EPR spectra of tris(trimethylsilyl)methyl(hydroxy)silyl radicals, $(Me_3Si)_3CSi(R)OH^{\bullet}$, and of tris(trimethylsilyl)methylsilanone radical anions, $(Me_3Si)_3CSi(R){=}O^{\bullet -}$ (R = H, Me, Et, Bu, Ph, F)

Alwyn G. Davies,[a,*] **Colin Eaborn,**[b,*] **Paul D. Lickiss**[b,†] **and Anthony G. Neville**[a]

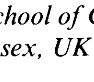
[a] *Chemistry Department, University College London, 20 Gordon Street, London, UK WC1H 0AJ*

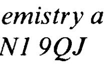
[b] *School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton, Sussex, UK BN1 9QJ*

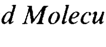
The EPR spectra are reported of the tris(trimethylsilyl)methylsilyl radicals $(Me_3Si)_3CSiH_{n-1}R_{3-n}$ (R = H, Et or F, n = 1, 2 or 3) which were prepared by abstraction of hydrogen atoms from the corresponding tris(trimethylsilyl)methylsilanes, $(Me_3Si)_3CSiH_nR_{3-n}$ by photolytically generated *tert*-butoxyl radicals in *tert*-butyl alcohol–di-*tert*-butyl peroxide as solvent. Similar reactions with the silanols $(Me_3Si)_3CSiH(R)OH$ (R = H, Me, Et, Bu, Ph, F) under neutral conditions gave the spectra of the corresponding hydroxysilyl radicals $(Me_3Si)_3CSi(R)OH^{\bullet}$, and, in the presence of potassium *tert*-butoxide, gave the spectra of the silanone radical anions $(Me_3Si)_3CSi(R){=}O^{\bullet -}$.

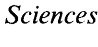
In recent years a number of compounds which show multiple bonding to silicon have been isolated.[1] These include silenes **1**, disilenes **2**, azasilenes **3** and phosphasilenes **4**, and in every case, kinetic stability has been achieved by the introduction into the molecules of at least three bulky groups R which inhibit oligomerisation.

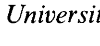
The intramolecularly coordinated silathiones shown in eqn. (1) (Ar = phenyl or 1-naphthyl) are stable but air-sensitive compounds, and the structure of the 1-naphthyl derivative has been determined by X-ray diffraction.[2] The related silaselenone (Ar = Ph) has also been isolated, but the corresponding silanone immediately trimerises.[2]

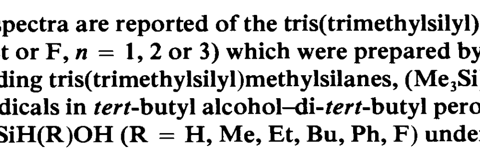

1


2


3


4


5


(1)

Monomeric silanones **5** have as yet been observed only in solid matrices;[3] apparently the presence of two bulky groups is not sufficient to prevent oligomerisation in fluid solution, but the formation of the silanones can be inferred from their reactions with traps such as dienes.[4] There is also evidence from kinetic studies of the transient formation of the silanone $Me_2Si{=}O$ by base cleavage of $RSiMe_2OH$ ($R = m\text{-}ClC_6H_4CH_2$ or $PhC{\equiv}C$) in aqueous methanol,[5] and of $(Me_3Si)_3CPhSi{=}O$ by reaction of $(Me_3Si)_3CPhSi(OH)I$ with NaOMe–MeOH[5] [and also of the related metasilicate ion $MeSi(O^-){=}O$ by base cleavage of $m\text{-}ClC_6H_4CH_2MeSi(OH)_2$ in aqueous Me_2SO or MeOH[6]].

$$\underset{\mathbf{7}}{\mathrm{Bu^t_2\dot{S}i{-}OH}} \xleftarrow{\mathrm{Bu^tO^{\bullet}}} \underset{\mathbf{6}}{\mathrm{Bu^t_2Si(H)OH}} \xrightarrow[\mathrm{Bu^tO^-}]{\mathrm{Bu^tO^{\bullet}}} \underset{\mathbf{8}}{\mathrm{Bu^t_2Si{=}O^{\bullet -}}} \qquad (2)$$

There is, however, good evidence from EPR spectroscopy for the existence of sterically stabilised silanone radical anions, $\mathbf{5}^{\bullet -}$, in solution.[7] If *tert*-butoxyl radicals are generated in solution, by photolysis of di-*tert*-butyl peroxide, in the presence of di-*tert*-butylsilanol **6**, the EPR spectrum of the di-*tert*-butylhydroxysilyl radical **7** can be observed, but if the reaction is carried out in the presence also of potassium *tert*-butoxide, a different spectrum which is assigned to the di-*tert*-butylsilanone radical anion **8** is generated.

We now report a study by a similar technique of the generation from tris(trimethylsilyl)methylsilanols, $(Me_3Si)_3CSiH(R)OH$, **9**, and some related compounds, of radicals by the removal of hydrogen atoms, and of radical anions by the removal of hydrogen atoms and protons. Much work in recent years has highlighted the unusual structures and novel reactions that can result from the presence of the tris(trimethylsilyl)methyl group, $(Me_3Si)_3C$[8] (frequently referred to below as the trisyl group, and denoted by Tsi), and a variety of derivatives are available where R in **9** is hydrogen, alkyl, halide, *etc.* It seemed possible that the presence of one tris(trimethylsilyl)methyl group would be sufficient to allow the observation of the silanone radical anions $(Me_3Si)_3CSi(R){=}O^{\bullet -}$, so that the effect of varying the group R could be investigated.

Results and discussion

It is often observed in photolytic EPR studies of sterically congested silicon-centred radicals that there is a problem with the spectra of unwanted persistent secondary radicals growing in intensity during periods of UV photolysis. In a previous study of tris(trimethysilylmethyl)silyl radicals,[9] this problem was overcome by modulating the irradiation at 3–4 Hz, and removing the unwanted signal by subtracting the spectrum obtained during the dark period from that obtained during photolysis. As only the persistent radical is present in the dark, its signal is removed by this process, and spectra of the radicals TsiSiRR′′(RR′ = H_2; Me,H; Ph,H; MePh; Me_2; Ph_2) were

---

[†] *Present address*: Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, UK SW7 2AY.

Table 1 EPR parameters of trisylhydroxysilyl radicals, trisylsilanone radical anions, and related trisylsilyl and trisylfluorosilyl radicals in *tert*-butyl alcohol at 250 K

No.	Radical	$a(n\text{H or F})$/G	a(27 H)/G	$a(^{29}\text{Si}\alpha)$/G	g
12	$(Me_3Si)_3CSi(H)OH^{\bullet}$	37.83 (1 H)[a]	0.13	212.2	2.002 48
13	$(Me_3Si)_3CSi(H){=}O^{\bullet-}K^+$	32.90 (1 H)	0.13	186.0	2.002 85
14	$(Me_3Si)_3CSi(Me)OH^{\bullet}$	4.55 (3 H)		208.1	2.002 29
15	$(Me_3Si)_3CSi(Me){=}O^{\bullet-}K^+$	4.25 (3 H)		172.1	2.002 72
16	$(Me_3Si)_3CSi(Et)OH^{\bullet}$	10.06 (1 H)[b]		199.0	2.002 32
17	$(Me_3Si)_3CSi(Et){=}O^{\bullet-}K^+$	8.70 (1 H)[b]		164.7	2.002 65
18	$(Me_3Si)_3CSi(Bu)OH^{\bullet}$	9.83 (1 H)[b]		198.5	2.002 33
19	$(Me_3Si)_3CSi(Bu){=}O^{\bullet-}K^+$	8.44 (1 H)[b]		164.8	2.002 65
20	$(Me_3Si)_3CSi(Ph)OH^{\bullet}$	0.11 (nH)[c]	0.11	< 102	2.002 31[d]
21	$(Me_3Si)_3CSi(Ph){=}O^{\bullet-}K^+$	0.11 (nH)[c]	0.11	< 75	2.002 65[d]
22	$(Me_3Si)_3CSi(F)OH^{\bullet}$	95.0 (1 F)[e]			2.001 67
23	$(Me_3Si)_3CSi(F){=}O^{\bullet-}K^+$	95.8 (1 F)[e]			2.001 91
24	$(Me_3Si)_3CSiH_2^{\bullet}$	14.1 (2 H)	0.2		
25	$(Me_3Si)_3CSiEtH^{\bullet}$	13.60 (1 Hα) 13.60 (1 Hβ) 2.6 (1 Hβ)			2.002 33
26	$(Me_3Si)_3CSiEtD^{\bullet}$	2.2 (1 D) 14.2 (1 Hβ) 2.5 (1 Hβ)			2.002 35
27	$(Me_3Si)_3CSiEt_2^{\bullet}$	10.4 (2 Hβ)			2.002 39
28	$(Me_3Si)_3CSiFH^{\bullet}$	40.7 (1 H) 61.4 (1 F)		241.4	2.002 61
29	$(Me_3Si)_3CSiFD^{\bullet}$	6.2 (1 D) 61.5 (1 F)			2.002 63
30	$(Me_3Si)_3CSiF_2^{\bullet}$	80.2 (2 F)			2.001 89

[a] Also a(1 H) 0.39 G. [b] Coupling is observed to only one of the two methylene protons. [c] Coupling to the phenyl protons had to be included to obtain convincing simulations. [d] At 280 K. [e] Coupling to α-fluorine.

Table 2 EPR parameters of silyl radicals[a]

Radical	$a(n\text{H})$/G	$a(n\text{F})$/G	$a(^{29}\text{Si}\alpha)$/G	g
$H_3Si^{\bullet}$	7.84		182	2.0032
$H_2SiF^{\bullet}$	34.6	55.2		2.0024
$HSiF_2^{\bullet}$	89.9	77.8		2.0013
$SiF_3^{\bullet}$		136.6	498	2.0003
$Me_3Si^{\bullet}$			181	
$Bu^t_3Si^{\bullet}$			160	
$PhSiH_2^{\bullet}$	10		169[b]	
$Ph_2SiH^{\bullet}$	14		160[b]	
$Ph_3Si^{\bullet}$			150[b,c]	

[a] C. J. Rhodes, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1475, and papers cited therein. [b] Recorded with the perdeuteriophenylsilanes. [c] An earlier value of 79.6 G appears to be in error (M. Geoffroy and E. A. C. Lucken, *Helv. Chim. Acta*, 1970, **53**, 813).

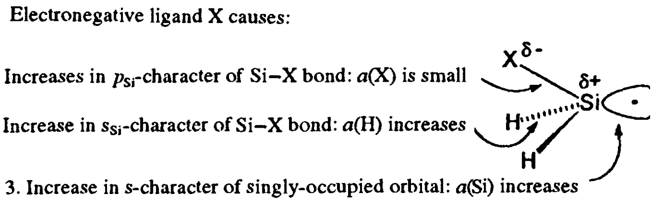
obtained. Although this works reasonably efficiently, it does require special instrumentation to perform the subtraction and it results in a significant loss of signal intensity and resolution. In the present work we have avoided the problem by the use of more conventional methods, as described below.

EPR studies have often been carried out by photolysing solutions of the silane in neat di-*tert*-butyl peroxide; we found that addition of an inert co-solvent such as cyclopentane or cyclopropane, or particularly *tert*-butyl alcohol, gave solutions which, on photolysis, were far less prone to produce secondary radicals, often with minimal loss of signal intensity. By this technique, particularly in some cases if it were combined with the use of Pyrex-filtered, rather than unfiltered, UV light, the rate of build up of unwanted signals could be reduced to such a level that electronic filtering of the spectra was unnecessary. In a number of the spectra, the ^{29}Si satellites (natural abundance ^{29}Si, 4.7%) could be detected.

This technique has been used in the present work. Neutral hydroxysilyl radicals **10** were generated by photolysis of di-*tert*-butyl peroxide in the presence of the silanol (Me$_3$Si)$_3$CSiH(R)–OH **9** in *tert*-butyl alcohol, and the silanone radical anions **11** by the same procedure with potassium *tert*-butoxide present in the solution. The spectra were analysed by computer simulation, and the results, together with those obtained from some related trisylsilyl and trisylfluorosilyl radicals, are presented in Table 1.

$$\underset{\mathbf{10}}{(Me_3Si)_3C\dot{S}i(R){-}OH} \xleftarrow{Bu^tO^{\bullet}} \underset{\mathbf{9}}{(Me_3Si)_3CSiH(R){-}OH} \xrightarrow[Bu^tO^-]{Bu^tO^{\bullet}} \underset{\mathbf{11}}{(Me_3Si)_3CSi(R){=}O^{\bullet-}} \quad (3)$$

EPR spectral data from the literature for some simple silyl radicals are presented in Table 2. These spectra are commonly rationalised in the following terms (Scheme 1).[10]


Electronegative ligand X causes:

1. Increases in p_{Si}-character of Si–X bond: a(X) is small
2. Increase in s_{Si}-character of Si–X bond: a(H) increases
3. Increase in s-character of singly-occupied orbital: a(Si) increases

Scheme 1

The value of $a(^{29}\text{Si})$ in the radicals H$_3$Si$^{\bullet}$ and Me$_3$Si$^{\bullet}$ (*ca.* 180 G) is about one quarter of the value expected for unit unpaired electron population of the Si-3s AO (*ca.* 800 G), therefore the orbital which carries the unpaired electron has about 1/4 s-character, and these radicals are pyramidal with 3sp^3-hybridised silicon (unlike alkyl radicals which are planar and 2sp^2-hybridised, with the unpaired electron in a *p*-orbital). Introduction of an electronegative ligand X such as fluorine into SiH$_3$ confers enhanced p-character on the Si–X bond, therefore increased s-character on the remaining Si–H bonds and the singly occupied orbital on silicon; the pyramidal character is enhanced, and both a(Hα) and $a(^{29}\text{Si})$ are increased. A second ligand X has a similar but smaller effect; a(Hα) and $a(^{29}\text{Si})$ increase further, and as the average polarity and p-character of the two Si–X bonds is lowered, the hyperfine coupling to the ligand, *e.g.* F, also increases. The introduction of phenyl ligands at the silicon apparently does not drastically affect the state of hybridisation of the silicon, though there is significant delocalisation of the unpaired electron into the aromatic rings.

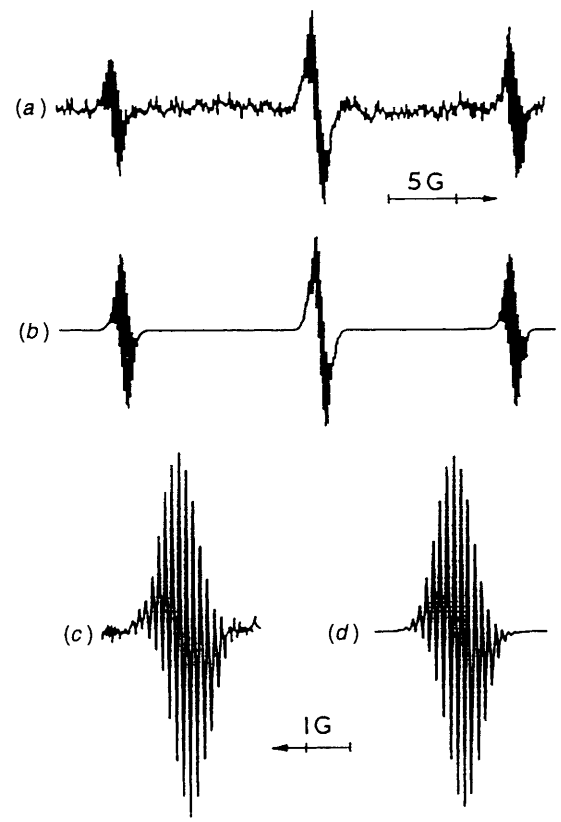


Fig. 1 (*a*) EPR spectrum of the trisylsilyl radical $\text{TsiSiH}_2^{\cdot}$ **24** in 1 : 1 $\text{Bu}^t\text{OH–Bu}^t{}_2\text{O}_2$ at 250 K; (*b*) computer simulation; (*c*) expansion of high-field multiplet; (*d*) computer simulation of (*c*) assuming 27 equivalent hydrogen atoms

The fact that the silyl radicals are pyramidal is supported by the observation that chiral radicals can retain their configuration throughout reactions.[11] The decrease in $a(^{29}\text{Si})$ which is observed with bulky ligands on silicon (*e.g.* $\text{Bu}^t{}_3\text{Sn}^{\cdot}$ *versus* $\text{Me}_3\text{Sn}^{\cdot}$) can be regarded as being the result of steric flattening of the pyramid, which puts more p-character into the SOMO, and thus provides supporting evidence for the connection between the hybridisation of the silicon and the structure of the radical.

This assumption that the changes in hybridisation can be related directly to the geometry at the radical centre has recently been challenged by Guerra.[12] *Ab initio* calculations, which accurately predicted the hyperfine coupling in a series of silyl radicals, revealed no relation between the structure at the radical site and the silicon hybridization in the SOMO. As yet, the structure of no silicon radical has been determined by direct experiment to check this conclusion, but for the time being, caution should be exercised in attempting to deduce structural information from trends in hyperfine coupling constants.

The spectra of the trisylsilyl radicals will now be discussed against this background.

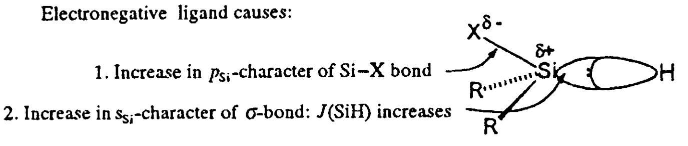
A comparison of the two techniques is provided by the spectrum of the trisylsilyl radical itself, $(\text{Me}_3\text{Si})_3\text{CSiH}_2^{\cdot}$, **24**. The spectrum which is shown in Fig. 1 was obtained using a 1 : 1 mixture of *tert*-butyl alcohol and di-*tert*-butyl peroxide by weight, with photolysis by Pyrex-filtered UV light; if unfiltered light was used, no recognisable signal could be obtained. The value of $a(2\text{H}\alpha)$ of 14.1 G obtained is similar to that reported previously (14.3 G),[10] but now the hyperfine coupling to the 27 trisyl protons can also be resolved.

For the hydroxysilyl radicals **10**, R = H, Me, Et or Bu, (**12**, **14**, **16**, **18**) and the fluorosilyl radical **28**, the hyperfine coupling to ^{29}Si could be measured (Table 1). For 10 silyl radicals not carrying Cl or Me_3Si ligands, it was shown previously that the value of $a(^{29}\text{Si})$ is related to that of $^1J(\text{SiH})$ in the parent silane by the eqn. (4); (note that both *a* and *J* have negative values).[13] The deviation of the points for the radicals $(\text{Me}_3\text{Si})_3\text{Si}^{\cdot}$ and $\text{Cl}_3\text{Si}^{\cdot}$ from this line was interpreted in terms of delocalisation of the unpaired electron on to the substituents.

$$a(^{29}\text{Si})/\text{G} = 1.625\,J(\text{SiH})/\text{Hz} + 123.9 \qquad (4)$$

From this equation, the values of $a(^{29}\text{Si})$, calculated from the NMR coupling constants (see Experimental), for our radicals are $(\text{Me}_3\text{Si})_3\text{CSi(Me)OH}^{\cdot}$ 210.0, $(\text{Me}_3\text{Si})_3\text{CSi(Bu)OH}^{\cdot}$ 205.7 and $(\text{Me}_3\text{Si})_3\text{CSiFH}^{\cdot}$ 246.6 G, in satisfactory agreement with the observed values of 208.1, 198.5 and 241 G, respectively. The phenyl-substituted radical $(\text{Me}_3\text{Si})_3\text{CSi(Ph)OH}^{\cdot}$ has an apparent value of $a(^{29}\text{Si})$ of less than 102 G, which is less than the value of 217.4 G which is calculated from the *J* parameters. A similar but much smaller effect is observed in the $\text{Ph}_3\text{Si}^{\cdot}$ radical, where the calculated and observed values of $a(^{29}\text{Si})$ are 198 and 150 G, respectively. As in the case of the Cl-substituents, this may indicate significant delocalisation into the phenyl rings, with a reduction of the spin density, and of the s character of the SOMO, at silicon.

This correlation between $J(\text{SiH})$ and $a(^{29}\text{Si})$ implies that the substituents at silicon have the same effect on the the singly occupied s-orbital in the radical (Scheme 1) and on the σ-bond in the silane, as illustrated in Scheme 2.



Scheme 2

We conclude that in the trisylsilyl radicals in Table 1, the unpaired electron occupies an orbital with about 25% of 3s character, and that, at least in the absence of a phenyl ligand, the radicals are pyramidal, though the precise geometry is open to question. A similar situation is obtained with the di-*tert*-butylhydroxysilyl radical **7**, which has $a(^{29}\text{Si})$ 186 G.[7] The high value of $a(^{29}\text{Si})$ in these hydroxysilanes presumably reflects the presence of the electronegative oxygen ligand.

The ^{29}Si coupling in the conjugate radical anions **11** was 33.7–36.2 G (**13**, **15**, **17**, **19**) less than that in corresponding radicals **10**. This difference is similar to that which was found for the radical **7**, $a(^{29}\text{Si})$ 186 G, and the radical anion **8**, $a(^{29}\text{Si})$ 151 G, Δa 35 G.[7] Again, these trisylsilanone radical anions **11**, like the di-*tert*-butylsilanone radical anion **8**, appear to be pyramidal at silicon. It is usually accepted that the high value of $a(^{13}\text{C})$ in the ketyl radical anions $\text{R}_2\text{C=O}^{\cdot -}$ [14] implies that these are likewise pyramidal at carbon.

In all the trisylsilanes studied, the *g* value for the radical anion **11** was 0.0002–0.0004 greater than that for the corresponding neutral radical **10**; again, the same situation was observed with the di-*tert*-butyl derivatives **7** (*g* 2.002 28) and **8** (*g* 2.0025).[7] This is consistent with the effect normally observed with an electronegative ligand (Table 2).

Trisylhydroxysilanyl radical 12 and trisylsilanal radical anion 13

The silanal radical anion **13** represents the first identification of a radical anion of a sila-aldehyde. In the spectra of **12** and **13**, the coupling to the 27 trisyl protons was resolved. All these protons appear to be equivalent at 300 K, implying rapid rotation of and within the trisyl group. The ^{1}H and ^{13}C NMR spectra of trisyl derivatives similarly show that the methyl groups are magnetically equivalent at room temperature, but, for example, $(\text{Me}_3\text{Si})_3\text{CSiCl}_3$ and $(\text{Me}_3\text{Si})_3\text{CSiBr}_3$ below 200 K show the presence of three magnetically distinct methyl groups, due to restriction of rotation.[15]

Of more significance is the fact that hyperfine coupling by the

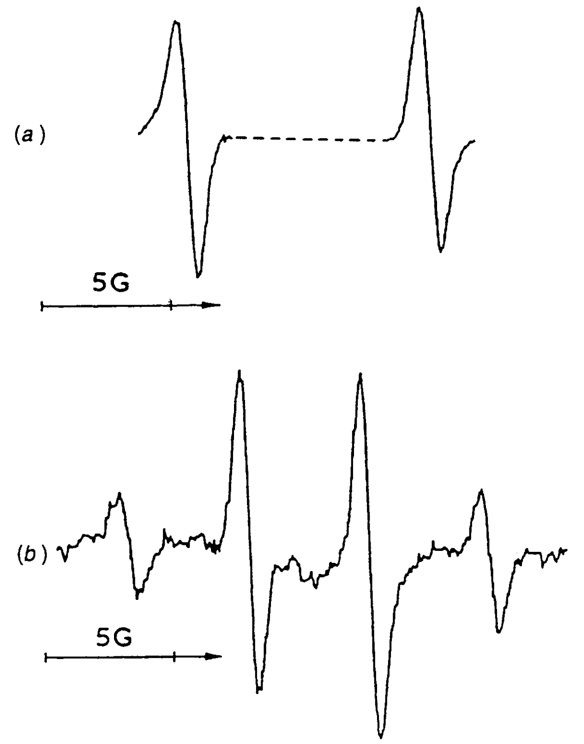
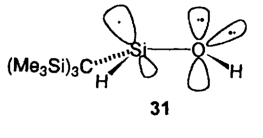
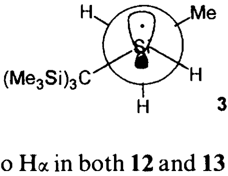


Fig. 2 EPR spectra of (*a*) the ethyltrisylsilanone radical anion (Me$_3$Si)$_3$CSiEt=O$^{\cdot-}$ (**17**); and (*b*) the methyltrisylsilanone radical anion (Me$_3$Si)$_3$CSiMe=O$^{\cdot-}$ (**15**)

OH group could be resolved in **12**, and is absent in the potassium salt **13**, supporting the contention that these two species are related as neutral radical and conjugate base. The low value of *a*(1 H) of 0.39 G implies that the OH bond lies close to the nodal plane of the singly occupied orbital, as illustrated in **31**. The same situation was encountered in **7**,[7] where *a*(1 H) was 0.87 G. No coupling to the potassium ion could be observed, but when sodium *tert*-butoxide was used as the base, the multiplet involving the 27 hydrogen atoms could no longer be resolved. This is probably best regarded as an inconclusive result, though it could arise from coupling by the sodium counter-ion leaving the spacing within the protic envelope too small to be resolved.


31


32

The magnitude of the coupling to Hα in both **12** and **13** (*ca.* 35 G) is larger than that in the radical Me$_2$SiH$^{\cdot}$[*a*(Hα) 17.0 G][10] but similar to that which is observed for silyl radicals carrying electronegative groups [*e.g.* H$_2$SiF$^{\cdot}$,[10] *a*(Hα) 34.6 G]. This may reflect an enhanced p-character in the Si–X bond, and a compensating increase in s-character in the H–Si bond (Scheme 1).

Methyl-, ethyl- and n-butyl-trisylhydroxysilanyl radicals 14, 16 and 18, and trisylsilanone radical anions, 15, 17 and 19

Fig. 2 shows the EPR spectra of the methyl- and ethyltrisylsilanone radical anions **15**, **17**; the spectrum of **19** was the same as that of **17**, except that the proton coupling was reduced from 8.7 to 8.4 G. It is immediately apparent that whilst the three hydrogens in the methyl group in **15** give rise to a binomial quartet as expected, with *a*(3 Hβ) 4.25 G, the methylene groups in the ethyl or butyl groups side chains of **17** and **19** give a doublet splitting rather than the anticipated triplet, with *a*(1 Hβ) 8.70 and 8.44 G, respectively. Qualitatively similar spectra were obtained from the neutral hydroxysilyl radicals **14**, **16** and **18**. Although coupling to the second β-hydrogen cannot be observed for either of these radical anions, the line-width is rather large, and so may be masking a small hyperfine coupling to this atom.

Table 3 Calculated dependence of spin density at Hβ on θ in alkylsilyl radicals

θ	ρ	θ	ρ
0°	0.117	210°	0.112
30°	0.085	240°	0.042
60°	0.027	270°	0.004
90°	0.004	300°	0.027
120°	0.042	330°	0.085
150°	0.112	360°	0.117
180°	0.144		

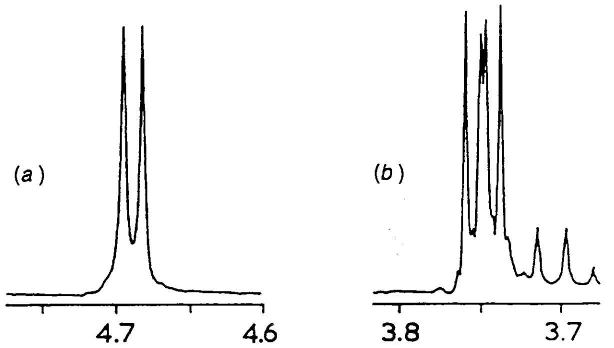


Fig. 3 Partial ^{1}H NMR spectra of (*a*) ethylhydroxytrisylsilane, and (*b*) ethyltrisylsilane

In order to investigate this anomaly, the radical (Me$_3$Si)$_3$CSi(Et)H$^{\cdot}$ (**25**) was generated by abstraction of hydrogen with the *tert*-butoxyl radical. It showed *a*(Hα) 13.60, *a*(1 Hβ) 13.60, *a*(1 Hβ) 2.6 G, *g* 2.002 33, and the assignment of the couplings was confirmed by generating the radical (Me$_3$Si)$_3$CSi(Et)D$^{\cdot}$ (**26**), which showed *a*(D) 2.2, *a*(1 Hβ) 14.2, *a*(1 Hβ) 2.5 G, *g* 2.002 35.

This non-equivalence of the methylene protons could reflect the fact that they are diastereotopic, or it could be the result of restriction of rotation about the Si–Et bond. The most stable conformation of the radical (Me$_3$Si)$_3$CSi(Et)H$^{\cdot}$ will be that in which the trisyl and methyl groups are located *trans*, as shown in **32**, and in which the dihedral angles θ between the two β-hydrogen atoms and the axis of the singly-occupied sp^3 orbital are 0° and 60°. The value of *a*(Hβ) will not depend on θ^2 as described by the Heller–McConnell equation[16] because that assumes that the electron is in a pure 2p orbital, therefore the relation between θ and the spin density (ρ) on Hβ was calculated by the INDO method using MNDO/3 optimised geometries. The results are given in Table 3, and show that the angular dependence of *a*(Hβ) is similar to that described by the Heller–McConnell equation for alkyl radicals, but the lower symmetry of the SOMO for the silyl radicals produces unequal maxima when $\theta = 0°$ or 180°.

Thus in **32** the proton with $\theta = 30°$ would be expected to give a small but non-zero coupling, whilst the other β-proton, with $\theta = 180°$, should show a large coupling, which is consistent with what is observed.

A similar magnetic inequivalence of the methylene protons is apparent in the ^{1}H NMR spectra. If the methylene protons were equivalent in the moiety RCH$_2$SiH, the SiH proton should give a triplet signal, but this is not observed. For example, in TsiSiEt(OH)H the Si*H* signal is a doublet as shown in Fig. 3(*a*). In TsiSiEtH$_2$, the methylene protons are not diastereotopic, yet they still show unequal coupling to the Si*H*$_2$ protons, as shown in Fig. 3(*b*), supporting the suggestion that the magnetic non-equivalence results from restricted rotation.

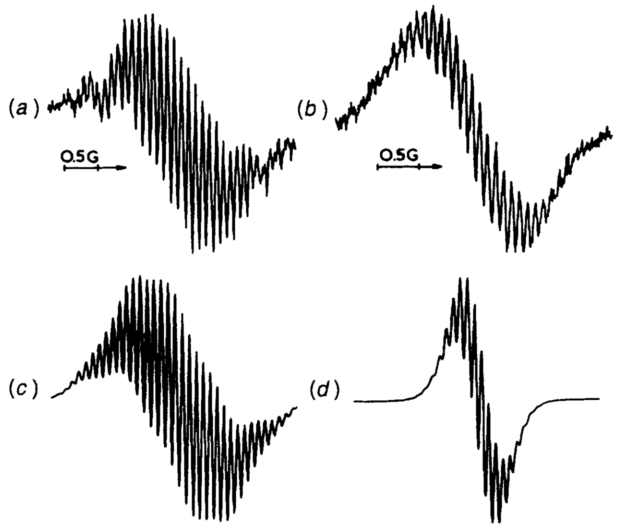


Fig. 4 (*a*) EPR Spectrum of the phenylhydroxytrisylsilyl radical, $(Me_3Si)_3CSi(Ph)OH^{\bullet}$ (**20**); (*b*) EPR spectrum of the phenyltrisylsilanone radical anion, $(Me_3Si)_3CSi(Ph){=}O^{\bullet -}$ (**21**); (*c*) possible simulation of the spectrum of **20** on the basis of *a*(27 H) 0.11, *a*(1 H) 0.43, *a*(3 H) 0.64 G; (*d*) simulation of spectrum with *a*(27 H) 0.11 G

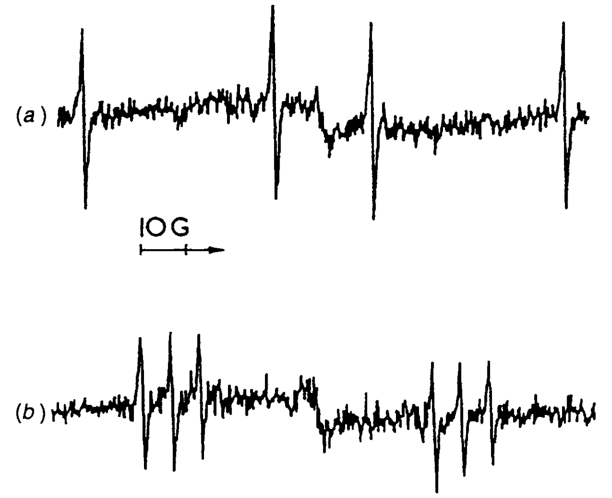


Fig. 5 EPR spectra of (*a*) the fluorotrisylsilyl radical, $(Me_3Si)_3CSiFH^{\bullet}$ (**28**), and (*b*) the fluorotrisylsilyl radical, $(Me_3Si)_3CSiFD^{\bullet}$ (**29**). The bottom spectrum is offset downfield to make it obvious that the smaller hyperfine coupling constant is changed on deuteriation.

Phenyltrisylhydroxysilanyl radical 20 and silanone radical anion 21

Of the 12 radicals detailed in Table 1, the neutral radical **20** and the radical anion **21** were the most prone to problems caused by the build-up of persistent secondary radicals, despite purification of the parent hydroxysilane by column chromatography. Spectra could not be recorded at 250 K, the temperature used for all the other observations, but at 280 K, with careful choice of the concentration of the di-*tert*-butyl peroxide and *tert*-butyl alcohol, reasonable spectra were obtained, as shown in Fig. 4.

The resolution is far better for the neutral radical than for the radical anion, but it is clear that in both spectra coupling to the trisyl protons is being observed, as it was for compounds **12** and **13**. The discussion that follows applies to the neutral radical only, as the poor resolution of the spectrum of the silanone radical anion does not allow a detailed treatment.

The simulation shown in Fig. 4(*d*) is that for 27 equivalent hydrogens, *i.e.* for the δ-hydrogens of the trisyl group, with the splitting shown in the spectrum of the phenylhydroxysilyl radical, Fig. 4(*a*). This simulation is clearly much too narrow. Inclusion of another coupling to a single hydrogen, *i.e.* the hydroxylic hydrogen, also does not give a fair simulation. It appears then that in this radical there is resolvable coupling to hydrogens in the phenyl ring. Since the spectrum which is obtained consists of a smooth envelope of peaks which is lacking in characteristic features, it is impossible to assign a unique simulation to the spectrum with any conviction, as various similar coupling parameters give quite close fits. However, the simulation presented in Fig. 4(*c*) which assumes coupling to two identical *ortho* and the *para* hydrogens, in addition to the hydroxylic and trisyl hydrogens, was judged to give the best match.

This indication of electron density in the phenyl ring might imply that unfavourable steric interactions between the very bulky trisyl group, the reasonably large phenyl ring, and the solvated hydroxylic group are causing the silyl radical to be less pyramidal than usual, so that the SOMO has more 2p character and can overlap with the aromatic π-system. If this were true, then the ^{29}Si coupling for this radical ought to be lower than normal, as both the increased p-character of this orbital and the delocalisation of the unpaired electron density away from the silicon atom would reduce the coupling. Unfortunately the build-up of permanent signals in the middle region of the spectrum prevented the identification of the ^{29}Si satellites, and it was possible to place only an upper limit on the coupling constant of *ca.* 100 G for the neutral radical and 75 G for the radical anion.

Fluorotrisylhydroxysilyl radical 22 and silanone radical anion 23

The spectrum of **23** represents the first example of the identification of the radical anion of a sila-acyl halide. Indeed no EPR spectra appear to be known of radical anions of acyl halides, $RCX{=}O^{\bullet -}$, probably because they readily dissociate into $RC{=}O^{\bullet}$ and X^-; in the case of the sila-acyl fluoride, dissociation is prevented by the strength of the Si–F bond.

Although there is little difference between the α-^{19}F coupling in the neutral radical (95.0 G) and in the radical anion (95.8 G), the difference in *g*-value supports the belief these are two separate species, and the concentration of the base could be greatly reduced without altering either the coupling or *g*-value of the radical anion.

The only EPR spectra of fluorosilyl radicals in the literature are of $FSiH_2^{\bullet}$, $F_2SiH^{\bullet}$ and $F_3Si^{\bullet}$, and of $Me_2SiF^{\bullet}$,[10] which show a large variation in *a*(^{19}F) and *g*-values (Table 2), and the radicals $TsiSiFH^{\bullet}$ **28** and $TsiSiF_2^{\bullet}$ **30** were therefore studied to give more information about the systematics of the coupling constants and *g*-values.

The spectrum of the radical $TsiSiFH^{\bullet}$ is shown in Fig. 5(*a*). In order to distinguish between the doublet coupling by ^1H and ^{19}F, the radical $TsiSiFD^{\bullet}$ **29** was also generated, and the spectrum is shown in Fig. 5(*b*) and coupling constants and *g*-values are given in Table 1. For **24**, **28** and **30**, the values of *a*(*n*Hα) and *a*(*n*Fα) increase, and that of *g* decreases, as fluorine ligands are progressively introduced. This endorses the generalisation which was inferred from the data for $FSiH_2^{\bullet}$, $F_2SiH^{\bullet}$ and $F_3Si^{\bullet}$ in Table 2, and related compounds, and is consistent with the model in Scheme 1.

Conclusions

This work has added a further six examples of silanone radical anions to the one which was already known, and includes the first radical anions of a sila-aldehyde and sila-acyl halide. There was no evidence for the rearrangements which trisylsilanes can show when siliconium ions are generated.[8,17] The radical anions are not long-lived under the experimental conditions, but the mechanism of decay, and the decay products, are not known. It would be interesting to investigate the UV photochemistry which does generate persistent radicals, and to identify the decay products, which could indicate the conditions under which the silanones themselves might be observable.

The radicals $(Me_3Si)_3CSiH_nF_{2-n}^{\bullet}$ represent only the second series of fluorosilyl radicals for which the EPR spectra have been described. The spectral parameters show the same trends as those reported for the radicals H_nSiF_{3-n}, and are consonant with the model (Scheme 1) for the interpretation of the hyperfine coupling constants which is based on the dependence of the hybridisation of the silicon on the electronegativity of the ligands.

Experimental

Unless otherwise reported, ^1H, ^2H and ^{13}C NMR spectra were recorded on solutions in $CDCl_3$ using a Varian VXR-400 spectrometer.

EPR Spectra were recorded on a Varian E-109 spectrometer. An Osram HBO-500 W/2 mercury discharge lamp in an Oriel Universal housing was focused on the cavity, and provided with neutral bronze gauze transmission filters, and Pyrex and soda-glass cut-off filters. Most of the spectra reported here were obtained using the Pyrex filter which cuts off the light below 300–350 nm.

Hydroxytrisylsilane,[18] methylhydroxytrisylsilane[19] ($^1J_{SiH}$ 205.5 Hz) and phenylhydroxytrisylsilane[20] ($^1J_{SiH}$ 210 Hz) were prepared by the methods as previously described.

Tris(trimethylsilyl)methane

Tris(trimethylsilyl)methane (TsiH) was prepared from Me_3SiCl, $HCBr_3$ and Mg[21] and purified by column chromatography.

[1,1,1-$^2H_3$]Trisylsilane

Trichlorotrisylsilane was made as described in ref. 21, and was reduced with lithium aluminium deuteride in THF to give [1,1,1-$^2H_3$]trisylsilane, which was sublimed at 100 °C/0.1 mmHg (59% yield). Its physical properties were similar to those of $TsiSiH_3$ prepared in the same way; $\delta_D(CHCl_3–CDCl_3)$ 3.7 (br s).

Ethyldichlorotrisylsilane

Ethyldichlorotrisylsilane was made by the route used for similar chlorosilanes.[22]

Trisyllithium was prepared[23] from TsiH (1.94 g, 8.3 mmol) and methyllithium (1.4 mol dm^{-3}; 9 cm^3, 12 mmol). Ethyltrichlorosilane (1.6 cm^3, 12 mmol) was added dropwise to the stirred solution at room temperature causing immediate precipitation. The mixture was heated under reflux for 1 h. The cooled solution was then quenched with saturated aq. ammonium chloride (20 cm^3). The inorganic layer was removed and washed with diethyl ether (2 × 20 cm^3). The combined organic solutions were then washed with water (2 × 20 cm^3) and dried (magnesium sulfate). Removal of the solvent under vacuum gave the crude dichlorosilane, which was purified by washing with cold methanol and sublimation (90–110 °C/0.005 Torr) (Found: C, 39.9; H, 8.9; Cl, 19.7. $C_{12}H_{32}Cl_2Si_4$ requires C, 40.08; H, 8.97; Cl, 19.72%); $\delta_H(CDCl_3)$ 0.35 [27 H, s, $Si(CH_3)_3$] and 1.13–1.21 (5 H, m, $SiCH_2CH_3$); $\delta_C(CDCl_3)$ 17.41 (CH_2CH_3), 7.98 (CSi_4) and 4.97 [CH_2CH_3, $Si(CH_3)_3$]; *m/z* 345 (M − Me, 82%), 343 (100), 235 (54), 221 (65) and 73 (79).

Ethyltrisylsilane

(*i*) THF (*ca.* 50 cm^3) was distilled from lithium aluminium hydride directly into the reaction vessel. Ethyldichlorotrisylsilane (829 mg, 2.31 mmol) was added, followed by lithium aluminium hydride (0.22 g, 5.8 mmol). The mixture was then refluxed for 48 h. TLC indicated the presence of the starting material, so a second portion of lithium aluminium hydride (0.22 g, 5.8 mmol) was added and the solution was refluxed for a further 24 h. This was repeated with a third sample of the reducing agent (0.18 g, 4.7 mmol) as TLC still indicated the presence of the starting material.

The reaction was quenched with wet diethyl ether (5 cm^3) followed by saturated aq. ammonium chloride (10 cm^3). Water (10 cm^3) was added and the aqueous layer extracted with diethyl ether (4 × 30 cm^3). The combined organic fractions were then washed with water (2 × 30 cm^3) and dried (magnesium sulfate). The solvent was removed under reduced pressure, and the crude mixture was carefully sublimed to give 106 mg of sublimate containing 90 mg (15% yield) of $EtTsiSiH_2$ as indicated by NMR spectroscopy. Recrystallisation (ethanol) gave pure ethyltrisylsilane (Found: C, 49.5; H, 11.9. $C_{12}H_{34}Si_4$ requires C, 49.57; H, 11.79%); $\delta_H(CDCl_3)$ 0.18 [27 H, s, $Si(CH_3)_3$], 0.79 (2 H, m, $SiCH_2$), 1.02 (3 H, t, *J* = 7.7 Hz, CH_2CH_3) and 3.77 (2 H, dd, *J* = 4.8, 5.2 Hz, SiH_2); *m/z* 276 (M − Me, 30%), 275 (100), 187 (30), 73 (57) and 59 (22).

(*ii*) To confirm the identity of the product, it was also prepared by a different method.

Ethyllithium solution (6.0 cm^3, 1.3 mmol) was added to a solution of trisylsilane (0.352 g, 1.3 mmol) in diethyl ether (20 cm^3) at 0 °C. The mixture was warmed to room temperature then stirred for 1 h, and quenched with water. The mixture was extracted with ether (3 × 20 cm^3) and the combined organic fractions were washed with water (2 × 30 cm^3) then dried ($MgSO_4$). Removal of the solvent, and recrystallisation of the residue from EtOH gave ethyltrisylsilane in 55% yield. It was identical to the material obtained above.

[1,1-$^2H_2$]-Ethyltrisylsilane

This was produced in 65% yield from [1,1,1-$^2H_3$]-trisylsilane as described immediately above. Its spectroscopic data were identical with those for $(Me_3Si)_3CSiH_3$ except for the obvious differences caused by deuteriation; $\delta_D(CHCl_3–CDCl_3)$ 3.6 (br s).

Diethyltrisylsilane

Ethyltrisylsilane was ethylated as described above to give diethyltrisylsilane in 62% yield; δ_H 0.20 (27 H, s, SiMe), 1.07 (6 H, t, *J* 7.6 Hz, CH_2CH_3), 0.86 (4 H, br m, CH_2CH_3) and 3.80 (1 H, t, *J* 5.4 H, SiH); *m/z* 301 (M − Me, 100%), 79 (45%), 302 (40%), 187 (38%) and 59 (29%).

Ethylhydroxytrisylsilane

Iodine monochloride (61 mg, 0.38 mmol) in CCl_4 (1 cm^3) was added dropwise to a stirred solution of ethyltrisylsilane (110 mg, 0.38 mmol) in CCl_4 (10 cm^3). The mixture was stirred for 15 min at room temperature, and the solvent was then removed under reduced pressure and replaced by a mixture of THF (40 cm^3) and water (1 cm^3). The mixture was stirred for 15 min, then the product was isolated as described for hydroxytrisylsilane,[18] and purified by chromatography (Merck kieselgel 60, eluted with chloroform 60–80 °C light petroleum, 50/50 by volume as eluent) to give ethylhydroxytrisylsilane (89 mg, 76%); δ_H 0.224 (27 H, s, $SiMe_3$), 0.801 (2 H, m, $SiCH_2$), 1.074 (3 H, t, *J* 5.8 Hz, CH_2CH_3) and 4.690 (1 H, d, *J* 4.9 Hz, SiH); the Si*OH* signal was not observed.

Butylhydroxytrisylsilane

Butyliodotrisylsilane[24] was heated under reflux in a mixture of acetone and water (1 : 1 v/v). The solution was cooled, and the volatile material was removed under reduced pressure. The residue was dissolved in light petroleum and the solution was shaken with aq. $NaHSO_3$. Evaporation of the solution left a solid which was sublimed to give TsiSiBu(OH)H (72% yield); δ_H 0.202 (27 H, s, $SiMe_3$), 0.86–0.96 (4 H, m, $SiCH_2CH_2$), 1.35–1.58 (5 H, m, CH_2CH_3) and 4.71 (1 H, d, *J* 4.9 Hz, SiH); the Si*OH* signal was not observed.

Fluorotrisylsilane

Trisylsilane (1.23 g, 4.7 mmol) was iodinated by the method described above. The iodide obtained was dissolved in diethyl ether containing silver tetrafluoroborate (1.02 g, 5.3 mmol), the mixture was stirred for 1 h, and the silver iodide then filtered off. The solvent was removed, giving fluorotrisylsilane, which was sublimed; δ_H(200 MHz, $CDCl_3$) 0.228 (27 H, s, $SiMe_3$), 4.868 (2 H, d, J_{HF} 52.0 Hz, SiH_2. The MS and IR spectra were identical to those obtained previously.[24]

[1,1-$^2H_2$]-Fluorotrisylsilane

The deuteriated fluoride was produced in 85% yield from [1,1,1-$^2H_3$]-trisylsilane as described above for the undeuteriated compound. The physical properties were identical to those of the undeuteriated compound except for the obvious differences caused by deuteriation.

Fluorohydroxytrisilylsilane

Fluorotrisylsilane was iodinated and the iodo-compound was hydrolysed as above to give the desired hydroxysilane, which was purified by column chromatography (Merck kieselgel 60, eluted with chloroform/60–80 light petroleum 75/25 by volume) in 75% yield over the two steps; δ($CDCl_3$) 0.356 (27 H, s, $SiMe_3$) and 4.96 (1 H, d, $^1J_{SiH}$ 210 Hz, $^2J_{HF}$ 71 Hz, SiH); the Si*OH* signal was not observed.

Difluorotrisylsilane

Fluorotrisylsilane was iodinated and fluorinated as described for the preparation of fluorotrisylsilane above. The crude difluoride was purified by column chromatography (Merck kieselgel 60, eluted with 60–80 light petroleum) and obtained in 67% yield.

EPR Experiments

The following examples illustrate the technique for obtaining the spectra of the neutral radicals and of the radical anions.

(*i*) Ethylhydroxytrisilylsilane (25 mg) was dissolved in a mixture of *tert*-butyl alcohol (172 mg) and di-*tert*-butyl peroxide (279 mg). The solution was degassed with a stream of nitrogen at room temperature, then transferred to a nitrogen-flushed Suprasil silica sample tube in the pre-cooled EPR cavity.

The sample was irradiated with Pyrex-filtered UV light, and a series of 12 spectra were recorded between 250 and 304 K.

(*ii*) Phenylhydroxytrisylsilane (31 mg) was dissolved in a mixture of *tert*-butyl alcohol (111 mg), di-*tert*-butyl peroxide (242 mg), and a solution of potassium (11 mg) in *tert*-butyl alcohol (115 mg). The sample was treated as above, and spectra were recorded between 250 and 290 K.

Acknowledgements

We acknowledge the provision by the SERC of a Research Studentship to A. G. N. and of a Grant towards the NMR and EPR instrumentation at UCL and one in support of the work at Sussex.

References

1 J. Chojnowski and W. Stanczyk, *Adv. Organomet. Chem.*, 1990, **30**, 243; N. C. Norman, *Polyhedron*, 1993, **12**, 2431; Y. Apeloig, in *The Chemistry of Organosilicon Compounds*, ed. S. Patai and Z. Rappoport, Wiley, Chichester, 1989, pp. 57–225.

2 P. Arya, J. Boyer, F. Carre, R. Corriu, G. Lanneau, J. Lapasset, M. Perrot and C. Priou, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1016.

3 R. Withnall and L. Andrews, *J. Phys. Chem.*, 1988, **92**, 594; V. N. Khabashesku, Z. A. Kerzina, A. K. Maltsev and O. M. Nefedov, *J. Organomet. Chem.*, 1989, **364**, 301.

4 G. Manuel, G. Bertrand and F. El Anba, *Organometallics*, 1983, **2**, 391; C. A. Arrington, R. West and J. Michl, *J. Am. Chem. Soc.*, 1983, **105**, 6176; V. N. Khabashesku, Z. A. Kerzina, E. G. Baskir, A. K. Maltsev and O. M. Nefedov, *J. Organomet. Chem.*, 1988, **347**, 277.

5 Z. H. Aiube, J. Chojnowski, C. Eaborn and W. A. Stanczyk, *J. Chem. Soc., Chem. Commun.*, 1983, 493.

6 C. Eaborn and W. A. Stanczyk, *J. Chem. Soc., Perkin Trans. 2*, 1984, 2099; C. J. Chmielecka, J. Chojnowski, W. A. Stanczyk and C. Eaborn, *J. Chem. Soc., Perkin Trans. 2*, 1989, 865.

7 A. G. Davies and A. G. Neville, *J. Organomet. Chem.*, 1992, **436**, 255.

8 C. Eaborn, in *Organosilicon and Bioorganosilicon Chemistry*, ed. H. Sakurai, Ellis Horwood, Chichester, 1985, p. 123; J. D. Smith, *Pure Appl. Chem.*, 1986, **58**, 623; A. R. Bassindale and P. G. Taylor, *The Chemistry of Organic Silicon Compounds*, Wiley, Chichester, 1989, p. 880; C. Eaborn and J. D. Smith, *Coord. Chem. Rev.*, in the press; C. Eaborn, K. Izod and J. D. Smith, *J. Organomet. Chem.*, 1995, **500**, 57.

9 A. I. Al-Wassil, C. Eaborn, A. Hudson and R. Jackson, *J. Organomet. Chem.*, 1983, **258**, 271.

10 C. J. Rhodes, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1475, and refs. therein cited.

11 H. Sakurai, M. Murakami and M. Kumada, *J. Am. Chem. Soc.*, 1969, **91**, 519.

12 M. Guerra, *J. Am. Chem. Soc.*, 1993, **115**, 11926. For similar arguments applied to carbon-centred radicals, see M. Guerra, *J. Phys. Chem.*, 1995, **99**, 81.

13 A. Hudson, R. A. Jackson, C. J. Rhodes and A. L. del Vecchio, *J. Organomet. Chem.*, 1985, **280**, 173.

14 A. G. Davies and A. G. Neville, *J. Chem. Soc., Perkin Trans. 2*, 1992, 163.

15 A. Avent, S. G. Bott, J. A. Ladd, P. D. Lickiss and A. Pidcock, *J. Organomet. Chem.*, 1992, **427**, 9.

16 C. Heller and H. M. McConnell, *J. Chem. Phys.*, 1960, **32**, 1535.

17 C. Eaborn, D. A. R. Happer, S. P. Hopper and K. D. Safa, *J. Organomet. Chem.*, 1980, **188**, 179.

18 R. I. Damja and C. Eaborn, *J. Organomet. Chem.*, 1985, **290**, 267.

19 C. Eaborn and D. E. Reed, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1695.

20 Z. H. Aiube, N. H. Buttrus, C. Eaborn, P. B. Hitchcock and J. A. Zora, *J. Organomet. Chem.*, 1985, **292**, 177.

21 R. L. Merker and M. J. Scott, *J. Am. Chem. Soc.*, 1963, **85**, 2243.

22 S. S. Dua, C. Eaborn, D. A. R. Happer, S. P. Hopper, K. D. Safa and D. R. M. Walton, *J. Organomet. Chem.*, 1979, **178**, 75.

23 M. A. Cook, C. Eaborn, A. E. Jukes and D. R. M. Walton, *J. Organomet. Chem.*, 1970, **24**, 529.

24 D. B. Azarian, C. Eaborn and P. D. Lickiss, *J. Organomet. Chem.*, 1987, **330**, 1.

Paper 5/05400A
Received 11*th August* 1995
Accepted 28*th September* 1995