

Dichlorodiphenylantimony(V) derivatives of oxo- and thioimidodiphosphinic acids, containing novel inorganic $\text{SbO}_2\text{P}_2\text{N}$ and SbOSP_2N rings: crystal and molecular structures of $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)(\text{XPPH}_2)\text{N}]$ ($\text{X} = \text{O}, \text{S}$)

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Abstract

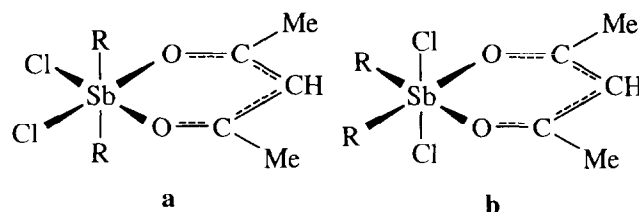
$\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)(\text{XPR}_2)\text{N}]$ ($\text{X} = \text{O}, \text{S}$; $\text{R} = \text{Me}, \text{Ph}$) were prepared by metathesis reactions between Ph_2SbCl_3 and an alkali metal salt of the corresponding imidodiphosphinic acid. All new compounds were characterized by IR, multinuclear NMR and mass spectrometry. The molecular structures of $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)_2\text{N}]$ (**1**) and $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)(\text{SPPH}_2)\text{N}]$ (**2**) were determined by X-ray diffraction. In both compounds the imidodiphosphinato ligand is coordinated through both chalcogen atoms to antimony ($\text{Sb}-\text{O}(1)$ 2.128(3), $\text{Sb}-\text{O}(2)$ 2.112(3) in (**1**), and $\text{Sb}-\text{O}(1)$ 2.113(3), $\text{Sb}-\text{S}(1)$ 2.614(2) Å in (**2**)), leading to novel, non-planar inorganic $\text{SbO}_2\text{P}_2\text{N}$ and SbOSP_2N rings respectively. In both cases the coordination geometry around the metal atom is slightly distorted octahedral, with the phenyl groups in axial positions ($\text{C}(1)-\text{Sb}-\text{C}(7)$ 173.5(2) and 176.8(2)° in (**1**) and (**2**) respectively).

Keywords: Antimony; Oxoimidodiphosphinic acids; Thioimidodiphosphinic acids; Crystal structure; Metallacycle

1. Introduction

NMR studies in solution for (acetylacetonato)dichlorodiorganantimony(V) complexes have been reported to be consistent with the presence of only cis-dichloro isomer (**a**) for $\text{R} = \text{Me}$ [1], and an equilibrium between cis-(**a**) and trans-dichloro (**b**) isomers for $\text{R} = \text{Ph}$ and substituted Ph [1,2]. However, only the cis-dichloro isomer (**a**) of $\text{Ph}_2\text{SbCl}_2[(\text{OCMe})_2\text{CH}]$ (two crystal forms which differ essentially only in the dihedral angle between the phenyl ring planes) could be isolated in solid

state as established by a single-crystal X-ray diffraction study [3,4].



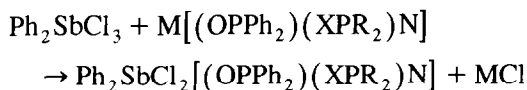
Our interest in organoantimony derivatives of phosphorus ligands [5–12] and inorganic (carbon-free) chelate rings [13] led us to investigate compounds of the type $\text{Ph}_2\text{SbCl}_2[(\text{XPR}_2)(\text{YPR}'_2)\text{N}]$ ($\text{X}, \text{Y} = \text{O}, \text{S}$; $\text{R}, \text{R}' = \text{Me}, \text{Ph}$), which are structurally related to the above acetylacetonato complexes. We report here on the synthesis, spectroscopic characterization and single-crystal

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X-ray diffractometry studies of some derivatives containing both symmetric and asymmetric ligands.

2. Results and discussion

The title compounds were obtained by reacting stoichiometric amounts of anhydrous Ph_2SbCl_3 and the alkaline salt of the corresponding phosphorus acid, in boiling toluene, according to the following equation:



$\text{M} = \text{Na}; \text{X} = \text{O}; \text{R} = \text{Ph}$

$\text{M} = \text{K}; \text{X} = \text{O}; \text{R} = \text{Me}$

$\text{M} = \text{K}; \text{X} = \text{S}; \text{R} = \text{Ph}$

The diphenylantimony(V) compounds were isolated after recrystallization from toluene as colorless, crystalline solids, soluble in organic solvents. They were characterized using IR, multinuclear NMR spectroscopy, and mass spectrometry. For the tetraphenylthioimidodiphosphinato derivative, the retention of toluene in the crystal, to give the composition $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)(\text{SPPH}_2)\text{N}] \cdot 0.5\text{CH}_3\text{C}_6\text{H}_5$, was suggested by elemental analysis, ^1H and ^{13}C NMR, and confirmed by X-ray diffractometry.

The IR spectra of $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)(\text{XPR}_2)\text{N}]$ exhibit strong absorptions in the regions 1240–1175, 1130–1010, 580–500 and 350–270 cm^{-1} . These were assigned to $\nu_{\text{as}}(\text{P}_2\text{N})$, $\nu(\text{PO})$, $\nu(\text{SbO})$ and $\nu(\text{SbCl})$ stretching vibrations by comparison with the spectra of the free acids, their alkali metal salts, and Ph_2SbCl_3 used as starting materials. Additionally, a strong absorption at 530 cm^{-1} was assigned to $\nu(\text{PS})$ in the spectrum of the monothio derivative. The values of $\nu(\text{PO})$ and $\nu(\text{PS})$ vibrations are in the characteristic range for single phosphorus–oxygen and phosphorus–sulfur bonds, in agreement with the bidentate coordination of the ligand, through both chalcogen atoms, established by X-ray diffractometry.

The ^1H NMR spectra of the title compounds show the expected resonances for the phenyl groups bonded to antimony and the organic groups attached to phosphorus. In all cases the lower field signal (δ ca. 8 ppm) is due to the ortho protons of the $\text{Sb}-\text{C}_6\text{H}_5$ groups. For $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)_2\text{N}]$ and $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)(\text{OPMe}_2)\text{N}]$ only one multiplet resonance (δ ca. 7.5 ppm) is present for the ortho protons of the $\text{P}-\text{C}_6\text{H}_5$, with a splitting pattern corresponding to phosphorus–proton and proton–proton couplings. For $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)(\text{OPMe}_2)\text{N}]$ a high field resonance ($\delta = 1.31\text{dd}$, $^2J(\text{PH}) 14.4$, $^4J(\text{PH}) 1.2$ Hz) is observed for the methyl protons.

The ^1H NMR spectrum of $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)(\text{SPPH}_2)\text{N}] \cdot 0.5\text{CH}_3\text{C}_6\text{H}_5$ is considerably more com-

plex, owing to the presence of four types of phenyl group, i.e. $\text{P}(\text{S})\text{C}_6\text{H}_5$, $\text{P}(\text{O})\text{C}_6\text{H}_5$, SbC_6H_5 and $\text{CH}_3\text{C}_6\text{H}_5$. However, in addition to the signal for the ortho $\text{Sb}-\text{C}_6\text{H}_5$ protons, two multiplet resonances, at $\delta = 7.55$ and 7.44 ppm (partially overlapped by resonances of other aromatic protons), were assigned to the two types of phenyl group bonded to phosphorus in a ligand unit. A singlet resonance at $\delta = 2.39$ ppm, assigned to the methyl protons of toluene, indicates the presence of toluene as crystallization solvent.

In the ^{13}C NMR spectra, resonances for the carbon atoms of the phenyl groups attached to both antimony and phosphorus are observed in the aromatic region and their assignment is based on HETCOR studies. The signals for $\text{P}-\text{C}_6\text{H}_5$ are generally split into two components of equal intensity due to phosphorus–carbon couplings. For the ipso carbons of the $\text{P}-\text{C}_6\text{H}_5$ groups the doublet of doublet pattern is due to $^1J(\text{PC})$ and $^3J(\text{PC})$ couplings. For the thioimidodiphosphinato derivative the assignments of the ipso carbon resonances for $\text{P}(\text{O})-\text{C}_6\text{H}_5$ and $\text{P}(\text{S})-\text{C}_6\text{H}_5$ are based on the magnitude of the $^1J(\text{PC})$ coupling constant. The spectrum of $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)(\text{OPMe}_2)\text{N}]$ exhibits a high field doublet of doublets resonance ($\delta = 19.84\text{dd}$, $^1J(\text{PC}) 96.8$, $^3J(\text{PC}) 2.9$) for $\text{P}-\text{CH}_3$.

The ^{31}P NMR spectra of the compounds containing asymmetric ligands show, as expected, two resonances. For $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)(\text{SPPH}_2)\text{N}] \cdot 0.5\text{CH}_3\text{C}_6\text{H}_5$ both signals exhibit a doublet pattern owing to $^2J(\text{PP})$ coupling, while in the case of $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)(\text{OPMe}_2)\text{N}]$ the phosphorus–phosphorus coupling is observed only for the Ph_2PO signal. The spectrum of $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)_2\text{N}]$, which contains a symmetrical ligand, shows a singlet resonance, thus suggesting the equivalence of the phosphorus atoms in the molecule on the NMR time scale.

Various ^1H NMR studies point to an equilibrium in solution between the cis- and trans-dichloro isomers of the related $\text{Ph}_2\text{SbCl}_2[(\text{OCMe})_2\text{CH}]$ [1,2]. By contrast, for the compounds investigated in this work there is no NMR evidence to suggest a similar behavior.

The presence of $\text{M} + \text{H}^+$ fragments, although of very low intensity, in the mass spectra of the compounds containing asymmetric ligands confirms their identity. In both cases the $\text{M} - \text{Cl}^+$ fragment is the base peak. For $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)_2\text{N}]$ the molecular ion is not observed and the base peak is Ph^+ ; however, the $\text{M} - \text{Cl}^+$ fragment is also of high intensity. In the case of $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)(\text{OPMe}_2)\text{N}]$, ions heavier than the molecular mass were also observed (860 (22) $\text{Ph}_6\text{Me}_4\text{P}_4\text{O}_4\text{N}_2\text{SbH}^+$; 859 (48) $\text{Ph}_6\text{Me}_4\text{P}_4\text{O}_4\text{N}_2\text{Sb}^+$; 705 (48) $\text{Ph}_4\text{Me}_4\text{P}_4\text{O}_4\text{N}_2\text{Sb}^+$) and were tentatively assigned to fragments containing a ligand:Sb ratio of 2:1. This indicates a rearrangement process which occurs during the fragmentation of the parent compound.

Crystals of $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)_2\text{N}]$ (1) and Ph_2-

Table 1

Relevant interatomic distances (Å) and angles (deg) in $\text{Pb}_2\text{SbCl}_2[(\text{OPPh}_2)_2\text{N}]$ (1) and $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)(\text{SPPPh}_2)\text{N}] \cdot 0.5\text{C}_6\text{H}_5\text{CH}_3$ (2)

	(1) X = O(2)	(2) X = S(1)		(1) X = O(2)	(2) X = S(1)
Sb–O(1)	2.128(3)	2.113(3)	O(1)–Sb–X	87.3(1)	90.5(1)
Sb–X	2.112(3)	2.614(2)	O(1)–Sb–Cl(2)	86.9(1)	88.7(1)
Sb–Cl(1)	2.452(1)	2.422(2)	X–Sb–Cl(1)	92.6(1)	86.7(1)
Sb–Cl(2)	2.420(1)	2.428(2)	Cl(1)–Sb–Cl(2)	93.2(1)	93.9(1)
Sb–C(1)	2.124(4)	2.146(7)	O(1)–Sb–Cl(1)	177.6(1)	176.3(1)
Sb–C(7)	2.131(4)	2.141(7)	X–Sb–Cl(2)	173.1(1)	176.7(1)
			C(1)–Sb–C(7)	173.5(2)	176.8(2)
P(1)–O(1)	1.546(3)	1.543(4)	C(1)–Sb–O(1)	88.4(2)	91.2(2)
P(1)–N	1.592(4)	1.582(4)	C(1)–Sb–X	89.6(1)	91.5(2)
P(2)–N	1.582(4)	1.587(4)	C(1)–Sb–Cl(1)	89.2(1)	91.4(2)
P(2)–X	1.539(3)	2.037(2)	C(1)–Sb–Cl(2)	94.1(1)	91.7(2)
			C(7)–Sb–O(1)	91.3(2)	87.4(2)
O(1)·····X	2.928	3.374	C(7)–Sb–X	83.9(1)	85.7(2)
			C(7)–Sb–Cl(1)	91.1(1)	89.9(1)
			C(7)–Sb–Cl(2)	92.3(1)	91.1(2)
			Sb–O(1)–P(1)	129.4(2)	132.6(2)
			O(1)–P(1)–N	115.3(2)	116.7(2)
			P(1)–N–P(2)	125.8(2)	132.3(3)
			X–P(2)–N	116.2(2)	117.9(2)
			Sb–X–P(2)	130.5(2)	106.1(1)

$\text{SbCl}_2[(\text{OPPh}_2)(\text{SPPPh}_2)\text{N}] \cdot 0.5\text{C}_6\text{H}_5\text{CH}_3$ (2), suitable for X-ray diffractometry studies were grown from toluene. Important interatomic distances and bond angles for both compounds are listed in Table 1. Figs. 1 and 2 show the three-dimensional representation of the molecular structures of (1) and (2), with the atom numbering scheme. In both cases the crystal contains discrete molecular units, separated by normal van der Waals distances.

The Sb–O bond lengths (ca. 2.11–2.13 Å) in both compounds (1) and (2) are of the same magnitude as in $\text{Me}_3\text{Sb}[\text{O}(\text{S})\text{PPh}_2]_2$ (Sb–O 2.111(5) Å), which contains the monothiophosphinic ligand bonded only through oxygen (the sulfur atom not being involved in sec-

ondary interactions to the metal, Sb···S av. 3.961 Å) [9]. The antimony–sulfur distance in (2) also corresponds to a normal Sb–S covalent bond (cf. $\text{Me}_3\text{Sb}[\text{S}(\text{S})\text{PPh}_2]_2$ av. Sb–S 2.611(5), Sb···S 3.79(7) Å [10]). Thus, the phosphorus ligand is coordinated to antimony through both chalcogen atoms, leading to a distorted octahedral geometry around the metal in both (1) and (2); the phenyl groups attached to the metal occupy trans positions, with pairs of chlorine atoms and chalcogen atoms, each in cis positions. In both compounds the Sb–C bond lengths are similar to those observed in the anhydrous Ph_2SbCl_3 (Sb–C 2.125(9) Å) [14]. By contrast, the magnitude of the Sb–Cl bonds

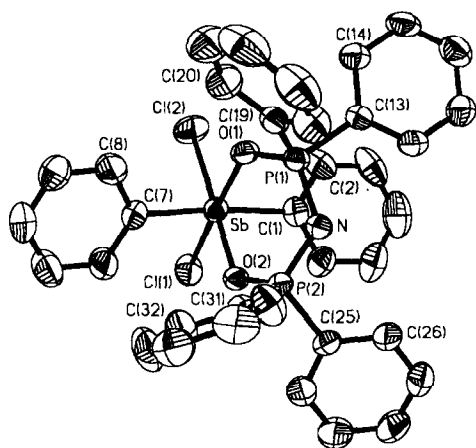


Fig. 1. Three-dimensional representation of the molecular structure of $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)_2\text{N}]$ (1).

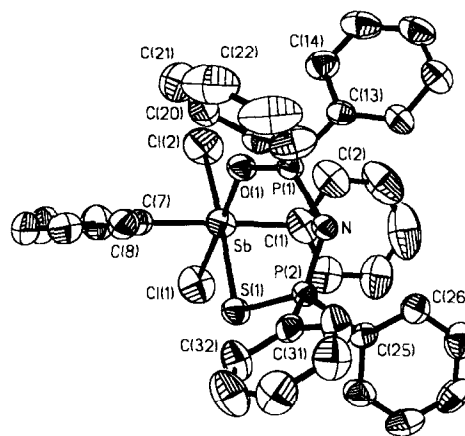


Fig. 2. Three-dimensional representation of the molecular structure of $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)(\text{SPPPh}_2)\text{N}] \cdot 0.5\text{C}_6\text{H}_5\text{CH}_3$ (2) (the toluene molecule is not shown).

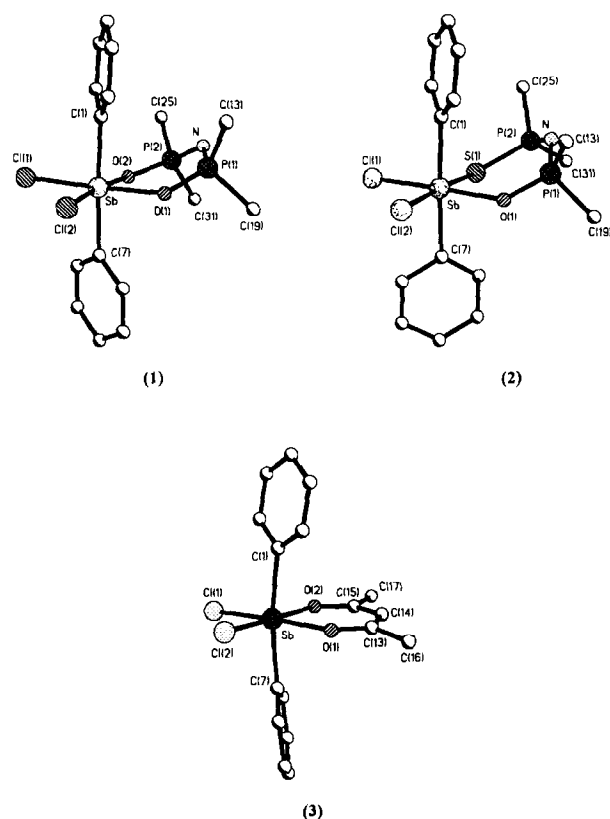


Fig. 3. Comparison of the metal coordination geometry and conformation of the six-membered chelate rings in $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)_2\text{N}]$ (1), $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)(\text{SPPPh}_2)\text{N}] \cdot 0.5\text{CH}_3\text{C}_6\text{H}_5$ (2) (this work), and $\text{Ph}_2\text{SbCl}_2[(\text{OCMe})_2\text{CH}]$ (3) [3] (for clarity only the ipso-carbons of the phenyl groups attached to phosphorus are shown).

(av. 2.436 and 2.425 Å in (1) and (2) respectively) are intermediate between terminal (av. 2.367 Å) and bridging ($\text{Sb}(1)\text{--Cl}$ 2.620, $\text{Sb}(2)\text{--Cl}$ 2.839 Å) antimony–chlorine bonds formed in the dimeric structure of anhydrous Ph_2SbCl_3 [14]. This reflects the weaker trans

influence of chalcogen atoms compared with chlorine atoms.

The SbC_2 fragment is almost linear ($\text{C}(1)\text{--Sb--C}(7)$ 173.5(2)° in (1) and 176.8(2)° in (2)), with the Sb--C bonds bent towards the $\text{O}(1) \cdots \text{X}$ ($\text{X} = \text{O}(2)$, $\text{S}(1)$) side of the equatorial plane (angles of $\text{C}(1)\text{--Sb}$ and $\text{C}(7)\text{--Sb}$ axes to the best SbCl_2OX plane: 87.5 and 86.0° in (1), and 89.8 and 87.0° in (2)). The SbCl_2OX ($\text{X} = \text{O}$, S) system is almost planar (deviation range from the best plane: -0.066 to 0.068 Å in (1), and -0.048 to 0.024 Å in (2)). The distortion of the coordination polyhedron is reflected in the magnitude of the angles between axial and equatorial bonds (Table 1).

The main difference between the molecular structures of (1) and (2) is the relative orientation of the phenyl groups attached to antimony. The dihedral angle between the phenyl ring planes is 29.2° in (1), while in (2) they are almost perpendicular, i.e. 85.7°.

The coordination geometry around antimony in $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)_2\text{N}]$ (1) and $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)(\text{SPPPh}_2)\text{N}]$ (2) is very similar to that observed in the related acetylacetonato complex, $\text{Ph}_2\text{SbCl}_2[(\text{OCMe})_2\text{CH}]$ (3) (Fig. 3). In the latter, some important molecular dimensions are: Sb--O (av.) 2.117, Sb--Cl (av.) 2.418, Sb--C (av.) 2.130 Å, $\text{C}(1)\text{--Sb--C}(7)$ 171.6(5), $\text{Cl}(1)\text{--Sb--Cl}(2)$ 95.7(1), $\text{O}(1)\text{--Sb--O}(2)$ 86.5(4), *cis* Cl--Sb--O (av.) 89.0, *trans* Cl--Sb--O 174.4°; the SbC_2 fragment is also bent towards the oxygen ligand (angles of $\text{C}(1)\text{--Sb}$ and $\text{C}(7)\text{--Sb}$ axes to the best SbCl_2O_2 plane: 85.6 and 86.0° — calculated from published atomic coordinates), while the dihedral angle between the phenyl ring planes is 38° [3].

In the OPNPX fragment of the ring, the phosphorus–oxygen and phosphorus–sulfur bonds (Table 1) are longer than in the parent free acid (i.e. $(\text{OPPh}_2)_2\text{NH}$ [15]: P--O 1.519(2) Å; $(\text{OPPh}_2)(\text{SPPPh}_2)\text{NH}$ [16]: P--O 1.491(4), P--S 1.935(2) Å) and their

Table 2

Comparative dihedral angles and least-square planes in the molecules (1), (2) (this work) and $\text{Ph}_2\text{SbCl}_2[(\text{OCMe})_2\text{CH}]$ [3]

	(1) X = O(2)	(2) X = S(1)	$\text{Ph}_2\text{SbCl}_2[(\text{OCMe})_2\text{CH}]$ ^a X = O(2)
Deviation (Å)			
From $\text{SbO}(1)\text{X}$ plane	P(1)	-0.685	C(13)
	P(2)	-0.484	C(14)
	N	-1.122	C(15)
From $\text{O}(1)\text{P}(1)\text{P}(2)\text{X}$ plane	O(1)	0.053	
	P(1)	-0.055	
	P(2)	0.055	
	O(2)	-0.053	
Dihedral angles (deg)			
$\text{SbO}(1)\text{X}/\text{O}(1)\text{P}(1)\text{P}(2)\text{X}$	22.4	34.6	
$\text{NP}(1)\text{O}(1)/\text{NP}(2)\text{X}$	27.1	27.2	

^a Calculated from the atomic coordinates published in Ref. [3].

magnitude suggests a predominant single bond character (cf. $\text{Ph}_2\text{P}(=\text{O})\text{OH}$ [17]: $\text{P}-\text{O}$ 1.526(6), $\text{P}=\text{O}$ 1.486(6) Å; $\text{Me}-\text{S}-\text{PPh}_2=\text{N}-\text{Ph}_2\text{P}=\text{S}$ [16]: $\text{P}-\text{S}$ 2.069(3), $\text{P}=\text{S}$ 1.956(3) Å). The two phosphorus–nitrogen bonds in the ring are equivalent and their lengths intermediate (range 1.582–1.592 Å) between single $\text{P}-\text{N}$ and double $\text{P}=\text{N}$ bonds (cf. $\text{Me}-\text{S}-\text{PPh}_2=\text{N}-\text{Ph}_2\text{P}=\text{S}$ [16]: $\text{P}-\text{N}$ 1.619(4), $\text{P}=\text{N}$ 1.568(4) Å), thus suggesting a partial double bond character, i.e. some π -electron delocalization over the $\text{P}-\text{N}-\text{P}$ fragment. The $\text{P}(1)-\text{N}-\text{P}(2)$ angle in (2) ($132.3(3)^\circ$) is of the same magnitude as in the free acid ($131.4(3)^\circ$) [14]. By contrast, the linear P_2N fragment observed in $(\text{OPPh}_2)_2\text{NH}$ [13] becomes angular ($125.8(2)^\circ$) in (1) to allow the chelation by the ligand.

The SbOXp_2N inorganic rings display a twisted boat conformation (Fig. 3, Table 2), with both phosphorus and nitrogen atoms on the same side with respect to SbOX plane. A similar conformation was observed for the SnOXp_2N rings in the related diorganotin(IV) complexes $^n\text{Bu}_2\text{Sn}[(\text{OPPh}_2)_2\text{N}]_2$ [18] and $\text{R}_2\text{Sn}[(\text{OPPh}_2)(\text{SPPH}_2)\text{N}]_2$ [19]. By contrast, in the β -diketonato analogue $\text{Ph}_2\text{SbCl}_2[(\text{OCMe})_2\text{CH}]$ the carbon-containing SbO_2C_3 ring is almost planar [3].

The chalcogen–chalcogen distance in the coordinated ligand is $\text{O}(1)\cdots\text{O}(2)$ 2.928 Å in (1) and $\text{O}(1)\cdots\text{S}(1)$ 3.374 Å in (2), shorter than in the related diorganotin containing the same ligand, i.e. $\text{O}\cdots\text{O}$ 3.073 Å in $^n\text{Bu}_2\text{Sn}[(\text{OPPh}_2)_2\text{N}]_2$ [18], $\text{O}\cdots\text{S}$ 3.772 Å in $\text{Me}_2\text{Sn}[(\text{OPPh}_2)(\text{SPPH}_2)\text{N}]_2$, and $\text{O}\cdots\text{S}$ 3.489 Å in $\text{Ph}_2\text{Sn}[(\text{OPPh}_2)(\text{SPPH}_2)\text{N}]_2$ [19]. The modification of the ligand ‘bite’ owing to the flexibility of the OPNPX skeleton explains the versatility of this type of ligand in responding to various coordination requirements of a metal atom, leading to cyclization.

3. Experimental details

3.1. Materials

Anhydrous Ph_2SbCl_3 was obtained by heating $\text{Ph}_2\text{SbCl}_3 \cdot \text{H}_2\text{O}$ [14]. The imidophosphinic acids and their alkali metal salts were prepared according to literature methods [20–23]. IR spectra were run in the range 4000–200 cm^{-1} on a Perkin–Elmer 283B spectrometer, as KBr disks. ^1H , ^{13}C and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded as CDCl_3 solutions using Varian VXR 300S or Gemini 200 instruments. The chemical shifts are reported in ppm relative to TMS and H_3PO_4 85% respectively. FAB(+) mass spectra were recorded using a Jeol SX-102A instrument.

3.2. Synthesis of $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)_2\text{N}]$ (1)

A mixture of Ph_2SbCl_3 (0.764 g, 2 mmol) and $\text{Na}[(\text{OPPh}_2)_2\text{N}]$ (0.85 g, 2 mmol) in 20 ml anhydrous

toluene was stirred under reflux for 1 h, then filtered hot to remove the resulting NaCl. On cooling, colorless crystals started to deposit. The filtrate was concentrated to ca. 10 ml and the solid product was separated by filtration. Recrystallization from hot toluene allowed separation of the title compound as colorless crystals. Yield: 0.94 g (62.7%, after recrystallization), m.p. 257°C . Anal. Found: C, 56.79; H, 3.98; N, 1.80. $\text{C}_{36}\text{H}_{30}\text{Cl}_2\text{NO}_2\text{P}_2\text{Sb}$. Calc.: C, 56.64; H, 3.93; N, 1.84%. IR (KBr): $\nu(\text{P}_2\text{N})$ 1210vs; $\nu(\text{PO})$ 1120s, 1020vs,br; $\nu(\text{PC})$ 750s, 740s, 720vs, 685vs; $\nu(\text{SbO})$ 550vs, 510s; $\nu(\text{SbCl})$ 340w, 285s. ^1H NMR (200 MHz): 6.95dd (4H, $\text{Sb}-\text{C}_6\text{H}_5$ -meta, $^3J(\text{HH})$ 7.8); 7.15t (2H, $\text{Sb}-\text{C}_6\text{H}_5$ -para, $^3J(\text{HH})$ 7.3); 7.26ddd (8H, $\text{P}-\text{C}_6\text{H}_5$ -meta, $^3J(\text{HH})$ 7.4, $^4J(\text{HH})$ 3.6); 7.40tt (4H, $\text{P}-\text{C}_6\text{H}_5$ -para, $^3J(\text{HH})$ 7.2, $^2J(\text{HH})$ 1.5); 7.51ddd (8H, $\text{P}-\text{C}_6\text{H}_5$ -ortho, $^3J(\text{PH})$ 13.2, $^3J(\text{HH})$ 6.9, $^4J(\text{HH})$ 1.5); 8.02dd (4H, $\text{Sb}-\text{C}_6\text{H}_5$ -ortho, $^3J(\text{HH})$ 8.5, $^4J(\text{HH})$ 1.2). ^{13}C NMR (50 MHz): 127.55s ($\text{C}_m(\text{Sb})$); 127.98d ($\text{C}_m(\text{P})$, $^3J(\text{PC})$ 13.9); 129.42s ($\text{C}_p(\text{Sb})$); 130.85s ($\text{C}_i(\text{Sb})$); 130.85d ($\text{C}_o(\text{P})$, $^2J(\text{PC})$ 11.8); 131.38s,br ($\text{C}_o(\text{Sb})$, $\text{C}_p(\text{P})$); 133.71dd ($\text{C}_i(\text{P})$, $^1J(\text{PC})$ 137.3, $^3J(\text{PC})$ 3.2). ^{31}P NMR (121.4 MHz): 25.5s. MS (m/e (%)): 726 (49) $\text{M}-\text{Cl}^+$; 614 (85) $\text{Ph}_5\text{P}_2\text{O}_2\text{NSb}^+$; 572 (14) $\text{Ph}_4\text{P}_2\text{O}_2\text{NSbCl}^+$; 537 (15) $\text{Ph}_4\text{P}_2\text{O}_2\text{NSb}^+$; 418 (67) $\text{Ph}_4\text{P}_2\text{O}_2\text{NH}_2^+$; 400 (11) $\text{Ph}_4\text{P}_2\text{ON}^+$; 275 (28) Ph_2Sb^+ ; 201 (65) Ph_2PO^+ ; 198 (11) PhSb^+ ; 185 (23) Ph_2P^+ ; 156 (8) SbCl^+ ; 154 (57) Ph_2^+ ; 137 (26) SbO^+ ; 121 (9) Sb^+ ; 77 (100) Ph^+ .

3.3. Synthesis of $\text{Ph}_2\text{SbCl}_2[(\text{OPPh}_2)(\text{SPPH}_2)\text{N}] \cdot 0.5\text{CH}_3\text{C}_6\text{H}_5$ (2)

A mixture of Ph_2SbCl_3 (0.764 g, 2 mmol) and $\text{K}[(\text{OPPh}_2)(\text{SPPH}_2)\text{N}]$ (0.942 g, 2 mmol) in 20 ml anhydrous toluene was stirred under reflux for 2 h, then filtered hot to remove the resulting NaCl. On cooling, colorless crystals started to deposit. The filtrate was concentrated to ca. 10 ml and the solid product was separated by filtration. Recrystallization from hot toluene allowed separation of the title compound as colorless crystals. Yield: 0.86 g (63.3%, after recrystallization), m.p. $254-5^\circ\text{C}$. Anal. Found: C, 57.53; H, 4.11; N, 1.71. $\text{C}_{36}\text{H}_{30}\text{Cl}_2\text{NOP}_2\text{SSb} \cdot 0.5\text{C}_7\text{H}_8$. Calc.: C, 57.47; H, 4.16; N, 1.69%. IR (KBr): $\nu(\text{P}_2\text{N})$ 1240 vs,br; $\nu(\text{PO})$ 1115s,br, 1010vs; $\nu(\text{PC})$ 730,sh, 720vs, 700s,sh, 685vs; $\nu(\text{PS})$ 530s; $\nu(\text{SbO})$ 545s, 500s; $\nu(\text{SbCl})$ 340w, 275vs,br. ^1H NMR (300 MHz): 2.39s (3H, $\text{CH}_3\text{C}_6\text{H}_5$); 7.01t (8H, $\text{Sb}-\text{C}_6\text{H}_5$ -meta, $^3J(\text{HH})$ 7.7); 7.1–7.48m (33H, complex signal — see text); 7.44dd (8H, $\text{P}(\text{O})\text{C}_6\text{H}_5$ -ortho, $^3J(\text{PH})$ 14.4 $^3J(\text{HH})$ 7.1 — partially overlapped); 7.55dd (8H, $\text{P}(\text{S})\text{C}_6\text{H}_5$ -ortho, $^3J(\text{PH})$ 13.3, $^3J(\text{HH})$ 7.2); 8.14d (8H, $\text{Sb}-\text{C}_6\text{H}_5$ -ortho, $^3J(\text{HH})$ 7.8). ^{13}C NMR (50 MHz): 21.35s ($\text{CH}_3\text{C}_6\text{H}_5$); 125.21s ($\text{CH}_3\text{C}_6\text{H}_5$ -para); 127.64s ($\text{C}_m(\text{Sb})$); 128.10d ($\text{C}_m(\text{C}_6\text{H}_5\text{PO}, \text{C}_6\text{H}_5\text{PS})$, $^3J(\text{PC})$ 13.9); 128.14s

(CH₃C₆H₅-*meta*); 128.93s (CH₃C₆H₅-*ortho*); 129.38s (C_p(Sb)); 130.44d (C_o, P(O)-C₆H₅, ²J(PC) 11.5); 130.77s (C_i(Sb)); 130.94d (C_o, P(S)-C₆H₅, ²J(PC) 10.4); 131.08s (C_o(Sb)); 131.23d (C_p(P-C₆H₅), ⁴J(PC) 3.5); 131.53d (C_p(P-C₆H₅), ⁴J(PC) 2.3); 133.56dd (C_i, P(O)-C₆H₅, ¹J(PC) 134.6, ³J(PC) 4.7); 135.23dd (C_i, P(S)-C₆H₅, ¹J(PC) 107.3, ³J(PC) 5.2); 137.72s (CH₃C₆H₅-*ipso*). ³¹P NMR (121.4 MHz): 26.5d (Ph₂PO, ²J(PP) 2.3); 32.1d (Ph₂PS, ²J(PP) 2.3). MS (*m/e*, (%)): 778 (1) M + H⁺; 745 (40) M - S⁺; 742 (100) M - Cl⁺; 707 (2) Ph₆P₂OSNSb⁺; 668 (9) Ph₅P₂ONSbCl₂⁺; 630 (51) Ph₅P₂OSNSb⁺; 588 (12) Ph₄P₂OSNSbCl⁺; 553 (3) Ph₄P₂OSNSb⁺; 433 (23) Ph₄P₂OSNH⁺; 432 (55) Ph₄P₂OSN⁺; 400 (56) Ph₄P₂ON⁺; 345 (14) Ph₂SbCl₂⁺; 275 (3) Ph₂Sb⁺; 217 (20) Ph₂PS⁺; 201 (38) Ph₂PO⁺; 154 (42) Ph₂⁺; 137 (19) SbO⁺; 121 (2) Sb⁺; 77 (14) Ph⁺.

3.4. Synthesis of Ph₂SbCl₂[(OPPh₂)(OPMe₂)N]

A mixture of Ph₂SbCl₃ (0.764 g, 2 mmol) and K[(OPPh₂)(OPMe₂)N] (0.662 g, 2 mmol) in 20 ml anhydrous toluene was stirred under reflux for 2 h, then filtered hot to remove the resulting NaCl. On cooling, colorless crystals started to deposit. The solid product was separated by filtration and recrystallized from hot toluene. Yield: 0.99 g (77%, after recrystallization), m.p. 236–7°C. Anal. Found: C, 48.72; H, 4.06; N, 1.80. C₂₆H₂₆Cl₂NO₂P₂Sb. Calc.: C, 48.86; H, 4.10; N, 2.19%. IR (KBr): ν(P₂N) 1230m, br; ν(PO) 1130vs,br, 1115s; ν(PC) 740mw, 730ms, 720ms, 685ms; ν(SbO) 530s, 490mw; ν(SbCl) 350w, 280s. ¹H NMR (300 MHz): 1.31dd (6H, CH₃, ²J(PH) 14.4, ⁴J(PH) 1.2);

7.23m (10H, P-C₆H₅-*meta* + *para*, Sb-C₆H₅-*meta*); 7.40tt (2H, Sb-C₆H₅-*para*, ³J(HH) 7.4, ⁴J(HH) 1.6); 7.46ddd (4H, P-C₆H₅-*ortho*, ³J(PH) 13.3, ³J(HH) 7.5, ⁴J(HH) 1.4); 8.12dd (4H, Sb-C₆H₅-*ortho*, ³J(HH) 8.1, ⁴J(HH) 1.6). ¹³C NMR (75 MHz): 19.84dd (CH₃, ¹J(PC) 96.8, ³J(PC) 2.9); 127.76s(C_m(Sb)); 128.00d (C_m(P), ³J(PC) 12.7); 128.90s (C_i(Sb)); 129.59s (C_p(Sb)); 130.72d (C_o(P), ²J(PC) 10.4); 131.24s (C_o(Sb)); 131.37d (C_p(P), ⁴J(PC) 2.3); 134.02dd (C_i(P), ¹J(PC) 138.6, ³J(PC) 2.9). ³¹P NMR (121.4 MHz): 25.0d (Ph₂PO, ²J(PP) 3.9); 46.0s, br (Me₂PO). MS (*m/e* (%)): 638 (1) M + H⁺; 602 (100) M - Cl⁺; 560 (2) M - Ph⁺; 490 (39) Ph₃Me₂P₂O₂NSb⁺; 448 (14) Ph₂Me₂P₂O₂NSbCl⁺; 413 (7) Ph₂Me₂P₂O₂NSb⁺; 345 (6) Ph₂Cl₂Sb⁺; 294 (6) Ph₂Me₂P₂O₂NH₂⁺; 275 (2) Ph₂Sb⁺; 233 (4) PhClSb⁺; 201 (4) Ph₂PO⁺; 154 (6) Ph₂⁺.

3.5. Crystal structure determinations

3.5.1. Crystal data

Crystal data and experimental conditions are listed in Table 3.

3.5.2. Structure determination

Data were collected at 293 K on a Siemens P4 four-circle diffractometer with graphite monochromator for 9630 and 11 152 reflections of which 9132 ($R_{int} = 2.86\%$) and 10996 ($R_{int} = 2.42\%$) were independent, and 6158 ($F > 3.0\sigma(F)$) and 6023 ($F > 4.0\sigma(F)$) for (1) and (2) respectively, were used in the full-matrix least squares refinement. The structures were solved using direct methods [24]. The molecule of toluene in

Table 3

Crystal data, details of intensity measurements and structure refinement for Ph₂SbCl₂[(OPPh₂)₂N] (1) and Ph₂SbCl₂[(OPPh₂)(SPPPh₂)N]·0.5CH₃C₆H₅ (2)

	Ph ₂ SbCl ₂ [(OPPh ₂) ₂ N] (1)	Ph ₂ SbCl ₂ [(OPPh ₂)(SPPPh ₂)N]·0.5CH ₃ C ₆ H ₅ (2)
Molecular formula	C ₃₆ H ₃₀ Cl ₂ NO ₂ P ₂ Sb	C _{39.5} H ₃₄ Cl ₂ NOP ₂ SSb
<i>M</i>	763.2	825.3
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	10.257(2)	37.030(5)
<i>b</i> (Å)	16.053(2)	10.642(2)
<i>c</i> (Å)	20.665(4)	19.642(2)
β(deg)	99.11(2)	101.59(2)
<i>V</i> (Å ³)	3359.6(6)	7582(2)
<i>Z</i>	4	8
<i>D</i> _{calc} (g cm ⁻³)	1.509	1.446
Crystal size (mm ³)	0.58 × 0.44 × 0.26	0.60 × 0.48 × 0.40
λ(Mo K α) (Å)	0.71073	0.71073
μ (Mo K α) (cm ⁻¹)	11.09	10.40
$R = \sum(F_o - F_c) / \sum F_o $ (%)	5.14	5.12
$wR = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$ (%)	5.70	5.85
GOF	1.09	1.12
<i>F</i> (000)	1536	3336
<i>T</i> (K)	293	293

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for (1)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Sb	1777(1)	1437(1)	3706(1)	36(1)
P(1)	-694(1)	2687(1)	3947(1)	35(1)
P(2)	1855(1)	3394(1)	4236(1)	35(1)
Cl(1)	3898(1)	1041(1)	3390(1)	55(1)
Cl(2)	723(2)	144(1)	3314(1)	61(1)
O(1)	-84(3)	1807(2)	3942(2)	41(1)
O(2)	2545(3)	2564(2)	4135(1)	38(1)
N	325(4)	3438(2)	3965(2)	39(1)
C(1)	1272(5)	2057(3)	2793(2)	43(1)
C(2)	142(6)	1838(4)	2374(3)	62(2)
C(3)	-195(7)	2255(5)	1788(3)	82(3)
C(4)	589(9)	2886(5)	1625(3)	90(3)
C(5)	1727(8)	3107(4)	2040(3)	76(3)
C(6)	2085(6)	2680(3)	2624(2)	54(2)
C(7)	2367(5)	946(3)	4666(2)	41(1)
C(8)	1455(6)	642(4)	5021(3)	62(2)
C(9)	1863(7)	338(4)	5648(3)	71(2)
C(10)	3148(7)	310(4)	5909(3)	65(2)
C(11)	4091(7)	623(4)	5566(3)	73(2)
C(12)	3691(6)	950(4)	4942(3)	62(2)
C(13)	-1953(4)	2858(3)	3250(2)	38(1)
C(14)	-3065(5)	2347(3)	3150(3)	52(2)
C(15)	-4087(5)	2501(3)	2643(3)	58(2)
C(16)	-4029(6)	3167(4)	2242(3)	62(2)
C(17)	-2930(6)	3677(4)	2327(3)	63(2)
C(18)	-1898(5)	3510(3)	2824(3)	51(2)
C(19)	-1611(4)	2690(3)	4622(2)	41(1)
C(20)	-1889(6)	1972(4)	4931(3)	65(2)
C(21)	-2686(7)	1982(5)	5409(3)	87(3)
C(22)	-3201(6)	2706(6)	5588(3)	92(3)
C(23)	-2920(7)	3442(5)	5295(3)	79(3)
C(24)	-2136(6)	3425(3)	4807(3)	61(2)
C(25)	2700(5)	4163(3)	3826(2)	43(1)
C(26)	2041(5)	4696(3)	3363(3)	59(2)
C(27)	2759(6)	5210(4)	3003(3)	73(2)
C(28)	4105(7)	5194(4)	3112(4)	85(3)
C(29)	4744(6)	4679(5)	3573(4)	108(4)
C(30)	4042(6)	4154(4)	3932(3)	79(3)
C(31)	2160(5)	3617(3)	5102(2)	41(1)
C(32)	3086(6)	3188(4)	5526(3)	65(2)
C(33)	3279(7)	3376(4)	6189(3)	79(3)
C(34)	2547(7)	3970(4)	6425(3)	69(2)
C(35)	1619(6)	4393(4)	6011(3)	70(2)
C(36)	1422(6)	4214(3)	5354(3)	62(2)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

(2) is placed in a special position '.2.' and exhibits an orientation disorder which was modelled considering two antipode orientations containing a common carbon atom. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were calculated as a riding model with fixed, isotropic temperature factor $U = 0.06 \text{\AA}^3$.

The final R values are $R = 5.14\%$ and $wR = 5.70\%$ ($R = 8.27\%$, $wR = 11.02\%$ for all data) for (1), and $R = 5.12\%$ and $wR = 5.85\%$ ($R = 9.97\%$, $wR = 7.14\%$ for all data) for (2), with weights $w^{-1} = \sigma^2(F) +$

$0.0008F^2$ for both structure determinations. The residual electron density from a final difference Fourier synthesis was in the range of $0.51, -0.41 \text{ e \AA}^{-3}$ for (1), and $0.79, -0.42 \text{ e \AA}^{-3}$ for (2). Refined values for the atomic coordinates are listed in Tables 4 and 5.

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for (2)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Sb	1345(1)	449(1)	7959(1)	48(1)
Cl(1)	1787(1)	-155(2)	8990(1)	80(1)
Cl(2)	817(1)	-267(3)	8413(1)	94(1)
S(1)	1904(1)	1352(2)	7489(1)	48(1)
P(1)	991(1)	1044(1)	6280(1)	37(1)
P(2)	1786(1)	1069(1)	6442(1)	34(1)
O(1)	978(1)	1087(4)	7060(2)	48(1)
N	1375(1)	708(4)	6090(2)	39(1)
C(1)	1397(2)	-1340(6)	7484(3)	60(2)
C(2)	1088(2)	-1963(8)	7136(4)	79(3)
C(3)	1127(3)	-3067(9)	6796(5)	105(4)
C(4)	1469(4)	-3558(9)	6815(5)	116(5)
C(5)	1779(3)	-2972(8)	7176(4)	90(4)
C(6)	1744(2)	-1854(7)	7510(4)	73(3)
C(7)	1306(1)	2281(7)	8389(3)	52(2)
C(8)	1300(2)	3349(7)	7986(3)	59(2)
C(9)	1304(2)	4537(8)	8300(4)	72(3)
C(10)	1308(2)	4627(10)	8999(4)	87(3)
C(11)	1307(2)	3573(11)	9393(4)	93(4)
C(12)	1306(2)	2399(9)	9093(3)	74(3)
C(13)	661(1)	-97(5)	5862(2)	40(1)
C(14)	341(2)	-304(7)	6104(3)	58(2)
C(15)	84(2)	-1165(7)	5777(4)	69(3)
C(16)	145(2)	-1803(7)	5202(4)	70(3)
C(17)	461(2)	-1585(7)	4954(4)	71(3)
C(18)	719(2)	-746(6)	5283(3)	56(2)
C(19)	817(1)	2530(5)	5923(3)	44(2)
C(20)	617(2)	3318(6)	6264(4)	63(2)
C(21)	465(2)	4416(8)	5954(6)	90(4)
C(22)	503(2)	4704(8)	5312(7)	99(4)
C(23)	690(2)	3947(10)	4942(5)	95(4)
C(24)	850(2)	2831(8)	5248(4)	70(3)
C(25)	2076(1)	-173(5)	6238(2)	36(1)
C(26)	1928(2)	-1171(6)	5819(3)	52(2)
C(27)	2156(2)	-2117(7)	5664(3)	66(2)
C(28)	2525(2)	-2081(7)	5931(3)	64(2)
C(29)	2673(2)	-1123(8)	6332(4)	67(2)
C(30)	2454(2)	-146(6)	6493(3)	57(2)
C(31)	1948(1)	2450(5)	6056(3)	40(2)
C(32)	2118(2)	3457(6)	6434(3)	64(2)
C(33)	2263(2)	4415(7)	6104(4)	79(3)
C(34)	2235(2)	4396(7)	5396(4)	72(3)
C(35)	2066(2)	3404(7)	5016(3)	68(3)
C(36)	1920(2)	2444(6)	5347(3)	60(2)
C(37)	0	3888(46)	7500	133(12) ^b sof = 0.25
C(38)	274(3)	4441(14)	7892(7)	140(4) ^b
C(39)	274(3)	5759(20)	7859(10)	99(6) ^b sof = 0.50
C(40)	0	6467(30)	7500	234(13) ^b sof = 0.50
C(41)	0	2503(26)	7500	198(10) ^b sof = 0.50
C(42)	0	5064(61)	7500	187(20) ^b sof = 0.25
C(43)	274(3)	3127(25)	7940(12)	121(7) ^b sof = 0.50

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor. ^b Isotropic iU .

Complete lists of bond lengths and angles and table of anisotropic displacement coefficients and H-atom coordinates have been deposited at the Cambridge Data Base.

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