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NCN Chelated Organoantimony(III) and Organobismuth(III) Phosphinates and Phosphites: Synthesis, Structure and Reactivity

Tomáš Svoboda,[a] Roman Jambor,[a] Aleš Růžička,[a] Zdeňka Padělková,[a] Milan Erben,[a] and Libor Dostál*[a]

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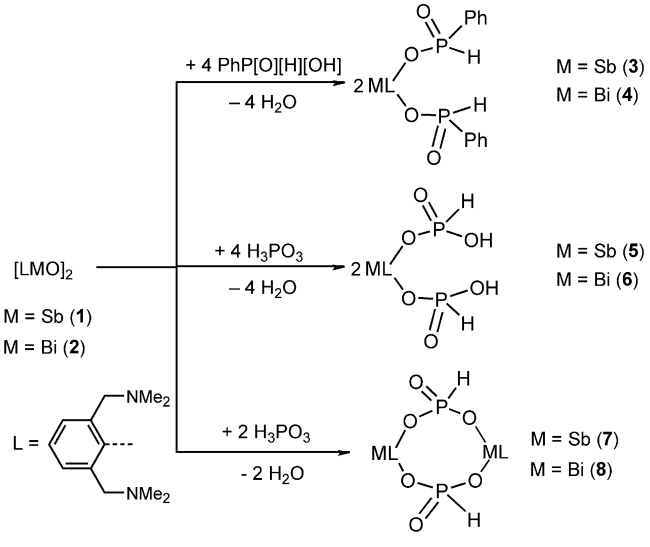
The reaction of the organoantimony and organobismuth oxides $[LSbO]_2$ (**1**) and $[LBiO]_2$ (**2**), where L = $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]^-$, with phenylphosphinic acid in a 1:4 molar ratio gave the molecular organoantimony and organobismuth phosphinates $LM[OP(H)(O)(Ph)]_2$ [M = Sb (**3**), Bi (**4**)]. Similarly, the reaction of **1** and **2** with H_3PO_3 gave the secondary phosphites $LM[OP(H)(O)(OH)]_2$ [M = Sb (**5**), Bi (**6**)] or the fully deprotonated phosphite $\{LM[O_2P(H)(O)]\}_2$ [M = Sb (**7**), Bi (**8**)] depending on whether the molar ratio of the starting materials was 1:4 or 1:2. The syntheses of novel mixed phosphinate-phosphite LSb[OP(H)(O)(OH)][OP(H)(O)(Ph)] (**9**), phosphonate-phoshinate LSb[OP(*t*Bu)(O)(OH)][OP(H)-(O)(Ph)] (**10**) and phosphonate-phosphite LSb[OP(*t*Bu)-(O)(OH)][OP(H)(O)(OH)] (**11**) compounds are also described. While the organoantimony compounds **3**, **5** and **7** are stable in solution, the organobismuth congeners showed only limited stability in solution and underwent a redox process involving to the reduction of the bismuth ions, and oxidation of the phosphorus ions from the +III to +V oxidation state. The reaction pathway associated with the redox process was studied with the system bismuth oxide **2** + $Ph_2P(O)H$, which gave compound $LBi[OP(O)(Ph)_2]_2$ (**14**) as a result of the oxidation of the phosphorus ion. All compounds were characterized by elemental analysis, ^1H, ^{13}C and ^{31}P NMR spectroscopy and IR spectroscopy. The solid-state molecular structures of compounds **3**, **5a** $\{LM[O_2P(H)(O)][(HO)_2P(H)-(O)]\}$ and **7** were determined by X-ray diffraction.

Introduction

Recently, we have started investigating the preparation of well-defined and soluble organoantimony(III) and organobismuth(III) oxides and sulfides, which are stabilized by coordination of the potentially tridentate NCN ligand[1] $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]^-$, denoted as L hereafter. The oxides are dimeric, $[LMO]_2$ (M = Sb, Bi), with a central four-membered ring system, which is similar to the solid-state structures discovered for the corresponding sulfides, $[LMS]_2$.[2] Interestingly, the sulfides were shown to be able to dissociate in solution to give the monomeric compounds that contained terminal metal–sulfur bonds, making them reactive to other substrates such as sulfur or carbon disulfide.[2c] The oxides are able to reversibly bind to carbon dioxide and react with trifluoromethanesulfonic acid with the formation of an ionic hydroxido compound containing terminal M–OH groups.[2b] These compounds are potential starting materials for the preparation, under relatively mild reaction conditions and starting from soluble and well-defined precursors, of other main group element oxido and sulfido compounds. We have also demonstrated that these NCN chelated organoantimony(III) and organobismuth-(III) oxides can be utilized as starting materials for the controlled and reliable preparation of organometallic molecular phosphonates.[3] In this way, we enriched the available knowledge of similar group 15 compounds, which is at this time still quite limited.[4] Studies dealing with this class of



Scheme 1.

[a] Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice,
Studentská 573, 53210 Pardubice, Czech Republic
Fax: +420-466-037-068
E-mail: libor.dostal@upce.cz

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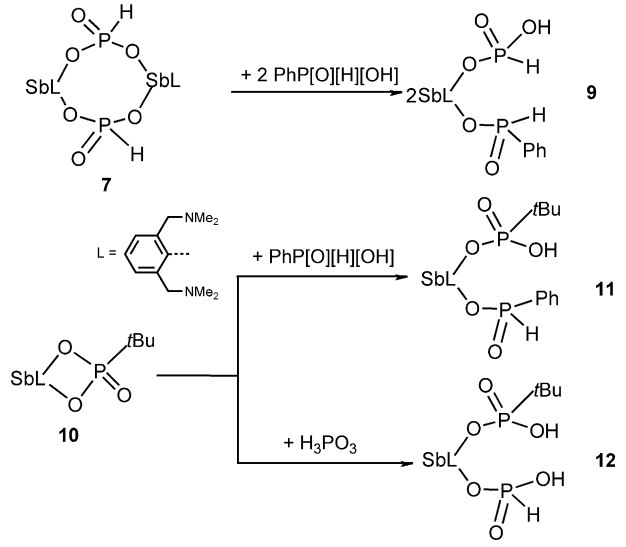
compounds are often hampered by their limited solubility. This problem seems to be solved in part by the presence of ligand L in the compounds of this type.

As a part of an ongoing investigation of main group compounds containing potentially tridentate pincer-type ligands, and as a logical continuation of studies in this field, we report herein the syntheses, structures and reactivity of organoantimony and organobismuth phosphinate and phosphite complexes (Scheme 1) that are stabilized by the NCN chelating ligand L. Previously we were able to synthesize mixed phoshonate compounds (i.e. complexes containing two different phosphonate groups),[3] and herein the syntheses of novel mixed phosphinate-phosphite, phosphonate-phoshinate and phosphonate-phosphite compounds are also described (Scheme 2).



Scheme 2.

Results and Discussion

Syntheses and Characterization of Compounds 3–8

The reaction of oxides **1** and **2** with 4 mol-equiv. of phenylphosphinic acid in dichloromethane resulted in organoantimony (**3**) and organobismuth (**4**) phenylphosphinates (Scheme 1). The ^{1}H NMR spectra of **3** and **4** in $CDCl_3$ revealed one set of sharp signals (singlets) for the NCH_2 and $N(CH_3)_2$ groups pointing to a symmetrical tridentate coordination mode for the NCN ligand. The presence of a PH group in the complexes was proven by observation in the ^{1}H NMR spectra of a doublet resonance peak at δ = 7.54 ppm ($^1J_{P,H}$ = 531 Hz) for **3** and at δ = 7.67 ppm ($^1J_{P,H}$ = 528 Hz) for **4**, and doublets at δ = 13.7 ppm for **3** and at δ = 15.5 ppm for **4** were observed in the ^{31}P NMR spectra of these complexes. Treatment of oxides **1** and **2** with phosphorous acid gave, depending on the molar ratio used (1:4 or 1:2), the secondary phosphites **5** and **6** or the fully deprotonated phosphites **7** and **8** (Scheme 1). One set of sharp signals (singlets) for the NCH_2 and $N(CH_3)_2$ groups was detected in the ^{1}H NMR spectra for compounds **5** and **6**. Doublet resonance peaks, corresponding to the PH groups, at δ = 6.84 ppm ($^1J_{P,H}$ = 653 Hz) for **5** and at δ = 7.07 ppm ($^1J_{P,H}$ = 643 Hz) for **6**, and broad singlets at low field [δ = 11.70 (**5**) and 10.61 ppm (**6**)] with integrated intensities of 2 that are attributable to POH groups, were observed in the ^{1}H NMR spectra, providing evidence for the proposed structures of **5** and **6**. The ^{31}P NMR spectra of **5** and **6** revealed doublets at δ = 4.5 ppm (**5**) and 5.2 ppm (**6**). In the ^{1}H NMR spectrum of the organoantimony phosphite **7**, the NCH_2 group signal has an AX pattern, and two singlets were detected for the $N(CH_3)_2$ groups, which is consistent with the ligand's donor atoms being in a pseudo-*cis* arrangement, as also determined from solid-state analyses (vide infra). Conversely, the corresponding signals in the ^{1}H NMR spectrum of the bismuth congener **8** are significantly broader. In both cases, the presence of the PH groups was established by the observation of doublet resonance peaks both in the ^{1}H NMR spectra at δ = 6.77 ppm ($^1J_{P,H}$ = 644 Hz) for **7** and 7.14 ppm ($^1J_{P,H}$ = 595 Hz) for **8**, and in the ^{31}P NMR spectra at δ = –0.5 ppm for **7** and 3.1 ppm for **8**. Any signals attributable to POH groups are absent from the ^{1}H NMR spectra of **7** and **8**.

The characteristic vibrations for PH groups in the 2240–2383 cm^{-1} regions of the IR spectra of compounds **3**–**8** proved the presence of this functionality in these complexes. Similarly, strong bands were detected in the PO vibration domain for all compounds. Both compounds **5** and **6** contain POH groups in their structure, which was reflected by observation of three broad bands (around 2700, 2300 and 1600 cm^{-1}) in their IR spectra, and splitting of the POH peaks points to strong hydrogen bonds between these POH moieties.[3,5]

We have recently reported so-called mixed antimony(III) and bismuth(III) phoshonates, in which two different phosphonate units are bonded to the same central ion.[3] We have also suggested that an analogous synthetic protocol may lead to similar phosphorus-antimony(bismuth) compounds containing either two phosphorus ions in a +III oxidation state, or with one phosphorus ion in a +III state and the other in a +V state. Compound **7** showed a propensity to react with acids, as demonstrated by a ^{1}H and ^{31}P NMR experiment, and when mixed with 2 equiv. of phosphorous acid compound **5** was produced.[6] This fact made us study the reactivity of **7** in more detail. The reaction of phosphite **7** with 2 mol-equiv. of phenylphosphinic acid gave the mixed phosphite-phosphinate **9** (Scheme 2). The ^{1}H and ^{13}C NMR spectra of **9** revealed sets of sharp signals consistent with the proposed structure, the ^{1}H NMR spectrum included two doublets corresponding to the phosphite PH group at δ = 6.84 ppm ($^1J_{P,H}$ = 656 Hz), a signal from the PH group of the phenylphosphinate group at δ = 7.56 ppm ($^1J_{P,H}$ = 536 Hz), and a broad signal at δ = 11.61 ppm attributable to the POH group. The ^{31}P NMR spectrum revealed, as expected, two doublets at δ = 3.9 ppm (phosphite) and 16.0 ppm (phenylphosphinate). The IR spectrum of **9** revealed bands at 2380 and 2351 cm^{-1} corresponding to the PH group, peaks at 2711, 2321, 1645 cm^{-1}

for the POH groups that point to possible hydrogen bonding,[5] and peaks at 1180, 1127, 977 cm^{-1} that are attributable to vibrations of the PO groups.

With phosphonate **10**[3] as a starting compound the mixed phosphonate-phosphite compounds **11** and **12** can be prepared, depending on which reagent is added, namely, phenylphosphinic or phosphorous acid (Scheme 2). The ^1H and ^{13}C NMR spectra of **11** and **12** are consistent with the proposed structures. In the ^1H NMR spectra the PH group signals were detected as doublets at δ = 7.59 ppm ($^1J_{P,H}$ = 536 Hz) for **11** and at δ = 6.84 ppm ($^1J_{P,H}$ = 656 Hz) for **12**. The presence of POH moieties was reflected by observation of broad singlets at 11.63 ppm for **11** and 11.57 ppm for **12**. The ^{31}P NMR spectra for both compounds revealed one singlet corresponding to the *tert*-butylphoshonate moiety (at δ = 36.9 ppm for **11** and at δ = 36.3 ppm for **12**) and one double at δ = 16.3 ppm for **11** (phenylphosphinate) and at δ = 6.3 ppm for **12** (phosphite). The IR spectra supported the proposed structures for both compounds (see Experimental Section).

Molecular Structures of 3, 5a and 7

Compound **3** crystallizes in space group $P2_1/c$, and its molecular structure with relevant structural parameters is depicted in Figure 1. Both phenylphosphinate groups are coordinated to the central antimony ion in a unidentate fashion with bond lengths of Sb1–O1 2.204(2) and Sb1–O3 2.223(2) Å, and both functional groups are located in a mutually *trans* fashion as demonstrated by the O1–Sb1–O3 angle of 163.87(7)°. The NCN ligand is coordinated in a tridenate fashion to the central ion, and the bond lengths describing the Sb–N dative connection are Sb1–N1 2.460(3) and Sb1–N2 2.400(3) Å. The coordination polyhedron around the central metal atom may be described as a strongly distorted tetragonal pyramid with the *ipso*-carbon atom (C1) at the apical position. The shapes of the coordination polyhedra of the phosphorus atoms remain essentially tetrahedral. There are no significant intermolecular contacts in the solid-state structure of **3**.

Attempts to obtain single crystals of compound **5** resulted in an isomeric compound $LSb[O_2P(H)(O)][(HO)_2P(H)(O)]$ (**5a**). The composition of **5** (Scheme 1) was formulated, in accordance with the NMR spectroscopic data, as containing two secondary phosphite groups that are only partially deprotonated, but the composition of **5a** (a single-crystalline material) must be described as containing one fully deprotonated phosphite group that forms a solvate with phosphorous acid (Figure 2). The compositional difference between **5** and **5a** is also reflected in their different solid-state IR spectra (see Experimental Section), and the fact that the single crystals (**5a**) are totally insoluble in $CDCl_3$ (probably reflecting the high complexity of the structure due to the presence of an extensive hydrogen-bond network), in which polycrystalline **5** is very soluble. To shed some light on this problem, we left compound **5** (after characterization by ^1H, ^{13}C and ^{31}P NMR spectroscopy) in dichloromethane for one week. A white insoluble precipitate formed during this time, which was shown to be **5a** by the excellent agreement of the X-ray powder diffractogram of this material with the simulated pattern determined from the single-crystal data (see the Supporting Information). These findings point, most probably, to the high fluxionality of the acidic POH hydrogen atoms when **5** is in solution, which leads to the crystallization (or precipitation) of **5a**.

The structure of **5a** (Figure 2) may be described as an aduct of a NCN chelated organoantimony phosphite with phosphorous acid, but due to extensive hydrogen bonding the complete structure is more complex. The monomeric unit is shown in Figure 2 (top). The central ion (Sb1) is coordinated by the NCN ligand in tridentate fashion [the bond lengths are Sb1–N2 2.4262(19) and Sb1–N1 2.4161(19) Å, and the bonding angle N1–Sb1–N2 is 149.17(6)°]. The phosphite group, which is fully deprotonated, is coordinated to the central ion through oxygen atom

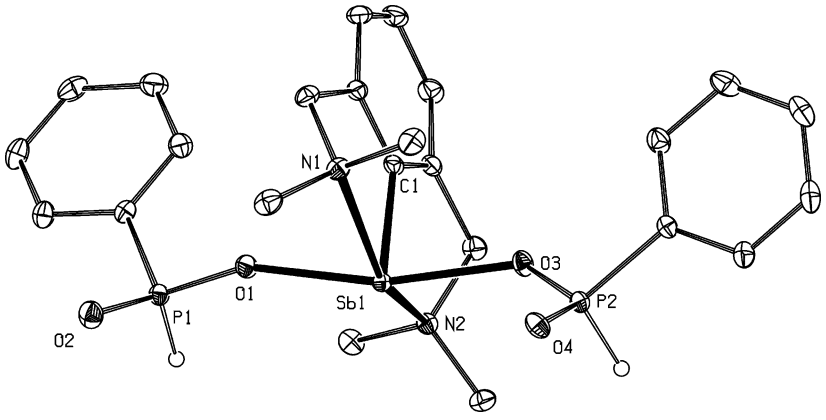


Figure 1. ORTEP diagram for compound **3** with the thermal displacement parameters at the 30% probability level. Hydrogen atoms, except those bonded to phosphorus atoms, are omitted for clarity. Selected distances [Å] and angles [°]: Sb1–C1 2.109(2), Sb1–N1 2.460(3), Sb1–N2 2.400(3), Sb1–O1 2.204(2), Sb1–O3 2.223(2), O1–P1 1.519(2), O2–P1 1.483(2), O3–P2 1.529(2), O4–P2 1.484(2), N1–Sb1–N2 149.44(7); C1–Sb1–N1 74.09(9), C1–Sb1–N2 75.42(9), C1–Sb1–O1 81.65(9), C1–Sb1–O3 82.22(9), O1–Sb1–O3 163.87(7).

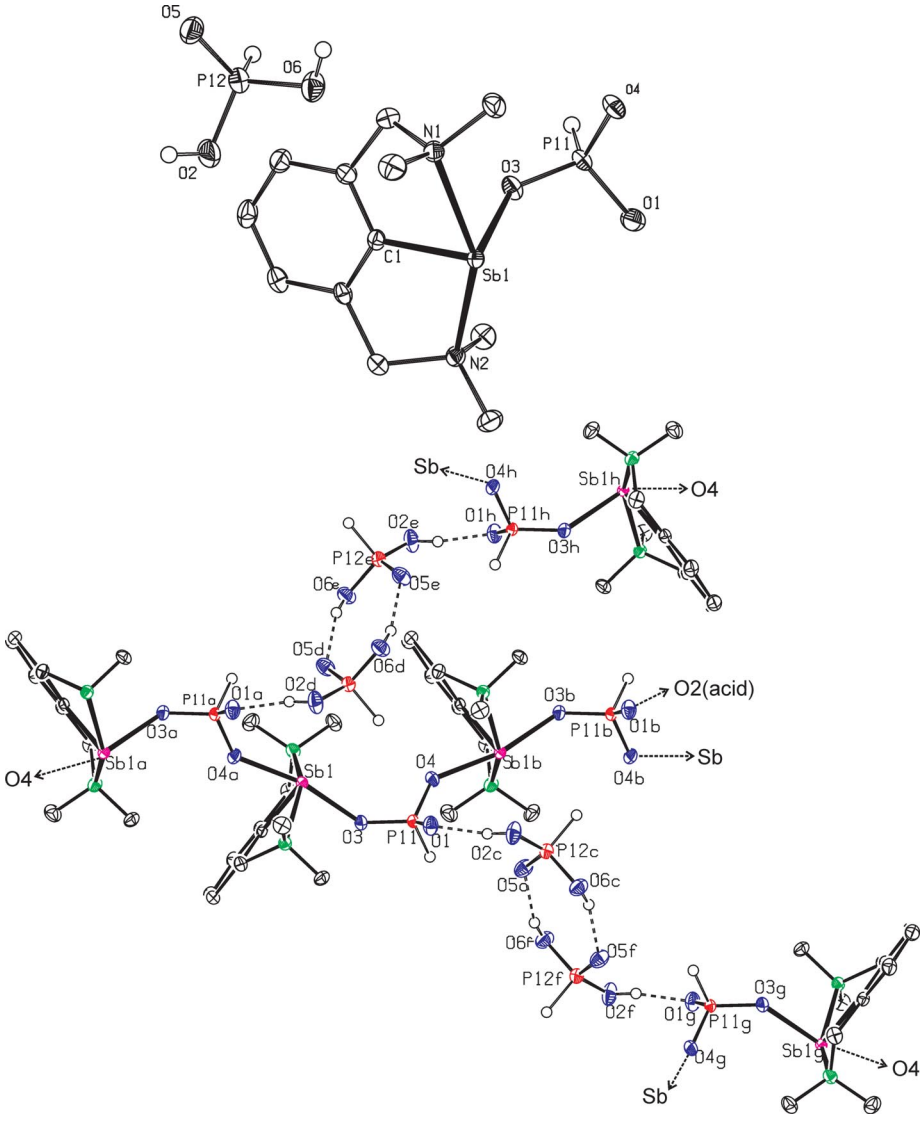


Figure 2. ORTEP diagram for compound **5a** (top: monomeric unit; bottom: hydrogen-bond network) with the thermal displacement parameters at 30% probability level. Hydrogen atoms, except those involved in hydrogen bonds and bonded to phosphorus atoms, are omitted for clarity. Selected distances [Å] and angles [°]: Sb1–C1 2.105(3), Sb1–N1 2.4161(19), Sb1–N2 2.4262(19), Sb1–O3 2.2519(15), Sb1–O4a 2.1961(17); C1–Sb1–N1 74.67(8), C1–Sb1–N2 74.52(8), C1–Sb1–O3 82.72(8), C1–Sb1–O4a 83.20(8), N1–Sb1–N2 149.17(6), O1–Sb1–O4a 165.92(6). Symmetry operators: a: x, 1/2 – y, –1/2 + z; b: x, 1/2 – y, 1/2 + z; c: –1 + x, 1/2 – y, 1/2 + z; d: –1 + x, y, z; e: 1 – x, 1 – y, 1 – z; f: 1 – x, 1/2 + y, 3/2 – z; g: –x, –y, 2 – z; h: – x, 1/2 + y, 3/2 – z. Hydrogen-bond distances [Å] and angles [°]: O1···O2c 2.453(3), O5c···O6f 2.515(3), O6c···O5f 2.515(3), O1···H(O2c)–O2c 161, O5c···H(O6f)–O6f 154, O5f···H(O6c)–O6c 154.

O3 [the Sb1–O3 bond length is 2.2519(15) Å], and the second deprotonated oxygen atom O4 is connected to the antimony atom of a neighboring molecule [Sb1b in Figure 2 (bottom)]. The coordination environment of the Sb1 atom is completed by phopsphite oxygen atom O4a [the bond length Sb1–O4a is 2.1961(17) Å]. This bonding arrangement leads to the formation of an infinite chain structure with alternating LSb (Sb1a, Sb1 and Sb1b ions) and phosphite (P11a, P11 and P11b ions) fragments as shown in Figure 2 (bottom). The coordination polyhedron around each antimony ion is best described as a distorted tetragonal pyramid with the *ipso*-carbon atom located at the apex and oxygen atoms in *trans* positions in the basal plane [the O3–Sb1–O4a angle is 165.92(6)°]. The third oxygen atom from the P=O group of each phosphite entity within these infinite chains is involved in a hydrogen bond with one of the POH groups of the phosphorous acid, O1···H(O2c), the length of this hydrogen bond (O–O distance) is 2.453(3) Å. Furthermore, the second POH group of the phoshorus acid is connected to a neighboring acid molecule via by additional hydrogen bonds, O5c···H(O6f) and O5f···H(O6c); both hydrogen bonds are 2.515(3) Å in length (O–O distance). The remaining POH group (O2f) of the second phosphorous acid is in turn bonded to atom O1g of a neighboring infinite NCN chelated organoanitmony phosphite chain. The complete structure may be summarized as infinite phosphite chains linked by dimers of phosphorous acid that are held together by hydrogen bonds. This bond-

ing arrangement is repeated throughout the whole structure leading to the formation of a polymeric structure containing alternating infinite antimony phosphite and phosphorous acid chains (see Figure S1 in the Supporting Information).

Compound **7** crystallizes in space group *P*2/*c*, and the unit cell contains two independent molecules, the structures of which are closely related. Only one molecule is depicted in Figure 3, and relevant structural parameters are given in the figure caption.

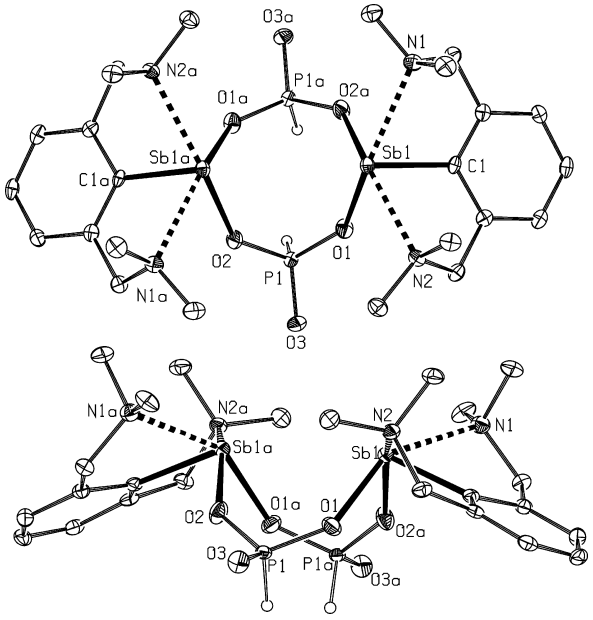


Figure 3. ORTEP diagram for compound **7** (only one of the two independent molecules is shown) with the thermal displacement parameters at the 30% probability level. Hydrogen atoms, except those bonded to phosphorus atoms and dichloromethane molecules, are omitted for clarity. Symmetry operator: a: 1 – *x*, *y*, 1/2 – *z*. Selected distances [Å] and angles [°]: Sb1–C1 2.117(7), Sb1–N1 2.613(5), Sb1–N2 2.543(7), Sb1–O1 2.075(5), Sb1–O2a 2.082(5), O1–P1 1.527(5), O2–P1 1.543(5), O3–P1 1.474(5); N1–Sb1–N2 121.2(2), C1–Sb1–N1 71.2(3), C1–Sb1–N2 72.1(2), C1–Sb1–O1 91.0(2), C1–Sb1–O2a 91.2(2), O1–Sb1–O2a 81.9(2), O1–P1–O2 111.7(3), O1–P1–O3 113.3(3), O2–P1–O3 127.7(2).

Compound **7** has a dinuclear molecular structure with a central eight-membered $Sb_2P_2O_4$ ring that has a boat conformation. This ring is a consequence of two phosphite groups, which are fully deprotonated, forming bridges between two antimony ions. These bridges are nearly symmetrical as demonstrated by the bond lengths Sb1–O1 2.075(5) and Sb1a–O2 2.082(5) Å. The angles involving the antimony ions within the ring (O1–Sb1–O2a 81.9(2)° and its symmetry-equivalent) are significantly more acute than the angles incorporating the phosphorus atoms; the O1–P1–O2 angle is 111.7(3)°. The NCN ligand is coordinated in a tridenate fashion to the central ion [the bond lengths are Sb1–N1 2.613(5) and Sb1–N2 2.543(7) Å], but in contrast to compounds **3** and **5a** where the donor atoms are in a *trans* position, in **7** it is bound in a pseudo-*cis* fashion with the N1–Sb1–N2 angle equal to 121.2(2)°. The coordinated pendant arms of the ligand may play an important role in stabilizing the central ring, and hence are situated above it. The presence of the ligand bound in such a way hinders oligomerization or polymerization of the phosphite complex. Also of interest is the position of the hydrogen atoms, which are orientated in the same direction. Furthermore, only one set of signals was observed in the solution ^{1}H, ^{31}P and ^{13}C NMR spectra suggesting that only this compound isomer is present in solution, although the second isomer with a different orientation of the hydrogen atoms and oxygen atoms O3 and O3a is possible.[7]

Decomposition Pathways for Organobismuth Phosphinates

Although antimony compounds **3**, **5** and **7** are stable in solution, the organobismuth compounds **4** and **8** have only limited stability in solution. Leaving compounds **4** and **8** for a long time in solution results in a black precipitate forming, which in part hampered attempts to obtain single crystals of these compounds. This insoluble solid was shown to be elemental bismuth suggesting that a redox process is taking place in solutions of these bismuth compounds.

Interestingly, Shimada et al. have recently reported the reaction of a CNC chelated organobismuth oxide (where the CNC ligand was 5,6,7,12-tetrahydrodibenz[*c*,*f*][1,5]azabismocine, Figure 4, denoted L′ hereafter) with $Ph_2P(O)(H)$ (in which phosphorus is in the +III oxidation state). The reaction proceeded as a redox process yielding the reduced compound L′BiBiL′ that contained a Bi–Bi bond and in which the phoshorus ions were oxidized to the V+ state, which led to the formation of the organobismuth phosphinate L′BiOP(O)(Ph_2).[8] Taking this fact into account, our compounds may decompose by the same pathway giving organobismuth(I) compounds and the corresponding organobismuth phosphonate complexes. To test this possibility the decomposition of compound **4** (which seemed to decompose easily) was studied in more detail, and the reaction of the oxide **2** with $Ph_2P(O)(H)$ was investigated and performed in a similar manner to Shimada et al.'s experiment.

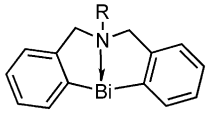
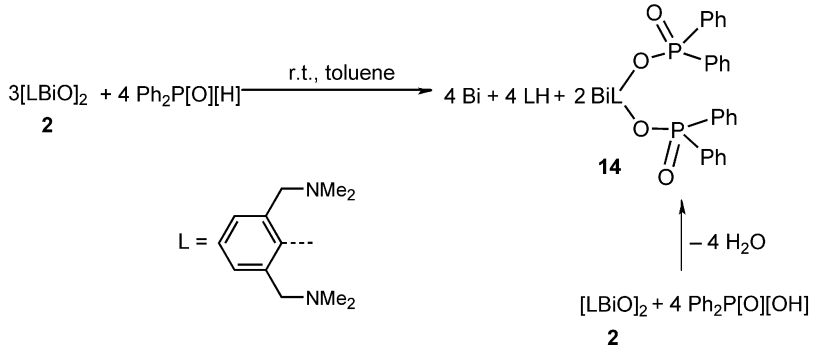


Figure 4. Structure of 5,6,7,12-tetrahydrodibenz[*c*,*f*][1,5]azabismocine ligand.

Compound **4** was heated in toluene to 60 °C, and within a few hours the solution started to change color and became slightly violet. This may suggest the presence of a reduced bismuth(I) compound in the solution, but this is unstable under these reaction conditions, and metallic bismuth was characterized by X-ray powder diffraction as the decomposition product after workup.[9–11] The ^{1}H NMR spectra of the reaction mixture revealed, besides signals associated with the starting compound **4**, signals that can be assigned to the free ligand that is a decomposition coproduct



Scheme 3.

of the bismuth(I) compound, and eventually a new set of signals emerge that are attributable to the phosphonate LBi[OP(Ph)(O)(OH)]$_2$ (**13**). Similarly, the ^{31}P NMR spectra revealed, in addition to the doublet resonance peak associated with **4** (δ = 15.5 ppm, $^1J_{H,P}$ = 528 Hz), an extra singlet at δ = 14.8 ppm with the lost of $^1J_{P,H}$ coupling, which provides evidence for the oxidation of the phosphorus ion to the +V state and the formation of **13**. This singlet increased in intensity over time giving ca. 30% conversion after 16 d (Figure 5). In the very early stages of the reaction, a compound that gave a signal at δ = 5.1 ppm in the ^{31}P NMR spectra was detected, but this signal disappeared over time, and the structure of this compound remains unknown. Compound **13** was also prepared by the conventional reaction of oxide **2** with 2 equiv. of phenylphosphonic acid, the analysis data for the product of this reaction coincided with all the analytical data for compound **13** that was formed from the decomposition of **4**.

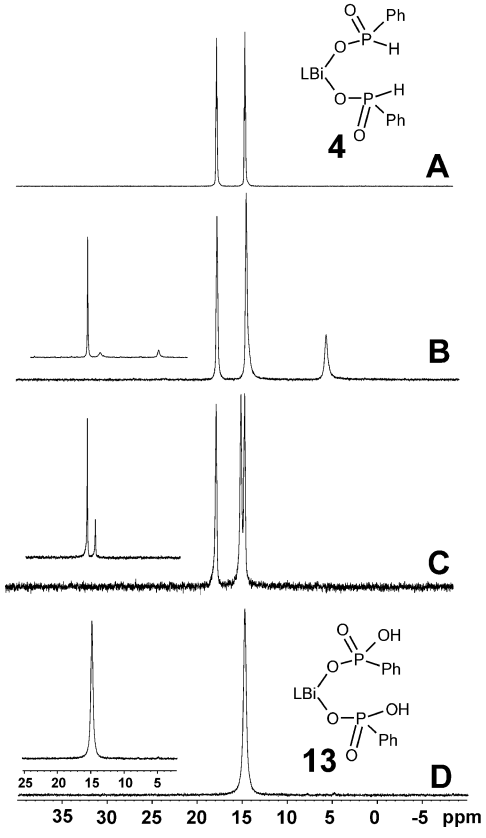


Figure 5. ^{31}P NMR spectra recorded to monitor the decomposition of compound **4** to give compound **13**: (A) at the start of the reaction – pure **4**; (B) after 30 min; (C) after 16 d; (D) compound **13** prepared from the reaction of **2** with phenylphosphonic acid. The inset spectra are ^{31}P{^{1}H} NMR data that show the coalescence of the signals that are split in the ^{31}P NMR spectra due to the presence of the PH group.

Mixing oxide **2** and $Ph_2P(O)(H)$ in 3:4 molar ratio in C_6D_6 at room temp. resulted in the reaction solution immediately exhibiting an intense violet color, which was followed by the precipitation of bismuth metal (Scheme 3). The reaction was monitored by ^{31}P NMR spectroscopy (see the Supporting Information), and the spectra revealed a doublet resonance peak associated with the starting material $Ph_2P(O)(H)$ (δ = 17.2 ppm, $^1J_{P,H}$ = 462 Hz) and a singlet (δ = 21.3 ppm) that corresponds to the product **14**, which contains an oxidized phosphorus ion. The reaction at room temp. is completed within 2 d as shown by the ^{31}P NMR spectra in which only signals from **14** are observed after this time. The ^{1}H NMR spectrum contained, besides the signal associated with **14**, signals arising from the free ligand. Compound **14** was also prepared by the direct reaction of oxide **2** with diphenylphosphonic acid.

Conclusions

The NCN chelating ligand L has been shown to be very efficient at stabilizing various types of organoantimony and organobismuth compounds that contain different types of oxido-phosphorus substituents. In most cases the compounds retain their discrete molecular structures and do not tend to oligomerize or polymerize (except **5a**), which promotes their solubility in organic solvents such as chloroform and dichloromethane. An investigation focused towards the targeted synthesis of other mixed antimony(bismuth)-oxido compounds containing elements other than phosphorus are currently underway in our laboratories.

Experimental Section

General Procedures: All air- and moisture-sensitive manipulations were carried out under argon with standard Schlenk tube tech-

niques. All solvents were dried by standard procedures and distilled prior to use. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded with a Bruker AMX360 spectrometer, with a 5 mm tunable broad-band probe. The shifts of the peaks in the ^{1}H and ^{13}C NMR spectra were measured relative to the residual signals of the solvent [$CDCl_3$: $\delta(^1H)$ = 7.27 ppm and $\delta(^{13}C)$ = 77.23 ppm; C_6D_5: $\delta(^1H)$ = 7.16 ppm]. The shift of the peaks in the ^{31}P NMR spectra were measured relative to an external standard, 85% H_3PO_4, $\delta(^{31}P)$ = 0.00 ppm. IR spectra were recorded over the 5000–400 cm^{-1} range, with the samples prepared as KBr pellets or as nujol mulls (**10**), with a Nicolet Magna 550 FT-IR spectrometer. The starting compounds: phenylphosphinic acid, diphenylphosphonic acid, phosphorous acid and diphenylphosphane oxide, were obtained from commercial suppliers and used as delivered. Compounds [2,6-$(Me_2NCH_2)_2C_6H_3SbO]_2$[2a] (**1**), [2,6-$(Me_2NCH_2)_2C_6H_3BiO]_2$[2b] (**2**) and 2,6-$(Me_2NCH_2)_2C_6H_3Sb[O_2P(O)tBu]$[3] (**12**) were prepared according to literature procedures.

2,6-$(Me_2NCH_2)_2C_6H_3Sb[OP(H)(O)Ph]_2$ (3): A dichloromethane (10 mL) solution of [2,6-$(Me_2NCH_2)_2C_6H_3SbO]_2$ (**1**) (79 mg, 0.12 mmol) was added to a suspension of phenylphosphinic acid (68 mg, 0.48 mmol) in dichloromethane (15 mL), and the resulting mixture was stirred at room temperature for 2 h. The reaction mixture was concentrated in vacuo, and the residue was washed with hexane (5 mL). The remaining white solid was recrystallized from a dichloromethane/toluene mixture to give **3** as white crystals (103 mg, 72%); m.p. 149 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.62 [s, 12 H, N(CH_3)$_2$], 4.00 (s, 4 H, NCH_2), 7.20 (d, 2 H, Ar-H3,5), 7.35 (m, 7 H, Ph-H3,4,5 and Ar-H4), 7.53 (m, 4 H, Ph-H2,6) 7.54 (d, $^1J_{P,H}$ = 531 Hz, 2 H, P*H*) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 25 °C): δ = 46.6 [s, N(*C*H_3)$_2$], 64.5 (s, N*C*H_2), 125.4 (s, Ar-C3,5), 128.3 [d, $^3J_{P,C}$ = 13 Hz, Ph-C3,5], 129.9 (d, $^2J_{P,C}$ = 12 Hz, Ph-C2,6), 130.5 (s, Ar-C4), 131.3 (s, Ph-C4), 136.4 (d, $^1J_{P,C}$ = 128 Hz, Ph-C1) 143.7 (s, Ar-C2,6), 155.3 (s, Ar-C1) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$, 25 °C): δ = 13.7 (d, $^1J_{H,P}$ = 531 Hz, *P*H) ppm. IR: $\tilde{\nu}$ = 2323 (s), 2305 (s, PH), 1205 (vs), 1123 (s, PO) cm^{-1}. $C_{24}H_{31}N_2O_4P_2Sb$ (595.22): calcd. C 48.4, H 5.3; found C 48.5, H 5.5.

2,6-$(Me_2NCH_2)_2C_6H_3Bi[OP(H)(O)Ph]_2$ (4): Compound **4** was prepared according to a similar procedure as described for the synthesis of compound **3**. A dichloromethane (10 mL) solution of [2,6-$(Me_2NCH_2)_2C_6H_3BiO]_2$ (**2**) (105 mg, 0.126 mmol) was mixed with phenylphosphinic acid (72 mg, 0.504 mmol) in dichloromethane (15 mL) to give **4** as white crystals (118 mg, 69%); m.p. 139 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.74 [s, 12 H, N(CH_3)$_2$], 4.36 (s, 4 H, NCH_2), 7.34 (m, 6 H, Ph-H3,4,5), 7.54 (m, 5 H, Ph-H2,6 and Ar-H4), 7.67 (d, $^1J_{P,H}$ = 528 Hz, 2 H, P*H*), 7.73 (d, 2 H, Ar-H2,6) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 25 °C): δ = 46.9 [s, N(*C*H_3)$_2$], 68.6 (s, N*C*H_2), 128.3 (s, Ar-C3,5), 128.4 (d, $^3J_{P,C}$ = 13 Hz, Ph-C3,5), 129.9 (s, Ar-C4), 130.1 (d, $^2J_{P,C}$ = 11 Hz Ph-C2,6), 131.1 (d, $^4J_{P,C}$ = 4 Hz, Ph-C4), 137.6 (d, $^1J_{P,C}$ = 128 Hz, Ph-C1), 152.1 (s, Ar-C2,6) ppm, an Ar-C1 signal was not observed. ^{31}P NMR (161.98 MHz, $CDCl_3$, 25 °C): δ = 15.5 (d, $^1J_{H,P}$ = 528 Hz, *P*H) ppm. IR: $\tilde{\nu}$ = 2283 (m, PH), 1176 (s), 1130 (s, PO) cm^{-1}. $C_{24}H_{31}BiN_2O_4P_2$ (682.44): calcd. C 42.2, H 4.6; found C 42.4, H 4.8.

2,6-$(Me_2NCH_2)_2C_6H_3Sb[OP(H)(O)(OH)]_2$ (5): A dichloromethane (10 mL) solution of [2,6-$(Me_2NCH_2)_2C_6H_3SbO]_2$ (**1**) (103 mg, 0.16 mmol) was added to a suspension of phosphorous acid (51 mg, 0.63 mmol) in dichloromethane (15 mL), and the mixture was stirred for 30 min. Concentration of the solution and washing with hexane (10 mL) gave **5** as white crystals (108 mg, 71%); m.p. 93 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.80 [s, 12 H, N(CH_3)$_2$], 4.00 (s, 4 H, NCH_2), 6.84 (d, $^1J_{P,H}$ = 653 Hz, 2 H, P*H*), 7.19 (d, 2 H, Ar-H3,5), 7.33 (t, 1 H, Ar-H4), 11.7 [s (br.), 2 H, PO*H*] ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 25 °C): δ = 46.4 [s, N(*C*H_3)$_2$], 64.4 (s, N*C*H_2), 125.4 (s, Ar-C3,5), 130.3 (s, Ar-C4), 144.0 (s, Ar-C2,6), 155.4 (s, Ar-C1) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$, 25 °C): δ = 4.5 (d, $^1J_{P,H}$ = 653 Hz, *P*H) ppm. IR: $\tilde{\nu}$ = 2800 (m), 2383 (s), 1637 (s br., POH), 2240 (m, PH), 1177 (vs), 1009 (vs br., PO) cm^{-1}. To obtain isomeric compound **5a** a clear dichloromethane (5 mL) solution of **5** was stirred for 24 h. During this period a white precipitate formed, which was filtered off and washed with hexane (15 mL). The remaining white powder was characterized as **5a** by powder X-ray diffraction (see the Supporting Information; it is noteworthy that the filtrate does not contain any significant amount of the NCN chelated compound, which suggests exclusive conversion of **5** to **5a**). The yield based on the starting material **5** was 90%; m.p. 148 °C. IR: $\tilde{\nu}$ = 2711 (vs), 2326 (m sh), 1630 (m, POH), 2383 (m, PH), 1030 (vs), 1005 (vs, PO) cm^{-1}. $C_{12}H_{23}N_2O_6P_2Sb$ (475.03): calcd. C 30.3, H 4.9; found C 30.4, H 5.2.

2,6-$(Me_2NCH_2)_2C_6H_3Bi[OP(H)(O)(OH)]_2$ (6): Compound **6** was prepared according to a similar procedure as described for the synthesis of compound **3**. A dichloromethane (10 mL) solution of [2,6-$(Me_2NCH_2)_2C_6H_3BiO]_2$ (**2**) (124 mg, 0.149 mmol) was mixed with phosphonic acid (49 mg, 0.59 mmol) in dichloromethane (15 mL) to give **6** as white crystals (108 mg, 64%); m.p. 133 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.90 [s, 12 H, N(CH_3)$_2$], 4.35 (s, 4 H, NCH_2), 7.07 (d, $^1J_{P,H}$ = 643 Hz, 2 H, P*H*), 7.52 (t, 1 H, Ar-H4), 7.72 (d, 2 H, Ar-H3,5), 10.61 [s (br.), 2 H, PO*H*] ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 25 °C): δ = 46.7 [s, N(*C*H_3)$_2$], 68.5 (s, N*C*H_2), 128.1 (s, Ar-C3,5), 129.8 (s, Ar-C4), 152.3 (s, Ar-C2,6) ppm, an Ar-C1 signal was not observed. ^{31}P NMR (161.98 MHz, $CDCl_3$, 25 °C): δ = 5.2 (d, $^1J_{P,H}$ = 643 Hz, *P*H) ppm. IR: $\tilde{\nu}$ = 2701 (m br.), 2244 (m br.), 1641 (s br., POH), 2383 (vs, PH), 1152 (vs), 1006 (vs br., PO) cm^{-1}. $C_{12}H_{23}BiN_2O_6P_2$ (562.25): calcd. C 25.6, H 4.1; found C 25.7, H 4.3.

2,6-$(Me_2NCH_2)_2C_6H_3Sb[O_2P(O)(H)]$ (7): Compound **7** was prepared according to a similar procedure as described for the synthesis of compound **3**. A dichloromethane (10 mL) solution of [2,6-$(Me_2NCH_2)_2C_6H_3SbO]_2$ (**1**) (101 mg, 0.153 mmol) was mixed with phosphonic acid (25 mg, 0.307 mmol) in dichloromethane (15 mL) to give **5** as white crystals (82 mg, 68%); m.p. 243 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.02 [s (br.), 6 H, N(CH_3)$_2$], 2.77 [s (br.), 6 H, N(CH_3)$_2$] 3.13 and 4.77 (AX pattern, $^2J_{H,H}$ = 13 Hz, 4 H, NCH_2), 6.77 (d, $^1J_{P,H}$ = 644 Hz, 1 H, P*H*), 7.06 (br., 2 H, Ar-H3,5), 7.11 (br., 1 H, Ar-H4) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 25 °C): δ = 41.1 [s, N(*C*H_3)$_2$], 44.6 [s, N(*C*H_3)$_2$], 62.4 (s, N*C*H_2), 125.1 (s, Ar-C3,5), 128.8 (s, Ar-C4), 146.8 (s, Ar-C2,6), 152.1 (s, Ar-C1) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$, 25 °C): δ = –0.5 (d, $^1J_{P,H}$ = 644 Hz, *P*H) ppm. IR: $\tilde{\nu}$ = 2355 (vs), 2319 (m, PH), 1199 (m), 1027 (vs), 1006 (vs), 981 (s, PO) cm^{-1}. $C_{12}H_{20}N_2O_3PSb$ (393.03): calcd. C 36.7, H 5.1; found C 36.5, H 4.9.

2,6-$(Me_2NCH_2)_2C_6H_3Bi[O_2P(H)(O)]$ (8): Compound **8** was prepared according to a similar procedure as described for the synthesis of compound **3**. A dichloromethane (10 mL) solution of [2,6-$(Me_2NCH_2)_2C_6H_3BiO]_2$ (**2**) (68 mg, 0.082 mmol) was mixed with phosphonic acid (13 mg, 0.163 mmol) in dichloromethane (15 mL) to give **8** as white crystals (56 mg, 72%); m.p. 198 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.78 [s, 12 H, N(CH_3)$_2$], 4.25 (s, 4 H, NCH_2), 7.14 (d, $^1J_{P,H}$ = 595 Hz, 1 H, P*H*), 7.41 (t, 1 H, Ar-H4), 7.60 (d, 2 H, Ar-H3,5) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 25 °C): δ = 46.8 [s, N(*C*H_3)$_2$], 68.6 (s, N*C*H_2), 127.9 (s, Ar-C3,5), 129.1 (s, Ar-C4), 152.1 (s, Ar-C2,6) ppm, an Ar-C1 signal was not

observed. ^{31}P NMR (161.98 MHz, $CDCl_3$, 25 °C): δ = 3.1 (d, $^1J_{P,H}$ = 595 Hz, *P*H) ppm. IR: $\tilde{\nu}$ = 2323 (s, PH), 1010 (vs), 1002 (s, PO) cm^{-1}. $C_{12}H_{20}BiN_2O_3P$ (480.25): calcd. C 30.0, H 4.2; found C 30.2, H 4.4.

2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$Sb[OP(H)(O)(OH)][OP(H)(O)(Ph)] (9): A dichloromethane (10 mL) solution of 2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$Sb-[O$_2$P(O)(H)] (**7**) (33 mg, 0.084 mmol) was added to a suspension of phenylphosphinic acid (12 mg, 0.084 mmol) in dichloromethane (15 mL). The reaction mixture was stirred at room temperature for 3 h and then concentrated in vacuo and the residue washed with hexane (5 mL). The product was recrystallized from a dichloromethane/hexane mixture. The resulting product was dried to give a white solid (37 mg, 84%); m.p. 99 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.70 [s, 12 H, N(C*H*$_3$)$_2$], 4.01 (s, 4 H, NC*H*$_2$), 6.84 (d, $^1J_{P,H}$ = 656 Hz, 1 H, P*H*) 7.20 (d, 2 H, Ar-H3,5), 7.40 (m, 4 H, Ph-H3,4,5 and Ar-H4), 7.56 (d, $^1J_{P,H}$ = 536 Hz, 1 H, P*H*), 7.57 (m, 2 H, Ph-H2,6), 11.61 (br., 1 H, PO*H*) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 25 °C): δ = 46.7 [s, N(*C*H$_3$)$_2$], 64.6 (s, N*C*H$_2$), 125.5 (s, Ar-C3,5), 128.5 (d, $^3J_{P,C}$ = 13 Hz, Ph-C3,5), 130.2 (d, $^2J_{P,C}$ = 12 Hz, Ph-C2,6), 130.5 (s, Ar-C4), 131.6 (s, Ph-C4), 136.4 (d, $^1J_{P,C}$ = 131 Hz, Ph-C1), 144.0 (s, Ar-C2,6), 155.5 (s, Ar-C1) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$, 25 °C): δ = 3.9 (d, $^1J_{H,P}$ = 656 Hz, *P*H), 16.0 (d, $^1J_{H,P}$ = 536 Hz, *P*H) ppm. IR: $\tilde{\nu}$ = 2711 (m br.), 2321 (s br.), 1645 (s br., POH), 2380 (s), 2351 (m, PH), 1180 (s br.), 1127 (s), 977 (vs, PO) cm^{-1}. $C_{18}H_{27}N_2O_5P_2Sb$ (535.12): calcd. C 40.4, H 5.1; found C 40.5, H 5.3.

2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$Sb[OP(*t*Bu)(O)(OH)][OP(H)(O)(Ph)] (11): A dichloromethane (10 mL) solution of 2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$Sb-[O$_2$P(O)*t*Bu] (**10**) (28 mg, 0.062 mmol) was added to a suspension of phenylphosphinic acid (8.8 mg, 0.062 mmol) in dichloromethane (15 mL). The reaction mixture was stirred at room temperature for 3 h. The reaction mixture was concentrated in vacuo, and the residue was washed with hexane (5 mL). The resulting product was dried to give a white solid (32 mg, 86%); m.p. 147 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.10 (d, $^3J_{P,H}$ = 16 Hz, 9 H, *t*BuP), 2.74 [s, 12 H, N(C*H*$_3$)$_2$], 3.98 (s, 4 H, NC*H*$_2$), 7.20 (d, 2 H, Ar-H3,5), 7.41 (m, 4 H, Ph-H3,4,5 and Ar-H4), 7.59 (d, $^1J_{P,H}$ = 536 Hz, 1 H, P*H*), 7.59 (m, 2 H, Ph-H2,6), 11.63 (br., 1 H, PO*H*) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 25 °C): δ = 25.2 (s, *C*H$_3$), 31.0 (d, $^1J_{P,C}$ = 143 Hz, *C*P), 46.6 [s, N(*C*H$_3$)$_2$], 64.6 (s, N*C*H$_2$), 125.2 (s, Ar-C3,5), 128.5 (d, $^3J_{P,C}$ = 13 Hz, Ph-C3,5), 130.3 (d, $^2J_{P,C}$ = 12 Hz, Ph-C2,6) that overlapped with the Ar-C4 signal at 131.5 (s, $^4J_{P,C}$ = 2 Hz, Ph-C4), 136.3 (d, $^1J_{P,C}$ = 128 Hz, Ph-C1), 144.1 (s, Ar-C2,6) ppm, an Ar-C1 signal was not observed. ^{31}P NMR (161.98 MHz, $CDCl_3$, 25 °C): δ = 16.3 (d, $^1J_{H,P}$ = 536 Hz, *P*H), 36.9 (s) ppm. IR: $\tilde{\nu}$ = 2707 (m br.), 2337 (s), 1648 (s br., POH), 2358 (s, PH), 1263 (s), 1127 (vs), 1095 (vs), 977 (vs, PO) cm^{-1}. $C_{22}H_{35}N_2O_5P_2Sb$ (591.23): calcd. C 44.7, H 6.0; found C 44.5, H 6.2.

2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$Sb[OP(*t*Bu)(O)(OH)][OP(H)(O)(OH)] (12): Compound **12** was prepared according to a similar procedure as described for the synthesis of compound **11**. A dichloromethane (10 mL) solution of 2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$Sb[O$_2$P(O)*t*Bu] (**12**) (59 mg, 0.131 mmol) was mixed with phosphonic acid (11 mg, 0.131 mmol) in dichloromethane (15 mL) to give **12** as white crystals (59 mg, 85%); m.p. 211 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.03 (d, $^3J_{P,H}$ = 16 Hz, 9 H, *t*BuP), 2.83 [s, 12 H, N(C*H*$_3$)$_2$], 3.98 (s, 4 H, NC*H*$_2$), 6.84 (d, $^1J_{P,H}$ = 656 Hz, 1 H, P*H*), 7.20 (d, 2 H, Ar-H3,5), 7.34 (t, 1 H, Ar-H4), 11.57 (br., 2 H, PO*H*) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 25 °C): δ = 25.2 (s, *C*H$_3$), 31.0 (d, $^1J_{P,C}$ = 146 Hz, *C*P), 46.5 [s, N(*C*H$_3$)$_2$], 64.4 (s, N*C*H$_2$), 125.1 (s, Ar-C3,5), 130.1 (s, Ar-C4), 143.9 (s, Ar-C2,6) ppm, an Ar-C1 signal was not observed. ^{31}P NMR (161.98 MHz, $CDCl_3$, 25 °C): δ = 6.3 (d, $^1J_{H,P}$ = 656 Hz, *P*H), 36.3 (s) ppm. IR: $\tilde{\nu}$ = 2708 (m br.), 2370 (s br.), 1655 (s br., POH), 2346 (s, PH), 1262 (s), 1127 (vs), 1095 (vs), 980 (vs, PO) cm^{-1}. $C_{16}H_{31}N_2O_6P_2Sb$ (531.13): calcd. C 36.2, H 5.9; found C 36.4, H 6.1.

2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$Bi[OP(O)(OH)Ph]$_2$ (13): A dichloromethane (10 mL) solution of [2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$BiO]$_2$ (**2**) (80 mg, 0.096 mmol) was added to a suspension of phenylphosphonic acid (61 mg, 0.384 mmol) in dichloromethane (15 mL). The reaction mixture was stirred at room temperature for 3 h. The reaction mixture was concentrated in vacuo, and the residue was washed with hexane (5 mL). The remaining white solid was recrystallized from a dichloromethane/hexane mixture to give **13** as white crystals (99 mg, 72%); m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.78 [s, 12 H, N(C*H*$_3$)$_2$], 4.29 (s, 4 H, NC*H*$_2$), 7.20 (m, 4 H, Ph-H3,5), 7.30 (t, 2 H, Ph-H4), 7.47 (t, 1 H, Ar-H4), 7.60 (m, 4 H, Ph-H2,6), 7.67 (d, 2 H, Ar-H3,5), 10.64 (br., 2 H, PO*H*) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 25 °C): δ = 46.6 [s, N(*C*H$_3$)$_2$], 68.4 (s, N*C*H$_2$), that was overlapped with the Ph-C3,5 signal (s, Ar-C3,5), 128.0 (d, $^3J_{P,C}$ = 15 Hz, Ph-C3,5), 129.4 (s, Ar-C4), 130.2 (s, Ph-C4), 130.9 (d, $^2J_{P,C}$ = 11 Hz, Ph-C2,6), 135.7 (d, $^1J_{P,C}$ = 103 Hz, Ph-C1), 152.4 (s, Ar-C2,6) ppm, an Ar-C1 signal was not observed. ^{31}P NMR (161.98 MHz, $CDCl_3$, 25 °C): δ = 14.8 (s) ppm. IR: $\tilde{\nu}$ = 2708 (m br.), 2359 (s br.), 2337 (s br.), 1647 (s br., POH), 1135 (vs), 1110 (vs), 1002 (vs), 910 (vs, PO) cm^{-1}. $C_{24}H_{31}BiN_2O_6P_2$ (714.44): calcd. C 40.3, H 4.4; found C 40.1, H 4.3.

2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$Bi[OP(O)(Ph)$_2$]$_2$ (14): A toluene (20 mL) solution of [2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$BiO]$_2$ (**2**) (132 mg, 0.159 mmol) was added to a toluene (20 mL) solution of diphenylphosphane oxide (43 mg, 0.212 mmol), and the resulting mixture was stirred at room temperature for 12 h. The reaction mixture was filtered, and the toluene filtrate was concentrated in vacuo, and the residue was washed with hexane (5 mL). The resulting product was dried to give a white solid (35 mg, 52%); m.p. 137 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.56 [s, 12 H, N(C*H*$_3$)$_2$], 4.33 (s, 4 H, NC*H*$_2$), 7.27 (m, 12 H, Ph-H3,4,5), 7.60 (m, 9 H, Ph-H2,6 and Ar-H4), 7.76 (d, 2 H, Ar-H2) ppm. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 2.32 [s, 12 H, N(C*H*$_3$)$_2$], 3.95 (s, 4 H, NC*H*$_2$), 7.04 (m, 12 H, Ph-H3,4,5), 7.26 (Ar-H4), 7.37 (d, 2 H, Ar-H2), 7.88 (m, 8 H, Ph-H2,6) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 25 °C): δ = 46.9 [s, N(*C*H$_3$)$_2$], 68.5 (s, N*C*H$_2$), 128.0 (d, $^3J_{P,C}$ = 13 Hz, Ph-C3,5), 128.1 (s, Ar-C3,5), 129.5 (s, Ar-C4), 130.2 (d, $^3J_{P,C}$ = 3 Hz, Ph-C4), 131.2 (d, $^2J_{P,C}$ = 10 Hz, Ph-C2,6), 139.0 (d, $^1J_{P,C}$ = 131 Hz, Ph-C1), 152.3 (s, Ar-C2,6) ppm, an Ar-C1 signal was not observed. ^{31}P NMR (161.98 MHz, $CDCl_3$, 25 °C): δ = 21.1 (s) ppm. ^{31}P NMR (161.98 MHz, C_6D_3, 25 °C): δ = 21.3 (s) ppm. IR: $\tilde{\nu}$ = 1181 (s), 1117 (vs), 988 (vs, PO) cm^{-1}. $C_{36}H_{39}BiN_2O_4P_2$ (834.63): calcd. C 51.8, H 4.7; found C 52.0, H 4.5.

X-ray Crystallography: Suitable single crystals of complexes **3**, **5a**, and **7** were mounted on glass fibers with oil and measured with a four-circle KappaCCD diffractometer equipped with a CCD area detector, with monochromated Mo-K_α radiation (λ = 0.71073 Å) at 150(1) K. Numerical absorption corrections[12] based on the crystal shapes were applied to the data for all crystals. The structures were solved by direct methods (SIR92)[13] and refined by a full-matrix least-squares procedure based on F^2 (SHELXL97).[14] Hydrogen atoms were fixed at idealized positions in the crystallographic models (riding model) and assigned temperature factors of H_{iso}(H) = 1.2 U_{eq}(pivot atom) or, in the case of the methyl moieties, with H_{iso}(H) = 1.5 U_{eq}(methyl C). The C–H bond lengths were fixed at 0.96, 0.97, and 0.93 Å for the methyl, methylene, and aromatic ring groups, respectively, and at 0.83 Å for the O–H bonds. The final

difference maps displayed no peaks of chemical significance as the highest peaks and holes are close (ca. 1 Å) to the locations of heavy atoms in the structures. CCDC-772345 (**3**), -772346 (**5a**), -772347 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystallographic Data for 3: $C_{24}H_{31}N_2O_4P_2Sb$, M = 595.20, monoclinic, $P2_1/c$, a = 9.2519(7), b = 21.1840(13), c = 14.4701(12) Å, β = 117.382(7), V = 2518.3(4) Å^3, Z = 4, T = 150(1) K, 21311 total reflections, 5759 independent reflections [R_{int} = 0.049, $R1$(obs. data) = 0.030, wR_2(all data) = 0.051].

Crystallographic Data for 5a: $C_{12}H_{23}N_2O_6P_2Sb$, M = 474.95, monoclinic, $P2_1/c$, a = 8.9871(4), b = 16.9291(6), c = 12.2810(7) Å, β = 106.332(5), V = 1793.08(14) Å^3, Z = 4, T = 150(1) K, 13630 total reflections, 4092 independent reflections [R_{int} = 0.032, $R1$(obs. data) = 0.024, wR_2(all data) = 0.045].

Crystallographic Data for 7: $C_{26}H_{44}Cl_4N_4O_6P_2Sb_2$, M = 955.89, monoclinic, $P2/c$, a = 22.6501(19), b = 6.1611(6), c = 27.6080(12) Å, β = 109.008(7)°, V = 3642.6(5) Å^3, Z = 4, T = 150(1) K, 46669 total reflections, 8306 independent reflections [R_{int} = 0.038, $R1$(obs. data) = 0.058, wR_2(all data) = 0.1180].

Supporting Information (see footnote on the first page of this article): Figures showing the polymeric structure and X-ray powder diffractogram of **5a**, ^{1}H and ^{31}P NMR spectra of compounds **5**, **9**, **10** and **11**, and ^{31}P NMR spectra recorded to monitor the reaction between compound **2** and $Ph_2P(O)(H)$.

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