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Structure of Bromo(4-iodo-1,2,3,4-tetraphenyl-1,3-butadienyl)diphenyltin(IV)

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Abstract. [SnBr(C_6H_5)$_2$($C_{28}H_{20}I$)], $M_r = 836 \cdot 19$, triclinic, $P\bar{1}$, $a = 10 \cdot 336\,(4)$, $b = 10 \cdot 582\,(5)$, $c = 16 \cdot 615\,(8)$ Å, $\alpha = 94 \cdot 65\,(4)$, $\beta = 98 \cdot 80\,(3)$, $\gamma = 108 \cdot 23\,(4)°$, $V = 1690\,(1)$ Å^3, $Z = 2$, $D_x = 1 \cdot 643$ g cm^{-3}, λ(Mo $K\alpha$) $= 0 \cdot 71073$ Å, $\mu = 27 \cdot 90$ cm^{-1}, $F(000) = 816$, $T = 298\,(2)$ K, $R = 0 \cdot 032$ for 4718 unique observed reflections. The butadiene is σ-bound to the Sn atom and the pendent I substituent of the butadiene is involved in a intramolecular interaction with the Sn, having Sn···I $= 3 \cdot 8835\,(5)$ Å (van der Waals radii for Sn and I are commonly $2 \cdot 2$ and $2 \cdot 0$ Å respectively). Whether this Sn···I interaction is attractive (bonding) or repulsive (steric), the presence of the I atom distorts the Sn coordination sphere from the ideal tetrahedron towards a trigonal bipyramid. The axial Br—Sn···I angle is $168 \cdot 45\,(2)°$. Like all 1,2,3,4-tetraphenylbutadienes, this one is non-planar with $72 \cdot 3\,(1)°$ between the two olefinic planes. The C1—C2—C3—C4 torsion angle of the butadiene backbone is $78 \cdot 7\,(5)°$. The phenyl groups on the 1, 2, 3 and 4 positions are canted with respect to their olefinic planes and the dihedral angles are $76 \cdot 7\,(2)$, $-46 \cdot 3\,(3)$, $57 \cdot 1\,(4)$ and $69 \cdot 8\,(3)°$, respectively.

Experimental. The title complex was prepared by the reaction of elemental iodine with hexaphenylstannole and tetrahydrofuran at 195 K under a nitrogen atmosphere and recrystallized from ether/trichloromethane. It should be noted that the presence of the Br atom was unexpected, as Br was not intentionally a part of the preparation and most likely part of an unknown impurity.

Colorless prismatic crystals, $0 \cdot 25 \times 0 \cdot 25 \times 0 \cdot 40$ mm; Nonius CAD-4 diffractometer, monochromated Mo $K\alpha$; $\theta/2\theta$ scans; $3 \leq 2\theta \leq 50°$; lattice parameters from 25 high-angle reflections ($2\theta > 20°$); Gaussian-integration absorption corrections applied with transmission coefficients $0 \cdot 40$–$0 \cdot 48$; $0 \leq h \leq 12$, $-12 \leq k \leq 12$, $-19 \leq l \leq 19$; three standard reflections fluctuated $2 \cdot 7\%$; 6093 total reflections, 5956 unique, 4718 observed with $I_o \geq 3 \cdot 0\sigma(I)$. Patterson methods; full-matrix refinement *via* *SHELX*76 (Sheldrick, 1976) on F's, minimizing $\sum w(|F_o| - |F_c|)^2$; all C atoms anisotropic; H atoms were placed in calculated positions (C—H $= 1 \cdot 08$ Å) and held invariant with U(H) set to $0 \cdot 08$ Å^2. Number of parameters varied was 388. For observed reflections $R = 0 \cdot 032$, $wR = 0 \cdot 045$, $S = 1 \cdot 66$, $w = (\sigma_F)^{-2}$. In a

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{eq}(\text{Å}^2)$
I	0·98303 (3)	−0·50462 (4)	0·83177 (2)	0·0605 (2)
Br	0·83220 (7)	0·02066 (6)	0·72440 (4)	0·0658 (3)
Sn	0·92511 (3)	−0·17500 (3)	0·77500 (2)	0·0381 (1)
C1	0·8289 (4)	−0·3403 (5)	0·6775 (3)	0·038 (2)
C2	0·7464 (4)	−0·4617 (5)	0·6860 (3)	0·038 (2)
C3	0·6963 (4)	−0·4986 (4)	0·7641 (3)	0·036 (2)
C4	0·7696 (4)	−0·5265 (4)	0·8287 (3)	0·037 (2)
C5	1·1398 (5)	−0·1006 (5)	0·7636 (3)	0·043 (2)
C6	1·1746 (6)	−0·0452 (7)	0·6946 (4)	0·070 (3)
C7	1·3115 (7)	−0·0021 (7)	0·6842 (4)	0·082 (3)
C8	1·4125 (6)	−0·0109 (6)	0·7429 (5)	0·073 (3)
C9	1·3802 (6)	−0·0637 (8)	0·8129 (5)	0·082 (3)
C10	1·2432 (6)	−0·1100 (6)	0·8219 (4)	0·063 (2)
C11	0·8797 (5)	−0·1731 (4)	0·8954 (3)	0·042 (2)
C12	0·9681 (5)	−0·1950 (5)	0·9612 (3)	0·050 (2)
C13	0·9388 (6)	−0·1868 (6)	1·0414 (3)	0·062 (2)
C14	0·8253 (7)	−0·1547 (6)	1·0546 (4)	0·064 (2)
C15	0·7376 (6)	−0·1335 (6)	0·9912 (4)	0·066 (2)
C16	0·7647 (5)	−0·1408 (5)	0·9113 (3)	0·052 (2)
C17	0·7211 (4)	−0·5781 (5)	0·9021 (3)	0·039 (2)
C18	0·6866 (5)	−0·4976 (5)	0·9585 (3)	0·047 (2)
C19	0·6444 (5)	−0·5466 (6)	1·0287 (3)	0·057 (2)
C20	0·6333 (6)	−0·6747 (6)	1·0415 (3)	0·060 (2)
C21	0·6648 (6)	−0·7579 (6)	0·9844 (4)	0·062 (2)
C22	0·7099 (6)	−0·7093 (5)	0·9152 (3)	0·053 (2)
C23	0·5448 (4)	−0·5168 (5)	0·7580 (3)	0·040 (2)
C24	0·4508 (5)	−0·6406 (6)	0·7636 (3)	0·056 (2)
C25	0·3092 (6)	−0·6592 (8)	0·7481 (4)	0·077 (3)
C26	0·2628 (6)	−0·554 (1)	0·7294 (4)	0·082 (3)
C27	0·3536 (7)	−0·4286 (8)	0·7264 (4)	0·077 (3)
C28	0·4979 (5)	−0·4135 (6)	0·7408 (4)	0·058 (2)
C29	0·8844 (5)	−0·3076 (5)	0·6011 (3)	0·043 (2)
C30	0·8387 (6)	−0·2252 (6)	0·5509 (3)	0·064 (2)
C31	0·8983 (8)	−0·1898 (7)	0·4828 (4)	0·082 (3)
C32	1·0001 (9)	−0·2361 (9)	0·4639 (4)	0·092 (4)
C33	1·0458 (7)	−0·3174 (7)	0·5127 (4)	0·076 (3)
C34	0·9892 (6)	−0·3538 (6)	0·5820 (3)	0·057 (2)
C35	0·6895 (5)	−0·5778 (5)	0·6187 (3)	0·042 (2)
C36	0·6323 (5)	−0·5614 (6)	0·5399 (3)	0·058 (2)
C37	0·5760 (7)	−0·6722 (7)	0·4794 (4)	0·074 (3)
C38	0·5748 (7)	−0·7971 (6)	0·4949 (4)	0·078 (3)
C39	0·6333 (7)	−0·8132 (6)	0·5727 (4)	0·072 (3)
C40	0·6864 (6)	−0·7047 (5)	0·6329 (3)	0·057 (2)

Table 2. Selected bond lengths (Å) and angles (°)

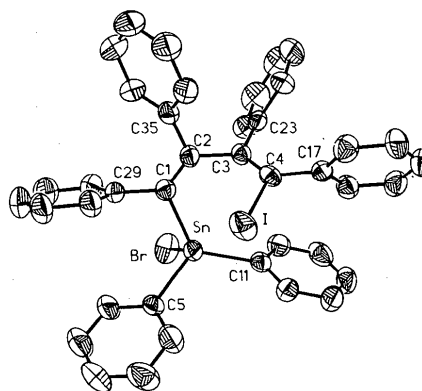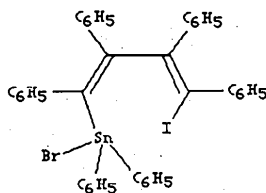|			
I—C4	2·136 (4)	C2—C3	1·504 (5)
Br—Sn	2·6824 (5)	C2—C35	1·493 (5)
Sn—C1	2·153 (4)	C3—C4	1·326 (5)
Sn—C5	2·154 (4)	C3—C23	1·502 (6)
Sn—C11	2·124 (4)	C4—C17	1·470 (5)
C1—C2	1·333 (5)	Sn⋯I	3·8835 (5)
C1—C29	1·492 (5)		
I—C4—C3	120·1 (3)	C2—C3—C4	125·5 (4)
I—C4—C17	112·2 (3)	C2—C3—C23	112·2 (3)
Br—Sn—C1	104·0 (1)	C3—C2—C35	111·2 (3)
Br—Sn—C5	101·98 (9)	C3—C4—C17	127·6 (4)
Br—Sn—C11	99·91 (9)	C4—C3—C23	121·9 (3)
Sn—C1—C2	125·3 (3)	C5—Sn—C11	117·6 (2)
Sn—C1—C29	110·3 (3)	C29—C30—C31	120·0 (5)
C1—Sn—C5	105·3 (1)	I⋯Sn—Br	168·45 (2)
C1—Sn—C11	124·5 (1)	I⋯Sn—C1	67·6 (1)
C1—C2—C3	124·5 (3)	I⋯Sn—C5	88·2 (1)
C1—C2—C35	124·3 (3)	I⋯Sn—C11	79·7 (1)
C2—C1—C29	123·7 (3)		

Fig. 1. ORTEP (Johnson, 1965) drawing at 50% probability of bromo(4-iodo-1,2,3,4-tetraphenyl-1,3-butadienyl)diphenyltin(IV) showing the adopted labeling.

final cycle: $(\Delta/\sigma)_{max} < 0·02$, $(\Delta\rho)_{max} = 1·1$ e Å^{-3} near the Br atom, $(\Delta\rho)_{min} = -0·7$ e Å^{-3}. No correction for extinction was applied. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). Table 1* gives the atomic coordinates and Table 2 lists bond distances and angles. Fig. 1 illustrates the geometry and labeling scheme. A diagram of the title molecule is shown below.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52833 (46 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Related literature. Four other very similar structures of Sn^{IV} have been examined, all possessing a 4-halo-1,2,3,4-tetraphenylbutadiene ligand. The complexes (4-bromo-1,2,3,4-tetraphenyl-1,3-butadienyl)dibromophenyltin (Hahn, Barnes, van der Helm & Zuckerman, 1990) and (4-bromo-1,2,3,4-tetraphenyl-1,3-butadienyl)dimethylbromotin (Boer, Doorakian, Freedman & McKinley, 1970) each show close contacts between Sn and the extant Br substituent of the butadiene, Sn⋯Br = 3·838 and 3·774 Å respectively. Intramolecular bonding has been postulated for both. On the other hand, two other complexes, (4-halo-1,2,3,4-tetraphenyl-1,3-butadienyl)dimethylphenyltin, where halo = Cl and Br, show the same gross geometry but long enough Sn⋯X distances (Sn⋯Cl = 4·282, Sn⋯Br = 4·346 Å) to preclude an intramolecular cyclization of the butadienyl moiety (Boer, van Remoortere, North & Reeke, 1971). A paper by Alcock & Sawyer (1977) summarizes and discusses weak interactions of adjacent molecules between Sn and halogen atoms in six-coordinate complexes and notes Sn⋯Br = 3·777 and Sn⋯I = 4·284 Å in the structures of $(CH_3CH_2)_2SnX_2$, $X = Br$,

I. They also discuss possible factors affecting secondary Sn—halo bonds.

This compound was prepared under the auspices of the late Professor J. J. Zuckerman, formerly of the Department of Chemistry, University of Oklahoma, Norman, OK 73019, USA.

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Structure of (3,5,7,13,15,17-Hexaethyl-2,8,12,18-tetramethylporphinato)copper(II)

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Abstract. [Cu($C_{36}H_{44}N_4$)], $M_r = 596.32$, monoclinic, $C2/c$, $a = 27.423$ (4), $b = 14.147$ (3), $c = 16.718$ (3) Å, $\beta = 107.60$ (1)°, $V = 6183$ (2) Å^3, $Z = 8$, $D_x = 1.281$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ(Mo $K\alpha$) = 0.768 mm^{-1}, $F(000) = 2536$, $T = 295$ K, $R = 0.0363$ for 5352 reflections [$|F_o| > 3\sigma(F_o)$]. The Cu^{II} ion is surrounded by four pyrrole N atoms of the porphinato ligand and the coordination plane defined by these atoms is virtually planar (to within 0.05 Å). The planar structure of the porphinato core is strongly distorted into a saddle-like form due to the steric hindrance between the *meso*-ethyl and β-pyrrolic ethyl substituents, the *meso*-C atoms being displaced from the coordination plane by 0.574 (3)–0.660 (3) Å.

Experimental. The compound was prepared by treatment of the free base porphyrin (Maruyama, Nagata & Osuka, 1988) with copper(II) acetate in a methanol–chloroform solution. Purple prismatic crystals were grown by the slow evaporation of a dichloromethane–hexane solution. A crystal with dimensions 0.54 × 0.62 × 0.51 mm was used for the X-ray diffractometry. Rigaku AFC-5 diffractometer operating at 50 kV, 20 mA, graphite-monochromated Mo $K\alpha$ radiation. Accurate cell parameters by least-squares fit using 41 reflections with 25

$< 2\theta < 30°$. Intensity data collected by θ–2θ scan, scan rate 3° min^{-1}, scan range $(1.3 + 0.5\tan\theta)°$, $2\theta_{max} = 55°$, h −38 to 38, k 0 to 19, l −23 to 0. Three standard reflections monitored every 50 reflections showed no crystal movement or decay. Intensity corrected by numerical absorption method based on Gaussian integration, transmission-factor range = 0.642–0.696. 7675 reflections measured, 5352 reflections with $|F_o| > 3\sigma(F_o)$ observed. The structure was solved by conventional heavy-atom method, refined on F by block-diagonal least squares. All the non-H atoms refined anisotropically. H atoms were located by difference synthesis and refined isotropically. Weighting scheme $w = [\sigma_c^2 + (0.030|F_o|)^2]^{-1}$; no extinction correction; $R(F) = 0.036$, $wR(F) =$
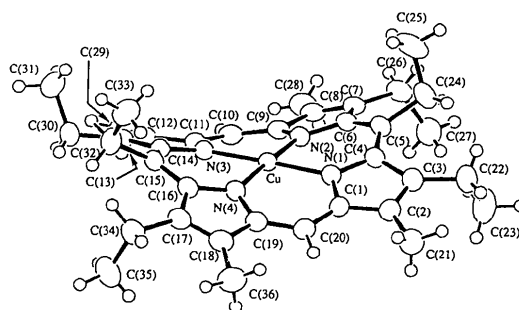

Fig. 1. *ORTEP* view of the molecule with the atom numbering. The thermal ellipsoids are given at 50% probability.