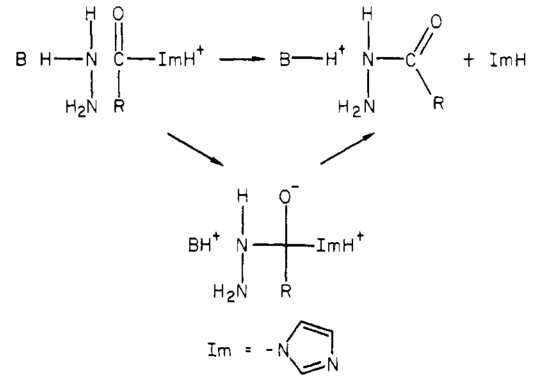
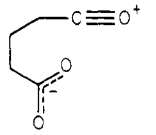
for breakdown provided by the electron pairs on the oxyanion and nitrogen atoms and the developing resonance of the amide product (eq 16).

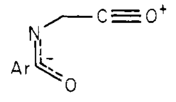


(16)

The acylium ions from the intramolecular reactions of succinate and glutarate half esters and of aryl benzoylglycinates possess highly electron-donating moieties (IX and X, respectively) which



IX



X

may act as stabilizing functions; the potential energy surface (Figure 9), usually highly asymmetric in favor of an addition–elimination mechanism, may therefore be rendered more symmetrical, shifting the reaction coordinate toward the top left corner favoring a concerted process. The free energy of the tetrahedral adduct in the intramolecular reaction will also be greater than that in the open chain because of a greater degree of internal rotational freedom in the latter; this also helps to promote a concerted displacement process.

Electron Spin Resonance Studies on Tris(3,5-di-*tert*-butylphenyl)silyl and -germyl Radicals[1]

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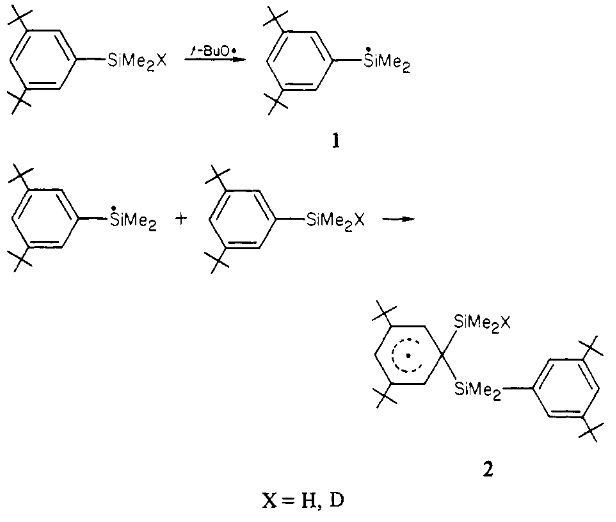
Contribution from the Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan. *Received February 20, 1980*

Abstract: Electron spin resonance spectra of tris(3,5-di-*tert*-butylphenyl)silyl, -germyl, and -methyl radicals in solution are recorded. The hyperfine coupling constants of the triarylsilyl radical are observed for the first time. The *g* values and hyperfine coupling constants, $A_{o\text{-H}}$ and $A_{p\text{-H}}$ (in gauss), are as follows: $Ar_3C\cdot$ (−40 °C), 2.0026, 2.58, 2.80; $Ar_3Si\cdot$ (−50 °C), 2.0027, 0.95, 1.17; $Ar_3Ge\cdot$ (−70 °C), 2.0056, 0.60, 0.95 (Ar = 3,5-di-*tert*-butylphenyl). The spin densities at the central atoms of $Ar_3M\cdot$ are estimated to be 0.50 (M=C), 0.78 (M = Si), and 0.82 (M = Ge), respectively.

Aryl-substituted radicals are of considerable interest to study by electron spin resonance (ESR) techniques, since ESR data give direct information about spin delocalization onto the aryl rings. Particularly interesting would be the ESR spectra of aryl-substituted group 4B radicals which could be compared with those of well-documented triarylmethyl radicals. These data could give useful information about the efficiency of spin delocalization from the central group 4B atom to 2p orbitals and may be related to the efficiency of C=M (M = Si, Ge, etc.) bonding which has been of current interest.

We have previously reported the ESR spectra of phenyl-substituted germyl radicals,[2] but, in spite of repeated experiments, we could not observe a neat spectrum of $Ph_3Si\cdot$ radicals. A reason that we failed to observe $Ph_3Si\cdot$ seemed to be the high reactivity of silyl radicals toward aromatic substitution.[3] The reaction of (3,5-di-*tert*-butylphenyl)dimethylsilane with the *tert*-butoxy radical gave a strong ESR signal of the ipso substituted radical (**2**) instead of the expected (3,5-di-*tert*-butylphenyl)dimethylsilyl radical (**1**).[4]

However, hydrogen abstraction from tris(3,5-di-*tert*-butylphenyl)silane gave the desired tris(3,5-di-*tert*-butylphenyl)silyl radical (**3**) successfully. In this paper, we report ESR studies on **3** and related methyl and germyl radicals.



(1)

1

(2)

2

X = H, D

Results and Discussion

The tris(3,5-di-*tert*-butylphenyl)silyl radical (**3**) was generated in an ESR cavity by abstraction of hydrogen from the corresponding hydrosilane using photochemically generated *tert*-butoxy radicals.[5,6]

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(1) Chemistry of Organosilicon Compounds. 133.

(2) (a) Sakurai, H.; Mochida K.; Kira, M. *J. Am. Chem. Soc.* **1975**, *97*, 929. (b) Sakurai, H.; Mochida, K.; Kira, M. *J. Organomet. Chem.* **1977**, *124*, 235.

(3) Sakurai, H.; Hosomi, A. *J. Am. Chem. Soc.* **1971**, *93*, 1709.

(4) Sakurai, H.; Nozue, I.; Hosomi, A. *Chem. Lett.* **1976**, 129.

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

(6) Hudson, A.; Hussain, H. A. *Mol. Phys.* **1969**, *16*, 199.

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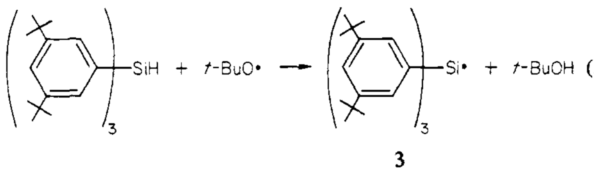


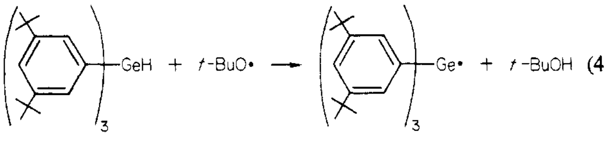
(3)

3

Figure 1a shows the spectrum of **3** at −50 °C that consists of 28 lines arising from a quartet (1.17 G due to parahydrogens) of septets (0.95 G due to ortho hydrogens). These coupling constants show temperature dependence as discussed later. The experimental spectrum was satisfactorily reproduced by computer simulation as shown in Figure 1b. So far as we know, this is the first spectrum of aryl-substituted silyl radicals in solution with well-resolved hyperfine coupling constants (hfcc). Geoffroy and Lucken reported ESR of Ph$_3$Si·, generated by X-ray irradiation of solid Ph$_3$SiH, with an average *g* value of 2.0029, but no hyperfine interaction was observed.[7] The isotropic *g* value of **3** was 2.0027. The radical **3** was not long-lived, disappearing rapidly after the light was shut off.

Three bulky 3,5-di-*tert*-butylphenyl groups are apparently necessary to prevent homolytic aromatic silylation efficiently, since cyclohexadienyl-type radicals similar to **2** were derived from bis(3,5-di-*tert*-butylphenyl)methylsilane. At −110 °C, a new radical with a different *g* value was observed which could be bis(3,5-di-*tert*-butylphenyl)methylsilyl but the spectrum could not be fully analyzed.

The tris(3,5-di-*tert*-butylphenyl)germyl radical (**4**) was also generated by a similar procedure. Experimental and computer-simulated spectra of **4** are shown in Figure 2.

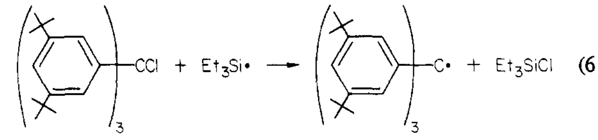


(4)

4

The corresponding methyl radical, tris(3,5-di-*tert*-butylphenyl)methyl (**5**), has been already reported by Schreiner, Berndt, and Baer,[8] but we have observed **5**, generated as depicted by reactions 5 and 6.

$$Et_3SiH + t\text{-}BuO\cdot \rightarrow Et_3Si\cdot + t\text{-}BuOH \qquad (5)$$



(6)

5

The radical **5** is long-lived, and the ESR spectrum is composed of a quartet (2.80 G, due to para hydrogens) of septets (2.58 G, due to ortho hydrogens). These hfcc values are in accord with those (2.80 and 2.57 G) reported by Schreiner et al.[8] Four sets of satellites due to ^{13}C were also observed for **5**.

Spectral data of **3**, **4**, and **5** are listed in Table I. From the spin densities of the triphenylmethyl radical calculated by the Hückel–McLachlan method,[2b] ^{13}C hfcc values are computed and listed in Table I.

As can be seen in the Table I, hyperfine coupling constants of ring protons decrease in the order of **5** > **3** > **4**. Since hfcc values are linearly correlated with spin densities by the McConnell equation,[9] the result indicates that the extent of spin delocalization from the central atom to benzene rings decreases in the same order. Thus, the spin density in the ring system of the aryl-substituted silyl radical is between those of the corresponding methyl and germyl radicals, in agreement with the expected order of π conjugation between the central atom and carbon.

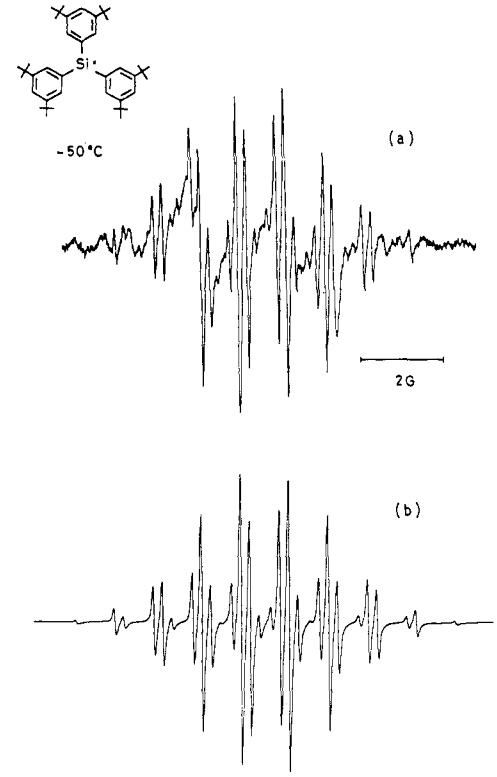


Figure 1. ESR spectra of tris(3,5-di-*tert*-butylphenyl)silyl radicals (**3**): (a) experimental at −50 °C; (b) simulated.

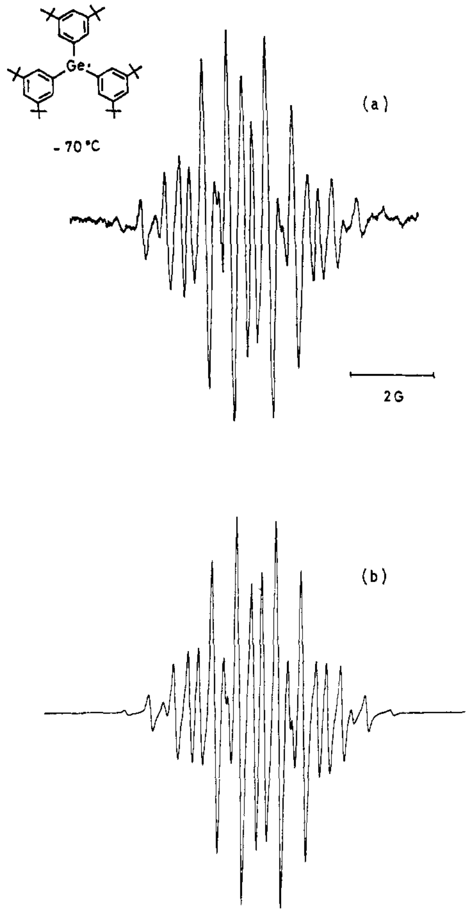


Figure 2. ESR spectra of tris(3,5-di-*tert*-butylphenyl)germyl radicals (**4**): (a) experimental at −70 °C; (b) simulated.

The second characteristic feature observed in the ESR data of the present series of radicals, in comparison with those of triphenylmethyl and triphenylgermyl radicals, is that the hfcc

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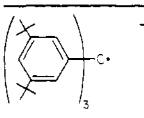
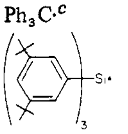
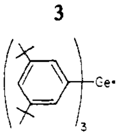
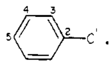
(7) Geoffroy, M.; Lucken, E. A. C. *Helv. Chim. Acta* **1970**, *57*, 813.

(8) Shreiner, K.; Berndt, A.; Baer, F. *Mol. Phys.* **1973**, *26*, 929.

(9) McConnell, H. M. *J. Chem. Phys.* **1956**, *24*, 632.

Table I. *g* Factors and Hyperfine Coupling Constants of $Ar_3M\cdot$ Radicals

			hfcc/G			
radical	T/°C	g value	o-H	p-H	other	
 **5**	−40	2.0026	2.58	2.80	11.3 $(C_2)^{a,b}$ 6.40 (C_3) 3.20 (C_4) 4.1 (C_5)	$(10.3)^c$ $(5.09)^c$ $(4.42)^c$ $(4.96)^c$
$Ph_3C\cdot^c$	20	2.0026	2.53	2.77	1.11 (m-H)	
 **3**	−50	2.0027	0.95	1.17		
 **4**	−70	2.0056	0.60	0.95		
$Ph_3Ge\cdot^d$	−30	2.0054	0.93	0.93	0.46 (m-H)	

[a] Numbering is as follows:  . [b] Schreiner et al.[8] reported following hfcc in G: C_2, 11.3; C_3, 6.5; C_4, 3.2; C_5, 4.1. [c] Calculated hfcc by using the equation of Karplus, M.; Fraenkel, G. *J. Chem. Phys.* **1976**, *35*, 1312, with spin densities reported in ref 2. [d] Reference 2b.

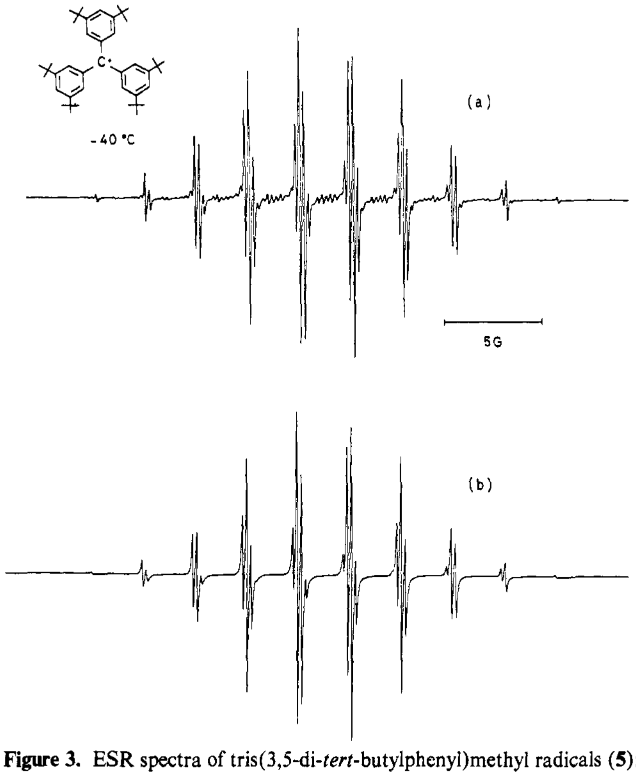


Figure 3. ESR spectra of tris(3,5-di-*tert*-butylphenyl)methyl radicals (**5**): (a) experimental at −40 °C; (b) simulated.

values for ortho hydrogens ($A_{o\text{-H}}$) are smaller than those of para hydrogens ($A_{p\text{-H}}$), and the ratio, $A_{o\text{-H}}/A_{p\text{-H}}$, is in the following order: **5** > **3** > **4**. Previously, we have observed almost the same hfcc values for ortho and para hydrogens in the spectra of both $Ph_3C\cdot$ and $Ph_3Ge\cdot$ (see Table I).

The Hückel molecular orbital calculations with the McLachlan approximation[10] for $Ph_3Ge\cdot$, $Ph_2MeGe\cdot$, $PhMe_2Ge\cdot$, and the corresponding methyl radicals reproduced hfcc values excellently,[2] when the resonance integral, β_{G-C}, was estimated to be 0.45 β_0. However, no satisfactory result was obtained on the calculation of spin densities for $Ar_3M\cdot$ radicals (Ar = 3,5-di-*tert*-butylphenyl) with a variety of combination of resonance and Coulomb integrals, observed hfcc values for ortho hydrogens being always too small.[11] This fact suggests that approximations used for the calculation of hfcc values of $Ph_3M\cdot$ (M=C and Ge) can be no longer valid for $Ar_3M\cdot$ because of increasing distortion from planarity of the radicals.

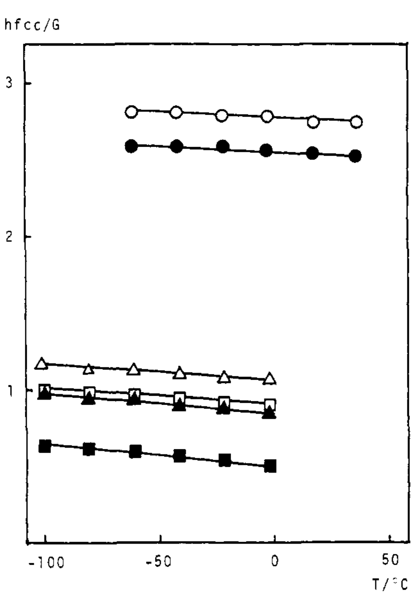


Figure 4. Temperature dependence of hfcc: ○, $A_{p\text{-H}}$ of **5**; ●, $A_{o\text{-H}}$ of **5**; △, $A_{p\text{-H}}$ of **3**; ▲, $A_{o\text{-H}}$ of **3**; □, $A_{p\text{-H}}$ of **4**; ■, $A_{o\text{-H}}$ of **4**.

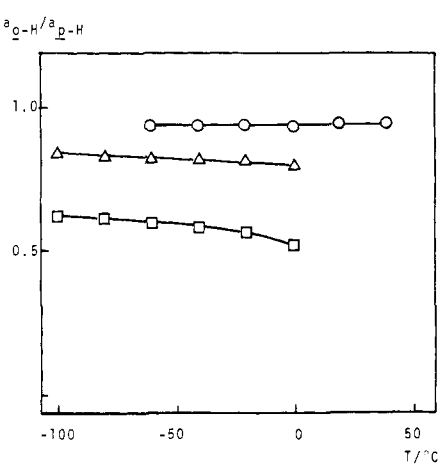


Figure 5. Temperature dependence of $A_{o\text{-H}}/A_{p\text{-H}}$. ○, **5**; △, **3**; □, **4**.

Calculation of hfcc of ring hydrogens by the McConnell equation is premised on the spin-polarization mechanism. However, methyl, silyl, and germyl radicals would loose their planarity either by twisting the substituent groups or by assuming a pyramidal structure, and nonbonded interaction between adjacent ortho hydrogen atoms in addition to the existence of bulky *tert*-butyl groups will favor most probably a propeller configuration for $Ar_3M\cdot$ radicals. The average angle between the benzene rings of the triphenylmethyl radical is estimated at about 30°.[12] The X-ray crystallographic analysis of the tris(p-nitrophenyl)methyl radical also indicates that the plane of the ring is twisted about 30°.[13] For nonplanar radicals, long-range through-space interaction between the p orbital of the central atom and ortho hy-

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(10) McLachlan, A. D. *Mol. Phys.* **1959**, *2*, 271.

(11) In the Hückel-McLachlan calculations, Coulomb ($\alpha = \alpha_0 + h\beta_0$) and resonance ($\beta = k\beta_0$) integrals are changed with $-0.6 \leq h \leq 0$ and $0.8 \leq k \leq 1.0$.

(12) (a) Samoilov, S.; Dyatkina, M. E. *Zh. Fiz. Khim.* **1948**, *22*, 1294. (b) Adrian, F. J. *J. Chem. Phys.* **1958**, *28*, 608.

(13) Anderson, P.; Klewe B. *Acta Chem. Scand.* **1962**, *16*, 1817.

drogens becomes more important as the spin density on the central atom increases. The through-space interaction and the spin polarization counteract each other to determine the magnitude of hfcc and, therefore, explain the relative magnitude of $A_{o\text{-H}}/A_{p\text{-H}}$ qualitatively. Thus, increasing nonplanarity with increasing localizing spin density on the central atom in the series of **5** → **3** → **4** results in increasing importance of the through-space spin delocalization to ortho hydrogens. Accordingly, $A_{o\text{-H}}/A_{p\text{-H}}$ decreases in the order of **5** > **3** > **4**.

hfcc values of ring hydrogens show small but definite temperature change as shown in Figures 4 and 5.

The *g* value of **3** is the smallest among those reported for other silyl radicals: H_3Si, 2.003,[14] 2.00332;[15,16] $MeSiH_2$, 2.0032;[15,17] $Me_2SiH\cdot$, 2.0031;[16] $Me_3Si\cdot$, 2.0031,[16] 2.0029;[15] $Et_3Si\cdot$, 2.0030.[16] This fact obviously indicates increased delocalization of the spin from the central silicon atom to substituents in the case of **3** as compared to the other silyl radicals.

In the triphenylgermyl radical, it is estimated that 82% of the spin is localized at germanium,[2] whereas in the corresponding triphenylmethyl radical the spin density at the central carbon is 42%.[18] Since the *g* value of **4** is almost identical with that of $Ph_3Ge\cdot$, the spin density of **4** can be assumed to be 82%. On the other hand, Schreiner et al. estimated the spin population at the central carbon of **5** to be 48 to ~53%.

From the McConnell equation ($A_H = Q\rho$), the spin density of the central atom (ρ_M) may be written as in eq 7. If one assumes

$$\rho_M = 1 - 3\left(\sum_{i=1}^{6}\rho_i\right) = 1 - (3/Q)(1/\rho_p)\left(\sum_{i=1}^{6}\rho_i\right)A_{p\text{-H}} \qquad (7)$$

that Q and $(1/\rho_p)(\sum_{i=1}^{6}\rho_i)$ are identical for **3**, **4**, and **5** (the latter term indicates the relative spin densities at aryl rings), ρ_M should be proportional to $A_{p\text{-H}}$. From the values of spin densities of **4** (0.82) and **5** (0.50), the spin density of **3** can be calculated as 0.78.

In spite of the very rough approximation, the value agrees quite nicely with the value (0.71) reported for solid $Ph_3Si\cdot$.[7]

Experimental Section

General Data. Microanalyses were performed by the Instrumental Analysis Center for Chemistry, Tohoku University. 1-Bromo-3,5-di-*tert*-butylbenzene[19] and methyl 3,5-di-*tert*-butylbenzoate[20] were prepared according to the references.

Tris(3,5-di-*tert*-butylphenyl)methanol. To a diethyl ether (40 mL) solution of (3,5-di-*tert*-butylphenyl)lithium, prepared from 1-bromo-3,5-di-*tert*-butylbenzene (26.9 g, 99.9 mmol) and lithium (1.8 g, 250 mmol), was added methyl 3,5-di-*tert*-butylbenzoate (9.89 g, 39.7 mmol) in ether (20 mL) during 30 min, and the mixture was refluxed for 8 h. Usual workup gave a white solid which was recrystallized from pentane to give pure crystals (18.5 g, 31.0 mmol, 78% yield), mp 156–157 °C. IR (KBr): 3605 cm^{-1} (ν_{OH}). NMR (CCl_4): δ 1.27 (s, 54 H), 2.32 (s, 1 H), 7.09 (m, 6 H), 7.29 (m, 3 H). Anal. Calcd for $C_{43}H_{64}O$: C, 86.51; H, 10.81. Found: C, 86.55; H, 10.84.

Tris(3,5-di-*tert*-butylphenyl)chloromethane. A benzene (20 mL) suspension of tris(3,5-di-*tert*-butylphenyl)methanol (1.10 g, 1.8 mmol) was heated at 80 °C under nitrogen. Addition of acetyl chloride (0.15 mL) to the mixture resulted in the formation of a homogeneous solution. After 5 min, additional acetyl chloride (0.4 mL) was added, and the mixture was refluxed for 30 min. The mixture was cooled with an ice bath, white crystals being precipitated by adding pentane (2 mL). Recrystallization from pentane gave 1.01 g (1.64 mmol, 91.4% yield) of pure compound; mp 186–187 °C. IR (KBr) 805 cm^{-1} ($\nu_{C\text{-}Cl}$). Anal. Calcd for $C_{43}H_{63}Cl$: C, 83.92; H, 10.32. Found: C, 84.09; H, 10.61.

Tris(3,5-di-*tert*-butylphenyl)silane. (3,5-Di-*tert*-butylphenyl)lithium, prepared from 1-bromo-3,5-di-*tert*-butylbenzene (3.56 g, 13.2 mmol) and lithium (0.22 g, 32 mmol) in 50 mL of ether was added to trichlorosilane (0.54 g, 4 mmol). After being stirred for 3 h at room temperature, the mixture was hydrolyzed and worked up to give white crystals. Recrystallization from methanol gave 0.90 g (1.5 mmol, 38%) of pure compound, mp 139–140 °C. IR (KBr) 2120 cm^{-1} ($\nu_{Si\text{-}H}$). Anal. Calcd for $C_{42}H_{64}Si$: C, 84.49; H, 10.80. Found: C, 84.34; H, 10.73.

Tetrakis(3,5-di-*tert*-butylphenyl)germane. (3,5-Di-*tert*-butylphenyl)lithium, prepared from 3,5-di-*tert*-butylbromobenzene (19.4 g, 72 mmol) and lithium (1.3 g, 0.18 mmol) in 300 mL of ether, was added to tetrachlorogermane (3.21 g, 15 mmol) in 50 mL of ether. After usual workup, white crystals were obtained. Recrystallization from toluene and washing with methanol gave 9.24 g (11.1 mmol, 74.2%) of pure crystals, mp 200–202 °C. Anal. Calcd for $C_{56}H_{84}Ge$: C, 81.05; H, 10.20. Found: C, 81.20; H, 10.17.

Tert(3,5-di-*tert*-butylphenyl)bromogermane. Bromine (1.4 g, 8.8 mmol), was added to a 1,2-dibromoethane (30 mL) solution of tetrakis(3,5-di-*tert*-butylphenyl)germane (6.64 g, 8 mmol), and the mixture was refluxed for 1 h. The solvent was removed in vacuo and the residual mass was extracted with benzene. After benzene was distilled off, a crude material was recrystallized from acetic acid to give white crystals, mp 208 °C. Anal. Calcd for $C_{42}H_{63}GeBr$: C, 70.02; H, 8.81. Found: C, 69.99; H, 8.87.

Tris(3,5-di-*tert*-butylphenyl)germane. The bromogermane (2.16 g, 3 mmol) in 50 mL of ether was added to $LiAlH_4$ (0.2 g, 5.3 mmol) in ether (100 mL). A usual workup gave the hydrogermane and recrystallization from pentane gave 1.73 g (2.70 mmol, 90%) of white crystals, mp 150–151 °C. IR (KBr) 2032 cm^{-1} ($\nu_{Ge\text{-}H}$). Anal. Calcd for $C_{42}H_{64}Ge$: C, 78.63; H, 10.06. Found: C, 78.93; H, 10.23.

ESR Spectra. ESR spectra were taken with a Varian E-12 spectrometer as described previously.[2b]

Acknowledgment is made to the Mitsubishi Foundation for the partial support to the work. We also thank Toshiba Silicone Co., Ltd., for gifts of chlorosilanes.

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