Structural Studies in Main-group Chemistry. Part VI.[1] Crystal and Molecular Structure of 2,2'-Bipyridyldichlorodiphenyltin

By **Philip G. Harrison,*** **Trevor J. King,** and **John A. Richards,** Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD

The crystal structure of the title compound has been determined by single-crystal X-ray diffraction. Crystals are monoclinic, space group $P2_1/n$, with $Z = 4$ in each unit cell of dimensions $a = 9\cdot5208(24)$, $b = 13\cdot1583(36)$, $c = 16\cdot5437(40)$ Å, $\beta = 93\cdot600(17)°$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares methods to R 0·049 for 1896 independent reflections. The tin atoms are octahedrally co-ordinated by a bidentate 2,2'-bipyridyl residue, two *cis*-chlorine atoms, and two phenyl groups which are mutually *trans*. The two tin–carbon bond distances are identical [mean r(Sn–C) 2·152 Å], as are the two tin–chlorine bond distances [mean r(Sn–Cl) 2·509 Å]. The bipyridyl group is not planar, one C_5H_4N ring being twisted 4·2° with respect to the other, with the two Sn–N distances unequal (2·344 and 2·375 Å). The bond angles subtended at tin by adjacent ligands all fall in the range 85·5—95·6°. The two phenyl groups are not exactly *trans* (C–Sn–C 173·5°), and are not equivalent. The plane of one phenyl group almost exactly bisects the Cl–Sn–Cl and N–Sn–N bond angles, whilst the other is rotated 79·5° with respect to the first.

THE stereochemistry adopted by five- and six-co-ordinate (organo)tin complexes and complex ions has been the subject of much investigation. In the absence of unequivocal structural data for the solid state from X-ray diffraction studies, it has been the usual convention to infer the stereochemistry from the application of spectroscopic techniques such as far i.r., Raman, Sn-119m Mössbauer, n.m.r., and dipole-moment studies. The combinations of far-i.r. and Raman data with activity predicted by group theoretical calculations, and the magnitude of the Mössbauer quadrupole splitting with the rather naïve (but surprisingly effective) point-charge calculation have been employed with apparent success. We have previously [2] applied the former method to species such as $Me_3SnX_2^-$ (I), $Me_2SnX_3^-$ (II), and $Me_2SnX_4^{2-}$ (III; X = Cl, Br, or I) and found the far-i.r. data to be consistent with the X-ray diffraction determined structures for the two five-co-ordinated species.[3,4] The stereochemistry of six-co-ordinate diorganotin species is intriguing, and depends on the nature (both steric and electronic) of the groups attached to tin. Here the value of the Mössbauer quadrupole splitting, Δ, can be a guide as to the disposition of the two organic groups about tin. Point-charge calculations show that for the two isomers, *cis*- and *trans*-SnX_2Y_4, Δ_{trans} is $2\Delta_{cis}$. By use of this criterion, Fitzsimmons *et al.*[5] have postulated the *trans*-structure for the bipyridyl and phenanthroline complexes of the diorganotin dihalides and the complex anions $R_2SnCl_4^{2-}$ (R = Me or Ph) and the *cis*-configuration for diorganotin bis(oxinates). With some electronegative substituents, however, the stereochemistry adopted is dependent on the organic group attached to tin. Thus, whilst the bipyridyl and phenanthroline adducts of dialkyltin di-isothiocyanates and dialkyltin bis(oxinates) and bis(acetylacetonates) exhibit large

quadrupole splittings (*ca.* 4 mm s^{-1}) and hence appear to possess the *trans*-configuration, the corresponding diphenyltin derivatives have only small quadrupole splittings (*ca.* 2 mm s^{-1}) characteristic of *cis*-geometry. Available structural data illustrate that a simple division into *cis*- and *trans*-geometries is far from an adequate representation of reality. Both dimethyltin dichloride (Δ 3·55 mm s^{-1}) [6] and dimethyltin bis(dimethyldithiocarbamate) [Δ 3·14 mm s^{-1} for $Me_2Sn(S_2CNEt_2)_2$] [7] have structures which in the solid phase are best described as intermediate between tetrahedral and octahedral, the Me–Sn–Me bond angles being only 123·5 (ref. 6) and 136° (ref. 8) respectively.

A problem of equal magnitude is the rationalisation of known stereochemistry. This is exemplified by the two closely related systems Me_2SnCl_2,L_2 (L = dimethyl sulphoxide or pyridine N-oxide). Whilst both have a *trans*-arrangement of methyl groups, the former possesses *cis* chlorine atoms and sulphoxide groups but the latter has the totally *trans*-configuration.

In order to gain insight into the factors controlling the structure and bonding involved, we are determining the crystal structures of a series of model compounds. We now report the X-ray crystal structure of the bipyridyl complex of diphenyltin dichloride, Ph_2SnCl_2-$(C_{10}H_8N_2)$.

EXPERIMENTAL

Crystals of Ph_2SnCl_2(bipy) suitable for intensity measurements were prepared by addition of a benzene solution of 2,2-bipyridyl to a benzene solution of diphenyltin dichloride, and were recrystallized from hot benzene. A crystal was mounted directly on a fine glass fibre, and was used for both cell data and subsequent intensity measurements.

Crystal Data.—$C_{22}H_{18}Cl_2N_2Sn$, $M = 500\cdot00$, $a = 9\cdot5208(24)$, $b = 13\cdot1583(36)$, $c = 16\cdot5437(40)$ Å, $\beta = 93\cdot600(17)°$, $U = 2068\cdot46$ Å^3, $Z = 4$, $F(000) = 992$.

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Space group $P2_1/n$ by systematic absences ($h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$).

The space group and initial cell parameters were determined from zero- and first-layer Weissenberg photographs obtained on an equi-inclination Weissenberg camera. The cell parameters were further refined and relative intensities were collected with Mo-K_α radiation on a Hilger and Watts single-crystal computer-controlled four-circle diffractometer Y 290. A crystal of cross-section $ca.$ 0.4×0.5 mm was used for the collection of intensity data up to θ $29.4°$. Each reflection was counted for 30 s and the associated two background counts for 10 s. The reflections were brought to the same relative intensities by reference re-

to 0.070 and a further four cycles of block-diagonal aniso-tropic and four cycles of full-matrix anisotropic least-squares refinement further reduced it to 0.052. A weight-ing scheme: $w = 1/[1 + (F_0 - 30)/23.3]^2$, was applied, and subsequently the 245 reflections with $F_c < 1/4\ F_0$ were omitted from the least-squares total. The positions of the hydrogen atoms could not satisfactorily be de-termined from a difference map, and although it was possible to estimate their positions, they were not intro-duced. Refinement was terminated after a further 6 cycles of full-matrix anisotropic least-squares, when the shifts were <0.35 for the positional parameters and μ_{ij}. The final value of R was 0.049 and R' $[=\Sigma w\Delta^2/\Sigma w F_0{}^2]$ 0.0068.

TABLE 1

Atomic co-ordinates and thermal parameters ($\times 10^3$), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.1142(8)	0.2540(7)	0.0293(4)	59(5)	67(5)	37(4)	3(4)	−6(3)	5(4)
C(2)	0.1256(9)	0.3570(8)	0.0089(6)	62(5)	80(7)	70(6)	5(5)	0(4)	23(5)
C(3)	0.1335(10)	0.3862(9)	−0.0718(7)	69(6)	94(7)	83(7)	7(5)	−7(5)	33(6)
C(4)	0.1304(11)	0.3087(11)	−0.1327(7)	82(7)	132(11)	66(6)	−7(7)	−16(5)	25(7)
C(5)	0.1187(12)	0.2093(11)	−0.1122(6)	99(7)	127(10)	50(5)	−13(8)	−12(5)	1(7)
C(6)	0.1090(10)	0.1811(8)	−0.0305(5)	83(6)	99(8)	50(5)	−11(5)	−3(4)	−7(5)
C(7)	0.1222(8)	0.1714(6)	0.2808(5)	50(4)	55(4)	52(4)	−3(3)	5(3)	2(4)
C(8)	0.0014(9)	0.1798(7)	0.3264(5)	73(6)	62(5)	58(5)	−5(4)	20(4)	1(4)
C(9)	0.0080(11)	0.1559(8)	0.4077(6)	105(8)	72(6)	60(5)	−8(6)	6(5)	−8(5)
C(10)	0.1345(11)	0.1231(8)	0.4460(6)	93(7)	77(6)	63(6)	−9(6)	9(5)	4(5)
C(11)	0.2516(10)	0.1141(6)	0.4008(5)	90(6)	53(5)	58(5)	−3(5)	2(4)	−1(4)
C(12)	0.2447(9)	0.1391(6)	0.3200(4)	70(5)	52(5)	47(4)	−2(4)	−1(4)	3(4)
C(13)	0.3652(9)	0.3702(6)	0.1919(4)	71(5)	51(4)	53(4)	−1(4)	−3(4)	4(4)
C(14)	0.4990(9)	0.4120(7)	0.1939(5)	61(5)	69(6)	58(5)	−4(4)	−4(4)	3(4)
C(15)	0.6074(10)	0.3492(8)	0.1695(5)	70(6)	75(6)	68(6)	−16(5)	−12(5)	23(5)
C(16)	0.5802(8)	0.2507(7)	0.1464(5)	54(5)	64(5)	72(6)	3(4)	5(4)	11(4)
C(17)	0.4431(7)	0.2133(6)	0.1479(4)	48(3)	55(4)	34(3)	9(4)	1(3)	4(4)
C(18)	0.4058(8)	0.1066(6)	0.1273(4)	59(4)	52(4)	39(4)	4(4)	3(3)	6(3)
C(19)	0.5071(9)	−0.0329(7)	0.1122(5)	71(5)	61(6)	66(5)	22(4)	12(4)	0(4)
C(20)	0.4637(10)	−0.0956(6)	0.0956(4)	87(6)	61(6)	71(6)	14(5)	21(5)	3(5)
C(21)	0.3219(10)	−0.0897(6)	0.0948(5)	93(6)	56(5)	56(5)	9(4)	12(4)	−5(4)
C(22)	0.2267(10)	−0.0150(6)	0.1128(5)	87(6)	52(5)	56(5)	11(4)	−2(4)	1(4)
N(1)	0.3373(6)	0.2726(4)	0.1695(3)	50(3)	40(4)	45(3)	−1(3)	0(2)	−3(3)
N(2)	0.2687(6)	0.0815(4)	0.1291(4)	62(4)	36(3)	50(3)	5(3)	−1(3)	−6(3)
Cl(1)	−0.1005(2)	0.0957(2)	0.1260(1)	52(1)	65(1)	88(1)	−7(1)	−6(1)	−7(1)
Cl(2)	−0.0074(2)	0.3777(2)	0.1891(1)	70(1)	57(1)	72(1)	18(1)	6(1)	−1(1)
Sn	0.10536(5)	0.21238(4)	0.15459(3)	49.7(2)	52.0(2)	51.9(2)	2.4(3)	−2.1(1)	−0.9(3)

flections taken for every hundred reflections recorded, the diffractometer being referenced every two hundred reflections recorded. The background counts were low and were included in the usual manner; intensities varied from 1 to 270,000. Of 3500 intensities, those with a cor-rected count $I < 3\ \sigma\ (I)$ were considered unobserved and were not further used, reducing the total number of re-flections to 2380. These reflections were further reduced to 2141 by eliminating the lower intensity reflections, to enable adequate computer storage for refinement. The intensities were corrected for Lorentz and polarization effects, but not for absorption correction. An approximate absolute scale factor was determined by inspection of the data.

Structure Determination and Refinement.—The positional parameters of the tin atom in the asymmetric unit were obtained from a Patterson synthesis, and were used to phase the initial structure-factor calculation. A Fourier synthesis established the positions of the remaining non-hydrogen atoms of the asymmetric unit, which complied with the chemically expected model. Four cycles of iso-tropic block-diagonal refinement reduced R from 0.749

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

Scattering factors (which were not modified) used in the refinement were those for neutral atoms.[9]

Positional and thermal parameters are listed in Table 1, bond distances and angles in Table 2. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21044 (11 pp., 1 microfiche).*

DISCUSSION

As can be seen from the Figure, the molecule contains octahedrally co-ordinated tin with *trans*-phenyl groups, as expected from the magnitude of the quadrupole splitting (Δ 3.90 mm s^{-1}).[5] The geometry is not ideally octahedral, the C–Sn–C bond angle being only $173.5°$, and the C–Sn–N and C–Sn–Cl angles all falling in the range $85.5—92.9°$. The two Sn–C bond lengths are equal (2.152 Å). Since this is the first Sn–C(Ph) bond distance measured for a six-co-ordinate species, no comparative values are available. The present values are in general larger than those obtained previously for four-co-ordinate compounds, and are of the same

9 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

TABLE 2

Intramolecular distances and angles with estimated
standard deviations in parentheses

(a) Distances (Å)

Sn–C(1)	2·151(7)	C(11)–C(12)	1·37(1)
Sn–C(7)	2·153(8)	C(12)–C(7)	1·37(1)
Sn–N(1)	2·344(6)	N(1)–C(13)	1·36(1)
Sn–N(2)	2·375(6)	N(1)–C(17)	1·34(1)
Sn–Cl(1)	2·511(2)	C(13)–C(14)	1·39(1)
Sn–Cl(2)	2·508(2)	C(14)–C(15)	1·40(1)
C(1)–C(2)	1·40(1)	C(15)–C(16)	1·37(1)
C(2)–C(3)	1·40(1)	C(16)–C(17)	1·40(1)
C(3)–C(4)	1·43(2)	C(17)–C(18)	1·48(1)
C(4)–C(5)	1·36(2)	N(2)–C(18)	1·35(1)
C(5)–C(6)	1·41(1)	N(2)–C(22)	1·35(1)
C(6)–C(1)	1·38(1)	C(18)–C(19)	1·40(1)
C(7)–C(8)	1·42(1)	C(19)–C(20)	1·36(1)
C(8)–C(9)	1·38(1)	C(20)–C(21)	1·39(1)
C(9)–C(10)	1·39(1)	C(21)–C(22)	1·38(1)
C(10)–C(11)	1·39(1)		

(b) Angles (°)

C(1)–Sn–C(7)	173·5(3)	C(10)–C(11)–C(12)	120·9(8)
C(1)–Sn–N(1)	85·5(2)	C(11)–C(12)–C(7)	121·6(8)
C(1)–Sn–N(2)	87·0(2)	C(12)–C(7)–C(8)	117·9(7)
C(1)–Sn–Cl(1)	92·9(2)	Sn–N(1)–C(17)	119·6(4)
C(1)–Sn–Cl(2)	92·4(2)	Sn–N(1)–C(13)	121·0(5)
C(7)–Sn–N(1)	88·3(2)	C(13)–N(1)–C(17)	119·0(6)
C(7)–Sn–N(2)	88·9(2)	N(1)–C(13)–C(14)	123·1(8)
C(7)–Sn–Cl(1)	92·3(2)	C(13)–C(14)–C(15)	116·9(8)
C(7)–Sn–Cl(2)	90·2(2)	C(14)–C(15)–C(16)	120·5(8)
N(1)–Sn–N(2)	69·0(2)	C(15)–C(16)–C(17)	119·2(8)
N(1)–Sn–Cl(1)	160·9(1)	C(16)–C(17)–N(1)	121·2(7)
N(1)–Sn–Cl(2)	95·6(1)	C(16)–C(17)–C(18)	122·7(7)
N(2)–Sn–Cl(1)	92·0(1)	N(1)–C(17)–C(18)	116·1(6)
N(2)–Sn–Cl(2)	164·5(1)	Sn–N(2)–C(18)	118·2(5)
Cl(1)–Sn–Cl(2)	103·5(1)	Sn–N(2)–C(22)	121·8(5)
C(1)–C(2)–C(3)	120·4(9)	N(2)–C(22)–C(21)	121·4(8)
C(2)–C(3)–C(4)	118·5(10)	C(22)–C(21)–C(20)	118·2(8)
C(3)–C(4)–C(5)	120·6(10)	C(21)–C(20)–C(19)	120·9(9)
C(4)–C(5)–C(6)	120·2(10)	C(20)–C(19)–C(18)	118·6(8)
C(5)–C(6)–C(1)	120·3(10)	C(19)–C(18)–N(2)	120·9(7)
C(6)–C(1)–C(2)	120·0(8)	C(19)–C(18)–C(17)	122·6(7)
C(7)–C(8)–C(9)	120·7(8)	C(17)–C(18)–N(2)	116·4(6)
C(8)–C(9)–C(10)	120·0(9)	C(18)–N(2)–C(22)	120·0(7)
C(9)–C(10)–C(11)	118·8(9)		

TABLE 3

(a) Equations of weighted least-squares planes, in the form
$PI + QJ + RK = S$, where I, J, K are orthogonal co-ordinates
related to the monoclinic co-ordinates by: $I = X + Z \cos\beta$,
$J = Y$, $K = Z \sin\beta$. Deviations * (Å) of atoms from the planes
are given in square brackets

	P	Q	R	S
Plane (1): C(13), C(17), N(1)				
	0·10739	−0·29324	0·94999	1·93321

[C(16) −0·0281, C(14) 0·0073, C(15) −0·0200, Sn −0·2374]

	P	Q	R	S
Plane (2): C(18), C(22), N(2)				
	0·07893	−0·22871	0·97029	2·01403

[C(19) 0·0563, C(20) 0·0501, C(21) 0·0088, Sn −0·1100]

	P	Q	R	S
Plane (3): Cl(1), Cl(2), Sn				
	−0·02463	−0·26534	0·096384	1·69793

[N(1) −0·0265, N(2) 0·0120]

	P	Q	R	S
Plane (4): C(1)—(6)				
	0·99209	−0·07474	0·1085	0·84061

[C(1) 0·0068, C(2) 0, C(3) −0·0050, C(4) 0·0034, C(5) 0·0032,
C(6) 0·0084, Sn 0·0438]

	P	Q	R	S
Plane (5): C(7)—(12)				
	0·23144	0·94599	0·22704	3·38875

[C(7) 0, C(8) −0·0027, C(9) 0·0004, C(10) 0·0047, C(11)
−0·0075, C(12) 0·0052, Sn 0·0293]

(b) Angles (°) between planes

(1)—(2) 4·2, (1)—(3) 7·77, (1)—(4) 77·04, (1)—(5) 87·89,
(2)—(3) 6·31, (2)—(4) 78·86, (2)—(5) 88·73, (3)—(4) 84·69,
(3)—(5) 87·83, (4)—(5) 79·53

* According to V. Schomaker, J. Waser, R. E. Marsh, and
G. Bergman, *Acta Cryst.*, 1959, **12**, 600.

TABLE 4

Comparison of bond distances (Å) in Ph_2SnCl_2(bipy)
with those in related compounds

(a) Sn–C(Ph) bonds

Compound	Geometry †	Distance
Ph_2SnCl_2(bipy) *	Oct	2·152(8)
Ph_4Sn [a,b]	Tet	2·14
Ph_3SnCl [c]	Tet	2·122(22)
Ph_2SnCl_2 [d] ‡	Tet	(i) 2·105(5), 2·119(5)
		(ii) 2·112(6), 2·118(5)
PhMe$_2$Sn–CPh:CPh·–PhC:PhC–X	Tet	(i) X = Cl, 2·116(9)
		(ii) X = Br, 2·141(13)
$Ph_2ISn[CH_2]_4SnIPh_2$ [f]	Tet	2·14(2), 2·16(2)
$Ph_2Sn·[O·CMe·O]_2·SnPh_2$ [g]	Trig bipy	2·15(2)
$Ph_3Sn(ONPh·CO·Ph)$ [h]	Trig bipy	Ax 2·18
		Eq 2·13, 2·14

(b) Sn–Cl bonds

Ph_2SnCl_2(bipy) *	Oct	2·508(2)
		2·511(2)
Ph_3SnCl [c]	Tet	2·318(15)
Ph_2SnCl_2 [d] ‡	Tet	(i) 2·336(2), 2·353(2)
		(ii) 2·336(2), 2·357(2)
Me_3SnCl(py) [i]	Trig bipy	2·42(4)
$Me_3SnCl(Ph_3PCH·CO·Me)$ [j]	Trig bipy	2·565
Me_2SnCl_2 [k]	Tet §	2·41(4) bridged, 3·54(5)
$Me_2SnCl_2(DMSO)_2$ [l]	Oct	2·48(1)
		2·53(1)
Me_2SnCl_2(py-O)$_2$ [m]	Oct	2·584(10)

(c) Sn–N bonds

Ph_2SnCl_2(bipy) *	Oct	2·344(6)
		2·375(6)
$Sn(NMe_2)_4$ [n]	Tet	2·045
$(Me_3Sn)_2N_2C$ [o]	Trig bipy	2·47
$Me_3SnN(CN)_2$ [p]	Trig bipy	2·336(9)
$SnCl_4(MeCN)_2$ [q]	Oct	2·33(2)
Me_2Sn(oxin)$_2$ [r]	Dist oct	2·31(1)
		2·38(1)
$[Me_2SnCl$(ter)$]^+$ [s]	Dist oct	2·29(3), 2·33(4)
		2·41(3)
$Me_2Sn(NCS)_2$(ter) [t]	Pent bipy	(i) Sn–NCS: 2·283(4)
		(ii) Sn–ter 2·479(3),
		2·497(3), 2·570(4)
Cl_2Sn^{IV}(phth) [u]	Oct	2·050(3)

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* This work.   † Oct = octahedral, Tet = tetrahedral, Trig
bipy = trigonal bipyramid, Dist = distorted, Pent bipy =
pentagonal bipyramid;   oxin = 8-hydroxyquinolato, ter =
terpyridyl, phth = phthalocyaninato.   ‡ The asymmetric unit
of Ph_2SnCl_2 contains two crystallographically different
molecules.   § Distorted towards octahedral.

magnitude as for the two five-co-ordinate derivatives. $Ph_4Sn_2(O_2CMe)_2$ (ref. 10) and $Ph_3SnONPh \cdot CO \cdot Ph$.[11]

The bipyridyl residue, the tin atom, and the two chlorine atoms are essentially coplanar (Table 3),
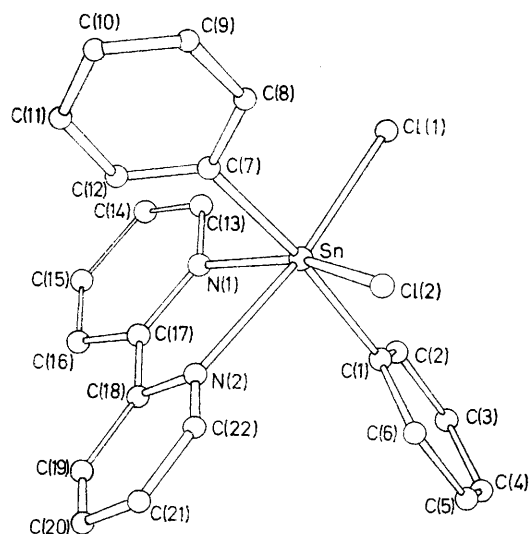
Structure of the molecule, showing the atom numbering used in the analysis

although the two rings of the bipyridyl are mutually twisted *ca.* 4·2°. Mutual repulsion of the two chlorine atoms opens the Cl–Sn–Cl bond angle to 103·5°, whilst N–Sn–N is only 69·0°.

The Sn–Cl distances are also equal (2·509 Å) and are substantially bigger than those in tetrahedral diphenyltin dichloride (2·34 and 2·36 Å), but within the range of values determined for other six-co-ordinate diorganotin dichloride complexes (Table 4). The Sn–N distances (2·344 and 2·375 Å) are also of a similar magnitude to those for other octahedral complexes, although the distance in octahedral dichloro(phthalocyaninato)tin(IV) is only 2·05 Å.

Unlike dimethyltin(IV) derivatives, where an increase in co-ordination number from four to six is accompanied by an increase in Sn–Cl bond distances but a decrease in the Sn–C bond distance as tin $5s$ electron density is preferentially concentrated in bonds to carbon, both Sn–Cl and Sn–C bond distances are increased in the complex formation between Ph_2SnCl_2 and bipyridyl. Presumably this difference is due to the increased electronegativity of the phenyl relative to the methyl group.

An unusual feature of the structure is the disposition of the two phenyl groups, which are not equivalent. The plane of one almost exactly bisects the Cl–Sn–Cl and N–Sn–N bond angles, whilst the plane of the other makes an angle of 79·5° with the first.

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