Axially Asymmetric Metal Alkyls. Part 2.[1] Synthesis of the Di-Grignard Reagent $[\{\text{Mg(thf)}_n\text{Cl}\}_2\text{R}]$ [thf = tetrahydrofuran, R = $(2\text{-CH}_2\text{C}_6\text{H}_4)_2{}^{2-}$] and 6,7-Dihydro-5*H*-dibenzo[*c,e*]-silepines and -stannepines; *X*-Ray Crystal Structures of $[\text{SnPh}_2\text{R}]$ and δ-*SS*- and λ-*RR*-$[\text{SnPh}_2\{[2\text{-CH(SiMe}_3)\text{C}_6\text{H}_4]_2\}]$†

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Reactions of Mg and Li with 2,2′-bis(chloromethyl)biphenyl in tetrahydrofuran (thf) yield respectively a new di-Grignard reagent, $[\{\text{Mg(thf)}_n\text{Cl}\}_2\{(2\text{-CH}_2\text{C}_6\text{H}_4)_2\}]$ (5), for rather critical conditions, and the intramolecular cyclization product, 9,10-dihydrophenanthrene which further reacts to form a radical anion (g = 2.0037, hydrogen hyperfine coupling unresolved). Substituted 6,7-dihydro-5*H*-dibenzo[*c,e*]-silepines and -stannepines derived from (5) and the dilithium complexes $[\{\text{Li(tmen)}\}_2\{(2\text{-CHRC}_6\text{H}_4)_2\}]$ (R = H or SiMe_3; tmen = *NNN′N′*-tetramethylethylenediamine) are also reported. The crystal structures of the compounds $[\text{SnPh}_2\{(2\text{-CHRC}_6\text{H}_4)_2\}]$ [R = H (8) or SiMe_3 (9)] have been determined. Sn–C (aromatic) distances are similar [2.139(8) and 2.149(9) Å in (8), *cf.* 2.136(4) Å in (9)] whereas the Sn–CHR distances are significantly different [2.157(8) and 2.159(9) Å in (8), *cf.* 2.184(4) Å in (9)]; the angles subtended by the bidentate ligands are 98.7(3)° in (8) and 99.4(2)° in (9) and the associated torsion angles along the biphenyl axis are respectively 66.0 and 70.8°. Compound (9) comprises a racemate of δ-*SS* and λ-*RR* isomers, in the solid, with the molecules lying on C_2 axes.

In Part 1 [1] of the current series lithium alkyl complexes derived from metallation of 2,2′-dimethylbiphenyl and its trimethylsilylmethylated compounds using Li(tmen)Bu^n (tmen = *NNN′N′*-tetramethylethylenediamine) were reported as well as their SiMe_3-substituted derivatives. Access to the dilithium species, $[\{\text{Li(tmen)}\}_2\{(2\text{-CHRC}_6\text{H}_4)_2\}]$ (1; R = H) and (2; R = SiMe_3) was with a view that they would be suitable precursors to axially asymmetric metallacycles *via* salt elimination reactions. This is explored in the present paper with reactions involving tin(IV) and to a lesser extent silicon alkyl chlorides.

For metallacycles of ring sizes up to and including six atoms in metallacyclohexanes, β-hydrogen elimination is attentuated, a consequence of the difficulty in achieving a low M–C–C–H dihedral angle. However, for a more flexible seven-membered ring, β-hydrogen elimination is reasonably facile as exemplified by the instability of $[\overline{\text{Pt}\{\text{CH}_2(\text{CH}_2)_4\text{C}}\text{H}_2\}(\text{PPh}_3)_2]$;[2] in consequence, the absence of β-hydrogen atoms is imperative for enhanced stability, a feature of the metallacycles derived from (1) and (2). Also, in principle, the ligand $(2\text{-CH}_2\text{C}_6\text{H}_4)_2{}^{2-}$ is capable of unusual bonding configurations similar to the related unidentate benzyl group,[3] and the ability to bridge two metal centres as found in the related bidentate *o*-xylidene ligand for a magnesium macrometallacycle.[4] Another important feature of the ligand is its potential for accommodating a wide variation in heteroatom size by torsion along the biphenyl axis.

Prior to this work, main-group heterocyclic derivatives of $(2\text{-CH}_2\text{C}_6\text{H}_4)_2{}^{2-}$ were prepared by reactions of 2,2′-bis(bromomethyl)biphenyl, (3), with K_2Se and $(\text{BrMg})_2\text{AsPh}$ for $\text{Se}[(2\text{-CH}_2\text{C}_6\text{H}_4)_2]$[5] and $\text{AsPh}[(2\text{-CH}_2\text{C}_6\text{H}_4)_2]$[6] respectively. It has been noted that a di-Grignard reagent of (3) would provide a more direct route to these classes of heterocycles,[7] but attempts to prepare such a reagent were unsuccessful, yielding the intramolecular cyclization product, 9,10-dihydrophenanthrene.[8] In this paper a successful synthesis of a di-Grignard reagent is described, based on 2,2′-bis(chloromethyl)biphenyl, (4), and although the synthesis of the lithium alkyl (1), an alternative source of the dianion $(2\text{-CH}_2\text{C}_6\text{H}_4)_2{}^{2-}$, is simpler[1] it has been demonstrated that lithium alkyls are less versatile as transfer reagents, particularly for transition-metal complexes.[9] Some of the results reported herein have appeared in a preliminary communication.[10]

Results and Discussion

Access to the di-Grignard reagent of α,α′-dichloro-*o*-xylene, albeit under rather critical conditions,[4] suggests that other previously inaccessible Grignard reagents may be available using similar conditions and precursors. We found the optimum conditions and choice of halide, chloride rather than bromide for the present system based on $(2\text{-XCH}_2\text{C}_6\text{H}_4)_2$, to be identical to those for the *o*-xylidene di-Grignard with yields typically greater than 90%. No di-Grignard reagent could be prepared for X = Br under the same conditions. Success of chlorides in general over bromides to restrict competing coupling reactions even from simple Grignards is well known. The predominant competing reaction for X = Cl is the formation of oligomers which, together with a high dilution requirement for generation of the Grignard (5), vindicates the coupling decomposition pathway to be intermolecular elimination of MgCl_2. Like the *o*-xylidene case the solvent used was tetrahydrofuran (thf) and attempts to prepare solutions of concentrations higher than *ca.* 0.1 mol dm^{-3} resulted in diminished yields. Concentrations of Grignard solutions were determined by quenching aliquots with excess aqueous HCl and back-titrating with base; the Grignard (5) was also subsequently derivatized as the bis(trimethylsilyl) compound, (6).

Using the same conditions as for the dichloride, the dibromide (3) yielded exclusively the intramolecular cyclization product 9,10-dihydrophenanthrene (Scheme 1), there

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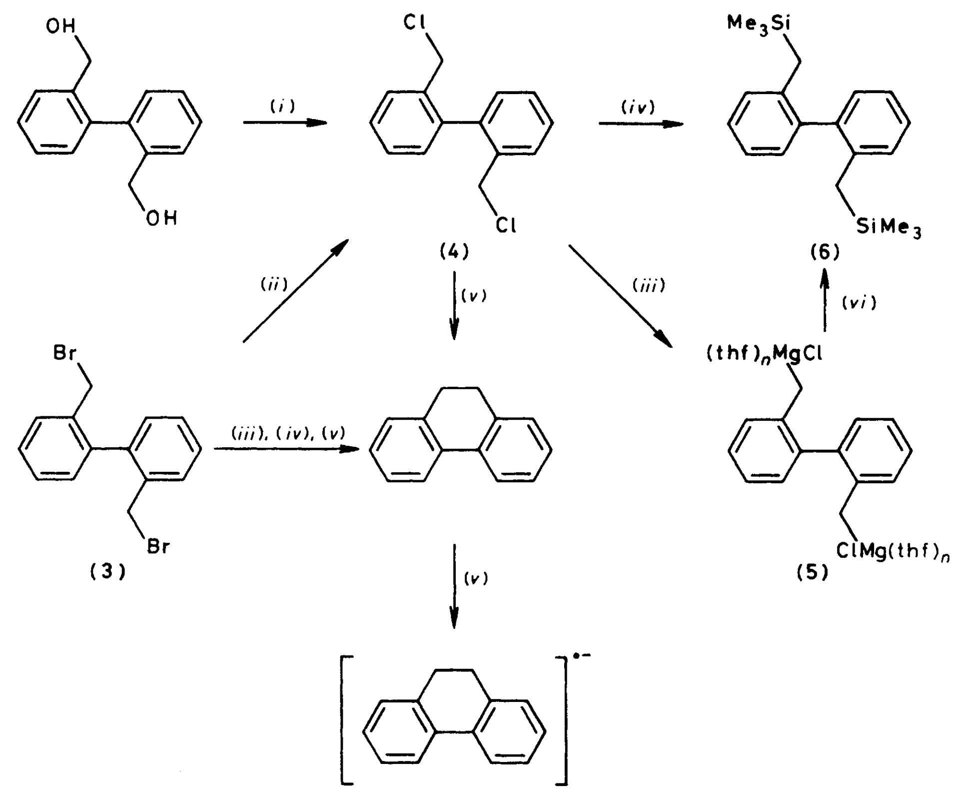
† 6,7-Dihydro-6,6-diphenyl- and 6,7-dihydro-6,6-diphenyl-5,7-bis(trimethylsilyl)-5*H*-dibenzo[*c,e*]stannepine.

Supplementary data available (No. SUP 23756, 21 pp.): structure factors, thermal parameters, least-squares planes, H-atom parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii–xix.

Non-S.I. unit employed: 1 mmHg = (101 325/760) Pa.



Scheme 1. (*i*) Concentrated $HCl-H_2SO_4$; (*ii*) LiCl, dmf; (*iii*) Mg, thf; (*iv*) Mg, thf-$SiMe_3Cl$; (*v*) Li, thf; (*vi*) $SiMe_3Cl$

being no Grignard activity. This has been noted previously [8] and more recently biphenyl ring-closure reactions involving Mg and aromatic substituted compounds of (3) have featured in organic syntheses.[11] A similar contrast between chloride and bromide reactivity is found in 1,8-bis(halogenomethyl)-naphthalene, the chloride resulting in oligomerization but with no Grignard formation using the same conditions, whereas the bromide afforded the intramolecular cyclization product, acenaphthylene.[12]

It thus appears that in benzylic type di-Grignard reactions the mono-Grignard initially formed is more stable towards intramolecular elimination of MX_2 for the chloride. The origin of this possibly relates to kinetic effects ($Br^{\bullet}$ is a better leaving group than $Cl^{\bullet}$), variation in Mg–X, XMg–C, and X–C bond energies, and the mechanism of Grignard formation, thought to involve free-radical intermediates.[13] In the case of saturated dihalides, di-Grignard reagents are readily accessible, as for example *cis*-$CH_2(CH_2)_3CH(CH_2MgCl)CH(CH_2MgCl)$ and $BrMgCH_2Si(CH_3)_2Si(CH_3)_2CH_2MgBr$,[14] although for 1,3-di-Grignards the yields are low.[15]

Reaction of (3) or (4) with lithium in thf afforded 9,10-dihydrophenanthrene, the cyclization product. [This contrasts with saturated alkyl halides (excluding iodides) which readily yield lithium alkyl complexes.] Further reaction with lithium occurs with the formation of a dark green solution containing a new persistent radical anion of 9,10-dihydrophenanthrene. The same species was also prepared by reacting an authentic sample of 9,10-dihydrophenanthrene with lithium in thf. Although no desired dilithium alkyl of (3) or (4) could be prepared an alternative approach to lithium alkyl synthesis, direct metallation using Li(tmen)Bu^n, was successful and is described in the preceding paper.[1]

The radical anion of 9,10-dihydrophenanthrene has been prepared as a product on protonation of the phenanthrene dianion, in turn derived from a reaction of the aromatic compound with Na or K.[16] However, no e.s.r. data were reported. The anion detected in the present study, $g = 2.0037$, shows poorly resolved hydrogen hyperfine coupling (Figure 1). (The g value of 2.0044 reported in a preliminary communication is in error.[10]) Attempts to enhance the resolution by dilution had only limited success and this was associated with the appearance of a spurious persistent sharp singlet (Figure 1) of increasing intensity with further dilution. The absence of well defined fine structure in the e.s.r. spectrum contrasts with that of a related radical anion in potassium 4,5,9,10-tetrahydropyrylide where all hydrogen hyperfine coupling is resolved.[17] It may be the nature of the anion–cation interaction, possibly of the ' contact ion-pair ' type that

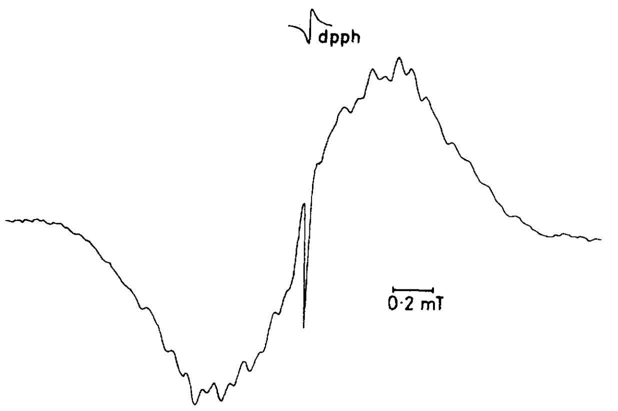
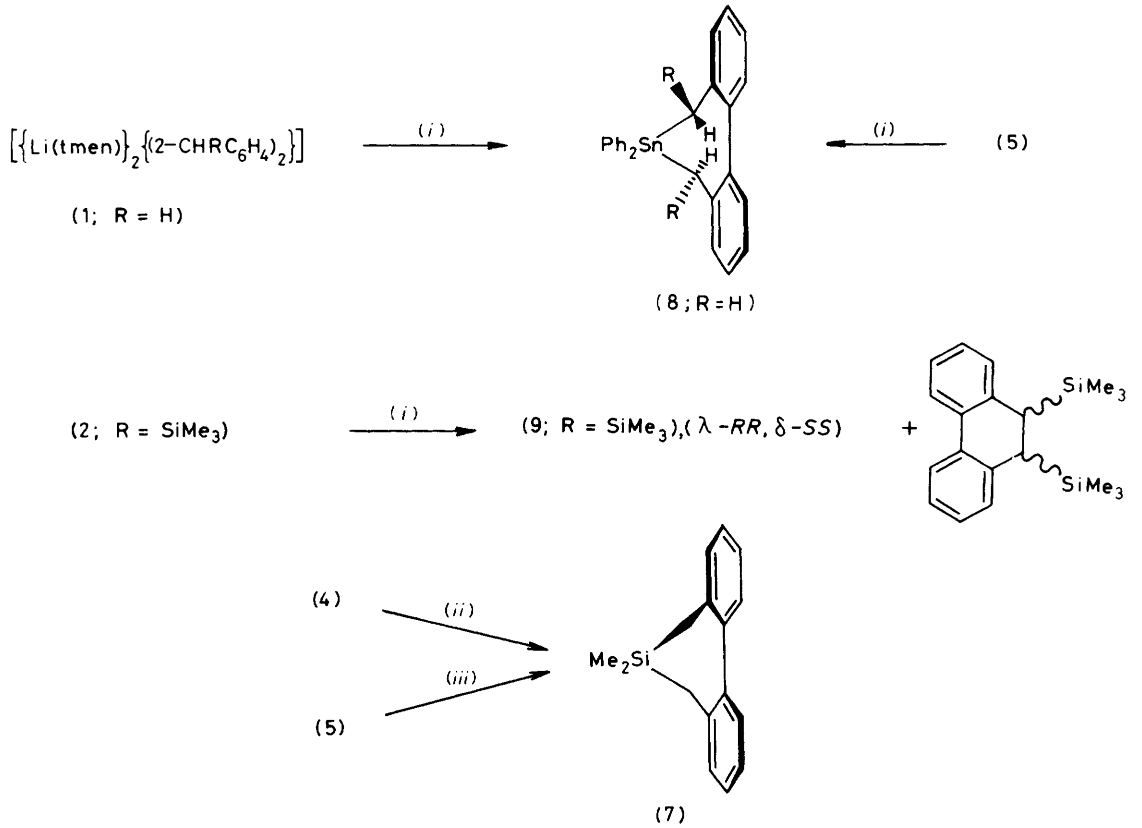
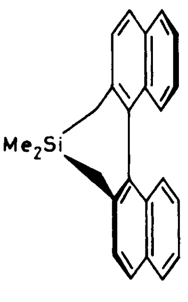


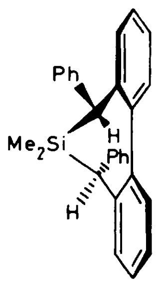
Figure 1. E.s.r. spectrum of the product of the reaction between 9,10-dihydrophenanthrene and lithium in thf at 20 °C (dpph = diphenylpicrylhydrazyl)



Scheme 2. (*i*) $SnPh_2Cl_2$, Et_2O; (*ii*) Mg, thf-$SiMe_2Cl_2$; (*iii*) $SiMe_2Cl_2$

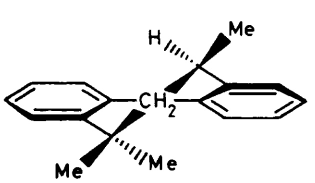


(10)



(δ-*RS*,λ-*RS*)

(12)



(11)

is common for aromatic complexes of lithium,[18] as opposed to solvent-separated ion pairs with Na^+ and K^+ as counter ions, that precludes the likelihood of obtaining detailed coupling information.

The chemistry of the O-centred, isoelectronic silicon and tin heterocyclic compounds of (7) and (8) is well established [19] and while heterocycles based on the present C-centred system are unusual, those of the isomeric series, dihydrodibenzo[*b,f*]-metallepines, are well documented, being in general prepared from 2,2′-dilithiodibenzyl and an appropriate halide, as in for example in the Group 4B dimethyl and diphenyl compounds (Si, Ge, Sn, Pb).[20] By far the most extensively studied class of tin metallepines are the metallacyclopentene complexes and unsaturated analogues such as $[Sn\{CHPh(CHPh)_2CHPh\}_2]$ [21] and $[Ph_2SnCH_2(CH)_2CH_2]$ [22] respectively.

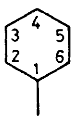
A previously attempted di-Grignard *in situ* reaction of (3) with $SiMe_2Cl_2$ yielded only small quantities of the silepine (7) and attempts to purify it were unsuccessful.[7] However, we find that by using the dichloride (7) is formed in 42% yield. Moreover, by quenching the di-Grignard reagent (5) with $SiMe_2Cl_2$, compound (7) was obtained in high yield. Using the alternative source of the dianion, $(2\text{-}CH_2C_6H_4)_2{}^{2-}$, the lithium complex (1), the same silepine was obtained in modest yield (44%) and was difficult to purify. The success of using (5) compared to (1) further illustrates the versatility of the Grignard reagent compared to the lithium complex,[9] although a related silicon heterocycle (10) has been prepared in good yield from a dilithium reagent (not isolated).[23] Reaction of the trimethylsilylalkyl lithium complex (2) with $SiMe_2Cl_2$ afforded the expected silepine although in low yield (9% based on a gas-chromatographic mass spectrum), and attempts to isolate the species were unsuccessful.

Unlike the silepine (7), the stannepine (8) was found to be accessible in good yield from either the di-lithium or di-Grignard reagent. The $SiMe_3$-substituted stannepine (9) was, however, only obtained in low yield (17%) as colourless crystals from pentane; the major products were 9,10-bis(trimethylsilyl)-9,10-dihydrophenanthrene (gas-chromatographic mass spectrum), and oligomeric and pentane-insoluble $SnPh_2$ [24] (Scheme 2). Formation of the latter possibly originates from a reductive elimination or metathesis pathway. Reduction of this type has been noted in the formation of a by-product, SnL, during the preparation of SnL_2 [L = *o*-$(Me_3SiCH)_2C_6H_4{}^{2-}$].[25]

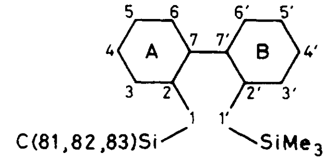
Of the three sets of isomers, δ- and λ-*RR*, δ- and λ-*SS*, and δ- and λ-*RS*, molecular models suggest that the δ-*RR* and λ-*SS* isomers (C_2) and the δ- and λ-*RS* isomers (C_s) possess unfavourable non-bonding interactions between the phenyl and $SiMe_3$ groups. The remaining isomers, the enantiomers δ-*SS* and λ-*RR*, are the observed isomers, as determined by an *X*-ray structure determination (see below). Conversion of these isomers to the enantiomeric pair δ-*RR* and λ-*SS*, *via* torsion along the biphenyl axis, is unlikely for reasons cited above and is further supported by variable-temperature ^1H n.m.r. spectroscopy which shows no fluxional behaviour over a wide temperature range (−80 to +100 °C). The presence of only one diastereoisomer may be a consequence of the steric compression requirements in the other isomers and if they are formed they may favour a reduction–elimination decomposition pathway.

Stereospecific formation of metallacycles in transmetallation reactions has been noted in the syntheses of $(SnL)_4$,[25] SnL_2,[25] and $[ML(\eta\text{-}C_5H_5)_2]$ (M = Ti, Zr, or Hf)[26] [L = *o*-$(Me_3SiCH)_2C_6H_4{}^{2-}$] where the chelating alkyl is always bound in the *meso* configuration, and in (12) where the stereochemistry is *cis*, δ- and λ-*RS*.[27] Although (12) and (9) possess different heteroatoms, it's likely that the smaller steric constraints associated with the substituents in (12) is sufficient to allow the otherwise unfavourable isomeric analogue of (9) to exist. Hydrogen-1 n.m.r. spectra of conformationally rigid 6,7-dihydro-5*H*-dibenzo[*c*,*e*]metallepines possess AB coupling patterns for the methylene protons since these protons are isotropic and anisochronous. This is so for the tin heterocycle (8), for temperatures in excess of 100 °C. Where there is conformational inversion, the energy barrier to this process appears to be related to the size of the heteroatom; the smaller the heteroatom, the lower is the energy required, which corresponds to the transition state with the least unfavourable distortions.[28,29] The associated coalescence temperatures lie within the range 34—87.5 °C for sulphur heterocycles and −9 to +17.5 °C for heterocycles of second-row elements.[29] In the present study, however, the silicon heterocycle (7) is not consistent with these results; for temperatures down to −100 °C there is no evidence for an AB pattern for the methylene protons. Although this is indicative of fluxional behaviour, in view of the n.m.r. characteristics of the above compounds, it may be a consequence of the resonances of the methylene protons almost being identical for the rigid molecule. The silicon heterocycle (12) is, however, fluxional at temperatures above −77 °C,[27] although its torsion lability is likely to be affected by the substituents. In another closely related compound, (10), where axial inversion is not expected because of steric hindrance, a well defined AB coupling pattern for the methylene protons is found;[23] in the methylene-substituted compound, (11), the predominant conformation is that shown[29] and, interestingly, the methyl disposition at the carbon bearing only one methyl group is that found for the $SiMe_3$ groups in the structure of (9) where the isomer is that predicted on consideration of intramolecular non-bonding contacts.

Structural Commentary.—Results are presented in Tables 1—4 and Figures 2 and 3 for compounds (8) and (9), showing unit cell content projections [2(*a*) and 3(*a*)] and molecular dispositions [2(*b*) and 3(*b*)] respectively. For comparative purposes, concerning the molecular geometry and bonding we note that a recent redetermination of the structure of tetraphenyltin(IV) gives tin–carbon distances (uncorrected for libration) of 2.143(5) Å, with angles subtended at the tin atom by the phenyl carbon atoms of 110.5(2) (about the crystallographic $\bar{4}$ axis) and 108.9(2)°.[30] ' Standard ' distances in a comparable unstrained compound could be considered to be represented by 1,1,6,6-tetraphenyl-1,6-distannacyclodecane, in which the mean Sn–C(phenyl) distance is 2.14 Å, while the mean Sn–C(alkyl) distance is 2.16 Å. The angle subtended at the tin by the phenyl carbon atoms is 108.2(3)°, while that subtended by the alkyl carbon is 111.0(3)°.[31] The atom numbering of (8) and (9) is shown below; hydrogen atom numbering follows that of the parent atom with suffixes a,b,c.



Phenyl ligand



Diphenyl ligand

Compound (8). This compound crystallizes in space group $P2_1/n$ with one complete molecule comprising the asymmetric unit of the structure. All tin–carbon distances lie within experimental error in the range for tetraphenyltin(IV) [2.139(8)—2.159(9) Å]. The angle subtended at the tin by the bidentate ligand is 98.7(3)°; in this context, it would be expected that there would be a concomitant increase in the other angles, above the tetrahedral values. Curiously, this increase is largely absorbed by one angle alone, *not* the angle between the two phenyl ligands. The molecular projection, along the bisector of the C(phenyl)–Sn–C(phenyl) angle, shows a total loss of symmetry within the molecule. It may be that this angular distortion relieves strain about the tin atom (which is brought about by increased crowding introduced by the alkyl hydrogen atoms) in spite of the smaller ' bite ' angle of the bidentate ligand. Regarding the latter, the angle at the aliphatic carbon is the usual tetrahedral angle, while at all aromatic ring junctions the angles do not deviate excessively from the expected trigonal values. The mean torsion angle about the bond between the two halves of the bidentate ligand is 66.0°, comparable with the value of 65.5° for the naphthyl–naphthyl dihedral angle in (*S*)-(+)-2,2'-(2,2-dimethylsilapropane-1,3-diyl)-1,1'-binaphthalene, (10), in which the Si–C(bidentate ligand) distances are 1.89 Å and the angle between them is 103.7°.[19] For the $d^{0,1,2}$ metallepines $[Nb\{(2\text{-}CH_2C_6H_4)_2\}(\eta\text{-}C_5H_5)_2]^x$ (x = 0,1, or −1), in which the torsion angle is affected by electronic as well as steric factors, the respective values are 78.4, 62.4, and 59.6°.[9]

Tin atom deviations from bidentate aromatic planes are 1.78 and 2.02 Å, and from the phenyl ligand planes, 0.14 and 0.09 Å.

Compound (9). This compound crystallizes in space group $C2/c$; a crystallographic two-fold axis passes through the tin atom and the midpoint of the bidentate ligand, so that only one-half of the molecule is crystallographically independent. The geometry about the tin atom is significantly different from that observed in (8); Sn–C(phenyl) distances may be slightly shorter [2.136(4) Å], but the Sn–C(alkyl) distances are very much longer [2.184(4) Å], presumably a consequence of steric constraints. The angle subtended by the bidentate ligand carbon atoms at the tin, however, is not significantly different [99.4(2)°]. Again, we find the other angles about the tin atom lying close to the tetrahedral value with one significant exception; the unusually large angle in this case lies between the two monodentate ligands, as expected [116.1(2)°]. Within the bidentate ligand, the torsion angle about the central bond (70.8°) is indicative of a similar relative disposition of the two aromatic rings to that of (8), and at the alkyl carbon atom, a value similarly close [106.5(3)°] to tetrahedral is observed; the increased torsion angle is consistent with the increased

Table 1. Molecular geometry (non-hydrogen atoms) for (8)

Distances (Å)

	Biphenyl ligand		Phenyl ligands	
	A	B	A	B
Sn–C(1)	2.157(8)	2.159(9)	2.139(8)	2.149(9)
C(1)–C(2)	1.49(1)	1.49(1)	1.41(1)	1.39(1)
C(2)–C(3)	1.40(1)	1.40(1)	1.37(1)	1.38(1)
C(3)–C(4)	1.37(2)	1.38(2)	1.36(2)	1.35(2)
C(4)–C(5)	1.37(1)	1.36(2)	1.36(2)	1.36(2)
C(5)–C(6)	1.38(1)	1.39(2)	1.36(1)	1.40(1)
C(6)–C(1,7)	1.37(1)	1.39(1)	1.37(1)	1.37(1)
C(2)–C(7)	1.39(1)	1.40(1)		
C(7)–C(7)	1.50(1)			

Angles (°)

	Biphenyl ligand		Phenyl ligands	
	A	B	A	B
Sn–C(1)–C(2)	110.8(5)	108.2(6)	119.6(6)	119.0(6)
Sn–C(1)–C(6)			124.0(7)	123.6(7)
C(2)–C(1)–C(6)			116.2(8)	117.3(8)
C(3)–C(2)–C(7)	117.7(7)	119.4(9)		
C(1)–C(2)–C(3)	119.7(7)	119.7(8)	120.1(9)	121.5(9)
C(1)–C(2)–C(7)	122.5(7)	120.8(8)		
C(2)–C(3)–C(4)	119.9(9)	120.8(10)	122.1(11)	119.5(10)
C(3)–C(4)–C(5)	121.9(9)	120.0(10)	117.7(9)	121.0(10)
C(4)–C(5)–C(6)	118.3(10)	120.4(12)	121.3(9)	119.3(10)
C(5)–C(6)–C(7,1)	121.1(9)	120.8(9)	122.4(9)	121.3(9)
C(6)–C(7)–C(2)	121.0(8)	118.5(8)		
C(6)–C(7)–C(7)	116.7(8)	119.2(8)		
C(2)–C(7)–C(7)	122.3(7)	122.2(8)		

Angles at Sn (°) (phenyl ligand atoms are italicized)

C(1A)–Sn–C(1B) 98.7(3), C(1A)–Sn–*C(1A)* 109.0(3)
C(1A)–Sn–*C(1B)* 110.5(3), C(1A)–Sn–*C(1B)* 117.3(3)
C(1B)–Sn–*C(1A)* 109.8(3), C(1B)–Sn–*C(1B)* 110.7(3)

Table 2. Molecular geometry (non-hydrogen atoms) for (9)

Distances (Å)

	Diphenyl ligands	Phenyl ligands		Diphenyl ligands	Phenyl ligands
Sn–C(1)	2.184(4)	2.136(4)	C(5)–C(6)	1.381(8)	1.391(11)
C(1)–C(2)	1.498(6)	1.379(7)	C(6)–C(1,7)	1.392(6)	1.393(7)
C(1)–Si	1.887(5)		Si–C(81)	1.848(8)	
C(2)–C(3)	1.392(6)	1.367(8)	Si–C(82)	1.855(8)	
C(2)–C(7)	1.410(6)		Si–C(83)	1.866(9)	
C(3)–C(4)	1.378(7)	1.375(12)	C(7)–C(7)	1.493(6)	
C(4)–C(5)	1.360(8)	1.331(12)			

Angles (°)

	Diphenyl ligands	Phenyl ligands		Diphenyl ligands
Sn–C(1)–C(2)	106.5(3)	118.6(4)	C(1)–Si–C(81)	107.5(3)
Sn–C(1)–C(6),Si	114.1(2)	124.0(4)	C(1)–Si–C(82)	111.3(4)
C(2)–C(1)–Si	120.8(3)		C(1)–Si–C(83)	113.1(4)
C(2)–C(1)–C(6)		117.3(5)	C(81)–Si–C(82)	107.6(4)
C(3)–C(2)–C(7)	117.2(4)		C(81)–Si–C(83)	107.5(4)
C(1)–C(2)–C(3)	122.0(4)	122.5(5)	C(82)–Si–C(83)	109.6(4)
C(1)–C(2)–C(7)	120.8(3)			
C(2)–C(3)–C(4)	121.6(5)	118.4(6)		
C(3)–C(4)–C(5)	121.3(5)	121.3(7)		
C(4)–C(5)–C(6)	118.6(5)	120.6(7)		
C(5)–C(6)–C(7,1)	121.5(5)	119.9(6)		
C(2)–C(7)–C(7)	121.1(3)			
C(6)–C(7)–C(7)	119.1(4)			
C(2)–C(7)–C(6)	119.8(4)			

Angles at Sn (°) (phenyl carbon atoms are italicized, atoms generated by the two-fold rotor are primed)

C(1)–Sn–*C(1)* 110.1(2), *C(1)*–Sn–*C(1′)* 116.1(2)
C(1)–Sn–C(1′) 99.4(2), C(1)–Sn–*C(1′)* 110.0(2)

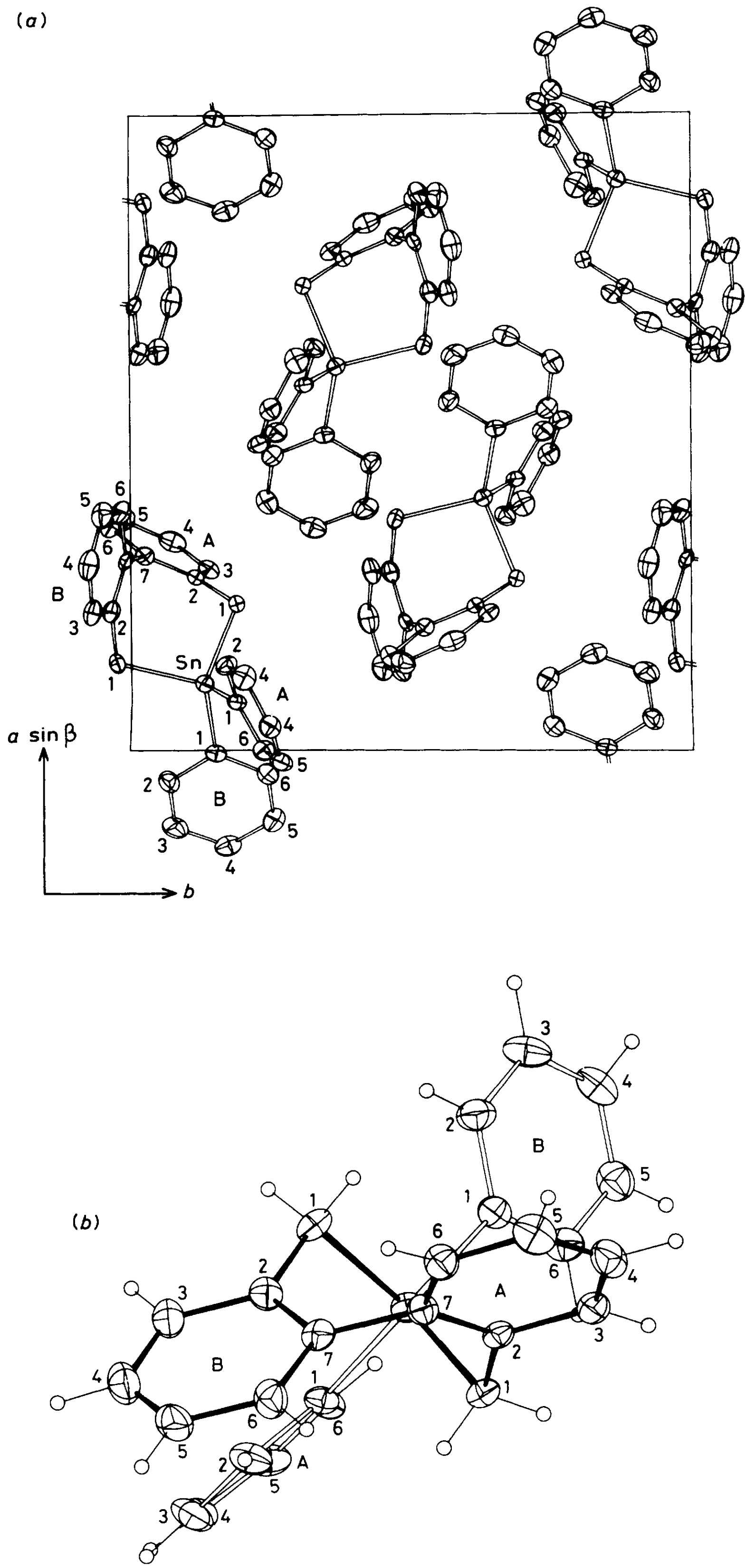


Figure 2. (a) Unit-cell contents of (8) projected down c; 20% thermal ellipsoids are shown for the non-hydrogen atoms. (b) A single molecule of (8) projected down the bisector of the angle subtended at the tin by the two phenyl carbon atoms. Hydrogen atoms have an arbitrary radius of 0.1 Å

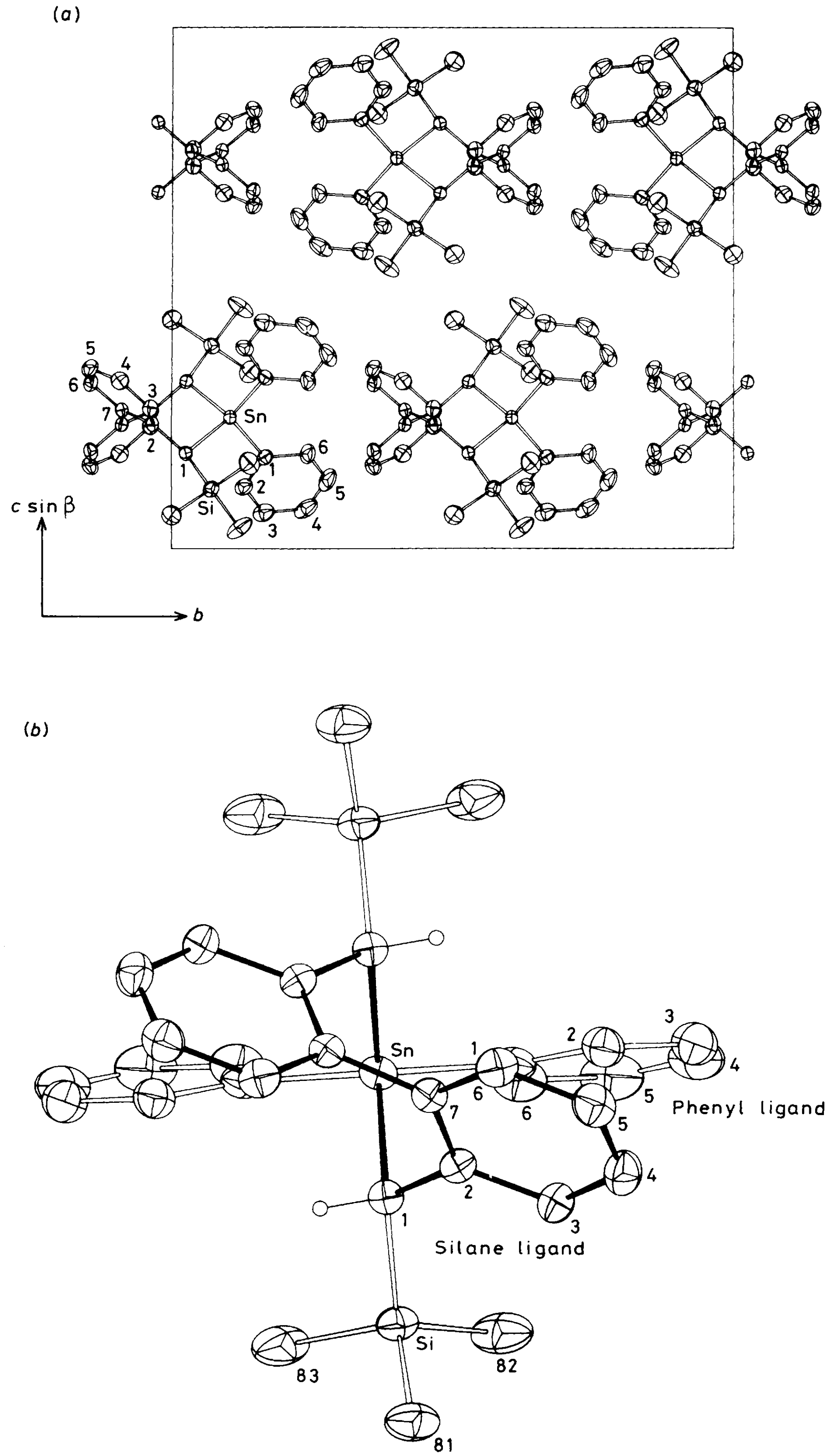


Figure 3. (*a*) Unit-cell contents of (9) projected down *a*. (*b*) A single molecule of (9) projected down the two-fold crystallographic axis

tin–carbon distance. However, some considerable deviations are observed at this carbon relative to the silicon atom; silicon–carbon distances lie in the range 1.848(8)—1.887(5) Å, with that to the ligating carbon being the longer. Si–C–Sn,C angles are 114.1(2) and 120.8(3)°, deviating considerably from tetrahedral. The tin atom deviates from the bidentate aromatic plane by 2.04 Å, and from the phenyl ligand plane by 0.08 Å. The silicon atom deviates by 0.75 Å from the bidentate aromatic ring plane, indicating a considerable degree of torsion about the C(1)–C(2) bond.

Experimental

General procedures and instrumentation have been described in the preceding paper.[1] Dichlorodiphenyltin(IV) [32] and 2,2′-bis(hydroxymethyl)biphenyl [33] were prepared according to the literature procedures. 2,2′-Bis(bromomethyl)biphenyl was obtained as a minor product from a reaction of 2,2′-bis-(methyl)biphenyl and *N*-bromosuccinimide, detailed in the previous paper [1] and by the method described in the literature.[33]

Synthesis of 2,2′-*Bis*(*chloromethyl*)*biphenyl*, (4).—*Method* 1. A mixture of concentrated $HCl-H_2SO_4$ (2 : 1, 600 cm^3) and 2,2′-bis(hydroxymethyl)biphenyl (22.7 g, 0.11 mol) was stirred at room temperature for 18 h. The separated brown oil was then extracted into hexane (2 × 200 cm^3) and the non-aqueous layer separated, dried, concentrated *in vacuo*, and distilled to afford a colourless liquid, b.p. 120 °C (0.2 mmHg), which upon standing crystallized (m.p. 46 °C). Yield 18.8 g, 71% (Found: C, 67.4; H, 5.15. Calc. for $C_{14}H_{12}Cl_2$: C, 66.95; H, 4.8%); ^1H n.m.r. (60 MHz, $CDCl_3$), τ 5.75 (AB, J_{AB} 12.0 Hz, 4 H), 2.70 (m, 8 H), ^{13}C n.m.r. (^1H decoupled, $CDCl_3$), δ 44.2 (CH_2), 128.4, 128.7, 129.0, 130.3, 135.9 (C_6H_4); mass spectrum, *m*/*e* 251 (P^+), 215 ($P - Cl^+$), 180 ($P - 2Cl^+$), 152 ($P - 2CH_2Cl^+$); i.r. (KBr disc), 3 070w, 3 030w, 2 970w, 2 870w, 1 478s, 1 445s, 1 272s, 1 262s, 1 200s, 1 160s, 1 005s, 952s, 898s, 830s, 810s, 778s, 765s, 755s, 705s, 665s, 575s, 540s, 368w, and 312m cm^{-1}.

Method 2. A mixture of LiCl (4.6 g, 0.11 mol), *NN*-dimethylformamide (dmf) (50 cm^3) and (3) (9.1 g, 0.03 mol) was stirred for 2 h at 20 °C and hexane (100 cm^3) and H_2O (70 cm^3) were added. Concentration of the hexane portion and distillation yielded a colourless liquid of the title compound. Yield 5.4 g, 80%.

Synthesis of the Di-Grignard Reagent, (5).—To a suspension of magnesium powder (2.43 g, 0.1 mol) in dry degassed thf (20 cm^3) was added 1,2-dibromoethane (0.5 cm^3), and the mixture stirred at room temperature until evolution of ethylene gas was evident. Stirring was then continued for 5 min. The thf was removed and replaced by fresh thf (50 cm^3) and the mixture stirred rapidly at room temperature, whereupon a solution of (4) (6.28 g, 0.25 mol) in thf (200 cm^3) was added over a period of 4 h. The solution became green and, after the addition was complete, the mixture was stirred for 18 h at room temperature. The di-Grignard solution was filtered into a calibrated Schlenk flask. Quenching 2 cm^3 aliquots with 0.1 mol dm^{-3} HCl (20 cm^3) and back-titrating with 0.1 mol dm^{-3} NaOH indicated a di-Grignard reagent (250 cm^3) concentration of 0.095 mol dm^{-3} (95%).

Preparation of 2,2′-*Bis*(*trimethylsilylmethyl*)*biphenyl*, (6).—To a solution of (5) (100 cm^3, 0.088 mol dm^{-3}, 8.8 mmol) at room temperature was added $SiMe_3Cl$ (2.5 cm^3, 19.7 mmol). After 2 h the thf was removed *in vacuo* and replaced with hexane (50 cm^3). Filtration then concentration and distillation afforded a colourless liquid, (6), the same compound as that formed in the reaction of (1) with $SiMe_3Cl$.[1]

Reaction of the Dihalides (3) *and* (4) *with* Li.—To a stirred suspension of Li powder (0.57 g, 0.08 mol) in thf (10 cm^3) was added dropwise a solution of (3) (3.50 g, 0.01 mol) in thf (100 cm^3) over 1 h. The mixture was then stirred at room temperature for 1 h during which it became dark green due to the formation of a radical anion ($g_{av.}$ = 2.0037, unresolved hyperfine structure), the same as that derived from a reaction of (4) (2.51 g, 0.01 mol) in place of (3), and also for a reaction of an authentic sample of 9,10-dihydrophenanthrene (0.3 g, 1.67 mmol) with Li (0.05 g, 6.7 mmol) in thf (20 cm^3) for 15 min at room temperature. Termination of reactions involving (3) and (4) prior to radical formation afforded 9,10-dihydro-

Table 3. Atomic co-ordinates for (8)

	Section A			Section B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Sn	0.104 21(4)	0.130 89(4)	0.189 56(6)			
Diphenyl ligand						
C(1)	0.229 2(5)	0.187 7(6)	0.272 5(8)	0.137 1(6)	−0.026 2(6)	0.181 3(9)
H(1a)	0.267(—)	0.200(—)	0.202(—)	0.145(—)	−0.054(—)	0.272(—)
H(1b)	0.223(—)	0.251(—)	0.316(—)	0.091(—)	−0.063(—)	0.134(—)
C(2)	0.273 3(5)	0.115 2(6)	0.369 9(8)	0.219 9(6)	−0.035 5(6)	0.117 2(9)
C(3)	0.285 2(5)	0.139 6(7)	0.506 6(8)	0.217 6(7)	−0.069 5(7)	−0.015 1(9)
H(3)	0.262(—)	0.203(—)	0.538(—)	0.162(—)	−0.090(—)	−0.064(—)
C(4)	0.329 4(7)	0.075 0(9)	0.596 0(9)	0.292 9(10)	−0.075 7(8)	−0.077 8(11)
H(4)	0.336(—)	0.094(—)	0.690(—)	0.292(—)	−0.096(—)	−0.171(—)
C(5)	0.363 2(7)	−0.013 8(9)	0.556 0(11)	0.370 9(8)	−0.050 2(8)	−0.010 4(12)
H(5)	0.393(—)	−0.059(—)	0.623(—)	0.425(—)	−0.058(—)	−0.054(—)
C(6)	0.352 8(6)	−0.037 3(7)	0.421 8(10)	0.375 2(6)	−0.017 3(7)	0.121 5(10)
H(6)	0.380(—)	−0.098(—)	0.393(—)	0.432(—)	0.003(—)	0.168(—)
C(7)	0.307 8(5)	0.025 0(6)	0.330 4(8)	0.300 0(6)	−0.008 1(6)	0.186 6(9)
Phenyl ligand						
C(1)	0.075 3(5)	0.188 4(6)	−0.008 9(8)	−0.004 4(5)	0.153 2(7)	0.304 4(8)
C(2)	0.133 2(6)	0.169 6(7)	−0.106 1(10)	−0.048 7(6)	0.070 0(7)	0.345 7(10)
H(2)	0.188(—)	0.136(—)	−0.079(—)	−0.026(—)	0.002(—)	0.328(—)
C(3)	0.113 0(8)	0.201 6(8)	−0.235 4(11)	−0.121 0(7)	0.079 9(8)	0.415 3(11)
H(3)	0.157(—)	0.190(—)	−0.298(—)	−0.151(—)	0.021(—)	0.445(—)
C(4)	0.036 4(7)	0.248 5(8)	−0.276 0(9)	−0.150 4(6)	0.172 5(8)	0.442 0(9)
H(4)	0.021(—)	0.264(—)	−0.371(—)	−0.203(—)	0.180(—)	0.489(—)
C(5)	−0.018 2(6)	0.269 6(8)	−0.181 1(12)	−0.110 0(7)	0.255 9(8)	0.401 9(10)
H(5)	−0.071(—)	0.309(—)	−0.208(—)	−0.132(—)	0.322(—)	0.422(—)
C(6)	−0.000 3(6)	0.238 1(7)	−0.052 5(10)	−0.036 7(6)	0.245 6(7)	0.331 9(10)
H(6)	−0.042(—)	0.252(—)	0.011(—)	−0.008(—)	0.306(—)	0.302(—)

Table 4. Atomic co-ordinates for (9)

Atom	*x*	*y*	*z*
Sn	0	0.102 71(2)	1/4
Diphenyl ligand			
C(1)	0.101 1(4)	0.025 2(2)	0.182 0(2)
H(1)	0.023(4)	0.010(2)	0.149(2)
C(2)	0.159 8(4)	−0.033 8(2)	0.237 6(2)
C(3)	0.298 4(5)	−0.037 3(3)	0.267 1(3)
H(3)	0.359(5)	−0.003(3)	0.252(3)
C(4)	0.351 3(6)	−0.091 0(3)	0.319 2(3)
H(4)	0.429(6)	−0.090(3)	0.334(3)
C(5)	0.270 3(6)	−0.143 6(3)	0.343 2(3)
H(5)	0.310(5)	−0.181(3)	0.380(3)
C(6)	0.132 3(5)	−0.142 1(3)	0.314 7(3)
H(6)	0.079(5)	−0.173(3)	0.332(3)
C(7)	0.075 2(4)	−0.087 4(2)	0.263 7(2)
Si	0.207 29(14)	0.069 82(7)	0.114 01(8)
C(81)	0.090 1(9)	0.120 8(5)	0.039 2(5)
H(81a)	0.053(9)	0.080(5)	0.012(5)
H(81b)	0.040(8)	0.147(5)	0.062(5)
H(81c)	0.154(8)	0.151(5)	0.007(4)
C(82)	0.296 4(8)	0.000 2(4)	0.062 5(5)
H(82a)	0.357(7)	−0.018(4)	0.098(4)
H(82b)	0.255(8)	−0.037(4)	0.054(5)
H(82c)	0.355(7)	0.025(4)	0.034(4)
C(83)	0.333 7(9)	0.136 9(5)	0.164 4(6)
H(83a)	0.296(8)	0.176(4)	0.182(5)
H(83b)	0.385(10)	0.115(5)	0.179(7)
H(83c)	0.369(8)	0.153(5)	0.124(5)
Phenyl ligands			
C(1)	−0.148 6(5)	0.164 7(2)	0.174 2(3)
C(2)	−0.237 8(6)	0.127 9(3)	0.118 1(3)
H(2)	−0.228(5)	0.078(3)	0.112(3)
C(3)	−0.338 8(6)	0.162 9(4)	0.068 9(4)
H(3)	−0.407(6)	0.138(4)	0.032(4)
C(4)	−0.352 6(9)	0.237 4(5)	0.076 5(5)
H(4)	−0.409(7)	0.260(4)	0.047(4)
C(5)	−0.270 8(10)	0.275 1(4)	0.130 7(6)
H(5)	−0.269(7)	0.320(4)	0.138(4)
C(6)	−0.167 1(7)	0.240 1(3)	0.180 6(4)
H(6)	−0.105(6)	0.262(3)	0.215(4)

phenanthrene quantitatively after removal of solvent *in vacuo* and washing with water to remove LiX (X = Cl or Br).

Preparation of 6,7-*Dihydro*-6,6-*dimethyl*-5H-*dibenzo*[c,e]-*silepine*, (7).—*Method* 1. To the di-Grignard reagent, (5) (0.095 mol dm^{-3}, 168 cm^3, 16 mmol) at 0 °C, was added dropwise $SiMe_2Cl_2$ (5 cm^3, 20 mmol) in thf (50 cm^3) over 1 h. After stirring for a further 1 h the solvent was removed *in vacuo* and the product washed with HCl (2 mol dm^{-3}, 10.0 cm^3) and extracted into hexane (100 cm^3). Concentration and distillation yielded a colourless liquid, b.p. 100—102 °C (0.3 mmHg). Yield 3.5 g, 90% (Found: C, 80.2; H, 7.75. Calc. for $C_{16}H_{18}Si$: C, 80.6; H, 7.6%); ^1H n.m.r. (60 MHz, $CDCl_3$), τ 9.95 (s, 6 H), 8.23 (s, 4 H), 2.89 (m, 8 H); ^{13}C n.m.r. (^1H decoupled, $CDCl_3$), δ −3.7 ($SiCH_3$), 23.4 (CH_2), 124.0, 127.6, 128.2, 129.8, 138.7, 140.6 (C_6H_4); mass spectrum, *m*/*e* 238 (P^+), 223 ($P - CH_3^+$), 195 ($P - SiCH_3^+$), 178 ($C_{14}H_{10}^+$), 165 ($C_{13}H_9^+$); i.r. (KBr disc), 3 075w, 3 030w, 2 972m, 2 908w, 1 500w, 1 480m, 1 450w, 1 410w, 1 252s, 1 200m, 1 070m, 1 155m, 1 010m, 942w, 850s, 750s, 820s, 715w, and 695w cm^{-1}.

Method 2. To a suspension of activated magnesium powder (0.80 g, 33 mmol) in thf (20 cm^3) and $SiMe_2Cl_2$ (2 cm^3, 15.5 mmol) was added dropwise over 2 h a solution of (4) (2.0 g, 8.0 mmol) in thf (80 cm^3). The procedure was then as for method 1. Yield 0.79 g, 42%.

Preparation of 6,7-*Dihydro*-6,6-*diphenyl*-5H-*dibenzo*[c,e]-*stannepine*, (8).—Tetrahydrofuran was removed *in vacuo* from a solution of (5) (0.088 mol dm^{-3}, 45 cm^3, 4.0 mmol). Dry Et_2O (100 cm^3) was then added and the solution cooled to −78 °C, whereupon a solution of $SnPh_2Cl_2$ (1.35 g, 3.9 mmol) in Et_2O (100 cm^3) was added over 30 min. After 15 min, the yellow solution was warmed to room temperature and stirred for 2 h. Filtration followed by concentration *in vacuo* to *ca.* 100 cm^3 and cooling to −30 °C afforded colourless crystals of (8) (m.p. 189 °C). Yield 0.82 g, 46% (Found: C, 68.75; H, 4.95. Calc. for $C_{26}H_{22}Sn$: C, 68.9; H, 4.9%); ^1H n.m.r. (60 MHz, $CDCl_3$), τ 7.5 (CH_2, J_{AB} 11.5 Hz, 4 H), 2.78 (m, 10 H), 2.63 (m, 8 H); ^{13}C n.m.r. (^1H decoupled, $CDCl_3$), δ 17.5 (CH_2), 124.8, 127.7, 128.7, 129.2, 129.9, 130.2, 138.8, 139.3, 140.1 (C_6H_4 and C_6H_5); mass spectrum, *m*/*e* 452 (P^+), 375 ($P - Ph^+$), 180 ($C_{14}H_{12}^+$); i.r. (KBr disc), 3 045w, 3 012w, 2 870w, 1 640w, 1 470m, 1 440m, 1 426s, 1 330w, 1 295w, 1 282w, 1 260s, 1 195m, 1 185m, 1 090s, 1 070m, 1 020w, 995m, 935m, 827s, 802s, 752s, 721s, 700vs, 570w, 499w, 455w, and 435s cm^{-1}.

Method 2. To a mixture of $SnPh_2Cl_2$ (1.87 g, 5.44 mmol) and $[\{Li(tmen)\}_2\{(2\text{-}CH_2C_6H_4)_2\}]$ (2.33 g, 5.46 mmol) at 30 °C was added boiling Et_2O (100 cm^3) and the resulting solution stirred for 2 h at room temp. Removal of solvent *in vacuo* was followed by the addition of CH_2Cl_2 (20 cm^3), filtration and concentration (2 cm^3) to afford crystals of (8). Yield 1.48 g, 60%.

6,7-*Dihydro*-6,6-*diphenyl*-5,7-*bis*(*trimethylsilyl*)-5H-*dibenzo*[c,e]*stannepine*, (9).—To a mixture of $[\{Li(tmen)\}_2\{[2\text{-}CH(SiMe_3)C_6H_4]_2\}]$ (2) (3.1 g, 5.5 mmol) and $SnPh_2Cl_2$ (1.7 g, 4.9 mmol) boiling Et_2O (30 cm^3) was added and the resulting solution stirred for 30 min at 35 °C. To this, MeOH (5 cm^3) was added after which the solvents were removed *in vacuo*. Hexane (20 cm^3) was added and the resulting solution filtered. Reduction in volume (10 cm^3) yielded a yellow solid (2 g, 68%). The mother-liquor was then reduced further (2 cm^3) and after standing at −40 °C for several days, colourless crystals of (9) were obtained (m.p. 184—186 °C). Yield 0.5 g, 17% (Found: C, 63.25; H, 6.6. Calc. for $C_{32}H_{38}Si_2Sn$: C, 64.35; H, 6.4%); ^1H n.m.r. (60 MHz, $CDCl_3$), τ 10.23 (s, 18 H), 7.99 (s, 2 H), 2.85 (m, 8 H), 2.72 (m, 10 H); ^{13}C n.m.r. (^1H decoupled, $CDCl_3$), δ 1.2 ($SiCH_3$), 21.1 (CHSi), 124.3, 127.5, 127.8, 128.7, 129.4, 129.7, 137.7, 140.4, 141.3, 142.3 (C_6H_4 and C_6H_5); mass spectrum, *m*/*e* 597 (P^+), 582 ($P - CH_3^+$), 520 ($P - Ph^+$), 324 ($P - SnPh_2^+$) 237, 221, 178, 135; i.r. (KBr disc), 3 060m, 3 030m, 2 965m, 2 910w, 1 600w, 1 585w, 1 487m, 1 478m, 1 434s, 1 338w, 1 305w, 1 254s, 1 200w, 1 164w, 1 075m, 1 025w, 1 004m, 840s, 755m, 728s, 698s, 620w, 565w, and 445m cm^{-1}.

Crystallography.—*Crystal data for* (8). $C_{26}H_{22}Sn$, *M* = 453.2, Monoclinic, space group $P2_1/n$ (variant of C_{2h}^5, no. 14), *a* = 15.42(1), *b* = 13.334(8), *c* = 10.042(8) Å, β = 95.90(6)°, *U* = 2 054(2) Å^3, *Z* = 4, D_c = 1.39 g cm^{-3}, *F*(000) = 912, μ_{Mo} = 11.8 cm^{-1}. Specimen: 0.20 × 0.12 × 0.06 mm. $2\theta_{max.}$ = 45°; *N*, N_o = 2 694, 1 621; *R*, *R'* = 0.037, 0.042.

Crystal data for (9). $C_{32}H_{38}Si_2Sn$, *M* = 597.4, Monoclinic, space group *C*2/*c* (C_{2h}^6, no. 15), *a* = 9.937(2), *b* = 18.231(3), *c* = 17.316(3) Å, β = 99.20(1)°, *U* = 3 097(1) Å^3, *Z* = 4, D_c = 1.28 g cm^{-3}, *F*(000) = 1 232, μ_{Mo} = 9.2 cm^{-1}. Specimen: 0.42 × 0.22 × 0.15 mm. $2\theta_{max.}$ = 50°; *N*, N_o = 2 738, 1 974; *R*, *R'* = 0.034, 0.040.

Structure determinations. Unique data sets were measured on crystals enclosed in capillaries (295 K) within a preset $2\theta_{max.}$ limit using a Syntex $P2_1$ four-circle diffractometer fitted with a monochromatic Mo-K_α radiation source (λ = 0.710 69 Å) and operating in conventional $2\theta/\theta$ scan mode. N Independent reflections were collected of which N_o with $I > 3\sigma(I)$ were considered 'observed' and used in the 9 × 9 block-diagonal least-squares refinement, after absorption correction and solution of the structures by the heavy-atom method. In (8), hydrogen atoms (x,y,z,U) were constrained at estimated values, while in (9), hydrogens (x,y,z) were satisfactorily refined. Reflection weights were $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f',f'').[34] Computation used the X-RAY 76 program system [35] implemented by S. R. Hall on a Perkin-Elmer 3240 computer. Atomic co-ordinates are in Tables 3 and 4.

Acknowledgements

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