data in Table I show that the α-^{13}C hfsc decreases regularly by about 2 G with each additional β-carbon on the substituent groups. This general trend was used to assign the larger ^{13}C hfsc to the smaller alkyl substituent in those rings with two types of alkyl groups.

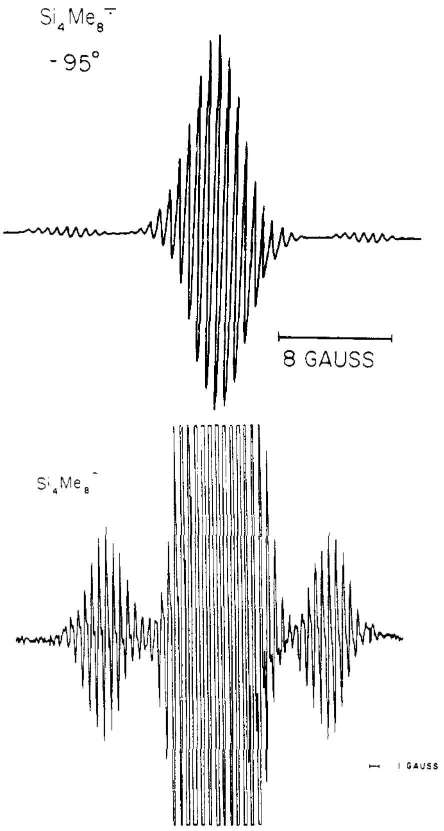

Figure 1. ESR spectrum of (Me$_2$Si)$_4^{-}\cdot$: above, low gain; below, high gain.

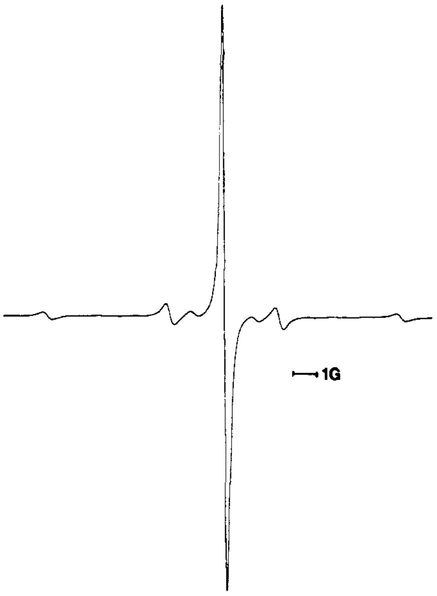

Figure 2. ESR spectrum of (Et$_2$Si)$_5^{-}\cdot$, low gain.

Results and Discussion

(Me$_2$Si)$_4$. Reduction of this highly reactive cyclosilane produced a blue anion radical showing a multiplet ESR spectrum (Figure 1), similar in form to those for (Me$_2$Si)$_5^{-}\cdot$ and (Me$_2$Si)$_6^{-}\cdot$.[1,2] Line intensities for the multiplet agree with those calculated for the center portion of a 25-line pattern, consistent with equal splitting by each of the 24 protons. A ^{13}C hyperfine splitting constant (hfsc) is also observed for (Me$_2$Si)$_4^{-}\cdot$ at 21.07 G, slightly larger than for the five- and six-membered ring analogues (Table I).

(Et$_2$Si)$_n$ Rings. The ESR spectrum of the five-membered ring anion (Et$_2$Si)$_5^{-}\cdot$ is unprecedented. The multiplet typical for methylcyclosilane anions is collapsed into a

---

(8) Carlson, C. W.; Zhang, X.-H.; West, R. *Organometallics* **1983**, *2*, 453.

(9) (a) Watanabe, H.; Muraoka, T.; Kohara, Y.; Nagai, Y. *Chem. Lett.* **1980**, 735. (b) Watanabe, H.; Muraoka, T.; Kageyama, M. *J. Organomet. Chem.* **1981**, *216*, C45. (c) Watanabe, H.; Muraoka, T.; Kageyama, M.; Yoshizumi, K.; Nagai, Y. *Organometallics* **1984**, *3*, 141.

(10) Glass, G. E.; West, R. *Inorg. Chem.* **1972**, *11*, 2847.

(11) Glarum, S. H. *Rev. Sci. Instrum.* **1965**, *36*, 771.

Table I. ESR Parameters for Cyclosilane Anion Radicals

radical anion	g value^{a}	color	hyperfine coupling constants, G $a(^{29}Si)$	 $a(\alpha\text{-}^{13}C)^{b}$	max^{c} a(H)	ΔH_{pp} central line
$(Me_2Si)_4$	2.0037	blue		20.97	0.67^{d}	
$(Et_2Si)_4$	2.0037	blue	4.70	18.40	0.14 (11)	0.78
$[(CH_2)_5Si]_4$	2.0034	purple	5.20	20.80	<0.51^{h}	4.32
$(i\text{-}Bu_2Si)_4$	2.0040	olive	3.8	17.6, [35/2]^{e}	0.17 (11)	0.92
$(i\text{-}Pr_2Si)_4$	2.0040	olive	3.8	18.58, 14.40, 16.49 (av)	0.31 (9)	1.38
$(s\text{-}Bu_2Si)_4$	2.0040	olive		18.36, 14.42, 16.39 (av)	0.41 (9)	1.86
$(t\text{-}BuMeSi)_4$ (a)	2.0039	olive		21.65, 14.0, [27.5]^{e}	0.28^{i}	
$(t\text{-}BuMe_4Si)$ (b)	2.0040	olive		23.3, 15.1	j	2.65
$(Me_2Si)_5$	2.0032	blue	5.18	16.03	0.53^{d}	
$(Et_2Si)_5$	2.0034	blue	4.46	14.10	0.04 (15)	0.29
$[(CH_2)_4Si]_5$	2.0031	blue		13.9	0.58^{d}	
$[(CH_2)_5Si]_5$	2.0031	blue	5.20	15.71	0.14^{k}	
$(n\text{-}Pr_2Si)_5$	2.0034	blue	4.0	13.36, [17.2 ± 0.5]^{f} [9.2 ± 5]^{g} [26.2±5]^{e}	0.18 (15)	1.36
$(n\text{-}Bu_2Si)_5$	2.0035	blue	4.44	13.40, [17.86]^{f} [8.89]^{g} [26.65]^{e}	0.10 (15)	0.72
$(n\text{-}PrSiMe)_5$	2.0034	blue		12.7, 18.63	j	1.60
$(i\text{-}BuMeSi)_5$	2.0035	blue		12.0, 19.6	j	1.90
$(Me_2Si)_6$	2.0028	yellow		14.60	0.44	

[a] Reproducible to ±0.0001. [b] For rings with two types of alkyl groups the larger ^{13}C hfsc is assigned to the smaller alkyl group, see text. Couplings in brackets result from molecules with two magnetic nuclei. [c] Values estimated from ΔH_{pp}. The number of lines expected to be observed are listed in parentheses, see text. [d] Exact values. [e] 2-^{13}C. [f] 1-^{29}Si and 1-^{13}C. [g] 2-^{29}Si overlapped with the peak from 1-^{29}Si and 1-^{13}C. [h] a(H) of either the α- or β-hydrogen, whichever is larger, estimated from ΔH_{pp}. See Experimental Section. [i] Exact a(H) obtained chemically at room temperature, see ref 4. [j] Estimate of a(H) not made in the case of differing alkyl substitutents, since the number of contributing hydrogens is now known. [k] Apparent a(H) produced from incompletely resolved α- and β-hydrogen hyperfine splittings.

single narrow line (Figure 2).[12] From the line width, the proton hfsc must be <0.04 G. The ESR spectrum of $(Et_2Si)_4^{-}\cdot$ is similar except that the central line is slightly wider; the unresolved ^{1}H hyperfine splittings contributing to the line width are <0.14 G (Table I).

The proton hfsc's of cyclosilane anion radicals may result from direct hydrogen 1s orbital participation in the singly occupied molecular orbital (SOMO) and/or from spin polarization of the C–H bonding electron pair. Both of these contributions to the hfsc are espected to be conformationally dependent. In $(Et_2Si)_5^{-}\cdot$, the spin polarization, which can result in a negative hfsc, and odd electron delocalization, which produces a positive hfsc for hydrogen, apparently almost exactly cancel and so produce a near-zero proton splitting. In $(Et_2Si)_4^{-}\cdot$, the cancellation is less exact so that the unresolved proton splittings broaden the center line somewhat.

Because the proton splittings in the ethylcyclosilanes are so small, there is no overlap with splittings due to other magnetic nuclei, which are therefore easily determined. Each of the three nuclei ^{29}Si, α-^{13}C, and β-^{13}C gives rise to a single pair of satellite lines, indicating that the Et_2Si groups are equivalent. Of the two splitting constants due to ^{13}C for each anion radical, the larger is assigned to the α-carbon, because the magnitudes are similar to those for the ^{13}C splitting constants in methylcyclosilanes.

The decline in α-^{13}C hfsc with increasing ring size found for the $(Me_2Si)_n^{-}\cdot$ series is also observed in the ethylcyclosilane anion radicals.[13] Small but significant hyperfine couplings are found for the β-carbon atoms in ethylcyclosilanes. The β-carbon hyperfine coupling is larger in $(Et_2Si)_5^{-}\cdot$ than in $(Et_2Si)_4^{-}\cdot$, reversing the trend for the α-carbon hfsc's.[14]

The equivalence of the $SiEt_2$ groups is further supported by the high gain spectrum of $(Et_2Si)_5^{-}\cdot$ (Figure 3), which shows additional low intensity doublet sidebands. The near-zero hydrogen hfsc allows resolution of secondary splittings which differ from each other only slightly. The hfsc expected for anion radicals containing two magnetic nuclei (^{29}Si or ^{13}C) are listed and compared with observed splittings in Table I. The correspondences are very close, and all of the low intensity lines are explained as due to species containing two ^{29}Si or ^{13}C atoms, rather than a result of unique Et_2Si groups in a nonplanar conformation.

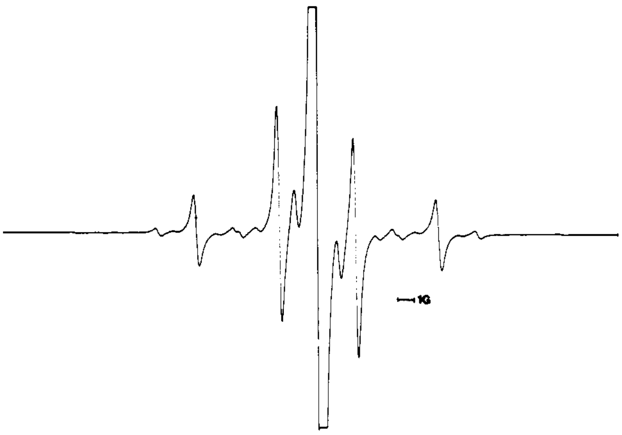

Figure 3. ESR spectrum of $(Et_2Si)_5^{-}\cdot$, high gain.

Reduction of $(Et_2Si)_6$ gave no ESR signal in repeated attempts over the range −110 to −70 °C, but electrolytic reduction of $(Et_2Si)_7$ gave the ESR spectrum of $(Et_2Si)_5^{-}\cdot$. Similar transformation to the five-membered ring anion radical is observed upon reduction of $(Me_2Si)_7$. These observations may explain the earlier results of Bukhtiyarov and co-workers, who reported the preparation of a diethylcyclosilane thought to be $(Et_2Si)_6$, and its reduction to an anion radical described as $(Et_2Si)_6^{-}\cdot$.[15] The ESR spectrum published by these workers is identical with that recorded by us for $(Et_2Si)_5^{-}\cdot$.

---

(12) The same spectrum was obtained by chemical and electrochemical reduction and over a wide range of concentrations, ruling out electron exchange as the cause of the narrow central line.

(13) The significance of the ^{13}C hfsc for these and other cyclosilane anion radicals are considered: Wadsworth, C. L.; West, R. *Organometallics*, following paper in this issue.

(14) The reasons for this are not well understood but may result from differences in the conformation of the alkyl substituents relative to the average plane of silicon atoms in each ring.[13]

(15) Bukhtiyarov, V. V.; Solodovnikov, S. P.; Nefedov, O. M.; Shiryaev, V. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, 1012. This paper contains an interpretation of the high gain spectrum similar to that presented here for $(Et_2Si)_5^{-}\cdot$. As explained elsewhere,[7] it is likely that the silane of Bukhtiyarov et al. was either $(Et_2Si)_6$ or $(Et_2Si)_7$.

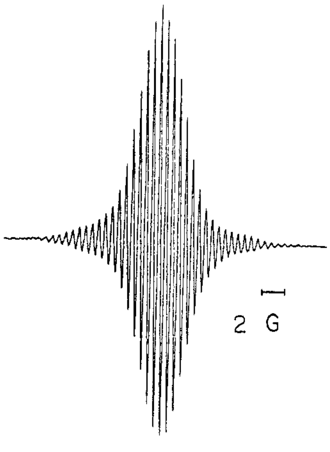

Figure 4. ESR spectrum of $[(CH_2)_4Si]_5^{-}\cdot$.

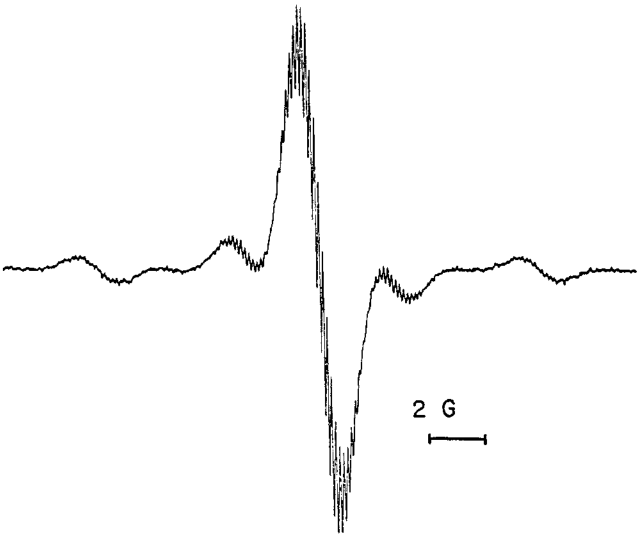

Figure 5. ESR spectrum of $[(CH_2)_5Si]_5^{-}\cdot$.

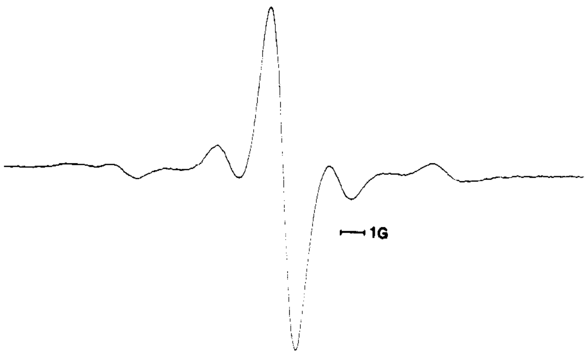

Figure 6. ESR spectrum of $(n\text{-}Pr_2Si)_5^{-}\cdot$.

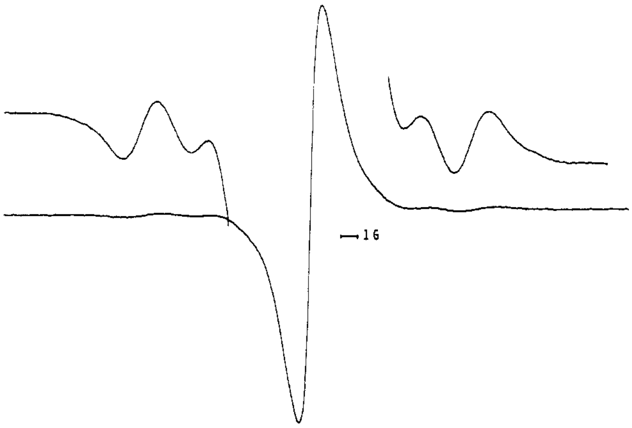

Figure 7. ESR spectrum of $(n\text{-}PrMeSi)_5^{-}\cdot$.

Organosilicon Rotanes.[8] In the cyclotetramethylenesilane series only one molecule $[(CH_2)_4Si]_5$ produced an anion radical. The ESR spectrum, shown in Figure 4, is a highly symmetrical pattern showing well-resolved hydrogen hyperfine coupling. Measurement of the line intensities showed that they are consistent with a 41-line pattern due to coupling by 40 equivalent hydrogens. Apparently in this anion radical the protons on both the α- and β-carbons couple to the odd electron, with splitting constants which fortuitiously have nearly the same absolute magnitude.

Splitting by β-hydrogens in cyclopolysilane anion radicals is unusual but has also been observed for *all-trans*-(t-BuMeSi)$_4$.[4] A conformational feature share by this compound and $[(CH_2)_4Si]_5$ is that the β-hydrogens lie near the mean plane of the ring silicon atoms. Perhaps this orientation leads to efficient β-proton coupling, but the mechanism is not known.

Indications of β-proton coupling are also seen in the ESR spectra of $[(CH_2)_5Si]_4^{-}\cdot$ and $[(CH_2)_5Si]_5^{-}\cdot$. For the latter species, proton splittings are partially resolved (Figure 5), and the number of lines in the multiplet is too large for the coupling to be due only to α-hydrogens. Apparently both α- and β-protons are coupled, and there is a near-integral relationship between their splitting constants. For $[(CH_2)_5Si]_5^{-}\cdot$, a single broad line is observed in the ESR. The line width is sufficiently large, 4.32 G, that if splitting by α-protons only were involved, the line should have been resolved into a multiplet. The broad line probably results from the combination of α- and β-proton splittings which are somewhat different so that they form an overlapping unresolved pattern.

The α-^{13}C hfsc in $[(CH_2)_5Si]_5^{-}\cdot$, which might be expected to be similar to that in $[(CH_2)_4Si]_5^{-}\cdot$ and $(Et_2Si)_5^{-}\cdot$, is actually slightly larger. A conformational effect of the cyclopentamethylenesilane substituent on the angle between the α-carbon and the cyclosilane ring may account for the increased electron delocalization onto the carbon atoms in $[(CH_2)_5Si]_5^{-}\cdot$. Several attempts were made to reduce other compounds in this class, $[(CH_2)_4Si]_6$, $[(CH_2)_4Si]_7$, and $[(CH_2)_5Si]_6$, but in no case was an ESR signal observed.

Other Cyclopentasilanes: (n-Pr$_2$Si)$_5$, (n-Bu$_2$Si)$_5$, (n-PrMeSi)$_5$, and (i-BuMeSi)$_5$. The spectra of the anion radicals of these cyclopentasilanes all consist of a principal central line with ^{13}C and ^{29}Si sidebands, indicating equivalence of the SiR$_2$ or SiRR′ units. A typical spectrum for an (SiR$_2$)$_5$ anion radical, $(n\text{-}Pr_2Si)_5^{-}\cdot$, is shown in Figure 6; only a single ^{13}C satellite line is observed. For (SiRR′)$_5$ anion radicals, two ^{13}C sidebands are found, indicating differing amounts of odd electron density at the α-carbon in the two types of alkyl substituents.[13] A typical example is $(n\text{-}PrMeSi)_5^{-}\cdot$, shown in Figure 7. The larger α-^{13}C hfsc is assigned to the methyl group in $(n\text{-}PrMeSi)_5^{-}\cdot$ and $(i\text{-}BuMeSi)_5^{-}\cdot$ and the smaller α-^{13}C hfsc to the n-Pr or i-Bu group, according to the trend of decreasing α-^{13}C with increasing substituent bulk (Table I).

These cyclopentasilane anion radicals, and the ones discussed earlier in this paper, may be either planar or pseudorotating at a rate which is fast compared to the ESR time scale. Rapid pseudorotation seems most likely, since the neutral cyclopentasilanes whose structure is known all adopt bent conformations,[16] and the barrier to pseudorotation for five-membered ring cyclosilanes is expected to be quite small.[17] All cyclopentasilane anion radicals have

---

[16] Carlson, C. W.; Zhang, X.-H.; Haller, K. J.; West, R. *J. Am. Chem. Soc.* **1984**, *106*, 5521.

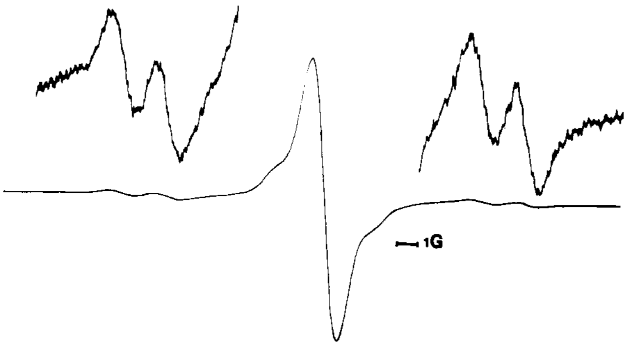

Figure 8. ESR spectrum of $(i\text{-Pr}_2\text{Si})_4^{-}\cdot$.

uniform *g* values and color suggesting that whichever conformation is adopted, it is probably similar for all of these species.

Other Cyclotetrasilanes: $(i\text{-Bu}_2\text{Si})_4$, $(i\text{-Pr}_2\text{Si})_4$, $(s\text{-Bu}_2\text{Si})_4$, and $(t\text{-BuMeSi})_4$. The anion radicals of these cyclotetrasilanes, all of which carry bulky substituents, are somewhat different from those of the unhindered species $(\text{Me}_2\text{Si})_4^{-}\cdot$, $(\text{Et}_2\text{Si})_4^{-}\cdot$, and $[(\text{CH}_2)_5\text{Si}]_4^{-}\cdot$ (Table I). The hindered Si_4 anion radicals are olive green rather than blue and show larger g values. Moreover, the ESR spectra of $(i\text{-Pr}_2\text{Si})_4^{-}\cdot$ (Figure 8) and $(s\text{-Bu}_2\text{Si})_4^{-}\cdot$ each show two equally intense ^{13}C hfsc,[18] which must be assigned to two types of α-carbons. This is to be expected only if the four-membered rings are *bent*, and inversion between equivalent bent forms is slow on the time scale of the ESR experiment; the pseudoaxial and pseudoequatorial carbons could then have different hfsc.

Factors that influence *g* values in cyclopolysilanes are not well understood but in general both the *g* value and absorption spectrum depend on the energy gap to the excited states of the anion radical,[19] so that both of these properties should vary with ground-state conformation. One possibility is that the olive-colored, hindered cyclotetralsilane anion radicals have bent conformations, while the blue unhindered species are planar.[20] The ESR spectrum for $(i\text{-Bu}_2\text{Si})_4^{-}\cdot$, has some characteristics in common with those of both the less hindered species $(\text{SiMe}_2)_4^{-}\cdot$ and $(\text{SiEt}_2)_4^{-}\cdot$ and the more hindered species $(i\text{-Pr}_2\text{Si})_4^{-}\cdot$ and $(s\text{-Bu}_2\text{Si})_4^{-}\cdot$. The color and *g* value resemble those for the hindered cyclotetrasilane anion radicals, but the single value of the ^{13}C hfsc found for $(i\text{-Bu}_2\text{Si})_4$ suggests that all of the *i*-Bu groups are equivalent on the ESR time scale. Possibly $(i\text{-Bu}_2\text{Si})_4^{-}\cdot$ exists in a folded conformation but is rapidly inverting.

The ESR spectrum for the all-trans isomer a of $(t\text{-BuMeSi})_4^{-}\cdot$ has been recorded earlier;[4] the spectrum for the cis, cis–trans,trans isomer b is shown in Figure 9.[21] Each isomer displays two equally intense ^{13}C hfsc, of which the larger one is probably due to the methyl carbon and the smaller to the α-*tert*-butyl carbon. The colors and *g* values for these species are again similar to those for $(i\text{-Pr}_2\text{Si})_4^{-}\cdot$ and $(s\text{-Bu}_2\text{Si})_4^{-}\cdot$, suggesting that the $(t\text{-BuMeSi})_4^{-}\cdot$ isomers also adopt folded conformations.[22] If the anion radical of isomer b is indeed bent, the ^{13}C hfsc provide evidence that it must undergo rapid ring inversion. Slow interconversion between two bent forms for isomer b would lead to a 3:1:3:1 pattern of ^{13}C hfsc.[23] The axial and equatorial couplings should differ by ~4 G, as for $(i\text{-Pr}_2\text{Si})_4^{-}\cdot$ and $(s\text{-Bu}_2\text{Si})_4^{-}\cdot$, and so should easily be resolved. However, even with line sharpening only two α-^{13}C hfsc were observed, with intensities corresponding to four carbon atoms each, as expected if isomer b is rapidly inverting.

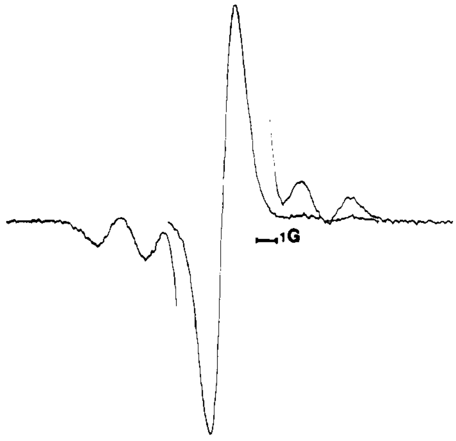

Figure 9. ESR spectrum of $(t\text{-BuMeSi})_4^{-}\cdot$, isomer b.

The α-^{13}C hfsc for the methyl and *tert*-butyl groups in isomer b are greater than the analogous values obtained for isomer a, indicating that more odd electron density is delocalized onto the substituents in isomer b.[13] The reasons for this are not known but may result from differing relative contributions among conformations with different degrees of bending.

The width of the center line in the ESR spectra for these compounds varies considerably. Presumably the line width depends on the magnitude of the unresolved hydrogen hfsc. The largest line widths are found for species which have two different groups attached to silicon or which are bent and not rapidly inverting. Either of these factors would produce more than one hydrogen hfsc value.

Conclusions

The cyclopentasilane anion radicals reported here, like those previously studied, all produce blue anion radicals with only single values for α-^{13}C hfsc, indicating that they are either planar or rapidly pseudorotating. The cyclotetrasilane anion radicals are more variable in their properties. Those with relatively small alkyl substituents $(\text{Me}_2\text{Si})_4^{-}\cdot$, $(\text{Et}_2\text{Si})_4^{-}\cdot$, and $[(\text{CH}_2)_5\text{Si}]_4^{-}\cdot$ show only a single α-^{13}C hfsc, indicating that these species are planar or un-

---

[17] Legan, A. C. *Chem. Rev.* **1989**, *80*, 231. Dunitz, J. D. In "X-Ray Analysis and the Structure of Organic Molecules"; Cornell University Press: Ithaca, NY, 1979; pp 429–431.

[18] The sidebands for $(i\text{-Pr}_2\text{Si})_4^{-}\cdot$ could be resolved without line sharpening, and therefore it was possible to determine that the intensity for each sideband relative to the central line was correct for four carbons. The intensity of the ^{13}C sidebands for $(s\text{-Bu}_2\text{Si})_4^{-}\cdot$ could not be determined accurately because resolution of the sidebands required line sharpening which in our setup precludes an accurate intensity determination.

[19] Atkins, P. W. In "Structure of Inorganic Radicals; An Application of Electron Spin Resonance to the Study of Molecular Structure"; Elsevier: New York, 1967; Chapter 2.2.

[20] In support of this suggestion, the crystal structure of $(\text{Me}_2\text{Si})_4$ shows that this molecule is planar: Kratky, C.; Schuster, H. G.; Hengge, E. *J. Organomet. Chem.* **1983**, *247*, 253.

[21] Chemical reduction of either a or b by Li or Na/K leads only to an ESR spectrum for the anion radical of a. Evidently active metals bring about rearrangement to the thermodynamically stable isomer a. The *g* value for the anion radical of a in Table I replaces the earlier published value.[4]

[22] The crystal structure of isomer a reveals a folded structure with a dihedral angle of 36.8°. See: Hurt, C. J.; Calabrese, J. C.; West, R. *J. Organomet. Chem.* **1975**, *91*, 273.

[23] A 3:1:3:1 pattern for the bent radical is expected if the only factors which influence the hfsc are the chemical identity of the alkyl group, i.e., methyl or *tert*-butyl, and its relative placement, pseudoaxial or pseudoequatorial. A still more complicated pattern would result if cis neighbors affected the α-^{13}C hfsc. Lack of a cis neighbor effect is demonstrated by the 1:1 ratio of hfsc, correct for four carbons, obtained for isomer b. Whether the anion radical of isomer b was planar or rapidly inverting, each of the above sidebands would break into a 1:2:1 pattern if cis neighbors affected the hfsc. A 1:2:1 pattern of couplings is in fact observed in the NMR spectrum for this isomer.[4]

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

Cynthia L. Wadsworth and Robert West*

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received October 11, 1984

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 $(\text{RR'Si})_4$ and $(\text{RR'Si})_5$,[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

---

(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°.

0276-7333/85/2304-1664$01.50/0