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FULL PAPER

Magnetic resonance spectroscopic studies of a tetraaryl-distannene and -digermene $[M_2R_4]$ (R = C_6HBu^t-2-Me_3-4,5,6 and M = Sn or Ge) †

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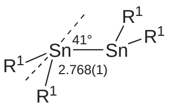
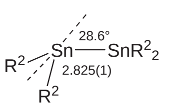
Tin-119 NMR spectral studies in the solid state and in solution of $[Sn_2R_4]$ (R = C_6HBu^t-2-Me_3-4,5,6) **3** are presented. The ambient temperature ^{119}Sn CP-MAS NMR spectrum displayed a single resonance at δ_{iso} 819, while variable-temperature spectra in toluene clearly indicated the existence of a rapid equilibrium between the loosely held dimer **3** and its monomer SnR_2. Photolysis of either **3** or its digermanium analogue in benzene yielded the persistent radicals $[MR_3]^\bullet$ (M = Ge or Sn), which were studied by ESR spectroscopy. The ESR parameters are compared with other trialkyl- and triamido-tin(III)- and -germanium(III)-centred radicals. Noteworthy is the first observation of ^{13}C hyperfine coupling for a Group 14 metal-centred radical, 18(1) G for $[SnR_3]^\bullet$ and 10(1) G for $[GeR_3]^\bullet$.

The red tetraaryldistannene $[Sn_2\{CH(SiMe_3)_2\}_4]$ **1** was the first compound reported to have a homonuclear (double) bond between heavier Group 14 elements.[1,2] Compound **1** was made and characterised by X-ray crystallography in 1976, but almost 20 years passed before two further molecules, both stable in the solid state, containing tin–tin bonds were reported: $[Sn_2\{Si(SiMe_3)_2\}_4]$ **2**[3] and $[Sn_2R_4]$ (R = C_6HBu^t-2-Me_3-4,5,6) **3**.[4] Although the tetraaryldistannene $[Sn_2(C_6H_2Pr^i_3$-2,4,6$)_4]$ had been prepared thermally and photochemically from the corresponding cyclotristannane $[\{Sn(C_6H_2Pr^i_3$-2,4,6$)_2\}_3]$, it had not been X-ray characterised, since it reverted completely to the three-membered ring precursor at room temperature.[5] A possible weak tin–tin interaction has been detected in $[Sn_2\{C_6H_2(CF_3)_3$-2,4,6$\}_4]$, which has close Sn···F contacts;[6a] however, the tin–tin separation of 3.64 Å is much too large for there to be significant Sn···Sn bonding.[6b]



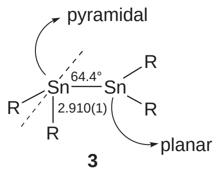
1

$R^1 = CH(SiMe_3)_2$



2

$R^2 = Si(SiMe_3)_3$



3

R = C_6HBu^t-2-Me_3-4,5,6

The three crystalline ditin compounds $[Sn_2R^x_4]$ **1**–**3** vary appreciably in their geometry, but the R^x–Sn–R^x angle at each of the tin atoms is identical. Although the centrosymmetric **1** has an undistorted *trans*-bent arrangement with a fold angle of 41° which closely approaches the theoretically predicted fold angles of between 46 and 51° for the parent compound $[Sn_2H_4]$,[2,7] the strongly distorted *trans*-bent compound **2** avoids steric strain imposed by its substituents by torsion about the Sn–Sn vector resulting in twist angles of 63.2°, the fold angle being 28.6°.[3] The nature of compound **3** is even more unusual: the somewhat large Sn–Sn bond length, as well as the differing environments of the two tin atoms, have been taken as evidence that in this case the bonding may be represented by a donor–acceptor interaction involving overlap between the occupied s orbital of one tin atom and an empty p orbital of the other.[4]

The tin–tin interaction in **1** has been described as representing a 'double bond', because of the compound's diamagnetism and its short Sn–Sn distance of 2.768(1) Å (*cf.* the Sn–Sn separation of 2.81 Å in tetrahedral tin).[1,2] However, the Sn–Sn bond in **1** is weak, as evident by the almost complete dissociation of **1** into the monomer $[Sn\{CH(SiMe_3)_2\}_2]$ **4** in both a dilute hydrocarbon solution and in the gas phase.[8,9]

The distannene **1** has been characterised by NMR spectroscopy in $[^2H_8]$toluene (^{13}C and ^{119}Sn)[9,10] and in the solid state (^{13}C and ^{119}Sn CP-MAS).[10] In summary, in solution there is a rapid $\mathbf{1} \rightleftharpoons 2 \times \mathbf{4}$ dissociative process, with ΔH −53.6 kJ mol^{-1} and ΔS −138.1 J K^{-1} mol^{-1}.[10] In solid **1**, the tin chemical shift was found at δ 692 at room temperature (and δ 613 at 77 K).[10] In $[^2H_8]$toluene, the ^{119}Sn-$\{^1H\}$ signal was located at δ 2315 at 375 K and assigned to the monomer **4**.[9,10] No signal was observed at room temperature (probably because of the fast $\mathbf{1} \rightleftharpoons 2 \times \mathbf{4}$ process), but two resonances were observed at 165 K at δ 740 and 725 attributed to **1** and its *cis* isomer.[10]

A solution of the distannene **3** in $[^2H_8]$toluene showed δ ^{119}Sn-$\{^1H\}$ 1401 at 373 K, assigned to the monomer SnR_2 **5**, while at a lower temperature no signal appeared.[4] Herein, we report a more detailed variable-temperature ^{119}Sn-$\{^1H\}$ NMR study of the equilibrium $\mathbf{3} \rightleftharpoons 2 \times \mathbf{5}$ and CP-MAS data for crystalline **3**.

Irradiation at ambient temperature of a benzene solution of **1** or of $[Ge_2\{CH(SiMe_3)_2\}_4]$ afforded the appropriate radical $[M\{CH(SiMe_3)_2\}_3]^\bullet$ (M = Sn or Ge) which was indefinitely persistent.[11,12] We describe below similar experiments on **3** and its germanium analogue.[13]

Results and Discussion

The ^{119}Sn-$\{^1H\}$ NMR spectrum of a $[^2H_8]$toluene solution of **3** was re-examined (*cf.* ref. 4). At 373 K, a sharp signal was found at δ 1401. Upon lowering the temperature, this was shifted to lower frequencies and was broadened until at temperatures between 238 and 218 K it was no longer apparent, Table 1. As the temperature was further decreased to 210 K, however, the resonance once again became observable, Fig. 1.

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† No reprints available.
Non-SI unit employed: G = 10^{-4} T.

Table 1 Temperature dependence ($\Delta\delta/\Delta T$) of the ^{119}Sn-{^{1}H} chemical shift (δ) and its linewidth ($\omega_{\frac{1}{2}}$) of **3** in [$^2H_8$]toluene

T/K	δ	$\omega_{\frac{1}{2}}$	$\Delta\delta/\Delta T$
373	1401	185	—
350	1379	400	0.96
320	1357	470	0.74
298	1329	520	1.27
279	1248	1500	4.26
258	1079	6000	8.05
238	*	—	—
218	*	—	—
210	798	4500	—

* Not observed.

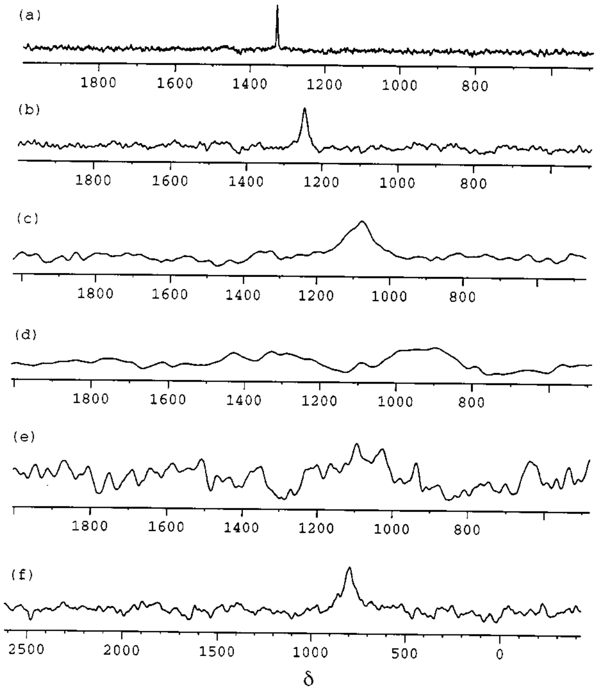


Fig. 1 Variable-temperature ^{119}Sn-{^{1}H} NMR spectra of $(SnR_2)_2$ (R = C_6HBu^t-2-Me_3-4,5,6) **3** in [$^2H_8$]toluene: (a) 298, (b) 278, (c) 258, (d) 238, (e) 218 and (f) 210 K

The non-linear temperature dependence, $\Delta\delta/\Delta T$, of the ^{119}Sn NMR chemical shift of the resonance observed in the solution state ^{119}Sn-{^{1}H} NMR spectra of **3** above 238 K indicates that (i) there is a rapid equilibrium between **3** and its monomer SnR_2 (R = C_6HBu^t-2-Me_3-4,5,6) **5**, and (ii) at 373 K there is a complete dissociation into the monomer **5**. As the temperature was lowered, not only did the exchange rate decrease, until at temperatures between 238 and 218 K the resonance was broadened over some 580 ppm, but the equilibrium concentration of **5** also decreased until at 210 K the equilibrium had shifted almost completely in favour of the dimer **3**. Based on a coalescence temperature of either 238 or 218 K, activation barriers of 33.8 and 33.9 kJ mol^{-1} place an upper and lower limit on this dissociative process. Thus, **3** dissociates significantly more readily than **1**, which is consistent with the structural data for these crystalline distannenes.

The ^{119}Sn CP-MAS NMR spectrum of **3**, also displayed a single resonance at δ_{iso} 819, Fig. 2. The associated span, Ω, compared well with that previously observed for the dimeric Sn^{II} species $[Sn_2\{CH(SiMe_3)_2\}_4]$ **1**.[10] The ^{119}Sn CP-MAS NMR spectral signal for crystalline **3** indicated the presence of only one Sn environment. This evidence does not support the previous description of the solid-state structure of this molecule in which a donor–acceptor dimer ($R_2Sn \leftarrow SnR_2$)[4] was proposed and for which two different ^{119}Sn NMR isotropic shifts would be anticipated. The suggestion of the donor–acceptor nature of this dimer was based on the different 'fold angles' determined for each Sn of **3**. These angles are, however, artefacts if each SnR_2 moiety is considered as an independent V-shaped monomer; the geometry of each is identical, as previously noted.[4] It is proposed that, as for the amide $[Sn\{N(SiMe_3)_2\}_2]$[14] and aryloxide $[Sn(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2]$,[15] **3** is a poorer Lewis acid or base than $[Sn\{CH(SiMe_3)_2\}_2]$ **4**, and hence exhibits little or no significant bonding interaction between the neighbouring Sn atoms. Further support for this conclusion derives from (i) the failure to detect any ^{117}Sn–^{119}Sn coupling in the ^{119}Sn CP-MAS NMR spectrum of **3**, in contrast to that (1.34 kHz) detected for **1**;[10] and (ii) the much smaller difference in chemical shifts between **3** and its monomer **5** than between **1** and **4**.

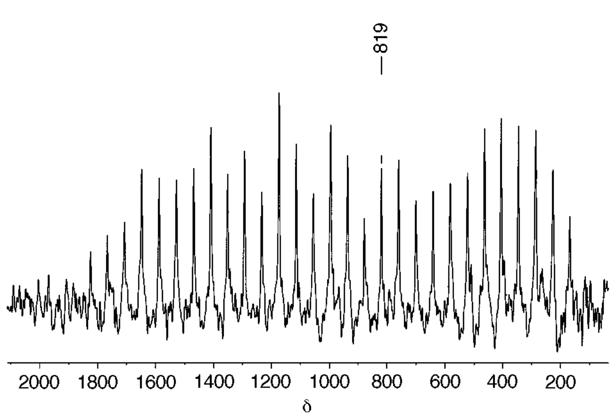


Fig. 2 The ^{119}Sn CP-MAS NMR spectrum of $(SnR_2)_2$ **3** at 298 K

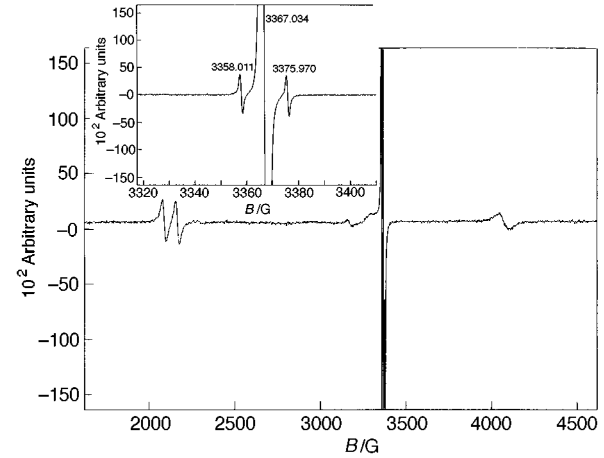


Fig. 3 The ESR spectrum of $[SnR_3]^{\bullet}$ **6** (R = C_6HBu^t-2-Me_3-4,5,6) in benzene at 298 K; the inset shows the satellites due to coupling with ^{13}C nuclei

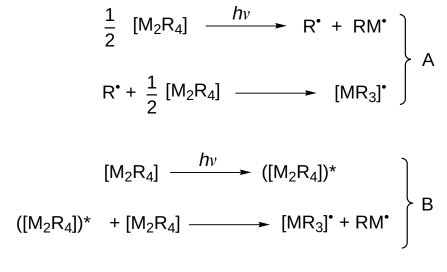
We have examined the distannene **3**, as well as the corresponding digermene $[Ge_2R_4]$ **7** (R = C_6HBu^t-2-Me_3-4,5,6)[13] by ESR spectroscopy. For **3**, a persistent radical species $[SnR_3]^{\bullet}$ **6** was readily detected, merely by exposing the diamagnetic tetraaryldistannene **3** to visible light, at room temperature. The ESR spectrum of a benzene solution, recorded at 298 K, showed a central isotropic resonance with g_{iso} = 2.0012(2) and two satellites assigned to the coupling of the unpaired electron with a ^{13}C nucleus [$a(^{13}C)$ = 18(1) G] (Fig. 3). Under conditions of higher gain, the ^{117}Sn and ^{119}Sn, satellite lines were detected (the natural abundance of each of these spin $I = \frac{1}{2}$ nuclei is 7.7 and 8.6%, respectively).

Owing to second-order effects, the satellite lines were not symmetrical about the central line and were shifted to higher frequency. The two low frequency satellite lines overlapped, consequently an ill-resolved broad signal was observed which was partially resolved by recording a second derivative spectrum at 343 K. The large central-atom hyperfine coupling constants

Table 2 Selected ESR parameters for some persistent tin- and germanium-centred radicals

Radical[a]	Solvent	g_{iso}	a(α-^{1}H) or a(N)/G	a(M)[b]/G	Ref.
$[Sn\{CH(SiMe_3)_2\}_3]^\bullet$	C_6H_6	2.0094	2.1	1698 (^{117}Sn) 1776 (^{119}Sn)	11,12
$[Ge\{CH(SiMe_3)_2\}_3]^\bullet$	C_6H_6	2.0078	3.8	92	12
$[Sn\{N(SiMe_3)_2\}_3]^{\bullet c}$	n-C_6H_{14}	1.9912	10.9	3139 (^{117}Sn) 3317 (^{119}Sn)	12,16
$[Ge\{N(SiMe_3)_2\}_3]^\bullet$	n-C_6H_{14}	1.9991	10.6	171	12,16
$[Sn\{N(SiMe_3)Bu^t\}_3]^\bullet$	n-C_6H_{14}	1.9928	12.7	—	12,16
$[Ge\{N(SiMe_3)Bu^t\}_3]^\bullet$	n-C_6H_{14}	1.9998	12.9	173	12,16
$[Sn\{N(GeMe_3)_2\}_3]^\bullet$	n-C_6H_{14}	1.9924	10.7	—	16
$[Ge\{N(GeMe_3)_2\}_3]^\bullet$	n-C_6H_{14}	1.9994	11.0	145	16
$[Sn\{N(GeEt_3)_2\}_3]^\bullet$	n-C_6H_{14}	1.9939	11.9	—	16
$[Sn(SR^3)_3]^\bullet$	n-C_6H_{14}	2.0064	—	—	17
$[Ge(SR^3)_3]^{\bullet d}$	n-C_6H_{14}	2.0096	—	131	17
$[Sn(R^4)_3]^\bullet$	MeC_6H_{11}	1.9966	3.4	—	18
6 $[Sn(C_6HBu^t\text{-}2\text{-}Me_3\text{-}4,5,6)_3]^\bullet$	MeC_6H_{11}	2.0012	(18)[e]	1756 (^{117}Sn) 1827 (^{119}Sn)	This work
8 $[Ge(C_6HBu^t\text{-}2\text{-}Me_3\text{-}4,5,6)_3]^\bullet$	MeC_6H_{11}	2.0049	(10)[e]	85	This work

[a] $R^3 = C_6H_2Bu^t_3$-2,4,6, $R^4 = C_6H_3(NMe_2)_2$-2,6. [b] a(^{117}Sn) ($I = \frac{1}{2}$, 7.7%), a(^{119}Sn) ($I = \frac{1}{2}$, 8.6%), a(^{73}Ge) ($I = \frac{9}{2}$, 7.6%), calculated using the Breit–Rabi equation. [c] The a(M) values are those reported in ref. 16, although in that article the a(^{117}Sn) and a(^{119}Sn) constants should clearly have been transposed. [d] $T = 193$ K. [e] In this case a(^{13}C).



Scheme 1 Alternative pathways **A** and **B** for the formation of the radicals $[MR_3]^\bullet$ (M = Ge or Sn); $RM^\bullet$ is assumed to be converted into a diamagnetic product

[a(^{117}Sn) = 1756(6) G, a(^{119}Sn) = 1827(6) G] were calculated by applying a Breit–Rabi correction, as described earlier for $[Sn\{CH(SiMe_3)_2\}_3]^\bullet$.[11,12] These data confirm the strong interaction of the unpaired electron with the tin nucleus.

After irradiating a sample in benzene with UV light (using a high-pressure mercury lamp) in the cavity of the ESR spectrometer, the signal intensity increased by a factor of *ca.* 12 after 4 min of irradiation and continued to grow when photolysis was stopped; a combination of irradiation (10 min) and heat (65 °C) caused an even more dramatic increase in the signal intensity (*ca.* 45 fold) and the initially dark red solution slowly turned to brown with no apparent deposition of a tin mirror or metallic precipitate.

The above a($^{117/119}$Sn) hyperfine couplings are of similar magnitude to those found for $[Sn\{CH(SiMe_3)_2\}_3]^\bullet$,[11,12] the parameters for which, together with those for other trialkyl- and triamido-tin(III) and -germanium(III)-centred radicals, are presented for comparison in Table 2.

Alternative mechanisms, **A** and **B** in Scheme 1, may be considered (*cf.* refs. 9, 11, 12) for the formation of the radicals $[MR_3]^\bullet$ (M = Sn or Ge). The absence of a deposit of metallic tin during irradiation implies that the tin(I) coproduct must be a diamagnetic oligomer, or reacts with solvent to yield a diamagnetic product, or is a mixture of such species. The use of a spin trap to capture $R^\bullet$ as required by **A** was considered, but both nitroso compounds or a nitrone reacted with $[M_2R_4]$; hence this approach was discarded.

It has recently been suggested that highly reactive transient intermediates such as $[SnR^2_3]^\bullet$ and $[SnR^2]$ ($R^2 = C_6H_3Et_2$-2,6) might be generated *via* the bimolecular disproportionation $2SnR^2_2 \longrightarrow SnR^2 + SnR^2_3{}^\bullet$; the monomeric stannylene species SnR^2_2 was postulated to have been formed by pyrolysis of the cyclotristannane $[(SnR^2_2)_3]$.[19] The mass spectra of sterically encumbered stannylenes $[SnR^x_2]$ have been reported to exhibit very intense peaks corresponding to $[SnR^x_3]^+$ ions; this is consistent with an easily occurring disproportionation of $[SnR^x_2]$ yielding an $[SnR^x_3]^\bullet$ radical, followed by its ionisation.

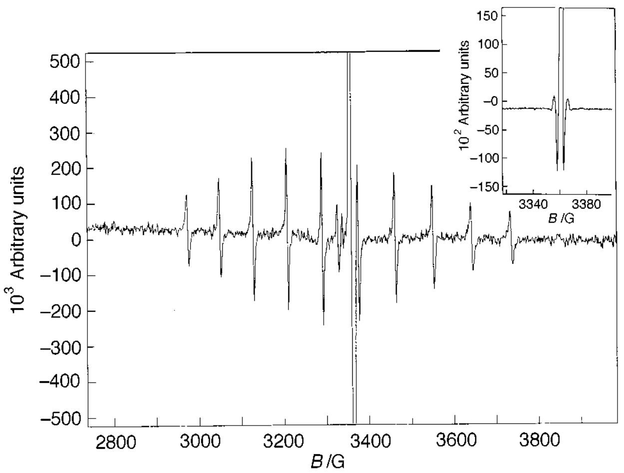


Fig. 4 The ESR spectrum of $[GeR_3]^\bullet$ **8** ($R = C_6HBu^t$-2-Me_3-4,5,6) in benzene at 298 K; the inset shows the enlargement around the central peak in the second derivative spectrum

The crystalline germanium complex $[Ge_2R_4]$ **7**, despite being isoleptic with **3**, has a quite different molecular structure, reflected in a short Ge–Ge bond length of 2.2521(8) Å, a completely planar environment for each of the two germanium atoms and fold angles of 7.9 to 10.4°.[13] This is surprising since, as for the distannane $[Sn_2H_4]$, fold angles between 35 and 47° have been calculated for the parent digermene, *trans*-$[Ge_2H_4]$.[2,7–9,20] By contrast, $[Ge_2\{CH(SiMe_3)_2\}_4]$ has l(Ge–Ge) 2.347(2) Å, a fold angle of 32° and the Ge atoms tend towards pyramidalisation by some 12°.[2,21] An almost planar environment, as in **7**, has been observed in $[Ge_2(C_6H_3Et_2\text{-}2,6)_4]$, with l(Ge–Ge) 2.213(2) Å and fold angle 12°,[22] as well as in the persilylated digermenes $[Ge_2(SiR^5)_4]$ ($SiR^5 = SiPr^i_2Me$, $SiBu^tMe_2$ or $SiPr^i_3$).[23]

Unlike the tin analogue **3**, the yellow-orange complex $[Ge_2R_4]$ **7** was not as sensitive to visible light and the non-irradiated, freshly prepared sample was ESR silent. Only by exposing the benzene solution of **7** to UV light was it possible to observe a strong central isotropic signal for $[GeR_3]^\bullet$ [$g_{iso} = 2.0049(2)$] due to the radical containing zero spin Ge nuclei and the ten satellites from the radical containing ^{73}Ge

Table 3 Experimental and calculated (Breit–Rabi equation) line positions (G) for $[GeR_3]^{\bullet}$ **8** (R = C_6HBu^t-2-Me_3-4,5,6)

m_I	Experimental values/G	Calculated values/G
$-\frac{9}{2}$	2974(3)	2976(4)
$-\frac{7}{2}$	3050(3)	3053(4)
$-\frac{5}{2}$	3128(2)	3131(4)
$-\frac{3}{2}$	3209(2)	3212(4)
$-\frac{1}{2}$	3291(2)	3295(4)
$\frac{1}{2}$	3376(2)	3380(4)
$\frac{3}{2}$	3462(2)	3467(4)
$\frac{5}{2}$	3552(2)	3556(4)
$\frac{7}{2}$	3643(3)	3648(4)
$\frac{9}{2}$	3737(3)	3741(4)

(natural abundance 7.8%, $I = \frac{9}{2}$), $a(^{73}Ge) = 85(4)$ G. Two satellites due to ^{13}C hyperfine coupling were also observed, $a(^{13}C) = 10(1)$ G (Fig. 4; seen most clearly in the second derivative spectrum, inset). The photochemical behaviour of **7** was thus similar to that of $[Ge_2\{CH(SiMe_3)_2\}_4]$.[12]

The heights of the inner satellites in the ESR spectrum of **7** in benzene were higher than those of the outer ones and their separation increased progressively. Table 3 shows the measured and calculated values of the ten satellites; the latter were calculated using the Breit–Rabi equation in the form suggested by Roncin and Debuyst.[24]

The germyl radical $[GeR_3]^{\bullet}$ **8** (R = C_6HBu^t-2-Me_3-4,5,6), like the isoleptic stannyl radical **6**, was persistent and exceptionally thermostable. Even after irradiation had ceased and upon heating the sample at 70 °C for 6 h, there was neither a significant decrease of the initial signal strength, nor a colour change; deposition of metal or other solid was not observed.

The observation of ^{13}C hyperfine couplings in **6** and **8** appears to be without precedent. In $[M\{CH(SiMe_3)_2\}_3]^{\bullet}$ (M = Sn or Ge) and $[Ge(C_6H_2Me_3\text{-}2,4,6)_3]^{\bullet}$[25a] it may not have been observed because of the intense $a(^1H)$ coupling either with the α- or methyl-protons while in the $[Sn(C_6H_2Me_3\text{-}2,4,6)_3]^{\bullet}$ case only a broad singlet was reported.[25b]

Experimental

All manipulations were performed by using standard Schlenk techniques under dry, oxygen-free argon. The compounds **3** and **4** were synthesized as previously described.[4,13]

The X-band (9.43 GHz) ESR spectrometers used were a Bruker ESP 300 equipped with a frequency meter to measure the *g* values and a Varian E-104 equipped with a 1 kW high pressure ultraviolet mercury–xenon Hanovia lamp for *in situ* photolysis. The intensity values reported refer to the relative intensity, namely the ratio between the height of each peak and the gain used to run the spectrum. All the compounds were air- and moisture-sensitive; hence, the samples were sealed *in vacuo* in quartz tubes (internal diameter = 3 mm, external diameter = 4 mm). For solid-state NMR spectroscopic analyses, a sample of **3** was ground in a glove-box operating at <1 ppm H_2O and <1 ppm O_2 and packed into zirconia rotors with Kel-F end caps and spun with N_2; the instrument used was a Bruker DMX-400 spectrometer (89 mm wide-bore magnet) with a 4 mm variable-temperature double-bearing probe. The irradiation and detection frequencies were 400.13 and 148.97 MHz for ^1H and ^{119}Sn, respectively. A standard ^1H–X cross-polarisation technique was employed [^1H 90° pulse duration of 3 μs and contact time of 6 ms (^{119}Sn)] with high-power ^1H decoupling applied during acquisition. An interscan delay of 10 s was used. At spin rates in excess of 8 kHz, a variable amplitude (triangular ramp ± 25%) cross-polarisation contact pulse was employed. The $^{119}Sn\text{-}\{^1H\}$ NMR spectral chemical shifts were measured relative to $SnMe_4$.

Acknowledgements

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