Measurement of the ^{29}Si Central Atom Couplings in Silicon-centred Radicals with Phenyl Substituents

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Following γ-irradiation of the completely deuteriated silicon compounds $C_6D_5SiD_3$, $(C_6D_5)_2SiD_2$ and $(C_6D_5)_3SiD$ at 77 K, features were detected by EPR spectroscopy from the ^{29}Si satellite transitions of the corresponding silicon-centred radicals, derived from Si–D bond cleavage. Thus the anisotropic ^{29}Si hyperfine tensors could be fully evaluated, leading to the conclusion that these are still pyramidal species, but are partially delocalised, rising to a maximum of *ca.* 30% spin transfer to the phenyl groups in the triphenylsilyl radical. The chloro-analogues, $C_6D_5SiCl_2^{\bullet}$ and $(C_6D_5)_2SiCl^{\bullet}$, were also studied, following γ-radiolysis of $C_6D_5SiCl_3$ and $(C_6D_5)_2SiCl_2$ at 77 K, the latter giving rise to both these radicals and indicating a radiolytic mechanism involving both Si–C and Si–Cl bond cleavage. In order to provide 'base' values for couplings in related species without phenyl substituents, the radicals $MeSiCl_2^{\bullet}$ and $HSiCl_2^{\bullet}$ were also studied as formed by the radiolysis of $MeSiCl_3$ and $HSiCl_3$.

The triphenylmethyl (trityl) radical is the archetypal stable free radical. The extent of this stability is reflected in the greatly reduced bond dissociation energies[1] of compounds of the general type Ph_3C–X from those of the analogues CH_3–X, and its source lies in part in the extensive delocalisation of the unpaired electron over the three aromatic rings, as attested to by results from EPR spectroscopy.[2] Bond energy measurements on the corresponding silicon compounds[3] (*e.g.* Ph_3Si–H) lead to the conclusion that the introduction of a phenyl substituent to a silane reduces the Si–H bond energy by *ca.* 2 kcal mol^{-1} and is taken to imply that there is some stabilising influence on the silyl radical thereby formed, although this is much less than that on a carbon-centred radical.*

No results from EPR spectroscopy are available to assess the degree of delocalisation in triphenylsilyl, since this species has never been observed in the liquid phase. However, Lappert[4] and Sakurai[5] have published independently their results for tris(3,5-di-*tert*-butyl)silyl[5] and trimesitylsilyl,[4] which indicate that 20% of the unpaired electron density is transferred from the silicon centre, according to the magnitude of the ring proton coupling constants. The most decisive piece of information that is required to probe the spin density at the silicon centre is the central atom ^{29}Si coupling constant, and an isotropic value of 135 G was reported by Lappert for the trimesitylsilyl radical.[4] There is, however, a complicating factor endemic to silyl radicals, which emanates from the fact that their configurations are, in contrast to many carbon-centred radicals, pyramidal. This means that a reduction in the isotropic ^{29}Si coupling from that in, say, the trimethylsilyl radical (*ca.* 180 G),[6–8] might reflect not only delocalisation of the unpaired electron, but also the development, by a change in substitution, of a more planar radical centre, leading in any case to a reduced 3s contribution to the SOMO. This uncertainty may be overcome by measurement of the EPR spectra of silyl radicals in the solid state so that the anisotropic components of the ^{29}Si hyperfine tensor can be determined. If this is accomplished, then the silicon 3s and 3p orbital populations may be determined by comparison with standard atomic hyperfine parameters,[9] leading to a direct determination of both the extent of delocalisation and, at least within the concept of complete orbital following, an estimate of the configuration of the radical centre.

Unfortunately, all our efforts prior to the present work had met with failure, since following γ-irradiation of the compounds $PhSiH_3$, Ph_2SiH_2 and Ph_3SiH as polycrystalline solids at 77 K, we were unable to locate unambiguously the desired ^{29}Si features. It occurred to us that the source of the problem could be that the tail of the intense central peak from silyl radicals with a non-magnetic silicon nucleus extended into the spectral regions where the satellite features were located, and thus obscured them. To reduce the width of this central peak, we resorted to the synthesis of the completely deuteriated phenyl silanes, taking the view that much of the peak width probably stems from unresolved proton hyperfine structure. Since the magnetogyric ratio of a deuteron is reduced to 1/6.514 from that of a proton, the width of the central peak should be reduced by 2/6.514, allowing for the difference in D/H nuclear spin, and hence the larger hyperfine multiplicity from the former nucleus. Additionally, the ^{29}Si features should also be sharpened and rendered easier to detect.

Results and Discussion

Our ^{29}Si hyperfine data for perdeuteriated phenyl-, diphenyl- and triphenyl-silyl radicals are shown in Table 1, along with those for structurally related chloro-derivatives. The $A_{\parallel}$ couplings for $Et_3Si^{\bullet}$ and $Bu^t_3Si^{\bullet}$ radicals are also given, but the corresponding perpendicular features were buried under more intense features from other radicals, and were not therefore detected. Some literature data are included additionally for the purpose of comparison.

$C_6D_5SiD_2^{\bullet}$, $(C_6D_5)_2SiD^{\bullet}$ *and* $(C_6D_5)_3Si^{\bullet}$ *Radicals.*—Following γ-radiolysis of the parent perdeuteriated phenylsilanes at 77 K, features from the title radicals were detected by EPR spectroscopy as shown in Figs. 1–3. In each case, there is an intense central feature, arising from silyl radicals with a non-magnetic Si nucleus, which is flanked by features in the wing regions of the spectrum with the correct intensity for ^{29}Si-centred radicals, considering the natural abundance of ^{29}Si (4.7%) and the degree of anisotropy present. As may be judged from the data in Table 1, the presence of a phenyl group reduces the isotropic ^{29}Si coupling from those typical for alkyl silyl radicals: *cf.* 181 G for $Me_3Si^{\bullet}$ and 169 G for $PhSi^{\bullet}D_2$. However, the anisotropic coupling also decreases slightly, from 52 G to 49 G. These parameters are both seen to decrease in a

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* 1 cal = 4.184 J.

Table 1 Hyperfine coupling data for silyl radicals

Radical	^{29}Si Hyperfine coupling constants[a]			
	$A_{\parallel}$	$A_{\perp}$	a	$2B$
$SiF_3^{\bullet}$[b]	562	501	521	41
$SiCl_3^{\bullet}$[c]	—	—	440	—
$MeSiCl_2^{\bullet}$	353	276	302 308[d]	51
$MeSiCl_2^{\bullet}$*[e]	296	228	251	45
$HSiCl_2^{\bullet}$	359	278	305	54
$Me_2SiCl^{\bullet}$[f]	290	199	229	61
$Me_3Si^{\bullet}$[f]	233	155	181	52
$Me_3Si^{\bullet}$[g]	223	160	181	42
$Et_3Si^{\bullet}$	221	[144]	170[h]	51
$Bu^t_3Si^{\bullet}$	215	[137]	163[i]	52
$C_6D_5SiD_2^{\bullet}$	218	144	169	49
$(C_6D_5)_2SiD^{\bullet}$	206	137	160	46
$(C_6D_5)_3Si^{\bullet}$	190	130	150	40
$C_6D_5SiCl_2^{\bullet}$	332	260	284	48
$(C_6D_5)_2SiCl^{\bullet}$	256	190	212	44

[a] In Gauss; 1 $G = 10^{-4}$ T. [b] M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 1976, 1568. [c] J. Roncin, *Mol. Cryst.*, 1967, **3**, 117. [d] C. Hesse, N. Leray and J. Roncin, *J. Chem. Phys.*, 1972, **57**, 749. [e] Tentative assignment, could also be $MeSiHCl^{\bullet}$ but for the bond angle data (Table 2). [f] J. H. Sharp and M. C. R. Symons, *J. Chem. Soc. A*, 1970, 3084. [g] Present data; it appears that the radical is rotating and partially averaging the A-anisotropy in Me_3SiCl, even at 77 K. [h] Isotropic coupling from R. A. Jackson, *J. Chem. Soc., Perkin Trans. 2*, 1983, 523; we could not resolve the perpendicular coupling because of intense signals from ethyl radicals, so that in parentheses is calculated from the observed parallel and the literature isotropic couplings. [i] Isotropic coupling from R. A. Jackson and H. Weston, *J. Organomet. Chem.*, 1984, **272**, 13; again, the perpendicular features were obscured so that the perpendicular coupling is calculated as in *h*.

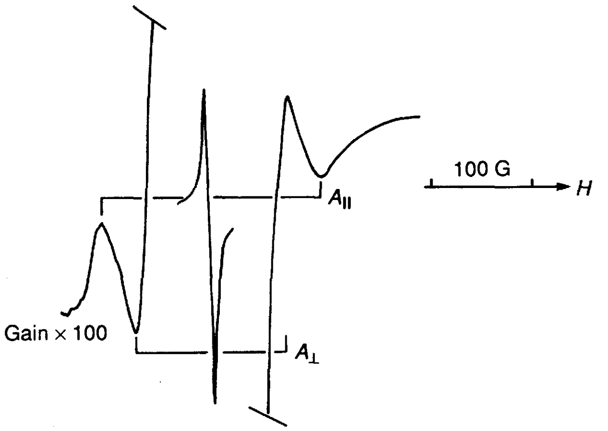


Fig. 1 ^{29}Si features from $C_6D_5SiD_2^{\bullet}$ formed by γ-irradiation of $C_6D_5SiD_3$ at 77 K. The hyperfine parameters were evaluated by computer simulation.

fairly monotonic fashion as the second and third phenyl groups are introduced. Thus it is clear that these are delocalised radicals, with up to 30% of the unpaired electron transferred to the aromatic rings in the case of triphenylsilyl (Table 2). Our anticipation was that any such delocalisation of the unpaired electron might render the silicon radical centres increasingly closer to planarity for the phenylsilyl series as partial π-bonding character developed between the silicon atom and the phenyl substituents. In order to evaluate the effect of these substituents on the configuration of the radical centre, we determined the 3p/3s hybridisation ratio of the SOMO (Table 2) and used the appropriate equation derived by Coulson[10] for C_{3v} symmetry [eqn. (1)] to estimate the average R–Si–R bond angle (θ) for each radical.

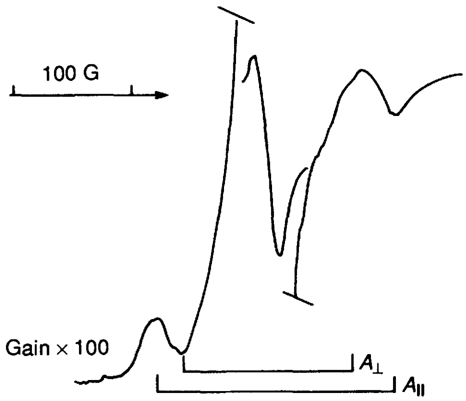


Fig. 2 ^{29}Si features from $(C_6D_5)_2SiD^{\bullet}$ formed by γ-irradiation of $(C_6D_5)_2SiD_2$ at 77 K. The hyperfine parameters were evaluated by computer simulation.

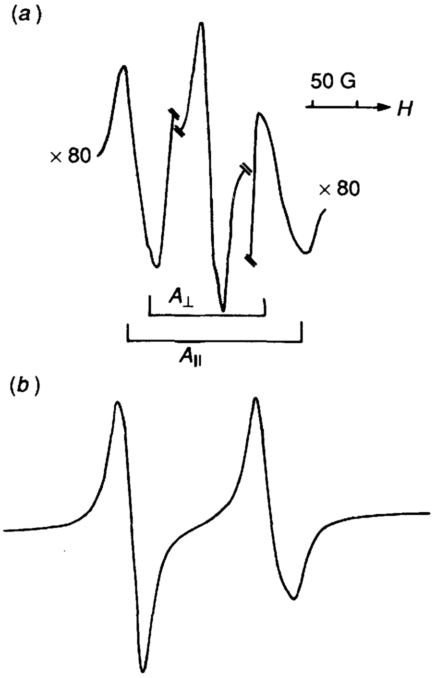


Fig. 3 (*a*) ^{29}Si feature from $(C_6D_5)_3Si$ formed by γ-irradiation of $(C_6D_5)_3SiD$. The hyperfine parameters were evaluated by computer simulation, shown in (*b*).

Table 2 Orbital populations and R–Si–R bond angles (θ) for silyl radicals

Radical	3s	3p	p/s ratio	θ/°
$SiF_3^{\bullet}$	0.43	0.59	1.38	103.8
$MeSiCl_2^{\bullet}$	0.25	0.74	2.96	109.4
$MeSiCl_2^{\bullet}$*,[a]	0.21	0.65	3.14	109.8
$HSiCl_2^{\bullet}$	0.25	0.78	3.10	109.7
$Me_2SiCl^{\bullet}$	0.19	0.88	4.66	112.2
$Me_3Si^{\bullet}$	0.15	0.75	5.03	112.6
$Et_3Si^{\bullet}$	0.14	0.74	5.25	112.9
$Bu^t_3Si^{\bullet}$	0.14	0.75	5.58	113.2
$C_6D_5SiD_2^{\bullet}$	0.14	0.71	5.07	112.7
$(C_6D_5)_2SiD^{\bullet}$	0.13	0.67	5.03	112.7
$(C_6D_5)_3Si^{\bullet}$	0.12	0.57	4.66	112.2
$C_6D_5SiCl_2^{\bullet}$	0.24	0.70	2.96	109.4
$(C_6D_5)_2SiCl^{\bullet}$	0.18	0.64	3.63	110.7

[a] Assignment tentative.

$$\theta = \cos^{-1}\{[1.5/2(p/s) + 3] - 0.5\} \qquad (1)$$

It is clear that the bond angles are all close to 112°, so that

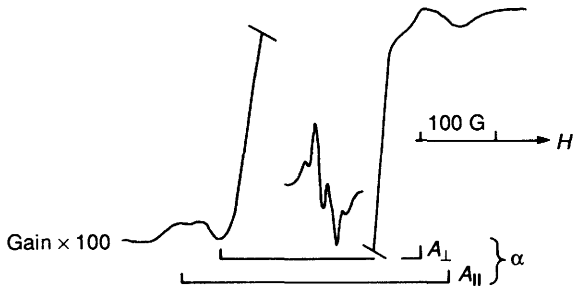


Fig. 4 ^{29}Si features from $C_6D_5SiCl_2^\bullet$ formed by γ-irradiation of $C_6D_5SiCl_3$

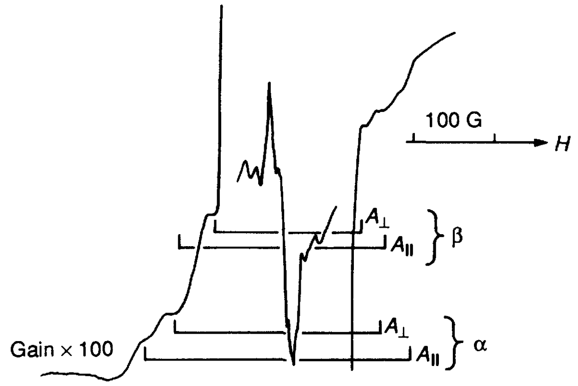


Fig. 5 ^{29}Si features from $C_6D_5SiCl_2$ (α) and $(C_6D_5)_2SiCl^\bullet$ (β) formed by γ-irradiation of $(C_6D_5)_2SiCl_2$

very little change in geometry is caused by the delocalisation; if anything, increasing the number of phenyl substituents actually renders the silicon radical centre fractionally more pyramidal, because the p/s ratios are seen to decrease slightly in this order. However, this situation is in some way reminiscent of the behaviour of chlorine substituents in which the p/s ratio decreases markedly (Table 2) from $Me_2SiCl^\bullet$ to $HSiCl_2^\bullet$, and the s-component clearly increases as shown by the rise in the isotropic couplings through the series $Me_2SiCl^\bullet$, $MeSiCl_2^\bullet$, $SiCl_3^\bullet$; nonetheless, these radicals are delocalised, as shown by deviations, to lower a^{29}Si values, from the straight line that may be drawn between the isotropic ^{29}Si couplings in the silyl radicals and the $^1J_{Si-H}$ couplings in the NMR spectra of the parent silanes [11] (see later). This may be explained in terms of the greater electron withdrawing power of Cl with respect to Si so that the Si–Cl bond orbitals take on more p-character and the radical centre bends. This effect overrides any possible planarising influence from partial multiple bonding. We can argue that the difference in (Pauling) electronegativity [12] between carbon (2.5) and silicon (1.8) acts similarly so that the phenyl groups attract more 3p character into the C–Si bonding orbitals and thus the radical centre bends slightly. The fall in the anisotropic couplings (*2B*) shows that the delocalisation increases with increasing number of phenyl groups. Thus, the gain in Si–Ph bonding energy [3] (*ca.* 2 kcal per phenyl group on the basis of bond energies) is insufficient to override the intrinsic energy barrier to increasing the planarity of the radical centres, calculated [13] to be 13 kcal mol^{-1} for $Me_3Si^\bullet$. Indeed, the argument of Pauling,[14] as with a related view of the situation in the terms of Perturbation MO theory,[15] predicts that this energy barrier will increase with increasing substituent electronegativity. The evidence for the methyl substituted series, $MeSiH_2^\bullet$, $Me_2SiH^\bullet$, $Me_3Si^\bullet$, is that increasing the number of methyl groups decreases the planarity of the radical centre,[16] thus reducing the p/s ratio; phenyl substituents, which bond to Si *via* sp^2 carbon orbitals would be expected to be somewhat more electronegative than methyl groups which bond *via* sp^3 orbitals.

$C_6D_5SiCl_2^\bullet$ *and* $(C_6D_5)_2SiCl^\bullet$.—Figs. 4 and 5 show the EPR spectra recorded following γ-irradiation at 77 K of $C_6D_5SiCl_3$ and $(C_6D_5)_2SiCl_2$, respectively. In the former case, ^{29}Si features are observed only from $C_6D_5SiCl_2^\bullet$ radicals, while both these and $(C_6D_5)_2SiCl^\bullet$ radicals are present following radiolysis of the latter compound. From the conversion of their hyperfine data into orbital populations (Table 2), it is clear that these radicals are slightly more delocalised in terms of the 3p population than are $C_6D_5SiD_2^\bullet$ and $(C_6D_5)_2SiD^\bullet$, but this difference is really only marginal. The greatest difference is found in the configurations of the radical centres which, as expected, are rendered more pyramidal by the chlorine substitution, and so these radicals occupy a structural mid-point between normal chlorosilyl radicals and the phenylsilyl species.

The formation of both radicals from the latter compound is interesting, and deserves comment. We believe that a dominant process in the radiolysis of chlorosilanes is dissociative electron capture, so that stray electrons, produced by ionisation, are captured by neutral chlorosilane molecules whose resulting radical anions then decompose [eqns. (2)–(4)]. This process

$$R_3SiCl \longrightarrow R_3SiCl^{\bullet+} + e^- \qquad (2)$$

$$e^- + R_3SiCl \longrightarrow [R_3SiCl]^{\bullet-} \qquad (3)$$

$$[R_3SiCl]^{\bullet-} \longrightarrow Cl^- + R_3Si^\bullet \qquad (4)$$

may be activated by the exoergicity of the electron addition step [eqn. (3)]. While this is highly reasonable for cleavage of a Si–Cl bond, similar cleavage of a Si–C bond is most unlikely, and we propose that the latter arises from electron return to a chlorosilane radical cation, leading to molecular excitation and bond homolysis [eqn. (5)].

$$R_3SiCl^{\bullet+} + e^- \longrightarrow [R_3SiCl]^* \longrightarrow R^\bullet + R_2SiCl^\bullet \quad (5)$$

Comparison with Other Radicals.—In a previous report,[17] EPR data were given for a radical pair formed in an X-irradiated single crystal of triphenylsilane. From the anisotropic ^{29}Si hyperfine tensor, it was concluded that the isotropic coupling was 80 G. However, the anisotropic hyperfine parameters in γ-irradiated polycrystalline perdeuteriated triphenylsilane (Table 1) provide an isotropic ^{29}Si coupling of 150 G, and we are forced to refute this previous interpretation. It is in any case clear from the spectrum shown,[17] that the lines assigned to ^{29}Si components are at least five times too intense, given the natural abundance of ^{29}Si, alluded to earlier. The liquid phase result for trimesityl reported by Lappert gives an isotropic ^{29}Si coupling of 135 G,[4] which is in much better accord with our result for $Ph_3Si^\bullet$: we suggest that the decrease in the former radical arises from steric hindrance between the mesityl groups which forces the radical centre into a more planar configuration than for the triphenylsilyl radical. A similar effect is found on comparison of $a(^{29}Si)$ for $Me_3Si^\bullet$ with $Bu^t{}_3Si^\bullet$, where there is a fall in the coupling from 181 G to 163 G and a small increase in the bond angle that may be derived for the latter radical. This must be due to steric effects since the 3p orbital population (Table 2) in the two radicals is the same.

It is interesting to compare the isotropic coupling in the silyl radicals with the corresponding members of the series of germanium-centred radicals (Table 3). Again the agreement is better with $a(^{29}Si)$ = 150 G than 80 G, but it is surprising that the delocalisation on to the three phenyl groups in $Ph_3Ge^\bullet$ is apparently so low. If this is correct, it must be almost entirely the steric effect of the three mesityl groups that reduces the germanium coupling from that in the other two members of the series.

Table 3 Comparison of isotropic hyperfine couplings for silicon- and germanium-centred radicals

R	$R_3Si^•$	$R_3Ge^•$
Me	181[a]	84.7[b]
Ph	150 (80)[c]	84.0[d]
mesityl	135[e]	68.4[e]

[a] S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson and K. D. J. Root, *J. Chem. Soc., A*, 1970, 348. [b] R. V. Lloyd and M. T. Rogers, *J. Am. Chem. Soc.*, 1973, **95**, 2459. [c] M. Geoffroy and E. A. C. Lucken; believed to be incorrect, see text. [d] M. Geoffroy, L. Ginet and E. A. C. Lucken, *Chem. Phys. Lett.*, 1976, **38**, 321. [e] M. J. S. Gynane, M. F. Lappert, P. I. Riley, P. Riviere and M. Riviere-Baudet, *J. Organomet. Chem.*, 1980, **202**, 5.

Table 4 α-Proton coupling constants for silyl radicals

Radical	α-H Coupling/*G*
$SiH_3^•$	7.84[a]
$MeSiH_2^•$	12.11[a]
$Me_2SiH^•$	17.29[a]
$PhSiH_2^•$	10
$Ph_2SiH^•$	14
$H_2SiF^•$	34.6[b]
$HSiF_2^•$	89.9[b]

[a] S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson and K. D. J. Root, *J. Chem. Soc., A*, 1970, 348. [b] M. Merritt and R. W. Fessenden, *J. Chem. Phys.*, 1972, **56**, 2353.

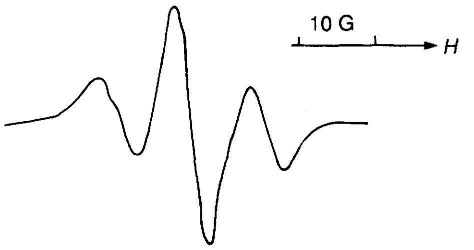


Fig. 6 Proton hyperfine structure from $PhSiH_2^•$ radicals formed by γ-irradiation of $PhSiH_3$ at 77 K

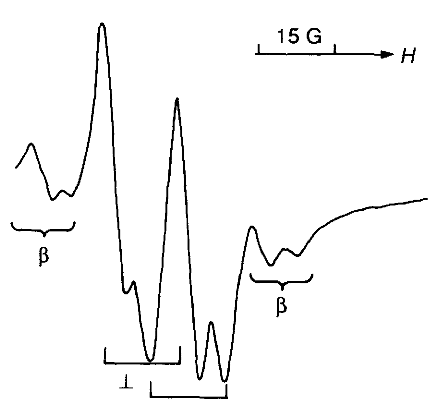


Fig. 7 Proton hyperfine structure from $Ph_2SiH^•$ radicals (α) formed by γ-irradiation of Ph_2SiH_2 at 77 K; (β) marks signals from an unassigned secondary radical

α-Proton Coupling Constants.—While we were unable to locate the ^{29}Si features from phenylsilyl radicals following γ-radiolysis of the non-deuteriated forms of $PhSiH_3$ and Ph_2SiH_2, there was no difficulty in detecting the α-proton structure from the silicon radical centres (Figs. 6 and 7); the coupling data are given in Table 4, along with those for other silyl radicals. In order to compare the α-proton couplings in the phenylsilyl radicals with those in the methylsilyl series,[7,8] we need to account for the effect of delocalisation in the following way. By taking as a base value the 3p spin population in the $Me_3Si^•$ radical, which is *ca.* 0.75, we can compensate for the delocalised nature of the phenylsilyl radicals by multiplying their α-H couplings by the ratio of the anisotropic couplings $2B(Me_3Si)/2B(PhSi)$, giving 'effective' α-proton couplings of 10.6 G and 15.8 G for $PhSiH_2^•$ and $Ph_2SiH^•$ respectively. Since these are very similar to the values for $MeSiH_2^•$ and $Me_2SiH^•$, evidence is provided that the configurations of the phenylsilyl radical centres are similar in configuration to the methyl series, and supports the view that Ph–Si π-delocalisation does not lead to significantly planar radical centres.

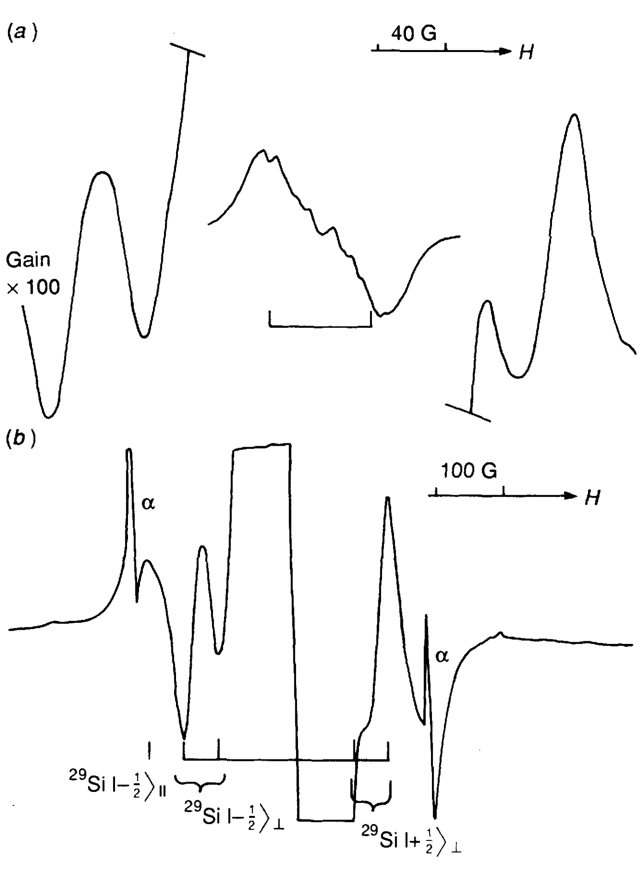


Fig. 8 EPR spectra from $HSiCl_2^•$ radicals, formed by γ-irradiation of $HSiCl_3$ at 77 K. (*a*) Recorded using a 400 G sweep, showing central region and part of ^{29}Si satellite features, recorded at higher gain. (*b*) Recorded using a 1000 G sweep, revealing full extent of ^{29}Si features and signals (α) from H-atoms.

Following radiolysis of $HSiCl_3$ at 77 K, the spectra shown in Fig. 8(*a*) and (*b*) were obtained. The former is recorded with a 400 G sweep, at low modulation, and shows an essential doublet splitting of *ca.* 58 G, superimposed on which is a complex incompletely resolved substructure. At increased gain and modulation, the substructure is lost and on the ^{29}Si features, which are now visible, there is a very clear doublet splitting of the same magnitude. We assign this spectrum to the $HSiCl_2^•$ radical, the highly bent radical centre (Table 2) now forcing the unique proton strongly into the positively coupled region. Fig. 8(*b*) is recorded with a 1000 G sweep and shows clearly the pair of perpendicular doublets: unfortunately the presence of signals from hydrogen atoms partially obscures the parallel regions, but by assuming that the coupling is nearly isotropic, the hyperfine data in Table 1 may be estimated, in good agreement with those for the $MeSiCl_2$ radical.[18] The complex substructure in Fig. 8(*a*) must arise from hyperfine coupling to the two chlorine nuclei, the hyperfine tensors for which are not parallel, and so the couplings will not be equivalent for all directions. In

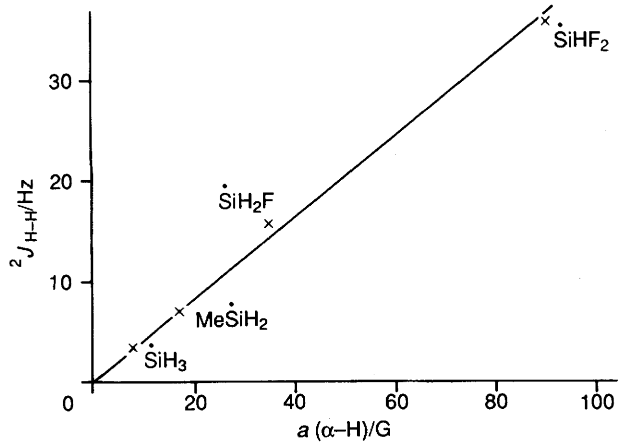


Fig. 9 Correlation of $^2J_{H-H}$ couplings in silanes H_2SiXY with a(α-H) couplings in the corresponding silyl radicals $HSiXY^•$. EPR data from refs. 7 and 21. NMR data from ref. 20 and E. A. V. Ebsworth and S. G. Frankiss, *Trans. Faraday Soc.*, 1962, **59**, 1518.

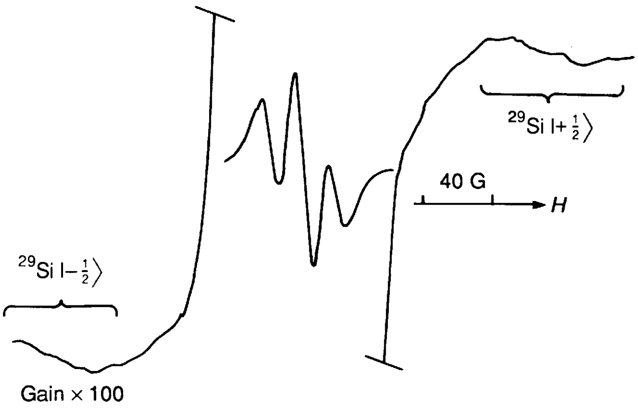


Fig. 10 EPR spectrum recorded at 77 K, following γ-irradiation of $MeSiCl_3$ at 77 K, showing broad ^{29}Si features from $MeSiCl_2^•$ radicals, and a central feature from H_2CSiCl_3 radicals

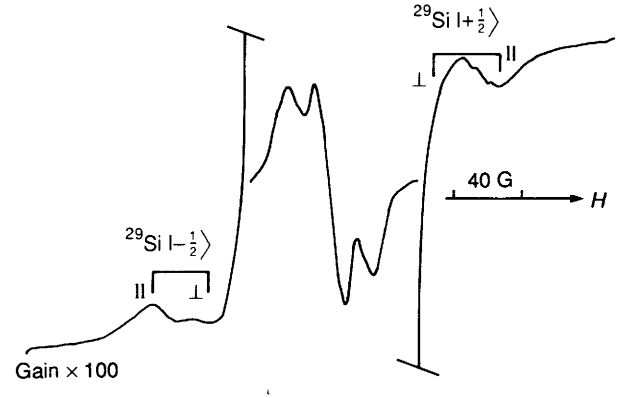


Fig. 11 EPR spectrum recorded at 77 K, following γ-irradiation of Me_3SiCl at 77 K, showing ^{29}Si features from $Me_3Si^•$ radicals, and a central feature from H_2CSiMe_2Cl radicals

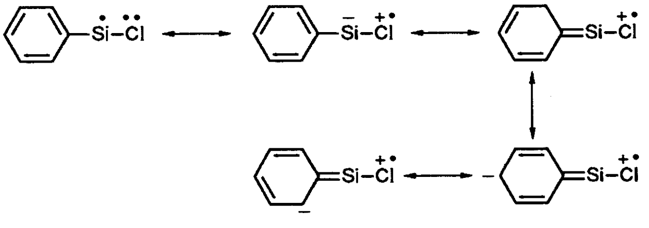
view of the incomplete resolution, we do not attempt further analysis of this.

Some years ago, Dobbs *et al.*[19] reported that there is a good linear correlation between the $^2J_{H-H}$ coupling in the NMR spectra of substituted methanes CH_2XY and the α-proton hyperfine coupling in the EPR spectra of the corresponding methyl radicals $CHXY^•$. Unfortunately the available data are far more limited for silanes and silyl radicals, but, as the plot in Fig. 9 shows, there does appear to be a similar relationship in this case also, if all a(α-H) couplings are taken as being positive. From the $^2J_{H-H}$ coupling of +12.7 Hz measured for the silane H_3SiCl,[20] a proton coupling of *ca.* 30 G is predicted for the $H_2SiCl^•$ radical, and the data for the fluoro-derivatives[21] $H_2SiF^•$ and $HSiF_2^•$ and their parent silanes show that the combined effect of two halogen substituents should be at least additive. Thus we expect a proton hyperfine coupling in the $HSiCl_2^•$ radical of *ca.* 60 G, which is not unreasonable given the observed value of 58 G.

Correlation of the $^1J_{Si-H}$ *Couplings in Silanes with the* $a(^{29}Si)$ *Hyperfine Couplings in the Corresponding Silyl Radicals.*—We have shown previously[11] that there is a linear relationship between the title couplings for a range of silicon species. However, substituents that are able to delocalise the unpaired electron in the silyl radicals lead to deviations to lower $a(^{29}Si)$ values than the correlation predicts. In this previous study, regression analysis of the data for weakly delocalising substituents gave eqn. (6). We discovered that the deviation from

$$a(^{29}Si) = 1.625\ (^1J_{Si-H}) + 123.9 \qquad (6)$$

this straight line amounted to *ca.* 20 G per Cl substituent, and we now find that phenyl substituents behave similarly, with an average deviation of *ca.* 14 G per group. Therefore, assuming only additivity, we would predict that the deviations for the radicals $Ph_2SiCl^•$ and $PhSiCl_2^•$ are 48 G and 54 G, respectively. The experimental values are a little greater than this, at 52 G and 64 G, and may reflect the presence of some 'captodative' stabilisation in which the electron acceptor property of the phenyl ring assists electron donation by the Cl substituents, as may be depicted by the canonical structures in Scheme 1.



Scheme 1

Interestingly, this may provide the first evidence that the captodative effect can operate in a σ-radical, although it has been fairly well documented for π-radicals.[22–26]

It is noteworthy that the sum of the 3s + 3p populations does not reflect the delocalisation proposed on the basis of the correlation, being generally larger than anticipated, although the 3p population alone seems to be a better measure of this. However, the standard procedure[9] for converting coupling constants into orbital populations relies upon the choice of a single parameterisation for each atom, regardless of the nature of the substituents. Clearly, this is a fault, since increasing the electronegativity of the substituents will result in orbital contraction, so that the populations derived in this way will be higher than they really are. This is probably the reason why the populations sum highest for the chlorine substituted radicals.

Radiolysis of $MeSiCl_3$, Me_3SiCl *and* $MeSiHCl_2$.—As shown in Figs. 10 and 11, in addition to the silyl radicals, $MeSiCl_2^•$ and $Me_3Si^•$, radiolysis of the first two compounds produced $H_2\dot{C}SiCl_3$ and $H_2\dot{C}SiMe_2Cl$, respectively, both signified by a 1:2:1 triplet pattern but differing slightly in their couplings of 21 G and 20 G. No such pattern was observed for $MeSiHCl_2$ (Fig. 12), and so this appears to form only a silyl radical. The source of this apparent resistance to C–H bond cleavage is not clear. It is interesting that the anisotropy of the ^{29}Si coupling in the Me_3Si radical is lower than reported in the literature,[16] but, since the derived isotropic coupling is the same, we assume that in our study the radical is rotating and partially averaging the

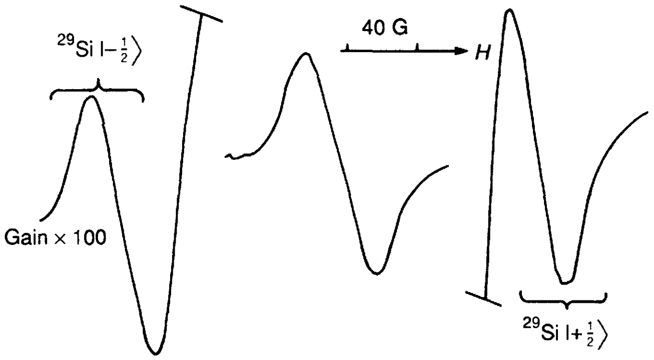


Fig. 12 EPR spectrum recorded at 77 K, following γ-irradiation of MeSiHCl$_2$ at 77 K. For assignment, see text.

^{29}Si tensor. Given the similarity in the derived bond angles (Table 3) in the silyl radicals, from MeSiCl$_3$ and MeSiHCl$_2$, it seems likely that the same species is produced, *i.e.* the MeSiCl$_2^{\bullet}$ radical, but there is greater reorientational mobility in the latter medium. Other assignments require that the number of chlorine substituents must differ for the two radicals, which seems incompatible with the data in Tables 1 and 2, where it is clear that common groups of bond angles and isotropic couplings occur for one, two or three chlorine substituents.

Experimental

The deuteriated phenyl silanes were prepared by lithium aluminium deuteride reduction of the appropriate phenylchlorosilanes, formed by the reaction of stoichiometric amounts of a solution of [^{2}H$_5$]phenylmagnesium bromide in tetrahydrofuran, as supplied by Aldrich, with tetrachlorosilane. All compounds were $>99\%$ pure according to GC analysis and showed satisfactory MS data ($>95\%$ deuteriation). EPR spectra were recorded using Bruker ER 200D or Varian E9 spectrometers from samples maintained at 77 K in a liquid nitrogen filled finger Dewar supported in the microwave cavity of the spectrometer. Radicals were formed, prior to EPR measurements, by γ-irradiation of samples frozen in spectrosil tubes at 77 K, using a ^{60}Co source. Other silanes and chlorosilanes were obtained from Aldrich and were used as supplied, following GC and MS analysis; all were $>98\%$ in purity. Triethylsilane and tri-*tert*-butylsilane were available from previous investigations.

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References

1 V. I. Veneneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev and Ye. L. Frankevich, *Bond Energies, Ionisation Potentials and Electron Affinities*, Arnold, London, 1966.
2 J. Sinclair and D. Kivelson, *J. Am. Chem. Soc.*, 1968, **90**, 5074.
3 R. Walsh, *Acc. Chem. Res.*, 1984, **14**, 246, and references cited therein.
4 M. J. S. Gynane, M. F. Lappert, P. I. Riley, P. Riviere and J. Riviere-Baudet, *J. Organomet. Chem.*, 1980, **202**, 5.
5 H. Sakurai, H. Umino and H. Sugiyama, *J. Am. Chem. Soc.*, 1980, **102**, 6837.
6 S. W. Bennett, C. Eaborn, A. Hudson, H. A. Hussain and R. A. Jackson, *J. Organomet. Chem.*, 1969, **16**, 36.
7 S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson and K. D. J. Root, *J. Chem. Soc. A*, 1970, 348.
8 P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 1969, **91**, 3938.
9 P. W. Atkins and M. C. R. Symons, *The Structure of Inorganic Radicals*, Elsevier, Amsterdam, 1967.
10 C. A. Coulson, *Volume Commemoratif Victor Henri, Contribution a l'etude de la Structure Moleculaire*, Desoer, Liege, 1948, p. 15.
11 A. Hudson, R. A. Jackson, C. J. Rhodes and A. L. Del Vecchio, *J. Organomet. Chem.*, 1985, **280**, 173.
12 J. E. Huheey, *Inorganic Chemistry, Principles of Structure and Reactivity*, 2nd edn., Harper and Row, New York, 1978.
13 F. K. Cartledge and R. V. Piccione, *Organometallics*, 1984, **3**, 299.
14 L. Pauling, *J. Chem. Phys.*, 1969, **51**, 2767.
15 W. Cherry, N. Epiotis and W. T. Borden, *Acc. Chem. Res.*, 1977, **10**, 167.
16 J. H. Sharp and M. C. R. Symons, *J. Chem. Soc. A*, 1970, 3084.
17 M. Geoffroy and E. A. C. Lucken, *Helv. Chim. Acta*, 1970, **53**, 813.
18 C. Hesse, N. Leray and J. Roncin, *J. Chem. Phys.*, 1972, **57**, 749.
19 A. J. Dobbs, B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc. A*, 1971, 124.
20 E. A. V. Ebbsworth and J. J. Turner, *J. Chem. Phys.*, 1962, **36**, 2628.
21 M. Merritt and R. W. Fessenden, *J. Chem. Phys.*, 1972, **56**, 2353.
22 H. G. Viehe, Z. Janousek, R. Merenyi and L. Stella, *Acc. Chem. Res.*, 1985, **18**, 148.
23 H. G. Viehe, R. Merenyi, L. Stella and Z. Janousek, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 917.
24 L. Sylvander, L. Stella, H.-G. Korth and R. Sustmann, *Tetrahedron Lett.*, 1985, **26**, 749.
25 H.-G. Korth, P. Lommes, R. Sustmann, L. Sylvander and L. Stella, in *Substituent Effects in Free Radical Chemistry*, eds. H. G. Viehe, Z. Janousek and R. Merenyi, Reidel, Dordrecht, 1986.
26 C. J. Rhodes and E. Roduner, *Tetrahedron Lett.*, 1988, **29**, 1437.

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