RECENT ADVANCES ON TWO CLASSICAL PROBLEMS OF ORGANOSILICON CHEMISTRY

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I. ORGANOSILICONIUM IONS

Silicon has a lower ionization potential and electronegativity than carbon, and so, other things being equal, silicon should be expected to bear a positive charge more easily than carbon. For this reason many workers have sought to prepare stable organosiliconium ions, analogous to the stable carbonium ions well-known in organic chemistry. However, these attempts have so far been unsuccessful.

The best known of stable carbonium ion species are the triaryl carbonium ions. Triphenylcarbonium ion is the simplest example; this ion can be generated by sulphuric acid solvolysis of triphenylcarbinol, or by dissociation of triphenylmethyl chloride in ionizing solvents. Considering first the sulphuric acid system, it is found that triphenylcarbinol gives an *i*-value near 4 in anhydrous sulphuric acid because of the following reaction:

$$Ph_3COH + 2H_2SO_4 \longrightarrow Ph_3C^+ + H_3O^+ + 2HSO_4^-, i = 4$$
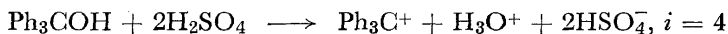
Organosilicon halides or oxygen compounds also give high *i*-values in sulphuric acid, and at one time this was thought to be due to the formation of siliconium ions in this solvent[1]. However, Flowers *et al.*[2] have recently shown that in fact reaction takes place to give covalent organosilyl hydrogen sulphate esters rather than siliconium ions:

$$R_3SiOH + 2H_2SO_4 \longrightarrow R_3SiOSO_3H + H_3O^+ + HSO_4^-, i = 3$$

The ionization of triphenylmethyl compounds into triphenylcarbonium ions is aided by the presence of electron-donating substituents which can promote delocalization of the positive charge onto the aromatic rings, and an especially powerful substituent for this purpose is the dimethylamino group. Thus the colourless compound tris(*p*-dimethylaminophenyl)carbinol is transformed by acids into the well-known, intensely purple carbonium ion dyestuff, "Crystal Violet". It seemed possible that the best chance for obtaining a triarylsiliconium ion might be with similar *p*-dimethylamino substitution. The first attempt following this reasoning was made by Gilman and Dunn[3], who prepared tris(*p*-dimethylaminophenyl)silanol. However, they found that this compound, unlike its carbon analogue, underwent essentially no spectral change upon treatment with acids, incidating that no delocalized siliconium ion species was formed. More recently tris(*p*-dimethylaminophenyl)chlorosilane, the silicon analogue of Crystal Violet itself, has been studied by Wannagat and Brandmair[4], and shown to behave as a typical covalent organosilyl chloride. Both the electronic spectrum and the chemical properties of the silicon analogue of Crystal Violet resemble those

of the covalent compounds triphenylchlorosilane and triphenylchlorome-thane, and are quite unlike the properties of ionic Crystal Violet (*Table 1.*) The perchlorate ion is quite nonpolarizable and enters into covalent bonding with reluctance. Triarylmethyl perchlorates are dark coloured compounds which appear to be completely ionic even as solids. However, Wannagat and Liehr[5] have shown that triphenylsilyl perchlorate is not at all ionic, but instead is a covalent ester of perchloric acid.

Table 1. Spectral properties of triphenylmethyl chlorides and their silicon analogues

Triphenylmethyl chlorides and their silicon analogues	λ_{max} (mμ)	Solvent
Ph$_3$CCl	282	Ether
Ph$_3$SiCl	273	Chloroform
(p-Me$_2$NPh)$_3$C$^+$Cl$^-$	590	Chloroform
(p-Me$_2$NPh)$_3$SiCl	283	Chloroform

Even if it proved impossible to prepare stable salts of organosiliconium ions, one could argue that organosilyl halides might nevertheless dissociate slightly to give siliconium ions in appropriate ionizing solvents. However, Thomas and Rochow[6] have carefully investigated the conductance of tri-phenylsilyl chloride in solution, and concluded that no significant ionization of this substance takes place, even in solvents like nitrobenzene–aluminium bromide and liquid sulphur dioxide, which cause extensive ionization of triphenylmethyl chloride (*Table 2*). The slight conductivity observed for triphenylchlorosilane in pyridine was attributed to the presence of traces of moisture in that solvent.

Table 2. Equivalent Conductances, mho-cm^2/mole

Solvent	Ph$_3$CCl	Ph$_3$SiCl
C$_5$H$_5$N	0·44	2·03
PhNO$_2$	0·14	0·07
PhNO$_2$–AlBr$_3$	18·85	0·14
SO$_2$	200·00	0·15

In spite of the lack of success of previous workers, a programme of research to obtain stable organosiliconium ions was initiated by Corey and West[7] in our laboratories in 1962. Our first experiments were designed to generate siliconium ions by hydride transfer from triphenylsilane to carbonium ions[7]; like all previous attempts, they proved unsuccessful. We then decided to attempt once more to obtain siliconium ions from triarylsilyl halides. Our tactical approach, however, differed in two respects from those used in the past. First, rather than the organosilyl chlorides which have been used in most previous studies, we planned to use silyl iodides and bromides, hoping to take advantage of the lower dissociation energy of the Si–Br or

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Si–I compared to the Si–Cl bond. Second, we planned to stabilize the organosiliconium species by the use of chelating agents.

Our first successful result was obtained when triphenylsilyl iodide was treated with 2,2'-bipyridine in dichloromethane. A pale yellow crystalline precipitate was obtained, which proved upon analysis to be a 1 : 1 complex of the two starting materials[8]:

$$Ph_3SiI + bipy \xrightarrow{CH_2Cl_2} Ph_3Si(bipy)I$$
$$(m.p.\ 172\text{–}74°)$$
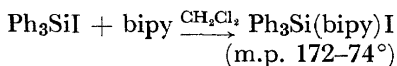
The resulting crystalline solid is very much less reactive than the starting material, triphenylsilyl iodide; it hydrolyzes only slowly in moist air. The properties of this substance indicate that it is an iodide salt of the pentacoordinate ion, $[Ph_3Si(bipy)]^+$. Two other related substances have been isolated and analyzed: the 1 : 1 adduct of triphenylsilyl bromide with 2,2'-bipyridine, which appears to be an ionic salt $[Ph_3Si(bipy)]^+Br^-$; and the 1 : 1 adduct of Ph_3SiBr with o-phenanthroline, which is probably also ionic but has not been fully studied as yet. Although these three compounds are the only stable organosiliconium salts yet obtained in pure form, evidence to be presented indicates that many other such species probably exist in solution.

The most convincing evidence for an ionic structure for $Ph_3Si(bipy)I$ in solution comes from conductometric studies in the solvent dichloromethane. *Figure 1* shows the equivalent conductance plotted against the square root of
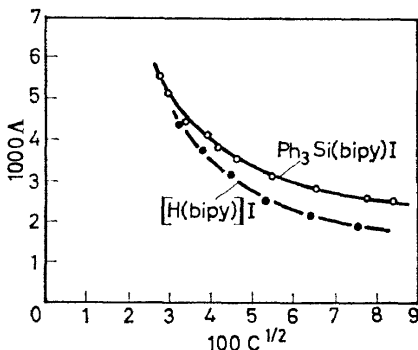

Figure 1. Plots of equivalent conductance against the square root of concentration for the triphenyliodide-bipyridine adduct and the mono-hydrogen iodide salt of bipyridine

concentration, for both the triphenylsilyliodide-bipyridine adduct and for the mono-hydrogen iodide salt of bipyridine, which is known to exist in ionic form as $(bipy\ H)^+\ I^-$. The silicon compound is a slightly better conductor than the hydrogen iodide salt, consistent with a greater degree of ion pairing of iodide with the protonated bipyridinium ion than with the siliconium ion. Conductivity data for several systems is shown in *Table 3*. As again indicated here, the $Ph_3Si(bipy)I$ has a higher equivalent conductance than $(bipy\ H)^+I^-$. The bromides corresponding to these compounds both show lower equivalent conductance than the iodides, probably because ion pairing is greater for the
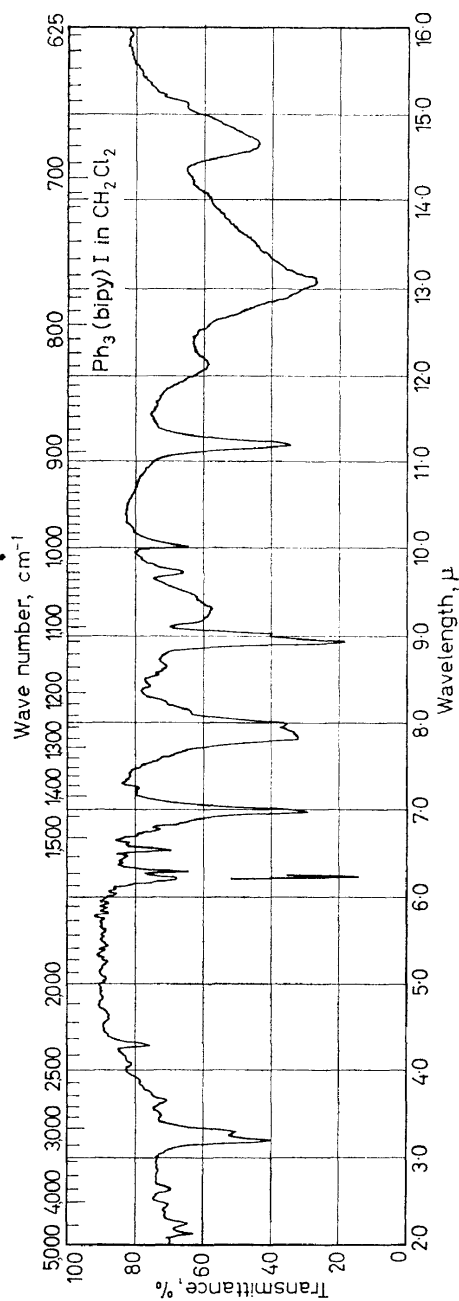
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Figure 2. Infrared spectrum in the sodium chloride region of triphenylsilyl iodide-bipyridine complex

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Table 3. Equivalent conductance of halides with 2,2'-bipyridine in dichloromethane

Compound	Conc., M $\times$ 10^2	Λ, mho-cm²/mole
HI	0·57	19·0
HBr	1·37	3·2
Ph₃SiI	0·85	25·0
Ph₃SiBr	0·81	4·0
Ph₃SiCl	3·30	< 0·2
Ph₂MeSiI	1·00	4·2
PhMe₂SiBr	4·60	1·5
Et₃SiBr	4·00	< 0·2

bromides than for the iodides. However, of the two bromides the silicon compound is once again a somewhat better conductor than the protonated bipyridinium bromide. Conductance measurements also provide evidence for at least partial dissociation in solution containing diphenylmethylsilyl iodide or phenyldimethylsilyl bromide with bipyridine. However, no conductivity could be observed for triphenylsilyl chloride or triethylsilyl bromide in the presence of 2,2'-bipyridine; if there is any ionization in the latter two solutions, it is not measurable by our technique.

Infrared spectral evidence is also consistent with an ionic formulation for the complexes. The infrared spectrum in the sodium chloride region of triphenylsilyl iodide-bipyridine complex is shown in *Figure 2*. The complex shows no absorption in the Si–O region near 1000 cm⁻¹ or in the O–H region, but if it is allowed to stand in air, slow hydrolysis takes place and bands appear in both of these regions. The complex shows bands at 1603 and 1520 cm⁻¹ which are not present in either of the starting materials. Absorption at 1600 cm⁻¹ is characteristic of heterocyclic nitrogen bases coordinated to metals[9].

A frequency range of particular importance is that from 300 to 600 cm⁻¹, where silicon-halogen stretching absorption bands are found. Data in this region for some silyl halides with and without 2,2'-bipyridine present are shown in *Figure 3*. Triphenylsilyl chloride, bromide and iodide each show a band near 500 cm⁻¹ and near 430 cm⁻¹, assigned to Si–C bending and to antisymmetric Si–C stretching modes, respectively[10]. In addition an Si-halogen stretching band is found for each compound: this appears at 417 cm⁻¹ for the iodide, 493 cm⁻¹ for the bromide, and 549 cm⁻¹ for the chloride[11].

Upon addition of bipyridine to the iodide and bromide, the Si-halogen and antisymmetric Si–C stretching bands both disappear, and a new absorption characteristic of the bipyridine group appears near 400 cm⁻¹. There is no evidence for complexing with triphenylsilyl chloride, for both the Si–Cl and antisymmetric Si–C bands appear with undiminished intensity in the presence of bipyridine. However, the spectra shown for diphenylmethylsilyl iodide indicate that complex formation takes place, for the Si–I at 409 cm⁻¹ mode disappears when bipyridine is added.

Ultraviolet spectral data are also of interest, for they indicate the configuration of the bipyridine moiety in the complexes. The bipyridine group is known to give electronic absorption bands at 239 and 283 mμ, when the two
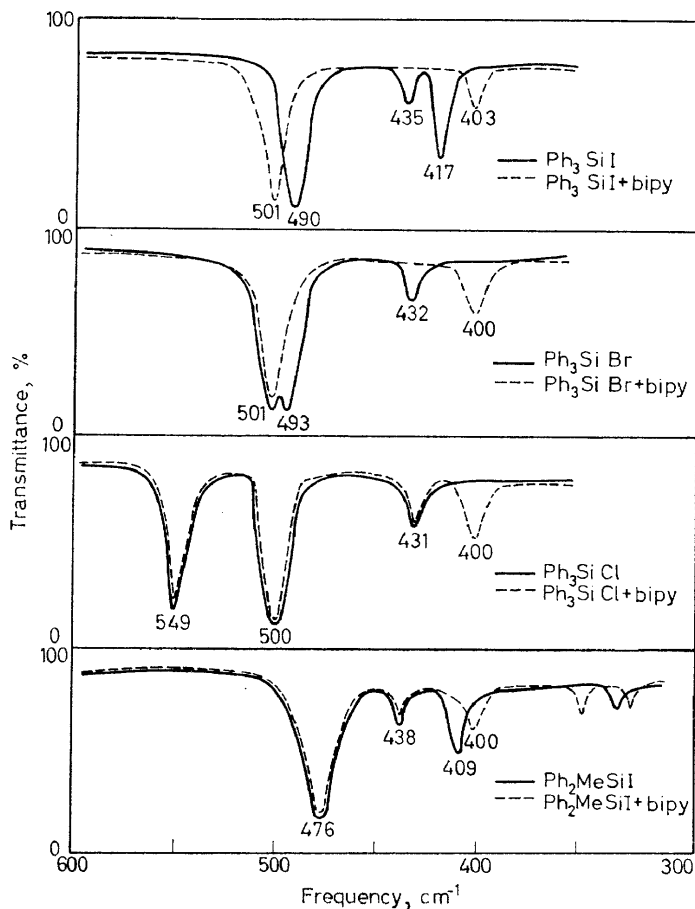
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Figure 3. Infrared absorption spectra of some silyl halides in the presence and absence of 2,2'-bipyridine

nitrogen atoms are in the *trans* configuration as in free bipyridine[12-14]. However, when the nitrogens are in the *cis* configuration as in chelate complexes of bipyridine these bands[13] appear near 245 and 301 mμ. Data in *Figure 4* show ultraviolet spectra for bipyridine and some of its complexes, in dichloromethane. The monohydrogen bipyridinium cation, which is known to exist in the *cis* chelated form (probably with a symmetrical N–H–N hydrogen bond), gives a spectrum identical with that of the triphenylsilyl bromide-bipyridine complex. Both are quite different from the spectrum of the 2,2'-bipyridine. The corresponding two species with iodine present in place of bromine also give identical spectra, but these differ from the bromides in that they show additional intensity at 243 mμ and in the end absorption below 220 mμ. As shown in the figure, this additional absorption corresponds to that for iodide ion[15]. Thus the ultraviolet evidence confirms the presence of iodide ion in solutions of $Ph_3Si(bipy)I$.

The spectral and conductometric evidence, taken as a whole, indicates that
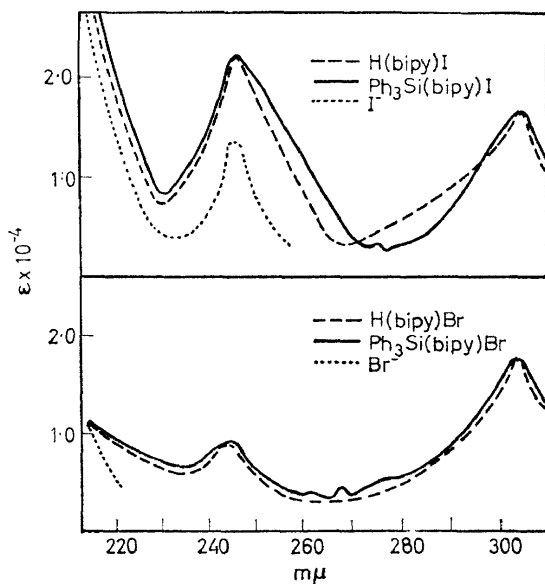
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Figure 4. Ultraviolet spectra, in dichloromethane, of bipyridine and some of its complexes

the complexes of triphenylsilyl bromide and iodide with 2,2'-bipyridine are ionic, and that the bipyridine moiety is in the *cis* configuration, and so is chelated to two coordination positions on the silicon. A pentacoordinate structure can be deduced for the chelated siliconium ion. One possibility is shown in structure (I). The two nitrogens of the bipyridine might occupy
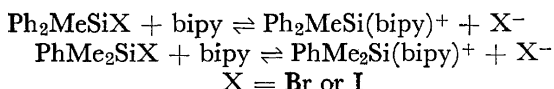

(I)
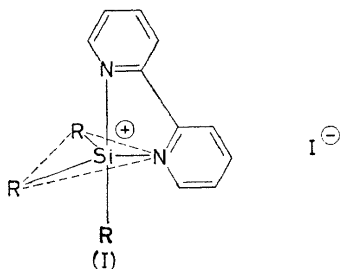
either an axial and an equatorial position as shown, or two equatorial positions, in trigonal bipyramidal coordination around the central silicon; and still other structural possibilities exist for pentacoordinate [Ph₃Si(bipy)]⁺. That the structure of the ion is indeed pentacoordinate, as deduced, is shown by an x-ray crystallographic study of solid triphenylsilyliodide-bipyridine carried out by Dr E. R. Corey of Cincinnati University. Although the data are incomplete and do not yet establish the exact arrangement of groups around silicon, they do show that the silicon atom is five-coordinate and that the ionic structure is maintained even in the solid. The Si–I distance in the

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solid is near 6·0 Å, so a hexacoordinate structure with iodine occupying one coordination position can be excluded.

The triphenyl(bipyridyl)siliconium ion is structurally related to the many pentacoordinate trialkyltin derivatives which have been studied in recent years. The fluoride, complex fluorides, the carboxylates, and even the perchlorate of trimethyltin have all been shown to have a bridged pentacoordinate structure, and there is now no evidence for the existence of free R_3Sn^+ ions in the solid state[16]. However, when trimethyltin perchlorate is complexed with two molecules of ammonia, the solid product appears to have the structure[17] $[Me_3Sn(NH_3)_2]^+ ClO_4^-$, in which the pentacoordinate cation is quite analogous to $[Ph_3Si(bipy)]^+$.

Pentacoordinate species have long been supposed to be intermediates in reactions of organosilicon compounds, and evidence for their participation is quite strong. However, stable pentacoordinate organosilicon species are very few†, and no others are known containing more than one organic group bonded to silicon. The triaryl siliconium ions can, therefore, be regarded as models for the pentacoordinate intermediates which are presumed to be important in so many reactions of organosilicon chemistry.

Although only two or three pentacoordinate siliconium ion salts have been isolated as solids, it appears from the evidence that others exist in solution. Organosilicon bromides and iodies containing at least one aromatic group bonded to silicon, such as, methyldiphenylsilyl and dimethylphenylsilyl iodides and bromides, give conducting solutions with 2,2'-bipyridine in dichloromethane, whose properties are similar to those of the known siliconium complexes. However, when the solvent is evaporated from these solutions, only the starting materials are recovered. It appears that an equilibrium may exist between free silyl halide and bipyridine on the one hand, and bipyridylsiliconium ion salts on the other:

$$Ph_2MeSiX + bipy \rightleftharpoons Ph_2MeSi(bipy)^+ + X^-$$
$$PhMe_2SiX + bipy \rightleftharpoons PhMe_2Si(bipy)^+ + X^-$$
$$X = Br \text{ or } I$$

These equilibria shift to the left when dichloromethane is removed. The evidence suggests that no appreciable ionization takes place for triphenylsilyl chloride, or for trialkylsilyl bromides. If equilibria like those shown in the equations exist for these molecules, they must lie well over to the side of the free neutral molecules.

The triphenylsilyl bromide and iodide cases are unique in that the solid siliconium ion salt precipitates from solution and can be isolated. A favourable crystallization energy is apparently an important factor. A chelating agent, rather than a monodentate amine ligand, also seems to be required for isolation of the siliconium ion salt. When triphenylsilyl bromide or iodide are treated with pyridine or 4-phenylpyridine in dichloromethane, electrically conducting solutions are formed but no crystalline complex can be isolated.

The charge distribution in these new silicon cations and the nomenclature

† A pentacoordinate structure is probable for the cage-type silicon derivatives of triethanolamine[18], and pentacoordinate anions of bis(o-arylenedioxy) organosiliconic acids are also known[19].

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which we have used to describe them call for some comment. The name "siliconium ion" was not originally intended to describe a particular charge distribution, but was employed because there is no other convenient and descriptive way to name the species. However, this term has been criticized by some on the grounds that the species is a silicon analogue of the N-alkyl-pyridinium ions, and so should be called an ammonium rather than a siliconium ion[20]. On the other hand, the same argument would apply equally well to such species as tris(2,2'-bipyridine)iron(III) ion, or even to hexam-mine iron(III) ion, $[Fe(NH_3)_6]^{3+}$. The latter two species are universally and logically classed as metal ion coordination complexes rather than as substituted pyridinium or ammonium ions. In true pyridinium ions, the majority of the positive charge is localized at nitrogen, although some slight delocalization will take place onto carbon atoms. In the iron(III) coordina-tion complexes, a major amount of positive charge is probably localized on the electropositive metal atom, although once again there will be some spreading of positive charge to nitrogen atoms. The organosiliconium ions represent an intermediate case, but because silicon is much closer in electro-negativity to metals like iron than to carbon, we believe that a substantial amount of positive charge is localized on silicon in $[Ph_3Si(bipy)]^+$, and that it is not therefore misleading to describe the species as a pentacoordinate organosiliconium ion.

It should be recognized, however, that the pentacoordinate siliconium ions are very different from the tricoordinate carbonium ions of organic chemistry. Tricoordinate siliconium ions truly analogous to organic carbo-nium ions are still unknown. The siliconium ions which we have prepared seem quite different both from conventional carbonium or pyridinium ions. However, there is close analogy to the chelate-stabilized diarylboronium ions described by Davidson and French[21]. The formation of stable organosili-conium ions provides a further indication of the well-known chemical simi-larity between boron and silicon. However, boronium ions appear to be somewhat more stable than siliconium ions. In particular, they can be made from boron–chlorine or boron–oxygen starting materials, whereas organo-siliconium ions have so far been made only from silyl iodides and bromides.

II. π-BONDING INVOLVING 3d-ORBITALS OF SILICON IN POLYSILANES

The participation of silicon d-orbitals in dative π-bonding, in compounds where the silicon is bonded to an atom bearing a lone pair of electrons, is now generally accepted. Convincing evidence for dative π-bonding from π-electron systems to silicon d-orbitals, as in organosilyl-substituted aromatic compounds, has also been presented previously by many of the participants in this symposium. Recently, some evidence has been presented for d-orbital participation in bonding in silicon compounds containing neither lone pairs, nor pi-electrons, i.e. in the permethylpolysilanes.

Organopolysilanes have been investigated especially by Professor Kumada and his group at Kyoto University, and also by Professors Macdiarmid and Gilman and their coworkers in the United States. In 1964, Gilman et al.[22] reported the striking observation that permethylpolysilanes exhibit strong ultraviolet absorption bands. Such electronic absorption in the near

ultraviolet region by molecules containing no lone pairs and no pi-electrons was quite unexpected and unprecedented. *Table 4* shows spectral data for some permethylpolysilanes. The principal absorption bands are seen to move to longer wavelength and to intensify with increasing chainlength.

The exact nature of the process responsible for u.v. absorption by permethylpolysilanes is not fully understood. However, it seems that the excitation must involve transfer of a bonding sigma electron into an antibonding molecular orbital of pi or delta type, made up of *d*-orbitals on adjacent silicon atoms. Thus *d*-orbital participation is indicated in these silanes which contain no donor groups, at least in the electronic excited state.

Table 4. Principal electronic absorption bands
of permethylpolysilanes, $CH_3[Si(CH_3)_2]_nCH_3$

n	λ *max* (Å)	ϵ
2	1950	—
3	2150	5,400
4	2350	14,700
5	2500	18,400
6	2600	21,100
8	2750	31,400

These observations led us to attempt to prepare a polysilane species containing an extra electron, i.e. a polysilane anion-radical, which might involve ground-state *d*-orbital bonding. The substrate which we chose for this work was dodecamethylcyclohexasilane (II), $[Si(CH_3)_2]_6$. Quite

(II)
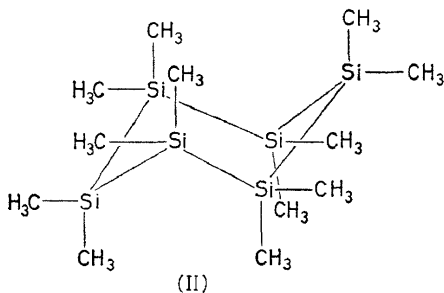
recently, Dr Ronald Husk of our laboratories has succeeded in obtaining what we believe to be anion-radicals of this and some other permethylpolysilanes[23]. The method employed involves solution of the polysilane in a 2 : 1 mixture of tetrahydrofuran and 1,2-dimethoxyethane, reduction with sodium-potassium alloy at $-100°C$, and detection by electron spin resonance (e.s.r.) spectroscopy at low temperatures. Oxygen must be strictly excluded and quite unusual purification of solvent and substrate is required. This technique is not easy, and over one full year of experimentation was required before we obtained our first successful observations and evidence for the anion-radical of $[Si(CH_3)_2]_6$.

When $[Si(CH_3)_2]_6$ is reduced under the conditions described it forms a blue-green solution which exhibits a strong e.s.r. pattern. The pattern becomes well resolved upon warming the sample to $-75°C$. *Figure 5* shows the e.s.r. spectrum of the anion-radical $[Si(CH_3)_2]_6^-$ at low gain. About nineteen equally-spaced lines can be observed, with spacing $0·53$ G, and line width
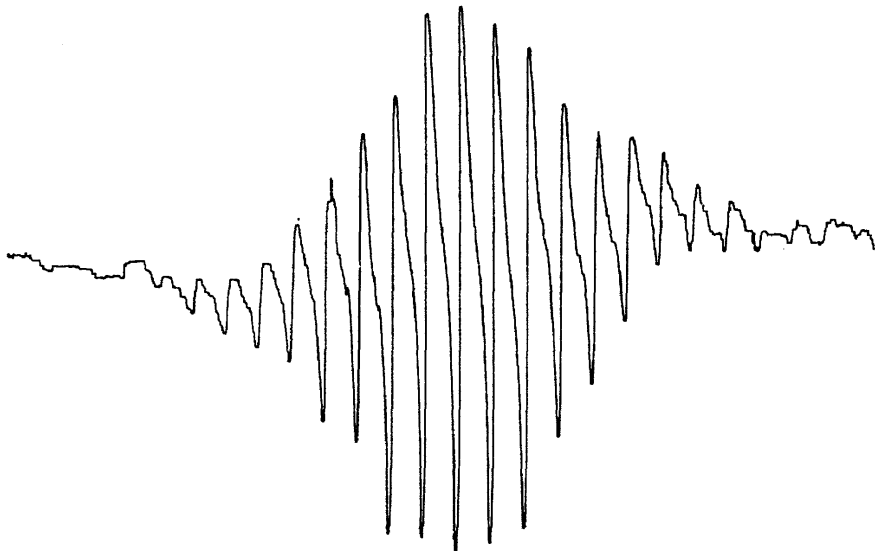

Figure 5. Electron spin resonance spectrum of the anion radical $[Si(CH_3)_2]_6^-$ at low gain

$0·11$ G. The intensity distribution is approximately correct for the centre lines of a 37-line pattern, which would be formed if the unpaired electron contacted each of the 36 protons of the molecule equally. Additional lines can be observed at higher amplification (*Figure 6*), and at best about 25 lines of the central pattern can be observed. At high gain the e.s.r. spectrum is complicated by the presence of two doublet satellite spectra, which form miniature replicas of the central pattern. One of these appears in *Figure 6*; it has a principal splitting of $15·8$ G and a line spacing of $0·53$ G. Each wing of the doublet has an intensity about 5 per cent of the main pattern. A second satellite can be observed overlapping the main pattern (*Figure 7*); it
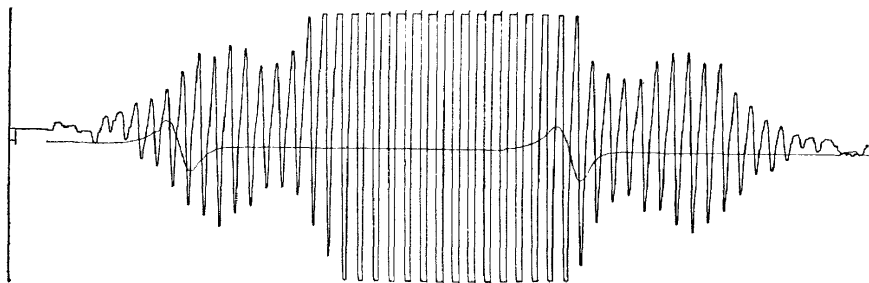

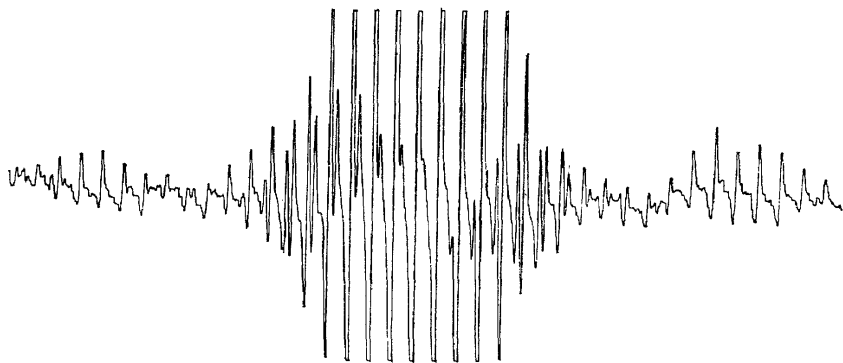*Figure 6.* Electron spin resonance spectrum at moderate gain showing satellite spectra with splitting $15·8$ G

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Figure 7. Electron spin resonance spectrum of $[Si(CH_3)_2]_6^-$ at high gain showing two doublet satellite spectra

has a splitting of 5·2 G and an intensity of about 12 per cent of the main pattern.

In the e.s.r. spectrum of $[Si(CH_3)_2]_6^-$, doublet satellite side bands are expected for both ^{13}C and ^{29}Si, each having a nuclear spin of 1/2. The assignment can be made on the basis of the observed intensity, which will depend on the isotopic abundance and the number of equivalent nuclei in the molecule. For ^{13}C the predicted intensity is 1·11 per cent × 12/2 or 6·7 per cent, whereas for ^{29}Si it is 4·7 per cent × 6/2 or 14·1 per cent. Accordingly the weaker satellite with splitting 15·8 gauss is assigned to interaction with ^{13}C, and the more intense satellite is assigned to ^{29}Si. Electron-nuclear hyperfine coupling constants of this type apparently have not been observed previously either for silicon or for carbon bonded to silicon; potentially they offer possibilities for significant theoretical interpretation.

The observed e.s.r. spectrum for the dodecamethylcyclohexasilane anion radical, and the form of the satellite spectra, indicate that the unpaired electron is delocalized in a molecular orbital extended equally over all six silicon atoms, just as the unpaired electron in aromatic anion-radicals is completely delocalized over the ring. In the silicon compound, because *d*-orbital combinations can be used to make up the molecular orbital holding the unpaired electron, it is not essential that the ring be planar for complete delocalization to occur. However, if the ring is nonplanar the environments of the methyl groups will be slightly different, and must, therefore, be equalized by rapid ring interconversion.

Dodecamethylcyclohexasilane can be reduced to its anion radical in the presence of excess benzene. Unlike polynuclear aromatic hydrocarbons, however, it cannot be reduced to the anion radical electrochemically in dimethoxyethane. Therefore, its electron affinity appears to lie between that of benzene and the polynuclear aromatic hydrocarbons such as biphenyl and naphthalene. As in the polyene series, cyclic structure is not necessary for anion-radical formation by methylpolysilanes. Although we have been unable to reduce hexamethyldisilane, linear decamethyltetrasilane gives a complex e.s.r. spectrum under the conditions described above. We plan to investigate many other related systems in the near future.

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CONCLUSION

π-bonding involving $3d$-orbitals of silicon was first seriously proposed about fifteen years ago. The past decade and a half have seen intensive efforts to prove or disprove the existence of this kind of interaction. The evidence for d-orbital bonding which has accumulated during this time is now overwhelming, and the recent findings that such bonding must take place even in the fully saturated permethylpolysilanes would seem to bring these efforts to their logical conclusion. Thus we may have reached the end of an era in organosilicon chemistry. Already, many workers in this field are turning their attention to the more difficult problem of elucidating the exact manner and extent of d-orbital involvement, in organosilicon compounds in ground, transition, and electronic excited states. These questions seem likely to be of increasing importance in the organosilicon chemistry of the future.

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