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Propeller rotation of aryl groups in triarylsilanes and triarylstannanes

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Rotation of aryl groups was studied in eight systems with the general structure Ar_3MX by changes in lineshapes as a function of temperature. Steric constraints were varied at each of the structural components (Ar, M, X). The barrier to rotation decreased as the central atom was changed from carbon to silicon to tin. When the substituent X was large (allyl or Cl), buttressing by the *meta* methyls in duryl raised the barrier. For X = H, however, buttressing decreased the barrier. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: NMR; dynamic NMR; aryl–carbon rotation; buttressing effect; propeller conformation; silanes; stannanes

INTRODUCTION

Attachment of three aryl groups to a saturated center (Ar_3MX) creates the stereochemical arrangement that has been termed the propeller. Repulsion between *ortho* substituents causes the three aryl groups to assume non-planar arrangements with respect to each other, in which one side of each aryl ring is above its neighbor while the other side is below the other neighbor. Such arrangements can generate chirality and create multiple isomers.

Racemization and interconversion of the isomers occur most commonly by the two-ring flip. In the transition state to this process, the planes of two rings are perpendicular to the plane formed by the three atoms attached to the saturated center, and the normal to the plane of the third ring is perpendicular to the plane of the three atoms. The details of these processes were examined by Finocchiaro *et al.*[1] and were reviewed by Ōki.[2]

Triphenylmethane (Ph_3CH) is the classical example of this genre. The interactions between the phenyl rings, and hence the barrier to aryl—C rotation, can be raised substantially by replacing the *ortho* hydrogens with methyls. Thus the barrier to two-ring flip for trimesitylmethane [tris-(2,4,6-trimethylphenyl)methane] is 21.9 kcal mol^{-1} (1 kcal = 4.184 kJ) at the coalescence temperature of 167 °C, whereas barriers for triphenyl systems are much lower.[1] Conversely, the interactions between the phenyl rings, and hence the barrier, can be lowered by replacing the central carbon atom with silicon, as the longer C—Si bonds increase distances between the *ortho* substituents. Only a single paper[3] has been published on the effect of silicon as the central atom in triaryl stereodynamics, and no reports have been published on tin.

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We report here a study of a series of triaryl systems Ar_3MX, with variation of three structural variables: (1) the central atom M is either silicon or tin, (2) the fourth substituent X is hydrogen, chlorine or allyl and (3) the aryl group is either mesityl or duryl (2,3,5,6-tetramethylphenyl). There have been no previous reports with duryl as the aryl group or with alkyl groups as the fourth substituent.

RESULTS

The following systems were prepared, in which Mes represents mesityl and Dur represents duryl: Mes_3SiH (**1**), Mes_3SiCl (**2**), Mes_3Si(allyl) (**3**), Dur_3SiH (**4**), Dur_3SiCl (**5**), Dur_3Si(allyl) (**6**), Dur_3SnBr (**7**) and Dur_3Sn(allyl) (**8**). The mesityl systems (**1**–**3**) were available from a previous study.[4] Durylsodium was reacted with trichlorosilane to produce tridurylsilane (**4**), which was converted to chlorotridurylsilane (**5**) by the action of phosphorus pentachloride. Reaction of allyllithium with **5** produced allyltridurylsilane (**6**). Reaction of duryllithium with tetrabromotin gave bromotridurylstannane (**7**), which was converted to allyltridurylstannane (**8**) by reaction with allylmagnesium bromide.

Variable-temperature NMR spectroscopy was utilized to examine the rates of aryl rotation. At rapid rotation on the NMR time-scale, the mesityl systems should exhibit two methyl resonances in the ratio 2 : 1 (*ortho:para*) and one aromatic resonance from the *meta* hydrogens. At slow rotation, the *ortho* methyls and *meta* hydrogens should become non-equivalent (one points toward X and the other away from X), leading to three methyl peaks (1 : 1 : 1) and two aromatic peaks (1 : 1). At rapid rotation, the duryl systems should exhibit two methyl resonances in the ratio 1 : 1 (*ortho:meta*) and one aromatic resonance from the *para* hydrogen. At slow rotation, both methyls become non-equivalent, leading to four methyl resonances (1 : 1 : 1 : 1). The duryl *para* hydrogen, like the *para* methyl group in the mesityl cases, lies along the axis of aryl rotation and produces an unchanged resonance

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at fast and slow exchange. The solvents selected for these experiments were toluene-d_8 and dichloromethane.

Figure 1 illustrates the spectral changes for chlorotrimesitylsilane (**2**). The highest frequency aromatic resonances (three peaks) are from residual protonated solvent (toluene). The lowest frequency aryl resonance, from the *meta* hydrogens, is one peak at high temperatures. It passes through coalescence at about −20 °C and splits into two peaks at low temperatures. The lower frequency methyl resonance undergoes no changes with temperature and therefore must come from the *para* group. The solvent methyl peak closely overlaps this peak. The higher frequency methyl resonance replicates the changes of the *meta* hydrogens, with a coalescence at about +25 °C. The much higher coalescence temperature results entirely from the larger slow exchange chemical shift difference. Trimesitylsilane (**1**) and allyltrimesitylsilane (**3**) undergo similar changes.

Figure 2 illustrates the spectral changes for chlorotridurylsilane (**5**). Again, the extra peaks derive from residual protonated solvent, toluene. No changes with temperature other than broadening occur in the aromatic region, as the only aromatic proton is *para* and hence unaffected by rotation. There are three methyl resonances at high temperatures, one of which belongs to the solvent. The highest frequency methyl resonance undergoes decoalescence with a coalescence temperature of about +25 °C. Surprisingly, the other duryl methyl resonance remains unchanged, presumably because of accidental overlap of the slow exchange resonances. The spectrum of allyltridurylsilane (**6**) exhibits a nearly identical set of spectral changes, with decoalescence of only a single methyl resonance. The spectrum of tridurylsilane (**4**), however, is independent of temperature down to −55 °C. The lower temperature permitted by dichloromethane-d_2 revealed decoalescence with a coalescence temperature of −71 °C and a relatively small chemical shift difference.

No decoalescence or even peak broadening was observed in either tin system (**7**, **8**). Although spectral degeneracies are

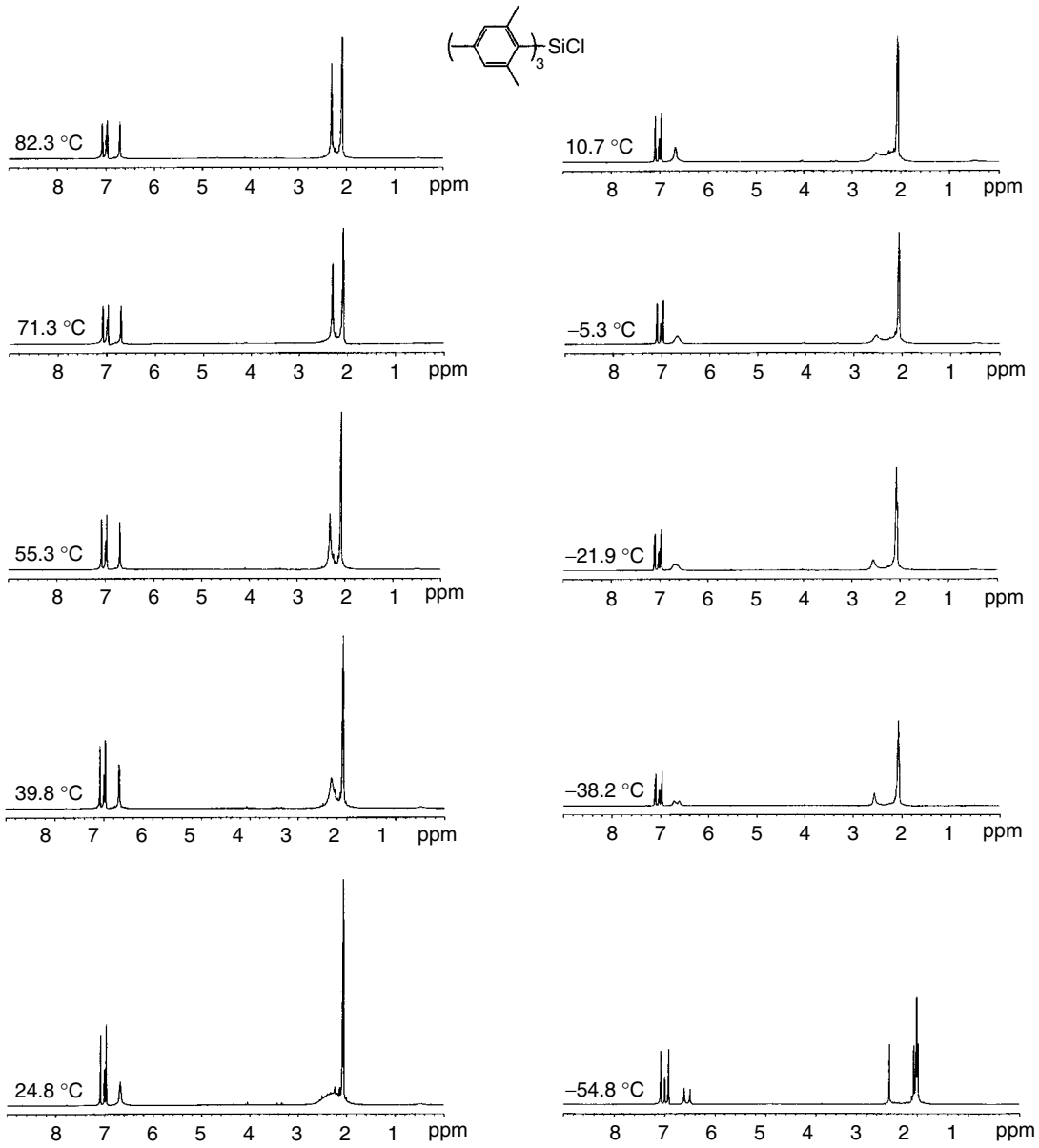

Figure 1. Variable-temperature, 500 MHz ^{1}H NMR spectrum of chlorotrimesitylsilene (**2**) in toluene-d_8.

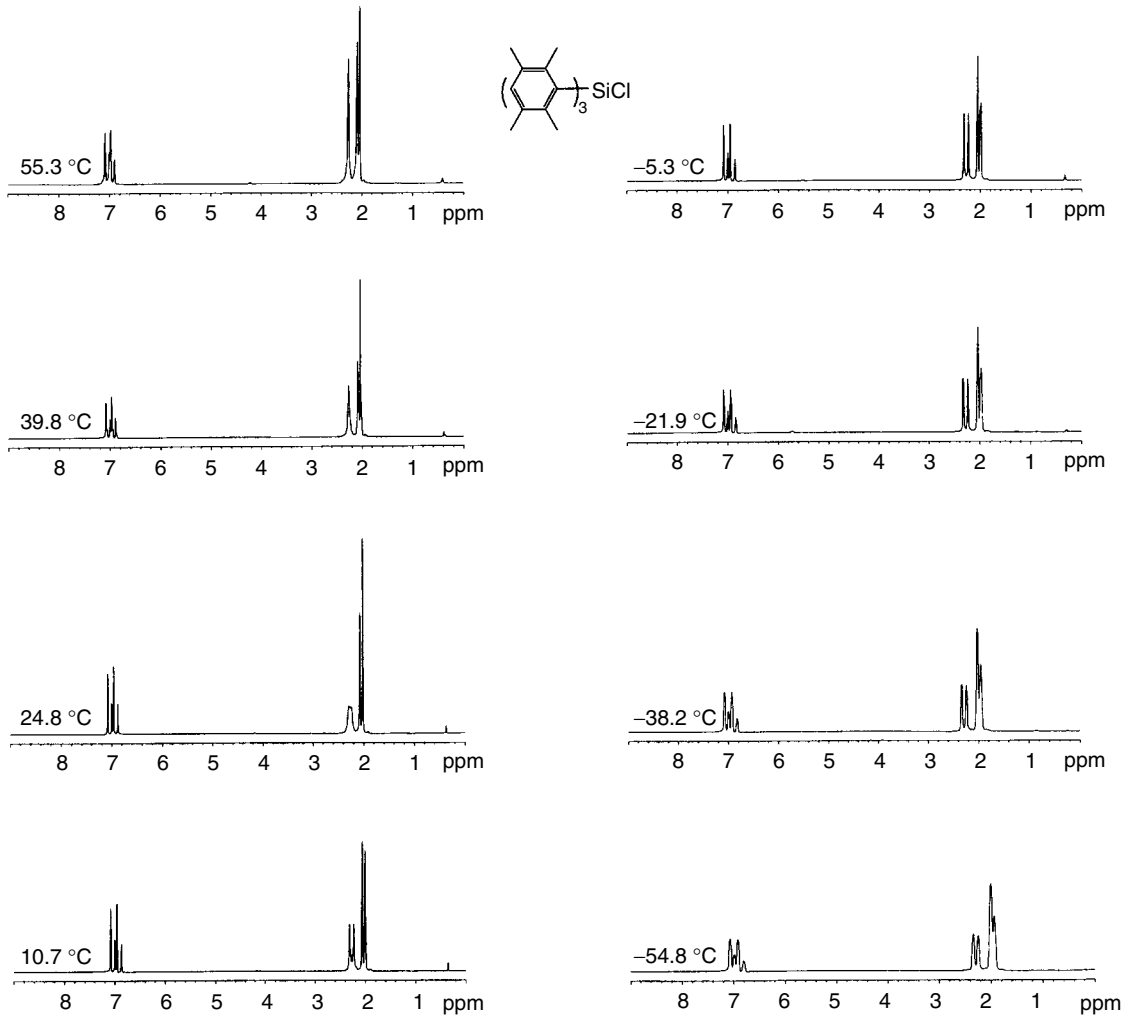

Figure 2. Variable-temperature, 500 MHz ^{1}H NMR spectrum of chlorotridurylsilane (**5**) in toluene-d_8.

Table 1. Spectral parameters for aryl rotation in triarylsilanes

			$\Delta\nu$ (Hz)		k_c (s^{-1})		T_c (K)		$\Delta G_c^{\ddagger}$ (kcal mol^{-1})	
System[a]	Ar	X	H[b]	Me[c]	H	Me	H	Me	H	Me
1	Mesityl	H	36.0	126	80	279	240	260	11.8	12.2
2	Mesityl	Cl	56.4	240	125	533	251	291	12.2	13.4
3	Mesityl	Allyl	46.2	58	102	129	224	230	10.9	11.1
4	Duryl	H		20		42		202		10.2
5	Duryl	Cl		44		98		303		15.0
6	Duryl	Allyl		83		184		278		13.4

[a] Solvent is toluene for **1**–**3**, **5** and **6** and CH_2Cl_2 for **4**.
[b] Aryl (*meta*) protons.
[c] Methyl protons.

possible, it is more likely that the barrier to aryl rotation is lower and that spectral changes do not occur in the temperature range observed (to −55 °C in toluene).

Free energies of activation were calculated from the Gutowsky–Holm equation, $k_c = \pi\Delta\nu/\sqrt{2}$ and $\Delta G_c^{\ddagger} = 2.3RT_c[10.32 + \log(T_c/k_c)]$, where k_c is the rate at the coalescence temperature, $\Delta\nu$ is the chemical shift difference between decoalesced peaks at the slow exchange limit, $\Delta G_c^{\ddagger}$ is the free energy of activation at the coalescence temperature and T_c is the coalescence temperature. This method is the most accurate and the least sensitive to systematic errors for uncoupled, two-site exchanges with equal populations. The values of these quantities are given in Table 1.

DISCUSSION

Substitution of silicon for carbon and then of tin for silicon progressively lowers the barrier for aryl rotation

in trimesityl-element systems. Whereas trimesitylmethane exhibits a barrier of 21.9 kcal mol^{-1},[1] the barrier for trimesitylsilane is ~12 kcal mol^{-1} and that for trimesitylstannane is below our range of observation (<~8 kcal mol^{-1}). As originally pointed out by Finocchiaro *et al.*,[1] this reduction is probably the result of the longer M—aryl bond lengths in the order C—C < C—Si < C—Sn (Finocchiaro *et al.*[1] did not discuss tin). As the aryl rings become more distant from the central atom, the methyl substituents at the *ortho* positions are further from the analogous groups on the adjacent aryl rings.

It is interesting that the first alkyl group to be examined in this context, allyl, has a lower barrier than chloro for both mesityl and duryl systems. Both coalescence temperature and barrier are slightly lower. Certainly the vinyl portion of the allyl group can be positioned away from the other groups attached to the central atom. Apparently the C—H bonds that then of necessity must point towards the respective groups on either side must not increase congestion around the central atom, compared with chloro.

The effect of duryl compared with mesityl has been discussed by Pinkus and Custard.[5] The *meta* methyls serve to enhance steric crowding around the *ortho* positions through buttressing. Although direct *meta–meta* interactions between adjacent rings should be small and not contribute to the aryl—M barrier, the presence of the *meta* methyls eliminates or diminishes angle distortions by the *ortho* methyl groups that might relieve *ortho–ortho* interactions. With enhanced crowding, the aryl—M barrier increases by ~2 kcal mol^{-1} for the chlorosilanes (X = Cl) and the allylsilanes (X = allyl).

The buttressing effect does not, however, operate in the same way for the hydrogen cases (X = H). One possible explanation is that the small size of X allows the *ortho* methyl group to distort towards H. The *meta* methyl pushes the *ortho* methyl towards H, thereby reducing inter-ring *ortho–ortho* interactions and the barrier to aryl rotation. Since this deformation does not occur for mesityl, the *ortho–ortho* interaction is higher.

There are not many systems in which the barrier can be measured at two different temperatures. The clear differences in coalescence temperatures (Table 1) translate into small differences in $\Delta G^{\ddagger}$, modulated by the values of $\Delta\nu$. These differences imply that $\Delta S^{\ddagger}$ is non-zero for these systems. Unfortunately, two-point kinetics yield very poor results. It is possible to approximate $\Delta S^{\ddagger}$ to the range −15 to −35 cal mol^{-1} K^{-1}. Aside from being negative, these numbers have errors that are too large to permit further interpretation.

In summary, barriers to aryl—M rotation in Ar_3MX systems decrease in the order C > Si > Sn for the central atom M. When X is large (allyl or Cl), buttressing from the *meta* methyls raises the barrier for duryl in comparison with mesityl. When X is small (H), the reverse occurs, whereby the duryl barrier is lower than the mesityl barrier. For H, buttressing reduces the barrier through angle deformation that lowers *ortho–ortho* interactions. Because buttressing varies with the substituent X, the barriers depend in a complex fashion on the substituent. Nonetheless, the chloro systems exhibit the highest barriers for both mesityl and duryl, suggesting that this spherical group offers no opportunity for steric reduction through M—X rotation. The anisotropic allyl group has several different faces that can allow the group to alter its steric interactions.

EXPERIMENTAL

Variable-temperature NMR experiments were carried out on a Varian INOVA spectrometer for which the frequency of ^{1}H was 500 MHz. The temperature of the probe was calibrated by measurement of peak positions of the methanol and ethylene glycol standards.

Tridurylsilane (4)

A 200 ml, three-necked, round-bottomed flask, equipped with a rubber septum, a condenser and a glass stopper, was charged with pieces of Na (2.4 g, 0.105 mol), bromodurene (6.39 g, 0.03 mol), dry benzene (75 ml) and a stirring bar. The flask was given an N_2 atmosphere and $HSiCl_3$ (1 ml, 0.01 mol) was added from a syringe. The mixture was heated to reflux and stirred overnight. The dark blue mixture was cooled and filtered through a Celite pad. The resulting yellow solution was concentrated by rotary evaporation. The dark yellow residue was crystallized from hexane to give white crystals: 1.2 g, 28%; ^{1}H NMR ($CDCl_3$), δ 2.24 (s, 18H), 2.37 (s, 18H), 5.93 (s, 1H), 7.18 (s, 3H); ^{13}C NMR ($CDCl_3$), δ 20.4, 21.3, 133.2, 134.0, 137.9, 140.8; ^{29}Si NMR ($CDCl_3$), δ−40.3.

Chlorotridurylsilane (5)

A 100 ml, round-bottomed flask was charged with tridurylsilane (1.49 g, 3.5 mmol), PCl_5 (1.12 g, 5.4 mmol), CCl_4 (30 ml) and a magnetic stirring bar. The mixture was heated at reflux under N_2 for 36 h. The resulting yellow solution was concentrated by rotary evaporation, and the residue was dissolved in 50 ml of hexane. Methanol (15 ml) was added slowly to decompose the unreacted PCl_5. The organic layer was separated, dried ($MgSO_4$) and concentrated by rotary evaporation to give a yellow solid. The solid was crystallized from hexane to produce a white powder: 1.25 g, 77%; ^{1}H NMR ($CDCl_3$), δ 2.18 (s, 18H), 2.22 (s, 18H), 7.05 (s, 3H); ^{13}C NMR ($CDCl_3$), δ 20.7, 22.4, 133.5, 133.7, 134.7, 139.3, 139.9, 141.1; ^{29}Si NMR, δ − 2.7. Anal. Calcd for $C_{30}H_{39}SiCl$, C 77.80, H 8.49; found, C 77.85, H 8.45%.

Allyltridurylsilane (6)

A 100 ml, round-bottomed flask fitted with a rubber septum was charged with allyltriphenylstannane (4.27 g, 11.0 mmol) and a stirring bar. Anhydrous tetrahydrofuran (25 ml) and (quickly) phenyllithium (1.8 M, 6.1 ml, 11.0 mmol) in diethyl ether–cyclohexane were added via a syringe. After 30 min, the suspension was transferred under N_2 through a wide-bore cannula to an enclosed glass frit and filtered into a 100 ml flask containing 1.50 g (3.2 mmol) of chlorotridurylsilane. The resulting dark red solution was stirred at room temperature for 3 days. The then yellow reaction mixture was quenched with H_2O and extracted twice with hexane. The organic portion was dried ($MgSO_4$) and concentrated by rotary evaporation. The residue was chromatographed over neutral alumina with hexane as eluent to give a white solid:

MRC

0.70 g, 46%; ^{1}H NMR (C_6D_6), δ 2.08 (s, 18H), 2.24 (s, 18H), 2.47–2.52 (m, 2H), 4.85–5.00 (m, 2H), 5.76–5.90 (m, 1H), 6.94 (s, 3H); ^{13}C NMR (C_6D_6), δ 21.2, 23.1, 30.5, 115.6, 133.4, 134.6, 138.9, 141.0, 142.3; ^{29}Si NMR ($CDCl_3$), δ − 17.4; MS (EI), *m/z* 468 (M^+, 1), 428 (38), 427 (M^+ − allyl, 100), 293 (16), 262 (21), 119 (8). Anal. Calcd for $C_{33}H_{44}Si$, C 84.55, H 9.46; found, C 84.81, H 9.33%.

Bromotridurylstannane (7)

To a solution of bromodurene (10.4 g, 48.8 mmol) in diethyl ether (80 mol) was added butyllithium (2.5 M, 23.6 ml, 58.9 mmol) in hexane at 0 °C under N_2. The mixture was warmed slowly to room temperature and then stirred for 3 h. Duryllithium precipitated very quickly, and the mixture became thick. A solution of tetrabromotin (5.94 g, 13.5 mmol) in 50 ml of toluene was transferred to the flask through a cannula. The mixture was stirred overnight at room temperature and then refluxed for 6 h. A white solid was removed by filtration, and the pale yellow solution was concentrated by rotary evaporation. The brown residue was washed with 30 ml of acetone to remove colored impurities. The resulting white powder consisted of 80% bromotridurylstannane and 20% dibromodidurylstannane. The mixture was stirred with 100 ml of acetone to dissolve all of the dibromodidurylstannane. The less soluble, desired bromotridurylstannane was isolated by filtration as a white powder: 3.3 g, 40.7%; ^{1}H NMR ($CDCl_3$), δ 2.19 (s, 18H), 2.31 (s, 18H), 6.99 (s, 3H); ^{13}C NMR ($CDCl_3$), δ 20.9, 23.9, 133.3, 134.7, 139.7, 148.3; ^{119}Sn NMR ($CDCl_3$), δ − 124.0. Anal. Calcd for $C_{30}H_{39}SnBr$, C 60.23, H 6.57; found, C 61.26, H 6.46%.

Allyltridurylstannane (8)

In a round-bottomed flask, allylmagnesium bromide (1.0 M, 3.6 ml, 3.6 mmol) was added to bromotridurylstannane (2.0 g, 3.3 mmol) in 80 ml of toluene. The solution was refluxed for 24 h and cooled to room temperature. To complete the reaction, additional allylmagnesium bromide (1.0 M, 3.6 ml, 3.6 mmol) was added. After refluxing overnight, the mixture was quenched with H_2O and 10% aqueous HBr. The organic portion was washed with H_2O, $NaHCO_3$ and again with H_2O. The solution was dried ($MgSO_4$), and the solvent was removed by rotary evaporation to give a white powder as the residue: 1.8 g, 96%; ^{1}H NMR (toluene-d_8), δ 2.06 (s, 18H), 2.29 (s, 18H), 2.42 (d, 2H), 4.83 (m, 2H), 5.94 (m, 1H), 6.82 (s, 3H); ^{13}C NMR ($CDCl_3$), δ 21.1, 23.6, 28.2, 113.3, 132.1, 133.8, 137.4, 140.1, 148.9; ^{119}Sn NMR ($CDCl_3$), δ − 161.7. Anal. Calcd for $C_{33}H_{44}Sn$, C 70.85, H 7.95; found, C 71.41, H 7.87%.

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