C19—P3—C25	104.7 (2)	C41—C42—C43	100.5 (6)
C19—P3—C31	105.1 (2)	C39—C43—C42	94.4 (5)
C25—P3—C31	101.4 (2)		

† *MP*1 and *MP*2 are the midpoints of the C37=C38 and C40=C41 double bonds, respectively.

Of the three tetrafluoroborate ions, one (that containing the B1 atom) was found to be well ordered, while the other two (those containing the B2 and B3 atoms) were found to be disordered in several orientations of three of the F atoms around the B—F bond to the fourth F atom. Ion 'B2' was modelled in three different orientations, *A*, *B* and *C* (with the sum of the occupation factors of these three being fixed as 100%), and ion 'B3' in four orientations, *A*, *B*, *C* and *D* (again with the sum of the occupation factors of these four being fixed as 100%). The refinement of these two ions was restrained to keep the geometry of the four F atoms around the B atom similar to the geometry of the ordered 'B1' ion. All the tetrafluoroborate atoms were refined with anisotropic displacement parameters; for disordered F atoms they were restrained by the commands *DELU* and *SIMU* of *SHELXL*93 (Sheldrick, 1993).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Xtal*3.0 (Hall & Stewart, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

The authors thank the Natural Sciences and Engineering Research Council of Canada for a research grant to MCB, the Alcan Aluminium Company of Canada for a fellowship to ER, and Johnson Matthey for a loan of rhodium trichloride.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1107). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Appleton, T. G., Clark, H. C. & Manzer, L. E. (1973). *Coord. Chem. Rev.* **10**, 335–422.

Bachechi, F., Ott, J. & Venanzi, L. M. (1989*a*). *Acta Cryst.* C**45**, 724–728.

Bachechi, F., Ott, J. & Venanzi, L. M. (1989*b*). *Acta Cryst.* C**45**, 876–879.

Ball, R. G. & Payne, N. C. (1977). *Inorg. Chem.* **16**, 1187–1191.

Cullen, W. R., Einstein, F. W. B., Huang, C.-H., Willis, A. C. & Yeh, E.-S. (1980). *J. Am. Chem. Soc.* **102**, 988–993.

Enraf–Nonius (1989). *CAD-4 Software*. Fortran Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Hall, S. R. & Stewart, J. M. (1990). Editors. *Xtal*3.0 *Reference Manual*. Universities of Western Australia, Australia, and Maryland, USA.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Renaud, E. & Baird, M. C. (1992). *J. Chem. Soc. Dalton Trans.* pp. 2905–2906.

Renaud, E. & Baird, M. C. (1993). *J. Mol. Catal.* **80**, 43–48.

Renaud, E., Russell, R. B., Fortier, S., Brown, S. J. & Baird, M. C. (1991). *J. Organomet. Chem.* **419**, 403–415.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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Acta Cryst. (1996). C**52**, 1362–1365

A Monoclinic Form of Tetrakis(1-methylimidazole-N^3)platinum(II) Diperchlorate

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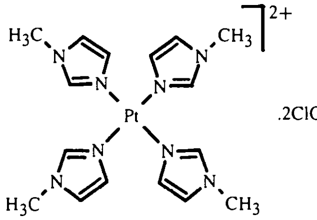
(*Received 31 October 1995; accepted 22 January 1996*)

Abstract

The monoclinic polymorph of the title compound, [Pt($C_4H_6N_2$)$_4$](ClO_4)$_2$, is reported. The two main differences between this form and the triclinic form reported previously lie in the conformation of the [Pt($C_4H_6N_2$)$_4$]$^{2+}$ cation and in the crystal packing. In both forms, the cation lies on an inversion center, but the orientations of the 1-methylimidazole (MeIm) ligands are different. In the present study, two *trans*-MeIm ligands are oriented perpendicular to the Pt coordination plane, while the other two are approximately coplanar with this plane. This is the first reported instance of coplanarity in an *N*-alkylimidazole–platinum(II) complex. The packing of the molecular cations in the monoclinic form involves no π-stacking, in contrast to the packing observed in the triclinic form.

Comment

The anticancer properties of some platinum(II) complexes are well known (*e.g.* Pasini & Zunino, 1987, and references therein). We have begun a study of the synthesis and characterization of a number of Pt^{II}–amine complexes (Clement, 1995; Buncel & Clement, 1995; Roszak, Clement & Buncel, 1996; Clement, Roszak & Buncel, 1996*a*,*b*) in continuation of our study of metal ion–biomolecule interactions (Buncel, Joly & Jones, 1986; Buncel, Joly & Yee, 1989; Buncel, Clement, Fan, Joly, Jones & Onyido, 1991; Buncel, Clement & Onyido, 1994; Buncel, Fan, Moir & Onyido, 1995). In this regard, we have recently described the triclinic form of the title compound, tetrakis(1-methylimidazole)platinum(II) diperchlorate, [Pt(MeIm)$_4$](ClO_4)$_2$, (I), where MeIm is the 1-methylimidazole ligand (Clement, Roszak & Buncel, 1996*a*). The complex was isolated as small colorless prisms from a methanolic solution of *cis*-[Pt(DMSO)$_2$Cl$_2$] and excess 1-methylimidazole, following the modified procedure of Reedijk and co-workers (Graves, Hodgson, van Kralingen & Reedijk, 1978). In the present study, a monoclinic form of (I) is described. In this work, the complex isolated from methanol was redissolved in water and allowed to crystallize slowly at room temperature over a period of one week, whereupon large colorless diamond-shaped block crystals were obtained.



(I)

In both polymorphic forms of (I), the molecular cation has a center of symmetry. In the monoclinic form (Fig. 1), the cation has exact square-planar Pt coordination, with Pt—N distances of 2.009 (5) Å and N—Pt—N angles of 90.2 (2) and 89.8 (2)°. In the triclinic form, the Pt—N distances were comparable [2.003 (6) and 2.006 (6) Å], while the N—Pt—N angles were more differentiated [91.6 (2) and 88.4 (2)°]. Previously, in the crystal structure of tetrakis(1,2-dimethylimidazole)-platinum(II) bis(triiodide) (Korte, Krebs, van Kralingen, Marcelis & Reedijk, 1981), the Pt—N distances were found to be 2.014 (5) and 2.009 (8) Å, and the N—Pt—N angles 91.4 (3) and 88.6 (3)°, while those in tetrakis(1-methylimidazole)platinum(II) hexachloroplatinate(IV) (Cingi, Lanfredi, Tiripicchio, van Kralingen & Reedijk, 1980) were 1.986 (14) and 2.012 (14) Å, and 92.6 (6) and 87.4 (6)°, respectively; in both complexes the tetrakis(imidazole)platinum(II) cation is centrosymmetric.

The major differences between the structures of the two polymorphic forms of (I) are the different conformations of the cation and the different crystal packing. In the triclinic form, one pair of MeIm ligands is approximately perpendicular to the Pt coordination plane [with a dihedral angle between the imidazole and Pt coordination planes of 83.7 (3)°], while the other pair of ligands is twisted out of this plane by 56.2 (4)° (Clement, Roszak & Buncel, 1996*a*). These angles are in the range of dihedral angles (40–90°) observed for 16 other platinum-coordinated *N*-alkylimidazoles obtained from the Cambridge Structural Database (Allen *et al.*, 1991). In the monoclinic form of (I), however, one pair of MeIm ligands (N11, C12, N13, C14, C15) is similarly perpendicular to the Pt coordination plane [dihedral angle 89.9 (2)°], while the other MeIm pair (N21, C22, N23, C24, C25) is almost coplanar with the PtN_4 plane [dihedral angle 5.8 (5)°]. The coplanar orientation of the MeIm ligand in the monoclinic form is therefore quite unique. The geometries of 'perpendicular' and 'coplanar' MeIm ligands differ significantly from each other in some bond distances and bond angles. The most striking is the shortening of the N13—C14 single-bond length to 1.324 (10) Å [*versus* 1.381 (9) Å for the N23—C24 bond], which is associated with significant changes in other bond lengths and angles in the ring. A comparison of bond lengths and angles for both imidazole moieties of (I) with those in the crystal structure of uncoordinated imidazole (McMullan, Epstein, Ruble & Craven, 1979) reveals that the imidazole moiety perpendicular to the plane of metal coordination is clearly affected by the coordinated Pt^{II} ion, whereas that in the coplanar orientation is not. The analogous N—C bond in uncoordinated imidazole, for example, is 1.381 Å, which is the same as the N23—C24 bond in the 'coplanar-oriented' imidazole moiety (see above). It is of note, however, that the geometries of the two crystallographically independent ligands in the triclinic form, which are both far from being coplanar with the Pt coordination plane, were found to be equal within two standard deviations and similar to the geometry of uncoordinated imidazole. The N13—C14 and N23—C23 bond lengths in the triclinic form were found to be 1.367 (11) and 1.383 (11) Å, respectively (Clement, Roszak & Buncel, 1996*a*). It is therefore uncertain if the orientation of ligands is responsible for the observed differences in the monoclinic form.

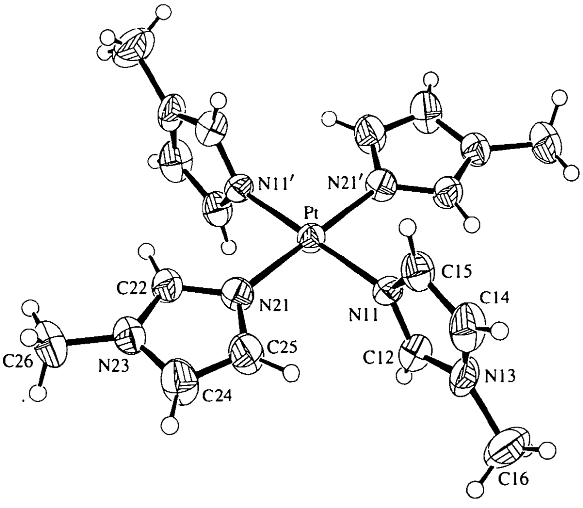


Fig. 1. The molecular structure of the title cation showing the atom-numbering scheme. The primed atoms are related to the unprimed atoms by the transformation $-x$, $-y$, $-z$. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as unlabeled spheres of arbitrary size.

In the triclinic form, the $[Pt(MeIm)_4]^{2+}$ cations are all packed in a parallel fashion and the dominant intermolecular interactions are the π-stacking interactions between the imidazole rings of adjacent molecules located at the four corners of the *ac* face of the unit cell (Clement, Roszak & Buncel, 1996*a*). In the monoclinic form described here (Fig. 2), the cation located at the center of the unit cell is not parallel to those located in the corners and the relative orientations of adjacent cations and their imidazole ligands is such that π-stacking effects are not present. Interestingly, the N11 MeIm ligands (*i.e.* containing atoms N11, C12, N13, C14, C15) of all cations are parallel to the (103) lattice plane, with the result that the 103 reflection is the strongest reflection in this structure. The perchlorate ions fill the space between the cations and, similar to the situation observed in the triclinic form, some short contacts between the perchlorate O atoms and imidazole C—H groups are present in this structure [*e.g.* C22···O1$(x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z)$ 3.162 (11) and C16···O4$(1-x, -y, -z)$ 3.141 (15) Å].

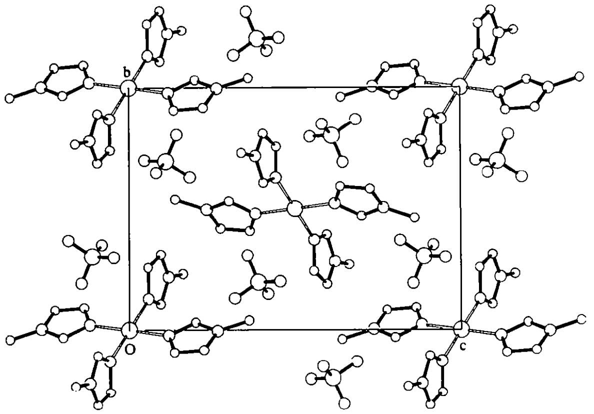


Fig. 2. The crystal packing of (I) projected along the *a* axis. H atoms are omitted for clarity.

Experimental

The title complex was obtained from a methanolic solution of *cis*-[Pt(DMSO)$_2$Cl$_2$] and excess 1-methylimidazole in methanol (Graves, Hodgson, van Kralingen & Reedijk, 1978; Clement, Roszak & Buncel, 1996*a*), and was recrystallized from water.

Crystal data

$[Pt(C_4H_6N_2)_4](ClO_4)_2$
$M_r = 722.42$
Monoclinic
$P2_1/n$
$a = 8.031 (2)$ Å
$b = 10.583 (2)$ Å
$c = 14.655 (4)$ Å
$\beta = 96.25 (3)°$
$V = 1238.2 (5)$ Å^3
$Z = 2$
$D_x = 1.938$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 15.1–18.8°$
$\mu = 5.94$ mm^{-1}
$T = 293 (2)$ K
Diamond-shaped block
0.40 × 0.35 × 0.30 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.62$, $T_{max} = 1.00$
2685 measured reflections
2685 independent reflections

1731 observed reflections [$I > 2\sigma(I)$]
$\theta_{max} = 26.98°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity variation: 5%

Refinement

Refinement on F^2
$R(F) = 0.0313$
$wR(F^2) = 0.0995$
$S = 1.052$
2685 reflections
162 parameters
H atoms riding with C—H 0.93–0.96 Å
$w = 1/[\sigma^2(F_o^2) + (0.0615P)^2 + 1.9360P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.035$ e Å^{-3}
$\Delta\rho_{min} = -0.743$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

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

	x	y	z	U_{eq}
Pt	0	0	0	0.03235 (12)
N11	0.1397 (6)	−0.1286 (5)	−0.0579 (3)	0.0346 (11)
C12	0.2792 (8)	−0.1067 (6)	−0.0953 (4)	0.0412 (14)
N13	0.3425 (7)	−0.2181 (6)	−0.1192 (4)	0.0465 (15)
C14	0.2437 (11)	−0.3102 (7)	−0.0960 (5)	0.056 (2)
C15	0.1133 (9)	−0.2574 (6)	−0.0564 (4)	0.0435 (15)
C16	0.5019 (11)	−0.2310 (10)	−0.1623 (6)	0.077 (3)
N21	0.1443 (7)	−0.0215 (5)	0.1198 (4)	0.0396 (13)
C22	0.1229 (9)	0.0305 (7)	0.2000 (5)	0.043 (2)
N23	0.2453 (8)	−0.0040 (5)	0.2653 (4)	0.0444 (12)
C24	0.3545 (10)	−0.0819 (7)	0.2251 (5)	0.057 (2)
C25	0.2889 (9)	−0.0919 (7)	0.1366 (5)	0.056 (2)
C26	0.2639 (13)	0.0386 (9)	0.3600 (5)	0.066 (2)
Cl	0.2947 (3)	0.3032 (2)	−0.11157 (14)	0.0597 (5)
O1	0.3411 (15)	0.3694 (13)	−0.1835 (6)	0.194 (6)
O2	0.1572 (14)	0.3506 (12)	−0.0826 (10)	0.206 (7)
O3	0.266 (3)	0.1933 (11)	−0.1446 (14)	0.327 (11)
O4	0.4104 (17)	0.299 (4)	−0.0460 (8)	0.43 (2)

Table 2. *Selected geometric parameters (Å, °)*

Pt—N21	2.009 (5)	C14—C15	1.370 (10)
Pt—N11	2.009 (5)	N21—C22	1.325 (9)
N11—C12	1.320 (7)	N21—C25	1.379 (8)
N11—C15	1.381 (8)	C22—N23	1.345 (9)
C12—N13	1.345 (8)	N23—C24	1.381 (9)
N13—C14	1.324 (10)	N23—C26	1.452 (9)
N13—C16	1.494 (9)	C24—C25	1.349 (10)
N21—Pt—N11	89.8 (2)	C14—C15—N11	105.7 (6)
N21—Pt—N11^i	90.2 (2)	C22—N21—Pt	127.6 (5)
C12—N11—Pt	126.5 (4)	C25—N21—Pt	127.7 (5)
C15—N11—Pt	124.7 (4)	C22—N21—C25	104.7 (6)
C12—N11—C15	108.5 (5)	N21—C22—N23	111.2 (6)
N11—C12—N13	108.5 (6)	C22—N23—C24	107.9 (6)
C12—N13—C14	108.9 (6)	C22—N23—C26	125.9 (7)
C12—N13—C16	123.7 (7)	C24—N23—C26	126.1 (7)
C14—N13—C16	127.4 (7)	N23—C24—C25	104.9 (6)
N13—C14—C15	108.4 (6)	C24—C25—N21	111.2 (6)
N21—Pt—N11—C12	−86.4 (5)	N11—Pt—N21—C22	−175.0 (6)
N21—Pt—N11—C15	86.6 (5)	N11—Pt—N21—C25	6.1 (6)

Symmetry code: (i) $-x, -y, -z$.

Systematic absences observed were those for the $P2_1/n$ space group but additionally the $h+k+l$ odd reflections were mostly weak due to the special position of the Pt atom and hence the relatively large number of unobserved data [$I < 2\sigma(I)$]. The perchlorate O atoms show large anisotropy consistent with some slight disorder, but their average positions show a tetrahedral arrangement around the Cl atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Xtal*3.0 (Hall & Stewart, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLUTON*92 (Spek, 1992). Software used to prepare material for publication: *SHELXL*93.

Financial support in the form of an operating grant from the Natural Science and Engineering Research Council of Canada (EB) is gratefully acknowledged. We also thank Queen's University for the award of a Graduate Scholarship (OC).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1141). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Davies, J. E., Galloy, J. J., Johnson, O., Kennard, O., Macrae, C. F., Mitchell, E. M., Mitchell, G. F., Smith, J. M. & Watson, D. G. (1991). *J. Chem. Inf. Comput. Sci.* **31**, 187–204.

Buncel, E. & Clement, O. (1995). *J. Chem. Soc. Perkin Trans.* 2, pp. 1333–1338.

Buncel, E., Clement, O., Fan, Y., Joly, H. A., Jones, J. R. & Onyido, I. (1991). *Synthesis and Applications of Isotopes and Isotopically Labelled Compounds*, Vol. 2, edited by J. R. Jones & G. W. Kabalka, pp. 309–316. Amsterdam: Elsevier.

Buncel, E., Clement, O. & Onyido, I. (1994). *J. Am. Chem. Soc.* **114**, 2679–2680.

Buncel, E., Fan, Y., Moir, R. Y. & Onyido, I. (1995). *Can. J. Chem.* **73**, 772–780.

Buncel, E., Joly, H. A. & Jones, J. R. (1986). *Can. J. Chem.* **64**, 1240–1245.

Buncel, E., Joly, H. A. & Yee, D. C. (1989). *Can. J. Chem.* **67**, 1426–1439.

Cingi, M. B., Lanfredi, A. M. M., Tiripicchio, A., van Kralingen, C. G. & Reedijk, J. (1980). *Inorg. Chim. Acta*, **39**, 265–270.

Clement, O. (1995). PhD thesis, Queen's University, Kingston, Ontario, Canada.

Clement, O., Roszak, A. W. & Buncel, E. (1996*a*). *J. Am. Chem. Soc.* **118**, 612–620.

Clement, O., Roszak, A. W. & Buncel, E. (1996*b*). *Inorg. Chim. Acta.* In the press.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Graves, B. J., Hodgson, D. J., van Kralingen, C. G. & Reedijk, J. (1978). *Inorg. Chem.* **17**, 3007–3011.

Hall, S. R. & Stewart, J. M. (1990). Editors. *Xtal*3.0 *Reference Manual*. Universities of Western Australia, Australia, and Maryland, USA.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Korte, H.-J., Krebs, B., van Kralingen, C. G., Marcelis, A. T. M. & Reedijk, J. (1981). *Inorg. Chim. Acta*, **52**, 61–67.

McMullan, R. K., Epstein, J., Ruble, J. R. & Craven, B. M. (1979). *Acta Cryst.* B**35**, 688–691.

Pasini, A. & Zunino, F. (1987). *Angew. Chem. Int. Ed. Engl.* **26**, 615–629.

Roszak, A. W., Clement, O. & Buncel, E. (1996). *Acta Cryst.* Submitted.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Spek, A. L. (1992). *PLUTON*92. *Molecular Graphics Program*. University of Utrecht, The Netherlands.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1996). C**52**, 1365–1367

2-Triphenylstannyl-1,2-benzisothiazol-3(2*H*)-one 1,1-Dioxide–Triphenylphosphine Oxide (1/1)

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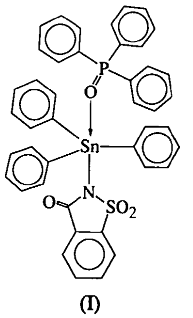
(*Received 15 August 1995; accepted 8 February 1996*)

Abstract

The Sn atom in the 1/1 2-triphenylstannyl-1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide–triphenylphosphine oxide complex, triphenyl(1,1,3-trioxo-2,3-dihydro-1,2-benzothiazol-2-yl)(triphenylphosphine oxide-*O*)tin, [Sn(C_6H_5)$_3$($C_7H_4NO_3S$){PO($C_{18}H_{15}$)}], shows *trans*-C_3SnNO trigonal bipyramidal coordination.

Comment

2-Triphenylstannyl-1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide forms 1/1 complexes with carbonyl (Ng, Kuthubutheen, Zainudin, Chen, Kumar Das, Schulze, Molloy, Yip & Mak, 1991), amine oxide (Ng, 1994) and sulfoxide (Ng, Chen & Kumar Das, 1992) donor ligands. The present phosphine oxide complex, (I), adopts a similar structure with the Sn atom displaying *trans*-C_3SnNO trigonal bipyramidal coordination. The Sn—O bond in this complex is somewhat shorter than those found in the complexes mentioned above, reflecting the greater Lewis basicity of triphenylphosphine oxide. This distance [2.341 (3) Å] compares well with that [2.391 (4) Å] found in chlorotriphenyltin triphenyl-



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Acta Crystallographica Section C
ISSN 0108-2701 © 1996