

# Bis(tetraphenylimidodiphosphinato)tin(II) and -tin(IV) Dihalides. Conversion of Pseudo Trigonal Bipyramidal to Octahedral Geometry

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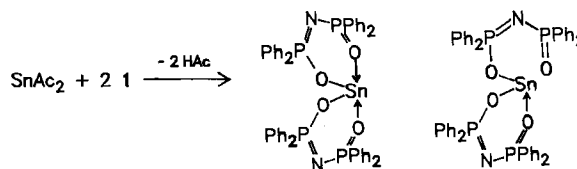
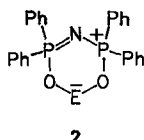
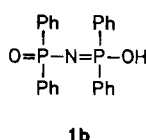
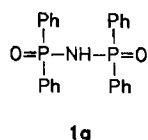
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The tetraphenylimidodiphosphinato [*N*-(*P,P*-diphenylphosphinoyl)-*P,P*-diphenylphosphinimidate] ion forms stable bis-chelates with Sn<sup>II</sup> and Sn<sup>IV</sup>. The Sn<sup>II</sup> compound [N(Ph<sub>2</sub>PO)<sub>2</sub>]<sub>2</sub>Sn (**3**) displays a distorted ψ-tbp structure in the solid state and is fluxional in solution. The bis(imidodiphosphinato)tin dihal-

ides **6** are *cis*-structured. A comparison of the X-ray structures of **3** and the diiodide [N(Ph<sub>2</sub>PO)<sub>2</sub>]<sub>2</sub>SnI<sub>2</sub> (**6c**) indicates the presence of a lone-pair stereochemical effect in **3** which is absent in **6c**.

Bis(diphenylphosphinoyl)amine (**1a**) is accessible by different routes<sup>1-3</sup>. In general, it is present in its tautomeric form **1b**. In accord with its acidic character it is commonly called tetraphenylimidodiphosphinic acid [name according to the IUPAC rules: *N*-(*P,P*-diphenylphosphinoyl)-*P,P*-diphenylphosphinimidic acid]. In the crystalline state molecules of **1b** are linked to each other by OH...O hydrogen bonds to infinite chains<sup>4</sup>. The polymeric nature makes **1** insoluble in most solvents. However, it is soluble in strongly protic or basic media in which this bonding can be overcome.



So far tetraphenylimidodiphosphinato [*N*-(*P,P*-diphenylphosphinoyl)-*P,P*-diphenylphosphinimidate] derivatives of **2** with E = Be<sup>5</sup>, Al<sup>6</sup>, Si, Ge<sup>7</sup>, Sn<sup>7,8</sup>, Sb<sup>9</sup>, Bi<sup>3</sup>, Mn<sup>6</sup>, Co, Ni<sup>6,10</sup>, Cu<sup>11</sup>, Zn<sup>12</sup>, Cd, Hg<sup>6</sup>, La, Pr, Nd, Eu<sup>13</sup>, Mo<sup>14</sup>, U<sup>6</sup>, and Re<sup>15</sup> are known. They have a chelate structure **2** and thus belong to the larger family of phosphazene heterocycles.

X-ray structure investigations have been reported recently of La, Mo and Re tetraphenylimidodiphosphinato complexes<sup>16</sup>. In this paper we report on the title compounds and their structures.

## Bis[tetraphenyl-imidodiphosphinato]tin<sup>8</sup> (**3**)

The crystalline tin compound **3** is easily obtained from tin(II) acetate and **1**. In contrast to **1**, it is readily soluble in

many polar organic solvents or even in benzene. Its <sup>31</sup>P-NMR spectrum at room temperature and at -80°C shows that all four phosphorus atoms are equivalent (δ = 17.9, broad signal, no tin satellites detectable). This suggests the existence of a bis-chelate structure **3a** in solution, as is found in the solid state (see below). Assuming that the ψ-trigonal-bipyramidal geometry surrounding the tin atom is preserved, the occurrence of a rapid pseudorotation which maintains the ring in axial-equatorial positions accounts for this equivalence.

Alternatively, the four-coordinate form **3a** might be present in a mobile equilibrium with a monocyclic form **3b** which contains a three-coordinate ψ-tetrahedral tin atom. For complexes of the type (R<sub>3</sub>PO)<sub>3</sub>Sn<sup>2+</sup> a rapid associative exchange of the phosphine oxide ligands has been found<sup>17</sup>.

An X-ray analysis shows that crystals of **3** consist of discrete molecules corresponding to **3a** (Figure 1). The two crystallographically independent imidodiphosphinato ligands chelate at axial-equatorial sites resulting in a distorted ψ-trigonal bipyramid at the tin atom. The geometry at the tin atom suggests the presence of a lone pair of electrons at the vacant equatorial site.

Five of the O—Sn—O angles (Table 3) are less than 90°<sup>18</sup>. The sixth one, which presents the diaxial angle, is 164.4° and describes the axial Sn—O bonds bent away from the equatorial lone pair position. The two respective Sn—O

bonds, which are axial in the  $\psi$ -trigonal bipyramid, are 0.22 Å longer than the two equatorial Sn–O bonds (Table 2). The average value of 2.24 Å agrees with known Sn–O distances in four-coordinate tin(II) compounds<sup>19</sup>.

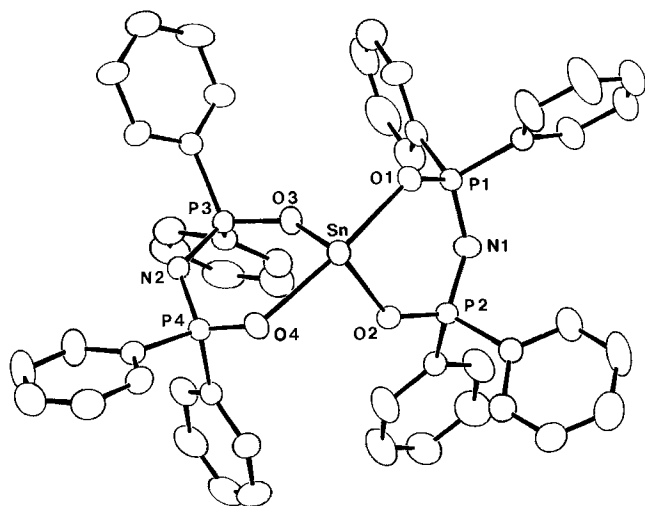


Figure 1. ORTEP plot of **3** with thermal ellipsoids at the 30% probability level; hydrogen atoms are omitted for clarity

Corresponding molecular structures are also found for other spirocyclic tin(II) chelates. In all cases the tin coordination may be understood in terms of trigonal bipyramids that are distorted towards square pyramids where all the angles at the tin atom are reduced by the influence of the lone-pair effect<sup>18</sup>. Table 1 lists known examples with four- to seven-membered rings and with S, P, and O as ligand atoms in the order of increasing diaxial angles. The list shows that **3** represents the least distorted case so far. Com-

Table 1. Structural data<sup>a)</sup> of spirocyclic tin(II)-chelated molecules with S, P, and O as the ligand atoms<sup>20</sup>

Chelating ligand	Dieq. angle	Diax. angle	Eq. b.l.	Ax. b.l.	Ax. elong.	Ref.
–S–C(NEt <sub>2</sub> )=S	96.2	139.6	2.574 2.592	2.756 2.819	8.1	21)
	96		2.57 2.58	2.78 2.83	8.9	22)
–S–C(OMe)=S	99.3	140.8	2.603 2.644	2.802 2.813	7.0	23)
–PMe <sub>2</sub> =C(PMe <sub>2</sub> )–PMe <sub>2</sub>	105.9	142.5	2.598 2.602	2.790 2.839	8.3	24)
–O–CO–CO–O	78.7	145.5	2.246	2.357	4.9	25)
–O–C(OMe)=[C <sub>5</sub> (CO <sub>2</sub> Me) <sub>3</sub> ]–C(OMe)=O	79.4	146.4	2.240	2.271	1.4	26)
–O–CPh=CH–CPh=O	85.8	146.8	2.151 2.167	2.263 2.345	6.7	27)
–O–CPh=CH–CMe=O	94.7	150.4	2.135	2.290	7.3	28)
–O–PPh <sub>2</sub> =N–PPh <sub>2</sub> =O	88.2	164.6	2.128 2.134	2.317 2.382	10.3	this work

<sup>a)</sup> Column headings: diequatorial and diaxial angles [°], equatorial and axial bond lengths [Å], and the (average) percentage elongation of axial bond lengths relative to that of equatorial bond lengths.

pound **3** also exhibits the longest axial bonds relative to equatorial bonds.

Table 2. Selected distances [Å] with estimated standard deviations in parentheses for **6c** and **3**

	<b>6c</b>	<b>3</b>
Sn–I1	2.7451(6)	
Sn–I2	2.7598(6)	
Sn–O1	2.082(3)	2.317(2)
Sn–O2	2.071(4)	2.134(3)
Sn–O3	2.069(4)	2.128(2)
Sn–O4	2.073(3)	2.382(3)
P1–O1	1.544(4)	1.515(3)
P1–N1	1.597(5)	1.591(4)
P2–O2	1.536(4)	1.528(3)
P2–N1	1.577(5)	1.582(3)
P3–O3	1.545(4)	1.529(2)
P3–N2	1.581(4)	1.580(3)
P4–O4	1.537(4)	1.513(2)
P4–N2	1.572(5)	1.596(3)

Table 3. Selected bond angles [°] with estimated standard deviations in parentheses for **6c** and **3**

	<b>6c</b>	<b>3</b>
I1–Sn–I2	93.69(2)	
I1–Sn–O1	92.9(1)	
I1–Sn–O2	88.0(1)	
I1–Sn–O3	172.9(1)	
I1–Sn–O4	93.1(1)	
I2–Sn–O1	92.5(1)	
I2–Sn–O2	177.2(1)	
I2–Sn–O3	92.8(1)	
I2–Sn–O4	93.1(1)	
O1–Sn–O2	89.7(1)	85.74(9)
O1–Sn–O3	84.0(1)	79.89(8)
O1–Sn–O4	171.5(1)	164.61(8)
O2–Sn–O3	85.6(1)	88.2(1)
O2–Sn–O4	84.5(1)	88.9(1)
O3–Sn–O4	89.4(1)	85.55(9)
O1–P1–N1	115.9(2)	117.3(2)
O2–P2–N1	115.2(2)	118.3(2)
O3–P3–N2	116.0(2)	116.9(1)
O4–P4–N2	116.5(2)	117.1(2)
Sn–O1–P1	128.8(2)	130.1(1)
Sn–O2–P2	130.3(2)	134.1(2)
Sn–O3–P3	131.1(2)	134.3(2)
Sn–O4–P4	132.1(2)	126.7(1)
P1–N1–P2	123.2(3)	128.0(2)
P3–N2–P4	129.5(3)	125.4(2)

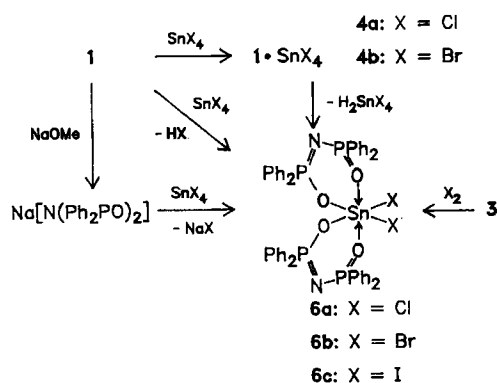
The bond lengths alternate in both of the chelate rings of **3**. At the ring side containing the longer (axial) Sn–O bond (Sn–O1/4) the P–O bonds are always somewhat shorter (average 1.51 Å) compared to the P–O bonds (average 1.53 Å) at the ring side containing the shorter (equatorial) Sn–O bonds (Sn–O2/3). The difference in the P–N bonds are not significant. When compared to **1b** (P–O 1.519 Å; P–N 1.535 Å<sup>4</sup>), the P–O bond lengths in **3** are approximately the same, but the P–N bonds in **3** are longer. The exceptionally short P–N distance in **1b** is associated with its linear P–N–P arrangement<sup>4</sup>.

While crystals of the related yellow bis(1,3-diketonato)tin(II) chelates (see Table 1) are air-sensitive and undergo rapid

hydrolysis<sup>27–30</sup>, crystals of **3** are colorless and stable in air for years.

### Bis(tetraphenylimidodiphosphinato)tin Dihalides **6**

Halogens add to **3** to give the corresponding tin(IV) compounds **6**. The latter are more conveniently prepared from the tin tetrahalides. SnCl<sub>4</sub> and SnBr<sub>4</sub> add to **1** in a 1:1 molar ratio. The products **4a, b** cannot be characterized by NMR due to their low solubility. By solvolysis in methanol or water they are converted into **6a, b**. Compounds **6** are also obtained by thermal condensation of the tetrahalides with two equivalents of **1** or by the action of the tetrahalides on the sodium salt **5**.



The <sup>119</sup>Sn-, <sup>31</sup>P-, and <sup>13</sup>C-NMR spectra of **6** (Table 4) consistently show two types of PPh<sub>2</sub> units each of which has two non-equivalent phenyl groups. However, the chemical shift differences are quite small and have not been detected in an earlier investigation<sup>8</sup>). The non-satellite <sup>31</sup>P-NMR signals are of the AA'BB' type with a PNP coupling constant  $J_{AB} = 3–4$  Hz, corresponding to  $J_{PNP}$  in phenyl-substituted cyclotriphosphazenes<sup>31</sup> ( $J_{AB}$ , can only be detected for **6c**). The spectra clearly indicate a *cis* structure of **6**.

In the order X = Cl, Br, I both <sup>31</sup>P-NMR signals are shifted to higher field in a rather parallel fashion. The most noticeable feature, however, are the two different SnOP coupling constants<sup>32</sup> resulting in a triple-triplet splitting of the <sup>119</sup>Sn-NMR signals of **6a, b, c**. Both coupling constants increase in the order X = Cl, Br, I, one of them increases much more, however, than the other. This coupling is assigned to the Ph<sub>2</sub>PO groups *trans* to the halogen atoms. A <sup>119</sup>Sn-NMR study of Bu<sub>3</sub>POSnCl<sub>5–n</sub>Br<sub>n</sub><sup>–</sup> and (Bu<sub>3</sub>PO)<sub>2</sub>SnCl<sub>4–n</sub>Br<sub>n</sub> demonstrates that a Cl/Br exchange *trans* to the phosphine oxide, in contrast to a *cis* exchange, generally increases  $J_{SnOP}$  to a significant extent<sup>33</sup>.

The <sup>119</sup>Sn-NMR signals of **6a, b, c** are found at rather high field, typical for six-coordinate tin, and they are shifted to higher field in the order X = Cl, Br, I, as is also well-known<sup>32</sup>). The Cl/Br exchange (**6a** → **6b**) is accompanied by a shift of  $\Delta\delta = -148$  per halogen atom (as compared to  $\Delta\delta \approx -200$  in the case of other compounds of six-coordinate tin). The shift of  $\Delta\delta = -523$  per halogen atom observed for the Cl/I exchange (**6a** → **6c**) seems to have no reported parallel so far<sup>32</sup>.

Table 4. NMR data of [N(Ph<sub>2</sub>PO)<sub>2</sub>]<sub>2</sub>SnX<sub>2</sub><sup>a)</sup>

		<i>cis</i> -Ph <sub>2</sub> PO <sup>b)</sup>		<i>trans</i> -Ph <sub>2</sub> PO <sup>b)</sup>		
<b>6a</b> , X = Cl	<sup>119</sup> Sn	$\delta$	–713			
	<sup>31</sup> P	$\delta$	29.3	30.3		
		${}^2J_{PP}$	4.0	4.0		
		${}^2J_{117,119SnP}$	66.1, 69.1	96.0, 100.6		
		${}^{2,3}J_{PC}$	11.0, 13.4	13.3, 19.0		
<b>6b</b> , X = Br	<sup>119</sup> Sn	$\delta$	–1008			
	<sup>31</sup> P	$\delta$	28.1	29.3		
		${}^2J_{PP}$	3.7	3.7		
		${}^2J_{117,119SnP}$	67.6, 70.6	115.6, 121.0		
		${}^{2,3}J_{PC}$	10.8, 13.4	11.0, 13.4		
<b>6c</b> , X = I	<sup>119</sup> Sn	$\delta$	–1759			
	<sup>31</sup> P	$\delta$	26.5	28.2		
		${}^{2,4}J_{PP}$	3.1	3.1, 0.3		
		${}^2J_{117,119SnP}$	71.0, 74.0	144.0, 150.2		
	<sup>13</sup> C- <i>i</i>	$\delta$ <sup>c)</sup>	135.9	135.6	135.1	134.8
		${}^1J_{PC}$	136.8	140.1	137.0	141.3
	<sup>13</sup> C- <i>o</i>	$\delta$	1.9	3.5	2.1	4.1
		${}^2J_{PC}$	131.8	129.9	131.5	130.8
	<sup>13</sup> C- <i>m</i>	$\delta$	10.9	10.8	11.1	11.2
		${}^4J_{PC}$		0.7		0.6
<sup>13</sup> C- <i>p</i>	$\delta$	128.5	127.9	128.5	127.9	
	${}^3J_{PC}$	13.7	13.5	13.7	13.7	
<sup>13</sup> C- <i>p</i>	$\delta$	131.9	131.7	131.2	130.9	
	${}^4J_{PC}$	3.0	3.0	3.0	3.0	

<sup>a)</sup> Chemical shifts  $\delta$  of <sup>119</sup>Sn, <sup>31</sup>P, and <sup>13</sup>C are relative to external Me<sub>4</sub>Sn, H<sub>3</sub>PO<sub>4</sub>, and internal Me<sub>4</sub>Si, respectively<sup>9</sup>), coupling constants  $J$  are in Hz. – <sup>b)</sup> *cis*- and *trans*-Ph<sub>2</sub>PO designate the position of the group relative to X. – <sup>c)</sup> The <sup>13</sup>C-NMR data are assigned to the individual Ph<sub>2</sub>PO group by a coupling constant comparison with the <sup>13</sup>C satellites of the <sup>31</sup>P-NMR signals; this assignment is not possible, however, for C-*p*.

The molecular structure of **6c** has been established by an X-ray investigation (Figure 2). The coordination at the tin atom is octahedral with the two iodine atoms in the *cis* positions. All the angles (Table 3) between *cis*-bonded atoms are close to ideal with the endocyclic and exocyclic O–Sn–O angles (average 89.6 and 84.7°, respectively) being somewhat smaller than 90° while the I–Sn–O angles (average 92.1°) and the I–Sn–I angles (93.7°) are somewhat larger than 90°.

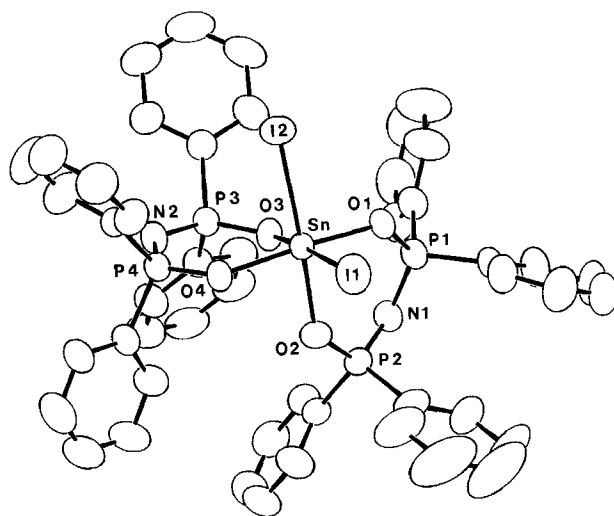
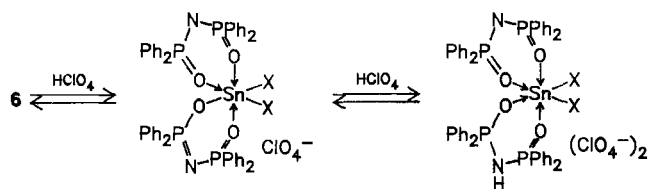


Figure 2. ORTEP plot of **6c** with thermal ellipsoids at the 30% probability level; hydrogen atoms are omitted for clarity

The diaxial O—Sn—O angle in **3**, on oxidation, increases from 164.6° to 171.6° in **6c**. At the same time, the Sn—O distances (Table 2) are shortened from 2.13 (equatorial and 2.35 Å (axial) in **3** to 2.07 Å in **6c**. The Sn—O bonds *trans* to iodine are only slightly shorter than those that are *cis* (which are axial in **3**). Thus, the Sn—O bond lengths in the structure do not account for the striking difference in *cis*- and *trans*- $J_{\text{SnOP}}$  values found in the NMR spectra. An even shorter Sn—O distance (average 2.058 Å) is found for the related bis(2,4-pentanedionato)tin *cis*-dichloride<sup>34</sup>.

Other bonds of the chelate rings of **6c** show the expected changes relative to the four-coordinate structure **3**. However, the changes are relatively slight. The P—O distance increases on the average from 1.52 Å to 1.54 Å, and the P—N distance decreases from 1.59 Å to 1.58 Å (Table 2).

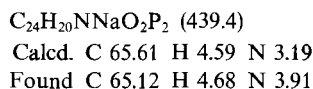
The compounds **6** can be protonated with perchloric acid at one or both nitrogen atoms<sup>8</sup>) to afford tin perchlorate chelates containing the neutral ligand **1a**.



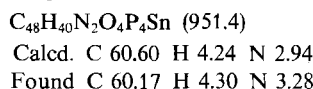
We thank Dr. Konstantin Karaghiosoff for his valuable help in recording the <sup>119</sup>Sn-NMR spectra. Support of this work by a NATO grant is gratefully acknowledged.

## Experimental

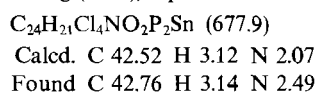
*Sodium N-(P,P-Diphenylphosphinoyl)-P,P-diphenylphosphinimidate (5)*: To 27.0 g (65 mmol) of **1** in 200 ml of ethanol a 0.5 M sodium ethoxide solution is added until a clear solution is obtained (ca. 130 ml). On standing, a fine colorless precipitate of **5** forms which is soluble in dimethylformamide and which can be recrystallized from acetonitrile; yield 23.0 g (80%).



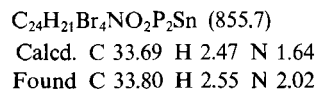
*Bis[N-(P,P-diphenylphosphinoyl)-P,P-diphenylphosphinimidato]tin<sup>8</sup> (3)*: A thorough mixture of 2.5 g (11 mmol) of freshly sublimed tin(II) acetate and 9.1 g (22 mmol) of **1** is heated in vacuo to 270°C until no more gas evolves from the melt. The product is dissolved in 20 ml of dichloromethane. After filtration, the addition of diethyl ether to the filtrate causes precipitation of 9.2 g (80%) of **3** as colorless crystals. In addition to their solubility in polar solvents, the crystals are soluble in benzene and may be recrystallized from ethyl acetate, mp 223–224°C.



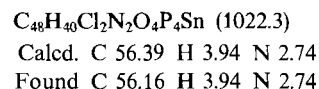
*Bis(diphenylphosphinoyl)amine-(Tin Tetrachloride) (4a)* and *-(Tin Tetrabromide) (4b)*: 7.1 g (17 mmol) of **1** and 4.4 g (17 mmol) of SnCl<sub>4</sub> are heated at reflux in 100 ml of acetonitrile for 1 h; **4a**, which is insoluble in the solvent, is separated and washed with acetonitrile; yield 10.8 g (95%), mp 286–292°C.



20.4 g (49 mmol) of **1** and 21.4 g (49 mmol) of SnBr<sub>4</sub> are heated at reflux in 150 ml of dichloromethane for 10 h; **4b**, which is insoluble in the solvent, is separated and washed; yield 41.3 g (100%), mp 278–280°C.



*Bis[N-(P,P-diphenylphosphinoyl)-P,P-diphenylphosphinimidato]tin Dichloride (6a)*: a) To 12.6 g (30 mmol) of **1** in 50 ml of dimethylformamide is added a sodium methoxide solution prepared from 0.7 g (30 mmol) of sodium and 10 ml of methanol. The mixture is heated at reflux until the methanol has evaporated and a clear solution results. After the addition of 3.9 g (15 mmol) of SnCl<sub>4</sub> to the cold solution, the solvent is removed by distillation. The residue is extracted with dichloromethane, and **6a** precipitates from the solution by the addition of ethanol; yield 10.9 g (70%), mp 325–327°C.

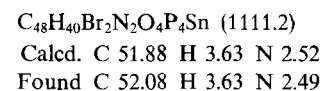


b) A mixture of 1.5 g (2 mmol) of **4a** and 0.9 g (2 mmol) of **1** is heated in vacuo to 270°C until no more gas evolves from the melt. On recrystallization from acetonitrile 1.8 g (80%) of **6a** is obtained.

c) **4a** gradually dissolves in boiling methanol. On cooling, crystals of **6a** separate from the filtrate.

*Bis[N-(P,P-diphenylphosphinoyl)-P,P-diphenylphosphinimidato]tin Dibromide (6b)*: a) To 1.4 g (1.5 mmol) of **3** in 10 ml of dichloromethane an excess of bromine (0.2 ml, 4 mmol) is added. Upon removal of the solvent and recrystallization of the residue from ethanol, 1.3 g (70%) of **6b** is obtained as colorless crystals which are identical with those from b).

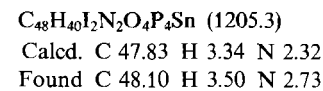
b) To 8.4 g (20 mmol) of **1** in 30 ml of dimethylformamide is added a sodium methoxide solution prepared from 0.5 g (20 mmol) of sodium and 7 ml of methanol. The mixture is heated until a clear solution results and the methanol has evaporated. After cooling and addition of 4.4 g (10 mmol) of SnBr<sub>4</sub>, the solvent is removed by distillation. From the residue, **6b** is extracted with dichloromethane and precipitated by the addition of ethanol; yield 9.5 g (85%), mp 283–285°C.



c) A mixture of 10.2 g (12 mmol) of **4b** and 4.9 g (12 mmol) of **1** is heated in vacuo to 270°C until no more gas evolves from the melt. Recrystallization from acetonitrile and from dichloromethane/methanol gives 6.8 g (50%) of **6b**.

d) 8.5 g (10 mmol) of **4b** is kept for 1 h in refluxing methanol and subsequently converts into 4.9 g (90%) of **6b**.

*Bis[N-(P,P-diphenylphosphinoyl)-P,P-diphenylphosphinimidato]tin Diiodide (6c)*: On heating at reflux of 18.6 g (45 mmol) of **1** and 14.4 g (23 mmol) of SnI<sub>4</sub> in 100 ml of dichloromethane, a brown solution is obtained. Upon addition of this solution to 300 ml of ethanol 25.9 g (95%) of yellow crystals of **6c** separate, mp 258–260°C.



*X-ray Crystallography*: All X-ray crystallographic studies were performed by using an Enraf-Nonius CAD 4 diffractometer and graphite-monochromated molybdenum radiation [ $\lambda(K\alpha_1) = 0.71073$  Å] at an ambient temperature of 23 ± 2°C. Details of the experimental procedures have been described previously<sup>35</sup>.

Crystals were mounted in thin-walled glass capillaries which were sealed. Data were collected by using the  $\Theta$ - $2\Theta$  scan mode. The structures were solved by use of the Patterson and difference Fourier techniques and refined by full-matrix least squares<sup>36</sup>. All computations were performed with a Microvax II computer using the Enraf-Nonius SDP system of programs.

**X-ray Structure Determinations of 3:** The colorless crystal used for data collection was cut from a larger plate and had the dimensions of  $0.19 \times 0.38 \times 0.49$  mm. Triclinic space group  $P\bar{1}$  (No. 2)<sup>37</sup>,  $a = 8.886(2)$ ,  $b = 12.106(2)$ ,  $c = 21.254(4)$  Å;  $\alpha = 92.57(1)$ ,  $\beta = 95.16(2)$ ,  $\gamma = 103.33(2)^\circ$ ;  $V = 2211(2)$  Å<sup>3</sup>;  $Z = 2$ ;  $D_{\text{calcd.}} = 1.429$  g/cm<sup>3</sup>;  $\mu(\text{Mo-K}\alpha) = 7.654$  cm<sup>-1</sup>. A total of 5734 independent reflections was measured ( $+h, \pm k, \pm l$ ;  $3^\circ \leq 2\Theta \leq 45^\circ$ ). An empirical absorption correction based on  $\psi$  scans was applied (relative transmission coefficients from 0.9133 to 0.9998 on  $I$ ). The 59 independent non-hydrogen atoms were refined anisotropically. The 40 independent hydrogen atoms were included in the refinement in ideal positions as fixed isotropic scatterers. The final agreement factors<sup>38</sup> were  $R = 0.028$  and  $R_w = 0.037$  for the 4527 reflections with  $I \geq 3\sigma_I$ . The maximum density on a final difference Fourier synthesis was  $0.30(5)$  e/Å<sup>3</sup>, and the ratio of observations to variables was 8.51.

Table 5. Selected fractional atomic coordinates and equivalent isotropic thermal parameters for 3

Atom	x	y	z	B eq
Sn	0.47032(3)	0.36484(2)	0.21401(1)	3.358(5)
P1	0.5098(1)	0.19396(8)	0.33952(4)	3.27(2)
P2	0.6237(1)	0.13455(8)	0.22455(5)	3.45(2)
P3	0.7868(1)	0.56752(8)	0.27309(4)	3.25(2)
P4	0.7346(1)	0.56560(8)	0.14004(5)	3.41(2)
O1	0.4250(3)	0.2736(2)	0.3064(1)	3.75(5)
O2	0.5935(3)	0.2385(2)	0.1920(1)	4.23(6)
O3	0.6708(3)	0.4528(2)	0.2740(1)	4.10(6)
O4	0.5864(3)	0.4726(2)	0.1325(1)	4.37(6)
N1	0.6068(4)	0.1289(3)	0.2979(1)	4.19(7)
N2	0.7878(3)	0.6283(2)	0.2088(1)	3.61(7)

Table 6. Fractional atomic coordinates and equivalent isotropic thermal parameters for 6c

Atom	x	y	z	B eq
I1	0.87136(4)	0.23585(2)	0.19156(2)	4.78(1)
I2	0.66980(4)	0.24930(2)	0.32905(2)	4.87(1)
Sn	0.74023(3)	0.15042(2)	0.25459(2)	2.641(8)
P1	0.5121(1)	0.10776(7)	0.15177(7)	3.23(3)
P2	0.7230(1)	0.03084(7)	0.15296(7)	3.23(3)
P3	0.6547(1)	0.04805(7)	0.35724(7)	2.95(3)
P4	0.9044(1)	0.08840(7)	0.37737(6)	2.94(3)
O1	0.5826(3)	0.1611(2)	0.1925(2)	3.19(8)
O2	0.7963(3)	0.0736(2)	0.2025(2)	3.44(8)
O3	0.6398(3)	0.0785(2)	0.2927(2)	3.20(8)
O4	0.8915(3)	0.1248(2)	0.3158(2)	3.06(8)
N1	0.5799(4)	0.0379(2)	0.1480(2)	3.4(1)
N2	0.7856(4)	0.0552(2)	0.3955(2)	3.5(1)

**X-ray Structure Determination of 6c:** The pale yellow crystal used for the study was cut from a large irregular chunk and had the approximate dimensions of  $0.25 \times 0.35 \times 0.35$  mm. Monoclinic space group  $P2_1/c$  (No. 14)<sup>39</sup>,  $a = 11.047(2)$ ,  $b = 20.089(5)$ ,  $c = 22.164(4)$  Å;  $\beta = 97.67(2)^\circ$ ;  $V = 4875(3)$  Å<sup>3</sup>;  $Z = 4$ ;  $D_{\text{calcd.}} = 1.642$  g/cm<sup>3</sup>, and  $\mu(\text{Mo-K}\alpha) = 19.503$  cm<sup>-1</sup>. A total of 5564 independent reflections was measured ( $+h, +k, \pm l$ ;  $3^\circ \leq 2\Theta \leq 43^\circ$ ). An empirical absorption correction based on  $\psi$  scans was applied (relative transmission coefficients from 0.9232 to 0.9999 on  $I$ ). The 61 in-

dependent non-hydrogen atoms were refined anisotropically. The 40 independent hydrogen atoms were treated as described for 3. The final agreement factors were  $R = 0.028$  and  $R_w = 0.037$  for the 4208 reflections with  $I \geq 3\sigma_I$ . The maximum density on a final difference Fourier synthesis was  $0.46(7)$  e/Å<sup>3</sup>, and the ratio of observations to variables was 7.65.

Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, by quoting the depository number CSD-54774, the names of the authors, and the journal citation.

#### CAS Registry Numbers

3: 15522-00-6 / 4a: 16960-81-9 / 4b: 16960-82-0 / 5: 135823-11-9 / 6a: 16960-83-1 / 6b: 16960-84-2 / 6c: 16960-85-3

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- <sup>39</sup> Ref. <sup>37</sup>, p. 99.

[263/90]