C(11)—N(11)	1.370 (8)	C(41)—N(41)	1.318 (9)
C(11)—N(12)	1.335 (7)	C(41)—N(42)	1.371 (8)
N(11)—C(13)	1.306 (9)	N(41)—C(43)	1.36 (1)
C(15)—N(12)	1.27 (1)	C(45)—N(42)	1.356 (9)
C(21)—N(21)	1.405 (9)	C(51)—N(51)	1.32 (1)
C(21)—N(22)	1.402 (8)	C(51)—N(52)	1.284 (9)
N(21)—C(23)	1.407 (7)	N(51)—C(53)	1.258 (8)
C(25)—N(22)	1.411 (8)	C(55)—N(52)	1.229 (8)
C(31)—N(31)	1.369 (9)	C(61)—N(61)	1.300 (9)
C(31)—N(32)	1.22 (1)	C(61)—N(62)	1.437 (9)
N(31)—C(33)	1.391 (9)	N(61)—C(63)	1.306 (9)
C(35)—N(32)	1.344 (9)	C(65)—N(62)	1.319 (9)
N(31)—Sn(1)—C(1)	83.7 (2)	N(61)—Sn(2)—C(5)	89.1 (2)
N(21)—Sn(1)—C(1)	82.2 (2)	N(51)—Sn(2)—C(5)	93.8 (2)
N(21)—Sn(1)—N(31)	71.8 (2)	N(51)—Sn(2)—N(61)	75.6 (2)
N(11)—Sn(1)—C(1)	90.2 (2)	N(41)—Sn(2)—C(5)	81.1 (2)
N(11)—Sn(1)—N(31)	76.1 (2)	N(41)—Sn(2)—N(61)	75.3 (2)
N(11)—Sn(1)—N(21)	147.6 (2)	N(41)—Sn(2)—N(51)	150.6 (2)
S(3)—Sn(1)—C(1)	144.3 (2)	S(6)—Sn(2)—C(5)	151.7 (2)
S(3)—Sn(1)—N(31)	60.6 (2)	S(6)—Sn(2)—N(61)	63.2 (2)
S(3)—Sn(1)—N(21)	86.1 (2)	S(6)—Sn(2)—N(51)	85.0 (2)
S(3)—Sn(1)—N(11)	81.9 (2)	S(6)—Sn(2)—N(41)	86.2 (2)
S(2)—Sn(1)—C(1)	107.9 (2)	S(5)—Sn(2)—C(5)	106.9 (2)
S(2)—Sn(1)—N(31)	131.3 (2)	S(5)—Sn(2)—N(61)	133.3 (2)
S(2)—Sn(1)—N(21)	63.8 (2)	S(5)—Sn(2)—N(51)	60.1 (2)
S(2)—Sn(1)—N(11)	147.5 (2)	S(5)—Sn(2)—N(41)	149.1 (2)
S(2)—Sn(1)—S(3)	96.6 (2)	S(5)—Sn(2)—S(6)	97.0 (1)
S(1)—Sn(1)—C(1)	109.4 (2)	S(4)—Sn(2)—C(5)	100.1 (2)
S(1)—Sn(1)—N(31)	134.2 (2)	S(4)—Sn(2)—N(61)	133.9 (2)
S(1)—Sn(1)—N(21)	151.2 (2)	S(4)—Sn(2)—N(51)	147.0 (2)
S(1)—Sn(1)—N(11)	60.8 (2)	S(4)—Sn(2)—N(41)	62.0 (2)
S(1)—Sn(1)—S(3)	97.0 (2)	S(4)—Sn(2)—S(6)	95.9 (2)
S(1)—Sn(1)—S(2)	87.4 (1)	S(4)—Sn(2)—S(5)	87.2 (2)
Sn(1)—S(1)—C(11)	89.9 (3)	Sn(2)—S(4)—C(41)	85.0 (3)
Sn(1)—S(2)—C(21)	85.3 (3)	Sn(2)—S(5)—C(51)	89.6 (3)
Sn(1)—S(3)—C(31)	92.7 (3)	Sn(2)—S(6)—C(61)	87.0 (3)
Sn(1)—N(11)—C(11)	99.9 (4)	Sn(2)—N(41)—C(41)	90.0 (4)
Sn(1)—N(11)—C(13)	144.0 (5)	Sn(2)—N(41)—C(43)	151.1 (4)
Sn(1)—N(21)—C(21)	91.7 (4)	Sn(2)—N(51)—C(51)	104.4 (4)
Sn(1)—N(21)—C(23)	148.4 (5)	Sn(2)—N(51)—C(53)	143.9 (5)
Sn(1)—N(31)—C(31)	94.8 (4)	Sn(2)—N(61)—C(61)	91.5 (4)
Sn(1)—N(31)—C(33)	150.2 (5)	Sn(2)—N(61)—C(63)	149.5 (5)
Sn(1)—C(1)—C(2)	113.9 (4)	Sn(2)—C(5)—C(6)	119.3 (5)

Systematic absences ($h0l$) $h + l = 2n + 1$, ($00l$) $l = 2n + 1$, ($h00$) $h = 2n + 1$ and ($0k0$) $k = 2n + 1$ were detected. The space group $P2_1/n$, at first suggested by SHELXTL-Plus (Sheldrick, 1987), had to be dismissed as the structure could not be solved in this space group, but was instead solved by examination of the Patterson function and by trial-and-error testing, coupled with electron-density and least-squares calculations. The structure was solved by standard Patterson and difference Fourier methods and refined satisfactorily in space group $P2_1$ (No.4) by full-matrix least-squares calculations employing SHELXTL-Plus. The H atoms were placed in geometrically calculated positions and refined with common isotropic displacement parameters for different C—H types (aryl H, alkyl H). The programs used were SHELXTL-Plus, PARST (Nardelli, 1983), PLATON (Spek, 1982) and MISSYM (Le Page, 1987).

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(2,2'-Biquinoline-$\kappa^2 N,N'$)chloro-(2,2':6',2''-terpyridine-$\kappa^3 N,N',N''$)-ruthenium(II) Hexafluorophosphate, [RuCl(C₁₈H₁₂N₂)(C₁₅H₁₁N₃)][PF₆]

Anthony L. Spek

Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Alessandra Gerli and Jan Reedijk

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands
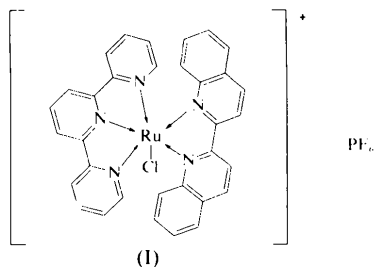
Abstract

The coordination geometry about Ru^II, involving one Cl and five N atoms, is distorted octahedral and shows several signs of interligand steric interactions. Ru—N distances are in the range 1.970 (7)–2.103 (6) Å and the Ru—Cl distance is 2.378 (2) Å.

Comment

The title compound (I) was synthesized and isolated as part of a program aimed at the development of new ruthe-

nium catalysts for the selective oxidation of carbohydrates. In this context, we investigated the syntheses of ruthenium complexes based on the 2,2':6',2''-terpyridine ligand (terpy). The present structure determination was

(I)

undertaken as a result of our interest in obtaining information on steric effects. To our knowledge, no structure of a ruthenium complex with the 2,2'-biquinoline (biq) ligand has been reported previously. The ligand environment about the Ru atom is distorted octahedral, with the terpy ligand coordinated in a meridional fashion, the biq ligand coordinated in a *cis* fashion and the Cl atom *trans* to one of the biq N atoms. The largest distortion of the octahedral geometry is due to the geometrical constraints of the terpy ligand, which exhibits small N—Ru—N angles [N31—Ru1—N41 = 80.3 (3) and N41—Ru1—N51 = 79.3 (3)°] and an Ru—N distance for the central pyridyl ring fragment shorter than those for the outer two. These values are in good agreement with those of other structures of ruthenium(II) complexes and the terpy ligand (Adcock, Keene, Smythe & Snow, 1984; Grover, Gupta, Singh & Thorp, 1992; Hecker, Fanwick & McMillin, 1991; Leising *et al.*, 1990; Thummel & Jahng, 1986).

The Ru—N distances of 2.071 (6)–2.103 (6) Å for the biq ligand and 2.060 (7)–2.065 (8) Å for the non-central terpy ring fragments are in the range found for other ruthenium(II) complexes with pyridyl-type ligands (Eggleston, Goldsby, Hodgson & Meyer, 1985; Hage *et al.*, 1990). The Ru—Cl distance of 2.378 (2) Å observed in this structure is similar to those found in other ruthenium complexes (Cathey, Constable, Hannon, Tocher & Ward, 1990; Clear *et al.*, 1980). The two Ru—N(biq) bond lengths are not significantly different, although N11 is *trans* to the 'sterically contracted' atom N41 and N21 is *trans* to the weak chloride. Similarly, no *trans* effect associated with the opposite N atom of the terpy ligand was observed in other mixed-ligand complexes involving terpy and Ru[II] (Hecker *et al.*, 1991; Leising *et al.*, 1990). The biq ligand has a −8.6 (13)° rotation about its C12—C22 bridging bond, *i.e.* the C13—C12—C22—C23 torsion angle. The angle between the adjacent pyridine ring fragments is 12.7 (4)° and the angle between the extreme phenyl ring fragments is 17.3 (4)°. In addition, the angle between the phenyl and pyridyl rings of the quinolyl fragment with N11 is 4.8 (4)° and that between similar rings of the quinolyl fragment with N21 is 7.4 (4)°.

These distortions from planarity are consistent with an overall banana-shaped curvature of the biq ligand, similar to that observed in biq complexes of other metals (Butcher & Sinn, 1977; Reagen & Radonovich, 1989; Sinn, 1976).

The coordination sphere about the Ru atom is crowded and shows several signs of interligand steric interactions. The quinolyl fragment with N21 has an H atom (from C28) pointing towards the Ru atom [H28⋯Ru1 3.064 (8) Å], the quinoline fragment with N11 has the corresponding H atom (from C18) pointing towards both the Ru and Cl atoms [H18⋯Ru1 3.025 (9) and H18⋯Cl2 2.499 (9) Å] and C18 pointing towards Cl2 [C18⋯Cl2 3.164 (9) Å]. Therefore, the biq ligand restricts the space around the metal atom. These steric features may prevent substitution reactions of the labile Cl atom by bulky ligands.

Analysis of the crystal packing reveals no stacking interactions between neighbouring molecules.
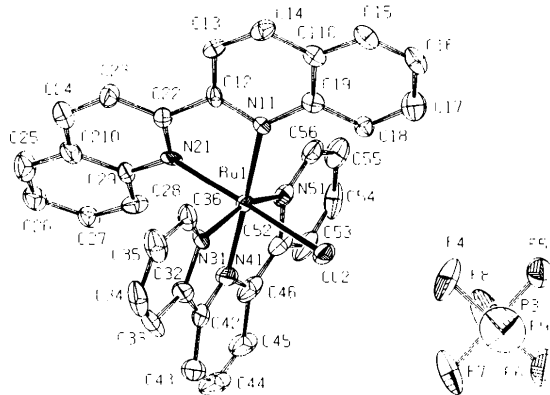

Fig. 1. Displacement ellipsoid plot at 50% probability, with H atoms omitted.

Experimental

The title compound was prepared following a procedure similar to that for the synthesis of [RuCl(terpy)(bpy)][PF$_6$] (Takeuchi, Thompson, Pipes & Meyer, 1984). Deep purple rod-shaped crystals were obtained by slow evaporation from ethanol.

Crystal data

[RuCl(C$_{18}$H$_{12}$N$_2$)- (C$_{15}$H$_{11}$N$_3$)][PF$_6$]	D_x = 1.681 Mg m^{-3}
M_r = 771.06	Mo $K\alpha$ radiation
Monoclinic	λ = 0.71073 Å
$P2_1/c$	Cell parameters from 25
a = 11.6712 (10) Å	reflections
b = 18.4964 (10) Å	θ = 11–14°
c = 15.4060 (10) Å	μ = 0.71 mm^{-1}
β = 113.660 (10)°	T = 150 K
V = 3046.2 (4) Å^3	Rod shaped
Z = 4	0.35 × 0.05 × 0.05 mm
	Dark purple

Data collection

Enraf–Nonius Turbo-CAD-4 diffractometer/rotating anode	3728 observed reflections [$I > 2.5\sigma(I)$] R_{int} = 0.049

$[RuCl(C_{18}H_{12}N_2)(C_{15}H_{11}N_3)][PF_6]$

$\omega/2\theta$ scans
Absorption correction:
   empirical (*DIFABS*;
   Walker & Stuart, 1983)
$T_{min} = 0.89$, $T_{max} = 1.08$
11 416 measured reflections
6984 independent reflections

$\theta_{max} = 27.5°$
$h = -14 \rightarrow 15$
$k = -24 \rightarrow 0$
$l = -16 \rightarrow 19$
3 standard reflections
   frequency: 60 min
   intensity variation: none

Refinement

Refinement on F
$R = 0.067$
$wR = 0.066$
$S = 3.79$
3728 reflections
425 parameters
H atoms refined as riding
   on carrier atoms with one
   common U_{iso}

$w = 1/[\sigma^2(F) + 0.000334F^2]$
$(\Delta/\sigma)_{max} = 0.3$
$\Delta\rho_{max} = 1.04$ e Å^{-3}
$\Delta\rho_{min} = -1.23$ e Å^{-3}
Atomic scattering factors
   from Cromer & Mann
   (1968)

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}
Ru1	0.84180 (7)	0.04348 (4)	0.21949 (5)	0.0209 (2)
Cl2	0.6962 (2)	0.13696 (11)	0.14339 (15)	0.0314 (7)
N11	0.8961 (6)	0.0801 (3)	0.3596 (4)	0.019 (2)
N21	0.9947 (6)	−0.0213 (3)	0.2938 (4)	0.022 (2)
N31	0.9678 (7)	0.1042 (4)	0.1870 (5)	0.028 (3)
N41	0.7979 (7)	0.0114 (4)	0.0881 (5)	0.031 (3)
N51	0.6977 (6)	−0.0271 (3)	0.2023 (5)	0.028 (2)
C12	1.0163 (7)	0.0640 (4)	0.4146 (6)	0.021 (3)
C13	1.0801 (8)	0.0939 (4)	0.5045 (5)	0.022 (3)
C14	1.0230 (8)	0.1423 (5)	0.5395 (6)	0.028 (3)
C15	0.8296 (9)	0.2061 (4)	0.5228 (6)	0.029 (3)
C16	0.7043 (9)	0.2162 (5)	0.4748 (7)	0.036 (3)
C17	0.6406 (9)	0.1794 (5)	0.3872 (7)	0.039 (3)
C18	0.7011 (7)	0.1342 (4)	0.3502 (6)	0.023 (3)
C19	0.8319 (8)	0.1237 (4)	0.3998 (6)	0.023 (3)
C22	1.0746 (7)	0.0107 (4)	0.3744 (6)	0.020 (3)
C23	1.2025 (8)	−0.0064 (5)	0.4180 (6)	0.031 (3)
C24	1.2494 (9)	−0.0587 (5)	0.3803 (7)	0.037 (3)
C25	1.2108 (10)	−0.1611 (5)	0.2708 (7)	0.042 (4)
C26	1.1273 (9)	−0.2025 (5)	0.2010 (7)	0.036 (3)
C27	0.9991 (8)	−0.1865 (4)	0.1615 (6)	0.027 (3)
C28	0.9542 (9)	−0.1258 (4)	0.1907 (6)	0.031 (3)
C29	1.0381 (8)	−0.0808 (4)	0.2618 (6)	0.022 (3)
C32	0.9575 (9)	0.0931 (5)	0.0958 (6)	0.034 (3)
C33	1.0356 (11)	0.1283 (5)	0.0628 (8)	0.050 (4)
C34	1.1268 (11)	0.1739 (6)	0.1208 (9)	0.054 (5)
C35	1.1381 (10)	0.1854 (5)	0.2115 (8)	0.048 (4)
C36	1.0560 (9)	0.1493 (5)	0.2414 (7)	0.033 (3)
C42	0.8546 (8)	0.0433 (5)	0.0371 (6)	0.036 (3)
C43	0.8163 (11)	0.0294 (6)	−0.0572 (7)	0.051 (4)
C44	0.7164 (12)	−0.0169 (6)	−0.0996 (7)	0.062 (5)
C45	0.6549 (10)	−0.0475 (6)	−0.0494 (6)	0.047 (3)
C46	0.6971 (9)	−0.0308 (5)	0.0472 (6)	0.041 (3)
C52	0.6429 (9)	−0.0546 (5)	0.1113 (6)	0.034 (3)
C53	0.5412 (9)	−0.1033 (5)	0.0869 (7)	0.045 (3)
C54	0.4960 (9)	−0.1213 (5)	0.1536 (8)	0.045 (4)
C55	0.5503 (9)	−0.0919 (5)	0.2423 (7)	0.042 (4)
C56	0.6484 (8)	−0.0459 (5)	0.2640 (6)	0.033 (3)
C110	0.8949 (8)	0.1579 (4)	0.4883 (6)	0.024 (3)
C210	1.1666 (9)	−0.1005 (5)	0.3025 (6)	0.032 (3)
P3	0.3661 (2)	0.28963 (14)	0.0172 (2)	0.0434 (10)
F4	0.4919 (7)	0.2673 (6)	0.0945 (6)	0.129 (4)
F5	0.3118 (5)	0.3031 (5)	0.0955 (4)	0.054 (2)
F6	0.2370 (6)	0.3164 (5)	−0.0627 (5)	0.095 (3)
F7	0.4169 (6)	0.2737 (4)	−0.0620 (5)	0.084 (3)
F8	0.3123 (8)	0.2111 (3)	0.0016 (7)	0.109 (4)
F9	0.4100 (8)	0.3700 (4)	0.0278 (6)	0.100 (4)

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

Ru1—Cl2	2.378 (2)	C19—C110	1.412 (12)
Ru1—N11	2.103 (6)	C22—C23	1.405 (13)
Ru1—N21	2.071 (6)	C23—C24	1.352 (14)
Ru1—N31	2.065 (8)	C24—C210	1.428 (13)
Ru1—N41	1.970 (7)	C25—C26	1.361 (14)
Ru1—N51	2.060 (7)	C25—C210	1.401 (14)
N11—C12	1.349 (11)	C26—C27	1.402 (15)
N11—C19	1.403 (11)	C27—C28	1.388 (12)
N21—C22	1.354 (10)	C28—C29	1.411 (12)
N21—C29	1.382 (10)	C29—C210	1.421 (14)
N31—C32	1.377 (11)	C32—C33	1.373 (16)
N31—C36	1.329 (13)	C32—C42	1.496 (13)
N41—C42	1.349 (12)	C33—C34	1.371 (17)
N41—C46	1.340 (13)	C34—C35	1.366 (17)
N51—C52	1.383 (11)	C35—C36	1.389 (16)
N51—C56	1.340 (12)	C42—C43	1.362 (13)
C12—C13	1.397 (11)	C43—C44	1.381 (17)
C12—C22	1.469 (12)	C44—C45	1.371 (17)
C13—C14	1.351 (13)	C45—C46	1.402 (12)
C14—C110	1.412 (14)	C46—C52	1.439 (14)
C15—C16	1.361 (15)	C52—C53	1.415 (15)
C15—C110	1.408 (13)	C53—C54	1.371 (16)
C16—C17	1.426 (14)	C54—C55	1.367 (15)
C17—C18	1.358 (13)	C55—C56	1.356 (14)
C18—C19	1.420 (13)		
Cl2—Ru1—N11	97.66 (18)	N11—Ru1—N51	103.3 (3)
Cl2—Ru1—N21	168.49 (18)	N21—Ru1—N31	84.8 (3)
Cl2—Ru1—N31	85.6 (2)	N21—Ru1—N41	101.8 (3)
Cl2—Ru1—N41	82.7 (2)	N21—Ru1—N51	100.5 (3)
Cl2—Ru1—N51	90.71 (19)	N31—Ru1—N41	80.3 (3)
N11—Ru1—N21	77.4 (2)	N31—Ru1—N51	159.6 (3)
N11—Ru1—N31	97.1 (3)	N41—Ru1—N51	79.3 (3)
N11—Ru1—N41	177.3 (3)		

Residual density in the final difference map was located in the PF_6 area, indicating some disorder. The structure contains a small potential solvent area at 0.451, 0.051, 0.367, sufficient to accommodate a water molecule of crystallization. However, no residual density was found. Data collection: locally modified *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *SET4* (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1993). Program(s) used to solve structure: *SIR92* (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *PLATON*.

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Comparison of the Structures of Two Trimesityltin Iodide Solvates and Triphenyltin Iodide

M. G. Simard

Département de Chimie, Université de Montréal, CP 6128, Succ. A., Montréal, Québec, Canada H3C 3J7

I. Wharf*

Department of Chemistry and Chemical Technology, Dawson College, 3040 Sherbrooke St W., Montréal, Québec, Canada H3Z 1A4

Abstract

The structures of iodotris(2,4,6-trimethylphenyl)tin-(IV) trichloro(^{2}H)methane hemisolvate, $[SnI(C_9H_{11})_3]_2.CDCl_3$ (I), iodotris(2,4,6-trimethylphenyl)-

tin(IV) toluene hemisolvate, $[SnI(C_9H_{11})_3]_2.C_7H_8$ (II), and iodotriphenyltin(IV), $[SnI(C_6H_5)_3]$ (III), have been determined by single-crystal X-ray diffraction. All three crystallize in the same space group ($P\bar{1}$) with Ar$_3$SnI molecules forming chains through the lattice using overlapping aryl groups. In (III), these are closely packed, but in (I) and (II), p-CH$_3$ groups prevent this, leaving voids which are filled by solvent molecules. Comparison of (I) and (II) with (III) shows the usual distortions due to o-CH$_3$ groups, except for the fact that distal methyls are closer to the Sn—I axis than expected, with the Sn—I distance increased by 0.05 Å. In Ar$_3$SnI, making the aryl group more sterically demanding has the same effect on the crystal structure as replacing iodine with a smaller halogen atom. Thus, $(p$-CH$_3$OC$_6$H$_4)_3$SnI (IV) crystallizes in the same space group as Ph$_3$SnBr ($P2_1/c$).

Comment

Replacement of phenyl groups in organometallics by mesityl (mes = 2,4,6-trimethylphenyl) often results in structural or chemical changes attributed to the steric effects of the two *ortho*-methyl groups. As examples in tin chemistry, we note that while compounds of the type Ph$_3$SnX, where X = OH (Glidewell & Liles, 1978), F (Tudela, Gutierrez-Puebla & Monge, 1992) or OAc (Molloy, Purcell, Quill & Newell, 1984), are polymeric with five-coordinate tin and planar C$_3$Sn moieties, the corresponding mesityl compounds, with X = OH or F (Reuter & Puff, 1989), or OAc (Wharf & Simard, 1992), are monomeric with pyramidal C$_3$SnX structures. Furthermore, while dehydrating Ph$_3$SnOH produces (Ph$_3$Sn)$_2$O (Kushlefsky, Simmons & Ross, 1963), the mesityl analogue in refluxing ethanol loses mesitylene to form (mes$_2$SnO)$_3$ (Weber, Pauls, Winter & Stegmann, 1982). These changes may well obscure the more subtle differences that might exist between phenyl- and mesityltin compounds with the same molecular structure.

In this paper, we compare two trimesityltin iodide solvates with the unsolvated triphenyl analogue. The former were prepared as part of an extension of earlier work on *para*-substituted triaryltin compounds (Wharf & Simard, 1991) to systems substituted at the *meta*- or *ortho*-positions. More recently, the crystal structure of Ph$_3$SnI was determined, confirming the prediction from infrared data in the phenyl ring region that it was not isomorphous with the corresponding chloride and bromide structures (Wharf, 1993).

Trimesityltin iodide was prepared from the bromide (Lapkin & Sedel'nikova, 1960) and a small sample of (II) was recrystallized from toluene. Since the m.p. (479 K, literature 485 K) suggested incomplete conversion, an X-ray structure determination