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TRIARYL-SILYL, -GERMYL, AND -STANNYL RADICALS $^{\cdot}MAr_3$ (M = Si, Ge, OR Sn AND Ar = 2,4,6-$Me_3C_6H_2$) AND $^{\cdot}Ge(2,6\text{-}Me_2C_6H_3)_3$: SYNTHESIS AND ESR STUDIES *

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Summary

The triarylmetal-centred radicals $^{\cdot}MAr_3$ (M = Si, Ge, or Sn; Ar = 2,6-$Me_2C_6H_3$ or 2,4,6-$Me_3C_6H_2$) have been prepared from the appropriate triarylmetal chloride, MAr_3Cl, and an electron-rich olefin $[\overline{RNCH_2CH_2NRC}{=}]_2$ (R = Me or Et) under UV irradiation in toluene at low temperature. The triarylgermyl radicals are persistent ($t_{1/2} > 24$ h, 20°C) whilst the analogous tin and silicon radicals are only stable under constant irradiation at temperatures below —20°C; the ESR spectra of the germanium radicals and of $^{\cdot}Si(2,4,6\text{-}Me_3C_6H_2)_3$ (which is the first triarylsilyl radical to be spectroscopically identified) show coincidental equivalence of all the proton couplings due to twisting of the aromatic rings into a "propeller" arrangement about the metal. The synthesis and characterisation of precursors to these radicals are also reported.

Introduction

Recently, considerable interest has been shown in persistent metal-centred radicals $^{\cdot}MX_3$ of the Main Group 4 elements [2]. Trialkyl- and triamido-metal-centred radicals $^{\cdot}MR_3$ (R = $CH(SiMe_3)_2$) and $^{\cdot}M(NR'R)_3$ (R = R' = Me_3Si or $GeMe_3$; and R = Me_3Si, R' = CMe_3) have been prepared for M = Ge or Sn (also the amide with R = $GeEt_3$ = R'_3) with half-lives greater than three months in hydrocarbon solvents at ambient temperature [3,4]. Others, however, although still

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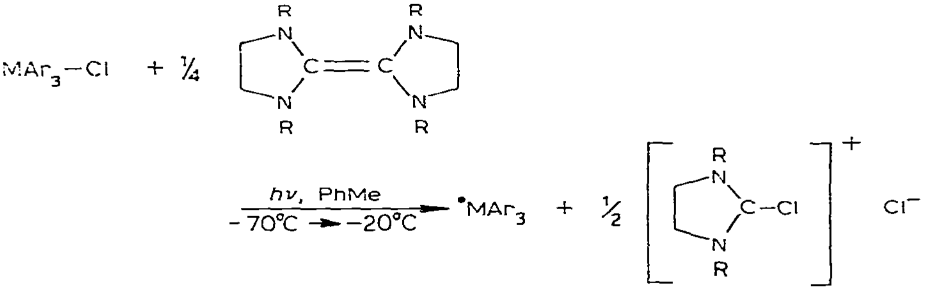
* See ref. 1 for a preliminary account of some of this work.

persistent, are significantly shorter lived, e.g., $^{\bullet}Si[CH(SiMe_3)_2]_3$ [3] and $^{\bullet}Sn(CH_2CMe_2Ph)_3$ [5]. We wish to report extensions of this work to persistent triaryl-silicon, -germanium, and -tin radicals. Preliminary data on the germanium compounds have appeared [1] and others have described complementary results [6,7]. There appears to be no previous report of the ESR spectrum of a triarylsilyl radical; it has been suggested [6] that this due to the high reactivity of silyl radicals towards aromatic substitution.

Results and discussion

The principal method used for the generation of the metal-centred radicals was the in situ irradiation of a solution of the appropriate triarylmetal chloride and an electron-rich olefin in toluene at low temperature in the cavity of an ESR machine according to eq. 1.



(M = Si, Ar = 2,4,6−$Me_3C_6H_2$; M = Ge, Ar = 2,4,6−$Me_3C_6H_2$, 3,4−$Me_2C_6H_3$, or 2,6−$Me_2C_6H_3$; M = Sn, Ar = 2,4,6−$Me_3C_6H_2$, R = Me or Et)

In all cases, during irradiation the solution became cloudy, presumably due to generation of the insoluble salt of eq. 1 (or $\{RNCH_2CH_2N(R)C\}_2Cl_2$); however, not all the triarylmetal-centred radicals which were presumably produced were detected by ESR spectroscopy. Trimesitylmetal radicals were observed for silicon, germanium, and tin, and the tri-2,6-xylylmetal radical only for germanium (see Table 1).

The ESR spectra of the trimesityl-silicon or -germanium radicals show a central eighteen line signal due to ^1H coupling, a(H), with satellites due to coupling

TABLE 1

ESR PARAMETERS FOR GROUP 4 TRIARYLMETAL RADICALS [a]

Radical	g	$a(^1H)$	a (M) [b]	$t_{1/2}$ at θ°C	θ (°C)
$^{\bullet}Si(2,4,6\text{-}Me_3C_6H_2)_3$	2.0027	0.070	13.50	20 s	−60
$^{\bullet}Ge(2,4,6\text{-}Me_3C_6H_2)_3$	2.0084 [d]	0.069	6.84	>24 h	20
$^{\bullet}Ge(2,6\text{-}Me_2C_6H_3)_3$	2.0080	0.065	6.69	>24 h	20
$^{\bullet}Sn(2,4,6\text{-}Me_3C_6H_2)_3$	2.0086	[c]	[c]	ca. 20 s	−60

[a] Generated according to eq. 1 in PhMe; coupling constants in mT. [b] ^{29}Si (I = 1/2, 4.7%), ^{73}Ge (I = 9/2, 7.6%), ^{117}Sn (I = 1/2, 7.9%), ^{119}Sn (I = 1/2, 8.6%). [c] Not observed; broad signal, ca. 0.5 mT. [d] 2.0066 according to ref. 6.

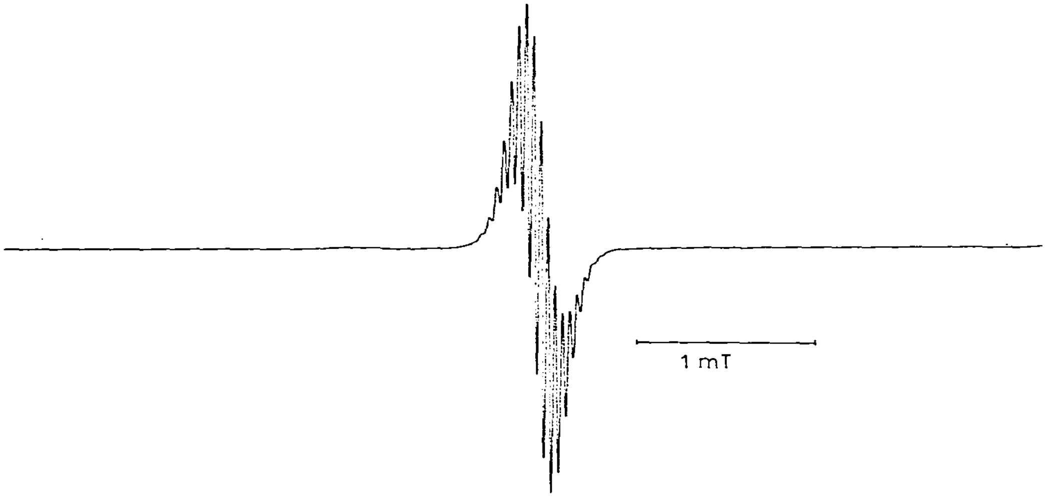


Fig. 1. The ESR spectrum of $^{\cdot}GeAr_3$ (Ar = 2,6-$Me_2C_6H_3$) in toluene at 20°C.

with ^{29}Si ($I = \frac{1}{2}$, 4.7%) or ^{73}Ge ($I = \frac{9}{2}$, 7.6%). The experimental spectra are identical with simulated ones assuming that a(H) for *meta*-H and the 2- or 6-Me groups are equivalent (i.e., coupling to 33 protons); thus the eighteen lines correspond in relative intensity to the central eighteen lines of the binomial expansion of 34. Similarly, the eighteen line central signal of $^{\cdot}Ge(2,6\text{-}Me_2C_6H_3)_3$ (Fig. 1) has relative intensities corresponding to the central eighteen lines of the binomial expansion of 28 (i.e., again all protons have identical coupling constants). This coincidence of CH_3 and aromatic CH proton coupling constants contrasts with the situation found for $^{\cdot}GePh_3$ where *o*-, *m*, and *p*-a(H)'s are 0.093, 0.046, and 0.093 mT, respectively [8]. This is attributed to the twisting of the aromatic rings to minimise unfavourable steric interactions, since it has been shown that such twisting causes a(*m*-H) to rise and a(*o*-H) and a(*p*-H) to fall [9].

The ESR spectrum of $^{\cdot}Ge(2,4,6\text{-}Me_3C_6H_2)_3$ has been reported previously, but prepared by a different route, with poorer resolution, no ^{73}Ge satellites being detected [6].

The ESR spectrum of $^{\cdot}Sn(2,4,6\text{-}Me_3C_6H_2)_3$ consists of a broad signal (line width 0.5 mT). Resolution of proton couplings was not detected and the signal was too weak for the identification of ^{117}Sn and ^{119}Sn satellites. An earlier paper [7] has described the formation of the triaryltin radicals $^{\cdot}SnAr_3$ (Ar = 2,4,6-$Me_3C_6H_2$, or 2,4,6-$Et_3C_6H_2$), obtained by high temperature reversible thermal dissociation of the corresponding hexa-aryldistannanes according to eq. 2.

$$Ar_3Sn\text{-}SnAr_3 \xrightleftharpoons{\text{heat } (t)} 2\ ^{\cdot}SnAr_3 \qquad (2)$$

(Ar = 2,4,6-$Me_3C_6H_2$, t = 180°C; or Ar = 2,4,6-$Et_3C_6H_2$, t = 100°C)

In both cases the ESR signal consisted of a broad (0.5 mT) signal at g = 2.0075 with proton couplings unresolved. *F*-strain due to the bulky aryl groups in the parent hexa-aryldistannanes was proposed to account for the weakening of the Sn—Sn bond to such an extent that reversible thermal dissociation occurred.

From Table 1 it can be seen that on descending Group 4 the *g*-factors increase from the free spin only values. This is not unexpected, since spin orbit coupling becomes increasingly important for heavier elements (ζ_{C} 29, ζ_{Si} 149, ζ_{Ge} 940) [10]. The trends found here are similar to those found for related radicals, notably $^{\bullet}\mathrm{M[CH(SiMe_3)_2]_3}$ [3,4], $^{\bullet}\mathrm{MH_3}$, and $^{\bullet}\mathrm{MMe_3}$. A decrease in *g* is also generally associated with a more pyramidal geometry for an $^{\bullet}\mathrm{MX_3}$ type radical.

Whereas the methyl radical is planar, there is considerable evidence that other Main Group 4 metal-centred radicals exhibit varying degrees of deviation from planarity. The principal evidence comes from hyperfine coupling to those isotopes of the central atom which possess non-zero spin (^{13}C, ^{29}Si, ^{73}Ge, ^{117}Sn, ^{119}Sn and ^{202}Pb). The metal coupling constant increases rapidly with bending as the *s*-character of the odd-electron orbital changes from zero to 25% on changing from sp^2 to sp^3 hybridisation [e.g., $^{\bullet}\mathrm{CH_3}$, $a(^{13}\mathrm{C})$ 3.8 mT, approximately planar; $^{\bullet}\mathrm{CCl_3}$, $a(^{13}\mathrm{C})$ 11.4 mT, approximately tetrahedral]. The values of $a(\mathrm{M})$ for the triarylmetal radicals reported here are slightly lower than those recorded for $^{\bullet}\mathrm{MH_3}$, $^{\bullet}\mathrm{MMe_3}$, and $^{\bullet}\mathrm{M[CH(SiMe_3)_2]_3}$ (typically $a(^{29}\mathrm{Si})$, 18—19 mT and $a(^{73}\mathrm{Ge})$, 7—8 mT), indicating a marked pyramidal deviation from planarity. In general, the greater the difference in electronegativity between the central atom and the atoms bonded to it, the more pyramidal will be the radical.

According to Sakurai et al. [6] there is a linear relationship between the *g* value of the metal-centred radical and the spin density on the metal (82% on Ge for each of triphenyl- and tri-*p*-tolyl-germane), whence we deduce that Ge has 90% or 87% of the spin density of trimesityl- or tri-2,6-xylyl-germane, respectively. Consistent with these conclusions of high spin densities on the metal is an argument, see ref. [6], based on proton hyperfine coupling constants. Thus, the ring proton coupling constants for germanium- or silicon-centred radicals are very small when compared to their carbon analogues, implying that there is much less tendency for $^{\bullet}\overset{\curvearrowright}{\mathrm{M}}\!-\!\mathrm{Ar}$ π-interaction when M is Si or Ge rather than M = C.

Numerous ESR studies have been concerned with the structure of carbon-centred radicals and many ingenious techniques have been devised to facilitate their observation, since their rates of dimerisation or disproportionation are essentially diffusion-controlled. In contrast, much less work has been reported on trivalent Si, Ge, Sn, and Pb species. However, it has become apparent that it is possible to increase the lifetime of unconjugated free radicals by using bulky substituents in order to "protect" the radical centre. For example, $^{\bullet}\mathrm{C(SiMe_3)_3}$ has a much longer lifetime than $^{\bullet}\mathrm{CMe_3}$ [11]; extensions of this concept are given in ref. 12.

The long half-lives of the tri-mesityl- and tri-2,6-xylyl-germyl radical (however, much shorter than of $^{\bullet}\mathrm{Ge[CH(SiMe_3)_2]_3}$) is attributed to steric constraints to dimerisation. The corresponding triaryltin radicals are less persistent, because the larger tin atom can more readily tolerate bulky substituents and this increases the facility for dimerisation, to give a hexa-aryldistannane.

From ESR measurements [7] on the thermal dissociation of the hexa-aryldistannanes $[\mathrm{Sn_2(C_6H_2R_3\text{-}2,4,6)_6}]$ (R = Me or Et) low Sn—Sn bond dissociation energies were derived (D(Sn—Sn) = 190 ± 8 kJ mol^{-1} (R = Me) and 125 ± 5 kJ mol^{-1} (R = Et)), which are considerably lower than the 210—240 kJ mol^{-1} found for Sn_2Me_6 [13]. This is indicative of a marked weakening of the Sn—Sn bond due to F-strain imposed by the bulky aryl groups. The silicon-centred radicals probably owe their lower stability to the greater facility with which they can abstract a hydrogen atom; this is due to the trend in M—H bond strengths (Si > Ge > Sn). However, the low values [14] of D(M—H) (C, 435; Si, 339; Ge, 305; Sn, 293 kJ mol^{-1}) may not favour hydrogen abstraction from the C—H bonds of the solvent.

The decay of $^{\bullet}Si(2,4,6\text{-}Me_3C_6H_2)_3$ in toluene at —60°C follows first-order kinetics. Its half-life is 20 ± 2 s, implying reaction with solvent or an intramolecular reaction; similarly $^{\bullet}Si[CH(SiMe_3)_2]_3$ decays in benzene at +20°C with first-order kinetics but has a much longer half-life of ca. 480 s even at the higher temperature [3]. The decay of $^{\bullet}C(SiMe_3)_3$ [11] and $^{\bullet}CH\text{-t-}Bu_2$ [14] have also been reported to follow first-order kinetics. The ESR characterisation of this triarylsilyl radical is noteworthy. We believe our success is largely due to the efficiency of reaction 1 compared with alternative methods of radical generation.

Other methods which we investigated for the generation of the triarylmetal-centred radicals are shown in eqs. 3 and 4. However, only for $Ge(2,4,6\text{-}Me_3\text{-}$

$$MAr_3H + \tfrac{1}{2}\,t\text{-}Bu_2O_2 \xrightarrow[n\text{-}C_6H_{14}\text{ or }PhMe]{h\nu,\ 0^\circ C} {}^{\bullet}MAr_3 + t\text{-}BuOH \qquad (3)$$

$$MAr_3H + (CH_2)_5C{=}O \xrightarrow[PhMe]{h\nu,\ 20^\circ C} {}^{\bullet}MAr_3 \qquad (4)$$

$C_6H_2)_3H$ were these two methods successful (with di-t-butyl peroxide, giving only a weak spectrum).

Photolysis of the "germylenes" $[GeAr_2]_n$ [15] in toluene did not produce $^{\bullet}GeAr_3$. This provides a contrast to the photochemical behaviour of Ge-$[CH(SiMe_3)_2]$ [3] or $[GePhCl]_n$ [16], which gave $^{\bullet}Ge[CH(SiMe_3)_2]_3$ or $^{\bullet}GePhCl_2$ (the latter identified as a spin-adduct, using a nitrone trap), respectively.

The synthesis and characterisation of tetravalent Group 4 metal compounds as radical precursors

Tri-mesityl- or -xylyl-Group 4 metal chlorides MAr_3Cl were obtained from MCl_4 and ArMgBr in refluxing THF (M = Ge or Sn). Tri-mesityl- or -xylyl-metal hydrides MAr_3H were prepared from the corresponding chlorides using the reduction reaction with $Li[AlH_4]$ in diethyl ether, but the silicon analogues $SiAr_3H$ were obtained directly by the reaction of ArMgBr with $SiCl_3H$. Pure samples of tri-mesityl or -xylyl-metal chlorides MAr_3Cl were obtained in good yield by the chlorination of the corresponding hydride with N-chlorosuccinimide or with CCl_4 in the presence of AIBN. Typical procedures are detailed in the experimental section.

The characterisation of the tetravalent metal compounds is summarized in Tables 2 and 3; data on 3,4-xylyl-metal chlorides and hydrides are included, although these compounds were not examined as radical precursors.

TABLE 2. TETRAVALENT GROUP 4 METAL PRECURSORS TO $^{\bullet}\mathrm{MAr_3}$

Compound [a]	Solvent for recryst.	Yield (%)	Analysis found (calcd.) (%)			M.p. (°C) (B.p. (°C/mmHg))	Ref.
			C	H	Cl		
$\mathrm{GeAr'_3H}$	MeOH	65				185—136 (198/0.05)	17, 18, 19
$\mathrm{GeAr'_3Cl}$	$\mathrm{CHCl_3/n\text{-}C_5H_{12}}$	88				167—169	18
$\mathrm{SiAr'_3H}$	—	60				198 (185/0.04)	20, 21
$\mathrm{SiAr'_3Cl}$	$\mathrm{CHCl_3/n\text{-}C_5H_{12}}$	68	77.0 (77.1)	7.90 (7.82)	8.42 (8.57)	155	b
$\mathrm{SnAr'_3H}$	$\mathrm{PhMe/n\text{-}C_5H_{12}}$	36				168	22
$\mathrm{SnAr'_3Cl}$	$\mathrm{C_6H_6}$	48	63.4 (63.2)	6.50 (6.45)	6.93 (7.17)	163	b
$\mathrm{GeAr''_3Cl}$	$\mathrm{PhMe/n\text{-}C_5H_{12}}$	73	68.1 (68.0)	6.43 (6.44)	8.37 (8.18)	143	b
$\mathrm{SnAr''_3H}$	$\mathrm{PhMe/n\text{-}C_5H_{12}}$	75	66.4 (65.9)	6.27 (6.21)		130	b
$\mathrm{SnAr''_3Cl}$	$\mathrm{C_6H_6}$	52	61.5 (61.2)	5.60 (5.57)	7.56 (7.71)	160	b
$\mathrm{GeAr'''_3H}$	MeOH	56				76	19
$\mathrm{GeAr'''_3Cl}$	$\mathrm{CHCl_3/n\text{-}C_5H_{12}}$	74	68.2 (68.3)	6.21 (6.14)	8.39 (8.43)	142—144	b
$\mathrm{SiAr'''_3H}$	—	67				58 (230/1)	19
$\mathrm{SiAr'''_3Cl}$	$\mathrm{C_6H_6}$	43	61.5 (61.3)	5.60 (5.52)	7.56 (7.68)	175—177	b

[a] Ar' = 2,4,6-$\mathrm{Me_3C_6H_2}$, Ar'' = 2,6-$\mathrm{Me_2C_6H_3}$, Ar''' = 3,4-$\mathrm{Me_2C_6H_3}$. [b] This work.

TABLE 3. SPECTROSCOPIC DATA FOR GROUP 4 METAL PRECURSORS TO $^{\bullet}\mathrm{MAr_3}$

Compound [a]	ν (M—H) [b] (cm^{-1})	^{1}H NMR chemical shifts (δ, in ppm rel. to $\mathrm{SiMe_4}$)					Solvent used
		M—*H*	Aromatic *H*'s	o-C*H*$_3$	p-C*H*$_3$	m-C*H*$_3$	
$\mathrm{GeAr'_3H}$	2052	5.83	6.75	2.15	2.23		$\mathrm{CCl_4}$
$\mathrm{GeAr'_3Cl}$			6.65	2.18	2.08		$\mathrm{CCl_4}$
$\mathrm{SiAr'_3H}$	2159	5.65	6.70	2.15	2.25		$\mathrm{C_6D_6}$
$\mathrm{SiAr'_3Cl}$			6.80	2.17	2.25		$\mathrm{CCl_4}$
$\mathrm{SnAr'_3H}$	1820	6.85	6.76	2.40	2.13		$\mathrm{C_6D_6}$
$\mathrm{SnAr'_3Cl}$			6.73	2.50	2.07		$\mathrm{C_6D_6}$
$\mathrm{GeAr''_3Cl}$			7.06	2.26			$\mathrm{CCl_4}$
$\mathrm{SnAr''_3H}$	1830	6.83	6.97	2.34			$\mathrm{C_6D_6}$
$\mathrm{SnAr''_3Cl}$			6.90	2.44			$\mathrm{C_6D_6}$
$\mathrm{GeAr'''_3H}$	2042	5.53	7.13		2.20	2.20	$\mathrm{CCl_4}$
$\mathrm{GeAr'''_3Cl}$			7.60		1.94 (or 1.96)	1.96 (or 1.94)	$\mathrm{CCl_4}$
$\mathrm{SiAr'''_3H}$	2125	5.27	7.43		2.20	2.20	$\mathrm{CCl_4}$
$\mathrm{SiAr'''_3Cl}$			7.10—7.66		1.97 (or 2.00)	2.00 (or 1.97)	$\mathrm{C_6D_6}$

[a] Ar' = 2,4,6-$\mathrm{Me_3C_6H_2}$, Ar'' = 2,6-$\mathrm{Me_2C_6H_3}$, Ar''' = 3,4-$\mathrm{Me_2C_6H_3}$. [b] Nujol mull.

Experimental

ESR spectra were recorded using Varian E3 and E104A spectrometers using manipulative techniques described in earlier papers [1,3,4]. Approximate g_{av}-values (Table 1) were obtained by comparison of the magnetic field at the centre of the spectrum with DPPH ($g = 2.0036$) and are uncorrected for second order hyperfine splitting. Typical procedures are listed below; see also Tables 2 and 3.

Preparation of $GeAr_3H$ *and* $GeAr_3Cl$

Crude trimesitylchlorogermane was prepared from $GeCl_4$ (2.15 g, 0.010 mol) and excess of mesitylmagnesium bromide (MesBr) (0.060 mol) in refluxing THF. After hydrolysis by 6 *M* aqueous HCl, extraction of the product with diethyl ether, and removal of solvent from the extract, the crude compound $GeClMes_3$ was obtained. Its reduction by $Li[AlH_4]$ (0.40 g, 0.010 mol) in diethyl ether at ca. 20°C gave, after hydrolysis and distillation, $GeHMe_3$ (2.86 g, 65%) [17,18].

A solution of $GeHMes_3$ (0.86 g, 0.002 mol) in CCl_4 (2 cm^3) was heated at 90°C during 2 h in a Carius tube with a trace of AIBN as catalyst. After evaporation of the mixture of CCl_4 and $CHCl_3$ in vacuo, the solid residue obtained was recrystallised from a minimum of n-pentane to give $GeClMes_3$ (0.82 g, 88%).

Preparation of $SiAr_3H$ *and* $SiAr_3Cl$

A solution of $SiCl_3H$ (4.0 g, 0.030 mol) and MesBr (24.0 g, 0.120 mol) in THF (100 cm^3) was added with stirring to a suspension of an excess of Li (3.0 g) in THF (100 cm^3). At the end of the exothermic reaction the mixture was refluxed for 12 h. The filtrate was hydrolysed using water, extracted with diethyl ether, and dried ($CaCl_2$). Distillation gave $SiHMe_3$ (7.15 g, 60%) [18].

A solution of $SiHMes_3$ (0.66 g, 0.0017 mol) in CCl_4 (5 cm^3) was irradiated under argon in a quartz vessel (35°C) until the Si—H bond was no longer observed (IR or NMR spectroscopy). After evaporation of CCl_4 and $CHCl_3$ in vacuo the crude $SiClMes_3$ was recrystallised with pentane to yield the pure material (68%). Chlorination of $SiHMes_3$ with *N*-chlorosuccinimide in THF (Carius tube, 100°C, 24 h) was also performed, to give the chloride (38%) in lower yield.

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