erably more planar and possess intermolecular separations on the order of 3.2 Å. Although the degree of oxidation of the TAAB complexes remains in question, these complexes do show larger than expected conductivities (especially when compared with the bisdioximates) along with an unusual pressure dependence, perhaps related to compression of the unit cell. Possible influences of the large percentage of iodine on the conductivity are currently being investigated in related systems with high iodine content.

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Supplementary Material Available: Table II, observed and calculated structure factors for $[Pd(TAAB)][BF_4]_2$ (37 pages). Ordering information is given on any current masthead page.

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Novel Organosilicon Radical Cations. One-Electron Oxidation of Permethylcyclopolysilanes[1]

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Abstract: The permethylcyclosilanes **1–4**, all of which exhibit low first ionization potentials, have been oxidized with $AlCl_3$ in CH_2Cl_2 to form the first examples of delocalized, σ-electron radical cations. These species have been studied by ESR spectroscopy. Unlike the well-known radical anion of **1**, the radical cation of dodecamethylcyclohexasilane ($\mathbf{1}^{+\cdot}$) gives an ESR spectrum which can be simulated only by assuming two sets of 18 equivalent protons, corresponding to 6 axial and 6 equatorial methyl groups which do not become equivalent on the ESR time scale. The high g value of 2.0093 observed for $\mathbf{1}^{+\cdot}$ suggests a considerable spin population in the Si_6 ring skeleton. The radical cations of **2**, **3**, and **4** show only overlapping signals in ESR, but their respective g values of 2.010, 2.0105, and 2.0063 are also consistent with spin delocalization into the σ_{Si-Si} system.

Peralkylpolysilanes have attracted interest because of their unique properties which distinguish these compounds from saturated catenates of carbon.[3] In particular, cyclic polysilanes resemble in their behavior aromatic hydrocarbons, in that they show long-wavelength ultraviolet absorption,[4] undergo one-electron reduction to radical anions,[5] form charge-transfer complexes with π acceptors,[6] and have low first ionization potentials.[7] Because the latter are similar to those of aromatic compounds like naphthalene and anthracene,[8] several attempts have been made to oxidize polysilanes to cation radicals.[9]

Recently, organosilicon compounds containing lone electron pairs or π-electron systems have been oxidized to persistent[10] radical cations in a straightforward way using the system $AlCl_3/CH_2Cl_2$. The redox potential of this mixture is sufficient to oxidize compounds which have a first (adiabatic) ionization potential below 8 eV. Examples containing silicon are shown in Chart I. Although permethylcyclopolysilanes contain neither π electrons nor lone pairs, the rather small effective nuclear charge of silicon leads to low (<8 eV) ionization potentials for Si-Si σ-bonding electrons. We find that compounds **1–4** (R = CH_3) can be oxidized by $AlCl_3/CH_2Cl_2$ at low temperatures

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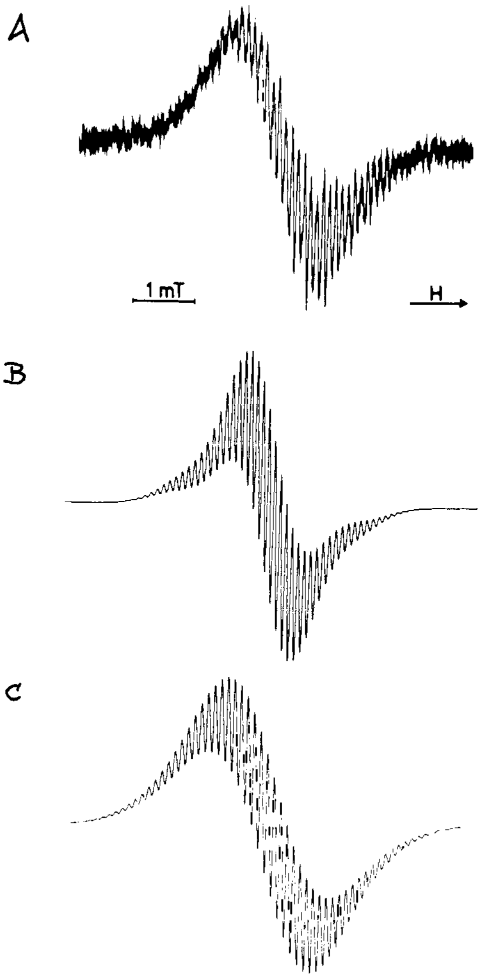

Figure 1. Optimum ESR spectrum of dodecamethylcyclohexasilane radical cation $1^{+\cdot}$ at 193 K (A) and its computer simulation assuming a ratio $a_{H,1} = 3a_{H,2}$ and a ^{29}Si coupling constant $a_{^{29}Si}$ of 0.7 (B) or 0 mT (C).

forming kinetically stable radical cations, $M^{+\cdot}$. In this paper, the ESR spectra of the cation radicals are reported and correlated with photoelectron spectra (PES) and with calculated values of ionization energies for the neutral molecules.


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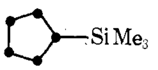

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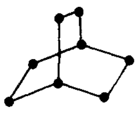
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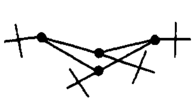
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Experimental Section

Dodecamethylcyclohexasilane (**1**) was obtained by condensation of dimethyldichlorosilane with sodium-potassium alloy.[16] The sample used was recrystallized three times from ethanol; it showed no impurity by gas chromatography and gave a singlet in the ^{1}H NMR spectrum at 0.132 ppm, in agreement with the previously reported value.[3] Nonamethyl(trimethylsilyl)cyclopentasilane was prepared by conversion of **1** to nonamethyl(chlorodimethylsilyl)cyclopentasilane[17] followed by methylation with methyl Grignard reagent.[18] It was purified by gas chromatography and showed spectral properties consistent with the known structure. Previous papers describe our syntheses of compounds **3**[19] and **4**,[20] which were also purified by gas chromatography.

Photoelectron spectra have been recorded on a Perkin-Elmer PS 16 spectrometer equipped with a heated inlet system and were calibrated using the Xe ($^2P_{3/2}$) = 12.13 eV and Ar ($^2P_{3/2}$) = 15.76 eV peaks.

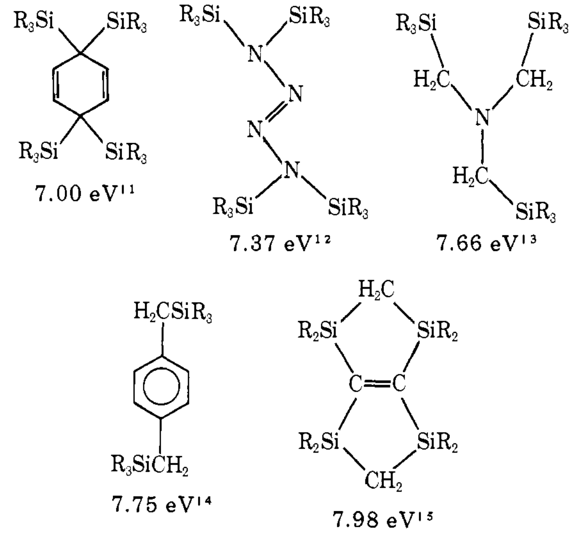
Radical cation generation was performed in 2-mm i.d. glass capillary tubes under N_2 by the following procedure: 1 mg of the compound was dissolved in 0.1 mL of oxygen-free dichloromethane which had been kept dry over $AlCl_3$, and ~5 mg of $AlCl_3$ was added to this solution. Because these peralkylcyclopolysilane radical cations decompose even at low temperatures, >190 ($1^{+\cdot}$ and $2^{+\cdot}$), >230 ($3^{+\cdot}$), and >250 K ($4^{+\cdot}$), this procedure was carried out in a cooling bath.

Table I. Properties of Cation Radicals of Permethylpolysilane

compd	*T* dec, K	a_H, mT	*g*	IE$_1$, eV
$1^{+\cdot}$	>190	0.282 (18 H), 0.094 (18 H), 0.188 (18 H), or 0.094 (18 H)	2.0093	7.79[7]
$2^{+\cdot}$	>190	singlet, ~1 mT[a]	2.010	7.81[c]
$3^{+\cdot}$	>230	singlet, ~1 mT[a,b]	2.0105	7.69[c]
$4^{+\cdot}$	>250	singlet, ~1.7 mT[a]	2.0063	7.42[20]

[a] Unresolved singlets with peak-to-peak line width as indicated. [b] A second singlet of ~1-mT width is observed at 90 K for a species with *g* = 2.004. [c] Estimated from regression described in Discussion section.

Chart I



Electron spin resonance spectra were recorded using a Varian E9 spectrometer equipped with an E-257 variable temperature unit, at 9.5-GHz frequency and 330-mT magnetic field, and with a field modulation of 100 kHz. The proton coupling constants for $1^{+\cdot}$ (Table I) are assumed to be correct within ±1%; calibration was performed with Fremy's salt ($2a_N$ = 2.618 mT). *g* values were determined by the double cavity technique using perylene radical anion in DME for calibration.[21]

ESR spectra simulation could be achieved using the program ESPLOT.[22] It contains some subroutines from the optimization program ESOP,[23] which has been kindly provided to us by Professor A. v. Zelewsky of the University Fribourg. Because of the unusual requirements for trimethylsilyl-containing radical cations, the program capacity has been extended to incorporate up to 10^4 theoretical lines from up to 10^2 equivalent nuclei of eight different sorts or isotopes.

Results and Discussion

Electron Spin Resonance Spectra of Radical Cations. Of the four radical cations obtained by oxidation with $AlCl_3$, only dodecamethylcyclohexasilane cation, $1^{+\cdot}$, gave a spectrum in which proton hyperfine splitting is resolved. The spectrum of $1^{+\cdot}$ is shown together with its computer simulation in Figure 1. The other three radical cations, $2^{+\cdot}$, $3^{+\cdot}$, and $4^{+\cdot}$, gave only broad, unresolved ESR lines. Typical of these is the ESR spectrum of $4^{+\cdot}$, shown in Figure 2. ESR data and decomposition temperatures for all the radical cations are reported in Table I.

The ESR spectrum observed for $1^{+\cdot}$ consists of 27 equally spaced lines at intervals of 0.094 mT. However, the line in-

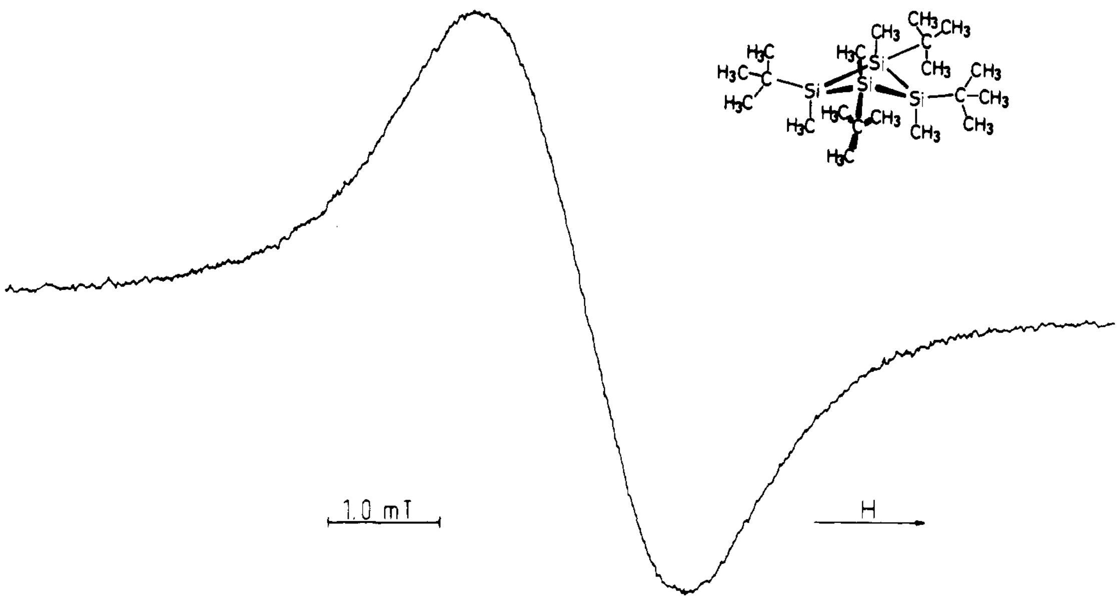


Figure 2. Unresolved ESR spectrum of tetra(*tert*-butyl)tetramethylcyclotetrasilane radical cation $4^{+\cdot}$ at 190 K.

tensities do not fit the binomial intensity pattern for a 37-tet, as expected if all 36 protons from the 12 methyl groups were coupled equally to the electron spin. Moreover, exhaustive attempts to simulate the spectrum by computer calculation failed if the splittings from all 36 protons were assumed to be equal. Satisfactory simulation could be achieved only when the protons were assumed to fall into two nonequivalent sets each containing 18 hydrogens. The near degeneracy of the proton splittings must result from a nearly integral ratio between the hydrogen hyperfine splittings, $a_{H_1} = na_{H_2}$. Two satisfactory solutions were found with different sets of splitting constants: (1) $a_{H_1} = 0.282$, $a_{H_2} = 0.094$, $a_{^{29}Si} < 0.9$ mT; (2) $a_{H_1} = 0.188$, $a_{H_2} = 0.094$, $a_{^{29}Si} = 2.05$ mT. (It is not necessary to include ^{13}C hyperfine splitting to achieve satisfactory simulation.)

Based on these results we assign the ESR spectrum from **1** to a radical cation $[Si(CH_3)_2]_6^{+\cdot}$ in which there are two different sets of six equivalent methyl groups. The neutral compound **1** is known to exist in the chair-cyclohexane conformation, with six axial and six equatorial methyl substituents,[24] which undergo rapid equilibration on the NMR time scale.[25] Our results suggest that in the cation radical $\mathbf{1}^{+\cdot}$ equilibration between equivalent chair conformers is slow on the ESR time scale of $\sim 10^{-5}$ s.

The ESR spectrum of $\mathbf{1}^{+\cdot}$ has a higher *g* value than for typical hydrocarbon cation radicals. This is consistent with the $[Si(CH_3)_2]_6^{+\cdot}$ structure, in which the unpaired electron is in contact with silicon atoms which have spin-orbit coupling constants larger than for carbon.[26] The spectrum changes slowly with time, with a broad, single line becoming superimposed on the resolved spectrum. Isomerization of **1** to **2** is known to take place under the influence of $AlCl_3$,[17] so the broad line may be the spectrum of $\mathbf{2}^{+\cdot}$ resulting from this slow isomerization.[27]

Although the ESR spectra of radical cations generated from the permethylcyclopolysilanes **2, 3,** and **4** show only broad-line ESR spectra with no observable hyperfine splitting, otherwise they resemble that for $\mathbf{1}^{+\cdot}$, having similar total line widths and *g* values (Table I). Data in Table I show that there is correspondence between the stabilities of the radical cations as measured by their decomposition temperatures and the ionization energies for their formation. As the first ionization potentials decrease the radical cations become more stable and their *g* values become smaller.

Photoelectron Spectra and LCBO–MO Calculations. The photoelectron spectrum (PES) for **1** has been reported previously.[7] Deconvolution of the spectrum gives ionization energies of 7.79, 8.96, 9.12, and 9.72 eV, all attributed to ionizations from the Si–Si σ orbitals. The observed 1:2:2:1 intensity pattern is consistent with an alternating system of six isoconjugate Si–Si bonds, having D_{3d} symmetry.

The PES of **2** and **3** were measured as a part of this study; that for **2** is shown in Figure 3. These compounds gave only partially resolved spectra, in which the various Si–Si σ states could not be fully separated. However, the spectra do indicate onset of ionization below 8 eV, the approximate limit above which oxidation to cation radicals by $AlCl_3$ does not take place.[10]

It is possible to calculate ionization energies for **2** and **3** using a previously derived LCBO (linear combination of bonding orbitals) MO model.[28] Assuming the validity of a Koopmans' relationship between ionization energies and HMO eigenvalue differences, the PES data for various permethylpolysilanes have been used to generate the correlation equation, $IE_n^{SiSi} = 8.69 + 0.5X_j^{HMO}$. Here IE_n^{SiSi} is the ionization energy of a particular level in eV, and X_j is the HMO eigenvalue from the LCBO calculation. In this correlation the Coulomb parameter α_{SiSi} is 8.69 eV and the slope of the SiSi bond interaction term, β_{SiSi}, is -0.5 eV.[7,28] This regression fits observed data very well, giving a quite small standard deviation SE = 0.02 eV.

Applying the LCBO model and the correlation equation to **2**, SiSi ionization energies are calculated at 7.81, 7.88, 8.28, 9.00, 9.26, and 9.99 eV. For **3**, similar calculations give 7.69 (d), 8.19 (d), 8.33, 9.19 (d), 9.69, and 10.06 eV (d = doubly degenerate state). The calculations are in qualitative agreement with the PES, and further indicate that ionization should occur below 8 eV, consistent with the generation of radical cations in our experiments.

The PES for **4** has also been determined previously. This highly strained tetra-*tert*-butyl compound does not follow the correlation equation, but instead shows a first ionization potential of 7.42 eV,[29] the lowest yet observed for a polysilane. This value is again consistent with oxidation to a radical cation. The lowered IE probably results both from electronic differences between methyl and *tert*-butyl groups and from the steric crowding in **4**.[29]

Comparison of the Radical Ions $[Si(CH_3)_2]_6^{+\cdot}$ and $[Si(CH_3)_2]_6^{-\cdot}$. In contrast to their carbon analogues the cyclic silicon catenates $(SiR_2)_n$ can be reduced to form the corresponding radical anions.[15] With information on both species

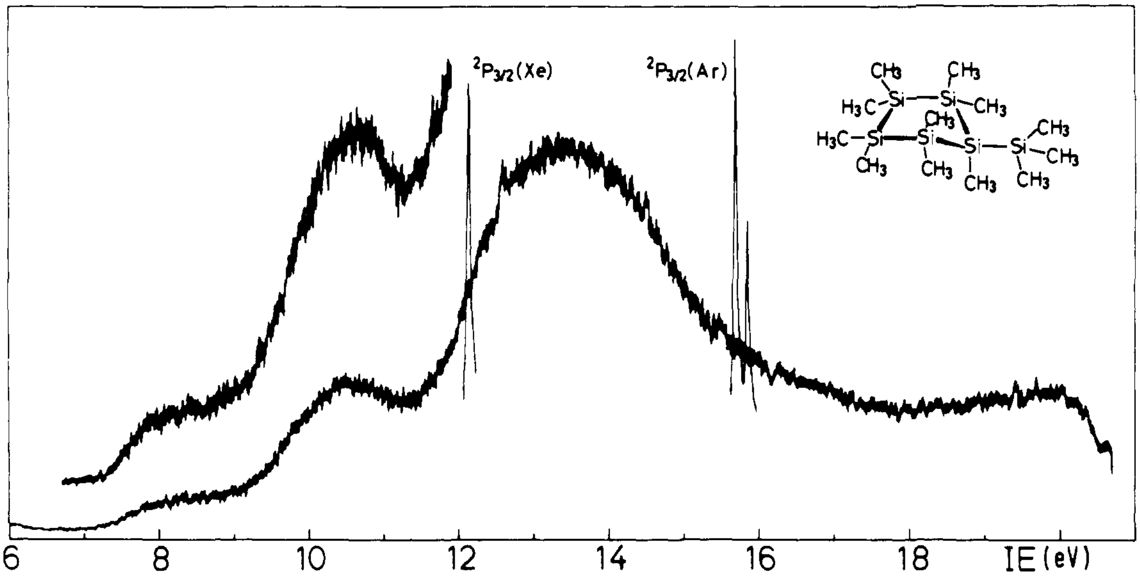


Figure 3. He(I) photoelectron spectrum of (trimethylsilyl)nonamethylcyclopentasilane (**2**).

$\mathbf{1}^{-\cdot}$ and $\mathbf{1}^{+\cdot}$ available, it is interesting to compare some of their respective ground-state properties. The ESR spectrum of the radical anion consists of a multiplet at a spacing of 0.049 mT, with correct intensities for the center lines of a 37-line pattern. In contrast to the radical cation, the radical anion must either interconvert rapidly between equivalent conformers or have a planar structure. The data suggest that $\mathbf{1}^{+\cdot}$ is a σ radical with direct (hyperconjugative)[30] delocalization, as also suggested by the isoconjugate LCBO MO model, whereas $M^{-\cdot}$ represents a π radical with spin distribution to silicon via polarization only.[25] Correspondingly, no ^{29}Si coupling has been observed for $M^{-\cdot}$—an estimate based on the Hunter-Symons relationship[31] yields 0.47 mT—and no ^{13}C coupling for $\mathbf{1}^{+\cdot}$. The rather high g value for $\mathbf{1}^{+\cdot}$ suggests considerable spin population in the σ_{SiSi} skeleton. In contrast, the g value of 2.0028 for $\mathbf{1}^{-\cdot}$, close to the free electron value, indicates that the spin—and presumably also the negative—charge is located away from the silicon atoms and closer to peripheral methyl groups. The differing charge distributions can be rationalized in terms of the low effective nuclear charge of silicon, favoring the loss of an electron rather than its acquisition.

The conclusions drawn from the ESR data (Table I) are in agreement with other observed properties of the dodecamethylcyclohexasilane radical ions $\mathbf{1}^{+\cdot}$ and $\mathbf{1}^{-\cdot}$. For radical anions the stability sequence $[Si(CH_3)_2]_5^{-\cdot} > C_6H_6^{-\cdot} > [Si(CH_3)_2]_6^{-\cdot} > [Si(CH_3)_2]_7^{-\cdot}$ has been established.[5] This is in accord with the assumed π character of advantageously planar species $M^{-\cdot}$, and also with the predominant spin population in the five-membered *silicon* ring of the phenyl-substituted radical anion $[(H_3C)_2Si]_4Si(CH_3)C_6H_5^{-\cdot}$.[32] On the other hand, the observed order of radical cation stability, $\mathbf{2}^{+\cdot} \sim \mathbf{1}^{+\cdot} < \mathbf{3}^{+\cdot} < \mathbf{4}^{+\cdot}$, parallels decreasing first ionization energies (Table I). $[Si(CH_3)_2]_6^{+\cdot}$ is apparently more stable than the unknown $[Si(CH_3)_2]_5^{+\cdot}$, because planarity does not play a decisive role for σ_{SiSi} radical cations.

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