Difluorenylsilanes, -germanes, and -stannanes Exhibiting an Unprecedented Parallel Arrangement of the Fluorene Units

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New, yet unprecedented molecular structures with parallel fluorene units were found by X-ray diffraction in (9,9′-disubstituted difluorenyl)(dimethyl) derivatives of group 14 elements $Me_2E(CR'R_2)(CR''R_2)$ (E = Si, R′ = Me, R″ = $SiMe_3$, **6a**; E = Ge, R′ = Me, R″ = $SiMe_3$, **6b**; and E = Sn, R′ = R″ = $SiMe_3$, **5c**; CR_2 = fluorene units). This is in sharp contrast with the structure of monosubstituted $Me_2Ge(CHR_2)(CR_2\text{-}SiMe_3)$ (**3b**) and disubstituted $Me_2E(CMeR_2)_2$ (E = Ge, **4b**; E = Sn, **4c**) derivatives where the two fluorene units are almost perpendicular. Intramolecular C−H⋯π interactions are revealed by solution ^1H NMR spectroscopy and supported by the AM1 molecular orbital calculations. Intermolecular (aryl, alkyl)C−H⋯π interactions leading to supramolecular associations are shown by the crystal structures of **3b**, **4b**, **4c**, **5c**, and **6a**. In **4b** and **5c** rather unusual CH⋯HC distances resembling the "dihydrogen" bonds are noticed. Synthesis, NMR spectra, and gas phase conformations predicted on the basis of AM1 semiempirical molecular orbital calculations are discussed for $Me_2E(CR'R_2)(CR''R_2)$ (E = Si, R′ = R″ = $SiMe_3$, **5a**; E = Ge, R′ = R″ = $SiMe_3$, **5b**; E = Sn, R′ = H, R″ = Me, **2c**; R′ = H, R″ = $SiMe_3$, **3c**; R′ = Me, R″ = $SiMe_3$, **6c**; CR_2 = fluorene units).

Introduction

In view of the special electronic and steric properties exhibited by a fluorenyl group bound to a main group element,[1−11] we have been interested in the last years in the influence brought by the presence of a second fluorenyl bound to the same element.

Many group 14 derivatives containing two fluorene groups substituted or not at the 9-position of the general formula $Me_2E(CR'R_2)(CR''R_2)$ (E = Si, Ge, Sn) have been studied.

$Me_2E(CHR_2)_2$ compounds (E = Si, **1a**; Ge, **1b**; Sn, **1c**; CHR_2 = 9-fluorenyl) were previously synthesized,[12] and the crystal and molecular structures of **1a**,[13] **2a**,[14] and **4a**[14] (see Chart 2) were reported by some of us. It was shown by molecular orbital calculations (AM1 level) on **1a**, **2a**, and **4a** that these systems can adopt four classes of conformations which differ by the relative orientations of the R′ and R″ groups toward the fluorenyl groups (Chart 1).[13,14]

An R′-*in*−R″-*out* conformation was found in both solid state and gas phase for **1a**, **2a**, and **4a**.[13,14] Gas phase conformations predicted on the basis of AM1 semiempirical molecular orbital calculations support the existence of intramolecular C−H⋯π interactions and correlate well with the temperature-dependent proton NMR

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Chart 1

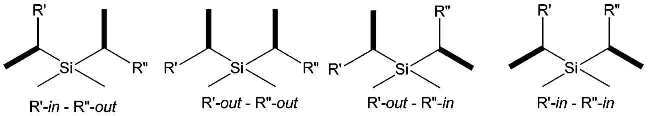
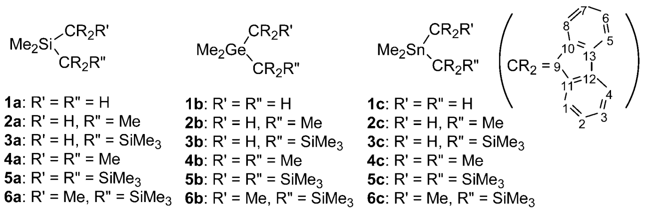


Chart 2



spectra. All these three silicon derivatives also exhibit extensive intermolecular C−H···π interactions leading to supramolecular associations in the solid state. Since so far, only the *in−out* conformers have been observed in the solid state,[13−15] it has been a challenge to obtain compounds having the two fluorenyl rings arranged in a parallel fashion: R′-*out*−R″-*out*. Such a conformation might be important in the synthesis of systems containing two fluorenyl groups coordinated to a strong Lewis acid center. Such compounds are of high technological interest, and significant industrial applications have been described in the literature since the discovery of new catalysts for the polymerization of ethylene or propylene based on fluorenylidene derivatives of zirconium.[1,16−23]

Herein we report the synthesis, NMR data, and semiempirical AM1 calculations for new derivatives **2c**, **3bc**, **4bc**, **5a**−**c**, and **6a**−**c** containing two substituted fluorene groups on metal 14 (Chart 2).

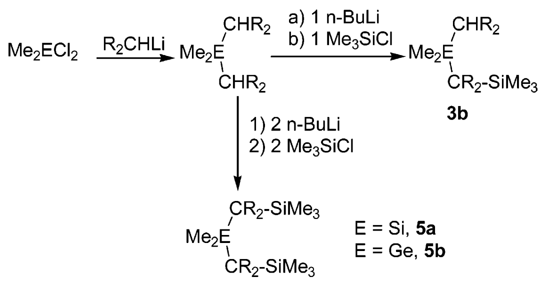
Crystal and molecular structures were determined by single-crystal X-ray diffraction for compounds **3b**, **4b**, **4c**, **5c**, **6a**, and **6b** and are discussed in relation with spectral data and conformational analysis.

Results and Discussion

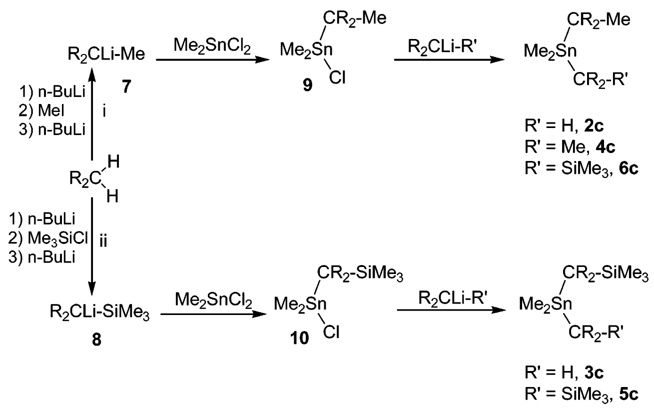
New monosubstituted **3b** and disubstituted **5a** and **5b** derivatives of silicon and germanium were prepared by the reaction of $Me_2E(CHR_2)_2$ with 1 or 2 equiv of *n*-butyllithium followed by addition of Me_3SiCl (1 or 2 equiv) to the reaction mixture (Scheme 1), as previously described by some of us for **2b** and **4b**.[12]

Such a route cannot be used in the case of tin due to an easy cleavage of the Sn−C(fluorenyl) bond by *n*-butyllithium leading to Me_2SnBu_2.[12] Thus, for tin derivatives, a different reaction pathway was used involving the successive addition of the lithiofluorenyl compound **7** or **8** to dimethyldichlorostannane then of $R_2C(Li)R'$ to the monosubstituted tin derivative **9** or **10** (Scheme 2).

Scheme 1



Scheme 2



The unsymmetrically substituted silicon and germanium compounds **6a** and **6b** have also been prepared using route (i) in Scheme 2.

Solution NMR Spectra and Conformational Analysis. The ^1H and ^{13}C NMR spectra of the novel synthesized 9-substituted (**2c**, **3bc**) and 9,9′-disubstituted (**4bc**, **5a**−**c**, **6a**−**c**) compounds have been recorded and compared to those of the already known **1a**−**c**, **2a**,**b**, **3a**, and **4a**.[12]

The remarkable change in the chemical shift of the proton bound to C9 in **2a** (3.05 ppm) compared to **1a** (4.25 ppm) has been related to a strong C−H···π interaction between H9 and the opposite fluorenyl ring.[13] Similar trends are also observed for 9-monosubstituted germanium **2b**, **3b** and tin **2c**, **3c** derivatives (3.15, 2.81 ppm for Ge and 3.50, 3.05 ppm for Sn, respectively, compared to 4.24 and 4.21 ppm in **1b** and **1c**). Note also that the ^1H NMR spectrum of **3a** (2.65 ppm) exhibits an even greater upfield shift of H9 than its methyl analogue **2a** (3.05 ppm). For the same substituent, the chemical shift for H9 increases from silicon to tin: from 3.05 to 3.50 ppm for methyl derivatives **2a**−**c** and from 2.65 to 3.05 ppm for trimethylsilyl derivatives **3a**−**c**. On the other hand, the chemical shifts of H9 for the three parent compounds (**1a**−**c**) are almost the same (4.25, 4.24, 4.21 ppm, respectively[12]). These lower field values in the parent systems **1a**−**c** could be related to a faster rotation around the E−C(fluorenyl) bonds than in their monosubstituted derivatives. A faster rotation means a shorter time spent by H9 in the field of the opposite fluorenyl group, which in turn means a smaller shielding exerted by the latter. Figure 1 shows the variation of these chemical shifts with the barrier of rotation around the H9−C(fluorenyl)−E−C(fluorenyl) torsion angles (which brings the H-*in*−R″-

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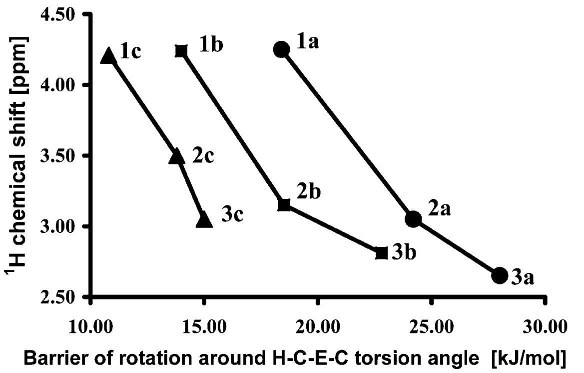

Figure 1. Variation of the ^{1}H chemical shifts with the barrier of *in*−*out* to *out*−*out* rotations around the H−$C_{(fluorenyl)}$−E−$C_{(fluorenyl)}$ (H−C−E−C) torsion angle.

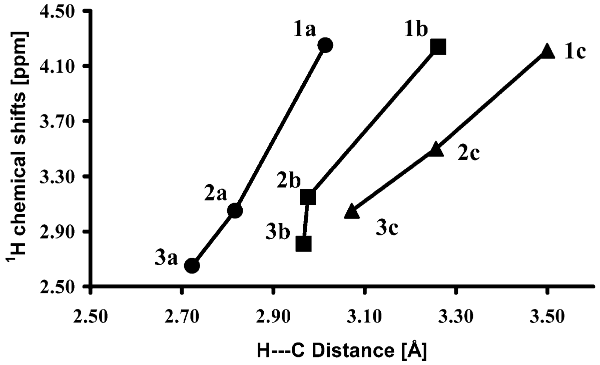

Figure 2. Variation of the ^{1}H chemical shifts with the H−$C_{reference}$ (see text) distances.

out into H-*out*−R″-*out* conformer), as calculated with the AM1 method.

These data show that, indeed, the lowest barriers of rotation are found in the unsubstituted **1a**−**c** (in relation to **2a**−**c** and **3a**−**c**), and these correlate with the downfield values of H9 in these systems. Upon substitution, the barriers of rotation increase. The largest barriers are found in **3a**−**c** (in relation to **1a**−**c** and **2a**−**c**), where a $SiMe_3$ group is on the second fluorenyl and the H9 chemical shifts go to upfield values, in accordance with slower rotation around the H9−C(fluorenyl)−E−C(fluorenyl) torsion angle, which causes a greater extent of shielding from the opposite fluorenyl.

The extent of shielding is also reflected through the distance between H9 and a reference point taken on the opposite fluorenyl ring in the *in*−*out* conformer. We have chosen this point as the closest carbon atom on the neighbor fluorenyl ring, and the variation of the ^{1}H chemical shifts with this distance for the three series of compounds **1a**−**c**, **2a**−**c**, and **3a**−**c** is given in Figure 2.

Note here that a shorter H9−$C_{reference}$ distance within the same metal series is indicative of a greater shielding.

The doublet of doublets at a surprisingly higher field (6.42 ppm) for aromatic protons in the ^{1}H NMR spectrum of $Me_2Si(CHR_2)(CMeR_2)$ (**2a**) was assigned on the basis of 2D NMR spectra to the protons bound to C1 and C8.[14] Similar signals are also present in the spectra of all other 9-substituted difluorenyl derivatives. Such high-field shifts for protons H1 and H8 are due to their interactions with the protons H2′ and H7′ of the opposite fluorenyl, as evidenced by NOE technique.

In the ^{1}H NMR spectra of $Me_2E(CMeR_2)_2$ (E = Si, Ge, Sn) there is only one signal for the two methyl groups at C9 and C9′; so, at least at room temperature, these groups (and the fluorenyl bearing them) are equivalent.

Solid State Structures. Data collection, crystal data, and refinement data for compounds **3b**, **4bc**, **5c**, and **6ab** are summarized in Table 1. Selected values of bond lengths and bond angles are listed in Tables 2 and 3, and Figures 3−8 show the molecular structure of these compounds.

a. Molecular Structures. The 9-substituted compound **3b** (Figure 3) adopts the *in*−*out* conformation, as does **1a** or **2a**.[12,13] The main feature here is the short (C)H9−fluorenyl (centroid of this ring) distance (2.887 Å) indicative of CH···π interaction.[24,25]

In compounds **4b** (Figure 4) and **4c** (Figure 5), as a consequence of the same *in*−*out* conformation, one proton of C16 (Me-*in*) comes close to the opposite fluorenyl ring (2.929 and 2.815 Å, respectively), making possible CH···π interactions which stabilize the *in*−*out* conformations of **4b** and **4c** and the corresponding silane **4a**.

Thus, with one trimethylsilyl group as in **3b**, or two methyl groups, as in **4b** or **4c**, only the *in*−*out* conformation is observed in the solid state. Note that the values of the dihedral angles between the two fluorenyl ring planes are 90.5° (**3b**), 126.1° (**4b**), and 119.9° (**4c**), respectively.

The Si2−C(fluorenyl) bond lengths in **6a** (Figure 6) (1.906(1), 1.925(5) Å) are similar to those reported for the unsubstituted compound **1a** (1.907(6), 1.923(9) Å)[13] but slightly shorter than in **2a** (1.929(3), 1.935(3) Å)[14] or **4a** (1.941(8), 1.940(8) Å).[14] The Si1−C9′ bond (1.930(1) Å) is slightly longer than the Si−C bonds formed around Si2. The two Si2−C(methyl) distances in **6a** (1.876(5), 1.867(2) Å) are in the same range as in **1a** (1.855(8), 1.862(8) Å), **2a** (1.857(3) Å), and **4a** (1.864(8), 1.871(8) Å). Thus, despite the differences in the relative orientation of the two fluorenyl groups, the corresponding Si−C(Me) bond lengths are very close in all four silicon derivatives **1a**, **2a**, **4a**, and **6a**.

The geometry around Si2 in **6a** is close to tetrahedral. However, there is a slight distortion brought by the C9−Si2−C9′ bond angle opened to 112.56(1)° and the C18−Si2−C19 bond angle closed to 105.25(1)°. The C(fluorenyl)−Si−C(fluorenyl) bond angle in **6a** (112.56°) is significantly larger than in **1a** (105.8°)[12] and **2a** (108.8°)[13] but smaller than in disubstituted derivative **4a** (116.2°).[14] Due to the steric demand of the trimethylsilyl group, the Si1−C9′−Si2 bond angle (115.75(3)°) is larger than the Si2−C9−C14 bond angle (108.1(4)°).

The main feature of the structure of **6a** is the parallel orientation of the two fluorene units. The angle between CR_2 planes is only 4.5°, and this is the first example of a monomeric $Me_2E(CR'R_2)(CR''R_2)$ system stabilized in the *out*−*out* conformation. The short distance (3.447 Å) between the fluorenyl rings suggest a possible π−π interaction (see ref 26 for a review). Similar π-stacked

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Table 1. Crystal and Collection Data

	3b	**4b**	**4c**	**5c**	**6a**	**6b**
empirical formula	$C_{31}H_{32}GeSi$	$C_{30}H_{28}Ge$	$C_{30}H_{28}Sn$	$C_{34}H_{40}Si_2Sn$	$C_{32}H_{34}Si_2$	$C_{32}H_{34}GeSi$
fw	505.25	460.72	507.21	623.54	474.77	519.27
cryst syst	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$C2/c$	$Fdd2$	$P2_1/n$	$P2_1/n$
a (Å)	8.5001(6)	13.1197(10)	22.377(4)	20.000(3)	9.9160(2)	10.0281(7)
b (Å)	10.0668(9)	7.4855(9)	13.344(2)	32.881(5)	15.6780(4)	15.8575(10)
c (Å)	15.399(2)	24.557(2)	18.147(4)	9.795(10)	16.9780(5)	17.1917(10)
α (deg)	85.918(8)	90.00	90.00	90.00	90.00	90.00
β (deg)	87.093(8)	99.833(9)	117.517(14)	90.00	92.202(1)	92.231(8)
γ (deg)	87.936(9)	90.00	90.00	90.00	90.00	90.00
V (Å^3)	1311.9(2)	2376.2(4)	4805.7(16)	6441.4(15)	2637.50(12)	2731.8(4)
Z	2	4	8	8	4	4
μ(Mo Kα) (mm^{-1})	1.230	1.303	1.077	0.888	0.153	1.183
2θ range (deg)	22.6–37.2	3.16–50	5.06–45.00	4.76–49.94	6.62–55.0	4.62–51.50
no. of reflns collected	5465	4274	2064	1643	19781	5400
no. of indep reflns [R(int)]	5101 [0.0212]	4165 [0.0395]	646 [0.0175]	1509 [0.0133]	5963 [0.0520]	5223 [0.0522]
no. of reflns obsd (>2σ)	3884	2305	3253	1367	4149	2652
$T_{\max}, T_{\min}$	0.8370, 0.5784	0.8807, 0.6958	0.551–0.506	0.8287, 0.8425	0.9849, 0.9730	0.7978, 0.6490
R_1, wR_2 [$I > 2\sigma(I)$]	0.0344, 0.0922	0.0340, 0.0799	0.0307, 0.0740	0.0210, 0.0521	0.0471, 0.0981	0.0483, 0.0956
R_1, wR_2 (all data)	0.0579, 0.1136	0.1128, 0.1016	0.0400, 0.0809	0.0250, 0.0535	0.0834, 0.1136	0.1651, 0.1248

Table 2. Selected Bond Lengths (Å) for 3b, 4b, 4c, 5c, 6a, and 6b

3b		**4b**		**4c**	
Ge–C9	2.004(5)	Ge–C9	2.015(4)	Sn–C9	2.231(4)
Ge–C9′	2.013(2)	Ge–C9′	2.020(4)	Sn–C9′	2.232(4)
Ge–C14	1.940(5)	Ge–C14	1.937(4)	Sn–C14	2.142(5)
Ge–C15	1.946(2)	Ge–C15	1.945(4)	Sn–C15	2.142(5)
Si–C9′	1.911(5)				
		C16–C9	1.539(5)	C16–C9	1.535(6)
		C17–C9′	1.533(5)	C17–C9′	1.538(7)
Si–C16	1.855(5)				
Si–C17	1.856(5)				
Si–C18	1.871(2)				
5c		**6a**		**6b**	
Sn–C9	2.195(5)	Si2–C9	1.906(1)	Ge–C9	1.987(4)
		Si2–C9′	1.925(5)	Ge–C9′	2.004(4)
Sn–C16	2.147(6)	Si2–C18	1.876(5)	Ge–C18	1.963(4)
		Si2–C19	1.867(2)	Ge–C19	1.944(5)
Si1–C9	1.908(4)	Si1–C9′	1.930(1)	Si1–C9′	1.923(4)
		C14–C9	1.545(5)	C14–C9	1.538(6)
Si1–C14	1.847(6)	Si1–C15	1.869(2)	Si–C15	1.872(5)
Si1–C15	1.858(5)	Si1–C16	1.869(2)	Si–C16	1.852(6)
Si1–C17	1.886(8)	Si1–C17	1.863(2)	Si–C17	1.874(5)

Table 3. Selected Bond Angles (deg) for 3b, 4b, 4c, 5c, 6a, and 6b

3b		**4b**		**4c**	
C9–Ge–C9′	103.2(7)	C9–Ge–C9′	116.09(16)	C9–Sn–C9′	113.15(15)
C14–Ge–C15	105.9(4)	C14–Ge–C15	109.4(2)	C14–Sn–C15	109.4(2)
C14–Ge–C9′	111.9(5)	C9–Ge–C14	107.61(18)	C9–Sn–C14	110.01(18)
C15–Ge–C9′	111.7(1)	C9–Ge–C15	107.95(17)	C9–Sn–C15	108.00(17)
C9–Ge–C14	112.2(2)	C9′–Ge–C14	109.87(17)	C9′–Sn–C14	107.6(2)
C9–Ge–C15	112.0(5)	C9′–Ge–C15	105.73(18)	C9′–Sn–C15	108.62(19)
Ge–C9′–Si	119.27(12)	C16–C9–Ge	111.4(3)	C16–C9–Sn	111.3(3)
		C17–C9′–Ge	106.9(3)	C17–C9′–Sn	107.1(3)
5c		**6a**		**6b**	
C9–Sn–C9′	109.2(2)	C9–Si2–C9′	112.56(1)	C9–Ge–C9′	112.44(17)
C16–Sn–C16′	107.1(4)	C18–Si2–C19	105.25(1)	C18–Ge–C19	105.5(2)
C9–Sn–C16	111.0(2)	C9′–Si2–C18	107.49(5)	C9′–Ge–C18	107.0(2)
Sn–C9–Si1	113.6(2)	C9′–Si2–C19	109.12(1)	C9′–Ge–C19	108.7(2)
		C9–Si2–C18	111.54(2)	C9–Ge–C18	111.8(2)
		C9–Si2–C19	110.56(2)	C9–Ge–C19	111.1(2)
		Si2–C9–C14	108.1(4)	Ge–C9–C14	107.3(3)
		Si2–C9′–Si1	115.75(3)	Ge–C9′–Si	115.0(2)

oligomers have been synthesized through an anionic initialized polymerization of dibenzofulvene.[27]

The germanium compound **6b** (Figure 7) adopts also an *out–out* conformation in the solid state, with the parallel arrangement of the two fluorene units (the angle between the CR_2 planes is 2.8°). The two Ge–C(fluorenyl) bonds are only slightly different (2.004(4), 1.987(4) Å), as are the two Ge–C(methyl) bonds (1.963(4), 1.944(5) Å). The C9–C14 bond has about the same length as in **6a**. Note that, due to the larger size of

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[27] Nakano T.; Yade T. *J. Am. Chem. Soc.* **2003**, *125*, 15474.

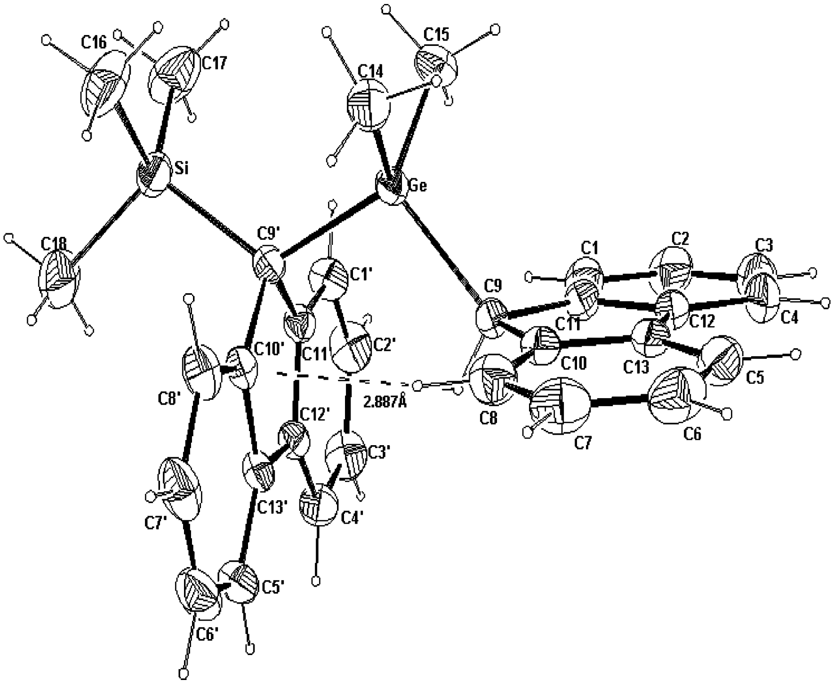

Figure 3. Molecular structure of $Me_2Ge(CHR_2)(CR_2\text{-}SiMe_3)$ (**3b**) showing the atom-numbering scheme. The short H9···π fluorenyl distance responsible for the *in*–*out* conformation is highlighted.

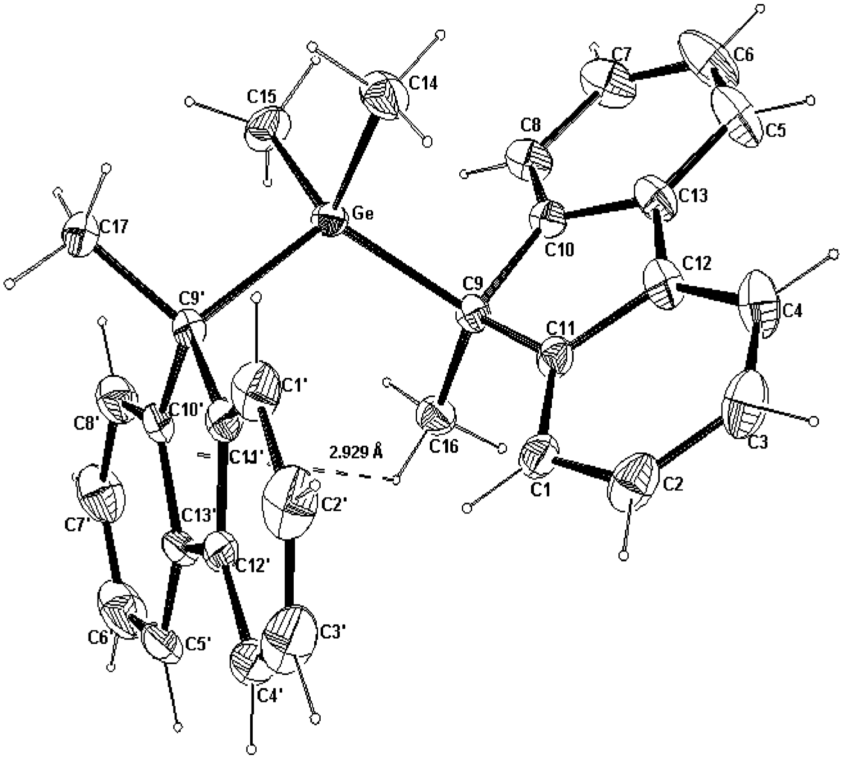

Figure 4. Molecular structure of $Me_2Ge(CMeR_2)_2$ (**4b**). Dotted lined is the (Me)H···π intramolecular distance.

germanium, the distance between the centroids of the two C5 rings of the fluorenyl groups (3.540 Å) is slightly longer than in the silicon analogue, but still is indicative of π–π interactions.

Parallel orientation of the two bulky fluorene units (angle between CR_2 planes: 0.9°) was found also in the symmetrically disubstituted derivative **5c** (Figure 8). The C(fluorenyl)–Sn–C(fluorenyl) angle is reduced to the normal tetrahedral value (109.2(2)° compared to **6a** and **6b** (ca. 112°)), and a similar trend is noted for the Sn–C9–Si angle (113.6(2)° compared to ca. 115° in **6a** and **6b**). The distance between the parallel fluorenyls (3.652 Å) (**5c**) does not exclude some π–π interactions.

Thus, the common feature of **5c**, **6a**, and **6b** is the *out*–*out* conformation, with two parallel fluorene units, which is in sharp contrast with **1a**, **2a**, **3b**, or **4b**,**c**, where the *in*–*out* conformation is adopted in the solid state. This *out*–*out* conformation is of course due to the great steric hindrance brought by a $SiMe_3$ and a Me (case of **6a** and **6b**) or two $SiMe_3$ (case of **5c**) groups.

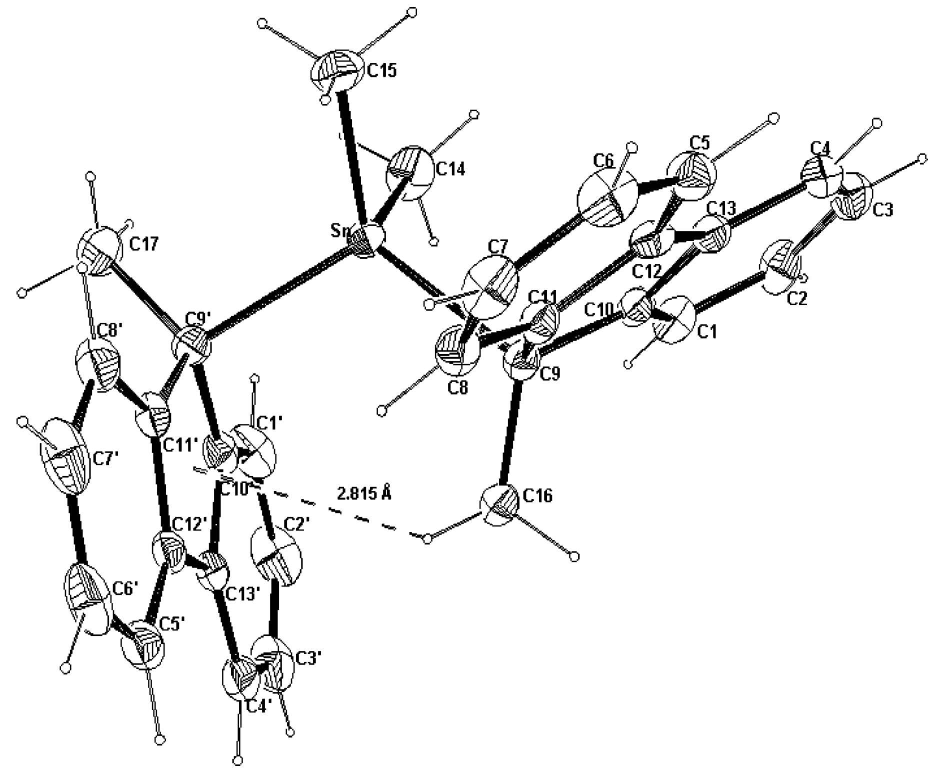

Figure 5. Molecular structure of $Me_2Sn(CMeR_2)_2$ (**4c**). Dotted lined is the (Me)H···π intramolecular distance.

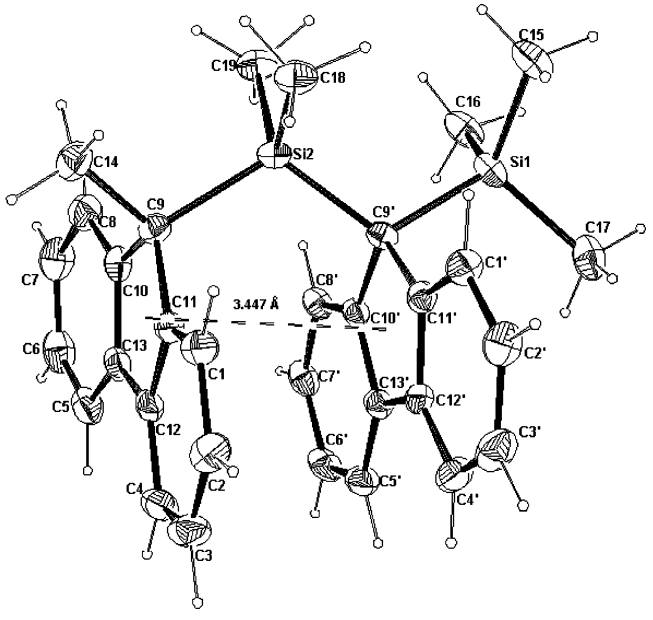

Figure 6. Molecular structure of $Me_2Si(CR_2\text{-}Me)(CR_2\text{-}SiMe_3)$ (**6a**) showing the parallel orientation of the two fluorenyl rings and the distances between the planes of these rings.

Interestingly, short CH···fluorene intramolecular contacts are observed between the Me-*out* with the fluorenyl group on which it is bound. The distances from the (Me-*out*)-hydrogen to the centroid of the C5 ring of the fluorenyl group are 2.640 Å in **6a**, 2.653 Å in **6b**, 2.691 Å in **4b**, and 2.766 Å in **4c** (close to the values found in **2a**, 2.775 Å,[14] and **4a**, 2.698 Å[14]) (Table 4). These contacts are also related to E−C(fluorenyl)−Centroid angles: the smaller the angle (from 125.87° in **6a** to 134.26° in **2a**), the shorter the contact. The shortest contacts involving a hydrogen belonging to the *out*-$SiMe_3$ group with the fluorenyl centroid are 2.898 Å in **3b**, 2.901 Å in **6a** and **6b**, and 3.104 Å in **5c**.

b. Crystal Packing. Two CH···π type short intermolecular contacts are responsible for packing in the solid state in **3b** (Figure 9): one of 2.822 Å (from H4 to C10) and another one of 2.892 Å (from a hydrogen of $GeMe_2$ and C3). Such short contacts (2.887 Å) have been observed in the crystal of 9,9′-bis(trimethylsilyl)-9,9′-bifluorene.[28]

The crystal structure of **4b** consists of parallel arrangements of columns formed by unexpectedly short CH···HC contacts of 2.691 Å between the (Me-*in*) and a hydrogen of the $GeMe_2$ fragment (Figure 10). Close H···H contacts (2.289 Å) are also displayed in a 9-trimethylsilyl-substituted fluorene derivative of germatrane,[29] a finding that might be relevant in view of the increased interest paid in the last years to such interactions.[30−32] Note that the above H···H distances correspond to the unrefined (calculated) positions of the hydrogen atoms, but molecular mechanics optimization (MMFF force field) of the structure by keeping fixed the positions of the heavy atoms leads to even shorter H···H contacts. Neighboring columns are in contact through H3···H7, with distances of 2.300 Å, which are below the sum of the van der Waals radii (2.40 Å[33]).

Loose dimeric units exhibiting contacts of 2.868 Å (close to the sum of the van der Waals radii[33]) were

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[28] Knjazhansky, S. Ya.; Moreno, G.; Cadenas, G.; Belsky, V. K.; Bulychev, B. M. *Tetrahedron* **1999**, *55*, 1639.

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[33] Winter, M.; WebElements, the periodic table on the Web, http://www.webelement.com.

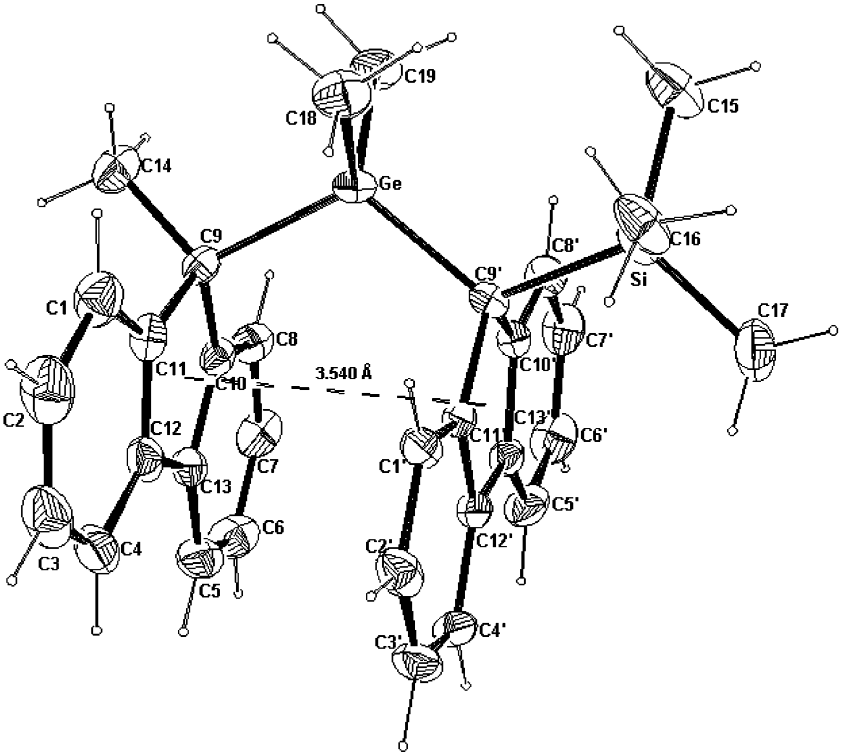


Figure 7. Molecular structure of $Me_2Ge(CR_2\text{-}Me)(CR_2\text{-}SiMe_3)$ (**6b**) showing the parallel orientation of the two fluorenyl rings and the distances between the planes of these rings.

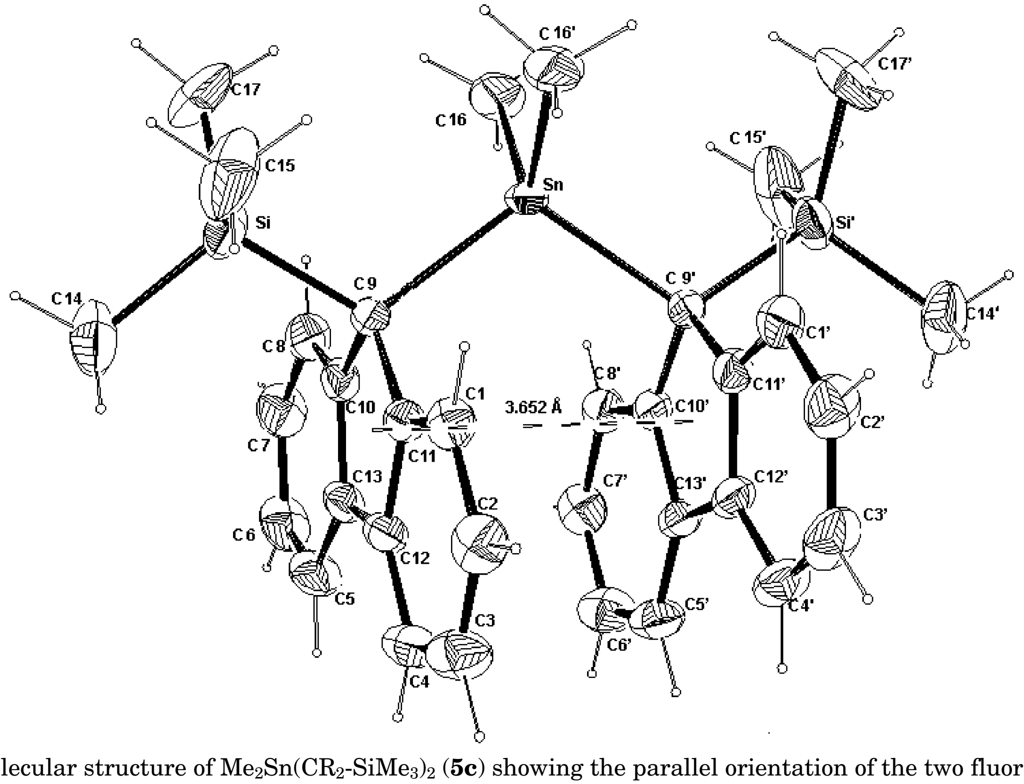


Figure 8. Molecular structure of $Me_2Sn(CR_2\text{-}SiMe_3)_2$ (**5c**) showing the parallel orientation of the two fluorenyl rings and the distance between the planes of these rings.

found in **4c** between H4 and a C of the fluorene moiety (Figure 11).

Remarkable short intermolecular CH···HC (H3···Me_3-Si) distances (2.282 Å) are found also in **5c** (Figure 12). Each molecule is interacting with four other neighbors through the CH bonds (coming from the $SiMe_3$ substituents) and two hydrogens (H3) of the fluorene moieties.

The basic unit of the crystal structure of **6a** is a chain (Figure 13), in which the molecules are separated by 2.390 Å ($SiMe_3$···H3) but are within the sum of van der Waals radii of hydrogen.

No significant interactions are noticed in the crystal of **6b**, as the shortest contacts are 2.667 Å for ($SiMe_3$)-CH···HC(Me), which are longer than the sum of van der Waals radii of hydrogen.

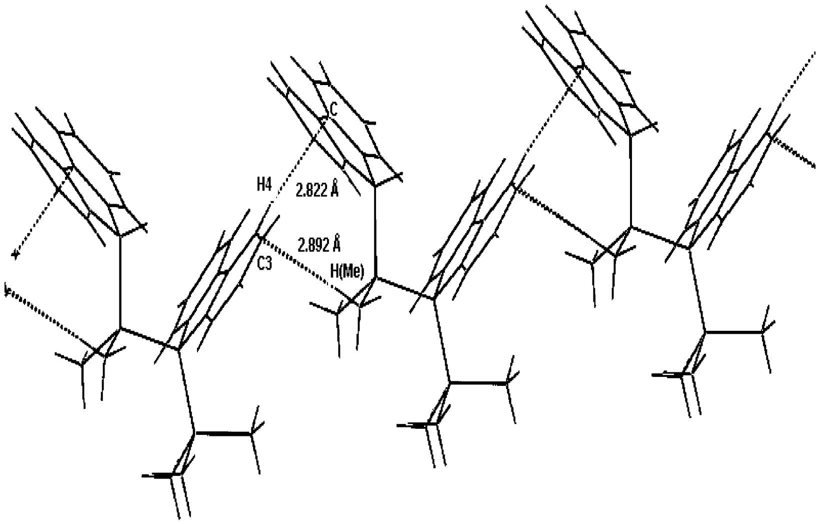
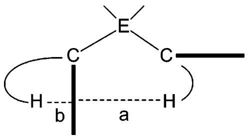


Figure 9. Crystal structure of **3b** showing the short intermolecular contacts.

Table 4. Some Significant Inter- and Intramolecular Distances in the Investigated Compounds



		intramolecular				
		type a		type b		intermolecular
	$\pi-\pi$	H-9$-\pi$	H(Me)$-\pi$	H(Me)$-\pi$	H(SiMe$_3$)$-\pi$	CH$-\pi$
2a		2.652		2.775		
4a			2.885	2.698		
3b		2.887			2.898	2.822, 2.892
4b			2.929	2.691		2.271
4c			2.818	2.766		2.868
5c	3.652				3.104	2.282
6a	3.447			2.640	2.901	2.390
6b	3.540			2.653	2.901	2.667

In conclusion, the investigated systems display a rather rich variety of arrangements in the solid state, ranging from discrete molecules (**6b**), dimers (**4c**), chainlike motifs as in **3b** and **6a**, double chains (**4b**), and three-dimensional supramolecular assemblies in **5c**.

Experimental Section

All manipulations were carried out using high-vacuum-line techniques. Diethyl ether, tetrahydrofurane, and pentane were freshly distilled from sodium benzophenone.

Bis(9-fluorenyl)dimethylsilane (**1a**) and -germane (**1b**) and Me$_2$Ge(CR$_2$-Me)$_2$ (**4b**) were prepared according to ref 12, 9-methylfluorene was prepared according to ref 34, and 9-trimethylsilylfluorene, according to ref 35. Me$_2$SiCl$_2$ and Me$_2$SnCl$_2$ were purchased from Aldrich, and Me$_2$GeCl$_2$ was prepared from Me$_4$Ge by redistribution with GeCl$_4$ in the presence of AlCl$_3$.[36]

^{1}H NMR spectra were recorded on Bruker AC 80 and AC 200 instruments at 80.1 and 200.1 MHz, respectively. ^{13}C NMR spectra were recorded on Bruker AC 200 and AC 250 instruments at 50.1 and 62.9 MHz and ^{119}Sn NMR spectra on a Bruker AC 400 at 288.18 MHz. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded at room temperature in CDCl$_3$. The 2D spectra were recorded on an Avance DRX 400 machine at 400 MHz.

Mass spectra were measured on a Hewlett-Packard 5989 A spectrometer by EI at 70 eV. Melting points were determined on a Leitz microscope heating stage 250.

Molecular orbital calculations have been performed at the AM1 semiempirical level[37] by using Spartan version 5.1.[38] The conformational space of the Me$_2$E(CR′R$_2$)(CR″R$_2$) systems has been searched by varying the R′$-$C9$-$E$-$C9′ angles from 0° to 180°, covering thus the *in−out* to *out−out* conformers. The conformations thus obtained were subject to RHF/AM1 optimizations maintaining the dihedral constraints. The constrained optimizations were exited when the drop in the energy was less than 0.001 kcal/mol and the gradient was smaller than 0.0001.

The crystal data were collected at room temperature (293 K) by using either an Enraf Nonius CAD4 diffractometer (**5c**) (no absorption corrections applied), a CAD4-Mach3 diffractometer (**3b**, **4b**, **4c**, **6b**), or a Nonius KappaCCD diffractometer (**6a**); in all cases graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) was used. The structures were solved by direct methods and refined by the full matrix least-squares

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(34) Murdoch, J. R.; Bryson, J. A.; McMillen, D. F.; Brauman, J. I. *J. Am. Chem. Soc.* **1982**, *104*, 600.

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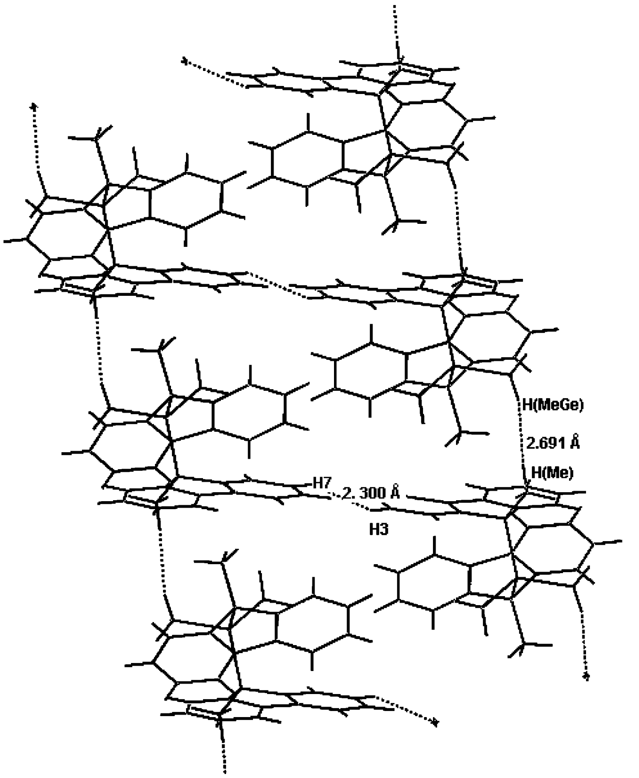

Figure 10. Double-chain arrangement of **4b** is shown, highlighting the short intra- and intercolumnar contacts.

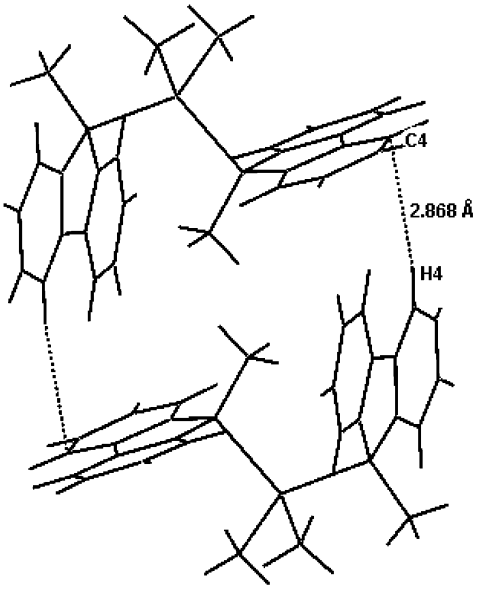

Figure 11. Dimeric units formed by short CH⋯π contacts found in the crystal structure of **4c**.

method using the SHELXTL-PC set of programs.[39] Hydrogen atoms were introduced at fixed positions.

The asymmetric unit of **5c** was found to consist of one-half of a molecule, the remaining portion being generated via a 2-fold rotation axis on which the central tin atom is located.

$Me_2Sn(CHR_2)(CR'R_2)$ (R′ = Me (2c), $SiMe_3$ (3c)). A solution of 9-methylfluorenyllithium or 9-trimethylsilylfluorenyllithium (2.00 mmol) obtained from the 1:1 stoichiometric amount of the corresponding 9-substituted fluorene and 2.00 mmol of *n*-BuLi (1.6 M in hexane) was added to a solution of dimethyldichlorostannane (0.44 g, 2.00 mmol) in diethyl ether at −78 °C. To the solution of chloro derivatives $Me_2Sn(Cl)(CR'R_2)$ thus obtained, 1 equiv of fluorenyllithium in diethyl ether (10 mL) was added and the resulting mixture was allowed to stir for 1 h. Lithium salts were eliminated by filtration and the solvents removed in vacuo. Recrystallization from pentane/Et_2O gave white crystals of **2c** and **3c**.

$Me_2Sn(CHR_2)(CMeR_2)$ (2c): 0.75 g, mp = 67 °C, 76%. ^1H NMR (ppm): −0.08 (s, 6H, Sn*Me*$_2$), 1.86 (s, 3H, C*Me*R$_2$) 3.50 (s, 1H, C*H*R$_2$), 6.42 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, *H* of CR$_2$,), 7.05−7.51 (m, 14H, *H* of CR$_2$). ^{13}C NMR (ppm): 1.16 (*Me*$_2$Sn), 18.28 (C*Me*R$_2$), 37.01 (R$_2$*C*), 42.52 (R$_2$*C*H) 119.96 ($C_{4,5}$), 124.10, 125.11 126.79, 127.01, 129.16 ($C_{1,2,3,6,7,8}$), 141.78, 143.30 ($C_{12,13}$), 149.07 ($C_{10,11}$). MS, *m/z*: 494 (M, 5) 299 (M − 2Me − CHR$_2$, 58), 165 (CHR$_2$, 100). Anal. Calcd for $C_{29}H_{26}Sn$ (*M* = 493.215): C, 70.62; H, 5.31. Found: C, 70.38; H, 5.27.

$Me_2Sn(CHR_2)(CR_2\text{-}SiMe_3)$ (3c): 0.68 g, mp = 76 °C, 62%. ^1H NMR (ppm): 0.03 (s, 9H, Si*Me*$_3$), 0.26 (s, 6H, Sn*Me*$_2$), 3.05 (s, 1H, C*H*R$_2$), 6.25 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, *H* of CR$_2$,), 6.97−7.80 (m, 14H, *H* of CR$_2$). ^{13}C NMR: −2.58 (*Me*$_3$-Si), 1.26 (*Me*$_2$Sn), 37.03 (*C*R$_2$), 42.84 (R$_2$CH), 119.99 ($C_{4,5}$), 124.10, 125.13, 125.29, 126.09, 126.82, 127.03 ($C_{1,2,3,6,7,8}$), 140.51, 141.81 ($C_{12,13}$), 143.32, 145.80 ($C_{10,11}$). MS, *m/z*: 552 (M, 8), 357 (M − 2Me − CHR$_2$, 47), 165 (CHR$_2$, 100). Anal. Calcd for $C_{31}H_{32}SiSn$ (*M* = 551.370): C, 67.53; H, 5.85. Found: C, 67.41; H, 5.67.

$Me_2Ge(CHR_2)(CR_2\text{-}SiMe_3)$ (3b). A diethyl ether solution of bis(9-fluorenyl)dimethylgermane (3.50 g, 8.10 mmol, in 20 mL of diethyl ether) was treated with *n*-BuLi (8 mmol, 5.2 mL, 1.6 M in hexane) at −78 °C to obtain the monolithiated derivative $Me_2Ge(CHR_2)(CLiR_2)$. After 20 min, Me_3SiCl (8.10 mmol, 5.7 mL) was added slowly. After 1 h of stirring at room temperature the reaction mixture was filtered and the solution concentrated in vacuo. On cooling, white crystals of $Me_2Ge(CHR_2)(CR_2\text{-}SiMe_3)$ (2.78 g) were obtained by recrystallization from ether/pentane (mp = 223 °C, 68%). ^1H NMR (ppm): −0.04 (s, 9H, Si*Me*$_3$), 0.21 (s, 6H, Ge*Me*$_2$), 2.81 (s, 1H, C*H*R$_2$), 6.20 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, *H* of CR$_2$), 6.97−7.52 (m, 14H, *H* of CR$_2$). ^{13}C NMR (ppm): −0.82 (Si*Me*$_3$), 0.10 (*Me*$_2$-Ge), 39.64 (R$_2$*C*H), 45.90 (R$_2$*C*), 119.49, 120,57 ($C_{4,5}$), 124.43, 124.66, 124.79, 124.91, 125.52, 126.29 ($C_{1,2,3,6,7,8}$), 139.72, 140.24 ($C_{12,13}$), 145.80, 147.60 ($C_{10,11}$). MS, *m/z*: 506 (M, 5), 491 (M − Me, 3), 434 (M − SiMe$_3$ + 1, 2), 341 (M − CHR$_2$, 32), 269 (Me$_2$GeCHR$_2$, 8), 165 (CHR$_2$, 100), 73 (Me$_3$Si, 61). Anal. Calcd for $C_{31}H_{32}GeSi$ (*M* = 505.271): C, 73.69; H, 6.38. Found: C, 73.41; H, 6.17.

$Me_2Sn(CR'R_2)_2$ (R′ = Me (4c), $SiMe_3$ (5c)). A solution of 9-methylfluorenyllithium or 9-trimethylsilylfluorenyllithium obtained from the corresponding 9-substituted fluorene (2 mmol) and *n*-BuLi (2 mmol) (1.6 M in hexane) was added to a solution containing the stoichiometric amount of dimethyldichlorostannane (1 mmol) in diethyl ether at −78 °C. The resulting mixture was stirred for 0.5 h and then filtered. The solvent was removed in vacuo. Crystallization from pentane/Et_2O afforded white crystals of **4c** and **5c**.

$Me_2Sn(CMeR_2)_2$ (4c): 0.36 g, mp = 149 °C, 71%. ^1H NMR (ppm): −0.24 (s, 6H, Sn*Me*$_2$), 1.36 (s, 6H, *Me*), 7.02−7.90 (m, 16H, CR$_2$). ^{13}C NMR (ppm): −10.75 (*Me*$_2$Sn), 18.39 (C*Me*R$_2$), 49.46 (R$_2$*C*) 119.98 ($C_{4,5}$), 122.15, 124.97, 126.22, ($C_{1,2,3,6,7,8}$), 137.80 ($C_{12,13}$), 150.78 ($C_{10,11}$). ^{119}Sn NMR (ppm): 33.9. MS: *m/z* 508 (M, 10), 329 (M − CMeR$_2$, 76), 299 (M − CMeR$_2$ − 2Me, 32), 179 (CMeR$_2$, 100). Anal. Calcd for $C_{30}H_{28}Sn$ (*M* = 507.242): C, 71.04; H, 5.56. Found: C, 70.88; H, 5.31.

$Me_2Sn(CR_2\text{-}SiMe_3)_2$ (5c): 0.54 g, mp = 122 °C, 86%. ^1H NMR (ppm): −0.44 (s, 18H, Si*Me*$_3$), 0.57 (s, 6H, Sn*Me*$_2$), 6.85−7.50 (m, 16H, CR$_2$). ^{13}C NMR (ppm): −3.73 (*Me*$_2$Sn), −1.52 (Si*Me*$_3$), 45.08 (R$_2$*C*) 119.98 ($C_{4,5}$), 123.23, 123.37, 125.13, ($C_{1,2,3,6,7,8}$), 138.98 ($C_{12,13}$), 147.17 ($C_{10,11}$). ^{119}Sn NMR (ppm): 10.5. MS: *m/z* 624 (M, 2), 387 (M − CR$_2$ − SiMe$_3$, 45), 237

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[39] Sheldrick, G. M. *SHELXS97*, Program for Crystal Structure Determination and *SHELXL97*, Program for the Refinement of Crystal Structures, University of Goettingen, 1997.

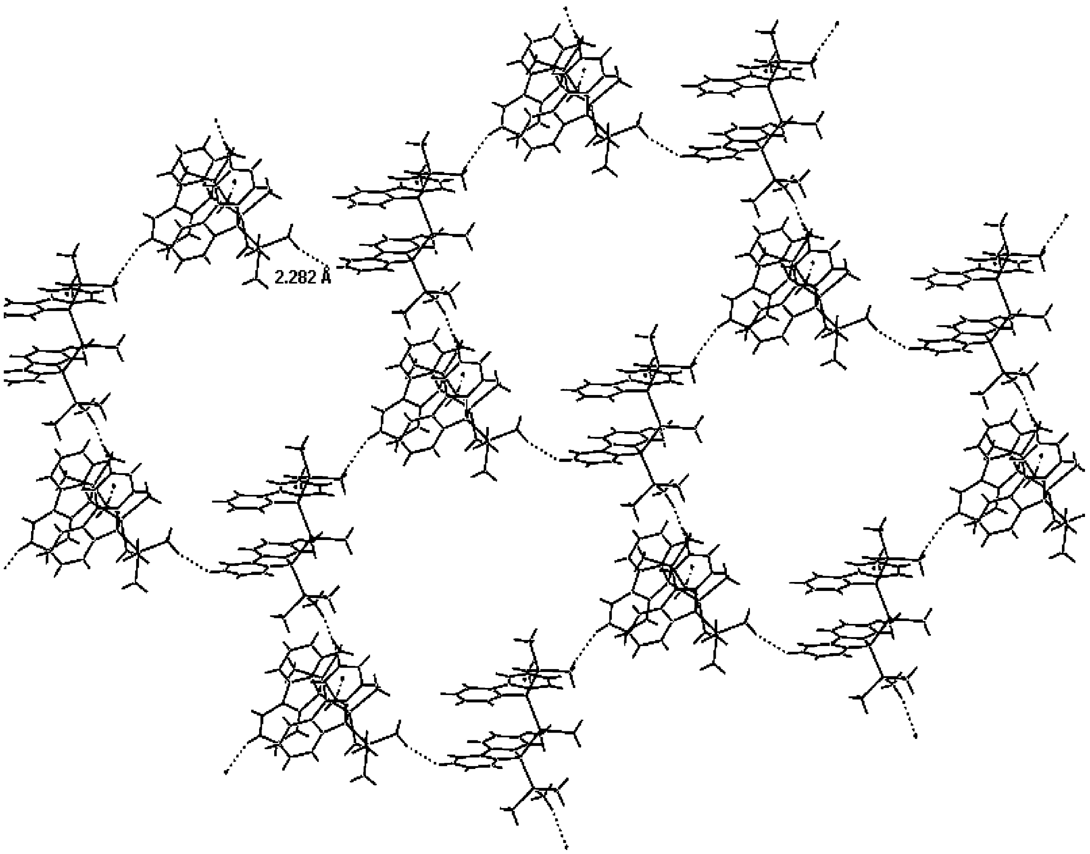

Figure 12. Top view of a layer formed by hexagonal chairlike rings in **5c** showing short H···H contacts (2.282 Å) between H($SiMe_3$) and H3(fluorenyl) atoms.

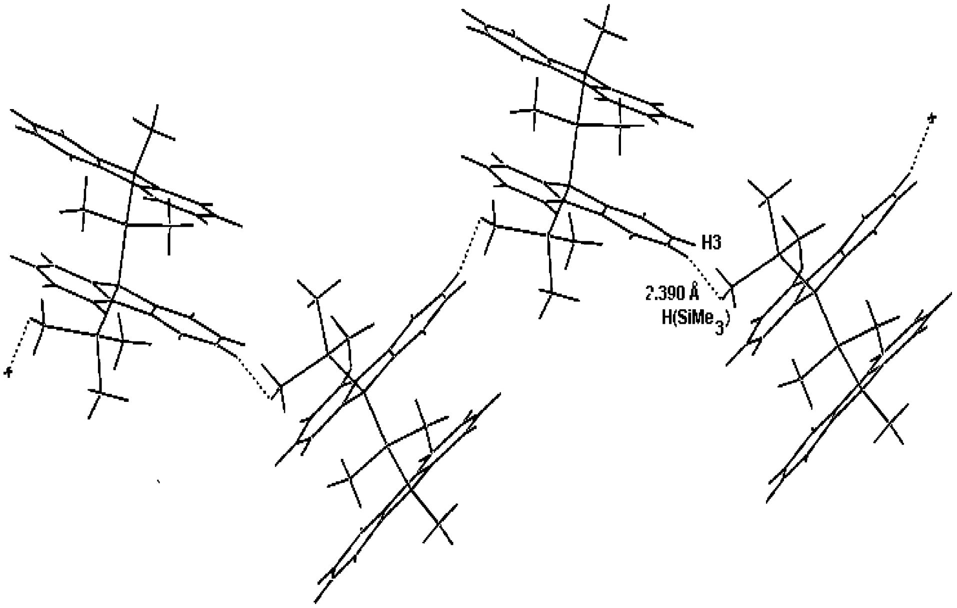

Figure 13. Crystal packing in $Me_2Si(CR_2Me)(CR_2SiMe_3)$ (**6a**). Note the zigzag chain formed through H($SiMe_3$)···H3-(fluorenyl) interactions.

(CR_2 − $SiMe_3$, 100), 73 ($SiMe_3$, 50). Anal. Calcd for $C_{34}H_{40}Si_2Sn$ (M = 623.55): C, 65.49; H, 6.47. Found: C, 65.11; H, 6.19.

$Me_2E(CR_2$-$SiMe_3)_2$ (E = Si (5a), Ge (5b)). Two equivalents of n-BuLi (12 mmol of a 1.6 M solution in hexane) was added to a solution containing 6 mmol of $Me_2E(CHR_2)_2$ (E = Si, Ge) in 20 mL of Et_2O at −78 °C. The dilithiated compound $Me_2E(CLiR_2)_2$ (E = Si, Ge) was stirred at 30 °C for 1 h and then cooled again at −78 °C; 10% excess of trimethylchlorosilane was added. After the ususal workup, **5a** (1.56 g, 49%) and **5b** (1.73 g, 50%) were obtained in about 90% purity. ^1H NMR (ppm) (**5a**): −0.37 (s, 9H, Si*Me*$_3$), 0.25 (s, 6H, Si*Me*$_2$), 6.30−7.91 (m, 16H, CR_2). ^1H NMR (ppm) (**5b**): −0.42 (s, 9H, Si*Me*$_3$), 1.14 (s, 6H, Ge*Me*$_2$), 6.71−7.30 (m, 16H, CR_2).

$Me_2E(CMeR_2)(CR_2$-$SiMe_3)$ (E = Si (6a), Ge (6b), Sn (6c)). An ethereal solution of 9-methylfluorenyllithium obtained at −78 °C from 9-methylfluorene (6.00 mmol) and n-BuLi (6.00 mmol) (1.6 M solution in hexane) was added in a 1:1 molar ratio to a solution of $\mathrm{Me_2ECl_2}$ (E = Si, Ge, Sn) (6.00 mmol) in diethyl ether to form a $\mathrm{Me_2E(CMeR_2)Cl}$ intermediate. The solution of 9-trimethylsilylfluorenyllithium obtained from 9-trimethylsilylfluorene in 20 mL of $\mathrm{Et_2O}$ and 2.83 mL of *n*-BuLi (1.6 M in hexane) was added via cannula, at −78 °C, to the solutions of $\mathrm{Me_2E(CMeR_2)Cl}$ (6.00 mmol). After 1 h of stirring at room temperature lithium salts were filtered and the solvents removed in vacuo.

$\mathbf{Me_2Si(CMeR_2)(CR_2\text{-}SiMe_3)}$ (6a). White crystals (1.97 g, mp = 80 °C, 69%) were obtained by recrystallization from diethyl ether/pentane. ^{1}H NMR (ppm): −0.38 (s, 9H, $\mathrm{Si}Me_3$), 0.67 (s, 6H, $\mathrm{Si}Me_2$), 1.06 (s, 3H, C*Me*), 6.75−7.63 (m, 16H, $\mathrm{CR_2}$). Anal. Calcd for $\mathrm{C_{32}H_{34}Si_2}$ (*M* = 474.793): C, 80.95; H, 7.22. Found: C, 80.56; H, 6.98.

$\mathbf{Me_2Ge(CMeR_2)(CR_2\text{-}SiMe_3)}$ (6b). White crystals (1.50 g, mp = 110 °C, 48%) were obtained by recrystallization from THF/pentane. ^{1}H NMR (ppm): −0.32 (s, 9H, $\mathrm{Si}Me_3$), 0.56 (s, 6H, $\mathrm{Ge}Me_2$), 0.96 (s, 3H, C*Me*), 6.64−7.67 (m, 16H, $\mathrm{CR_2}$). ^{13}C NMR (ppm): −1.41 ($Me_3\mathrm{Si}$), −0.81 ($Me_2\mathrm{Ge}$), 19.66 ($\mathrm{C}Me\mathrm{R_2}$), 43.16 and 47.76 ($\mathrm{R_2}C$), 119.46, 120.03 ($\mathrm{C_{4,5}}$), 122,96, 124.20, 125.11, 125.44, ($\mathrm{C_{1,2,3,6,7,8}}$), 138.86, 139.85 ($\mathrm{C_{12,13}}$), 146.72, 150.28 ($\mathrm{C_{10,11}}$). MS, *m/z*: 520 (M, 1), 341 (M − $\mathrm{CMeR_2}$, 100), 237 ($\mathrm{CR_2}$-$\mathrm{SiMe_3}$, 32), 179 ($\mathrm{CMeR_2}$, 55), 73 ($\mathrm{Me_3Si}$, 49). Anal. Calcd for $\mathrm{C_{32}H_{34}GeSi}$ (*M* = 519.297): C, 74.01; H, 6.60. Found: C, 73.83; H, 6.41.

$\mathbf{Me_2Sn(CMeR_2)(CR_2\text{-}SiMe_3)}$ (6c). White crystals (2.07 g, 61%) were obtained by recrystallization from THF/pentane (purity about 90%). ^{1}H NMR (ppm): 0.03 (s, 9H, $\mathrm{Si}Me_3$), 0.12 (s, 6H, $\mathrm{Sn}Me_2$), 1.26 (s, 3H, C*Me*), 7.08−7.89 (m, 16H, $\mathrm{CR_2}$).

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Supporting Information Available: The CIF files for structures of compounds **3b**, **4b**, **4c**, **5c**, **6a**, and **6b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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