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NCN-Chelated Organoantimony(III) and Organobismuth(III) Phosphonates: Syntheses and Structures

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The reactions 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 selected organophosphonic acids in a 1:4 molar ratio gave molecular organoantimony and organobismuth phosphonates $LM[OP(R)(O)(OH)]_2$ [M = Sb, R = Et (**3**), Ph (**4**), *t*Bu (**5**); M = Bi, R = *t*Bu (**8**)]. Similarly, the reactions of **1** and **2** with $tBuP(O)(OH)_2$ in a 1:2 molar ratio resulted in $LM[O_2P(tBu)(O)]$ [M = Sb (**6**), M = Bi (**9**)]. Reactions of **6** and **9** with $EtP(O)(OH)_2$ yielded mixed phosphonates LM[OP(Et)(O)(OH)][OP(*t*Bu)(O)(OH)] [M = Sb (**7**), M = Bi (**10**)]. All compounds were characterized by elemental analysis, ESI mass spectrometry, ^1H, ^{13}C and ^{31}P NMR spectroscopy and IR spectroscopy. Molecular structures of compounds **4**, **5**, **8** and **9** were determined by using X-ray single-crystal diffraction in the solid state. Secondary phosphonates **4**, **5** and **8** form weakly bonded dimeric units through hydrogen bridges of the type PO–H···O=P. On the other hand, compound **9** is trimeric in the solid state with the central 12-membered ring formed by three $LBi[O_2P(tBu)(O)]$ building blocks through intermolecular Bi···O=P contacts.

Introduction

The chemistry organophosphinates and organophosphonates of heavier group 15 elements (Sb and Bi) was studied to some extent in the past,[1] but the number of isolated and well-defined compounds of this type is still limited. Nevertheless, it seems that this field has started to revive recently. Mehring et al. reported on the solid-state structure of the first bismuth phosphonate cluster compound[2] $[(tBuPO_3)_{10}(tBuPO_3H)_2Bi_{14}O_{10}\cdot 3C_6H_6\cdot 4H_2O]$ prepared by the reaction of $BiPh_3$ with $tBuPO_3H_2$ in a 1:1 molar ratio. The same working group isolated sterically encumbered organobismuth phosphinate ArBiBrOP(O)(H)Ar (Ar denotes the 2,6-Mes-4-*t*Bu-C_6H_2 ligand) as well.[3] In a significant breakthrough, Winpenny et al. succeeded in preparing mixed antimonate–phosphonate compounds by mixing of *p*-chlorophenylstibonic acid and phenylphosphonic acid in toluene. The resulting products were, with success, used as ligands for selected transition metals.[4] A nonanuclear organostiboxane cage was isolated by using the 1,1,2,3,3-pentamethyltrimethylene phosphinate as an ancillary ligand recently.[5] The reaction of CNC intramolecularly coordinated organobismuth oxide, containing the 5,6,7,12-tetrahydrodibenz[*c*,*f*]-[1,5]azabismocine fragment, with $Ph_2P(O)(H)$ proceeded as a redox reaction, leading to the formation of Bi–Bi bonds and oxidation of the phosphorus atom to the +V state; the corresponding phosphonates were isolated.[6]

Nevertheless, other well-defined reaction paths for the preparation of mixed antimony (or bismuth) – phosphorus oxido compounds are still missing. Recently, we started the investigation and preparation of well-defined and soluble organoantimony[7] and organobismuth[8] oxides that hold potential as starting materials for the preparation of such mixed main group element oxido compounds by using relatively mild reaction conditions. As part of this investigation, we report here on the controlled preparation of both antimony and bismuth phosphonates by the reaction of the parent antimony and bismuth oxides $[LSbO]_2$ (**1**) and $[LBiO]_2$ (**2**), where L = $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]^-$, with selected organophosphonic acids. Compounds of the type $LM[OP(R)(O)(OH)]_2$ [M = Sb, R = Et (**3**), Ph (**4**), *t*Bu (**5**); M = Bi, R = *t*Bu (**8**)] and $LM[O_2P(tBu)(O)]$ [M = Sb (**6**), M = Bi (**9**)] were isolated, as were the mixed phosphonates LM[OP(Et)(O)(OH)][OP(*t*Bu)(O)(OH)] [M = Sb (**7**), M = Bi (**10**)]. All compounds were characterized by elemental analysis, ESI mass spectrometry, ^1H, ^{13}C and ^{31}P NMR spectroscopy and IR spectroscopy. The molecular structures of compounds **4**, **5**, **8** and **9** were determined by using X-ray single-crystal diffraction in the solid state.

Results and Discussion

The reactions of organoantimony oxide **1** with selected organophosphonic acids in a molar ratio of 1:4 (Scheme 1)

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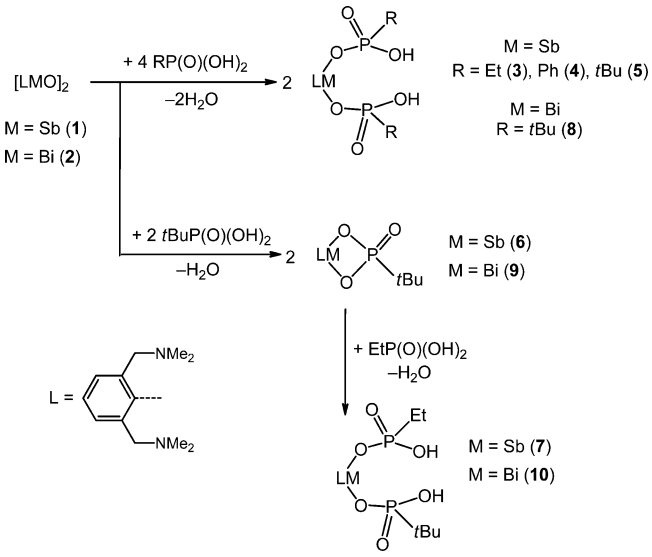
gave, independently of the substituent R on the phosphorus atom, secondary phosphonates **3**–**5** in good yields under mild reaction conditions (r.t., CH_2Cl_2). According to the molar ratio used, the acids were not fully deprotonated and each of the phosphorus functionalities carries one POH acidic hydrogen atom (Scheme 1). Compounds **3**–**5** are white solids soluble in chlorinated solvents.



Scheme 1. Reactivity of compounds **1** and **2**.

Changing the stoichiometry between **1** and *tert*-butylphosphonic acid to 1:2 resulted in complete deprotonation of the *tert*-butylphosphonic acid, giving compound **6** as the only isolable product (Scheme 1). This compound can be further converted into secondary phosphonate **5** by treatment with an additional equivalent of *tert*-butylphosphonic acid. More interestingly, if **6** had been reacted with one equivalent of ethylphosphonic acid, compound **7** containing two different phosphonates moieties in its structure could be isolated in reasonable yield as the sole product of the reaction. Similar reactions with *tert*-butylphosphonic acid can be performed by starting from bismuth oxide **2** (Scheme 1). In this way, secondary phosphonates **8** and mixed compound **10** were isolated, as was compound **9** prepared by the reaction of **2** with *tert*-butylphosphonic acid in the molar ratio 1:2.

All compounds were characterized by satisfactory elemental analysis and mass spectrometry (ESI). The most important ions observed in the full-scan negative-ion mass spectra were $[M - H]^-$, $[M + OPO_2HtBu]^-$ and $[M + OPO_2HEt]^-$ detected only for bismuth phosphonates (compounds **8**, **9** and **10**). The second mechanism of ion formation observed in the mass spectra of all studied compounds was the cleavage of the most labile bond between Sb (Bi) and the oxygen atom in the phosphonate groups, yielding two complementary ions, where the cationic part of the molecule $[M - OPO_2HR]^+$ was present in the positive-ion mode and the anionic part $[OPO_2HR]^-$ in the negative-ion mode (R = Et, *t*Bu, Ph). It is also noteworthy that the presence of two different phosphonate moieties in the structure of compounds **7** and **10** was verified on the basis of the ion formation mechanism. So both the $[M - OPO_2HEt]^+$ and $[M - OPO_2HtBu]^+$ ions were detected in the positive-ion mode and the $[OPO_2HEt]^-$ and $[OPO_2HtBu]^-$ ions were present in the negative-ion mode (see the Experimental Section). Moreover, some hydrolyzed adducts were observed in the spectra as a result of using water as the solvent.

The ^1H and ^{13}C NMR spectra of all secondary phosphonates **3**–**5**, **7**, **8** and **10** revealed only one set of sharp signals (singlets) for both the NCH_2 and $N(CH_3)_2$ groups at room temperature, indicating symmetrical (tridentate) coordination of the NCN chelating ligands in all compounds (similarly to the molecular structures determined in the solid state vide infra). Only one set of signals was observed for the organic substituent of the phosphonate groups in the ^1H and ^{13}C NMR spectra of **3**–**5**, **7**, **8** and **10**. The ^1H NMR spectra also revealed broaden signals (shifted to lower field) with an integral value of 2, proving the presence of acidic POH protons in the structure of these compounds. The ^{31}P NMR spectra showed one sharp signal in the case of all compounds at δ = 29.3 (**3**), 15.0 (**4**), 32.2 (**5**) and 32.5 ppm (**8**) (i.e., compounds containing only one type of phosphonate group). On the contrary, mixed species **7** and **10** displayed two signals in a mutual 1:1 ratio in the ^{31}P NMR spectra at δ = 34.2 and 30.8 ppm for **7** and δ = 32.7 and 29.7 ppm for **10** (reflecting the presence of two different phosphorus atoms).

The signal of the NCH_2 group is observed as an AX pattern in the ^1H NMR spectrum of **6**, and also two singlets were detected for the $N(CH_3)_2$ groups at room temperature. This indicates, most probably, that the rigid chelating coordination of the phosphonate (as depicted in Scheme 1), leading to nonsymmetrical coordination of the central antimony atom, results in nonequivalence of the arms of the ligand. The ^1H NMR spectrum of bismuth congener **9** revealed one set of significantly broaden signals for the NCH_2 and $N(CH_3)_2$ groups, pointing to a fluxional behaviour of **9** at ambient temperature. In both cases, the signal of the acidic POH protons are absent in the ^1H NMR spectra, proving full deprotonation of the *tert*-butylphosphonic acid used in the reaction (this was proven by IR spectroscopy vide infra). Only one signal was observed in the ^{31}P NMR spectra of **6** (δ = 41.0 ppm) and **9** (δ = 35.7 ppm).

IR spectra were recorded to manifest the presence of the acidic POH moieties in the structure of compounds **3**–**5**, **7**, **8** and **10**. Three broaden bands (around 2700, 2300 and 1700 cm^{-1}, see the Experimental Section) were observed for each POH group (this means six bands could be found in most spectra of the compounds due to the presence of two POH groups in their structure). This splitting of the POH vibration points to a strong hydrogen bonding between these POH moieties as demonstrated for other secondary phosphonates earlier.[9] This presumption was later verified by the determination of the molecular structure of selected compounds **4**, **5** and **8** in the solid state by X-ray diffraction (vide infra), where the presence of two crystallographically independent POH groups was established. On the contrary, any bands assignable to the POH vibrations are absent in

the IR spectra of compounds **6** and **9**. In the case of all compounds **3**–**10**, the presence of the phosphonate functionalities was also corroborated by strong absorption bands in the PO_3 vibration region 1150–950 cm^{-1} (see the Experimental Section).

The solid-state molecular structures of compounds **4**, **5**, **8** and **9** were determined by X-ray single-crystal diffraction. The molecular structures of both organoantimony phosphonates **4** and **5** are closely structurally related (Figures 1 and 2).

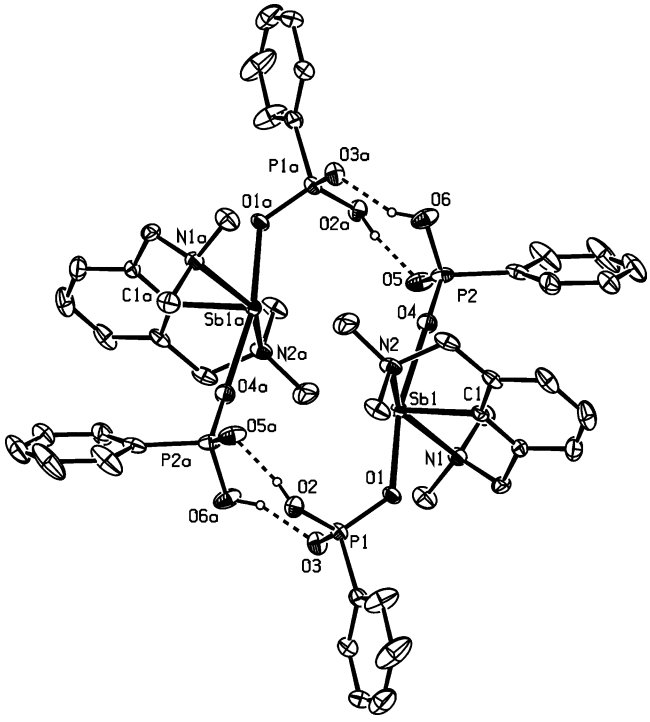


Figure 1. ORTEP diagram of compound **4** with thermal displacement parameters at 30% probability; hydrogen atoms, except those involved in hydrogen bonds, are omitted for clarity. Symmetry operator a = 2 – *x*, 1 – *y*, 1 – *z*. Selected distances [Å] and angles [°]: Sb1–C1 2.103(3), Sb1–N1 2.454(3), Sb1–N2 2.396(3), Sb1–O1 2.198(3), Sb1–O4 2.229(3), O2 – O5a 2.477(2), O3 – O6a 2.508(5), C1–Sb1–N1 74.31(13), C1–Sb1–N2 74.73(13), C1–Sb1–O1 83.11(12), C1–Sb1–O4 81.94(12), N1–Sb1–N2 149.04(12), O1–Sb1–O4 164.93(10), O2–H(O2)–O5a 170, O3–H(O6a)–O6a 156.

In both cases, the central antimony atom is coordinated by the NCN chelating ligand in a tridentate fashion [the range of the Sb–N bond lengths in **4** and **5** is 2.385(7)–2.464(8) Å]. The coordination polyhedron around the central atom can be described as a strongly distorted tetragonal pyramid with the *ipso* carbon atom C1 occupying the apical position. The basal plane is formed by two nitrogen atoms N1 and N2 [the bonding angle N1–Sb–N2 is 149.04(12)° for **4** and 148.3(3)° for **5**] and two oxygen atoms O1 and O4 [the range of the Sb–O bond lengths in **4** and **5** is 2.184(5)–2.229(3) Å, the bonding angle O1–Sb1–O4 equals 164.93(10)° for **4** and 164.6(2)° for **5**]. As established for **4** and **5** in solution, each of the coordinated phosphonate groups carries one POH moiety (oxygen atoms O2 and O6). These functionalities are involved in effective hydrogen

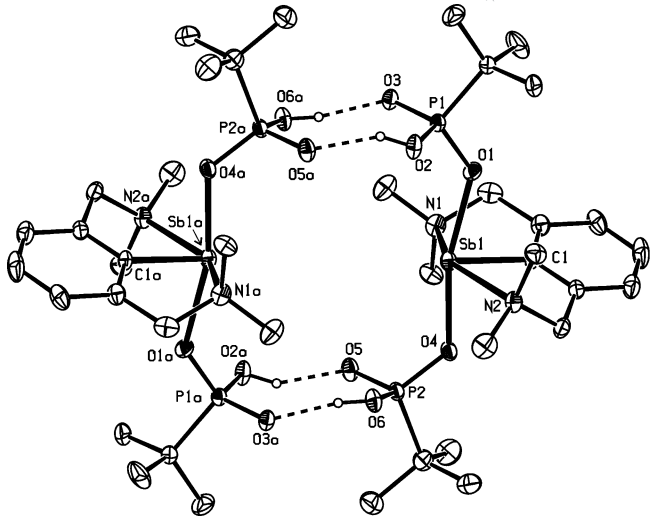


Figure 2. ORTEP diagram of compound **5** with thermal displacement parameters at 30% probability; hydrogen atoms, except those involved in hydrogen bonds, are omitted for clarity. Symmetry operator a = 1 – *x*, –*y*, –*z*. Selected distances [Å] and angles [°]: Sb1–C1 2.092(8), Sb1–N1 2.385(7), Sb1–N2 2.464(8), Sb1–O1 2.204(5), Sb1–O4 2.184(5), O2–O5a 2.495(9), O3–O6a 2.517(8), C1–Sb1–N1 74.6(3), C1–Sb1–N2 74.03, C1–Sb1–O1 81.2(3), C1–Sb1–O4 83.5(3), N1–Sb1–N2 148.3(3), O1–Sb1–O4 164.6(2), O2–H(O2)–O5a 153, O3–H(O6a)–O6a 168.

bonding with the P=O oxygen atoms O5a and O3a from the neighbouring molecule [the bond lengths O2–O5a and O6–O3a are, respectively, 2.477(2) and 2.508(5) Å for **4** and 2.495(9) and 2.517(8) Å for **5**, the bonding angles O2–H(O2)–O5a and O6–H(O6)–O3a are, respectively, 170 and 156° for **4** and 153 and 168° for **5**]. This hydrogen bonding is also answered by the POH groups from the second molecule, leading to four PO–H···O=P bridges and the formation of a dimeric structure.

The molecular structure of bismuth secondary phosphonate **8** is similar to that of its antimony congeners (Figure 3). The NCN chelating ligand coordinates the bismuth atom in a tridentate fashion with Bi–N bond lengths of 2.510(5) and 2.500(5) Å and a bonding angle N1–Bi1–N2 of 146.17(17)°. The oxygen atoms of the phosphonate groups are located mutually in *trans* positions [the bonding angle O1–Bi1–O4 equals 162.62(14)°]. The coordination polyhedron of the central atom might be described as a distorted tetragonal pyramid. Compound **8** forms a similar dimeric structure, as determined for compounds **4** and **5**, through linking two neighbouring molecules through hydrogen bridges between the O2–O5a atoms [2.533(6) Å, bonding angle 168°] and the O6–O3a atoms [2.541(6) Å, bonding angle 172°].

The hydrogen bonds seem to be nearly equivalent in all secondary phosphonates **4**, **5** and **8**, as demonstrated by the respective oxygen–oxygen bond lengths, although these become a bit longer along this set of compounds for **4** [2.477(2), 2.508(5) Å], for **5** [2.495(9), 2.517(8) Å] and for **8** [2.553(6), 2.541(6) Å]. It is also noteworthy that one of the hydrogen bonds is in all cases shorter than the second one. This is particularly evident in compound **4**. The hydrogen

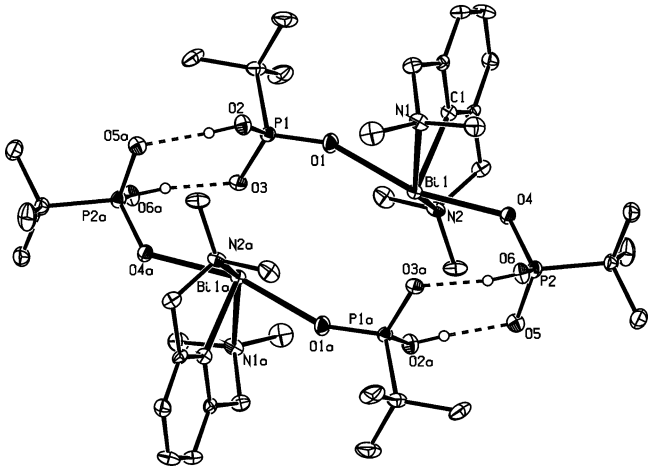


Figure 3. ORTEP diagram of compound **8** with thermal displacement parameters at 30% probability; hydrogen atoms, except those involved in hydrogen bonds, are omitted for clarity. Symmetry operator a = –*x*, –*y*, 1 – *z*. Selected distances [Å] and angles [°]: Bi1–C1 2.177(6), Bi1–N1 2.510(5), Bi1–N2 2.500(5), Bi1–O1 2.353(4), Bi1–O4 2.270(4), O2–O5a 2.553(6), O3–O6a 2.541(6), C1–Bi1–N1 72.6(2), C1–Bi1–N2 73.60(19), C1–Bi1–O1 79.12(19), C1–Bi1–O4 83.62(18), N1–Bi1–N2 146.17(17), O1–Bi1–O4 162.62(14), O2–H(O2)–O5a 168, O3–H(O6a)–O6a 172.

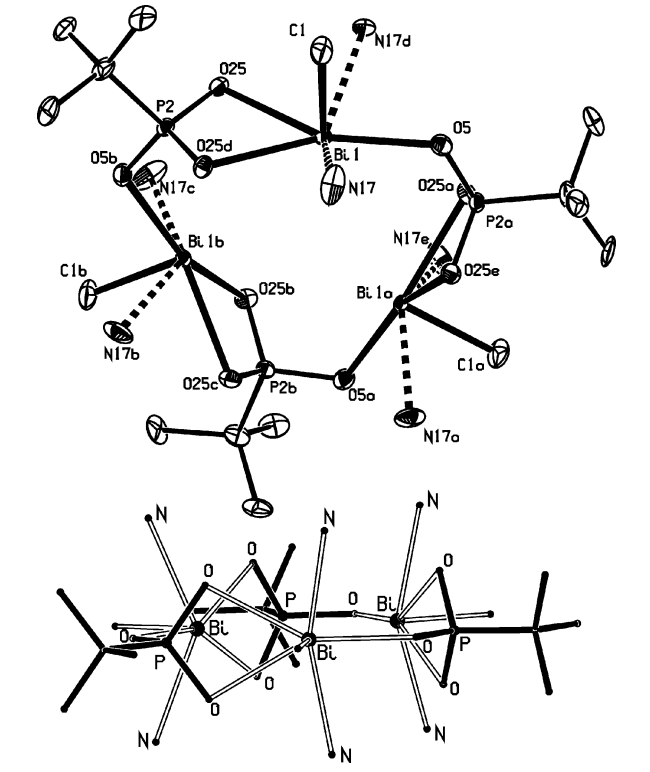


Figure 4. ORTEP diagram of compound **9** with thermal displacement parameters at 30% probability and view of the central ring system. The disordered ligands (except the nitrogen donor atoms and the *ipso* carbon atoms) and the hydrogen atoms are omitted for clarity. Symmetry operators a = 1 – *y*, *x* – *y*, *z*; b = 1 – *x* + *y*, 1 – *x*, *z*; c = 1 – *x* + *y*, 1 – *y*, 1/2 – *z*; d = *x*, *y*, 1/2 – *z*; e = 1 – *y*, *x* – *y*, 1/2 – *z*. Selected distances [Å] and angles [°]: Bi1–C1 2.178(11), Bi1–N17 2.60(2), Bi1–O5 2.313(17), Bi1–O25 2.518(8), C1–Bi1–N17 71.4(6), C1–Bi1–O5 89.8(5), C1–Bi1–O25 88.5(3), N17–Bi1–N17d 136.2(8), N17–Bi1–O5 78.7(4), N17–Bi1–O25d 73.1(5).

bonds in **4**, **5** and **8** are shorter in comparison with the hydrogen bonds found in the organophosphonic acids (i.e., 2.541–2.646 Å in *tert*-butylphosphonic acid and 2.546–2.607 Å in phenylphosphonic acid).[10]

The molecular structure of compound **9** is depicted in Figure 4. As postulated in solution (vide supra), the phosphonate groups in **9** are fully deprotonated and are coordinated to the central metal Bi1 in a chelating mode [oxygen atoms O25 and O25d, the Bi–O bond lengths are 2.518(8) Å]. The third oxygen atom O5b of the same phosphonate group is involved in a intermolecular connection with the bismuth atom Bi1b of the neighboring molecule [the Bi–O bond length is 2.313(17) Å]. This bonding situation is repeated for other molecules as well, leading to a trimeric structure built up from three LBi[O_2P(*t*Bu)(O)] subunits (Figure 4) and closure of the 12-membered ring. The organic groups, that is, ligands L and the *t*Bu groups, are arranged alternately along this core and are orientated outside the central ring. The pendant arms of the ligands are located above and below the ring and are coordinated to the bismuth atoms. This tridentate coordination of the central metals by the ligands L [the Bi–N bond lengths are 2.60(2) Å, the bonding angle N1–Sb–N2 is 136.2(8)°] leads to an increase in the coordination number of the bismuth atom to six. The coordination polyhedron around the bismuth may be described as a distorted pentagonal pyramid and the shapes of the coordination polyhedra around the phosphorus atoms remain essentially tetrahedral.

Conclusions

In conclusion, we have demonstrated that NCN-chelated antimony and bismuth oxides **1** and **2** are useful starting materials for the preparation of the corresponding phosphonates. The reaction of **1** and **2** with selected organophosphonic acids gave, in a controlled and predictable manner, depending on the molar ratio, either the secondary phosphonates **3**–**5** and **8** or fully deprotonated phosphonates **6** and **9**. Compounds **3**–**5** and **8** contain in their structure two acidic POH hydrogen atoms that are promising in regard to the investigation of their further reactivity. Furthermore, phosphonates **6** and **8** react with ethylphosphonic acid with formation of mixed compounds **7** and **10** containing two different organic groups on the phosphorus atoms, interestingly, without any evidence for scrambling of these ligands. These findings make compounds **6** and **9** possible precursors for the preparation of other mixed compounds containing either three different main group central atoms or mixed antimony (bismuth) phosphonate – phosphinate compounds. This investigation is currently underway in our laboratory.

Experimental Section

General Procedures: ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded with a Bruker AMX360 spectrometer, by using a 5-mm tunable broad-band probe. Appropriate chemical shifts in ^{1}H and ^{13}C

NMR spectra were related to the residual signals of the solvent [$CDCl_3$: $\delta(^1H)$ = 7.27 ppm and $\delta(^{13}C)$ = 77.23 ppm]. The ^{31}P NMR spectra were related to external 85% H_3PO_4 $\delta(^{31}P)$ = 0.00 ppm. Positive-ion and negative-ion electrospray ionization (ESI) mass spectra were measured with an ion trap analyzer Esquire 3000 (Bruker Daltonics, Bremen, Germany) in the range *m*/*z* = 50–1000. The samples were dissolved in a mixture of acetonitrile/water (1:1) and analyzed by direct infusion at a flow rate of 5 μL min^{-1}. The ion source temperature was 300 °C, the tuning parameter compound stability was 100% and the flow rate and the pressure of nitrogen were 4 L min^{-1} and 10 psi, respectively. Infrared spectra were recorded in the range 4000–400 cm^{-1} as KBr pellets or Nujol mulls with an FTIR spectrometer Nicolet Magna 550. The starting compounds ethylphosphonic acid (98%), phenylphosphonic acid (98%) and *tert*-butylphosphonic acid (98%) were obtained from commercial suppliers and used as delivered. The compounds [2,6-$(Me_2NCH_2)_2C_6H_3SbO]_2$[7] (**1**) and [2,6-$(Me_2NCH_2)_2C_6H_3BiO]_2$[8] (**2**) were prepared according to literature procedures.

2,6-$(Me_2NCH_2)_2C_6H_3Sb[OP(O)(OH)Et]_2$ (3): A solution of [2,6-$(Me_2NCH_2)_2C_6H_3SbO]_2$ (**1**; 100 mg, 0.152 mmol) in dichloromethane (10 mL) was added to a suspension of ethylphosphonic acid (67 mg, 0.61 mmol) in dichloromethane (15 mL), and the resulting mixture was stirred for an additional 2 h at room temperature. The reaction mixture was evaporated in vacuo, and the residue was washed with hexane (5 mL). The remaining white solid was recrystallized from dichloromethane/hexane to give **3** as white crystals (116 mg, 72%). M.p. 203–205 °C. MS (ESI+): *m*/*z* (%) = 749 (55) $[L_2Sb_2O(OPO_2HEt)]^+$, 421 (19) $[M - OPO_2HEt]^+$, 329 (100) $[LSbOH]^+$. MS (ESI–): *m*/*z* (%) = 219 (100) $[2HOPO_2HEt - H]^-$, 109 (16) $[OPO_2HEt]^-$. ^1H NMR (360 MHz, $CDCl_3$, 25 °C): δ = 0.99 (m, 6 H, PCH_2CH_3), 1.46 (m, 4 H, PCH_2CH_3), 2.85 [s, 12 H, $N(CH_3)_2$], 4.00 (s, 4 H, NCH_2), 7.20 (d, 2 H, Ar-H3,5), 7.34 (t, 1 H, Ar-H4), 11.55 (br. s, 2 H, POH) ppm. ^{13}C NMR (90.56 MHz, $CDCl_3$, 25 °C): δ = 7.6 (s, PCH_2CH_3), 20.8 (d, $^1J_{P,C}$ = 142 Hz, PCH_2CH_3), 46.3 [s, $N(CH_3)_2$], 64.3 (s, NCH_2), 124.9 (s, Ar-C3,5), 129.5 (s, Ar-C4), 143.8 (s, Ar-C2,6), 157.0 (s, Ar-C1) ppm. ^{31}P NMR (145.79 MHz, $CDCl_3$, 25 °C): δ = 29.3 (s) ppm. IR: $\tilde{\nu}$ = 2723 (m), 2389 (m), 2328 (m), 1738 (m), 1676 (s, POH), 1136 (vs), 1099 (vs), 1036 (vs), 987 (vs, PO_3) cm^{-1}. $C_{16}H_{31}N_2O_6P_2Sb$ (531.13): calcd. C 36.2, H 5.9; found C 36.3, H 6.2.

2,6-$(Me_2NCH_2)_2C_6H_3Sb[OP(O)(OH)Ph]_2$ (4): Prepared by a procedure similar to that described for compound **3**. [2,6-$(Me_2NCH_2)_2C_6H_3SbO]_2$ (**1**; 95 mg, 0.14 mmol) in dichloromethane (10 mL) and phenylphosphonic acid (91 mg, 0.58 mmol) in dichloromethane (15 mL) gave **4** as white crystals (135 mg, 75%). M.p. 234–237 °C. MS (ESI+): *m*/*z* (%) = 797 (20) $[L_2Sb_2O(OPO_2HPh)]^+$, 469 (3) $[M - OPO_2HPh]^+$, 329 (100) $[LSbOH]^+$. MS (ESI–): *m*/*z* (%) = 315 (14) $[2HOPO_2HPh - H]^-$, 157 (100) $[OPO_2HPh]^-$. ^1H NMR (360 MHz, $CDCl_3$, 25 °C): δ = 2.75 [s, 12 H, $N(CH_3)_2$], 4.01 (s, 4 H, NCH_2), 6.78 (br. s, 2 H, POH), 7.23 (m, 6 H, Ph-H3,4,5), 7.32 (d, 2 H, Ar-H3,5), 7.39 (t, 1 H, Ar-H4), 7.52 (m, 4 H, Ph-H2,6) ppm. ^{13}C NMR (90.56 MHz, $CDCl_3$, 25 °C): δ = 46.2 [s, $N(CH_3)_2$], 64.3 (s, NCH_2), 125.2 (s, Ar-C3,5), 127.8 (d, $^3J_{P,C}$ = 14 Hz, Ph-C3,5), 130.0 (s, Ar-C4), 130.1 (s, Ph-C4), 130.6 (d, $^2J_{P,C}$ = 10 Hz, Ph-C2,6), 135.5 (d, $^1J_{P,C}$ = 187 Hz, Ph-C1), 144.3 (s, Ar-C2,6), 156.2 (s, Ar-C1) ppm. ^{31}P NMR (145.79 MHz, $CDCl_3$, 25 °C): δ = 15.0 (s) ppm. IR: $\tilde{\nu}$ = 2723 (m), 2686 (m), 2385 (m), 2318 (s), 1670 (s, POH), 1134 (vs), 1093 (vs), 1001 (vs), 950 (vs), 957 (vs, PO_3) cm^{-1}. $C_{24}H_{31}N_2O_6P_2Sb$ (627.22): calcd. C 46.0, H 5.0; found C 46.1, H 5.2.

2,6-$(Me_2NCH_2)_2C_6H_3Sb[OP(O)(OH)tBu]_2$ (5): Prepared by a procedure similar to that described for compound **3**. [2,6-$(Me_2NCH_2)_2C_6H_3SbO]_2$ (**1**; 340 mg, 0.517 mmol) in dichloromethane (10 mL) and *tert*-butylphosphonic acid (286 mg, 2.07 mmol) in dichloromethane (15 mL) gave **5** as white crystals (417 mg, 73%). M.p. 300 °C (decomp.). MS (ESI+): *m*/*z* (%) = 777 (27) $[L_2Sb_2O(OPO_2HtBu)]^+$, 449 (28) $[M - OPO_2HtBu]^+$, 329 (100) $[LSbOH]^+$. MS (ESI–): *m*/*z* (%) = 275 (99) $[2HOPO_2HtBu - H]^-$, 137 (100) $[OPO_2HtBu]^-$. ^1H NMR (360 MHz, $CDCl_3$, 25 °C): δ = 0.98 [d, $^3J_{P,H}$ = 18 Hz, 18 H, $PC(CH_3)_3$], 2.88 [s, 12 H, $N(CH_3)_2$], 3.99 (s, 4 H, NCH_2), 7.19 (d, 2 H, Ar-H3,5), 7.36 (t, 1 H, Ar-H4), 11.10 (br. s, 2 H, POH) ppm. ^{13}C NMR (90.56 MHz, $CDCl_3$, 25 °C): δ = 25.6 [s, $PC(CH_3)_3$], 31.2 [d, $^1J_{P,C}$ = 143 Hz, $PC(CH_3)_3$], 46.4 [s, $N(CH_3)_2$], 64.3 (s, NCH_2), 125.5 (s, Ar-C3,5), 128.4 (s, Ar-C4), 143.6 (s, Ar-C2,6), 157.7 (s, Ar-C1) ppm. ^{31}P NMR (145.79 MHz, $CDCl_3$, 25 °C): δ = 32.2 (s) ppm. IR: $\tilde{\nu}$ = 2725 (s), 2679 (m), 2385 (m), 2330 (m), 1672 (br. m, POH), 1130 (s), 1091 (vs), 1033 (s), 1001 (vs), 985 (vs, PO_3) cm^{-1}. $C_{20}H_{39}N_2O_6P_2Sb$ (587.24): calcd. C 40.9, H 6.7; found C 41.2, H 6.8.

2,6-$(Me_2NCH_2)_2C_6H_3Sb[O_2P(O)tBu]$ (6): A solution of [2,6-$(Me_2NCH_2)_2C_6H_3SbO]_2$ (**1**; 114 mg, 0.156 mmol) in dichloromethane (10 mL) was added to a suspension of *tert*-butylphosphonic acid (43 mg, 0.31 mmol) in dichloromethane (15 mL), and the resulting mixture was stirred for an additional 3 h at the room temperature. The reaction mixture was evaporated in vacuo, and the residue was washed with hexane (5 mL). The remaining white solid was extracted with toluene (10 mL). The toluene filtrate was evaporated to give **6** as white crystals (95 mg, 68%). M.p. 179–181 °C. MS (ESI+): *m*/*z* (%) = 777 (100) $[L_2Sb_2O(OPO_2HtBu)]^+$, 449 (5) $[M + H]^+$, 329 (86) $[LSbOH]^+$. MS (ESI–): *m*/*z* (%) = 275 (28) $[2HOPO_2HtBu - H]^-$, 137 (100) $[OPO_2HtBu]^-$. ^1H NMR (360 MHz, $CDCl_3$, 25 °C): δ = 0.93 [d, $^3J_{P,H}$ = 15Hz, 9 H, $PC(CH_3)_3$], 2.13 [s, 6 H, $N(CH_3)_2$], 2.73 [s, 6 H, $N(CH_3)_2$], 3.39 and 4.43 (AX pattern, $^2J_{H,H}$ = 14 Hz, 4 H, NCH_2), 7.13 (d, 2 H, Ar-H3,5), 7.31 (t, 1 H, Ar-H4) ppm. ^{13}C NMR (90.56 MHz, $CDCl_3$, 25 °C): δ = 25.9 [s, $PC(CH_3)_3$], 31.3 [d, $J^1_{P,C}$ = 129 Hz, $PC(CH_3)_3$], 42.5 [s, $N(CH_3)_2$], 45.7 [s, $N(CH_3)_2$], 63.2 (s, NCH_2), 125.6 (s, Ar-C3,5), 130.6 (s, Ar-C4), 146.8 (s, Ar-C2,6), 152.6 (s, Ar-C1) ppm. ^{31}P NMR (145.79 MHz, $CDCl_3$, 25 °C): δ = 41.0 (s) ppm. IR: $\tilde{\nu}$ = 1132 (s), 1095 (vs), 1031 (m), 1001 (m), 987 (s, PO_3) cm^{-1}. $C_{16}H_{28}N_2O_3PSb$ (449.14): calcd. C 42.8, H 6.3; found C 42.9, H 6.4.

2,6-$(Me_2NCH_2)_2C_6H_3Sb[OP(O)(OH)tBu][OP(O)(OH)Et]$ (7): A solution of **6** (68 mg, 0.15 mmol) in dichloromethane (20 mL) was added to a suspension of ethylphosphonic acid (17 mg, 0.15 mmol) in dichloromethane (15 mL), and the resulting mixture was stirred for an additional 1 h at room temperature. The reaction mixture was evaporated in vacuo, and the residue was washed with hexane (5 mL). The remaining white solid was recrystallized from dichloromethane/hexane to give **7** as white crystals (60 mg, 71%). M.p. 237 °C (decomp.). MS (ESI+): *m*/*z* (%) = 449 (4) $[M - OPO_2HEt]^+$, 421 (2) $[M - OPO_2HtBu]^+$, 329 (100) $[LSbOH]^+$. MS (ESI–): *m*/*z* (%) = 137 (100) $[OPO_2HtBu]^-$, 109 (16) $[OPO_2HEt]^-$. ^1H NMR (360 MHz, $CDCl_3$, 25 °C): δ = 0.93 [d, $^3J_{P,H}$ = 9 Hz, 9 H, $PC(CH_3)_3$], 0.99 (m, 3 H, PCH_2CH_3) – overlap with the signal of the $PC(CH_3)_3$ group, 1.40 (m, 2 H, PCH_2CH_3), 2.82 [s, 12 H, $N(CH_3)_2$], 3.95 (s, 4 H, NCH_2), 7.14 (d, 2 H, Ar-H3,5), 7.29 (t, 1 H, Ar-H4), 11.63 (br. s, 2 H, POH) ppm. ^{13}C NMR (90.56 MHz, $CDCl_3$, 25 °C): δ = 7.6 (s, PCH_2CH_3), 21.3 (d, $^1J_{P,C}$ = 143 Hz, PCH_2CH_3), 25.5 [s, $PC(CH_3)_3$], 30.6 [d, $^1J_{P,C}$ = 142 Hz, $PC(CH_3)_3$], 46.4 [s, $N(CH_3)_2$], 64.4 (s, NCH_2), 124.9 (s, Ar-C3,5), 129.5 (s, Ar-C4), 143.9 (s, Ar-C2,6), 157.2 (s, Ar-C1) ppm. ^{31}P NMR (145.79 MHz, $CDCl_3$, 25 °C): δ = 34.2, 30.8 ppm. IR: $\tilde{\nu}$ = 2730 (m), 2707 (br. m), 2386 (br. m), 2330 (br. m), 1733 (s), 1668 (s, POH), 1133 (vs), 1099 (vs), 1033 (vs), 999 (vs, PO_3) cm^{-1}.

$C_{18}H_{35}N_2O_6P_2Sb$ (559.18): calcd. C 38.7, H 6.3; found C 38.9, H 6.5.

2,6-$(Me_2NCH_2)_2C_6H_3Bi[OP(O)(OH)tBu]_2$ (8): Prepared by a procedure similar to that described for compound **3**. [2,6-$(Me_2NCH_2)_2$-$C_6H_3BiO]_2$ (**2**; 443 mg, 0.532 mmol) in dichloromethane (10 mL) and *tert*-butylphosphonic acid (295 mg, 2.13 mmol) in dichloromethane (15 mL) gave **8** as white crystals (467 mg, 65%). M.p. >350 °C. MS (ESI+): *m*/*z* (%) = 537 (100) $[M - OPO_2HtBu]^+$, 417 (77) $[LBiOH]^+$. MS (ESI–): *m*/*z* (%) = 811 (8) $[M+OPO_2HtBu]^-$, 673 (21) $[M - H]^-$, 137 (100) $[OPO_2HtBu]^-$. ^1H NMR (360 MHz, $CDCl_3$, 25 °C): δ = 0.99 [d, $^3J_{P,H}$ = 16 Hz, 18 H, $PC(CH_3)_3$], 2.90 [s, 12 H, $N(CH_3)_2$], 4.26 (s, 4 H, NCH_2), 7.47 (t, 1 H, Ar-H4), 7.65 (d, 2 H, Ar-H3,5), 10.37 (br. s, 2 H, POH) ppm. ^{13}C NMR (90.56 MHz, $CDCl_3$, 25 °C): δ = 25.7 [s, $PC(CH_3)_3$], 31.3 [d, $^1J_{P,C}$ = 141 Hz, $PC(CH_3)_3$], 46.4 [s, $N(CH_3)_2$], 67.8 (s, NCH_2), 127.6 (s, Ar-C3,5), 129.0 (s, Ar-C4), 151.6 (s, Ar-C2,6) ppm, (Ar-C1) not observed. ^{31}P NMR (145.79 MHz, $CDCl_3$, 25 °C): δ = 32.5 (s) ppm. IR: $\tilde{\nu}$ = 2726 (m), 2671 (m), 2387 (br. s), 2329 (br. m), 1732 (s), 1662 (m, POH), 1128 (s), 1101 (vs), 1029 (s), 1001 (s), 989 (vs, PO_3) cm^{-1}. $C_{20}H_{39}BiN_2O_6P_2$ (674.47): calcd. C 35.6, H 5.8; found C 35.7, H 5.9.

2,6-$(Me_2NCH_2)_2C_6H_3Bi[O_2P(O)tBu]$ (9): Prepared by a procedure similar to that described for compound **6**. [2,6-$(Me_2NCH_2)_2$-$C_6H_3BiO]_2$ (**2**; 495 mg, 0.60 mmol) in dichloromethane (15 mL) and *tert*-butylphosphonic acid (164 mg, 1.19 mmol) in dichloromethane (15 mL) gave **9** as white crystals (306 mg, 48%). M.p. 292 °C (decomp.). MS (ESI+): *m*/*z* (%) = 537 (55) $[M + H]^+$, 417 (100) $[LBiOH]^+$. MS (ESI–): *m*/*z* (%) = 673 (15) $[M + OPO_2HtBu]^-$, 571 (15) $[M + Cl]^-$, 137 (100) $[OPO_2HtBu]^-$. ^1H NMR (360 MHz, $CDCl_3$, 25 °C): δ = 0.47 (v br. s, 9 H), 2.75 [br. s, 12 H, $N(CH_3)_2$], 4.24 (br. s, 4 H, NCH_2), 7.39 (t, 1 H, Ar-H4), 7.52 (d, 2 H, Ar-H3,5) ppm. ^{31}P NMR (145.79 MHz, $CDCl_3$, 25 °C): δ = 35.7 (s) ppm. IR: $\tilde{\nu}$ = 1089 (m), 1062 (vs), 1031 (s), 1014 (s), 950 (vs, PO_3) cm^{-1}. $C_{16}H_{28}BiN_2O_3P$ (536.37): calcd. C 35.8, H 5.3; found C 35.6, H 5.5.

2,6-$(Me_2NCH_2)_2C_6H_3Bi[OP(O)(OH)tBu][OP(O)(OH)Et]$ (10): Prepared by a procedure similar to that described for compound **7**. Compound **9** (61 mg, 0.11 mmol) in dichloromethane (20 mL) and ethylphosphonic acid (13 mg, 0.11 mmol) in dichloromethane (15 mL) gave **10** as a white solid (53 mg, 72%). M.p. 279 (decomp.). MS (ESI+): *m*/*z* (%) = 537 (100) $[M - OPO_2HEt]^+$, 509 (25) $[M - OPO_2HtBu]^+$, 417 (15) $[LBiOH]^+$. MS (ESI–): *m*/*z* (%) = 783 (32) $[M + OPO_2HtBu]^-$, 755 (16) $[M + OPO_2HEt]^-$, 645 (18) $[M - H]^-$, 137 (100) $[OPO_2HtBu]^-$, 109 (15) $[OPO_2HEt]^-$. ^1H NMR (360 MHz, $CDCl_3$, 25 °C): δ = 0.98 [d, $^3J_{P,H}$ = 9 Hz, 9 H, $PC(CH_3)_3$], 0.98 (m, 3 H, PCH_2CH_3) – overlap with the signal of the $PC(CH_3)_3$ group, 1.47 (m, 2 H, PCH_2CH_3), 2.90 [s, 12 H, $N(CH_3)_2$], 4.28 (s, 4 H, NCH_2), 7.48 (t, 1 H, Ar-H4), 7.65 (d, 2 H, Ar-H3,5), 11.00 (br. s, 2 H, POH) ppm. ^{13}C NMR (90.56 MHz, $CDCl_3$, 25 °C): δ = 8.2 (s, PCH_2CH_3), 21.8 (d, $^1J_{P,C}$ = 139 Hz, PCH_2CH_3), 25.9 [s, $PC(CH_3)_3$], 31.5 [d, $^1J_{P,C}$ = 141 Hz, $PC(CH_3)_3$], 46.5 [s, $N(CH_3)_2$], 68.1 (s, NCH_2), 127.8 (s, Ar-C3,5), 129.1 (s, Ar-C4), 151.6 (s, Ar-C2,6) ppm. (s, Ar-C1) not observed. ^{31}P NMR (145.79 MHz, $CDCl_3$, 25 °C): δ = 32.7, 29.7 ppm. IR: $\tilde{\nu}$ = 2726 (m), 2667 (m), 2391 (s), 2323 (s), 1735 (s), 1654 (br. s, POH), 1099 (vs), 1022 (vs, PO_3) cm^{-1}. $C_{18}H_{35}BiN_2O_6P_2$ (660.44): calcd. C 34.6, H 5.7; found C 34.7, H 5.9.

X-ray Crystallography: Suitable single crystals of **4**, **5**, **8** and **9** were mounted on a glass fibre with oil and measured with a four-circle diffractometer KappaCCD instrument with a CCD area detector and monochromated Mo-K_α radiation (λ = 0.71073 Å) at 150(1) K. The numerical[11] absorption corrections from crystal shape were applied for all crystals. The structures were solved by the direct methods (SIR92)[12] and refined by a full-matrix least-squares procedure based on F^2 (SHELXL97).[13] Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2U_{eq}$ (pivot atom) or of $1.5U_{eq}$ for the methyl moiety with C–H = 0.96, 0.97 and 0.93 Å for methyl, methylene and hydrogen atoms in the aromatic ring, respectively, and 0.83 Å for the O–H bonds. The final difference maps for **4**, **5** and **8** displayed no peaks of chemical significance, as the highest peaks and holes are in close vicinity (≈1 Å) to the heavy atoms. In **9**, there is a large peak (≈4 e A^{-3}) that has no chemical significance, and even after use of different software techniques (Platon-SQUEEZE) in order to explain it, no better model was obtained. In the same crystal, all phenyl rings of the NCN chelating ligands are disordered. These were split into three approximately equivalent positions; nevertheless, the positions of all heavier atoms, including the whole phosphonate groups, were well modelled.

CCDC-755837 (for **8**), -755838 (for **5**), -755839 (for **4**) and -755840 (for **9**) 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 4: $C_{24}H_{31}N_2O_6P_2Sb$, M = 627.20, triclinic, $P\bar{1}$, a = 9.60110(6) Å, b = 10.8722(6) Å, c = 12.6439(5) Å, α = 87.654(4)°, β = 88.544(5)°, γ = 84.612(5)°, V = 1312.57(12) $Å^3$, Z = 2, T = 150(1) K, 24003 total reflections, 5987 independent [R_{int} = 0.054, R_1 (obs. data) = 0.039, wR_2 (all data) 0.091].

Crystallographic Data for 5: $C_{21}H_{41}Cl_2O_6N_2P_2Sb$, M = 627.15, triclinic, $P\bar{1}$, a = 8.5612(5) Å, b = 13.3846(3) Å, c = 14.6761(12) Å, α = 69.384(4)°, β = 83.020(7)°, γ = 80.004(5)°, V = 1546.79(16) $Å^3$, Z = 2, T = 150(1) K, 27187 total reflections, 7040 independent [R_{int} = 0.386, R_1 (obs. data) = 0.077, wR_2 (all data) 0.160].

Crystallographic Data for 8: $C_{20}H_{39}N_2O_6P_2Bi$, M = 674.045, monoclinic, $P2_1/c$, a = 9.6582(4) Å, b = 14.8608(10) Å, c = 18.3442(12) Å, β = 90.251(4)°, V = 2632.8(3) $Å^3$, Z = 4, T = 150(1) K, 25111 total reflections, 5999 independent [R_{int} = 0.114, R_1 (obs. data) = 0.048, wR_2 (all data) 0.079].

Crystallographic Data for 9: $C_{48}H_{84}N_6O_9P_3Bi_3$, M = 1609.06, hexagonal, $P6_3/m$, a = 17.1000(19) Å, b = 17.1000(19) Å, c = 14.5642(7) Å, V = 3688.1(6) $Å^3$, Z = 2, T = 150(1) K, 20587 total reflections, 2919 independent [R_{int} = 0.136, R_1 (obs. data) = 0.069, wR_2 (all data) 0.24].

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