Substituent Effects on the Electron Spin Resonance Spectra of Cyclopentadienyl Radicals. Removal of Degeneracy by Organosilyl Groups[1]

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Abstract: Cyclopentadienyl and five silyl-substituted cyclopentadienyl radicals (XC_5H_4) were generated from the corresponding cyclopentadienes (XC_5H_5) by hydrogen abstraction with the *tert*-butoxy radical and were characterized by ESR. Spin densities at C(1) for these radicals calculated at −105 °C follow: Ph_2MeSi-, 0.056; $PhMe_2Si$-, 0.098; Me_3Si-, 0.130; H, 0.200; $Me_3SiSiMe_2$-, 0.327; $Me_3SiMe_2SiMe_2Si$-, 0.353. These data of the spin density at the point of substituent attachment (C_1), which is quite sensitive to the electronic nature of the substituent, indicate that Ph_2MeSi-, $PhMe_2Si$-, and Me_3Si- are electron accepting owing to d_π-p_π conjugation and that Me_5Si_2- and Me_7Si_3- groups are electron donating owing to σ-π mixing. Analyses of the temperature-dependent spectra revealed thermal equilibration between radicals with the spin in the symmetric and in the antisymmetric bonding orbitals.

Monocyclic π electron radicals such as $C_nH_n\cdot$ ($n = 3, 5, 7, \ldots$) and $C_nH_n^{\pm\cdot}$ ($n = 4, 6, 8, \ldots$) are the objects of particular interest for electron spin resonance (ESR) studies. For ideal n-membered ($n \geq 5$) electron ring systems of symmetry D_{nh}, the lowest antibonding and the highest bonding orbitals are both doubly degenerate. The orbital degeneracy is removed when a perturbation due to the substitution is introduced, so that the form of the ESR spectra depends critically on the symmetry properties of the orbital in which the unpaired electron resides. A number of ESR spectra of cyclic π hydrocarbon radicals,[2] especially of substituted benzene radical anions,[2a] have been studied and the effect on the spectra by the electronic properties due to the substituents has been elucidated. Typically, the ESR studies on the group 4B metal-substituted benzene anions[3] have substantiated that both trimethylsilyl and trimethylgermyl groups are electron accepting owing to significant conjugation between the low-lying vacant orbitals such as d orbitals and the aromatic π orbital[4,5] while the *tert*-butyl group is electron donating.[3a]

These studies are interesting since the differences in the properties of the group 4B substituents are clearly demonstrated. However, the conclusion from these studies is limited only to the problem of perturbation to the π^* orbital, since the unpaired electron occupies an antibonding orbital in the π systems. Therefore, the observed substituent effects must overemphasize the role of the vacant orbitals.[6] For example, the pentamethyldisilanyl group was regarded as an electron-accepting group, similar to the trimethylsilyl group, from the comparison of the ESR spectrum of the phenylpentamethyldisilane radical anion with that of the phenyltrimethylsilane radical anion,[3b] although photoelectron,[7] charge-transfer,[8] and ultraviolet[9] spectroscopic studies on phenylpentamethyldisilane revealed that the pentamethyldisilanyl group is electron donating to the π system owing to σ(SiSi)-π conjugation overcoming the possible (p-d)π conjugation.

In cyclopentadienyl radicals, however, an unpaired electron must occupy the bonding π orbital as shown in Figure 1, and therefore the substituent effects on the cyclopentadienyl radical were expected to be different from those on benzene radical anions, giving useful information for substituent effects on bonding π orbitals. We now report the first observation of some silyl-substituted cyclopentadienyl radicals by ESR and discuss the substituent effects based on the simple Hückel MO theory.

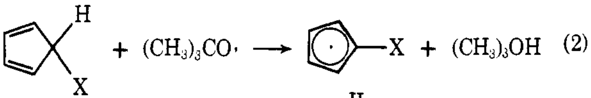
Results and Discussion

The ESR Spectra of Silyl-Substituted Cyclopentadienyl Radicals. The ESR spectra have been studied with the parent cyclopentadienyl radical generated by several routes such as γ-irradiation on both crystalline[10a,b] and liquid cyclopentadiene,[10c] by pyrolysis of a molecular beam of ferrocene and azobenzene,[10d] and recently by hydrogen abstraction of cyclopentadiene with the *tert*-butoxy radical in solution.[10e,f] The last method appeared in general as a method of generating the substituted cyclopentadienyl radicals such as alkyl-substituted ones in solution. However, the method has been actually limited only to the parent cyclopentadienyl radical, since radicals formed by the addition of the *tert*-butoxy radical to cyclopentadiene contaminate the desired radical. Therefore, no study on the substituted cyclopentadienyl radicals has been reported.

We have found that a series of silyl-substituted cyclopentadienyl radicals can be generated from the corresponding cyclopentadiene by hydrogen abstraction with the photochemically generated *tert*-butoxy radical (Figures 2-6).

In contrast to the spectrum from Ia,[10e] no additional paramagnetism such as in *tert*-butoxycyclopentenyl was found in the spectra obtained from Ib-f. The spectra of IIb-f consisted of two sets of 1:2:1 triplets due to two sets of two equivalent protons on the cyclopentadienyl ring. Spectra of IId and IIe showed, in addition, a small multiplet splitting due to methyl protons on silicon atoms.

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{h\nu} 2(CH_3)_3CO\cdot \qquad (1)$$



I

II

a, X = H; b, X = $SiMePh_2$; c, X = $SiMe_2Ph$; d, X = $SiMe_3$;
e, X = $SiMe_2SiMe_3$; f, X = $SiMe_2SiMe_2SiMe_3$

Two interesting features can be noted. First, the total spread of the spectrum strongly depends on the electronic properties of a substituent. Second, significant temperature dependence of the total spread of the spectrum as well as the individual hyperfine coupling constants (hfcc) was observed. Although the assignment of the two triplet hfcc values itself is not unequivocal at the first glance, these spectroscopic features can be explained, at least qualitatively, and the hfcc values can be assigned within a framework of the Hückel molecular orbital (HMO) theory.

The spin distribution in the substituted cyclopentadienyl radicals is determined by several factors: removal of the degeneracy by the interaction between the ring and the substit-

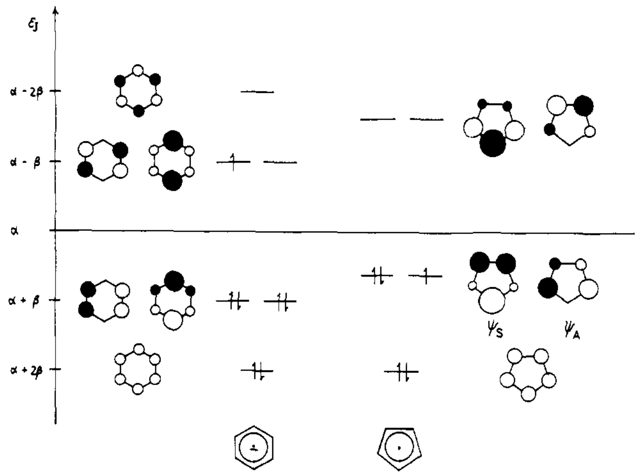


Figure 1. HMO energy diagram for cyclopentadienyl and benzene anion radicals.

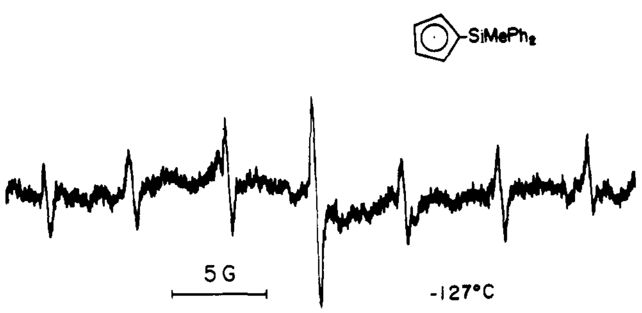


Figure 2. ESR spectrum of the diphenylmethylsilylcyclopentadienyl radical.

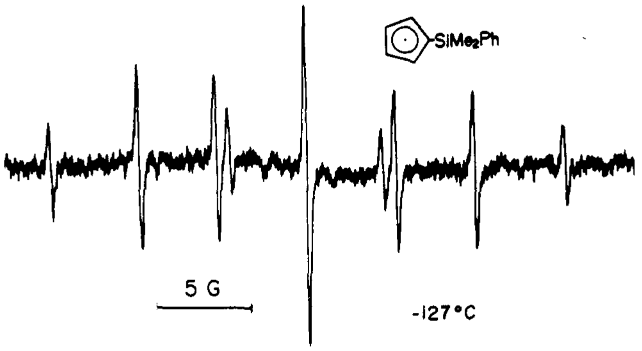


Figure 3. ESR spectrum of the phenyldimethylsilylcyclopentadienyl radical.

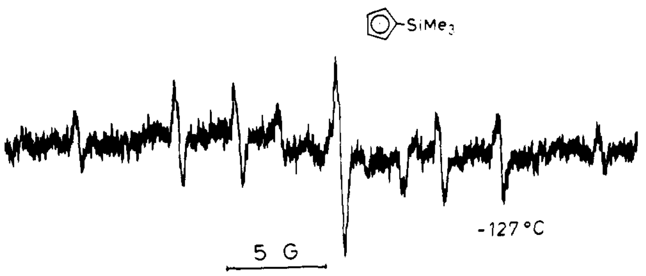


Figure 4. ESR spectrum of the trimethylsilylcyclopentadienyl radical.

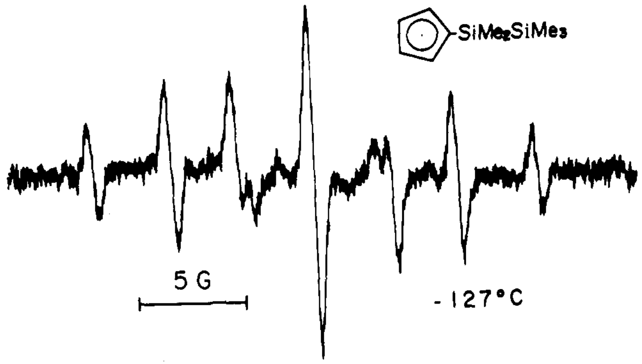


Figure 5. ESR spectrum of the pentamethyldisilanylcyclopentadienyl radical.

Figure 6. ESR spectrum of the *n*-heptamethyltrisilanylcyclopentadimethyl radical.

uent; thermal averaging; and vibronic coupling. It is reported that, for example, the realistic description of the benzene and substituted benzene anion radicals may require inclusion of vibronic coupling between ground and excited states.[11] We discuss, however, the substituent effects by the Hückel molecular orbital model without taking into consideration the effect of extensive configuration interactions and vibronic coupling. This simple treatment will be useful to draw the character of the substituent qualitatively, especially for a series of monosubstituted cyclopentadienyl radicals.

HMO Model for Substituted Cyclopentadienyls. The lowest energy π-electron configuration of the planar, symmetrical cyclopentadienyl radical $C_5H_5\cdot$ is doubly degenerate, having an evenly distributed spin population $\rho_i = {}^1/_5$. There are two equienergetic configurations corresponding to equally probable locations of the unpaired electron in either one of the two degenerate bonding orbitals:

$$\psi_S = \sum_{i=1}^{5} c_{S,i}x_i = 0.632x_1 + 0.195(x_2 + x_5) - 0.512(x_3 + x_4) \quad (3)$$

$$\psi_A = \sum_{i=1}^{5} c_{A,i}x_i = 0.602(x_2 - x_5) + 0.372(x_3 - x_4) \quad (4)$$

which are schematically depicted in Figure 1. If substitution for hydrogen on the cyclopentadienyl ring is considered to be essentially a weak electronic perturbation, the amount of such a perturbation should be proportional to the square of the coefficient of the atomic orbital at the perturbation center according to the first-order treatment.[12] The extent of the perturbation energy, $\Delta\epsilon$ shown in Figure 7, is described as

$$\Delta\epsilon = \frac{c_i^2\beta'^2}{|\epsilon_\pi - \epsilon_X|} \quad (5)$$

where ϵ_π and ϵ_X refer to the energy levels for the unperturbed

Table I. Calculated Spin Populations of the Cyclopentadienyl Radical

			McLachlan			
	HMO		$\lambda = 0.75^a$		$\lambda = 1.20$	
Position	ρ_S	ρ_A	ρ_S	ρ_A	ρ_S	ρ_A
1	0.4000	0.0000	0.4808	−0.0908	0.5228	−0.1468
2,5	0.0382	0.3618	−0.0332	0.4300	−0.0764	0.4681
3,4	0.2618	0.1382	0.2928	0.1154	0.3150	0.1052

[a] $\lambda = 0.75$ was selected so as to give the best fit between the observed five-membered ring proton hfcc values for the indenyl radical and the McLachlan calculation. Proton hfcc values of the indenyl radical which was generated by the photolysis of the mixture of di-*tert*-butyl peroxide and indene at −60 °C were observed as follows: $a_1 = (-)11.91$ G, $a_2 = (+)2.18$ G, $a_5 = (-)2.18$ G, and $a_6 = (-)1.47$ G. Similar hfcc values for this radical were reported by A. Atto, A. Hudson, R. A. Jackson, and N. P. C. Simmons, *Chem. Phys. Lett.*, **33**, 477 (1975).

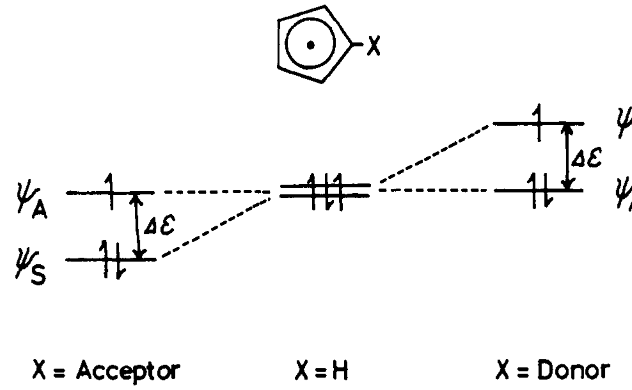


Figure 7. Splitting of degeneracy of the highest occupied molecular orbitals in the monosubstituted cyclopentadienyl radical.

π MO and a substituent π-type orbital with the pertinent symmetry, respectively; c_i is the coefficient of the atomic orbital at the point of substituent group attachment in the π MO; and β' is a resonance integral between the pπ and the π type orbital of χ.

In monosubstituted derivatives of the cyclopentadienyl radical in which the substituent occupies the position 1, the value of $c_{S,1}{}^2$ is large (0.400) for the symmetric orbital ψ_S, whereas in the antisymmetric orbital ψ_A, there is a nodal plane through the center 1, and hence $c_{A,1}{}^2 = 0$. The orbital ψ_S should therefore be strongly perturbed by monosubstitution, but according to this model, ψ_A should be unaffected. An electron-donating substituent raises the ψ_S level and prefers the electronic configuration $\Psi_A{}^2\Psi_S{}^1$ (S form), while an electron-accepting substituent lowers the Ψ_S level and prefers the $\Psi_S{}^2\Psi_A{}^1$ configuration (A form) (Figure 7).

When the energy difference between the two configurations is small, appreciable mixing of the two forms occurs just as in the case of the deuterated benzene anion radical.[13] For example, $\Psi_A{}^2\Psi_S{}^1$ (S form), the electronic configuration of the cyclopentadienyl radical with an electron-donating substituent, should be mixed with $\Psi_A{}^1\Psi_S{}^2$ (A form).

$$\Psi_A{}^2\Psi_S{}^1 \overset{\Delta E}{\rightleftharpoons} \Psi_A{}^1\Psi_S{}^2$$

The observed spectrum is a result of the rapid exchange between S and A forms. According to the assumption, the spin density ρ_i at position i of a substituted radical is given by

$$\rho_i = P_S\rho_i{}^S + P_A\rho_i{}^A \qquad (6)$$

$$P_S + P_A = 1 \qquad (7)$$

where P_S and P_A are the relative probabilities that the radical is in the S and A forms, respectively, at a particular temperature, and $\rho_i{}^S$ and $\rho_i{}^A$ are the spin densities at position i in the S and A forms of cyclopentadienyl, respectively. On the assumption that the familiar McConnell relationship,[14] $a_i{}^m = Q_H\rho_i{}^m$, holds for each electronic configuration m,[15] the equivalent relation to eq 6 for the hyperfine splitting is

$$a_i = P_Sa_i{}^S + P_Aa_i{}^A \qquad (8)$$

where a_i is the proton splitting in the radical at position i, and $a_i{}^S$ and $a_i{}^A$ are the proton splittings at position i in the S and A forms of the cyclopentadienyl radical, respectively. For the unsubstituted parent radical, two forms of the cyclopentadienyl radical are degenerate, and $P_S = P_A = {}^1\!/_2$, so that

$$a_i = {}^1\!/_2 Q_H(\rho_i{}^S + \rho_i{}^A) = {}^1\!/_5 Q_H(\text{for all } i\text{'s}) \qquad (9)$$

Since the total π electron spin density must be unity,

$$\rho_1 = 1 - \sum_{i=2}^{5} \rho_i \qquad (10)$$

and if Q_H is assumed to be constant for all substituted cyclopentadienyls,[15] the equation

$$a_1{}^* = Q_H - \sum_{i=2}^{5} a_i \qquad (11)$$

can be defined where $a_1{}^*$ is the imaginary proton splitting corresponding to the spin density at position 1. Here, we should note that the summation of a_2 to a_5 corresponds to the total spread of the spectrum.

One can calculate P_A and P_S, from the measured value of Q_H for the cyclopentadienyl radical, the calculated values of $a_1{}^*$ and other a_i's, and the spin densities $\rho_i{}^S$ and $\rho_i{}^A$, which are calculated based on both HMO and McLachlan[14] methods. Table I lists the calculated spin populations of the parent cyclopentadienyl radical by both HMO and McLachlan methods. Since our basic assumptions imply that the S and A forms are in thermal equilibrium,

$$P_A/P_S = \exp(-\Delta E/kT) \qquad (12)$$

Values of ΔE can be calculated from the temperature dependence of P_A/P_S.

The Values of $a_1{}^*$ as a Measure of Substituent Effects. The Q value of the cyclopentadienyl radical can be estimated to be 30.20 G from the observed sextet with hfcc value of 6.04 G and therefore, $a_1{}^*$ defined in eq 11 can be calculated to be 12.08 G for the S form and 0 G for the A form based on the HMO spin densities. The value of $a_1{}^*$ should increase from 0 to 12.08 G with increasing population of the S form, P_S, from 0 to 1. Therefore, when a substituent is more electron donating than hydrogen, P_S should be larger than 0.5 and hence $a_1{}^*$ should be larger than 6.04 G for a substituted cyclopentadienyl radical while for a substituted cyclopentadienyl radical with a more electron-accepting group, $a_1{}^*$ should be less than 6.04 G. Therefore, $a_1{}^*$ offers a measure of the electronic effect of a substituent. We can also assign each hfcc for IIb–f unequivocally by referring $a_1{}^*$ values as shown in Table II (see Experimental Section). We can obtain the following spectrum of $a_1{}^*$ values by systematically changing the electronic properties of

Table II. Proton Hyperfine Coupling Constants and Spin Densities (ρ) for Monosubstituted Cyclopentadienyl Radicals at −105 °C

		a_1*,[a] G	(ρ_1)[b]	$a_{2,5}$,[c] G	$(\rho_{2,5})$[b]	$a_{3,4}$,[c] G	$(\rho_{3,4})$[b]	Others, G
H	(IIa)	6.04	(0.200)	6.04	(0.200)	6.04	(0.200)	
Ph_2MeSi	(IIb)	1.70	(0.056)	9.53	(0.316)	4.72	(0.156)	
$PhMe_2Si$	(IIc)	2.96	(0.098)	8.75	(0.290)	4.87	(0.161)	
Me_3Si	(IId)	3.94	(0.130)	7.94	(0.263)	5.19	(0.172)	0.12[d]
Me_5Si_2	(IIe)	9.88	(0.327)	3.73	(0.124)	6.43	(0.213)	0.11[e]
n-Me_7Si_3	(IIf)	10.66	(0.353)	3.22	(0.107)	6.55	(0.217)	

[a] See the text for the definition of a_1*. [b] Spin densities are calculated with Q = 30.20 G. [c] Hfcc values are assigned to ring positions so as to give the best fit of theory and experiments. See also the Experimental Section. All values are reported to ±0.02 G. [d] The splitting is assigned to the methyl protons on a silicon. [e] Two types of methyl proton hfcc values may be included.

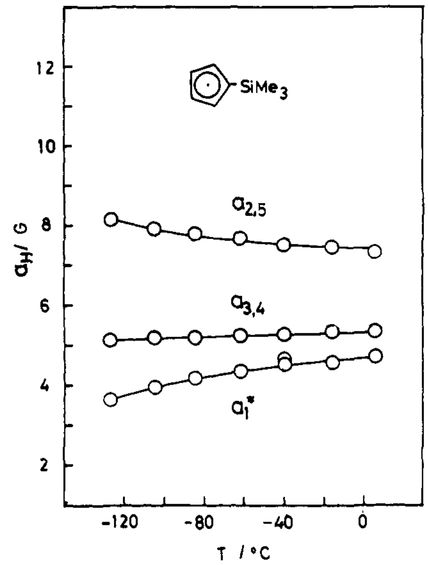


Figure 8. Temperature dependence of the ring proton coupling constants in the trimethylsilylcyclopentadienyl radical (IId).

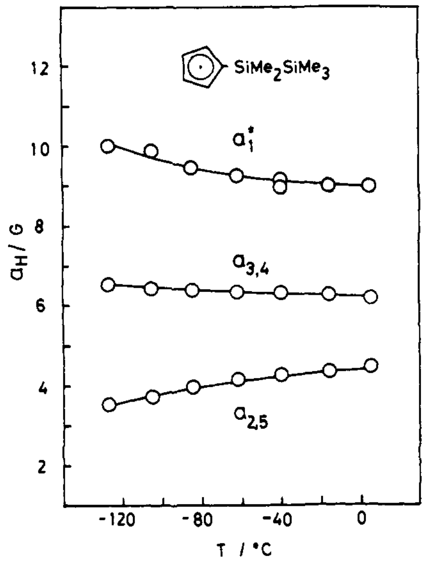


Figure 9. Temperature dependence of the ring proton coupling constants in the pentamethyldisilanylcyclopentadienyl radical (IIe).

the substituents:

$$\begin{array}{ccccc} X = \text{a strong donor} & \leftarrow & X = H & \rightarrow & X = \text{a strong acceptor} \\ a_1^* \simeq 12.1\ \text{G} & \leftarrow & a_1^* = 6.04\ \text{G} & \rightarrow & a_1^* \simeq 0\ \text{G (HMO)} \\ a_1^* \simeq 14.5\ \text{G} & & a_1^* = 6.04\ \text{G} & & a_1^* \simeq -2.7\ \text{G} \\ & & & & (\text{McLachlan}, \lambda = 0.75) \end{array}$$

The values of a_1* derived from $\sum_{i=2}^{5} a_i$ for IIb–f at −105 °C were spread from 1.70 G for IIb to 10.66 G for IIf with the order being IIf > IIe > IIa > IId > IIc > IIb.

These facts can be reasonably interpreted by the difference in the electronic properties of substituents. Thus, both n-Me_7Si_3 and Me_5Si_2 groups are electron donating owing to the predominant contribution of σ(SiSi)–π conjugation. The magnitude of electron-donating ability of the Me_5Si_2 group is smaller than that of the n-Me_7Si_3 group, which is in accord with the conclusion from the TCNE charge-transfer absorption maxima for various arylpolysilanes.[17]

In contrast, all monosilyl groups are electron accepting for a singly occupied molecular orbital (SOMO) of the cyclopentadienyl radical. Population of the A form for IId is estimated t be 0.70 at −105 °C, while the population of the ground state configuration for the phenyltrimethylsilane anion is nearly unity at −50 to −100 °C as estimated by the hfcc value of the para proton.[3] The trimethylsilyl group is concluded to be still electron accepting for the SOMO of the cyclopentadienyl radical, although the magnitude of the electron-accepting property is rather reduced from that observed for the SOMO of the benzene anion. The stepwise replacement of methyl on trimethylsilyl to phenyl is found to increase electron-accepting ability of the silyl group as judged by the magnitude of a_1* and this fact suggests either d-orbital contraction by the introduction of electronegative groups on silicon[18] or the lowering of σ* orbital level by the contribution of phenyl sp^2 hybrid orbitals to the σ* orbital. Unlike the substituent effects on benzene anion, these on cyclopentadienyl can be taken as a measure of electronic properties of substituents on a bonding π orbital, at least qualitatively. Again, it is interesting to note that pentamethyldisilanyl and heptamethyltrisilanyl groups are electron donating for the cyclopentadienyl, while these act as an accepting group for the benzene anion radical. Such a duality[19] may be attributed partly to the less effective conjugation between silicon and carbon which in turn makes the substituent effects sensitive to the energy differences between interacting silyl π type orbitals (both occupied and unoccupied orbitals) and a π orbital of the π system under consideration as expected from perturbation theory (cf. eq 4).

Temperature Dependence of Ring Proton Hfcc Values Including a_1*. Ring proton hfcc values of the cyclopentadienyl (IIa) did not change in the temperature range of −127 to 28 °C, although significant temperature dependence of hfcc values has been reported for other cyclic π radicals, such as benzene anion[10c] and cycloheptatrienyl radicals.[19] Rigid ring structure and no ion pair interaction may be responsible for the temperature independence of the proton splitting in $C_5H_5\cdot$.

On the other hand, ring proton hfcc values as well as a_1*'s for substituted cyclopentadienyl radicals changed significantly with temperature. Representative values of these splittings for IId and IIe are plotted in Figures 8 and 9, respectively. These temperature dependencies can also be interpreted within a framework of the HMO theory. As a simple approximation,

Table III. Splitting of Degeneracy of S and A Forms in Substituted Cyclopentadienyls XC_5H_4

		HMO[a]		McLachlan (λ = 0.75)[a]		McLachlan (λ = 1.20)[a]	
		ΔE,[b] cal/mol	ΔS,[c] eu	ΔE,[b] cal/mol	ΔS,[c] eu	ΔE,[b] cal/mol	ΔS,[c] eu
Ph_2MeSi	(IIb)	−590 ± 70	0.09 ± 0.30	−320 ± 80	0.33 ± 0.20	−260 ± 70	0.33 ± 0.17
$PhMe_2Si$	(IIc)	−360 ± 40	0.25 ± 0.20	−220 ± 30	0.28 ± 0.14	−180 ± 20	0.26 ± 0.11
Me_3Si	(IId)	−230 ± 20	0.21 ± 0.12	−150 ± 20	0.18 ± 0.08	−130 ± 10	0.16 ± 0.09
Me_5Si_2	(IIe)	300 ± 40	−0.44 ± 0.20	180 ± 20	−0.38 ± 0.11	150 ± 20	−0.33 ± 0.09
n-Me_7Si_3	(IIf)	500 ± 70	0.13 ± 0.36	280 ± 40	−0.15 ± 0.19	230 ± 30	−0.16 ± 0.16

[a] The type of approximation used to calculate the spin densities (see Table I). [b] ΔE's were estimated from the slopes of the straight lines given by the plots of log (P_A/P_S) vs. $1/T$. Errors are 2.5 times standard deviation. [c] ΔS's were estimated from the intercepts of the straight lines given by the plots of log (P_A/P_S) vs. $1/T$. Although these values should correspond to $R \ln (Q_A/Q_S)$, where Q_S and Q_A are the partition functions of S and A forms, respectively, they are meaningless under the present conditions. Errors are 2.5 times standard deviation.

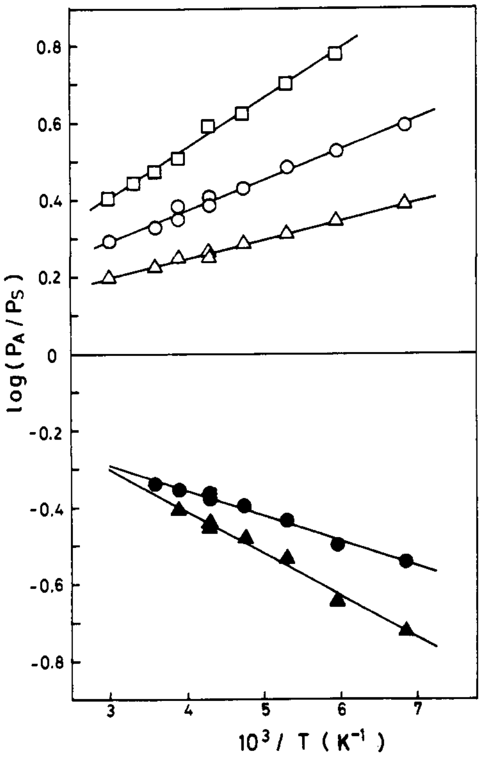


Figure 10. Plots of log (P_A/P_S) against $1/T$: (□), IIb; (○), IIc; (△), IId; (●), IIe; (▲), IIf.

a high-energy electronic configuration $\Psi_A{}^1\Psi_S{}^2$ of a cyclopentadienyl radical with an electron-donating group, for example, will mix more with $\Psi_A{}^2\Psi_S{}^1$ at a higher temperature. Therefore, expectedly, P_S and then $a_1{}^*$ of a donor-substituted cyclopentadienyl radical such as IIe decreased with increasing temperature, while $a_1{}^*$ of an acceptor-substituted one such as IId increased. The assignment of $a_{2,5}$ and $a_{3,4}$ based on the optimum fit of observed hfcc values with HMO theory (see Experimental Section) is confirmed by the temperature dependence. Thus, representatively in the case of IId, it was found that $a_{2,5}$ decreased and $a_{3,4}$ increased with increasing temperature (therefore, with increasing P_S), while the situation was inverted in the case of IIe. Excellent linear relationships between log (P_A/P_S) and $1/T$ for IIb-f were observed, as expected from eq 12 (Figure 10). Values of ΔE were calculated from the gradients of these linear lines. ΔE values based on various spin density calculations are listed in Table III.

Although the absolute values of ΔE depend markedly on the method of spin density calculation employed, the order and the sign of ΔE values do not change. It should be noted that separation of two electronic configurations is very small spreading only from ca. −590 to 500 cal/mol based on HMO, but the electronic properties of the substituents are fully responsible for such separation.

Experimental Section

Materials. Di-*tert*-butyl peroxide was washed with an acidic aqueous solution of potassium iodate and then with water, dried over anhydrous magnesium sulfate, and distilled at reduced pressure.

Trimethylsilyl- (Id),[21] pentamethyldisilanyl- (Ie),[22] and heptamethyltrisilanylcyclopentadiene (If)[23] were prepared by essentially the same method as described in the literature.

Diphenylmethylsilylcyclopentadiene (Ib). Diphenylmethylchlorosilane (23.3 g, 0.10 mol) in ether was added to a cyclopentadienylmagnesium bromide solution which was prepared by the reaction of ethylmagnesium bromide (0.10 mol) with freshly distilled cyclopentadiene (6.6 g, 0.10 mol) in an ether-benzene mixed solution. After refluxing for 6 h and workup, diphenylmethylsilylcyclopentadiene (4.85 g, 18.5%) was obtained, bp 128 °C (0.5 mm). This was purified by preparative GLC, MS *m/e* 262 (M^+). The NMR spectrum in CCl_4 (60 MHz) was satisfactory for the structure but two types of SiMe signal (δ 0.17 and 0.68) were observed, indicating that 5-(diphenylmethylsilyl)cyclopentadiene was contaminated with small amounts of the 2 and 3 isomers (up to 10%). The isomeric mixture is completely satisfactory for ESR experiments and therefore it was used without further purification. Anal. Calcd for $C_{18}H_{18}Si$: C, 82.38; H, 6.91. Found: C, 82.25; H, 7.15.

The yield was improved to 41% by replacing cyclopentadienyl Grignard reagent with sodium cyclopentadienide.

Phenyldimethylsilylcyclopentadiene (Ic). This was prepared by essentially the same method as above from cyclopentadienylmagnesium bromide and phenyldimethylchlorosilane in 22% yield, bp 127-130 °C (18 mm). An analytical sample was obtained by preparative GLC, MS *m/e* 200 (M^+). The isomeric mixture of phenyldimethylsilylcyclopentadiene (mainly 5 isomer) was used for ESR experiments without further purification. Anal. Calcd for $C_{13}H_{16}SI$: C, 77.93; H, 8.05. Found: C, 77.93; H, 8.04.

ESR Spectrometry. A degassed solution of di-*tert*-butyl peroxide and an appropriate cyclopentadiene in a sealed quartz tube was placed in a cavity of a Varian E-12 ESR spectrometer and irradiated with a 500-W Ushio super-high-pressure mercury lamp. The light was focused with a quartz lens. Temperature was controlled by the use of a Varian variable temperature accessory. The temperature was calibrated by a copper-constantan thermocouple. The temperature should be accurate to ±2 °C. The measurement of lower temperature than −30 °C was carried out by using cyclopropane as a cosolvent. The field sweep of the spectrometer was calibrated with an aqueous solution of Fremy's salt (a_N = 13.07 G).[23]

The Procedure for Assignment of Splittings and for Determination of P_S. Two hfcc values, a_α and a_β, are obtained by analysis of the spectrum at the particular temperature. The assignment of the two hfcc to ring positions is not decisive but $2(a_\alpha + a_\beta)$ should be $\sum_{i=2}^{5} a_i$. The $a_1{}^*$ can be calculated from the following equation resulting from transformation of eq 11

$$a_1{}^* = 30.20 - 2(a_\alpha + a_\beta) \qquad (13)$$

Within a framework of the HMO theory, the value of $a_1{}^*$ determines the initial P_S ($P_S{}^0$) from the equation

$$a_1{}^* = 12.08P_S{}^0 \qquad (14)$$

Then a_2 and a_3 values can be calculated from eq 15 and 16 derived from eq 8.

$$a_2 = a_5 = a_2^{\mathrm{A}} + (a_2^{\mathrm{S}} - a_2^{\mathrm{A}})P_{\mathrm{S}}^0 = 10.93 - 9.77P_{\mathrm{S}}^0 \quad (15)$$

$$a_3 = a_4 = a_3^{\mathrm{A}} + (a_3^{\mathrm{S}} - a_3^{\mathrm{A}})P_{\mathrm{S}}^0 = 4.17 + 3.73P_{\mathrm{S}}^0 \quad (16)$$

The experimental coupling constants, a_α and a_β, are assigned to the respective ring positions so as to give the best fit to the values obtained from eq 15 and 16. The final P_{S} values are determined by the technique of the least squares, so as to minimize $\sum_{i=1}^{5} \{a_i(\text{calcd}) - a_i(\text{obsd})\}^2$, in which a_1 should mean $a_1{}^*$. The equilibrium constants $P_{\mathrm{A}}/P_{\mathrm{S}}$ ($\equiv K$) are then calculated from the final P_{S} values. Different sets of K and P_{S} values are similarly obtained with ρ_i values calculated by the McLachlan method (Table I). These values lead to ΔE and ΔS values listed in Table III.

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Computer Simulation of Intramolecular Electron Transfer in $\alpha\mathrm{N(CH_2)}_n\alpha\mathrm{N}^{-}\cdot$ System

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Abstract: This paper is concerned with the theoretical treatment of intramolecular electron transfer in $\alpha\mathrm{N(CH_2)}_n\alpha\mathrm{N}$ radical anions reported by Shimada and Szwarc. By using both static and dynamic models, rate expressions are developed for intramolecular reactions. The equations involve the probability of finding the polymeric chain in favorable conformations for the electron transfer, and we calculate it by the direct enumeration method and the Monte Carlo method. The model considered for a polymethylene chain is that of the g–t rotational isomeric state. In order to determine the stable conformations of the terminal naphthylmethyl group, semiempirical potential functions are applied to n-propyl-α-naphthalene. The calculated frequencies of the intramolecular electron transfer divided by those of the corresponding intermolecular electron transfer agree excellently with the experimental values obtained in hexamethylphosphoric triamide and 1,2-dimethoxyethane solutions. The dynamic model is well supported by the fact that the activation energy of electron transfer is substantially higher than that of the calculated probability of the favorable conformations. The average lifetime of conformations favorable for intramolecular electron transfer is independent of the connecting chain length and is equal to the lifetime of the two naphthyl groups being in favorable positions for intermolecular electron transfer. The significance of the calculated results is reported and discussed.

The intramolecular reaction between terminal groups attached to a polymeric chain molecule is a convenient gauge of the flexibility of the connecting chain molecule.[1-11] There have been several authors who examined such a problem. In most of the cases, however, the activation energy of the end-to-end reaction is intrinsically high and the intramolecular reaction