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Di(*p-tert*-butylphenyl)-*N*,*N*-di-(*iso*-butyl)carbamoylmethylphosphine oxide and its organotin and uranyl adducts: structural and spectroscopic characterization†

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The single-crystal structure of the hydrophobic actinide extractant di(*p-tert*-butylphenyl)-*N*,*N*-di-(*iso*-butyl)carbamoylmethylphosphine oxide (CMPO, 1) has been determined, as has that of its 1 : 1 chelate complex with uranyl nitrate (2), its 1 : 1 monodentate complexes with Ph_3SnCl (3) and Me_2SnCl_2 (4) bonding via the P═O group. A 1 : 1 bidentate complex with Ph_2SnCl_2 bonding via both P═O and C═O functionalities (5) was obtained which in solution exhibits a C═O → Sn bond dissociation to exist as the monodentate isomer coordinating only through the P═O group. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: carbamoylphosphine oxide; CMPO; organotin chlorides; uranyl

INTRODUCTION

Diaryl-*N*-dialkylcarbamoylmethylphosphine oxides are widely recognized actinide extractants with important complexation selectivities.[1–11] We recently reported an efficient, relatively large-scale, one-pot synthesis of a hydrophobic example of this class of material, di(*p-tert*-butylphenyl)-*N*,*N*-di-*iso*-butylcarbamoylmethylphosphine oxide (**1**),[12] an extractant that has proven qualities for large-scale actinide extraction.[13] Several structures of related CMPO complexes of the actinides, lanthanides and transition metals have been reported,[14–18] but to our knowledge no main group complexes are known. In view of our general interest in organotin complexation,[19–24] we have explored the coordination of **1** to various organotin chlorides, where it acts as both an effective mono- and bi-dentate ligand in the solid state but apparently only as monodentate, via the P═O group, in solution.

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†Dedicated to the memory of Professor Colin Eaborn who made numerous important contributions to the main group chemistry.
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EXPERIMENTAL

All reactions were performed in dry, oxygen-free solvents in atmospheres of nitrogen or argon. The CMPO was prepared by using the previously published procedure.[12] Me_2SnCl_2, Ph_2SnCl_2 and Ph_3SnCl were purchased from Gelest/Aldrich and were used as received. NMR spectra of all compounds were recorded on a Bruker 300 MHz spectrometer in $CDCl_3$. Elemental analyses were performed by Galbraith Laboratories.

Reaction of 1 with Me_2SnCl_2, Ph_2SnCl_2 and Ph_3SnCl

A 10 ml warm ethanol/methanol solution of **1** (5 mmol) was combined with an equimolar amount of the respective organotin compound in 10 ml of warm ethanol/methanol solution and the mixture was stirred overnight. A white material slowly precipitated from solution. These solids, CMPO·Ph_3SnCl (**3**), CMPO·Me_2SnCl_2 (**4**) and CMPO·Ph_2SnCl_2 (**5**), were recrystallized from a methanol/ethanol–hexane or tetrahydrofuran (THF)–hexane solvent mixture in overall yields of between 70 and 80%.

A similar reaction, in ethanol, with a 1:1 mixture of **1** and uranyl nitrate, $UO_2(NO_3)_2{\cdot}6H_2O$, and crystallization from the same solution by slow evaporation of the solvent, yielded $CMPO{\cdot}UO_2(NO_3)_2$ (**2**) as a yellow crystalline material.

M.p.: **3**, 155–157 °C; **4**, 116–118 °C; **5**, 184–186 °C; **2**, 180–182 °C. Anal. Found (Calc.): **3**, C, 66.3 (65.9); H, 7.07 (6.90). **4**, C, 54.6 (55.5); H, 7.45 (7.49). **5**, C, 61.0 (60.8); H, 6.82 (6.85). **2**, C, 41.1 (41.3); H, 5.28 (5.69); N, 4.79 (4.83).

^{31}P NMR (ppm, $CDCl_3$, 298 °C): **1**, 29.3; **3**, 35.00; **4**, 35.09; **5**, 39.35; **2**, 44.3. ^{119}Sn NMR (ppm, $CDCl_3$, 298 °C): **3**, −104.5 (bd); **4**, −72.0 (bd); **5**, −239.3 (bd).

IR (ν CO, cm^{-1}, THF): **1**, 1633; **3**, 1633; **4**, 1635, **5**, 1633, **2**, 1597.

CRYSTAL AND MOLECULAR STRUCTURES

X-ray quality single crystals were obtained for the free ligand, **1**, and its adducts with uranyl nitrate (**2**), triphenyltin chloride (**3**), dimethyltin dichloride (**4**), and diphenyltin dichloride (**5**).

Data collections for **1, 2, 3** and **5** were performed on a Bruker Smart APEX diffractometer, and for **4** on a Siemens R3m/V diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). Absorption corrections based on multiple reflection scans[25] were applied to the **1, 2, 3** and **5** data sets, and an empirical psi-scan absorption correction[26] was applied to **4**. The structures were solved by direct methods and refined by anisotropic full-matrix least squares on F^2.[27,28]

Molecule **1** crystallizes with one molecule of hexane in the unit cell (half a molecule/asymmetric unit). The solvent molecule is extensively disordered, and no acceptable connectivity could be established. To treat the disordered solvent, the method of van der Sluis and Spek[29] was applied using the SQUEEZE function of the PLATON program.[30] The potential solvent-accessible void of 321.7 Å^3 is typical of a small molecule. The electron count/cell was 38. Subsequent SHELXL least squares with the modified data set converged smoothly. We modified the empirical formula, $F(000)$ and the density by adding the solvent molecule.

The uranyl complex **2** provides crystals of low quality due to the disordered *tert*-butyl groups and one phenyl ring in one of the molecules of the asymmetric unit. Several data sets were collected from different crystals but none of them provided better results. The disorder could not be modeled adequately; therefore, constraints were applied on atomic displacement parameters. The C4 and C5 atoms are disordered in **3** (the site occupation factor is 0.679 for the major disorder component). An extinction coefficient of 0.0130(5) was refined for **4** and the absolute structure parameter for the non-centrosymmetric structure **5** was refined to 0.003(11).

Crystal data, data collection and refinement parameters are presented in Table 1, the molecular diagrams[30] with the numbering of the atoms are depicted in Figs 1–5.

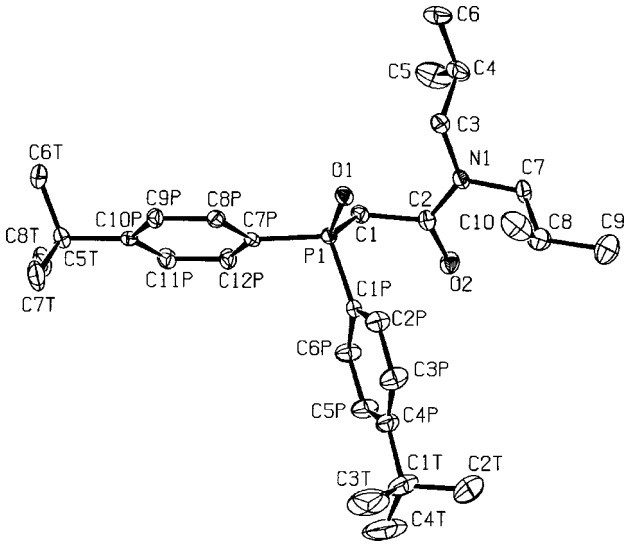


Figure 1. Crystal structure of **1**.

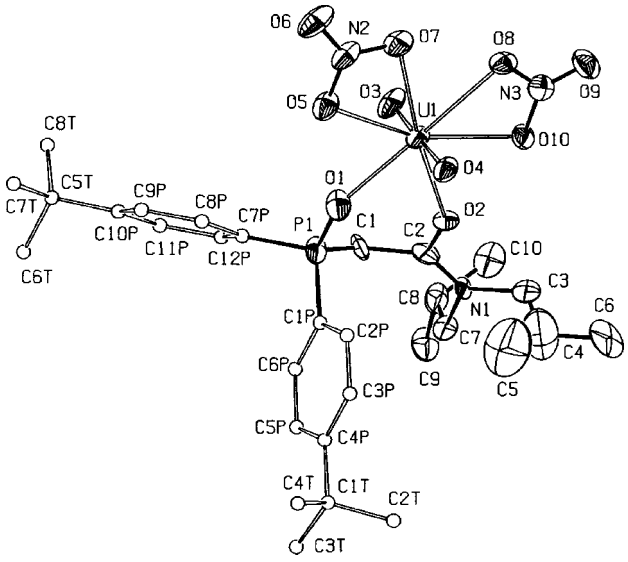


Figure 2. Crystal structure of **2**.

RESULTS AND DISCUSSION

As expected, di(*p-tert*-butylphenyl)-*N*,*N*-di-(*iso*-butyl)carbamoylmethylphosphine oxide readily formed complexes with actinide and lanthanide ions simply by mixing in a common solvent system. In the present study involving uranyl nitrate and the organotin halides Ph_3SnCl, Me_2SnCl_2 and Ph_2SnCl_2, only 1:1 complexes were obtained. In each case the yields were high and crystalline compounds were obtained, permitting complete characterization.

Spectroscopic characterization

The use of ^{31}P NMR data for characterization of the phosphine and phosphine oxide complexes is well established and is

Table 1. Crystal data and structure refinement

	1	2	3	4	5
Empirical formula	$C_{30}H_{46}NO_2P.1/2(C_6H_{14})$	$C_{30}H_{46}N_3O_{10}PU$	$C_{48}H_{61}ClNO_2PSn$	$C_{32}H_{52}Cl_2NO_2PSn$	$C_{42}H_{56}Cl_2NO_2PSn$
Formula weight	526.8	877.70	869.09	703.31	827.44
Temperature, K	123(2)	100(2)	123(2)	293(2)	293(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$Pna2_1$
Unit cell dimensions					
a (Å)	13.379(4)	29.828(3)	9.917(1)	9.736(4)Å	11.452(2)
b (Å)	13.535(4)	14.178(2)	10.499(1)	29.103(10)Å	21.698(3)
c (Å)	18.610(6)	18.904(2)	43.429(5)	13.134(7)Å	34.171(5)
α (°)	70.059(6)				
β (°)	84.205(6)	105.528(2)	91.667(2)	103.65(3)	
γ (°)	82.428(5)				
Volume (Å^3)	3134.7(17)	7702.5(14)	4520.1(10)	3616(3)	8491(2)
Z	4	8	4	4	8
Density (calc.) (Mg m^{-3})	1.116	1.514	1.277	1.292	1.295
Absorption coefficient μ (mm^{-1})	0.116	4.307	0.697	0.925	0.799
$F(000)$	1106	3472	1816	1464	3440
Crystal size (mm^3)	0.20 × 0.08 × 0.08	0.20 × 0.10 × 0.05	0.35 × 0.25 × 0.20	0.50 × 0.44 × 0.36	0.16 × 0.16 × 0.03
Max./min. transmission	0.991/0.978	0.915/0.175	0.974/0.852	0.953/0.765	0.976/0.883
θ range for data collection (°)	$1.17 \le \theta \le 28.54$	$1.42 \le \theta \le 23.34$	$0.94 \le \theta \le 28.31$	$2.12 \le \theta \le 25.10$	$1.11 \le \theta \le 28.32$
Reflections collected	35 744	49 005	27 962	7531	95 200
Independent reflections, R_{int}	9641, 0.0701	34 029, 0.1385	10 439, 0.0365	7288, 0.0243	20 248, 0.0447
Reflections $I > 2\sigma(I)$	6743	17 737	9258	6210	19 604
Data/restraints/parameters	9641/0/634	34 029/174/830	10 439/0/503	7288/0/356	20 248/1/903
Goodness-of-fit on F^2	1.021	0.996	1.155	1.069	1.203
Final R indices $[I > 2\sigma(I)]R_1$,wR_2	0.0708, 0.1438	0.0825, 0.1685	0.0512, 0.1059	0.0415, 0.1027	0.0414, 0.0885
R indices (all data) R_1,wR_2	0.1073, 0.1584	0.1673, 0.2066	0.0601, 0.1097	0.0500, 0.1083	0.0434, 0.0893
Max. and mean shift/esd	0.000; 0.000	0.167; 0.004	0.001; 0.000	0.001; 0.000	0.004; 0.000
Largest diff. peak/hole, (e$^-$ Å^{-3})	0.441/−0.257	1.784/−1.496	1.159/−0.606	0.672/−0.546	1.221/−0.907

useful to characterize the complexes between **1** and the chlorostannanes and uranyl nitrate. The free ligand ^{31}P resonance for **1** at 29.3 ppm shifts upon coordination in a monodentate manner ~6 ppm downfield to 35.00 ppm and 35.09 ppm for complexes **3** and **4** respectively. For the solid-state bidentate ligand complex **5** a slightly greater shift occurs to 39.35 ppm, and it is further shifted to 44.3 ppm upon complexation to uranyl nitrate, complex **2**.

The ^{119}Sn NMR spectra of **3, 4** and **5** exhibit very substantial chemical shift movements upon coordination, since there is a possible geometrical change from tetrahedral to either trigonal bipyramidal or octahedral geometry. The resonances (which in general are broad) at −104.5 ppm and −72.0 ppm for the trigonal bipyramidal complexes **3** and **4** respectively represent upfield shifts from the free chlorostannane of −56 for **3** and −210 ppm for **4**. These are very similar to the shifts reported upon simple phosphine oxide coordination to Ph_3SnCl (*ca* −55 ppm) and Et_2SnCl_2 (−240 ppm).[31] In the case of the solid-state hexacoordinate tin in **5**, the observed solution resonance at −239.3 ppm represent a shift of −201 ppm,

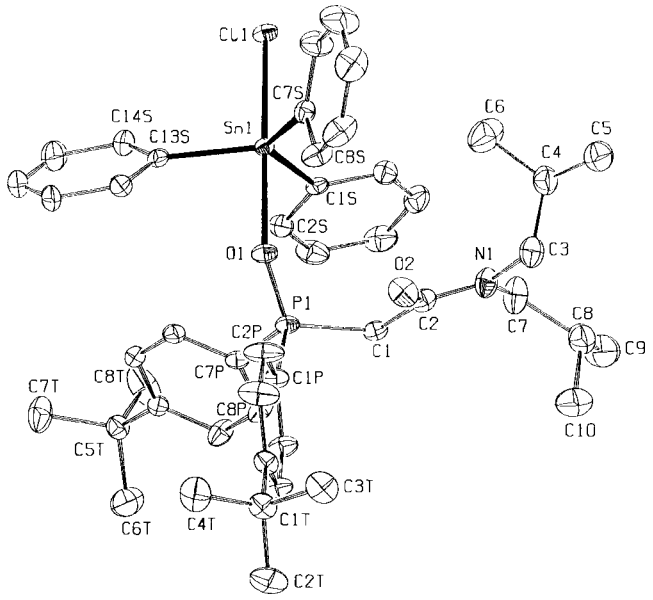


Figure 3. Crystal structure of **3**.

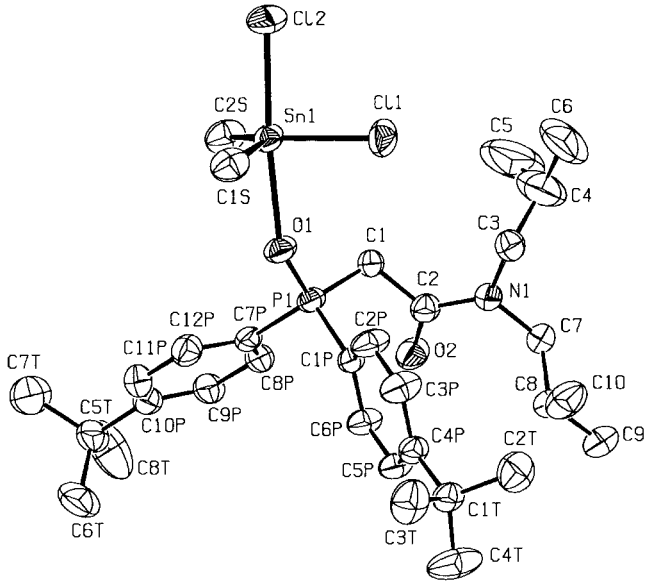


Figure 4. Crystal structure of **4**.

which compares poorly to a bis-phosphine oxide·Ph_2SnCl_2 reported shift of >450 ppm.[31–33] This much-reduced shift compared with other six-coordinate complexes suggests some dissociation of the C**=O** → **Sn** in solution. Furthermore, since the ^{119}Sn resonances are broad there is a distinct possibility of some dynamic process in solution, and we plan to perform some low-temperature and solid-state spectroscopic analysis in the future.

The ^{13}C and ^{1}H NMR data, available from the authors, are little changed from the resonances for the free ligand.[12] The ketonic group has resonances in the range at 165.6

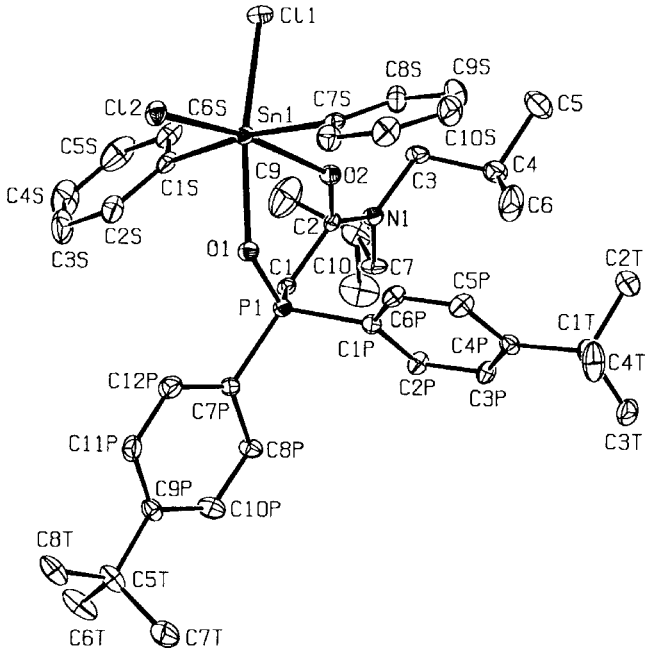


Figure 5. Crystal structure of **5**.

to 166.0 ppm, i.e. no discernable influence of the metal coordination for complexes **3, 4** and **5**. In the case of **5** this further reinforces the notion that in solution the C**=O** → **Sn** linkage is in the dissociated form. By way of comparison, in the ^{13}C spectrum for the uranyl complex **2** the ketonic resonance is has shifted to 172.5 ppm and appears as a doublet, presumably split by the phosphorus atom of the ligand, a splitting that it is not possible to observe in either the uncomplexed form of the ligand or complex **5**. The average aryl $^{119/117}$Sn–^{13}C coupling constants for **3** and **5** exhibit changes compared with the parent Ph_3SnCl, and Ph_2SnCl_2 compounds that are similar to those observed for their respective dimethylsulfoxide complexes.[32,33] The average ^{1}J, ^{2}J, ^{3}J and ^{4}J ($^{117/119}$Sn–^{13}C) values for **3** (with those of the parent tin chlorides in parentheses) are 636 (610) Hz, 49 (49) Hz, 65 (68) Hz and 14 (12) Hz respectively and 1062 (785) Hz, 67 (63) Hz, 100 (90) Hz and 21 (16) Hz for **5**. The ^{1}J values show a significant increase upon complexation, but the effect is attenuated as the Sn–C internuclear distance increases. Similarly, the ^{1}J value for **4**, 728 Hz, is significantly larger than that of the parent Me_2SnCl_2, 481 Hz, in the same solvent, illustrating the greater impact upon complexation for the dichlorotin compounds.[33]

A final piece of evidence to back up the lack of solution coordination of the keto group in **5** is the infrared region for the carbonyl stretching frequency. In the free ligand and for complexes **3, 4** and **5** the CO stretch is unchanged at 1633 cm^{-1}, showing no coordination of this group. A uranyl complex **2** exhibits a low-frequency shift to 1597 cm^{-1}, as expected upon coordination to the actinide metal center. The P=O stretching frequency of the parent CMPO ligand at 1192 cm^{-1}

changed to the lower values of 1155 cm^{-1} and 1151 cm^{-1} for the bidentate complexes **2** and **5** respectively, but remained essentially unaltered for the monodentate complex **3**.

Structural characterization

*Di(p-*tert*-butylphenyl)-*N,N*-di-(*iso*-butyl) carbamoylmethylphosphine oxide*

The parent ligand, **1**, contains two independent molecules in the asymmetric unit with a hexane solvent molecule (half a molecule/asymmetric unit) trapped within the two units, illustrative of its hydrophobic nature. Since there are no parametric differences between the two molecules, only molecule **1a** is discussed. The interatomic distances indicate a P═O bond length of 1.481(2) Å and a C═O bond length of 1.231(3) Å, both well within the norms for these linkages.[34] The carbon–nitrogen bond adjacent to the carbonyl group (N1–C2) with an internuclear distance of 1.352(3) Å is considerably shorter than the carbon–nitrogen bonds in the isobutylamino moiety (N1–C3, 1.469(4) Å; N1–C7, 1.458(3) Å), as expected for an amidic bond. Furthermore, as usual for such species, the nitrogen atom N1 is trigonal planar, as is the carbonyl-group carbon atom (sum of bond angles 360°). The bond angles around phosphorus P1 (in the range from 106.9(1) to 113.5(1)°) indicate distorted tetrahedral geometry, with the larger values displayed by the O–P–C angles (Table 2).

The related (diethylcarbamoylmethyl)-diphenylphosphine-oxide (**1c**)[34] has a similar conformation to that of CMPO. The O2–C2–C1–P1, N1–C2–C1–P1 and the C2–C1–P1–O1 torsion angles (77°, −103°, 65°) compare with those of the CMPO molecules: −100°, 78°, −68° (molecule 1) and 100°, −80°, 61° (molecule 2). The P═O and C1–C2 bonds are slightly longer (1.490 Å, 1.529 Å) and the C═O bond is slightly shorter (1.226 Å).

The relative positions of the O1 and O2 atoms are best described as their distances from the plane formed by the atoms P1, C1, and C2. In the free ligands **1** and **1c**, both oxygen atoms are on different sides of the plane (**1**/1: O1 −1.263 Å, O2 1.058 Å; **1**/2: O1 1.192 Å, O2 −1.062 Å; **1c**: O1 −1.224 Å, O2 1.044 Å). This arrangement is noted in Figure 6, illustrating a Newman projection along the virtual P–C2 bond with an average angular relationship of 136° between O═P and C═O.

Uranyl complex 2

The structure of **2**, illustrated in Fig. 2, shows a 1:1 complex with the CMPO acting as a bidentate ligand. Contrary to the free ligand noted above, the two oxygen atoms are now on the same side of the plane formed by P1, C1, and C2 (**2**/1: O1 −1.154 Å; O2: −0.864 Å; **2**/2: O1 −1.284 Å; O2: −0.765 Å; Fig. 6), resulting in an average dihedral angle of 13°. The structure of **2** may be directly compared with published structures for closely related uranyl complexes: *N,N*-diethylcarbamoylmethyl-phenyl-ethyl-phosphinate-*O,O′*)-(dinitrato-*O,O′*)-dioxo-uranium(VI) (**2a**), (*N,N*-diethylcarbamoylmethyl-diphenyl-phosphine-oxide)-(dinitrato-*O,O′*)-dioxo-uranium(VI) (**2b**), and (1-*N,N*-diethylcarbamoyl-2-phenylethyl(diphenyl)phosphonato-*O,O′*)-dioxo-bis(nitrato-*O,O′*)-uranium(VI) (**2c**).[35,36] All four structures exhibit the same bonding patterns and no unusual structural features can be noted for the respective U═O, U–O, P═O and C═O bond lengths (the values for **2** lie within the ranges observed for the other complexes).

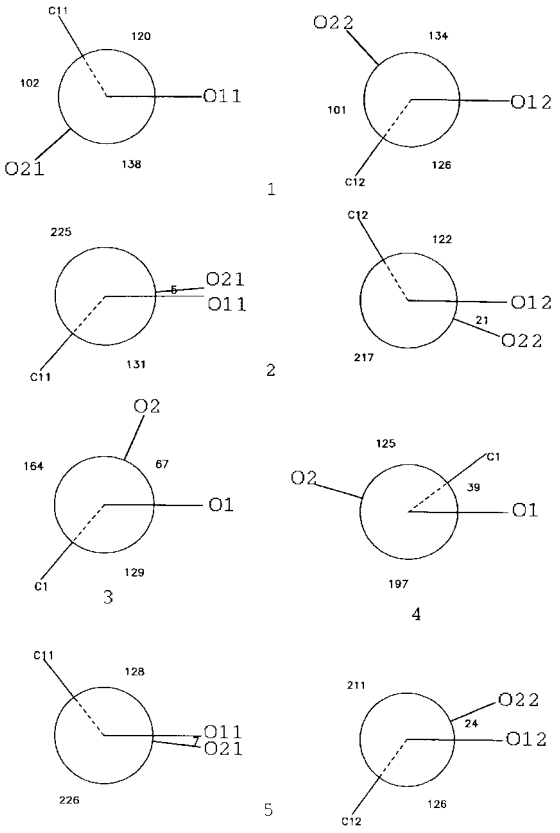


Figure 6. Spatial arrangement of the O═P and C═O groups along the virtual P–C2 bond in **2**,**5** (with two molecules in each of their corresponding asymmetric units) **3** and **4**.

Monodentate complexes 3 and 4

The parent ligand has two donor oxygen atoms, P═O and C═O, but in both the triphenyltin chloride adduct **1**·Ph_3SnCl (**3**) and, more surprisingly, in the dimethyltin dichloride adduct **1**·Me_2SnCl_2 (**4**), the ligand is monodentate, coordinating only through the more basic P═O moiety. Correspondingly, the tin atom is five-coordinate, with distorted trigonal bipyramidal geometry, where the axial positions are occupied by the electronegative chlorine and oxygen atoms. The monodentate coordination of **1** to tin results in limited changes in the molecular structure of the ligand, namely an expected lengthening of the P═O bond from 1.481(2) Å to 1.510(2) Å in **3** and to 1.504(2) Å in **4**.

The **P═O → Sn** dative bond lengths in **3** and **4** are 2.324(2) Å and 2.347(2) Å respectively, similar to

Table 2. Selected bond lengths (Å) and angles (°) for complexes **1**–**5**

	1		**2**[a]				**5**	
	a	**b**	**a**	**b**	**3**	**4**	**a**	**b**
P1–O1	1.481(2)	1.479(2)	1.523(7)	1.517(7)	1.510(2)	1.504(2)	1.508(2)	1.512(2)
P1–C1	1.821(3)	1.822(3)	1.79(1)	1.77(1)	1.813(3)	1.806(4)	1.819(3)	1.817(3)
C1–C2	1.511(4)	1.514(4)	1.51(1)	1.48(1)	1.525(4)	1.523(5)	1.534(4)	1.524(4)
C2–O2	1.231(3)	1.231(3)	1.23(1)	1.28(1)	1.221(4)	1.225(4)	1.250(4)	1.247(4)
N1–C2	1.358(3)	1.352(3)	1.31(1)	1.31(1)	1.354(4)	1.347(4)	1.319(4)	1.331(4)
O1–P1–C1	113.5(1)	113.4(1)	109.8(4)	109.3(5)	113.3(1)	110.7(2)	111.5(1)	114.3(1)
P1–C1–C2	111.3(2)	114.1(2)	110.0(8)	110.2(9)	110.8(2)	115.4(2)	108.9(2)	110.7(2)
C1–C2–O2	119.4(2)	118.7(2)	117.0(9)	117(1)	118.8(3)	118.8(3)	119.0(3)	117.5(3)
C1–C2–N1	119.8(2)	120.0(2)	124(1)	123(1)	119.3(3)	119.9(3)	121.3(3)	121.3(3)
N1–C2–O2	120.8(2)	121.2(3)	118.7(9)	119(1)	121.9(3)	121.3(3)	119.6(3)	121.2(3)
P1–O1–U1			135.1(4)	134.2(4)				
C2–O2–U1			141.2(7)	145.8(7)				
U1–O1			2.341(7)	2.354(8)				
U1–O2			2.394(6)	2.391(7)				
Sn1–Cl1					2.5214(8)	2.356(1)	2.4748(9)	2.5043(9)
Sn1–Cl2						2.462(1)	2.4753(8)	2.4526(9)
Sn1–O1					2.324(2)	2.347(2)	2.278(2)	2.252(2)
Sn1–O2							2.314(2)	2.342(2)
Sn1–C1s					2.136(3)	2.098(5)	2.145(3)	2.133(3)
Sn1–C2s						2.102(4)		
Sn1–C7s					2.133(3)		2.127(3)	2.139(3)
Sn1–C13s					2.134(3)			
P1–O1–Sn1					142.2(1)	144.9(2)	130.4(1)	126.4(1)
C2–O2–Sn1							135.8(2)	134.7(2)
Cl1–Sn1–O1					176.65(5)		171.12(6)	166.68(6)
Cl1–Sn1–O2							93.09(6)	88.13(6)
Cl1–Sn1–C1s					88.86(8)	108.1(1)	91.08(9)	92.2(1)
Cl2–Sn1–C1s							93.37(9)	92.2(1)
Cl1–Sn1–C2s						118.3(1)		
Cl1–Sn1–C7s					94.84(9)		92.06(9)	91.5(1)
Cl2–Sn1–C7s							94.09(8)	94.2(1)
Cl1–Sn1–C13s					94.30(9)			
Cl1–Sn1–Cl2						90.32(5)	99.68(3)	100.81(3)
O1–Sn1–O2							78.26(8)	78.60(8)
O1–Sn1–Cl2							89.04(6)	92.48(6)
O2–Sn1–Cl2							167.08(6)	170.98(6)
O1–Sn1–C1s					88.01(9)	86.3(1)	90.1(1)	85.9(1)
O2–Sn1–C1s							84.4(1)	86.3(1)
O1–Sn1–C2s						84.2(1)		
O1–Sn1–C7s					88.1(1)		85.6(1)	88.3(1)
O2–Sn1–C7s							87.3(1)	84.2(1)
O1–Sn1–C13s					85.8(1)			
C1s–Sn1–C7s					129.1(1)		171.3(1)	169.7(1)
C1s–Sn1–C2s						131.3(2)		
C1s–Sn1–C13s					112.8(1)			
C7s–Sn1–C13s					117.4(1)			

[a] The U═O bond distances range from 1.727(9)–1.746(8) Å; the U–O–N bond distances range from 2.482(7)–2.538(6) Å.

those reported for the five-coordinate tin atoms in $ClPh_3Sn{\cdot}OPPh_2CH_2CH_2PPh_2O{\cdot}SnPh_3Cl$ (**6**), 2.357(3) Å.[37] These bond lengths, however, are in contrast to those in the related triphenylphosphine oxide adducts. For example, in $Ph_3PO{\cdot}SnPh_3Cl$[38] and $Ph_3PO{\cdot}SnPh_2Cl_2$[39] the P═**O** → **Sn** bond lengths are 2.392 Å 2.278(2) Å respectively, i.e. significantly longer and shorter respectively than in **3** and **4**! When the coordination number increases to six seems, stronger (i.e. shorter) P═**O** → **Sn** interactions are observed, as evidenced by the value 2.214 Å for *trans*-$(Ph_3PO)_2{\cdot}SnPh_2Cl_2$[39] and 2.230(2) Å in the six-coordinate polymeric $[Cl_2Me_2Sn{\cdot}OPPh_2CH_2CH_2PPh_2O{\cdot}SnMe_2Cl_2]_n$.[40]

The relative orientation of the P═O and C═O oxygen atoms, with an average dihedral angle of 127°, resembles that of the free ligand rather than that noted in the bidentate uranyl complex form.

Bidentate complex 5

In **1**·Ph_2SnCl_2 (**5**) the ligand acts in the bidentate chelating mode toward tin via both P═O and C═O groups to form a six-membered SnO_2PC_2 ring and distorted octahedral coordination geometry at tin. The crystal contains two independent molecules, **5a** and **5b**, in the asymmetric unit. An analysis of the chelate six-membered ring conformation reveals a peculiar feature: the two independent molecules are in different conformations. Thus, molecule **5a** displays a boat conformation while molecule **5b** displays a twist-boat conformation.[41]

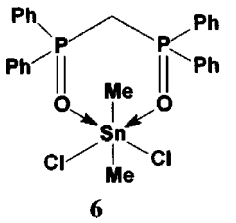
The bond angles in the molecular skeleton of the coordinated CMPO ligand in **5**, compared with the free ligand and complexes **3** and **4**, are strongly influenced by chelate ring formation. Thus, the P1–C1–C2 (108.9(2)°) and Sn1–O1–P1 (130.4(1)°) bond angles are significantly reduced in **5a** and **b** in comparison with **1, 3** and **4**.

The coordinated P═O and C═O bond lengths of **5a/5b**, 1.508(2)/1.512(2) Å and 1.250(4)/1.247(4) Å respectively, are both longer than in the free ligand, as expected. The P═O bond lengths are the similar to those noted above in **3** and **4**; however, the P═**O** → **Sn** bond lengths in **5a** and **5b** of 2.278(2) and 2.252(2)Å are significantly shorter than the equivalent bonds in **3** and **4** noted above, suggesting a stronger interaction with the tin atom. This observation illustrates the stronger phosphine oxide coordination in the chelate system, probably due to the greater Lewis acidity of Ph_2SnCl_2 cf. Ph_3SnCl and Me_2SnCl_2. However, as noted above for $Ph_3PO{\cdot}SnPh_2Cl_2$ and $(Ph_3PO)_2{\cdot}SnPh_2Cl_2$, the six-coordinated P═**O** → **Sn** bond length is significantly shorter than the five-coordinate species, 2.278(2) vs 2.214(2) Å. As expected, the relationship between the two coordinated oxygen atoms resembles that of the uranyl complex (Figure 6), with an average dihedral angle of 15°.

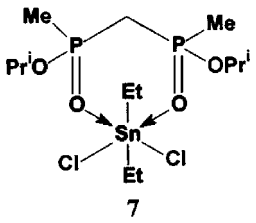
Comparison of the C═**O** → **Sn** bond length in **5** with other monodentate C═**O** → **Sn** bond lengths further emphasizes the strengthening of the individual components of the chelate over their monodentate equivalents. Thus, the C═**O** → **Sn** bonds in **5**, of 2.314(2) and 2.342(2) Å, may be compared with a bond length of 2.399(11) Å for a reported lactam derivative of Ph_3SnCl.[42] Unfortunately, we cannot find a dichlorotin/amide/lactam derivative to assess whether this is only true for the more Lewis acidic dihalo complexes. Overall, the data lead to the strong conclusion that there is a non-entropic stabilization of the bonding interactions upon chelation with both stronger P═O and C═O coordination bonds to tin.

The two phenyl groups are almost coplanar, with dihedral angles of 10.8° in **5a** and 21.7° in **5b**. A search of the Cambridge Crystallographic Database[43] for six-coordinate tin complexes Ph_2SnX_4 (X is any atom, non-ionic, non-polymeric, error-free structure that contains no transition metals) revealed that in each case the phenyl rings are coplanar in all structures, e.g. bis(triphenylphosphine oxide) diphenyltindichloride.[39] There are four crystal structures within this set involving tin coordinated by two chlorine and two oxygen atoms ($Ph_2SnCl_2O_2$), but in none of these are the oxygen atoms part of a chelate ring. Complex **5** is unique in this aspect.

The structure of the chelate complex **5** can be compared with that of other phosphine oxide chelate compounds, e.g. bis(diphenylphosphineoxo)methane dimethyltindichloride, $OPh_2PCH_2PPh_2O{\cdot}Me_2SnCl_2$ (**6**)[40] and bis[methyl(isopropoxy) phosphineoxo]methane diethyltin dichloride adduct, $[Me(^iPrO)P(O)]_2CH_2{\cdot}Et_2SnCl_2$ (**7**).[44] Complexes **6** and **7** have P═**O** → **Sn** bonds in the range 2.26 to 2.54 Å, with corresponding P═O bond lengths in the range 1.49 to 1.57 Å. The related bond lengths in **5** are within these ranges.



6



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