Chemistry of *o*-Xylenediyl–Metal Complexes. Part 5.[1] Silicon and Tin Metallacycles derived from o-$\mathrm{C_6H_4(\bar{C}HR)_2}$ (R = H or $\mathrm{SiMe_3}$) *

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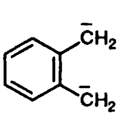
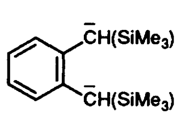
Treatment of $\mathrm{SnCl_2Ph_2}$ with [Mg(LL)(thf)] **6** or $[\mathrm{Li(tmen)}]_2[o\text{-}\mathrm{C_6H_4\{CH(SiMe_3)\}_2}]$ **7** in $\mathrm{OEt_2}$ yields the stannacycle $[\overline{\mathrm{Sn(LL}}\mathrm{)Ph_2}]$ **1** or $[\overline{\mathrm{Sn(L'L'}}\text{-}meso\mathrm{)Ph_2}]$ **2** $\{(\mathrm{LL})^{2-} = o\text{-}\mathrm{C_6H_4(\bar{C}H_2)_2}$, $(\mathrm{L'L'})^{2-} = o\text{-}\mathrm{C_6H_4[\bar{C}H(SiMe_3)]_2}$, thf = tetrahydrofuran, tmen = $\mathrm{Me_2N[CH_2]_2NMe_2}\}$. Likewise, $\mathrm{SnCl_4}$ with **6** or **7** at 30 °C in $\mathrm{OEt_2}$ affords exclusively the stannaspirobicycle $[\overline{\mathrm{Sn(LL}}\mathrm{)_2}]$ **3** or $[\overline{\mathrm{Sn(L'L'}}\text{-}meso)_2]$ **4**; by contrast $\mathrm{SnCl_4}$ with **7** at −78 °C gives, together with **4** (52%), the yellow, diamagnetic tin(II) metallacycle $[\{\overline{\mathrm{Sn(L'L'}}\text{-}meso)\}_4](Sn\text{–}Sn)$ **5** (14%). Compound **5** is more conveniently prepared by treating $\mathrm{Sn(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2}$ with **7**; it is tetrameric in the solid and in solution, but monomeric in the gas phase and has a low first ionisation energy (7.6 eV). The compound $[\overline{\mathrm{Si(LL}}\mathrm{)Me_2}]$ **8** is obtained by an *in situ* Grignard reaction from $\mathrm{SiCl_2Me_2}$, $o\text{-}\mathrm{C_6H_4(CH_2Cl)_2}$ and Mg in thf, while $[\overline{\mathrm{Si(L'L'}}\text{-}meso\mathrm{)Me_2}]$ **9** is prepared from $\mathrm{SiCl_2Me_2}$ and **7**. Each of the metallacycles derived from the ligand $(\mathrm{L'L'})^{2-}$ was obtained stereospecifically as the *meso* diastereoisomer. X-Ray structure determinations of complexes **1**–**5** have been performed. The α,α′-unsubstituted metallacycles have shorter $\langle \mathrm{Sn–C_\alpha} \rangle$ distances (2.14_4 in **1**, 2.14_7 Å in **3**) than the corresponding α,α′-bis(trimethylsilyl) derivatives (2.16_6 in **2**, 2.17_4 Å in **4**). The $\mathrm{C_6C_\alpha C_{\alpha'}}$ *o*-xylenediyl plane is folded relative to the $\mathrm{MC_\alpha C_{\alpha'}}$ plane, the 'fold angle' θ being 8.5 (**1**), 19.8 (**2**), 0.8 and 11.9 (**3**), 24.1 and 23.0 (**4**) and 20.8° (**5**). The larger θ values for the $\overline{\mathrm{Sn^{IV}(L'L'}})$ complexes **2** and **4** than for the their $\overline{\mathrm{Sn^{IV}(LL}})$ counterparts **1** and **3** (as for comparable $\mathrm{Sn–C_\alpha}$ distances) is attributable to greater interligand strain and crowding around the metal centre in **2** and **4**. Molecules of **5** have $\bar{4}$ symmetry, with Sn–Sn 2.852(3), $\mathrm{Sn–C_\alpha}$ 2.15(3) and $\mathrm{Sn–C_{\alpha'}}$ 2.09(4) Å.

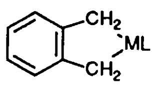
This Series is concerned with metal complexes of the *o*-xylenediyl ligands **A** and **B**. The starting materials have been (*i*) the diGrignard reagent $o\text{-}\mathrm{C_6H_4(CH_2MgCl)_2}$ or its chloride-free derivatives $[\{\mathrm{Mg(\mu\text{-}CH_2C_6H_4CH_2\text{-}}o)(\mathrm{thf})_n\}_m]$ ($n = 2$, $m = 3$; or $n = 1$, m unknown; thf = tetrahydrofuran)[2] or (*ii*) $[\mathrm{Li(tmen)}]_2[o\text{-}\mathrm{C_6H_4\{CH(SiMe_3)\}_2}]$ (tmen = $\mathrm{Me_2N[CH_2]_2NMe_2}$);[3] full preparative details are in ref. 4. Previous papers have dealt *inter alia* with the synthesis and in many cases also the X-ray structures of $[\{\mathrm{Mg(LL)(thf)_2}\}_3]$ [in which $(\mathrm{LL})^{2-}$ is a bridging ligand],[2,4] and the chelate complexes $[\overline{\mathrm{M(LL}})(\eta\text{-}\mathrm{C_5H_4R})_2]$ (R = H, M = Ti, Zr or Hf; or R = $\mathrm{SiMe_3}$, M = Nb),[5] $[\overline{\mathrm{Zr(L'L'}}\text{-}meso)(\eta\text{-}\mathrm{C_5H_5})_2]$,[1] $[\overline{\mathrm{Si(L'L'}}\text{-}meso)\mathrm{X_2}]$ (X = Ph or Cl),[6] $[\overline{\mathrm{Ti(L'L'}}\text{-}meso)(\eta\text{-}\mathrm{C_5H_5})\mathrm{Cl}]$,[6] $[\overline{\mathrm{Zr(L'L'}}\text{-}meso)(\eta\text{-}\mathrm{C_5H_5})(\mu\text{-}\mathrm{Cl})_2\mathrm{Li(tmen)}]$,[6] $[\overline{\mathrm{W(LL}})_3]$,[7] $[\{\overline{\mathrm{W(LL}})_2\mathrm{O}\}_2\mathrm{Mg(thf)_4}]$,[7] $\overline{\mathrm{P(L'L'}}\text{-}meso)\mathrm{Ph}$,[6] and *trans*-$[\mathrm{PtCl_2}\{\overline{\mathrm{P(L'L'}}\text{-}meso)\mathrm{Ph}\}_2]$.[6] These chelates may be regarded as 2-metalla-indans **A′** or 1,3-bis(trimethylsilyl)-2-metallaindans **B′**. Since in **B′** the α- and α′-carbon atoms ($\mathrm{C^1}$ and $\mathrm{C^5}$ of the metallaindan) are chiral there are in principle *meso* and *rac* diastereoisomers. Each of the above L′L′ metal complexes has been found to have the *meso* configuration **B″**, no doubt for steric reasons, as was evident from their ^{1}H and ^{13}C NMR spectra in solution and in the crystal (with two exceptions, for which data are not available) by X-ray crystallography. The complex $[\overline{\mathrm{Zr(L'L'}}\text{-}meso)(\mu\text{-}\eta\!:\!\sigma\text{-}\mathrm{C_5H_4})_2\mathrm{Zr}(\eta\text{-}\mathrm{C_5H_5})_2]$ probably has a similar configuration (but X-ray data are not available).[1]



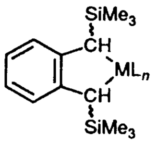
A [abbreviated as $(\mathrm{LL})^{2-}$]



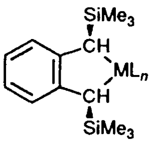
B [abbreviated as $(\mathrm{L'L'})^{2-}$]



A′



B′



B″

An item of interest with both types of metal complexes relates to the nature of the metal–ligand bonding shown in **A′**, **B′** and **B″** as formally from a dicarbanionic ligand $(\mathrm{LL})^{2-}$ or $(\mathrm{L'L'})^{2-}$

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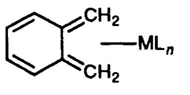
* Previous Parts of this Series had the generic title 'Chemistry of *o*-Xylidene Metal Complexes'. No reprints available.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: eV ≈ 1.60×10^{-19} J



C′

to a dicationic metal centre. However, the tungsten metallacycles of unusually high metal oxidation states of 5 or 6, $[\{W(LL)_2O\}_2Mg(thf)_4]$ and $[W(LL)_3]$ (LL = $CH_2C_6H_4CH_2$-*o*), showed a departure of the ligand bonding from such a bis(sigma) mode towards the η^4 (pi) mode C′ which was evident by substantial folding of the C_8 *o*-xylenediyl plane relative to the MC_2 plane, presumably to allow interaction of the electron-rich benzene ring with the metal centre.[7] This feature was also found in $[Zr(L'L'$-*meso*$)(\eta$-$C_5H_5)_2]$.[1]

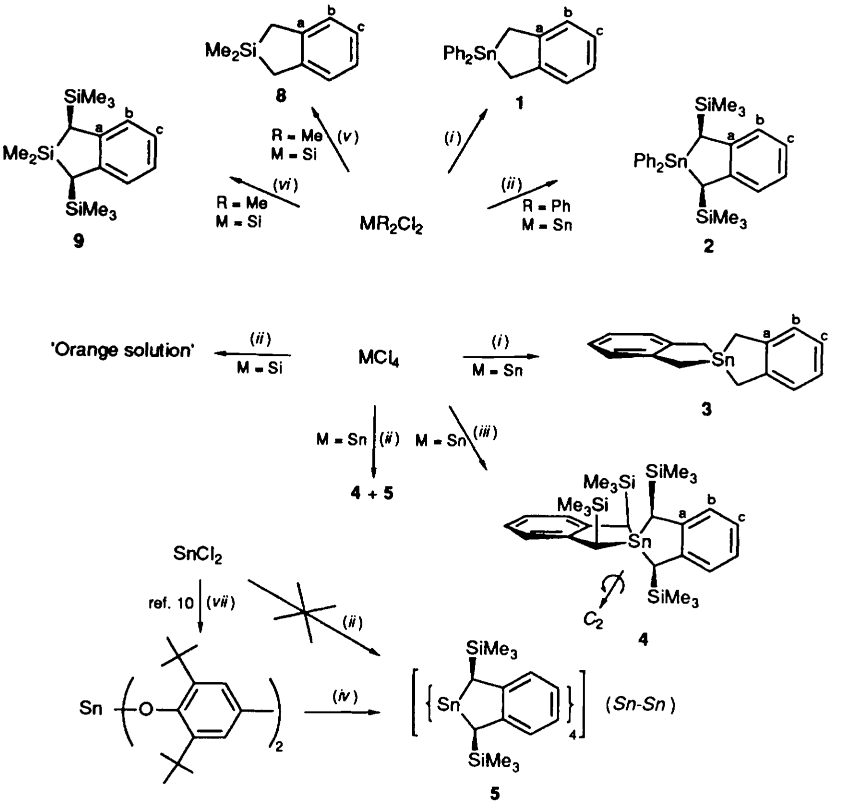
An aim of the present work was to prepare and authenticate structurally some main group IV (Group 14, Oländer numbering) metallacycles derived from the ligands $(LL)^{2-}$ and $(L'L')^{2-}$, where η^4-type interactions are unlikely, as a means of defining a baseline for comparison of the fold angle with those of transition-metal complexes. Additionally, we sought to ascertain the effect of incorporating bulky trimethylsilyl substituents at the C_α and $C_{\alpha'}$ positions of the *o*-xylenediyl moiety of the metallaindan, both on the fold angle and the metal environment, and any diastereoisomeric preference. We now report the synthesis and X-ray structure determinations of (*a*) the tin(IV) metallacycles $[Sn(LL)Ph_2]$ **1**, $[Sn(L'L'$-*meso*$)Ph_2]$ **2**, $[Sn(LL)_2]$ **3** and $[Sn(L'L'$-*meso*$)_2]$ **4** and (*b*) the tin(II) metallacycle $[\{Sn(L'L'$-*meso*$)\}_4]$ **5**. Compounds **1**–**5** were prepared from $[Mg(LL)(thf)]$ **6**[2,4] or $[Li(tmen)]_2[L'L']$ **7**.[3,4] Also reported is the synthesis of $[Si(LL)Me_2]$ **8** and $[Si(L'L'$-*meso*$)Me_2]$ **9**.

Other objectives of this work were to explore (*i*) the potential of the tin(IV) metallacycles as transfer reagents of the ligands $(LL)^{2-}$ or $(L'L')^{2-}$, and (*ii*) the synthesis of bivalent Group 14 metallacycles. As for (*i*), we note that aryltin(IV) compounds readily undergo chloride–aryl exchange with certain platinum(II) chlorides.[8] Regarding (*ii*), we were particularly interested to determine the degree of molecular aggregation *n* of tin(II) complexes such as $[\{Sn(L'L')\}_n]$ and their stereochemistry. The syntheses and X-ray structures of the highly substituted spirocyclic complexes **4** and **5** have already been briefly described.[9]

Results and Discussion

Methods for the synthesis of the tin-(IV) and -(II) *o*-xylenediyl metallacycles **1**–**5** and some related silicon heterocycles **8** and **9** are summarised in Scheme 1. Except for $[\{Sn(L'L'$-*meso*$)\}_4]$ **5** and $[Si(LL)Me_2]$ **8**, the compounds were prepared by the reaction of $[Mg(LL)(thf)]$ **6** or $[Li(tmen)]_2[L'L']$ **7** with the appropriate Group 14 metal(IV) chloride. A Grignard *in situ* trapping reaction was effective for **8**, and **5** was obtained either as the exclusive tin-containing metathesis product of treating **7** with $Sn(OC_6H_2Bu^t{}_2$-2,6-Me-4$)_2$,[10] or as a minor by-product when $[Sn(L'L'$-*meso*$)_2]$ **4** was prepared from $SnCl_4$ and **7** at low temperature.

The metallacycles **1**–**5** and **8** and **9** were characterised by microanalyses, NMR (^1H and ^{13}C) spectroscopy, mass spectrometry, and X-ray structure determinations (**8** and **9** excepted); they are air-stable, except for the tin(II) complex **5** which is moderately air-stable in the solid but somewhat more sensitive in hydrocarbon solution. Dialkyl- and diaryl-tin(IV) metallacycles are well known.[11] However, few spirobicyclic compounds have previously been described, and compounds $[Sn(LL)_2]$ **3** and $[Sn(L'L'$-*meso*$)_2]$ **4** are therefore of particular interest. Those previously described include $[Sn\{(CH_2)_5\}_2]$,[12] $[Sn\{(o$-$C_6H_4)_2\}_2]$,[13] and $[Sn\{(CPh)_4\}_2]$;[14] these, like **3** and **4** and the monocyclic compounds $[Sn(LL)Ph_2]$ **1** and $[Sn(L'L'$-*meso*$)Ph_2]$ **2** are the most common metallacyclic types, containing either five- or six-membered rings; a larger ring



Scheme 1 (*i*) $[Mg(CH_2C_6H_4CH_2$-*o*$)(thf)]$ **6**, OEt_2, −78 °C; (*ii*) $[Li(tmen)]_2[o$-$C_6H_4\{CH(SiMe_3)\}_2]$ **7**, OEt_2, −78 °C; (*iii*) **7**, OEt_2, 30 °C; (*iv*) **7**, OEt_2, 0 °C; (*v*) *o*-$(ClCH_2)_2C_6H_4$, Mg, $SiCl_2Me_2$, thf, <40 °C; (*vi*) **7**, OEt_2, 20 °C; (*vii*) $[\{Li(\mu$-$OC_6H_2Bu^t{}_2$-2,6-Me-4$)(OEt_2)\}_2]$, OEt_2

system has only been found in $[Sn\{(o\text{-}CH_2C_6H_4)_2\}Ph_2]$,[15] while a smaller one is represented by the stannacyclobutanes.[16] The latter were reported to be highly reactive, polymerising at room temperature, a probable consequence of the strain in the four-membered ring.

Salt-elimination reactions, involving Grignard or organolithium reagents, are used extensively in the synthesis of tin(IV) stannacycles, as here for compounds **1**–**4**. Both $[Sn(LL)Ph_2]$ **1**[17] and $[Si(LL)Me_2]$ **8**[18] had previously been reported but without synthetic or spectroscopic details, although some related alkyl- and aryl-silicon *o*-xylenediyls have been described more fully;[18,19] their synthesis involved multistep routes. A brief note on the germanium analogue of **8**, $[Ge(LL)Me_2]$, has appeared.[19]

Although the diGrignard reagent $o\text{-}C_6H_4(CH_2MgCl)_2$ is suitable for the synthesis of $[Si(LL)Me_2]$ **8**, the one-pot *in situ* Grignard reaction [(*v*) in Scheme 1] proved to be highly effective. The related heterocycle $[Si(CH_2C_{10}H_6CH_2\text{-}1,8)Me_2]$ has been prepared from 1,8-bis(chloromethyl)naphthalene using the same strategy,[20] although the appropriate diGrignard reagent is available.[21] It is noteworthy that the reactive benzylic sites associated with heterocycle formation in both $o\text{-}C_6H_4(CH_2Cl)_2$ and $1,8\text{-}C_{10}H_6(CH_2Cl)_2$ are in close proximity (they are marginally closer in the naphthalene case); rather high dilution, *ca.* 0.3 mol dm^{-3}; thf solvent, and the use of chlorides (rather than other halides) is essential for high yields (see refs. 2 and 20). The *in situ* trapping reaction involving 2,2′-bis(chloromethyl)biphenyl, however, was found to be ineffective for metallacycle formation, possibly because the reactive sites are well separated, a consequence of torsion along the biphenyl axis, favouring oligomerisation.[20]

Silicon- or tin-based metallacycles **2**, **4**, **5** and **9** based on the substituted *o*-xylenediyl ligand $o\text{-}C_6H_4[\bar{C}H(SiMe_3)]_2$ $[(L'L')^{2-}]$ were invariably isolated with L′L′ in the *meso* configuration **B**″, as found previously for complexes of transition metals, Si, and P (see above). Although it is not inevitable that the *meso* diastereoisomer is thermodynamically more stable than the *rac* analogue, the former may be the kinetic product because of the planar conformation of the $C_6H_4(C_\alpha)_2$ moiety in the organodilithium precursor **7**.[3]

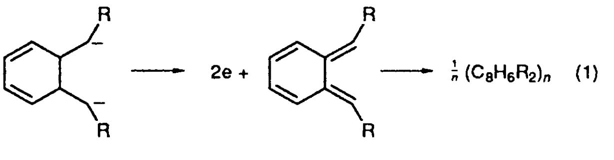
While for $[M(L'L')R_2]$ (M = Sn, R = Ph **2**; or M = Si, R = Me **9**) the alternative *rac* configuration is feasible on steric grounds, for the spirobicycle $[Sn(L'L'\text{-}rac)_2]$ unfavourable non-bonding interactions between interligand bulky $SiMe_3$ groups would be likely, a view supported by inspection of molecular models. A molecule of $[Sn(L'L'\text{-}meso)_2]$ **4** possesses a non-crystallographic C_2 symmetry axis that relates the two ligands (Scheme 1); consequently there are two different $SiMe_3$ and $C_\alpha H$ sites in the crystalline material, as also borne out by both ^1H and ^{13}C NMR solution data; the significant chemical shift differences for the alternative $SiMe_3$ and $C_\alpha H$ groups are attributed to differences in their proximity to the aromatic π clouds. For the case of **9**, magnetic inequivalence of the methyls of the Me_2Si group but equivalence of the pairs of $SiMe_3$ and $C_\alpha H$ groups is the basis of our assignment of its *meso* configuration. A similar assignment for **2** rests on the observation of two distinct phenyl groups (^{13}C NMR spectra and X-ray structure determination), while for $[\{Sn(L'L'\text{-}meso)\}_4]$ **5** this derives from its X-ray structure determination. The pairs of $SiMe_3$ and $C_\alpha H$ groups in each of **2** and **5** were found to be equivalent by ^1H, and for **2** also by ^{13}C, NMR spectroscopy; the limited solubility of **5** precluded the acquisition of ^{13}C NMR spectroscopic data. Stereospecificity of metallacycle formation has also been noted in the synthesis of the metallacycles $[Si(L''L''\text{-}meso)Me_2]$[20] and $[M(L''L''\text{-}meso)(\eta\text{-}C_5H_5)_2]$ (M = Zr or Hf)[22] from the appropriate organodilithium reagent based on $1,8\text{-}C_{10}H_6[\bar{C}H(SiMe_3)]_2[\equiv(L''L'')^{2-}]$.

Whereas the reaction of $[Mg(LL)(thf)]$ **6** with $SnCl_4$ gave the hydrocarbon-soluble metallaspirobicycle $[Sn(LL)_2]$ **3**, the reaction of an isoleptic transition-metal chloride MCl_4 (M = Ti, Zr or Hf) inevitably yielded an insoluble *o*-xylenediyl derivative as the thf adduct $M(LL)_2(thf)$, probably of oligomeric structure with bridging hydrocarbyl groups.[5]

As to the objective of utilising tin(IV) complexes as *o*-xylenediyl transfer agents, $[Sn(LL)_2]$ **3** with $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ failed to yield the known[5] red zirconacycle $[Zr(LL)(\eta\text{-}C_5H_5)_2]$ under the following conditions: thf and/or toluene, −78 °C then room temperature, with or without $Ag[ClO_4]$. This behaviour has some precedent in that certain platinum(II) chlorides failed to react with $SnPhMe_3$.[8]

Subvalent Chemistry.—Treatment of tin(IV) chloride with $[Li(tmen)]_2[o\text{-}C_6H_4\{\bar{C}H(SiMe_3)\}_2]$ **7** at −78 °C gave the stannaspirobicycle $[Sn(L'L'\text{-}meso)_2]$ **4** in modest yield (52%) and some reduced co-product $[\{Sn(L'L'\text{-}meso)\}_4]$ (*Sn–Sn*) **5** (14%). To our knowledge, **5** is the first tin(II) metallacycle. At 30 °C **4** was the sole product. That the lithium compound **7** can act as a reducing agent has been noted previously in the context of $Pt^{II} \longrightarrow Pt^0$ or $Hg^{II} \longrightarrow Hg$ conversion,[2] or transformation of zirconocene(IV) chloride to a reduced zirconium hydrocarbyl complex of unknown composition.[1] Reduction of Zr^{IV} occurred only at low temperatures (−78 °C), as in the formation of **5** from $SnCl_4$. Such a temperature effect for an organolithium reagent has precedent, as for example in the reaction between $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ and $LiPPh_2$.[23] A reagent related to **7**, $[Li(tmen)]_2[o\text{-}\bar{C}H(SiMe_3)C_6H_4]_2$ reduced $SnCl_2Ph_2$ to oligomeric '$SnPh_2$', even at 30 °C, the hydrocarbyl co-product being 9,10-dihydro-9,10-bis(trimethylsilyl)phenanthrene, derived from ring closure.[15] It is well established that Grignard reagents are less reducing than organolithium counterparts; not surprisingly, therefore, the diGrignard reagent **6**, while favouring reduction during alkylation of $WOCl_4$,[1] converted $SnCl_4$ exclusively into the tin(IV) product $[Sn(LL)_2]$ **3**.

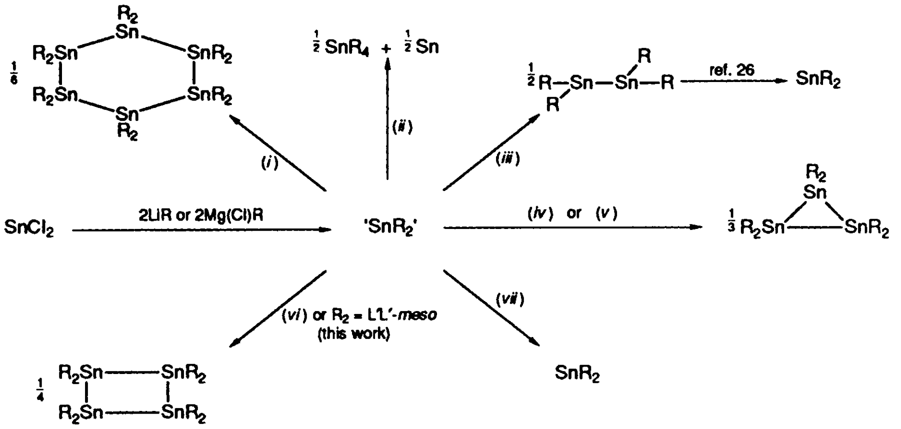
The mechanism of reduction when employing the lithium reagent **7** (or the magnesium counterpart **6**) probably involves an electron-transfer step *via* an unstable 5,6-dimethylenecyclohexa-1,3-diene, equation (1) (R = H or $SiMe_3$).



(1)

Reactions of $GeCl_4$ or $SiCl_4$ with compound **7** at low temperature were investigated under the conditions which had yielded **5** from $SnCl_4$, in order to ascertain whether subvalent compounds of Ge or Si might likewise prove to be accessible by this route. Although there was circumstantial evidence for reduction, from the brown (Ge) or orange (Si) colours of the resulting reaction mixture and detection of a persistent radical for the latter (broad multiplet at g_{av} = 2.005), no clearly defined products were isolated.

The tin(II) compound $[\{Sn(L'L'\text{-}meso)\}_4]$ (*Sn–Sn*) **5** proved not to be accessible from $SnCl_2$ and the lithium reagent **7** at −78 °C; there was reduction to elemental tin, further highlighting the reducing potential of **7**. By contrast, $GeCl_2\cdot C_4H_8O_2$ gave a brown solution, but no reduction to elemental germanium was evident. Treatment of **7** with $Sn(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2$[10] in diethyl ether afforded **5** in modest yield (44%), together with $[\{Li(\mu\text{-}OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)(OEt_2)\}_2]$;[24] a minor surprise was that the latter was the co-product rather than $Li(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)(tmen)$. The same strategy for germanium, using $Ge(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2$[10]



Scheme 2 Typical reaction products obtained by treating $SnCl_2$ with 2LiR or 2Mg(Cl)R. R = Me (*i*),[11] Ph (*ii*),[11] $CH(SiMe_3)_2$ (*iii*),[29] η-$C_{14}H_7$ (*iv*),[25] $C_6H_2Pr^i_3$-2,4,6 (*v*),[30] CH_2SiMe_3 (*vi*),[27] $C_5H_4N[C(SiMe_3)_2]$-2 (*vii*),[32] $C_6H_2(CF_3)_3$-2,4,6 (*vii*)[31b] or $C(SiMe_3)_2(CH_2)_2C(SiMe_3)_2$ (*vii*)[31c]

and 7, failed; the product was an intractable oil. The above tin reactions leading to the tin(II) spirobicycle **5** from $SnCl_4$ or $Sn(OR)_2$ (R = aryl) may be contrasted with existing methods for preparing other tin(II) alkyls, which include: (*i*) reduction of SnR_2Cl_2, *e.g.* R = 9-phenanthryl[25] or $CH(SiMe_3)_2$;[26] (*ii*) reaction of SnR_2X_2 with SnR_2H_2 (eliminating HX), *e.g.*[27] R = CH_2SiMe_3; or (*iii*) treatment of $SnCl_2$ with an alkylating agent, *e.g.*[26] $SnCl_2 + Li[CH(SiMe_3)_2]$. However, the $Sn(OR)_2$ route has been used for the preparation of $[\{Sn[CH(SiMe_3)_2]_2\}_2]$ (*Sn–Sn*).[26] The success of the present reductive alkylation of $SnCl_4$ for the preparation of **5** prompted us to investigate the reaction of $SnCl_4$ with $Li_2C_4Ph_4$ with a view to generating '$Sn[(CPh)_4]$'. Under similar conditions, however, only the spirobicycle $[Sn\{(CPh)_4\}_2]$[14c,d] was obtained; surprisingly, $Li_2C_4Ph_4$ with $Sn(OC_6H_2Bu^t_2$-2,6-Me-4$)_2$ gave the same product.

The tin(II) alkyl [{Sn(L'L'-*meso*)}₄] (*Sn–Sn*) **5** is yellow, diamagnetic, and a tetramer both in the solid (X-ray structure) and in C_2Cl_6 (vapour-phase osmometry), whereas in the gas phase it appeared to dissociate into the monomer. The He I photoelectron spectrum at 130–136 °C was dominated by the ligand features, as shown by comparing it with that of the spectrum of *o*-$(Me_3SiCH_2)_2C_6H_4$, which has a first ionisation energy of 8.2 eV. There were, however, additional bands at 7.6, 9.5 and 11.8 eV, the first of these probably due to ionisation from the metal-centred lone pair of the monomer, *cf.*[28] 7.42 eV for gaseous $[Sn\{CH(SiMe_3)_2\}_2]$. Further evidence for a gas-phase monomer derives from (*i*) its red colour and (*ii*) a monomeric parent ion in the electron impact (EI) mass spectrum. Interestingly, when the related crystalline tetramer $[\{Sn(CH_2SiMe_3)_2\}_4]$ (*Sn–Sn*) was heated at 80–160 °C there was a colour transition from white to yellow, with concomitant formation of a radical.[27] Assuming that there is a relationship between the steric requirements of the hydrocarbyl groups and the degree of aggregation of the corresponding tin(II) alkyl, we conclude that the substituted bidentate *o*-xylenediyl ligand *o*-C_6H_4-$[\bar{C}H(SiMe_3)]_2$ is sterically similar in its demands to that of two $\bar{C}H_2SiMe_3$ groups. For the more hindered ligand $\bar{C}H(SiMe_3)_2$, the crystalline tin(II) alkyl is a dimer (a tin analogue of an alkene),[29] which dissociates readily to the monomer in dilute cyclohexane solution or in the gas phase.[26] Crystalline trimers $[(SnR_2)_3]$ include R = 9-phenanthryl[25] or $C_6H_2Pr^i_3$-2,4,6.[30] The compound $[Sn\{C_6H_3(CF_3)_2$-2,6$\}_2]$ was alleged to be a crystalline monomeric tin(II) hydrocarbyl on the basis of ^{119}Sn Mössbauer data;[31a] X-ray data on monomeric species $[Sn\{C_6H_2(CF_3)_3$-2,4,6$\}_2]$[31b] and $[Sn\{C(SiMe_3)_2(CH_2)_2C(SiMe_3)_2]$[31c] have recently been published. Another X-ray-substantiated homoleptic crystalline tin(II) alkyl SnR_2 is that in which R = $C_5H_4N[C(SiMe_3)_2]$-2, having three-co-ordinate tin.[32]

It is clear that the reactions of $SnCl_2$ with 2 equivalents of an organolithium or organomagnesium hydrocarbyl (R^-) transfer reagent are complicated; the product depends on the nature of the hydrocarbyl ligand, and especially its steric or, to a lesser extent, electronic requirements. The data can be rationalised by assuming that the kinetic product is SnR_2 but that its subsequent fate is, with a single exception to date,[32] dependent on associative processes leading either to the oligomer $(SnR_2)_n$ or to disproportionation products. Typical data are summarised in Scheme 2.

Attempts were made to generate and characterise a tin-centred radical formed either by photolysis or electrochemical reduction of (in turn) one of the tin(IV) compounds **1–4**. Photolysis of [Sn(L'L'-*meso*)Ph₂] **2** or [Sn(L'L'-*meso*)₂] **4** in the presence of $Me_3SiO_2SiMe_3$ gave a broad ESR signal with no clearly defined hyperfine coupling. In general, alkyltin-centred radicals have broad spectra and are difficult to detect,[33] unlike readily identified tin(III) hindered alkyls or amides, *e.g.* $\dot{S}n[CH(SiMe_3)_2]_3$[34] or $\dot{S}n[N(SiMe_3)_2]_3$[35] which are indefinitely stable in hydrocarbon solution at ambient temperature. Photolysis of a stannacyclopentane yielded ESR-detectable *C*-centred radicals (^1H hyperfine coupling observed), consistent with there having been Sn–C bond rupture, but there was no evidence for a tin-centred co-radical.[33]

None of the compounds **1–4** was electrochemically responsive to reduction in thf solution, showing no reduction peak in the cyclic voltammogram down to the limits of background decomposition. This is unexceptional for an organotin(IV) compound. Each of the compounds $[Sn\{(CH_2)_n\}Ph_2]$ (*n* = 4 or 5), related to [Sn(LL)Ph₂] **1** and [Sn(L'L'-*meso*)Ph₂] **2**, underwent anionic cleavage of an Sn–Ph rather than an Sn–CH_2 bond at a mercury electrode using polarographic techniques.[36]

Structural Commentary.—Single-crystal X-ray diffraction data are provided for each of [Sn(LL)Ph₂] **1**, [Sn(L'L'-*meso*)Ph₂] **2**, [Sn(LL)₂] **3**, [Sn(L'L'-*meso*)₂] **4** [{Sn(L'L'-*meso*)}₄] (*Sn–Sn*) **5**, illustrated in Figs. 1–5, respectively, with atom coordinates in Tables 1–5 and selected geometric parameters for (*a*) the tin environment in Tables 6 (**1** and **2**), 7 (**3** and **4**), and 8 (**5**) and (*b*) the ligand skeleton in Tables 9–12, respectively.

The results are consistent with the stoichiometries and connectivities proposed above for compounds **1–4**, with a proviso in the case of **2** that residual peaks have been modelled in terms of a molecule of hexane solvent per molecule of complex, but with site occupancy of 0.5. Each complex has a single molecule as the asymmetric unit, so that in no case does the molecule contain crystallographic symmetry elements.

Invariably, for each of compounds **1–4** the immediate tin(IV)

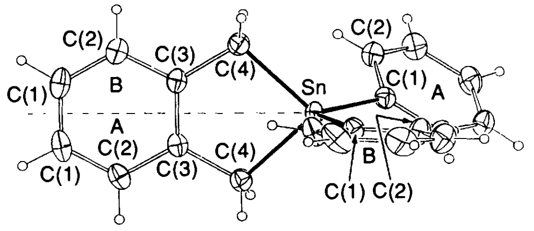


Fig. 1 A single molecule of [Sn(LL)Ph$_2$] **1**. 20% Thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å

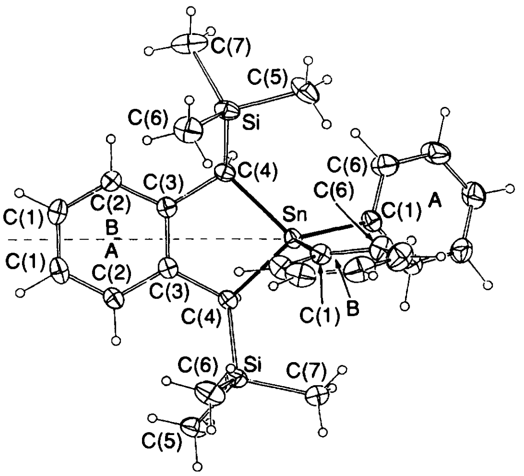


Fig. 2 A single molecule of [Sn(L′L′-*meso*)Ph$_2$] **2**

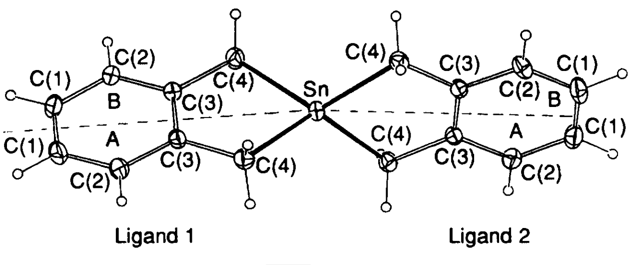


Fig. 3 A single molecule of [Sn(LL)$_2$] **3**

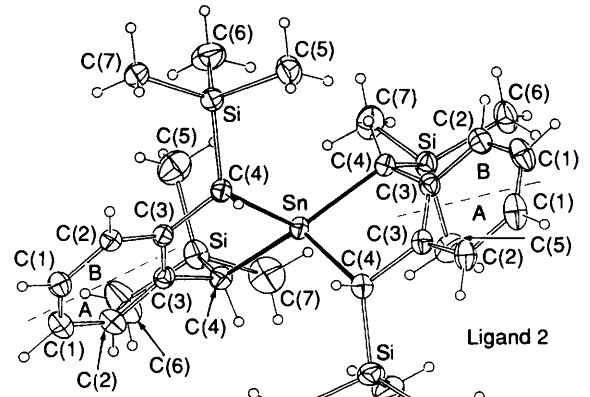


Fig. 4 A single molecule of [Sn(L′L′-*meso*)$_2$] **4**

environment is comprised of four carbon atoms; in **1** and **2**, two of these are associated with phenyl groups, and, as only minor variations in tin–carbon distances are observed, we take the Sn–C distance for tetraphenyltin as 2.143(5) Å [redetermined (without libration correction)] as a convenient reference point for comparison.[37] The spirobicycle [Sn(LL)$_2$] **3** provides a baseline for discussion of the Sn–C bond lengths in complexes of the *o*-xylenediyl chelate ligand (LL)$^{2-}$; this distance 2.143(5)–2.152(5) Å, mean 2.14_7 Å in **3**, is essentially the same as Sn–C in SnPh$_4$, probably because while there is contrast between Sn–C(sp^2) and Sn–C(sp^3), in the latter **3** there is a considerable reduction in the chelate angle below that of the tetrahedral value.

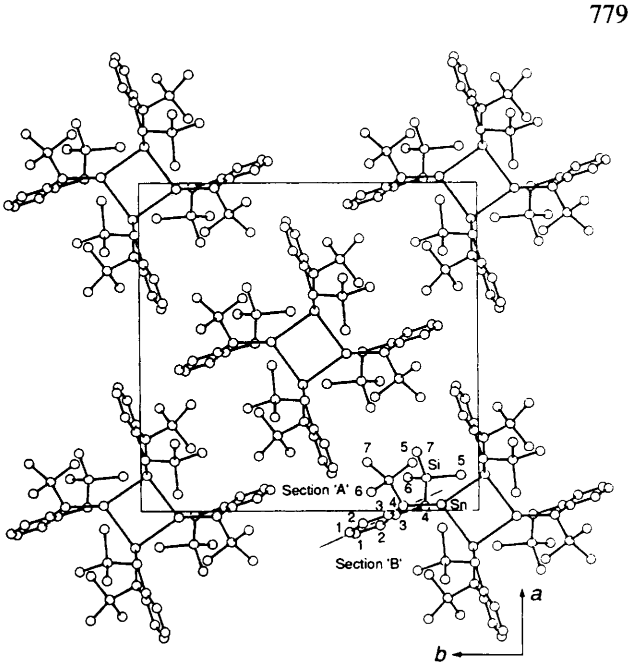


Fig. 5 Unit-cell contents of [{Sn(L′L′-*meso*)}$_4$] (*Sn–Sn*) **5** projected down *c*

A further parameter useful in defining the disposition of the *o*-xylenediyl ligand in relation to the metal atom is the 'fold angle' (θ) of the ligand. Given the aromatic component of the *o*-xylenediyl ligand, with a preference for the C$_6$C$_2$ moiety being coplanar, it might have been expected that any strain within the five-membered ring created by chelation to the metal atom should be minimised by the adoption of an envelope configuration within the ring, with the metal atom out of the C$_6$H$_4$C$_2$ plane; the 'fold angle' θ is a convenient measure of such departure, and on steric grounds it should be small for a small metal atom. However, electronic factors may intervene, the extremes representing the metal as a bis(σ-bond) (as in **A′**) or a bis(π-bond) (as in **C′**) acceptor; for a main-group metal the latter effect may not be especially important.

In [Sn(LL)Ph$_2$] **1** the chelate ring Sn–C (4A,B) distances are 2.150(4) and 2.138(4) Å, mean 2.14_4 Å, a value essentially identical to that found in the spirobicycle [Sn(LL)$_2$] **3** (taken as the norm), and enclosing a similar angle at the metal. The tin atom lies 0.23_3 Å out of the C$_6$H$_4$C$_2$ plane with θ = 8.5° in **1**, compared with 0.01_9 and 0.33_1 Å with θ = 0.8 and 11.9° for **3**. It seems likely, since no other contributing factor is immediately evident, that the 'fold angle' θ of the (LL) system is a relatively flexible parameter, susceptible to the influence of the lattice forces to the extent of at least 11°. The Sn–C(phenyl) [Sn–C(1A,B)] distances of 2.131(4) and 2.126(3) Å, mean $2.12_9(3)$ Å, are shorter than in the tetraphenyltin(IV) reference, presumably as a consequence of the diminished crowding about the metal because of the incorporation of two of the carbon atoms within the chelate ring, with all other angles at Sn being well above the tetrahedral value. For comparison, Sn–C(phenyl) distances of 2.14_4 Å are found in the unstrained compounds [Sn{(*o*-CH$_2$C$_6$H$_4$)$_2$}Ph$_2$][15] and [Ph$_2$Sn(CH$_2$)$_4$Sn{(CH$_2$)$_3$CH$_2$}Ph$_2$].[33] The angles subtended at the methylenic carbons C(3)–C(4)–Sn in **1** are 104.5(2) and 104.9(2)°, mean

Table 1 Atom coordinates for $[\mathrm{Sn(LL)Ph_2}]$ **1**

Ligand/Section	A			B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Sn	0.151 83(1)	0.056 23(2)	0.079 51(4)			
o-Xylenediyl ligand $(\mathrm{LL})^{2-}$						
C(1)	0.0384(2)	0.4161(3)	0.2355(8)	0.0801(2)	0.4220(3)	0.4126(7)
C(2)	0.0398(2)	0.3340(3)	0.0840(7)	0.1233(2)	0.3452(3)	0.4379(6)
C(3)	0.0834(2)	0.2540(2)	0.1103(6)	0.1264(2)	0.2593(2)	0.2893(5)
C(4)	0.0829(2)	0.1624(3)	−0.0541(7)	0.1748(2)	0.1760(3)	0.3230(6)
Phenyl ligands						
C(1)	0.2220(2)	0.0209(3)	−0.1433(5)	0.1152(2)	−0.0808(3)	0.2316(6)
C(2)	0.2715(2)	0.0889(3)	−0.1530(7)	0.1320(2)	−0.1837(3)	0.1836(6)
C(3)	0.3152(2)	0.0748(3)	−0.3061(8)	0.1089(2)	−0.2696(3)	0.2954(8)
C(4)	0.3120(2)	−0.0089(4)	−0.4527(7)	0.0691(2)	−0.2545(4)	0.4594(9)
C(5)	0.2639(2)	−0.0773(3)	−0.4451(7)	0.0513(2)	−0.1548(4)	0.5125(9)
C(6)	0.2193(2)	−0.0627(3)	−0.2940(6)	0.0743(2)	−0.0688(3)	0.3997(8)

Table 2 Atom coordinates for $[\mathrm{Sn(L'L'}\text{-}meso\mathrm{)Ph_2}]$ **2**

Ligand/Section	A			B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Sn	0.319 60(1)	0.492 73(2)	0.0183(2)			
o-Xylenediyl ligand $(\mathrm{L'L'})^{2-}$						
C(1)	0.2667(2)	0.1398(4)	−0.1360(3)	0.3215(2)	0.1177(4)	−0.0878(3)
C(2)	0.2438(2)	0.2303(4)	−0.1263(3)	0.3539(2)	0.1873(4)	−0.0286(3)
C(3)	0.2757(2)	0.3011(3)	−0.0671(2)	0.3326(2)	0.2796(3)	−0.0173(2)
C(4)	0.2482(2)	0.3979(3)	−0.0556(2)	0.3696(2)	0.3536(3)	0.0475(2)
Si	0.189 52(5)	0.461 76(10)	−0.140 84(7)	0.444 75(6)	0.367 70(12)	0.072 31(8)
C(5)	0.1223(2)	0.3850(4)	−0.1794(3)	0.4735(2)	0.4888(5)	0.1278(3)
C(6)	0.2029(3)	0.4865(4)	−0.2229(3)	0.4525(2)	0.3725(5)	−0.0175(3)
C(7)	0.1756(2)	0.5852(4)	−0.1040(3)	0.4884(2)	0.2594(6)	0.1351(4)
Phenyl ligand						
C(1)	0.3200(2)	0.5645(3)	0.1178(2)	0.3422(2)	0.6088(3)	−0.0396(3)
C(2)	0.2783(2)	0.6305(4)	0.1119(3)	0.3454(2)	0.5884(4)	−0.1072(3)
C(3)	0.2809(2)	0.6764(4)	0.1773(3)	0.3627(2)	0.6637(5)	−0.1420(3)
C(4)	0.3245(2)	0.6588(5)	0.2485(3)	0.3764(2)	0.7600(5)	−0.1099(4)
C(5)	0.3649(2)	0.5932(6)	0.2558(3)	0.3731(3)	0.7816(4)	−0.0441(4)
C(6)	0.3630(2)	0.5458(5)	0.1916(3)	0.3570(2)	0.7076(4)	−0.0083(3)

Table 3 Atom coordinates for $[\mathrm{Sn(LL)_2}]$ **3**

	Ligand 1			Ligand 2		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Sn	0.296 69(2)	0.158 67(3)	0.025 14(2)			
Section A						
C(1)	0.5437(5)	0.6220(5)	0.1862(3)	0.0435(4)	−0.3284(5)	−0.0884(4)
C(2)	0.4274(4)	0.5720(5)	0.1597(3)	0.0876(4)	−0.2501(5)	−0.0058(3)
C(3)	0.4056(4)	0.4304(4)	0.1160(3)	0.1445(3)	−0.1089(5)	−0.0129(3)
C(4)	0.2779(4)	0.3804(5)	0.0871(3)	0.1947(4)	−0.0288(5)	0.0790(3)
Section B						
C(1)	0.6471(5)	0.5300(6)	0.1701(4)	0.0549(4)	−0.2672(5)	−0.1816(4)
C(2)	0.6224(3)	0.3893(5)	0.1285(3)	0.1097(4)	−0.1267(5)	−0.1904(3)
C(3)	0.5059(4)	0.3376(4)	0.1004(3)	0.1558(3)	−0.0472(4)	−0.1072(3)
C(4)	0.4893(4)	0.1815(4)	0.0552(3)	0.2181(4)	0.1038(5)	−0.1194(3)

104.8 . There is no systematic variation of bond lengths throughout the *o*-xylenediyl moiety, indicative of the extension of aromaticity beyond that of the benzene ring. Exocyclic angles at the quaternary carbon atoms C(3A,B) are almost exactly 120°, as is also the case in $[\mathrm{Sn(LL)_2}]$ **3** where the angles at C(4) are 104.7(3)–105.0(3)°, mean 104.$_8$°. No significant interspecies

Table 4 Atom coordinates for [Sn(L′L′-*meso*)$_2$] **4**

	Ligand 1			Ligand 2		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Sn	0.167 63(2)	0.222 28(2)	0.122 35(4)			
Section A						
C(1)	−0.0047(4)	0.4235(3)	0.1687(7)	0.2540(4)	0.0283(3)	0.4680(6)
C(2)	0.0103(3)	0.3738(2)	0.0742(6)	0.1907(4)	0.0644(3)	0.4221(6)
C(2)	0.0750(3)	0.3366(2)	0.0942(6)	0.1904(3)	0.1064(3)	0.3021(6)
C(4)	0.0869(3)	0.2809(2)	−0.0120(6)	0.1236(2)	0.1511(3)	0.2685(5)
Si	0.1014(1)	0.3058(1)	−0.2066(2)	0.0269(1)	0.1204(1)	0.2206(2)
C(5)	0.1912(5)	0.3472(4)	−0.2235(4)	0.0102(4)	0.0967(4)	0.0232(9)
C(6)	0.0258(5)	0.3619(5)	−0.2832(8)	0.0010(5)	0.0494(5)	0.3332(11)
C(7)	0.0942(5)	0.2324(4)	−0.3256(9)	−0.0365(4)	0.1891(4)	0.2592(8)
Section B						
C(1)	0.0439(3)	0.4369(3)	0.2890(7)	0.3169(4)	0.0339(3)	0.3939(7)
C(2)	0.1075(3)	0.4004(3)	0.3131(6)	0.3173(3)	0.0748(3)	0.2752(6)
C(3)	0.1246(3)	0.3504(3)	0.2189(6)	0.2538(3)	0.1113(3)	0.2241(6)
C(4)	0.1915(3)	0.3070(3)	0.2597(6)	0.2598(2)	0.1557(3)	0.0908(6)
Si	0.2897(1)	0.3378(1)	0.2751(2)	0.267 33(10)	0.113 42(8)	−0.0909(2)
C(5)	0.3450(4)	0.2749(3)	0.3845(9)	0.1792(4)	0.0698(3)	−0.1494(7)
C(6)	0.3306(4)	0.3475(4)	0.0937(9)	0.3416(4)	0.0494(3)	−0.0787(8)
C(7)	0.2986(4)	0.4169(3)	0.3735(8)	0.2942(4)	0.1734(4)	−0.2300(8)

Table 5 Atom coordinates for [{Sn(L′L′-*meso*)}$_4$] (*Sn–Sn*) **5**

	Section A			Section B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Sn	0.0183(1)	0.1108(1)	−0.0224(2)			
C(1)	−0.065(2)	0.383(2)	−0.113(4)	−0.069(2)	0.366(2)	−0.232(3)
C(2)	−0.039(2)	0.344(2)	−0.025(4)	−0.045(2)	0.292(2)	−0.262(3)
C(3)	−0.013(1)	0.269(1)	−0.046(3)	−0.013(2)	0.247(2)	−0.160(3)
C(4)	0.015(2)	0.224(2)	0.048(3)	0.014(2)	0.159(2)	−0.193(4)
Si	0.0943(6)	0.2666(6)	0.1397(12)	0.1006(7)	0.1548(6)	−0.2836(11)
C(5)	0.149(3)	0.195(3)	0.217(5)	0.109(2)	0.053(2)	−0.333(4)
C(6)	0.057(3)	0.318(3)	0.264(4)	0.101(3)	0.210(3)	−0.424(4)
C(7)	0.150(2)	0.330(2)	0.038(4)	0.182(2)	0.182(2)	−0.185(4)

Table 6 Tin atom environments for [Sn(LL)Ph$_2$] **1** and [Sn(L′L′)Ph$_2$] **2** *

	r(Sn–L)	*C(4B)*	C(1A)	C(1B)
C(4A)	2.150(4) [2.167(4)]	87.3(2) [87.7(1)]	114.9(1) [117.1(2)]	112.8(1) [116.3(2)]
C(4B)	2.138(4) [2.165(4)]		114.4(1) [113.1(2)]	115.6(1) [114.5(2)]
C(1A)	2.131(4) [2.155(5)]			113.3(1) [107.4(2)]
C(1B)	2.126(3) [2.142(5)]			

* *r*(Sn–L) is the tin–ligand atom distance (Å); the other entries in the matrices are the angles (°) subtended at the tin atom by the relevant ligand atoms. Xylenediyl ligand atoms are italicised. Values for complex **2** are in square brackets.

contacts are observed in either [Sn(LL)Ph$_2$] **1** or **3**. In each of the tin(IV) compounds **1**–**4** the C–C bond lengths at the *o*-xylenediyl chelate ring periphery are systematically shortened, presumably as a consequence of the lack of libration correction.

On passing from [Sn(LL)Ph$_2$] **1** to [Sn(L′L′-*meso*)Ph$_2$] **2** a number of interesting effects upon stereochemistry may be observed, compounded by further variation on passing from [Sn(LL)$_2$] **3** to [Sn(L′L′-*meso*)$_2$] **4**. In **2** the two silicon atoms lie to one side of the *o*-xylenediyl plane, with deviations of 0.71$_2$ and 0.97$_0$ Å; the tin atom deviates to the same side of the plane by 0.49$_8$ Å (θ = 19.8°). Two of the methyl substituents at each silicon atom are situated outward from the plane further in this direction (2.46$_7$, 0.63$_4$; 1.27$_7$, 2.62$_1$ Å) with one atom of each pair being further from the plane and from the tin atom. The third methyl substituent is situated in the opposite direction and is nearly coplanar with the *o*-xylenediyl ring (−0.24$_6$, 0.012 Å). Hence, there is considerable atomic crowding on the tin side of the *o*-xylenediyl system; the phenyl ring which lies to this side of the plane is disposed so as to lie snugly between the hydrogen atoms of the two pairs of methyl substituents. No hydrogen-ring contacts shorter than van der Waals distances are observed, but the angles C(3)–C(4)–Si are well above the tetrahedral value, 118.9(4) and 120.7(3)°, mean 118.7°; methyl–phenyl contacts may contribute towards this enlargement. The other phenyl ring is tucked away at the back of the molecule.

Since *each* tin–carbon distance in [Sn(L′L′-*meso*)Ph$_2$] **2** is longer than its counterpart in [Sn(LL)Ph$_2$] **1** a steric explanation seems likely, as supported by the decrease in the angle subtended at Sn by the two phenyl ligands from 113.3(1) in **1** to 107.4(2)° in **2**. A longer Sn–C(sp^3) but a similar Sn–C(sp^2) distance in [Sn{*o*-CH(SiMe$_3$)C$_6$H$_4$}$_2$Ph$_2$] compared with its unsilylated analogue is noteworthy.[15] Other geometric parameters are unexceptional; the C(3)–C(4) bond is marginally longer in **2** than in **1**.

For each ligand in [Sn(L′L′-*meso*)$_2$] **4** the tin atom out-of-plane deviation or 'fold angle' θ is greater than in [Sn(LL)$_2$] **3**, being 0.67 and 0.64 Å or 24.1 and 23.0°, respectively. The silicon atoms lie on the same side of the ligand plane, but on the

Table 7 Tin atom environments for [$\overline{\mathrm{Sn(LL}}\mathrm{)}_2$] **3** and [$\overline{\mathrm{Sn(L'L'}}$-*meso*)$_2$] **4***

	r(Sn–L)	C(B4)	*C*(*A4*)	*C*(*B4*)
C(A4)	2.143(5) [2.186(5)]	87.3(2) [88.6(2)]	120.1(2) [117.2(2)]	121.3(2) [138.6(2)]
C(B4)	2.147(5) [2.164(5)]		122.7(2) [104.8(2)]	122.2(2) [117.3(2)]
C(*A4*)	2.152(5) [2.164(5)]			86.9(2) [88.4(2)]
C(*B4*)	2.144(5) [2.182(5)]			

* *r*(Sn–L) is the tin–ligand atom distance (Å); the other entries in the matrices are the angles (°) subtended at the tin atom by the relevant ligand atoms. Atoms derived from the xylenediyl ligand 2 are italicised. Values for complex **4** are in square brackets.

Table 8 Tin atom environments for [{$\overline{\mathrm{Sn(L'L'}}$-*meso*)}$_4$] (*Sn–Sn*) **5***

	r(Sn–L)	C(B4)	Sn$^{\mathrm{I}}$	Sn$^{\mathrm{II}}$
C(A4)	2.15(3)	88(1)	133.9(9)	116.6(9)
C(B4)	2.09(4)		121(1)	111(1)
Sn$^{\mathrm{I}}$	2.852(3)			88.21(8)

* *r*(Sn–L) is the tin–ligand atom distance (Å); the other entries in the matrices are the angles (°) subtended at the tin atom by the relevant ligand atoms. Symmetry operations I *y*, *x*, *z*; II *y*, *x*, *z*.

Table 9 *o*-Xylenediyl ligand non-hydrogen geometry (distances in Å, angles in °) for [$\overline{\mathrm{Sn(LL}}$)Ph$_2$] **1***

C(1)–C(1)	1.370(6)
C(1)–C(2)	1.374(6), 1.359(6)
C(2)–C(3)	1.397(5), 1.403(5)
C(3)–C(3)	1.395(5)
C(3)–C(4)	1.513(5), 1.505(5)
C(1)–C(1)–C(2)	120.7(4), 119.3(4)
C(1)–C(2)–C(3)	120.5(4), 122.3(4)
C(2)–C(3)–C(3)	119.3(3), 117.9(3)
C(4)–C(3)–C(3)	120.1(3), 121.4(3)
C(2)–C(3)–C(4)	119.6(3), 120.6(3)
C(3)–C(4)–Sn	104.5(2), 104.9(2)

* The two values in each entry are for Parts A and B respectively.

opposite side to that of the tin atom (deviations 1.50 and 1.24, or 1.17 and 1.58 Å). That these deviations are markedly greater in **4** than **3** is presumably a consequence of the greater 'envelope' distortion of the chelate ring, and/or the disposition of the Si atoms on the opposite side to that of the tin atom. Methyl atom deviations from the *o*-xylenediyl plane (2.94$_7$, 1.88$_5$, 1.04$_6$; 0.21$_2$, 2.58$_8$, 1.74$_4$ Å) are all to the same side as that of the silicon atoms. The endocyclic angles at the benzylic carbon atoms Sn–C(4)–C(3) are reduced still further, 99.9(4)–102.2(3)° (mean 101.$_1$°), and several contacts between the methyl groups of different moieties are now evident at the van der Waals limit. The Sn–C(sp^3) [Sn–C(4A,B)] bond lengths are even longer than in **1** or **2**, 2.164(5)–2.186(5) Å (mean 2.17$_4$ Å), with a considerable spread in the interligand C–Sn–C angles which range from 104.8(2) to 138.6(2)°. It is of interest that the largest of these angles about the pseudo-two-fold projection axis of the molecule 'contains' a pair of SiMe$_3$ groups, while the smaller ('*trans*') to it contains none. This molecular distortion has a steric origin, consequent upon chelation of a pair of *R*,*S* chiral centres in each ligand to a tin atom which deviates from the ligand plane in an opposite sense from that of the silicon atoms.

The single-crystal X-ray structure of [{$\overline{\mathrm{Sn(L'L'}}$-*meso*)}$_4$] (*Sn–Sn*) **5** shows the presence of a tetranuclear species with the above stoichiometry and connectivity. In space group $I\bar{4}$, the tetramer lies disposed about the $\bar{4}$ crystallographic axis with one quarter of the molecule (*i.e.* one tin atom and one ligand) comprising the asymmetric unit of the structure, Fig. 5. The molecular geometry is lower in precision than that determined for **1**–**4**; hence the Sn–C distances of 2.15(3) and 2.09(4) Å (mean 2.12 Å) cannot be said to differ significantly from those determined in **1**–**4**. In [{Sn(CH$_2$SiMe$_3$)$_2$}$_4$] (*Sn–Sn*), which is similar in structure to **5**, the Sn–C distances average 2.19$_5$ Å (corrected for thermal vibration).[27] The 'fold-angle' θ of the ligand in **5** is 21°, similar to the 19.8° in **2**. The Sn–Sn bonds, subtending an angle of 88.21(8)° at the tin atoms, are slightly longer at 2.852(3) Å than their counterparts (2.83$_5$ Å) in [{Sn(CH$_2$SiMe$_3$)$_2$}$_4$] (*Sn–Sn*) with ⟨Sn–Sn–Sn⟩ 90.0°,[27] but appreciably longer than in hexameric [(SnPh$_2$)$_6$], mean 2.78$_0$ Å, in which the mean ring angle is 112.5°.[38] At the lower limit of aggregation, in [{Sn[CH(SiMe$_3$)$_2$]$_2$}$_2$] (*Sn–Sn*), the Sn–Sn distance is 2.764(2) Å.[29]

We shall now consider the trends in the variation of the 'fold angle' θ with M–C$_\alpha$ distances in a wider series of complexes derived from the *o*-xylenediyl ligands (LL)$^{2-}$ and (L'L')$^{2-}$: **1**–**5**, [$\overline{\mathrm{M(LL}}$)(η-C$_5$H$_5$)$_2$] (M = Ti **10**, Zr **11** or Hf **12**),[5] [$\overline{\mathrm{Nb(LL}}$){η-C$_5H_4$(SiMe$_3$)}$_2$] **13**,[5] [$\overline{\mathrm{Zr(L'L'}}$-*meso*){(η-C$_5H_4$(SiMe$_3$)}$_2$] **14**,[1] [$\overline{\mathrm{W(LL}}$)$_3$] **15**,[1] [{$\overline{\mathrm{W(LL}}$)$_2$O}$_2$Mg(thf)$_4$] **16**,[7] [$\overline{\mathrm{Ti(L'L'}}$-*meso*)(η-

Table 10 *o*-Xylenediyl ligand non-hydrogen geometry (distances in Å, angles in °) for [$\overline{\mathrm{Sn(L'L'}}$-*meso*)Ph$_2$] **2***

C(1)–C(1)	1.364(7)
C(1)–C(2)	1.385(8), 1.396(6)
C(2)–C(3)	1.403(6), 1.393(7)
C(3)–C(3)	1.412(6)
C(3)–C(4)	1.532(6), 1.519(4)
C(4)–Si	1.873(4), 1.883(5)
Si–C(5)	1.879(6), 1.852(6)
Si–C(6)	1.855(8), 1.870(8)
Si–C(7)	1.854(7), 1.867(7)
C(1)–C(1)–C(2)	120.2(4), 119.1(5)
C(1)–C(2)–C(3)	121.4(4), 122.5(4)
C(2)–C(3)–C(3)	118.9(4), 117.9(4)
C(4)–C(3)–C(3)	121.2(3), 121.5(4)
C(2)–C(3)–C(4)	119.9(4), 120.7(4)
C(3)–C(4)–Si	120.7(3), 118.9(4)
C(3)–C(4)–Sn	102.1(3), 102.7(2)
Si–C(4)–Sn	117.6(2), 117.5(2)
C(4)–Si–C(5)	112.6(2), 109.7(3)
C(4)–Si–C(6)	112.9(3), 111.4(2)
C(4)–Si–C(7)	106.4(2), 111.8(3)
C(5)–Si–C(6)	108.1(3), 108.4(3)
C(5)–Si–C(7)	106.4(3), 107.0(3)
C(6)–Si–C(7)	110.3(3), 108.4(3)

* The two values in each entry are for parts A and B respectively.

Table 11 Ligand non-hydrogen geometries (distances in Å, angles in °) for [$\overline{\mathrm{Sn(LL}}$)$_2$] **3**

	1		2	
Section	A	B	A	B
C(1)–C(1)	1.380(7)	—	1.385(7)	—
C(1)–C(2)	1.382(7)	1.374(7)	1.376(7)	1.387(6)
C(2)–C(3)	1.396(6)	1.394(6)	1.399(6)	1.395(6)
C(3)–C(4)	1.505(6)	1.511(5)	1.505(6)	1.512(6)
C(3)–C(3')	1.403(6)	—	1.400(6)	—
C(1)–C(1)–C(2)	119.7(4)	119.6(5)	119.8(4)	119.4(4)
C(1)–C(2)–C(3)	121.8(4)	121.5(4)	121.8(4)	121.2(4)
C(2)–C(3)–C(3)	118.0(4)	119.4(4)	118.3(4)	119.4(4)
C(2)–C(3)–C(4)	120.3(4)	119.6(4)	120.2(4)	119.9(4)
C(3)–C(3)–C(4)	121.7(3)	121.0(3)	121.4(4)	120.6(4)
Sn–C(4)–C(3)	104.8(3)	104.8(3)	104.7(3)	105.0(3)

Table 12 Ligand non-hydrogen geometries (distances in Å, angles in °) for [$\mathrm{Sn(L'L'}$-*meso*$)_2$] **4**

	1		2	
Section	A	B	A	B
C(1)–C(1)	1.375(9)		1.360(10)	
C(1)–C(2)	1.373(9)	1.371(8)	1.395(10)	1.368(9)
C(2)–C(3)	1.391(8)	1.385(8)	1.390(8)	1.414(8)
C(3)–C(3)	1.417(7)		1.399(8)	
C(3)–C(4)	1.521(7)	1.520(7)	1.523(8)	1.526(8)
C(4)–Si	1.878(6)	1.868(6)	1.867(6)	1.879(6)
Si–C(5)	1.839(9)	1.870(7)	1.862(8)	1.862(7)
Si–C(6)	1.873(10)	1.864(8)	1.860(10)	1.869(7)
Si–C(7)	1.854(9)	1.857(7)	1.862(8)	1.853(8)
C(1)–C(1)–C(2)	120.2(6)	119.4(6)	119.6(6)	119.7(6)
C(1)–C(2)–C(3)	121.8(5)	121.8(5)	121.4(6)	122.2(6)
C(2)–C(3)–C(3)	117.7(5)	119.2(5)	119.3(5)	117.8(5)
C(2)–C(3)–C(4)	119.0(5)	119.4(4)	119.2(5)	118.3(5)
C(3)–C(3)–C(4)	123.3(5)	121.1(5)	121.2(5)	123.8(5)
Sn–C(4)–C(3)	100.2(3)	102.2(3)	102.2(3)	99.9(4)
Sn–C(4)–Si	123.0(3)	117.5(3)	117.4(3)	120.6(3)
C(3)–C(4)–Si	115.3(4)	123.0(4)	123.3(4)	115.8(4)
C(4)–Si–C(5)	112.8(3)	105.5(3)	113.2(3)	111.1(3)
C(4)–Si–C(6)	111.8(3)	113.6(3)	113.7(3)	111.7(3)
C(4)–Si–C(7)	108.6(3)	112.3(3)	105.7(3)	109.4(3)
C(5)–Si–C(6)	107.5(4)	108.4(3)	107.2(4)	105.4(3)
C(5)–Si–C(7)	110.5(4)	109.0(3)	108.8(3)	112.5(3)
C(6)–Si–C(7)	105.4(4)	107.8(3)	108.0(4)	106.7(3)

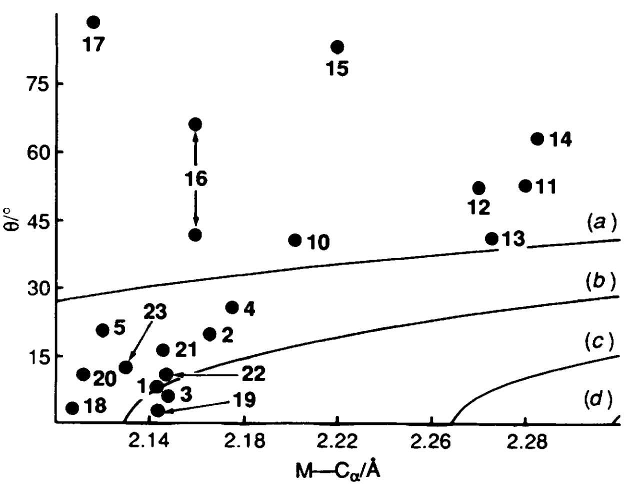


Fig. 6 Plot of 'fold angle' θ (°) *versus* the M–C_α distance (Å) for the *o*-xylenediylmetallacycles **1–6** and **10–23**; the solid lines represent calculated values of θ assuming the C_α–$C_{\alpha'}$ distance to be 2.96 Å and M–C_α–C (or C_6H_4) of 100 (*a*), 104.7 (*b*), 108 (*c*) and 109.47° (*d*)

$C_5H_5)Cl]$ **17**,[6] [$\mathrm{M(LL)(PMe_2CH_2CH_2PMe_2)_2}$] **18**,[39] [$\mathrm{Te(LL)I_2}$] **19**,[40] [$\mathrm{Te(LL)Me}$][$\mathrm{BPh_4}$] **20**,[41] [$\mathrm{Te(LL)(C_3H_5)Br}$] **21**,[42] [$\mathrm{Te(LL)(CH_2COPh)}$]Br **22**[42] and [$\mathrm{Te(LL)(CD_3)I}$] **23**.[42]

Among the parameters to be noted are (*i*) the effect of incorporating bulky trimethylsilyl substituents rather than H at C_α and $C_{\alpha'}$, and (*ii*) the formal valence electron count at the metal centre. Fig. 6 is a plot of θ against the M–C_α distance for the *o*-xylenediyl-metal and -metalloid complexes **1–5** and **10–23**; the solid lines represent calculated fold angles, assuming the $C_\alpha \cdots C_{\alpha'}$ distance to be constant at 2.96 Å (the value for the simplest of the stannacycles, **1** with M–C_α–C (of C_6H_6) varying from 100 [curve (*a*)] to 109.47° (*d*). While this is an idealised situation, and the $C_\alpha \cdots C_{\alpha'}$ distance does in practice vary considerably, fixing it at 2.96 Å provides a baseline for considering experimental data. The expected trend, in the absence of steric and electronic factors, is an increase in θ with an increase in M–C_α as is geometrically required when incorporating a larger metal atom in an isoleptic five-membered chelate ring containing a smaller metal atom.

Of the *o*-xylenediyl transition-metal derivatives **10–18**, those with an anomalously high 'fold angle' are the electron-deficient (12-electron complexes) **15–17**. These possess metal–hydrocarbyl interactions close to η^4 (**C′**), and hence a significant contribution from the 5,6-dimethylenecyclohexa-1,3-diene resonance form, equation (1). Two complexes having a distinct η^4-*o*-xylenediyl bonding mode have been structurally characterised, namely [$\mathrm{Fe(\eta^4\text{-}LL)(CO)_2(PPh_3)}$][43] and [$\mathrm{Ru(\eta^4\text{-}LL)(PPhMe_2)_3}$].[44] {An interesting variant is the η^4-M bonding to the four C(H) ring carbon atoms in [$\mathrm{Ru(\eta^4\text{-}LL)(\eta\text{-}C_5Me_5)}$].[45]} For the zirconium(IV) complex **14** and for one of the two independent ligands in the tungsten(V) complex **16** (also a 12-electron species) the bonding is intermediate between η^4 and bis(sigma), and this is reflected in their observed relatively high fold angles. For the other complexes listed in Fig. 6 there is a progressive increase in θ with increase in M–C_α terminating in the 17-electron manganese(II) complex **18** which has the shortest M–C_α distance. The *o*-xylenediyl–main group metal complexes based on the ligand $(LL)^{2-}$ are **1**, **3** and **19–21**. These, and some related telluracycles based on 3,4-quinoxalino-1-tellura(II)cyclopentane,[46] are clustered in Fig. 6 at low 'fold angle' with M–C_α almost within the 10° range for the two ligands in the spirobicycle **3**, the 'error bar' associated with the 'fold angle'. Each of the bis(trimethylsilyl)-*o*-xylenediyl $(L'L')^{2-}$ stannacycles **2**, **4** and **5** has a slightly greater 'fold angle' than its $(LL)^{2-}$ counterpart. Here θ might have been expected to depend on whether the $SiMe_3$ substituents are disposed axially (*i.e.* with the silicons on the opposite sides of the ligand plane to that of tin) or equatorially (*i.e.* the converse); the former situation might have been expected to result in greater crowding within the ligand, thereby tending to flatten it and draw the tin atom more closely to the ligand plane, consistent with the present results, although in the case of **4** interligand effects may be significant.

Experimental

General procedures have been described in Part 1.[2] Proton and $^{13}C\text{-}\{^1H\}$ NMR spectra were recorded in C_6D_6, unless otherwise stated, on Varian T60 and JEOL PFT 100 spectrometers, respectively. Synthetic procedures for the new compounds are given below. The $MgCl_2$-free derivative of the diGrignard reagent of 1,2-bis(chloromethyl)benzene **6**,[2,4] [Li(tmen)]$_2$[*o*-$C_6H_4\{CH(SiMe_3)\}_2$] **7**[34] $SnCl_2Ph_2$,[47] and $Sn(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2$[10] were prepared according to literature methods.

Preparations.—[$\mathrm{Sn(CH_2C_6H_4CH_2}$-*o*$)\mathrm{Ph_2}$] **1**. A solution of $SnCl_2Ph_2$ (2.21 g, 6.4 mmol) in OEt_2 (100 cm^3) was added dropwise at −78 °C to a stirred suspension of [$\mathrm{Mg(CH_2C_6H_4CH_2}$-*o*)(thf)] **6** (1.29 g, 6.4 mmol) in OEt_2 (10 cm^3). The mixture was allowed to warm to room temperature and was stirred for 12 h. A white precipitate was filtered off and volatiles were removed from the filtrate *in vacuo*. The residue was dissolved in OEt_2 (50 cm^3) and cooled to −40 °C to afford white crystals of *complex* **1** (0.92 g, 38%) (Found: C, 63.7; H, 4.7. $C_{20}H_{18}Sn$ requires C, 63.7; H, 4.8%), m.p. 55 °C. NMR: ^1H, δ 2.52 [s, 4 H, CH_2, $^2J(^{119}Sn\text{-}^1H)$ 20 Hz] and 7.15 (m, 4 H, C_6H_4); ^{13}C, δ 17.8 (CH_2), 125.8 and 129.3 (C_b and C_c, not separately assigned), 142.7 (C_a), 109.8, 129.0, 131.4 and 137.1 (C_6H_5). Mass spectrum: *m*/*z* 378, $[P]^+$; 301, $[P - Ph]^+$; and 104, $[C_8H_8]^+$.

meso-[$\mathrm{Sn\{CH(SiMe_3)C_6H_4CH(SiMe_3)}$-*o*$\}\mathrm{Ph_2}$] **2**. Diethyl ether (50 cm^3) was added to a mixture of $SnCl_2Ph_2$ (0.58 g, 1.7 mmol) and the organolithium reagent **7** (0.85 g, 1.7 mmol) at −78 °C. The stirred mixture was rapidly warmed to room temperature, and after *ca.* 1 h volatiles were removed *in vacuo*. The residue was extracted into pentane (100 cm^3), filtered, concentrated (to *ca.* 50 cm^3), and cooled to −40 °C yielding colourless crystals which were recrystallised (C_5H_{12} at −40 °C) and identified as *complex* **2** (0.55 g, 62%) (Found: C, 60.0; H, 6.7. $C_{26}H_{34}Si_2Sn$ requires C, 59.9; H, 6.6%), m.p. 85 °C. NMR: ^{1}H, δ 0.13 (s, 18 H, $SiMe_3$), 2.34 (s, 2 H, SiCH), 7.10 (m, 10 H, C_6H_5) and 7.36 (m, 4 H, C_6H_4); ^{13}C, δ 1.4 ($SiMe_3$), 23.8 (SiCH), and 130.6 (C_b and C_c, not separately assigned), 145.0 (C_a), 129.0, 136.9, 138.1 and 139.3 (C_6H_5). Mass spectrum: *m/z* 521, $[P]^+$; 506, $[P - Me]^+$; 444, $[P - Ph]^+$; 356; 298; and 196.

$[Sn(CH_2C_6H_4CH_2\text{-}o)_2]$ **3**. A solution of $SnCl_4$ (2.69 g, 10 mmol) in OEt_2 (100 cm^3) was added slowly to a stirred suspension of $[Mg(CH_2C_6H_4CH_2\text{-}o)(thf)]$ **6** (4.14 g, 20 mmol) in OEt_2 (30 cm^3) at −78 °C. The mixture was warmed to room temperature and stirred overnight. Filtration and removal of volatiles *in vacuo* from the filtrate afforded a white solid which was extracted into OEt_2 (100 cm^3). Cooling to −40 °C yielded colourless crystals of *complex* **3** (1.04 g, 31%) (Found: C, 58.6; H, 4.95. $C_{16}H_{16}Sn$ requires C, 58.8; H, 4.9%), m.p. 171 °C (decomp.). NMR: ^{1}H, δ 2.21 [s, 8 H, CH_2, $^2J(^{119}Sn-^1H)$ 20 Hz] and 7.10 (m, 8 H, C_6H_4); ^{13}C, δ 16.9 (CH_2), 125.6 and 131.2 (C_b and C_c, not separately assigned) and 142.8 (C_a). Mass spectrum: *m/z* 328, $[P]^+$; 224, $[P - C_8H_8]^+$; and 104, $[C_8H_8]^+$.

$[Sn\{meso\text{-}CH(SiMe_3)C_6H_4CH(SiMe_3)\text{-}o\}_2]$ **4**. Diethyl ether (50 cm^3) was added to a stirred mixture of $SnCl_4$ (0.5 g, 1.93 mmol) and the organolithium reagent **7** (2.15 g, 4.9 mmol) at 30 °C. After *ca.* 1 h at 30 °C volatiles were removed *in vacuo* and the residue was extracted into pentane (200 cm^3); the extract was filtered, and the filtrate concentrated (to *ca.* 20 cm^3) and cooled (−40 °C) to yield colourless crystals of *complex* **4** (0.9 g, 76%) (Found: C, 54.7; H, 7.9. $C_{28}H_{48}Si_4Sn$ requires C, 54.6; H, 7.8%), m.p. 115 °C. NMR: ^{1}H, δ 0.03 (s, 18 H, $SiMe_3$), 0.18 (s, 18 H, $SiMe_3$), 1.75 (s, 2 H, SiCH), 2.58 (s, 2 H, SiCH) and 6.97 (m, 8 H, C_6H_4); ^{13}C, δ 1.4, 2.6 ($SiMe_3$), 26.3, 28.1 (SiCH) 124.9 and 130.8 (C_b and C_c, not separately assigned) and 143.8 (C_a). Mass spectrum: *m/z*, 616, $[P]^+$; 368, $[P - C_8H_6(SiMe_3)_2]^+$; and 353.

$[\{Sn\{meso\text{-}CH(SiMe_3)C_6H_4CH(SiMe_3)\text{-}o\}_4]$ **5**. *Method* 1. Diethyl ether (50 cm^3) was added to a mixture of $SnCl_4$ (0.5 g, 1.93 mmol) and the organolithium reagent **7** (1.90 g, 3.85 mmol) at −78 °C. The stirred mixture was slowly (*ca.* 1 h) warmed to room temperature and stirring was continued for 1 h. Volatiles were removed *in vacuo* and the residue was extracted into pentane (200 cm^3); the extract was filtered and the filtrate concentrated (to *ca.* 100 cm^3) and cooled to −40 °C to give crystals of *complex* **5** (0.15 g, 14%) (Found: C, 44.4; H, 6.85. $C_{14}H_{24}Si_2Sn$ requires C, 45.8; H, 6.60%), m.p. 210 °C (decomp.). ^{1}H NMR: δ 0.13 (s, 18 H, $SiMe_3$), 3.07 (s 2, H, SiCH), and 7.17 (m, 4 H, C_6H_4). Mass spectrum: *m/z*, 368, $[P]^+$; 353, $[P - Me]^+$; and 248, $[C_8H_6(SiMe_3)_2]^+$. Further concentration of the mother-liquor (to *ca.* 50 cm^3) and cooling (−40 °C) yielded complex **4** (0.62 g, 52%).

Method 2 (*by* Dr. A. J. Thorne). The organolithium reagent **7** (1.64 g, 3.31 mmol) was added over 1 h to a stirred and cooled (0 °C) suspension of $Sn(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2$ (1.85 g, 3.31 mmol) in OEt_2 (50 cm^3). The mixture slowly became dark brown and a yellow precipitate was formed. After *ca.* 45 min the mixture was warmed to room temperature and stirring was continued for *ca.* 12 h. The yellow precipitate was filtered off, washed with OEt_2 (2 × 5 cm^3), dried *in vacuo*, and identified as complex **5** (0.53 g, 44%).

$[Si(CH_2C_6H_4CH_2\text{-}o)Me_2]$ **8**. 1,2-Dibromoethane (0.2 cm^3) was added to a suspension of magnesium powder (1.5 g, 61.7 mmol) in thf (10 cm^3). The mixture was warmed until gas (C_2H_4) evolution was evident, whereafter the mixture was stirred for 5 min. More thf (10 cm^3) was added followed by $SiCl_2Me_2$ (1.98 g, 15.3 mmol). 1,2-Bis(chloromethyl)benzene (2.60 g, 14.9 mmol) in thf (40 cm^3) was slowly added to this mixture at such a rate as to maintain the temperature close to 40 °C. Stirring was continued overnight at room temperature. Volatiles were removed *in vacuo*, and the residue was extracted into hexane (100 cm^3). The filtrate was concentrated and distilled to yield the colourless liquid *compound* **8** (1.93 g, 78%), b.p. 25 °C (0.3 mmHg, *ca.* 40 Pa) (Found: C, 73.1; H, 8.7. $C_{10}H_{14}Si$ requires C, 74.0; H, 8.7%); NMR ($CDCl_3$): ^{1}H, δ − 0.24 (s, 6 H, CH_3), 1.55 (s, 4, H, CH_2) and 6.52 (m, 4 H, C_6H_4); ^{13}C, δ −2.2 (CH_3), 21.4 (CH_2), 125.9 and 129.5 (C_b and C_c, not separately assigned) and 142.4 (C_a). Mass spectrum: *m/z* 162, $[P]^+$; and 147, $[P - CH_3]^+$.

meso-$[Si\{CH(SiMe_3)C_6H_4CH(SiMe_3)\text{-}o\}Me_2]$ **9**. The compound $SiCl_2Me_2$ (0.60 g, 4.7 mmol) was added to a stirred solution of the organolithium reagent **7** (2.0 g, 4 mmol) in OEt_2 (50 cm^3) at *ca.* 20 °C. After *ca.* 1 h volatiles were removed *in vacuo* and the residue was extracted into pentane (50 cm^3). The filtrate was concentrated (to *ca.* 5 cm^3) and cooled to −40 °C to yield colourless crystals of *compound* **9** (8.06 g, 65%) (Found: C, 61.5; H, 9.7. $C_{16}H_{30}Si_3$ requires C, 62.7; H, 9.85%). NMR ($CDCl_3$): ^{1}H, δ 0.07 (s 3, H, $SiMe_2$), 0.13 (s, 18 H, $SiMe_3$), 0.17 (s, 3 H, $SiMe_2$) and 6.95 (m, 4 H, C_6H_4); ^{13}C, δ −1.3 ($SiMe_2$, other not observed), 1.2 ($SiMe_3$), 24.2 (SiCH), 127.3 and 130.6 (C_b and C_c, not separately assigned) and 135.4 (C_a). Mass spectrum: *m/z*, 306, $[P]^+$; 218, $[P - SiMe_4]^+$; and 203.

Crystallography.—Unique data sets for each of the complexes **1**–**5** were measured at 295 K using Syntex $P\bar{1}$ and $P2_1$ four-circle diffractometers in conventional 2θ–θ scan mode. Graphite-monochromated Mo-Kα radiation sources were used (λ = 0.7106$_9$ Å). *N* Independent reflections were measured within a $2\theta_{max}$ limit determined by the scope of the data; N_o with $I > 3\sigma(I)$ were considered 'observed' and used in the (basically) 9 × 9 block-diagonal least-squares refinement after solution of the structures by the heavy-atom method and the application of an analytical absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were refined for complex **1** and constrained in the other cases at estimated values. At convergence, *R* and *R′* on |*F*| are quoted. Reflection weights were $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral atom complex scattering factors were used;[48] computation used the X-Ray 76 program system[49] implemented by S. R. Hall on a Perkin-Elmer 3240 computer. Specimens were mounted in sealed capillaries for the crystallographic work.

Abnormal features. Solvent molecules present in compound **2** were disordered and modelled as carbon atoms in constrained sites obtained from difference maps with population 0.5.

Crystal data. $[Sn(LL)Ph_2]$ **1**. $C_{20}H_{18}Sn$, $M = 377.1$, monoclinic, space group $P2_1/n$ [C_{2h}^5, no. 14 (variant)], $a = 22.039(8)$, $b = 12.603(4)$, $c = 5.956(2)$ Å, $\beta = 92.61(3)°$, $U = 1653(1)$ Å^3, D_c ($Z = 4$) = 1.51 g cm^{-3}, $F(000) = 752$, $\mu_{Mo} = 14.4$ cm^{-1}. Specimen 0.12 × 0.18 × 0.23 mm, $2\theta_{max} = 50°$; N, N_o = 2916, 2149; R, R' = 0.023, 0.029.

$[Sn(L'L'\text{-}meso)Ph_2]$ **2**·$0.5C_6H_{14}$. $C_{29}H_{41}Si_2Sn$, $M = 564.5$, monoclinic, space group $C2/c$ (C_{2h}^6, no. 15), $a = 27.41(1)$, $b = 12.931(4)$, $c = 19.57(1)$ Å, $\beta = 118.82(3)°$, $U = 6076(3)$ Å^3, D_c ($Z = 8$) = 1.23 g cm^{-3}, $F(000) = 2344$, $\mu_{Mo} = 8.8$ cm^{-1}. Specimen 0.24 × 0.04 × 0.20 mm, $2\theta_{max} = 55°$; N, N_o = 6965, 4047; R, R' = 0.037, 0.047.

$[Sn(LL)_2]$ **3**. $C_{16}H_{16}Sn$, $M = 327.0$, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), $a = 11.032(8)$, $b = 8.815(5)$, $c = 13.533(8)$ Å, $\beta = 93.64(5)°$, $U = 1313(1)$ Å^3, D_c ($Z = 4$) = 1.65 g cm^{-3}, $F(000) = 648$, $\mu_{Mo} = 18.0$ cm^{-1}. Specimen 0.45 × 0.45 × 0.35 mm, $2\theta_{max} = 65°$; N, N_o = 4462, 3387; R, R' = 0.048, 0.061.

$[Sn(L'L'\text{-}meso)_2]$ **4**. $C_{28}H_{48}Si_4Sn$, $M = 615.8$, monoclinic, space group $P2_1/n$, $a = 17.955(4)$, $b = 20.533(4)$, $c = 9.086(2)$ Å, $\beta = 94.21(2)°$, $U = 3341(1)$ Å^3, D_c ($Z = 4$) = 1.22 g cm^{-3}, $F(000) = 1288$, $\mu_{Mo} = 9.3$ cm^{-1}. Specimen cuboid ≈ 0.4 mm, $2\theta_{max} = 45°$; N, N_o = 4402, 3184; R, R' = 0.036, 0.045.

$[\{Sn(L'L'\text{-}meso)\}_4]$ (*Sn*–*Sn*) **5**. $C_{56}H_{96}Si_8Sn_4$, $M = 1468.8$, tetragonal, space group $I\bar{4}$ (S_4^2, no. 82), $a = 17.684(8)$, $c = 11.239(7)$ Å, $U = 3515(3)$ Å^3, D_c ($Z = 2$) = 1.39 g cm^{-3},

$F(000) = 1488$, $\mu_{\text{Mo}} = 14.7\ \text{cm}^{-1}$. Specimen 0.12 × 0.18 × 0.33 mm, $2\theta_{\text{max}} = 40°$; $N, N_o = 882, 615$; $R, R' = 0.066, 0.067$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, solvent coordinates for **2**, thermal parameters and remaining bond lengths and angles.

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