Preparation and NMR Investigation of 1,2-Distannyl Aromatics and Heteroaromatics, 1,2-Distannylcycloalkenes and 1,2-Distannylcycloalkanes

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A series of 1,2-distannylated aromatics, heteroaromatics and cycloalkenes was prepared by treating the dibromo precursors with Me_3SnNa in tetraglyme. The latter were converted into the corresponding cycloalkanes by diimine reduction. Multinuclear NMR data are reported and discussed.

Introduction

The explosive growth of applications of the Stille−Migita reaction in organic synthesis[1] has mainly involved the use of vinyl- and aryltins. Although in most cases substrates which bear only one organotin moiety have been employed, there is increasing interest in applications involving bisstannylated compounds. The methods available for the synthesis of such compounds are still relatively limited, in particular when the two stannyl moieties are to be located on adjacent carbon atoms. Thus while *Z*-1,2-distannyl-l-alkenes can be prepared by the palladium-catalysed addition of ditins (in fact in practice only hexamethylditin) to 1-alkynes,[2] the extension of this methodology to internal alkynes leads to problems involving both regio- and stereochemistry.[3]

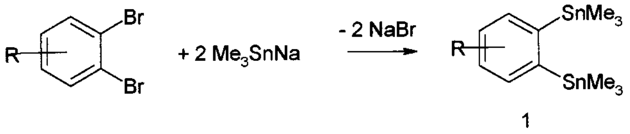
Structurally related 1,2-distannylaromatics are also not readily available: thus the preparation of *ortho*-bis(trimethylstannyl)benzene was first described by Seyferth in 1966 (via a Diels−Alder reaction between bis(trimethylstannyl)ethyne and (α-pyrone),[4] but attempts to prepare it by more appealing routes starting from *ortho*-dibromobenzene (Pd-catalysed reaction with Me_6Sn_2, reaction with Me_3SnLi or formation of the dimagnesium or dilithium reagents and reaction of these with Me_3SnCl) are all unsuccessful.[5]

A much more promising approach was described by Kuivila,[6] who was successful in reacting Me_3SnNa with *ortho*-dibromobenzene in tetraglyme. We decided to apply this methodology to other dibromoaromatics and to the related dibromocycloalkenes and to carry out NMR-spectroscopic studies on the products thus obtained. Of particular interest hereby is the three-bond tin-tin coupling constant.

Results and Discussion

1. 1,2-Distannyl-Substituted Aromatics and -Heteroaromatics 1

A series of 1,2-dibromoaromatics and -heteroaromatics was subjected to the reaction with Me_3SnNa in tetraglyme: as expected from the mechanistic discussion provided by Kuivila[6] the yields were not particularly good, lying generally between 40 and 60%. Since our work was completed, an improved procedure for the preparation of 1,2-bis(trimethylstannyl)benzene has been reported by Jurkschat et al.,[7] who obtained the material in 67% yield. The general reaction as illustrated for a monosubstituted 1,2-dibromobenzene is shown in Scheme 1.



Scheme 1

The nature of the starting materials was dictated by availability, and various substitution patterns were used; in addition, derivatives of naphthalene, furan, thiophene and imidazole were prepared. The structures of the compounds **1a−h** and the values of the three-bond tin-tin coupling constant are given in Table 1. If the stannyl moieties are located on benzene or naphthalene rings, ^3J lies between 220 and 290 Hz; in one case a 1,3-dibromo derivative was used as the starting material, the four-bond coupling constant in the highly substituted product molecule being 87 Hz.

The coupling constants in 2,3-bis(trimethylstannyl)furan (31 Hz) and -thiophene (130 Hz) are much lower, paralleling the behaviour of the corresponding interproton couplings in benzene, furan and thiophene. An intermediate value (80 Hz) is observed for 1-methyl-4,5-bis(trimethylstannyl)imidazole. Carbon-13 and proton NMR data are given in the Experimental Section.

2. 1,2-Distannylcycloalkenes 2

1,2-Distannylcycloalkenes should in theory be available by Pd-catalysed tin−tin addition to cycloalkynes. However, because of the instability of the latter in the case of small rings the alternative route via 1,2-dibromocycloalkenes, which are readily available, is much more attractive.

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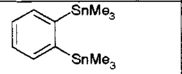
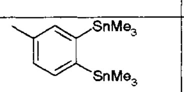
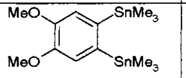
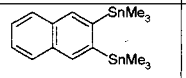
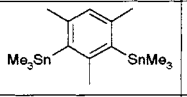
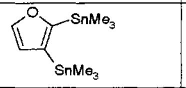
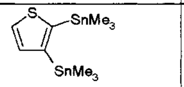
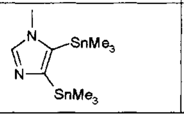
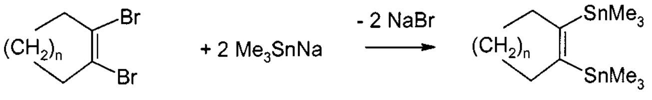
1434−193X/99/0909−2413 $ 17.50+.50/0

Table 1. Tin-119 NMR Data for Distannylaromatics and Heteroaromatics

Compound	Structure	$\delta(^{119}Sn)$	$^3J(^{119}Sn,^{119}Sn)$
1a		-25.7	286
1b		-32.2, -32.9	228
1c		-28.3	223
1d		-28.9	228
1e		-49.8	85*
1f		-42.4, -52.6	31
1g		-32.4, -42.2	131
1h		-52.2, -53.5	80

[a] ^4J(Sn,Sn).



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Scheme 2

We were able to carry out the reaction successfully for 5- to 8-membered rings ($n = 1-4$), the yields again being moderate (32−70%). The three-bond tin−tin coupling constants for compounds **2a−d** vary between 245 and 531 Hz; we had earlier observed values for acyclic derivatives in the range 400−500 Hz for *cis*- and 750−1000 Hz for *trans*-distannylalkenes.[2] The complete NMR data for these compounds are given in Table 2.

3. 1,2-Distannylcycloalkanes 3

As expected, 1,2-dibromocycloalkanes do not give the corresponding distannyl derivatives when treated with Me_3SnNa in tetraglyme. The distannylcycloalkanes are , however, available using the diimine reduction protocol originally introduced by Kuivila[8] and later used by Rahm,[9] which we have successfully applied to 1,2-distannyl-1-alkenes.[10] The yields are fair (62 and 70%, respectively), only a single isomer being observed in each case.

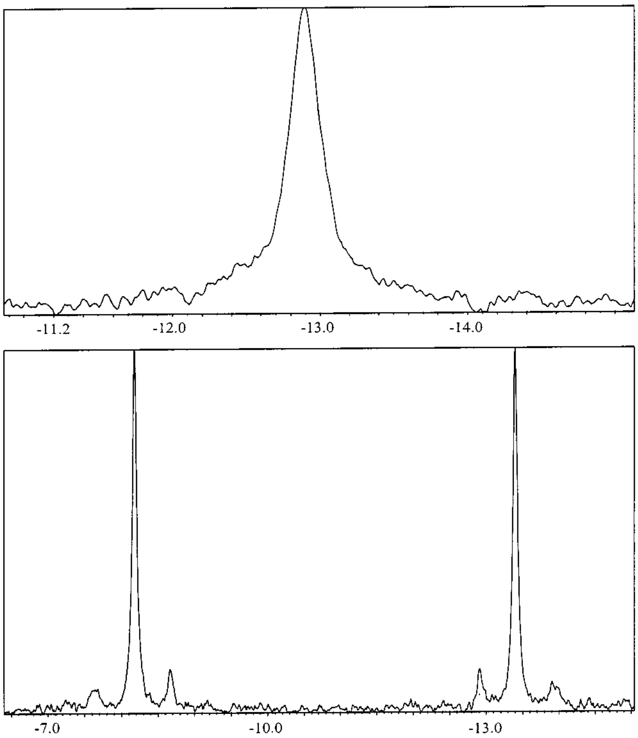
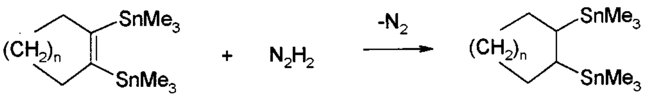


Figure 1. ^{119}Sn-NMR spectra of 1,2-bis (trimethylstannyl)cyclohexane **3b** at room temperature (top) and −50°C (bottom)



3

Scheme 3

4. Dynamic Behaviour of 1,2-Distannylcycloalkanes 3

Closer inspection of the spectra reveals that some resonances in the spectra of the 1,2-distannylcycloalkanes **3** are broad, suggesting the presence of dynamic equilibria. The diimine reduction is considered to be a stereospecific *cis* reaction and should thus afford only the *cis*-distannylcycloalkanes. In the case of the *1,2-distannylcyclohexane* **3b**, these should, according to the principles of conformational analysis, bear one axial and one equatorial stannyl moiety, so that the dihedral angle between the two should lie close to 60°; however, at room temperature only a single tin resonance is observed (Figure 1), suggesting at first that the *trans* isomer is obtained.

However, both stannyl groups in this isomer will presumably prefer equatorial positions, again leading to a dihedral angle close to 60°. The Karplus relation proposed by us for ^3J(Sn,Sn)[11] indicates that a coupling constant close to 340 Hz is to be expected for such a dihedral angle.

We thus carried out low-temperature ^{119}Sn NMR measurements, starting with the 1,2-distannylcyclohexane **3b**. Here the single broad signal observed at room temperature is split into two at −25°C, and at −50°C the coupling constant can be measured, the value of $^3J(^{119}Sn,^{119}Sn)$ being

Table 2. NMR Data for 1,2-Distannylcycloalkenes $C_nH_{2n-4}(SnMe_3)_2$

Compound	**2a**, $n = 5$	**2b**, $n = 6$	**2c**, $n = 7$	**2d**, $n = 8$
δ(Sn)	−57.2	−59.1	−50.7	−54.5
$^3J(^{119}\mathrm{Sn},^{119}\mathrm{Sn})$	246	528	491	518
$\delta(\mathrm{Sn}C\mathrm{H_3})$	−9.5	−7.6	−6.9	−7.0
$\delta(\mathrm{Sn}C\mathrm{H_3})$	340	320	321	319
$\delta(C_1)$	155.2	153.3	161.4	157.8
$^nJ(^{119}\mathrm{Sn},^{13}\mathrm{C})$	504/75	509/64	n. o./69	n. o.
$\delta(C_2)$	42.7	36.0	36.4	33.3
$^nJ(^{119}\mathrm{Sn},^{13}\mathrm{C})$	73/83	61/86	69/96	n. o.
$\delta(C_3)$	23.0	23.8	32.7[a]	29.0[b]
$^nJ(^{119}\mathrm{Sn},^{13}\mathrm{C})$	33	37/10	80	n. o.
$\delta(\mathrm{SnC}H_3)$	0.15	0.12	0.00	0.14
$^2J(^{119}\mathrm{SnC}H_3)$	54	52	52	51
$\delta(\mathrm{C}H_2)$	1.67, 2.51	1.59, 2.25	1.36, 1.74, 2.45	1.41, 2.50

[a] $\delta(C_4)$ 26.2. − [b] $\delta(C_4)$ 26.2, ^5J(Sn,H) 13. n. o. = not observed. − Ring carbon atoms are numbered as follows: C_1 refers to tin-bearing (vinylic) carbons, C_{2-4} to carbons at increasing distances.

Table 3. NMR Data for 1,2-Distannylcycloalkanes $C_nH_{2n-2}(SnMe_3)_2$

Compound	**3a**, $n = 5$	**3b**, $n = 6$	**3c**, $n = 7$	**3d**, $n = 8$
δ(Sn)	−7.5	−12.7 (room temp.) −6.7, −12.0 (−50°C)	−5.8	−3.0 (room temp.) 4.5, −5.4 (−50°C)
$^3J(^{119}\mathrm{Sn},^{119}\mathrm{Sn})$	289	159*	52	107*
$\delta(\mathrm{Sn}C\mathrm{H_3})$	−9.3	−8.9 −7.6, −10.8 (−50°C)	−9.0	−9.4 (room temp.) −9.7, −8.8 (−50°C)
$^1J(^{119}\mathrm{Sn},^{13}\mathrm{C})$	301	291 288, 298 (−50°C)	296	296
$\delta(C_1)$	32.6	33.6 31.8, 33.0 (−50°C)	33.9	34.6
$^1J(^{119}\mathrm{Sn},^{13}\mathrm{C})$	418	413 410, n. o. (−50°C)	395	n. o.
$\delta(C_2)$	24.5	32.5 29.2, 34.2 (−50°C)	35.6	28.1 (broad)
$^3J(^{119}\mathrm{Sn},^{13}\mathrm{C})$	38	n. o. 72, 69 (−50°C)	56	
$\delta(C_3)$	31.0	28.1 26.2, 29.7 (−50°C)	30.1	26.9
$^3J(^{119}\mathrm{Sn},^{13}\mathrm{C})$	45	n. o.	52	
$\delta(C_4)$			26.0	
$\delta(\mathrm{SnC}H_3)$			0.04, 0.06[a]	
$^2J(^{119}\mathrm{SnC}H_3)$			50, 48[a]	
$\delta(\mathrm{C}H_2)$			1.3−1.9	

[a] −50°C. − Ring carbon atoms are numbered as follows: C_1 refers to tin-bearing carbons, C_{2-4} to carbons at increasing distances.

159 Hz (Figure 1). The presence of two signals makes it clear that the *cis* isomer is formed, thus providing a further proof that the diimine hydrogenation occurs in a *cis* manner.

In the case of the corresponding *cycloheptane* derivative **3c** the sharp signal observed at room temperature broadens on cooling but is not resolved into two, even at −50°C, though the tin-tin coupling constant can of course be measured and is equal to only 52 Hz.

The *distannylcyclooctane* **3d**, however, again exhibits two signals at −25°C; these sharpen on further cooling, but at −50°C the well-separated signals are not of equal height, the high-field signal having a linewidth three times greater than its low-field equivalent. The value of ^3J(Sn,Sn) is again low (107 Hz).

In contrast, the *distannylcyclopentane* **3a** gives a signal which does not broaden when the sample is cooled from room temperature to −50°C, though ^3J varies slightly with temperature, decreasing from 289 to 277 Hz over this temperature range.

This wide range of ^3J(Sn,Sn) within a series of formally similar structures indicates that the presence of two relatively bulky organotin moieties in neighbouring positions on the carbocyclic ring leads to considerable deviations from ideal geometry; in order to compare the torsion angles *Sn−C−C−Sn* we have performed semiempirical geometry optimizations using PM3[12] for the distannylcycloalkanes.

The resulting values are 37° (cyclopentane), 59° (cyclohexane), 76° (cycloheptane) and 75° (cyclooctane); thus there is a clear Karplus-type dependence, though the J values deviate from those calculated using our previously proposed equation.[11] This is in fact not altogether surprising, as it is known that a ″Karplus band″ rather than a single curve reflects the true situation.

For the distannylcyclohexane the ring bond lengths, angles and torsion angles obtained using a density functional geometry optimisation are in good agreement with the PM3 calculations, so that we consider PM3 to be adequate for our task: thus for example the density functional calculation also gives 59° as the torsion angle *Sn−C−C−Sn*.

Low-temperature proton NMR measurements provided no useful information, since the ring proton multiplets, which are broad and complex at room temperature, only broaden further on cooling.

The ^{13}C spectra are much more informative. The *distannylcyclopentane* spectra remain virtually unchanged on cooling, while the *distannylcyclohexane* gives a total of 6 lines for the ring carbons at −50°C. Low-temperature ^{13}C spectra for the related *cis*-1,2-dimethylcyclohexane were reported by Schneider et al. in 1971.[13] The number of lines (4) remains constant on cooling for the *distannylcycloheptane* **3c**. The most curious behaviour is observed for the *distannylcyclooctane* **3d**, where one resonance, that for the tin-bearing carbons, is absent at room temperature; thus the greatest flexibility of the molecule apparently involves the tin-bearing carbons.

Table 3 contains the NMR data for the compounds studied; ^{13}C values obtained at room temperature are contrasted with those recorded at −50°C in a number of cases.

Experimental Section

General: All manipulations involving organotins and sodium were carried out under argon. − NMR: Bruker DPX-300 or DRX-400 spectrometers with CDC1$_3$ as solvent and internal lock. ^{13}C multiplicities were determined with the help of DEPT spectra. External TMS and Me$_4$Sn were used as standards. − Density functional calculations were carried out using the ADF basis set IV[14] and the local exchange-correlation functional of Vosko et al.[15] with Becke's nonlocal exchange correction[16] and Perdew's nonlocal correlation correction[17] including scalar relativistic effects (see[14d] and references contained therein). The inner core shells up to 4*p* for Sn and 1*s* for C were treated with the frozen-core approximation.[14d]

General Procedure for Reactions of the Dibromoaromatics and Dibromoalkenes with Me$_3$SnNa: A solution of the dibromoaromatic or dibromoalkene (3.5 mmol) in tetraglyme (4 mmol) was cooled to 0°C and a solution of Me$_3$SnNa (7 mmol) in tetraglyme (8.8 mL) was slowly added dropwise with stirring. The mixture was stirred overnight and treated with saturated NH$_4$Cl solution followed by three extractions with ether. The organic phase was separated and washed four times with water to remove traces of tetraglyme. After phase separation the organic solution was dried with MgS0$_4$ and volatiles removed at 12 Torr. The following compounds were prepared according to this procedure.

1,2-Bis(trimethylstannyl)benzene (1a): Yield 1.47 g (52%), pale yellow oil, b.p. 90°C/0.01 Torr. − C$_{12}$H$_{22}$Sn$_2$ (403.7): calcd. C 35.70, H 5.49; found C 35.95, H 5.20. − ^{13}C NMR: δ = −7.7 (SnMe$_3$, ^{1}J(SnC) = 342 Hz), 127.3 (C^3, C^6, ^{2}J(Sn,C) = 47 Hz), 136.6 (C^4, C^5, ^{3+4}J(Sn,C) = 64 Hz), 151.1 (C^1, C^2, ^{2}J(Sn,C) = 72 Hz). − ^{1}H NMR: δ = 0.24 (s, 18 H, SnMe$_3$, ^{2}J(Sn,H) = 52 Hz), 7.17 (m, 2 H), 7.44 (m, 2 H).

3,4-Bis(trimethylstannyl)toluene (1b): Yield 1.36 g (48%), pale yellow oil, b.p. 100°C/0.008 Torr. − Anal. Calcd. for C$_{13}$H$_{24}$Sn$_2$ (417.7): C, 37.38, H 5.79, found C 37.60, H 5.63). − ^{13}C NMR: δ = −7.1 (SnMe$_3$, ^{1}J(SnC) 339 Hz), 21.3 (Me), 128.5 (CH), 136.8 (CH), 137.0 (C$_q$), 137.8 (CH), 147.6 (C$_q$), 151.6 (C$_q$). − ^{1}H NMR: δ = 0.23, 0.24 (both s, 9 H, SnMe$_3$, ^{2}J(Sn,H) 53 Hz), 2.24 (s, 3 H, Me), 7.02 (d, 1 H, *J* = 7.5 Hz, CH), 7.27 (s, 1 H, CH), 7.34 (d, 1 H, *J* = 7.5 Hz, CH, ^{3}J(Sn,H) 45 Hz).

1,2-Bis(trimethylstannyl)-4,5-dimethoxybenzene (1c): Yield 1.40 g (43%), yellow oil, b.p. 150°C/0.02 Torr. − Anal. Calcd. for C$_{14}$H$_{26}$O$_2$Sn$_2$ (463.7): C 36.26, H 5.65, found C 36.70, H, 5.45. − ^{13}C NMR: δ = −7.0 (SnMe$_3$, ^{1}J(SnC) 342 Hz), 55.6 (OMe), 119.7 (CH, ^{3}J(Sn,C) 58 Hz), 142.8 (C$_q$), 148.4 (C$_q$). − ^{1}H NMR: δ = 0.31 (s, 18 H, SnMe$_3$, ^{2}J(Sn,H) 53 Hz), 3.87 (2, 6 H, OMe), 7.05 (s, 2 H, CH, ^{3}J(Sn,H) 48 Hz, ^{4}J(Sn,H) 11 Hz).

2,3-Bis(trimethylstannyl)naphthalene (1d): Yield 1.40 g (44%) after purification by column chromatography [A1$_2$O$_3$/petroleum ether, boiling range 30−60°C], pale yellow crystals, m.p. 106−107°C. − Anal. Calcd. for C$_{16}$H$_{24}$Sn$_2$ (453.8): C 42.35, H 5.33, found C 42.20, H, 5.25. − ^{13}C NMR: δ = −6.6 (SnMe$_3$, ^{1}J(SnC) 341 Hz), 126.6 (CH), 127.8 (CH), 132.9 (C$_q$), 136.8 (CH, *J*(SnC 46 Hz), 148.2 (C$_q$). − ^{1}H NMR: δ = 0.31 (s, 18 H, SnMe$_3$, ^{2}J(Sn,H) 54 Hz), 7.45 (m, 2 H, CH), 7.75 (m, 2 H, CH), 7.97 (s, 2 H, CH, ^{3}J(Sn,H) 53 Hz, ^{4}J(Sn,H) 11 Hz).

2,6-Trimethylstannyl-1,3,5-trimethylbenzene (1e): Yield 1.87 g (60%), b.p. 95−105°C/0.008 Torr. − Anal. Calcd. for C$_{15}$H$_{28}$Sn$_2$ (445.8): C 40.41, H 6.33, found C 40.50, H, 6.20. − ^{13}C NMR: δ = −4.7 (SnMe$_3$, ^{1}J(SnC) 338 Hz; 25.9 (Me), 30.5 (Me), 128.4 (CH, ^{4}J(Sn,C) 38 Hz), 139.1 (C$_2$, *J*(Sn,C) 28 Hz), 145.7 (C$_q$, *J*(Sn,C) 9 Hz), 152.2 (C$_q$, ^{1}J(SnC 528 Hz). − ^{1}H NMR: δ = 0.27 (s, 18 H, SnMe$_3$, ^{2}J(Sn,H) 53 Hz), 2.29 (s, 6 H, Me, ^{4}J(Sn,H) 6 Hz), 2.43 (s, 3 H, Me, ^{4}J(Sn,H) 6 Hz; 6.80 (s, 1 H, CH, ^{4}J(Sn,H) 16 Hz).

2,3-Bis(trimethylstannyl)furan (1f): Yield 1.56 g (62%), yellow oil, b.p. 68−75°C/0.1 Torr. − Anal. Calcd. for C$_{10}$H$_{20}$OSn$_2$ (358.5): C 30.51, H 5.12, found C 30.50, H, 5.20. − ^{13}C NMR: δ = −5.8 (SnMe$_3$, ^{1}J(SnC) 365 Hz), −5.7 (SnMe$_3$, ^{1}J(SnC) 373 Hz), 114.9 (CH, *J*(Sn,C) 36 Hz, 45 Hz), 127.1 (C$_q$, ^{1}J(Sn,C) 482 Hz, ^{2}J(Sn,C) 93 Hz), 146.1 (CH, *J*(Sn,C) 34 Hz, 43 Hz), 165.7 (C$_q$, ^{1}J(Sn,C) 520 Hz, ^{2}J(Sn,C) 104 Hz). − ^{1}H NMR: δ = 0.39 (s, 9 H, SnMe$_3$, ^{2}J(Sn,H) 56 Hz), 0.45 (s, 9 H, SnMe$_3$, ^{2}J(Sn,H) 57 Hz), 6.53 (d, 1 H, CH, ^{3}J(H,H) 1.6 Hz, ^{3}J(Sn,H) 14 Hz), 7.92 (d, 1 H, CH, ^{3}J(H,H) 1.6 Hz).

2,3-Bis(trimethylstannyl)thiophene (1g): Yield 1.20 g (42%), pale yellow oil, b.p. 88−95°C/0.1 Torr. − Anal. Calcd. for C$_{10}$H$_{20}$SSn$_2$ (409.7): C 29.32, H 4.92, found C 29.30, H, 4.90. − ^{13}C NMR: δ = −7.6 (SnMe$_3$, ^{1}J(SnC) 352 Hz), −6.9 (SnMe$_3$, ^{1}J(SnC) 366 Hz), 129.6 (CH, ^{2}J(Sn,C) 15 Hz, ^{3}J(Sn,C) 54 Hz), 132.7 (C$_q$,), 135.2 (CH, ^{3}J(Sn,C) 62 Hz, 75 Hz), 147.0 (C$_q$, ^{2}J(Sn,C) 59 Hz), 150.9 (C$_q$, ^{1}J(SnC) 514 Hz). − ^{1}H NMR: δ = 0.42 (s, 9 H, SnMe$_3$, ^{2}J(Sn,H) 55 Hz), 0.50 ((s, 9 H, SnMe$_3$, ^{2}J(Sn,H) 56 Hz), 7.45 (d, 1 H, CH, ^{3}J(H,H) 4.4 Hz, ^{3}J(Sn,H) 15 Hz, ^{4}J(Sn,H) 6 Hz), 7.82 (d, 1 H, CH, ^{3}J(H,H) 4.4 Hz, ^{4}J(Sn,H) 10 Hz).

1-Methyl-4,5-Bis(trimethylstannyl)imidazole (1h): Yield 0.91 g (32%), pale yellow crystals, m.p. 39−41°C. − Anal. Calcd. for C$_{10}$H$_{22}$N$_2$Sn$_2$ (407.7): C 29.46, H 5.44, N 6.87, found C 29.50, H 5.70, N 6.55. − ^{13}C NMR: δ = −7.9 (SnMe$_3$, ^{1}J(SnC) 362 Hz), −7.3 (SnMe$_3$, ^{1}J(SnC) 370 Hz), 34.7 (Me), 138.1 (C$_q$), 142.7 (CH, ^{3}J(Sn,C) 31 Hz), 151.7(C$_q$). − ^{1}H NMR: δ = 0.28 (s, 9 H, SnMe$_3$, ^{2}J(Sn,H) 57 Hz), 0.34 (s, 9 H, SnMe$_3$, ^{2}J(Sn,H) 57 Hz), 3.67 (s, 3 H, NMe), 7.76 (s, 1 H, CH, ^{4}J(Sn,H) 5 Hz).

1,2-Bis(trimethylstannyl)cyclopentene (2a): Yield 0.96 g (35%), b.p. 60°C/0.008 Torr. − Anal. Calcd. for $C_{11}H_{24}Sn_2$ (393.7): C 33.56, H 6.14, found C 32.60, H, 5.90.

1,2-Bis(trimethylstannyl)cyclohexene (2b): Yield 2.00 g (70%), colourless highly viscous oil, b.p. 100°C/0.5 Torr. − Anal. Calcd. for $C_{12}H_{26}Sn_2$ (407.7): C 35.35, H 6.43, found C 35.50, H, 6.40.

1,2-Bis(trimethylstannyl)cycloheptene (2c): Yield 1.83 g (62%), colourless highly viscous oil, b.p. 80°C/0.02 Torr (kugelrohr). − Anal. Calcd. for $C_{13}H_{28}Sn_2$ (421.8): C 37.02, H 6.69, found C 37.30, H, 6.50.

1,2-Bis(trimethylstannyl)cyclooctene (2d): Yield 1.31 g (43%), yellow highly viscous oil, boiling range 100−120°C/0.002 Torr (kugelrohr). − Anal. Calcd. for $C_{14}H_{30}Sn_2$ (435.8): C 38.59, H 6.94, found C 40.00, H 6.80).

Procedure for the Diimine Reduction: The distannylcycloalkene (2 mmol) was dissolved in ethanol (5 mL). The solution was cooled to 0°C and treated with a l% solution of $CuSO_4$ and an 80% solution of hydrazine followed by slow dropwise addition of 30% hydrogen peroxide. The mixture was stirred for 1 h, the solvent removed and the residue dissolved in $CDC1_3$. This procedure was used to prepare the following compounds:

***cis*-1,2-Bis(trimethylstannyl)cyclopentane (3a):** Yield 0.36 g (46%), boiling range 50−54°C/0.007 Torr. − Anal. Calcd. for $C_{11}H_{26}Sn_2$ (395.7): C, 33.39, H 6.62, found C 33.35, H 6.50.

***cis*-1,2-Bis(trimethylstannyl)cyclohexane (3b):** Yield 0.29 g (35%), colourless oil, boiling point 80°C/0.02 Torr. − Anal. Calcd. For $C_{12}H_{28}Sn_2$ (409.7): C, 35.18, H 6.89, found C 34.60, H 6.50 .

***cis*-1,2-Bis(trimethylstannyl)cycloheptane (3c):** Yield 0.25 g (30%), colourless highly viscous oil, boiling range 120−125°C/0.07 Torr (kugelrohr). − Anal. Calcd. for $C_{13}H_{30}Sn_2$ (423.8): C 36.84, H 7.14, found C 37.00, H 6.85.

***cis*-1,2-Bis(trimethylstannyl)cyclooctane (3d):** Yield 0.53 g (60%), colourless highly viscous oil, boiling range 80−90°C/0.003 Torr (kugelrohr). − Anal. Calcd. for $C_{14}H_{32}Sn_2$ (437.8): C, 38.40, H 7.37, found C 40.70, H 7.70).

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