$CH_3C{\equiv}CSiMe_3$, $Me_3SiCH_2C{\equiv}CSiMe_3$, $(Me_3Si)_2CHC{\equiv}CSiMe_3$, and $(Me_3Si)_2C{=}C{=}CHSiMe_3$.

Enough $Me_3SiCH_2C{\equiv}CSiMe_3$ was collected for characterization; nmr resonances at τ 9.88 and 8.50 in the ratio of 9:1.

Anal. Calcd for $C_9H_{20}Si_2$: C, 53.26; H, 10.89; Si, 35.85. Found: C, 53.34; H, 10.83; Si, 35.78.

Lithiation of 1,3-Bis(trimethylsilyl)propyne. To a solution of 1,3-bis(trimethylsilyl)propyne, 1.8 g (0.01 mol), in 10 ml of hexane was added 12.5 ml of 1.6 *M* *n*-BuLi (0.02 mol). The ir spectrum of the solution showed a strong band at 2190 cm^{-1} for the $C{\equiv}C$ stretching band of the starting material. After 10 min at room temperature the original $C{\equiv}C$ intensity was decreased and new bands appeared at 1850 and 1790 cm^{-1}. After 18 hr, only a single strong band at 1790 cm^{-1} was observed. The assignments for these frequencies are listed in Table I. Derivatization of the final solution with trimethylchlorosilane gave 2.9 g (89%) of **1**.

Electron Spin Resonance of Group IV Organometallic Alkyl Radicals in Solution

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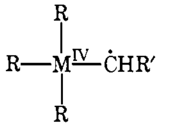
Abstract: Esr spectra have been obtained from a series of alkyl derivatives of group IV metals—silicon, germanium, and tin—by hydrogen abstraction with photochemically generated *t*-butoxy radicals. Abstraction occurs predominantly from the carbon atom α to the metal. In the tetraethyl derivatives, abstraction from the carbon atom β to the metal is also observed. Radicals produced by the latter process have also been observed by addition of trialkylmetal radicals to ethylene. The trends in the coupling constants for these series of α- and β-substituted alkyl radicals are discussed. In the methoxy derivatives of analogous organometallic compounds abstraction occurs from the ethereal methyl group. Line-broadening effects caused by hindered internal rotation are also reported.

Multiple bonding between ligand and the metals of the main group IV elements has been the subject of considerable discussion,[2] and a variety of physical techniques have been brought to bear on this problem. Electron spin resonance (esr) spectra of a number of stable aromatic ion-radical complexes of these metals have been investigated with relation to the possibility of p_π–d_π bonding.[3] Organometallic radicals related to I



$$R_3M^{IV}\dot{C}HR'$$

I, R = alkyl, aryl; R′ = H, CH_3; M = group IVB

(particularly M = Si) have also been discussed in an attempt to delineate radical rearrangements in organometallic derivatives analogous to those found in corresponding hydrocarbon radicals.[4a] Heretofore there has been no direct physical evidence for the existence of organometallic radicals of this type in solution.[4b,c]

Experimental Section

Esr spectra were taken with a modified Varian X-band spectrometer utilizing 100-kHz modulation. The microwave bridge was designed around a three-port ferrite circulator. A backward diode (Philco L4154B) was employed as detector in conjunction with a low-noise preamplifier. The magnetic field of a 12-in. magnet was swept by a Varian V3506 magnet flux stabilizer equipped with a modified Varian V3507 slow-sweep unit and was measured by a Harvey-Wells nmr gaussmeter in conjunction with a frequency counter and marker.[5] An unsilvered dewar (fused silica) system of conventional design was used to vary the temperature of the sample. The light source was a water-cooled 2-kW mercury discharge lamp (Pek Labs A-1-B) with an optical system consisting of two fused silica lenses and a spherical mirror. To increase the uv flux at the sample, the optical transmission end plate of a Varian V4531 rectangular cavity was replaced by a similar end plate with wider slots without appreciable loss of *Q*. The preparation and handling of the sample is described elsewhere.[5]

All of the compounds employed in this study were reagent grade commercial samples which were used without further purification. The di-*t*-butyl peroxide was obtained from Wallace and Tiernan Co. and was also used without further purification.

Results and Discussion

We have generated a series of transient organometallic radicals of the general structures I (R = alkyl, R′ = H, CH_3) and the oxygenated analogs II (R, R′ = CH_3, $CH_3CH_2CH_2CH_2$) in solution (ethane, cyclopro-

$$R_n(R'O)_{3-n}MOCH_2\cdot$$

II

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[1] (a) E. I. du Pont de Nemours and Co.; (b) Indiana University; (c) originally submitted (March 15, 1969) as a communication.

[2] For some leading references, see (a) D. R. Eaton and W. R. McClellan, *Inorg. Chem.*, **6**, 2134 (1967); (b) V. Chvalovsky, "Organosilicon Chemistry," IUPAC, Prague, Butterworth and Co., Ltd., London, 1966, pp 231 ff; (c) R. S. Drago, *Rec. Chem. Progr.*, **26**, 157 (1965).

[3] (a) M. D. Curtis and A. L. Allred, *J. Am. Chem. Soc.*, 87, 2554 (1965); (b) J. A. Bedford, J. R. Bolton, A. Carrington, and R. H. Prince, *Trans. Faraday Soc.*, **59**, 53 (1963); (c) R. D. Cowell, G. Urry, and S. I. Weissmann, *J. Am. Chem. Soc.*, **85**, 822 (1963); *J. Chem. Phys.*, **38**, 2028 (1963); (d) G. R. Hush and R. West, *J. Am. Chem. Soc.*, **87**, 3993 (1965); (e) L. Goodman, A. H. Konstam, and L. H. Sommer, *ibid.*, **87**, 1012 (1965).

[4] (a) J. W. Wilt, O. Kolewe, and J. F. Kraemer, *ibid.*, **91**, 2625 (1969). (b) The esr spectrum of III in a rigid matrix has been recently reported: J. Roncin, *Mol. Cryst.*, **3**, 117 (1967); I. I. Chkheidze, Y. Molin, V. Mironov, E. Chernyshev, N. Buben, and V. V. Voevodskii, *Kinet. Katal.*, 7, 230 (1966). (c) Related tin radicals have also been observed in the solid state: K. Höppner and G. Lassmann, *Z. Naturforsch.*, 23a, 1758 (1968).

[5] P. J. Krusic and J. K. Kochi, to be published.

pane). The esr spectra of these short-lived radicals are well resolved and show high signal-to-noise ratios. The technique for the generation of these radicals has been previously employed with a variety of substrates,[6] and involves abstraction of hydrogen from the tetralkylmetal derivative with photochemically generated *t*-butoxy radicals. The latter is a selective reagent for removal of the hydrogen atoms attached to the carbon

$$R_4M + (CH_3)_3CO\cdot \longrightarrow R_3M\dot{C}HR' + (CH_3)_3COH \qquad (1)$$

atom bonded directly to the metal.

The esr spectrum of the trimethylsilylmethyl radical III[4b,c] generated from tetramethylsilane and *t*-butoxy radicals is composed of a triplet due to the α-hydrogens which is further split into ten lines by the γ-hydrogens

$$(CH_3)_4Si + (CH_3)_3CO\cdot \longrightarrow \underset{\text{III}}{(CH_3)_3Si\dot{C}H_2} + (CH_3)_3COH \qquad (2)$$

(CH_3).[7] The same spectrum was obtained in both neat tetramethylsilane and in cyclopropane solutions. We observed no significant line broadening over the temperature range −34 to −137°.

Spectra similar to that of III were also obtained with tetramethylgermane and stannane.[7] The pertinent hyperfine coupling constants of these radicals are given in Table I along with those of the carbon analog for comparison.

Table I. Hyperfine Coupling Constants for Organometallic Radicals of Group IVB

R_4M	Radical	Temp, °C	Coupling constants, G	
			—R = methyl—	
			a_{CH_2}	a_{CH_3}
$(CH_3)_4C$	$(CH_3)_3C\dot{C}H_2$[a]	−58	21.81	1.00
$(CH_3)_4Si$	$(CH_3)_3Si\dot{C}H_2$	−126	20.88	0.41
$(CH_3)_4Ge$	$(CH_3)_3Ge\dot{C}H_2$	−115	20.85	<0.02[b]
$(CH_3)_4Sn$	$(CH_3)_3Sn\dot{C}H_2$	−107	20.84	0.17
			—R = ethyl—	
			a_{CH}	a_{CH_3}
$(CH_3CH_2)_4C$	$(CH_3CH_2)_3C\dot{C}HCH_3$[c]	−30	(21.7)	(24.9)
$(CH_3CH_2)_4Si$	$(CH_3CH_2)_3Si\dot{C}HCH_3$	−77	20.22	25.15
$(CH_3CH_2)_4Ge$	$(CH_3CH_2)_3Ge\dot{C}HCH_3$	−107	20.65	25.72
$(CH_3CH_2)_4Sn$	$(CH_3CH_2)_3Sn\dot{C}HCH_3$	−104	20.41	25.89

[a] Neopentyl radicals were generated from the photolysis of *t*-butylacetyl peroxide.[8] Neopentyl radical was originally observed by R. H. Fessenden and R. W. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963). However, they were unable to resolve the hyperfine structure due to γ-protons. [b] Unresolved. Envelope of each multiplet was 0.13 G wide (peak to peak). [c] See Fessenden and Schuler, footnote *a*. Because of poor signal-to-noise ratio these constants are accurate to ±0.3 G.

It is noteworthy that these tetramethyl group IV metals reacted with *t*-butoxy radical (eq 1, $R = CH_3$) to generate radical species I in sufficiently high concentration to observe their esr spectra, since the carbon analog, neopentane, did not afford an esr spectrum of comparable quality under the same conditions.[8] We deduce from this behavior that the presence of Si, Ge, or Sn either enhances the reactivity of the methyl group toward hydrogen abstraction or stabilizes the resultant radical I. The latter is in accord with the known reluctance of α-silyl radicals to undergo rearrangement and can be attributed to stabilization of such species by d_π–p_π electron delocalization.[9]

The tetraethyl derivatives of silicon, germanium, and tin also reacted with *t*-butoxy radicals under these conditions to generate the homologous radicals IV (Table I) by hydrogen abstraction from the *methylene* position.

$$(CH_3CH_2)_4M + (CH_3)_3CO\cdot \longrightarrow (CH_3CH_2)_3M\dot{C}HCH_3 \qquad (3)$$

$$\text{IV, M = Si, Ge, Sn}$$

The esr spectrum of each of these secondary radicals consisted of an eight-line pattern with the correct intensity ratios of a doublet (–CH–) split further into a quartet ($-CH_3$). The hyperfine splitting constants of the hydrogens located on the ethyl groups were not large enough to lead to resolvable fine structure.[10] A typical esr spectrum is reproduced in Figure 1 for the germanium analog.

The presence of a second paramagnetic species as a minor component is also shown in Figure 1. Similar additional lines were present in the spectra obtained from tetraethylsilane and tetraethylstannane. In each case the splitting pattern consisted of a triplet of triplets. We assign these lines to the radical V resulting from abstraction of a *primary* hydrogen from the methyl group of the tetraethyl derivatives. This assignment is

$$(CH_3CH_2)_3MCH_2CH_2\cdot$$

$$\text{V, M = Si, Ge, Sn}$$

confirmed by an independent experiment (Figure 2) in which triethylsilyl radicals (eq 4) *add* to ethylene (eq 5),

$$(CH_3)_3CO\cdot + (CH_3CH_2)_3SiH \longrightarrow (CH_3CH_2)_3Si\cdot + (CH_3)_3COH \qquad (4)$$

$$(CH_3CH_2)_3Si\cdot + CH_2{=}CH_2 \longrightarrow (CH_3CH_2)_3SiCH_2CH_2\cdot \qquad (5)$$

when a mixture of triethylsilane, ethylene, and di-*t*-butyl peroxide (1:1:1 by volume) is photolyzed. Significantly, no triethylsilyl radicals[11] were detected in these experiments, indicating that the addition of these silicon-centered radicals to ethylene is a very facile process.[12] The hyperfine coupling constants for these ethyl radicals substituted in the β position with group IV metals are listed in Table II.

In previous studies,[6] we were unable to detect esr spectra of primary alkyl radicals from alkanes by hydrogen abstraction. The detection of the primary radical species V from the tetraethyl derivatives of the group IV metals is quite unique. We ascribe the stabilization of these radicals to hyperconjugative effects represented by

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(6) P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, **90**, 7155 (1968).

(7) A second paramagnetic species of greater *g* value ($\Delta g 0.00 = 075$) than III grew in the early stages of irradiation. The hyperfine splitting pattern consisted of a doublet (a = 17.84 G) split further into at least 11 lines (a = 0.31 G) of approximately binomial intensity distribution. We tentatively assign the spectrum of the second component to $(CH_3)_3Si\dot{C}HSi(CH_3)_3$, formed by an undetermined mechanism. We cannot rigorously exclude the possibility of trace impurities, undetected by nmr and gas chromatographic analysis, leading to this species. Similar components were also present in the spectra obtained from tetramethylstannane and germane (*vide infra*).

(8) J. K. Kochi and P. J. Krusic, *J. Am. Chem. Soc.*, **91**, 3940 (1969).

(9) E. A. V. Ebsworth, "Organometallic Compounds of Group IV Elements," Vol. 1, A. G. MacDiarmid, Ed., M. Dekker, Inc., New York, N. Y., 1968, Chapter 1.

(10) The lines were broader (*ca.* 0.6 G) than usual presumably because of unresolved fine structure.

(11) P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, **91**, 3938 (1969).

(12) E. Y. Lukevits and M. G. Voronkov, "Organic Insertion Reactions of Group IV elements," Consultants Bureau, New York, N. Y., 1966.

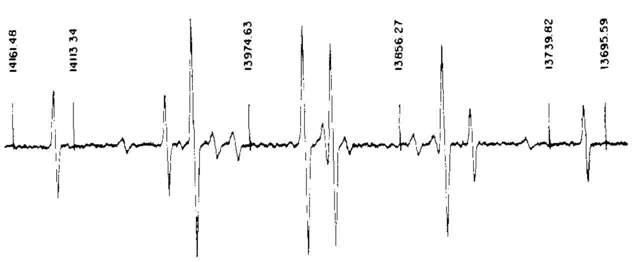


Figure 1. Esr spectrum of $(C_2H_5)_3Ge\dot{C}HCH_3$ (doublet of quartets) in cyclopropane solution at −107°. The minor components of the spectrum (triplet of triplets) are due to $(C_2H_5)_3GeCH_2\dot{C}H_2$ resulting by abstraction of a primary hydrogen from tetraethylgermane. The proton nmr field markers are in kilohertz.

the valence bond structures VI.[13] This is also consis-

$$[R_3M{-}CH_2\dot{C}H_2 \longleftrightarrow R_3\dot{M}\,CH_2{=}CH_2] \quad \text{VI}$$

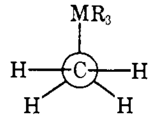
tent with the larger ^{29}Si splitting in the β-substituted radical V ($M = Si$, $a_{Si} = 37.4$ G) compared to the α-substituted radical IV ($M = Si$, $a_{Si} = 15.2$ G).

Table II. Hyperfine Coupling Constants for $(CH_3CH_2)_3MCH_2\dot{C}H_2$[a]

$(CH_3CH_2)_3MCH_2CH_2\cdot$	Temp, °C	Coupling constant, G	
		a_α	a_β
$(CH_3CH_2)_3SiCH_2CH_2\cdot$	−102	20.97	17.87
$(CH_3CH_2)_3GeCH_2CH_2\cdot$	−107	20.55	16.71
$(CH_3CH_2)_3SnCH_2CH_2\cdot$	−96	19.77	16.12

[a] From the photolysis of $(CH_3CH_2)_4M$ and di-*t*-butyl peroxide in cyclopropane solutions.

The β hyperfine splittings for the series of primary alkyl radicals V (Table II) are much smaller in magnitude than the β coupling constants observed for most acyclic alkyl radicals.[14] These reduced β splittings are no doubt caused by the presence of a twofold potential hindering the rotation about the bond between the α and β carbons with a minimum at the conformation in which the group IV metal is eclipsed by the p orbital on the α carbon. Anisotropic averaging of the well-known angular dependence for the β coupling constants (eq 6) about this equilibrium conformation will lead to values for a_β which are substantially less than the free rotation limit observed for the ethyl radical ($a_\beta = 26.87$ G), and it will also require a positive temperature coefficient for a_β which is indeed observed.[13]



$$a_\beta = B + A\cos^2\theta \qquad (6)$$

The coupling constants for the radical species I presented in Table I can be related to analogous α-substituted ethyl radicals, $CH_3\dot{C}HX$, according to Fischer's[15] interpretation which is based on the proportionality (eq 7) of the coupling constant for the β-methyl group

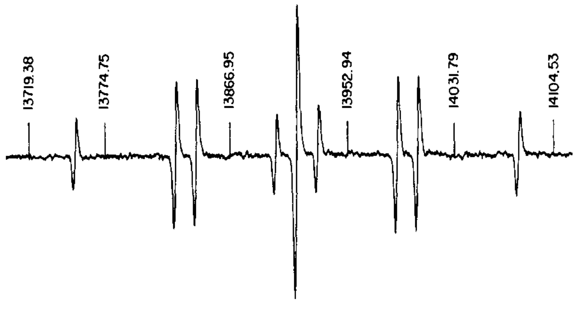


Figure 2. Esr spectrum of $(C_2H_5)_3SiCH_2\dot{C}H_2$ obtained by addition of $(C_2H_5)_3\dot{S}i$ to ethylene at −148°.

(a_{CH_3}) and the spin density (ρ_α) on the α-carbon as originally suggested by Fessenden and Schuler.[14] Values

$$a_{CH_3} = Q^{CH_3}\rho_\alpha = 29.30\rho_\alpha \qquad (7)$$

for ρ_α for the series of organometallic radicals I ($R = CH_3CH_2$; $R' = CH_3$) calculated using eq 7 are tabulated in Table III, together with Q^α and ΔX. The former is a parameter defined by a relation analogous to eq 7 for a_α but is not a true constant. The latter is an empirical parameter describing the effect of the substituent X in the series of radicals $CH_3\dot{C}HX$ and is defined by the product rule (eq 8).[15]

Table III. Parameters Related to α-Substituted Ethyl Radicals

Substituent X	T, °C	a_α	a_{CH_3}	Q^α	ρ_α	ΔX
$H^{a,b}$	−180	22.38	26.87	24.4	0.917	0.00
$(CH_3CH_2)_3Sn$	−104	20.41	25.89	23.1	0.884	0.038
$(CH_3CH_2)_3Ge$	−107	20.65	25.72	23.5	0.878	0.045
$(CH_3CH_2)_3Si$	−77	20.22	25.15	23.5	0.859	0.065
$(CH_3CH_2)_3C^{a,b}$	−30	21.7	24.9	25.5	0.850	0.076
$CH_3{}^{a,b}$	−85	22.11	24.68	26.2	0.842	0.081
$CH_3CH_2{}^{a,b}$	−98	21.8	24.5	26.1	0.836	0.090

[a] See Table I, footnote *a*. [b] H. Fischer, *Z. Naturforsch.*, **20a**, 428 (1965).

$$\rho_\alpha = \prod_{i=1}^{3}(1 - \Delta X_i) = 0.919(1 - \Delta X) \qquad (8)$$

It is apparent from the examination of Table III that group IV metal atoms as α substituents in ethyl radicals exert an influence which is intermediate between hydrogen and alkyl groups.

The γ coupling constants of α-substituted methyl radicals I ($R = CH_3$) show a pronounced variation in the series $(CH_3)_3CCH_2\cdot$, $(CH_3)_3SiCH_2\cdot$, $(CH_3)_3GeCH_2\cdot$, and $(CH_3)_3SnCH_2\cdot$. The mechanism of long-range interactions is insufficiently understood in order to interpret this trend.[16] It is probable, however, that the γ-coupling constant changes sign between the silicon and tin radicals in this series (Table I).

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(13) A more complete esr study of ethyl radicals substituted in the β position with group IV metals, sulfur, and oxygen will be reported later.

(14) See Table I, footnote *a*.

(15) See Table III, footnote *b*.

(16) Recently Lin and Williams (*J. Phys. Chem.*, 72, 3707 [1968]) have suggested on the basis of a large coupling constant of only three equivalent protons ($a_{\gamma\text{-}CH_3} = 4.0$ G) that neopentyl radicals at −145° in the solid state exists in a preferred conformation in which one of the γ-methyl groups is eclipsed by the p orbital. On the other hand, Fessenden and Schuler[14] at −13° do not observe any resolvable hyperfine structure for the γ-methyl groups, but estimate the coupling constant to be in the range 0.4–0.5 G from the over-all line width. Our value[8] is intermediate ($a_{\gamma\text{-}CH_3} = 1.0$) at −58° in solution. It appears, therefore, that the γ-coupling constant is strongly dependent on the temperature, probably due to hindered rotation. The decreased magnitude of the coupling constants of the group IV analogs *may* reflect lower barriers to rotations.

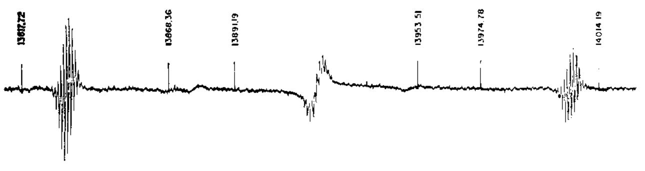
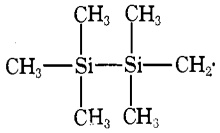


Figure 3. Esr spectrum of $(CH_3)_3SiSi(CH_3)_2CH_2\cdot$ in cyclopropane solution at −95°.

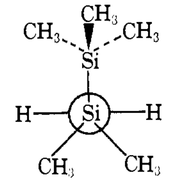
Transient radical species were also derived from disilanes. For example, the esr spectrum obtained from hexamethyldisilane is shown in Figure 3. There are two striking features of this spectrum: (1) a fine structure consisting of an *even number* of more than ten lines of approximately binomial intensity distribution and (2) the pronounced broadening of the central multiplet. We attribute this spectrum to radical species VII in which at least 9 methyl protons, but more probably all 15 protons are equally coupled. Examination of molecular models reveals that the γ and δ hydrogens are essentially equidistant from the radical center. The broadening of the central multiplet in the spectrum of VII is temperature dependent and associated with hindered rotation about the C–Si bond causing a fluctuation of the α-coupling constants.[17] Interestingly, the rotational conformation leading to the optimum steric arrangement of groups as shown below cannot be the conformation at the minimum of the potential barrier. In this equilibrium conformation the



$$(CH_3)_3Si{-}Si(CH_3)_2CH_2\cdot$$

VII

$a_{CH_2} = 20.15$ G
$a_{CH_3} = 0.24$ G
$T = -95°$



α protons are equivalent and no line-width broadening is expected. We cannot distinguish at this juncture among the other conformations leading to inequivalence of methylene hydrogens. We have also examined hexamethyldisiloxane in which an oxygen atom is interposed between the two trimethylsilyl moieties. As expected, no long-range interactions are observed and the spectrum consists of a triplet of septets assigned to species VIII.

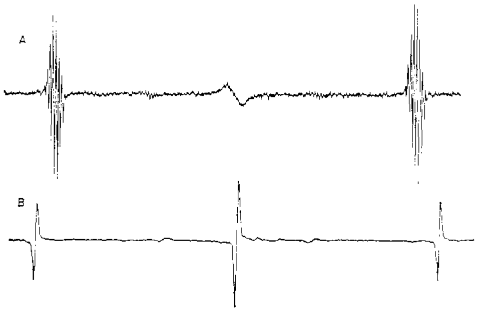
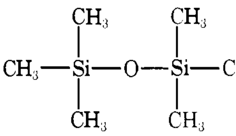


Figure 4. (a) Esr spectrum of $(CH_3)_3CO\dot{C}H_2$ in cyclopropane solution at −107°; (b) esr spectrum of $(CH_3)_3SiO\dot{C}H_2$ in cyclopropane solution at −155°.



$$(CH_3)_3Si{-}O{-}Si(CH_3)_2CH_2\cdot$$

VIII

$a_{CH_2} = 21.09$ G
$a_{CH_3} = 0.78$ G
$T = -108°$

Methoxy derivatives of the organometallic derivatives of group IV metals listed in Table IV yield only radicals of the general structure $R_n(CH_3O)_{3-n}MO\dot{C}H_2$, resulting from hydrogen abstraction exclusively at the methoxy group. The esr spectra are simply triplets without further resolved fine structure. The spectrum of the related *t*-butoxymethyl radical, on the other hand, shows resolved γ couplings and a pronounced temperature-dependent broadening of the central multiplet due to hindered internal rotation about the C–O bond.[17, 18] Figure 4 illustrates the magnitude of this effect at −107°. In marked contrast, the spectrum of the silicon analog shows no change even at temperatures as low as −155° (Figure 4). The difference in behavior between these carbon and silicon radicals can be accounted for by a larger oxygen bond angle in the latter, probably due to contribution from d_π–p_π bonding.

Table IV. Coupling Constants for Radicals from Methoxy Derivatives of Group IVB Compounds

$R_nM(OCH_3)_{4-n}$	$R_nM(OCH_3)_{3-n}OCH_2\cdot$	Temp, °C	a_{CH_2}, G
$(CH_3)_3COCH_3$	$(CH_3)_3COCH_2\cdot$	−102	17.29[a]
$(CH_3)_3SiOCH_3$	$(CH_3)_3SiOCH_2\cdot$	−109	19.08
$(CH_3O)_4Si$	$(CH_3O)_3SiOCH_2\cdot$	−22	19.69
$(CH_3O)_4Ge$	$(CH_3O)GeOCH_2\cdot$	−58	19.13
$(CH_3)_2Si(OCH_3)_2$	$(CH_3)_2(CH_3O)SiOCH_2\cdot$	−90	19.27
$(n\text{-}C_4H_9)_3SnOCH_3$	$(n\text{-}C_4H_9)_3SnOCH_2\cdot$	−40	16.30

[a] $a_{CH_3} = 0.28$.

Acknowledgment. We wish to thank Mr. K. Eaby for technical assistance.

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[17] Line width effects in esr spectroscopy have been reviewed recently: D. H. Geske, *Progr. Phys. Org. Chem.*, **4**, 125 (1967); G. K. Fraenkel, *J. Phys. Chem.*, **71**, 139 (1967); A. Hudson and G. R. Luckhurst, *Chem. Rev.*, **69**, 191 (1969).

[18] P. J. Krusic, to be published.