

# Crystal Structures and Vibrational and Solution and Solid-State (CPMAS) NMR Spectroscopic Studies in Triphenyl Phosphine, Arsine, and Stibine Silver(I) Bromate Systems, $(R_3E)_xAgBrO_3$ (E = P, As, Sb; $x = 1-4$ )

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Adducts of triphenyl phosphine, triphenyl arsine, and triphenyl stibine with silver(I) bromate have been synthesized and characterized both in solution (<sup>1</sup>H and ESI MS spectroscopy) and in the solid state (IR, single-crystal X-ray structure analysis). The triphenyl phosphine complexes have been also investigated by <sup>31</sup>P{<sup>1</sup>H} solution and <sup>31</sup>P cross-polarization magic-angle-spinning (CPMAS) NMR spectroscopy. The topology of the structures in the solid state was found to depend on the nature of EPh<sub>3</sub> and on the stoichiometric ratio AgBrO<sub>3</sub>/EPh<sub>3</sub>. In AgBrO<sub>3</sub>/PPh<sub>3</sub> (1:1)<sub>4</sub> (**1**) and AgBrO<sub>3</sub>/PPh<sub>3</sub> (1:2) (**2**), the bromate is in the unfamiliar and hitherto structurally uncharacterized role of coordinating ligand, the complex having a mononuclear form in **2** and a less familiar tetrameric form in **1**. In AgBrO<sub>3</sub>/AsPh<sub>3</sub> (1:4)·CH<sub>3</sub>OH (**7**) and AgBrO<sub>3</sub>/SbPh<sub>3</sub> (1:4)·C<sub>2</sub>H<sub>5</sub>OH (**11**), the cations are the familiar homoleptic [Ag(EPh<sub>3</sub>)<sub>4</sub>]<sup>+</sup> array with the bromate role simply that of counterion. The AgBrO<sub>3</sub>/AsPh<sub>3</sub> (1:2)<sub>2</sub>·0.7H<sub>2</sub>O derivative (**6**) is binuclear L<sub>2</sub>Ag(μ-BrO<sub>3</sub>)<sub>2</sub>AgL<sub>2</sub> with a four-membered ring core (L = AsPh<sub>3</sub>).

## Introduction

The coordination chemistry of tertiary phosphines is a well-established field of research that allows systematic investigation of the possible coordination modes of oxyanions such as NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, and NO<sub>2</sub><sup>-</sup> to Ag(I)<sup>1-4</sup> and Cu(I) ions.<sup>5</sup> It is well-known that interesting structural variations within

the series MX/(PR<sub>3</sub>)<sub>n</sub> result from the different coordination modes of the anions. By comparison, the chemistry of tertiary stibines and arsines has only been investigated sparsely, though there has been increased interest recently.<sup>4,6,7</sup> AgBrO<sub>3</sub> is a useful oxidant for the transformation of tetrahydropyranyl ethers to carbonyl compounds,<sup>8</sup> and AgBrO<sub>3</sub> has been efficiently employed to transform ethylene acetals to aldehydes in refluxing carbon tetrachloride in high yields.<sup>8</sup> However, severe regulations on the use of bromate salts have been imposed in the past few years by health and environmental protection authorities,<sup>9</sup> their uses in some cases being prohibited. In some cases, however, bromate salts provide substantial advantage in yield and reaction conditions over

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the use of other reagents for bromination such as  $Br_2$ , so that their use can be economically justified.<sup>10</sup> Nevertheless, to date no studies have been reported describing the simple coordination chemistry of  $AgBrO_3$ , the possibility of extracting it from reaction solution by using Lewis bases, and the stability of  $AgBrO_3$  complexes both in the solid and solution states. Following our current interest in silver(I) complexes,<sup>11</sup> we have decided to extend our studies to the investigation of the interaction of the “softer” group 15 donor ligands with  $AgBrO_3$ . Here, we describe a series of  $AgBrO_3$  adducts with unidentate triorgano phosphines, arsines, and stibines  $EPh_3$  ( $E = P, As, Sb$ ). Six single-crystal X-ray studies have been also reported to assist in understanding the relationships between structural type, coordinating ability of  $BrO_3^-$ , and donating ability of the ancillary ligand. Our results demonstrate that remarkably stable neutral silver complexes showing different silver(I) coordination environments and  $BrO_3^-$  coordination modes can be easily synthesized: mononuclear forms with bromate *O, O'*-bidentate containing two ancillary donors, binuclear and tetranuclear aggregates in which bromate oxygen atoms are the bridging atoms, and ionic derivatives containing four ancillary ligands. The stabilities of the species in chlorinated and acetonitrile solutions have been examined by way of variable temperature  $^{31}P$  NMR experiments.

## Experimental Section

**Materials and Methods.** All reactions were carried out under an atmosphere of dry oxygen-free dinitrogen, under standard Schlenk techniques and protected from light. Solvents were used as supplied or distilled using standard methods. All chemicals were purchased from Aldrich (Milwaukee) and used as received. Elemental analyses (C, H, N, S) were performed with a Fisons Instruments 1108 CHNS-O elemental analyzer. IR spectra were recorded from 4000 to  $100\text{ cm}^{-1}$  with a Perkin-Elmer system 2000 FT-IR instrument.  $^1H$  and  $^{31}P$  solution NMR spectra were acquired at room temperature on a VXR-300 Varian spectrometer operating at a field strength of 7.05 T (300 MHz for  $^1H$  and 121.4 MHz for  $^{31}P$ ). Proton chemical shifts are reported in parts per million versus  $Me_4Si$ , while phosphorus chemical shifts are reported in parts per million versus 85%  $H_3PO_4$ .  $^{31}P$  CPMAS solid state NMR spectra were acquired at room temperature on a Bruker MSL-400 spectrometer operating at a field strength of 9.40 T (400.13 MHz for  $^1H$  and 161.924 MHz for  $^{31}P$ ). Conventional cross-polarization and magic-angle-spinning techniques, coupled with spin temperature alternation to eliminate spectral artifacts, were implemented using a Bruker 4 mm double-air-bearing probe in which MAS frequencies of  $>10\text{ kHz}$  were achieved. A recycle delay of 30 s, a  $^1H-^{31}P$  contact period of 10 ms, and a  $^1H\ \pi/2$  pulse length of 3  $\mu s$  were used in these measurements. No spectral smoothing was invoked prior to Fourier transformation. Chemical shifts were externally referenced to 85%  $H_3PO_4$  via solid triphenyl phosphine ( $\delta$ ,  $-9.9$ ). The electrical conductances of the  $CH_2Cl_2$  solutions were measured with a Crison CDTM 522 conductimeter at room temperature. The positive and negative electrospray mass spectra were obtained with a series 1100 MSD detector HP spectrometer, using an acetonitrile

mobile phase. Solutions (3 mg/mL) for electrospray ionization mass spectrometry (ESI-MS) were prepared using reagent grade methanol. For the ESI-MS data, masses and intensities were compared to those calculated using IsoPro Isotopic Abundance Simulator, version 2.1.<sup>12</sup> Peaks containing silver(I) ions are identified by the peak of highest intensities in the isotope distribution pattern.

**Syntheses of Complexes.  $AgBrO_3/PPh_3$  (1:1)<sub>4</sub> (1).** Silver(I) bromate (0.236 g, 1 mmol) was added to an ethanol solution (30 mL) of  $PPh_3$  (0.262 g, 1 mmol) at 60 °C. After the addition, the solution was stirred for 48 h at 60 °C and then concentrated with a rotary evaporator and stored at 4 °C for 3 days. A colorless precipitate was formed which was isolated by filtration, washed with ethanol ( $3 \times 5\text{ mL}$ ), and shown to be compound **1**. Recrystallization from ethanol gave X-ray quality crystals. Yield 78%. Mp: 122–124 °C.  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ , 293 K):  $\delta$  29.5 (s), 6.1 (s).  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ , 213 K):  $\delta$  29.6 (s),  $-8.9$  (s, br) 3.4 (dd,  $^1J(^{109}Ag-^{31}P)$  644.5 Hz;  $^1J(^{107}Ag-^{31}P)$  559.0 Hz).  $^{31}P\{^1H\}$  NMR ( $CD_3CN$ , 293 K): 22.13 (s),  $-8.36$  (s).  $^{31}P\{^1H\}$  NMR ( $CD_3CN$ , 233 K): 22.7 (s),  $-8.9$  (s).  $\Lambda_{mol}$  ( $CH_2Cl_2$ , concentration =  $1.30 \times 10^{-3}\text{ M}$ ):  $0.7\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ . Anal. Calcd for  $C_{18}H_{15}AgBrO_3P$ : C, 43.56; H, 3.05. Found: C, 43.21; H, 3.10.

**$AgBrO_3/PPh_3$  (1:2) (2).** Compound **2** has been synthesized similarly to **1**, by using  $AgBrO_3$  (0.236 g, 1 mmol) and  $PPh_3$  (0.787 g, 3 mmol), and was recrystallized from ethanol yielding X-ray quality crystals. Yield 40%. Mp: 118–119 °C.  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ , 293 K):  $\delta$  29.5 (s).  $^{31}P\{^1H\}$  NMR ( $CD_3CN$ , 293 K): 22.13 (s), 6.0 (s).  $^{31}P\{^1H\}$  NMR ( $CD_3CN$ , 233 K): 22.9 (s), 6.4 (br), 4.1 (br), 2.5 (br).  $\Lambda_{mol}$  ( $CH_2Cl_2$ , concentration =  $0.70 \times 10^{-3}\text{ M}$ ):  $0.2\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ . Anal. Calcd for  $C_{36}H_{30}AgBrO_3P_2$ : C, 56.87; H, 3.98. Found: C, 56.54; H, 4.16.

**$AgBrO_3/PPh_3$  (1:3) (3).** Silver(I) bromate (0.236 g, 1 mmol) was added to an ethanol solution (30 mL) of  $PPh_3$  (1.06 g, 4.0 mmol) at 60 °C. After the addition, the solution was stirred for 24 h at 60 °C. A colorless precipitate was formed which was isolated by filtration and washed with ethanol ( $3 \times 5\text{ mL}$ ). Recrystallization from ethanol gave complex **3** as a microcrystalline solid in 75% yield. Mp: 123–124 °C.  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ , 293 K):  $\delta$  29.7 (s), 6.7 (s).  $^{31}P\{^1H\}$  NMR ( $CD_3CN$ , 293 K): 22.13 (s), 5.4 (br).  $\Lambda_{mol}$  ( $CH_2Cl_2$ , concentration =  $1.10 \times 10^{-3}\text{ M}$ ):  $0.4\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ . Anal. Calcd for  $C_{54}H_{45}AgBrO_3P_2$ : C, 63.42; H, 4.44. Found: C, 63.69; H, 4.69.

**$AgBrO_3/PPh_3$  (1:4)·2 $H_2O$  (4).** Compound **4** has been synthesized similarly to **3**, by using  $AgBrO_3$  (0.236 g, 1 mmol) and excess  $PPh_3$  (1.311 g, 5 mmol), and was recrystallized from ethanol. Yield 77%. Mp: 166–167 °C.  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ , 293 K):  $\delta$  29.7 (s), 6.5 (s).  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ , 213 K):  $\delta$  29.7 (s),  $-9.1$  (s, br), 3.4 (dd,  $^1J(^{109}Ag-^{31}P)$  645.1 Hz;  $^1J(^{107}Ag-^{31}P)$  560.0 Hz).  $\Lambda_{mol}$  ( $CH_2Cl_2$ , concentration =  $1.00 \times 10^{-3}\text{ M}$ ):  $1.2\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ . Anal. Calcd for  $C_{72}H_{64}AgBrO_5P_4$ : C, 65.47; H, 4.88. Found: C, 65.50; H, 5.16.

**$AgBrO_3/AsPh_3$  (1:1) (5).** Compound **5** has been synthesized similarly to **3**, by using  $AgBrO_3$  (0.236 g, 1 mmol) and  $AsPh_3$  (0.306 g, 1 mmol). Compound **5** was recrystallized from ethanol. Yield 39%. Mp: 178–180 °C.  $\Lambda_{mol}$  ( $CH_2Cl_2$ , concentration =  $1.00 \times 10^{-3}\text{ M}$ ):  $1.1\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ . Anal. Calcd for  $C_{18}H_{15}AgAsBrO_3$ : C, 39.89; H, 2.79. Found: C, 39.50; H, 2.53.

**$AgBrO_3/AsPh_3$  (1:2)<sub>2</sub>·0.7“ $H_2O$ ”(6).** Compound **6** has been synthesized similarly to **3**, by using  $AgBrO_3$  (0.236 g, 1 mmol) and  $AsPh_3$  (0.612 g, 2 mmol), and was recrystallized from ethanol

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yielding X-ray quality crystals. Yield 28%. Mp: 177–178 °C.  $\Lambda_{\text{mol}}$  ( $\text{CH}_2\text{Cl}_2$ , concentration =  $0.40 \times 10^{-3}$  M):  $2.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Anal. Calcd for  $\text{C}_{72}\text{H}_{61.4}\text{Ag}_2\text{As}_4\text{Br}_2\text{O}_{6.7}$ : C, 50.60; H, 3.62. Found: C, 50.67; H, 3.64.

**AgBrO<sub>3</sub>/AsPh<sub>3</sub> (1:4)·CH<sub>3</sub>OH (7).** Compound **7** has been synthesized similarly to **3**, by using AgBrO<sub>3</sub> (0.236 g, 1 mmol) and AsPh<sub>3</sub> (1.226 g, 4 mmol), and was recrystallized from ethanol, with X-ray quality crystals being obtained from methanol. Yield 37%. Mp: 192–195 °C.  $\Lambda_{\text{mol}}$  ( $\text{CH}_2\text{Cl}_2$ , concentration =  $0.80 \times 10^{-3}$  M):  $2.3 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Anal. Calcd for  $\text{C}_{73}\text{H}_{64}\text{AgAs}_4\text{BrO}_4$ : C, 58.74; H, 4.32. Found: C, 58.73; H, 4.51.

**AgBrO<sub>3</sub>/SbPh<sub>3</sub> (1:1) (8).** Compound **8** has been synthesized similarly to **3**, by using AgBrO<sub>3</sub> (0.236 g, 1 mmol) and SbPh<sub>3</sub> (0.706 g, 2 mmol). Compound **8** was recrystallized from ethanol. Yield 82%. Mp: 143–145 °C.  $\Lambda_{\text{mol}}$  ( $\text{CH}_2\text{Cl}_2$ , concentration =  $0.90 \times 10^{-3}$  M):  $0.2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Anal. Calcd for  $\text{C}_{18}\text{H}_{15}\text{AgBrO}_3\text{Sb}$ : C, 36.72; H, 2.57. Found: C, 36.91; H, 2.62.

**AgBrO<sub>3</sub>/SbPh<sub>3</sub> (1:2) (9).** Compound **9** has been synthesized similarly to **3**, by using AgBrO<sub>3</sub> (0.236 g, 1 mmol) and SbPh<sub>3</sub> (1.059 g, 3 mmol), and was recrystallized from ethanol. Yield 28%. Mp: 144–146 °C.  $\Lambda_{\text{mol}}$  ( $\text{CH}_2\text{Cl}_2$ , concentration =  $0.80 \times 10^{-3}$  M):  $0.1 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Anal. Calcd for  $\text{C}_{36}\text{H}_{30}\text{AgBrO}_3\text{Sb}_2$ : C, 45.91; H, 3.21. Found: C, 45.87; H, 3.09.

**AgBrO<sub>3</sub>/SbPh<sub>3</sub> (1:3) (10).** Compound **10** has been synthesized similarly to **3**, by using AgBrO<sub>3</sub> (0.236 g, 1 mmol) and SbPh<sub>3</sub> (1.412 g, 4 mmol), and was recrystallized from ethanol. Yield 35%. Mp: 146–149 °C.  $\Lambda_{\text{mol}}$  ( $\text{CH}_2\text{Cl}_2$ , concentration =  $0.60 \times 10^{-3}$  M):  $1.2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Anal. Calcd for  $\text{C}_{54}\text{H}_{45}\text{AgBrO}_3\text{Sb}_3$ : C, 50.09; H, 3.50. Found: C, 50.14; H, 3.76.

**AgBrO<sub>3</sub>/SbPh<sub>3</sub> (1:4)·C<sub>2</sub>H<sub>5</sub>OH (11).** Compound **11** has been synthesized similarly to **3**, by using AgBrO<sub>3</sub> (0.236 g, 1 mmol) and SbPh<sub>3</sub> (1.765 g, 5 mmol), and was recrystallized from ethanol yielding X-ray quality crystals. Yield 30%. Mp: 145–147 °C.  $\Lambda_{\text{mol}}$  ( $\text{CH}_2\text{Cl}_2$ , concentration =  $0.60 \times 10^{-3}$  M):  $3.3 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Anal. Calcd for  $\text{C}_{74}\text{H}_{66}\text{AgBrO}_4\text{Sb}_4$ : C, 52.47; H, 3.93. Found: C, 52.16; H, 3.87.

**AgBrO<sub>3</sub>/PPh<sub>3</sub>/AsPh<sub>3</sub> (1:1:1) (12).** Silver(I) bromate (0.236 g, 1 mmol) was added to an acetonitrile solution (30 mL) of PPh<sub>3</sub> (0.262 g, 1 mmol) and AsPh<sub>3</sub> (0.306 g, 1 mmol) at 50 °C. After the addition, the solution was stirred for 24 h at 50 °C and then concentrated with a rotary evaporator. A colorless precipitate was formed which was isolated by filtration, washed with acetonitrile (3 × 5 mL), and shown to be compound **12**. Yield 95%. Mp: 139 °C, dec.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 293 K):  $\delta$  10.9 br.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 218 K):  $\delta$  10.8 d,  $^1\text{J}(\text{Ag}-^{31}\text{P})$  633 Hz; 10.0 d,  $^1\text{J}(\text{Ag}-^{31}\text{P})$  444 Hz.  $\Lambda_{\text{mol}}$  ( $\text{CH}_2\text{Cl}_2$ , concentration =  $1.30 \times 10^{-3}$  M):  $0.2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Anal. Calcd for  $\text{C}_{36}\text{H}_{30}\text{AgAsBrO}_3\text{P}$ : C, 53.76; H, 3.76. Found: C, 53.55; H, 3.93.

**AgBrO<sub>3</sub>/PPh<sub>3</sub>/SbPh<sub>3</sub> (1:1:1) (13).** This compound has been prepared as **12** was, by using PPh<sub>3</sub> (0.262 g, 1 mmol) and SbPh<sub>3</sub> (0.353 g, 1 mmol). Yield 65%. Mp: 149 °C, dec.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 293 K):  $\delta$  10.0 br.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 218 K):  $\delta$  10.9 dd,  $^1\text{J}(\text{Ag}-^{31}\text{P})$  322 Hz,  $^1\text{J}(\text{Ag}-^{31}\text{P})$  279 Hz.  $\Lambda_{\text{mol}}$  ( $\text{CH}_2\text{Cl}_2$ , concentration =  $1.30 \times 10^{-3}$  M):  $0.3 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Anal. Calcd for  $\text{C}_{36}\text{H}_{30}\text{AgBrO}_3\text{Psb}$ : C, 50.80; H, 3.55. Found: C, 50.43; H, 3.63.

**AgBrO<sub>3</sub>/AsPh<sub>3</sub>/SbPh<sub>3</sub> (1:1:1) (14).** This compound has been prepared as for **12** by using AsPh<sub>3</sub> (0.306 g, 1 mmol) and SbPh<sub>3</sub> (0.353 g, 1 mmol). Yield 95%. Mp: 171 °C, dec.  $\Lambda_{\text{mol}}$  ( $\text{CH}_2\text{Cl}_2$ , concentration =  $1.22 \times 10^{-3}$  M):  $0.2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Anal. Calcd for  $\text{C}_{36}\text{H}_{30}\text{AgAsBrO}_3\text{Sb}$ : C, 48.31; H, 3.38. Found: C, 47.98; H, 3.21.

**Crystal Structure Determinations.** Full spheres of CCD area-detector diffractometer data were measured (Bruker AXS instrument,  $\omega$ -scans; monochromatic Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å;  $T$  ca. 153 K), yielding  $N_{\text{(total)}}$  reflections, these merging to  $N$  unique ( $R_{\text{int}}$  quoted) after “empirical”/multiscan absorption correction (proprietary software),  $N_o$  with  $F > 4\sigma(F)$  considered “observed” and used in the full-matrix least-squares refinements (non-hydrogen atom displacement parameter forms anisotropic;  $(x, y, z, U_{\text{iso}})_{\text{H}}$  included constrained). Conventional residuals  $R$ ,  $R_w$  (weights:  $(\sigma^2(F) + 0.0004F^2)^{-1}$ ) at convergence are cited. Neutral atom complex scattering factors were employed within the context of the Xtal 3.7 program system.<sup>13</sup> Pertinent results are presented in the following section and in Tables 1–7 and the figures, the latter depicting displacement envelopes with 50% probability amplitude, hydrogen atoms having arbitrary radii of 0.1 Å. Individual diversities in procedure (etc.) are described as follows.

**Compound 2.**  $(x, y, z, U_{\text{iso}})_{\text{H}}$  were refined.

**Compound 6.** A difference map residue was modeled in terms of a (water molecule) oxygen atom, site occupancy refining to 0.347(6).

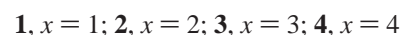
**Compound 7.** “Thermal motion” on the bromate oxygen atoms was high, and meaningful refinement could only be achieved refining the isotropic form, disorder not being resolvable. Difference map residues were modeled in terms of methanol C, O.

**Compound 11.** The bromate oxygen atoms were modeled with O(1) fully occupied and O(2)–O(4) (disordered) with occupancies  $2/3$ . The C and O of the ethanol were refined with isotropic displacement parameter forms.

**Compound 12.** Despite some inauspicious features (crystals exhibited some twinning and were opalescent rather than clear), the material diffracted well and was found to be isomorphous with **6** and refined with the same cell and coordinate settings. Refinement of P,As occupancies gave values not significantly different from 0.5 each at each of the two sites; resolution of individual P, As components was not possible, and the ligands were refined as nondisordered (in this respect) composites. Comparison of  $U_{\text{eq}}$  values with those of **6** showed, in general, close similarity between the values for the ligands with values for the central AgBrO<sub>3</sub> component exalted by ca. 50%. The “water molecule oxygen” residue also refined to a site occupancy 0.5. Attempts at refinement in lower symmetry were unrewarding.

## Results and Discussion

**Syntheses.** From the interaction of one equivalent of AgBrO<sub>3</sub> and one equivalent of PPh<sub>3</sub> in ethanol at 60 °C, adduct **1** was obtained in high yield (eq 1), compounds **2–4** being afforded when higher ligand-to-metal ratios were employed.



It is worthy of note that an excess of phosphine must be always employed, perhaps in consequence of the strong oxidizing power of the BrO<sub>3</sub><sup>−</sup> group; in some cases, Ph<sub>3</sub>P=O and [AgBr(PPh<sub>3</sub>)<sub>*x*</sub>] were obtained as byproduct.<sup>14–16</sup> The 1:2, 1:3, and 1:4 adducts **2**, **3**, and **4** in crystalline form slowly appeared also from the same reaction solution at different

(13) *The Xtal 3.7 System*; Hall, S. R., du Boulay, D. J., Olthoff-Hazekamp, R., Eds.; University of Western Australia: Australia, 2001.



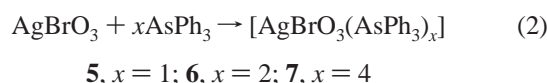
**Table 1.** Crystal/Refinement Data

	<b>1</b> AgBrO <sub>3</sub> /PPh <sub>3</sub> (1:1) <sub>4</sub>	<b>2</b> AgBrO <sub>3</sub> /PPh <sub>3</sub> (1:2)	<b>6</b> AgBrO <sub>3</sub> /AsPh <sub>3</sub> (1:2) <sub>2</sub> ·0.7H <sub>2</sub> O	<b>7</b> AgBrO <sub>3</sub> /AsPh <sub>3</sub> (1:4)·CH <sub>3</sub> OH	<b>11</b> AgBrO <sub>3</sub> /SbPh <sub>3</sub> (1:4)·EtOH	<b>12</b> AgBrO <sub>3</sub> /PPh <sub>3</sub> /AsPh <sub>3</sub> (1:1:1) <sub>2</sub> ·H <sub>2</sub> O
formula	C <sub>72</sub> H <sub>60</sub> Ag <sub>4</sub> Br <sub>4</sub> O <sub>12</sub> P <sub>4</sub>	C <sub>36</sub> H <sub>30</sub> AgBrO <sub>3</sub> P <sub>2</sub>	C <sub>72</sub> H <sub>60</sub> Ag <sub>2</sub> As <sub>4</sub> Br <sub>2</sub> - O <sub>6</sub> ·0.7H <sub>2</sub> O	C <sub>73</sub> H <sub>64</sub> AgAsBrO <sub>4</sub>	C <sub>74</sub> H <sub>66</sub> AgBrO <sub>4</sub> Sb <sub>4</sub>	C <sub>72</sub> H <sub>60</sub> Ag <sub>2</sub> As <sub>2</sub> Br <sub>2</sub> - O <sub>6</sub> P <sub>2</sub> ·H <sub>2</sub> O
M <sub>r</sub>	1992.2	760.4	1709.4	1492.8	1694.1	1926.6
cryst syst	triclinic	triclinic	triclinic	triclinic	monoclinic	triclinic
space group	P $\bar{1}$ (C <sub>1</sub> <sup>1</sup> , No. 2)	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	P <sub>2</sub> /c (C <sub>2</sub> <sup>5</sup> <sub>2h</sub> , No. 14)	P $\bar{1}$
a (Å)	8.850(2)	10.3399(6)	12.1898(5)	11.8708(9)	12.051(2)	12.2074(8)
b (Å)	14.086(3)	12.1874(7)	12.5186(5)	14.562(1)	23.289(4)	12.5651(8)
c (Å)	14.738(3)	13.7166(8)	13.3410(6)	18.613(1)	23.547(4)	13.3979(7)
α (deg)	81.066(4)	92.118(1)	67.135(1)	88.874(1)		66.689(1)
β (deg)	73.708(4)	90.725(1)	63.685(1)	87.088(2)	90.005(4)	63.036(1)
γ (deg)	86.966(4)	113.314(1)	65.875(1)	84.518(2)		65.126(1)
V (Å <sup>3</sup> )	1742	1586	1611	3198	6608	1608
D (g cm <sup>-3</sup> )	1.89 <sub>9</sub>	1.59 <sub>2</sub>	1.76 <sub>2</sub>	1.55 <sub>0</sub>	1.70 <sub>2</sub>	1.68 <sub>0</sub>
Z	1 tetramer	2	1 dimer	2	4	1 dimer
μ (mm <sup>-1</sup> )	3.6	2.0	3.9	3.0	2.6	3.0
specimen (mm)	0.45 × 0.25 × 0.08	0.50 × 0.40 × 0.14	0.30 × 0.25 × 0.18	0.30 × 0.25 × 0.20	0.20 × 0.14 × 0.12	0.32 × 0.17 × 0.13
"T" <sub>min</sub> /max	0.50	0.57	0.66	0.87	0.68	0.69
2θ <sub>max</sub> (deg)	58	75	75	58	58	69
N <sub>t</sub>	35023	32031	33292	65997	105980	33191
N (R <sub>int</sub> )	17654 (0.057)	16079 (0.031)	16569 (0.025)	16958 (0.058)	17551 (0.080)	13684 (0.032)
N <sub>o</sub>	13359	12775	11507	11149	12417	9413
R <sup>a</sup>	0.038	0.029	0.028	0.069	0.062	0.045
R <sub>w</sub> <sup>b</sup>	0.043	0.035	0.029	0.088	0.066	0.069

$${}^a R = \Sigma \Delta / \Sigma |F_o|, {}^b R_w = (\Sigma w \Delta^2 / \Sigma w F_o^2)^{1/2}.$$

times, whereas the 1:1 adduct was obtained only when equimolar quantities of AgBrO<sub>3</sub> and PPh<sub>3</sub> were employed.

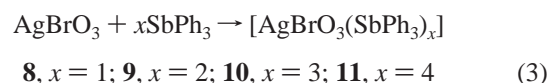
From the interaction of AgBrO<sub>3</sub> with AsPh<sub>3</sub> in ethanol at 60 °C, complexes **5–7** were, respectively, obtained (eq 2):



Oxidation of AsPh<sub>3</sub> to Ph<sub>3</sub>As=O was also observed when the reaction was carried out with Schlenk techniques, so that excess ligand is again often necessary to obtain the desired product.

We were not able to isolate the AgBrO<sub>3</sub>/AsPh<sub>3</sub> 1:3 adduct by using different solvents, or a different ligand-to-metal ratio. The 1:4 adduct **7** was obtained also when the reaction was conducted in the presence of an excess (>4 equiv) of the ancillary ligand.

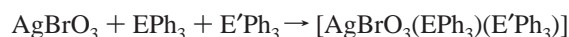
From the interaction of AgBrO<sub>3</sub> with SbPh<sub>3</sub> in ethanol at 60 °C, adducts **8–11** were obtained (eq 3):



The 1:1 adduct **8** was obtained also when 2 equiv of SbPh<sub>3</sub> was employed, whereas the 1:2 and 1:3 adducts, **9** and **10**, respectively, were obtained only when 3 and 4 equiv of SbPh<sub>3</sub> were, respectively, employed. The 1:4 adduct **11** was obtained when the reaction was conducted in the presence of an excess (>4 equiv) of the ancillary ligand. The low yields of the syntheses and, in a few instances, less than ideal

analyses, may also be consequent on the oxidation of EPh<sub>3</sub> by AgBrO<sub>3</sub>, as confirmed from the NMR data (see in a following paragraph).

Finally, from the interaction in acetonitrile of AgBrO<sub>3</sub> with equimolar quantities of PPh<sub>3</sub> and AsPh<sub>3</sub>, PPh<sub>3</sub> and SbPh<sub>3</sub>, and AsPh<sub>3</sub> and SbPh<sub>3</sub>, derivatives **12–14** were, respectively, obtained according to eq 4.



**12**, E = P, E' = As; **13**, E = P, E' = Sb;

**14**, E = As, E' = Sb (4)

All derivatives **1–14** show good solubility in chlorinated solvents, acetonitrile, acetone, and DMSO but are insoluble in diethyl ether, alcohols, and aromatic and aliphatic hydrocarbons. They are nonelectrolytes in CH<sub>2</sub>Cl<sub>2</sub> solution, the Λ<sub>m</sub> values being always less than 3.3 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. In the case of the 1:4 adducts **4**, **7**, and **11**, the lack of conductivity may be due to formation in solution of a solvated ionic pair or, perhaps alternatively, to dissociation of EPh<sub>3</sub> ligands from the silver with consequent reassociation of the counterion (see in a following paragraph).

**Structural Studies.** Low temperature single crystal X-ray structure determinations have confirmed the identities of compounds **1**, **2**, **7**, and **11** as adducts of silver(I) bromate diversely with EPh<sub>3</sub> (E = P, As, Sb). In two of these adducts (**7**, **11**), the cations (Table 2) are the familiar homoleptic [Ag(EPh<sub>3</sub>)<sub>4</sub>]<sup>+</sup> array with the bromate role simply that of counterion; in the other two (**1**, **2**), of diminished ligand stoichiometry, the bromate is found in the unfamiliar and hitherto structurally uncharacterized role of coordinating ligand, the complex having a familiar mononuclear form in **2** and a less familiar tetrameric form in **1**. The structures of [Ag(AsPh<sub>3</sub>)<sub>4</sub>](BrO<sub>3</sub>) (**7**) and [Ag(SbPh<sub>3</sub>)<sub>4</sub>](BrO<sub>3</sub>) (**11**) are

(14) Teo, B.-K.; Calabrese, J. C. *J. Chem. Soc., Chem. Commun.* **1976**, 185.

(15) Teo, B.-K.; Calabrese, J. C. *J. Am. Chem. Soc.* **1975**, 97, 1256.

(16) Bowmaker, G. A.; Effendy; Hanna, V. J.; Healy, P. C.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1993**, 1387.

**Table 2.** Selected  $[\text{Ag}(\text{EPh}_3)_4]^+$  Cation Geometries (**7**, **11**)<sup>a</sup>

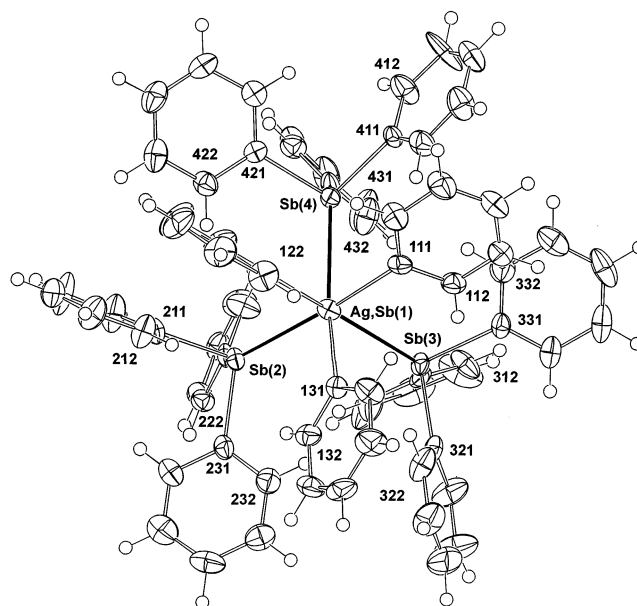
atoms	parameter	atoms	parameter
Distances (Å)			
Ag–E(1)	2.655(1), 2.7154(8)	Ag–E(3)	2.659(1), 2.7169(8)
Ag–E(2)	2.637(1), 2.7113(8)	Ag–E(4)	2.644(1), 2.7379(8)
Ag–E(n)	2.649(10), 2.720(12)		
Angles (deg)			
E(1)–Ag–E(2)	109.03(4), 112.57(3)	E(2)–Ag–E(3)	108.68(3), 106.84(3)
E(1)–Ag–E(3)	109.47(3), 110.88(3)	E(2)–Ag–E(4)	110.62(3), 108.70(3)
E(1)–Ag–E(4)	108.46(3), 107.34(3)	E(3)–Ag–E(4)	110.56(3), 110.51(3)
Ag–E(n)–C(nm1)–C(ortho) (Acute) Torsion Angles (deg) <sup>b</sup>			
11	–29.4(7), –60.0(7)	31	–30.1(8), –49.1(8)
12	–54.5(7), –1.1(8)	32	–32.8(8), –38.0(8)
13	–47.0(8), –40.5(7)	33	–43.9(9), –13.7(7)
21	–32.3(9), –55.3(7)	41	–52.9(8), –25.4(8)
22	–51.6(8), –35.4(7)	42	–24.7(8), –23.3(7)
23	–40.7(8), –16.1(8)	43	–28.8(8), –46.3(8)

<sup>a</sup> The two values in each entry are for E = As, Sb, respectively. <sup>b</sup> nm listed under “atoms”.

both modeled as alcohol monosolvates (methanol, **7**; ethanol, **11**); despite the not infrequent approach of the cation symmetry to its maximum/potential 32, here one formula unit, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure in each case. The two complexes are not isomorphous. However, a survey of the forms adopted by  $[\text{M}(\text{EPh}_3)_4]$  (oxyanion) (M = univalent coinage metal) arrays as recorded recently<sup>17</sup> shows the E = Sb complex, **11**, to be isomorphous with its copper(I) perchlorate counterpart, obtained as a chloroform monosolvate; the latter structure was modeled as fully ordered, albeit with high anion and solvent displacement parameters, using the cell and coordinate setting of ref 17. The present complex **11** has also been recorded as a tetrafluoroborate dichloromethane monosolvate, isomorphous with these.<sup>18</sup> Reference 17 also describes the structure determination of  $[\text{Ag}(\text{AsPh}_3)_4](\text{NO}_3) \cdot 4\text{EtOH}$  in a monoclinic  $C2/c$  lattice; the present **7** is not isomorphous with it and is seemingly of a new lattice type for  $[\text{M}(\text{EPh}_3)_4](\text{oxyanion})$ . Previously described structural characterizations of  $[\text{Ag}(\text{EPh}_3)_4](\text{oxyanion})$  (E = As, Sb) arrays have been less precisely definitive of these  $\text{AgE}_4$  environments than desirable, as defined in their unsolvated forms which crystallize in the widespread rhombohedral  $R\bar{3}$  lattice with unusual cation disorder; the  $[\text{Ag}(\text{AsPh}_3)_4](\text{NO}_3) \cdot 4\text{EtOH}$  structure does not suffer from this disadvantage, the cation being fully ordered. In the  $R\bar{3}c$  structures, each cation is disposed on a crystallographic 3-axis which passes through the M–E vector of one ligand, relating the other three, so that the cation symmetry is 3; in  $[\text{Ag}(\text{AsPh}_3)_4](\text{NO}_3) \cdot 4\text{EtOH}$ , the cation symmetry is (crystallographic) 2, the two independent Ag–As distances being equal (2.649–(2), 2.650(2) Å), and the As–Ag–As angles ranged between 108.22(4)° and 111.41(6)°. In the present, **7**, the spread of angles is more compact (108.68(3)–110.62(3)°), but the Ag–E(a) distance range is slightly more diverse (2.637(1)–2.659–(1) Å), although the mean (2.649(10) Å) is unchanged, despite the cation symmetry being quasi-3. In **11**, ranges of both distances and angles are more diverse, and more diverse

(17) Bowmaker, G. A.; Effendy, Hart, R. D.; Kildea, J. D.; de Silva, E. N.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1997**, *50*, 539.

(18) Hill, A. M.; Levason, W.; Webster, M. *Inorg. Chem.* **1996**, *35*, 3428.

**Figure 1.**  $[\text{Ag}(\text{SbPh}_3)_4]^+$  cation of **11**, showing its quasi-32 symmetry.**Table 3.** Selected  $[(\text{Ph}_3\text{P})_2\text{Ag}(\text{O}_2\text{BrO})]$  Geometries (**2**)

atoms	parameter	atoms	parameter
Distances (Å)			
Ag–P(1)	2.4177(5)	Ag–O(1)	2.473(1)
Ag–P(2)	2.4339(4)	Ag–O(2)	2.550(1)
Br–O(1)	1.663(1)	Br–O(3)	1.633(1)
Br–O(2)	1.658(1)		
Angles (deg)			
P(1)–Ag–P(2)	134.80(1)	P(2)–Ag–O(1)	112.93(3)
P(1)–Ag–O(1)	110.97(3)	P(2)–Ag–O(2)	97.15(3)
P(1)–Ag–O(2)	112.67(4)	O(1)–Ag–O(2)	61.80(3)
Ag–O(1)–Br	99.35(5)	O(3)–Br–O(1)	106.22(8)
Ag–O(2)–Br	96.58(5)	O(3)–Br–O(2)	105.94(8)
O(1)–Br–O(2)	101.98(5)		
Ag–P(n)–C(nm1)–C(ortho) (Acute) Torsion Angles (deg)			
11	–25.6(1)	21	24.3(2)
12	30.6(1)	22	28.2(1)
13	–83.9(2)	23	47.4(2)

than found in the same cation in ref 18 (Ag–Sb 2.7200–(6)–2.7297(6) Å,  $\langle \rangle$  2.725(4) Å; Sb–Ag–Sb, 108.34(2)–110.95(2)°, these values and the present ( $\langle \text{Ag–Sb} \rangle$  2.72 (1) Å) providing the first descriptions of undisordered  $[\text{Ag}(\text{SbPh}_3)_4]^+$  cations (Figure 1), albeit with disorder further afield in the lattice. In both **7** and **11**, the anion definition is influenced by disorder/high displacement parameters and of little interest.

While numerous adducts of the form  $[(\text{Ph}_3\text{P})_2\text{AgX}]$  have been structurally defined, examples for X = oxyanion, uni- or bidentate (or between), are more restricted; the present example is of particular interest in establishing the coordination mode of the bromate to be quasisymmetrical bidentate (Table 3, Figure 2). As discussed, this quasisymmetry is corroborated by the <sup>31</sup>P CPMAS NMR spectrum of  $[(\text{Ph}_3\text{P})_2\text{AgBrO}_3]$  (**2**) (see in a following paragraph), which exhibits very strong AB-type <sup>2</sup>J(<sup>31</sup>P–<sup>31</sup>P) coupling between the multiplets associated with each P site. Table 4 compares the present  $\text{AgO}_2\text{X}$  geometries in this array with counterpart  $\text{P}_2\text{–AgO}_2$  parameters in related  $[(\text{Ph}_3\text{P})_2\text{Ag}(\text{O}_2\text{X})]$  species, for simple oxyanions. There are strong suggestions that anion-

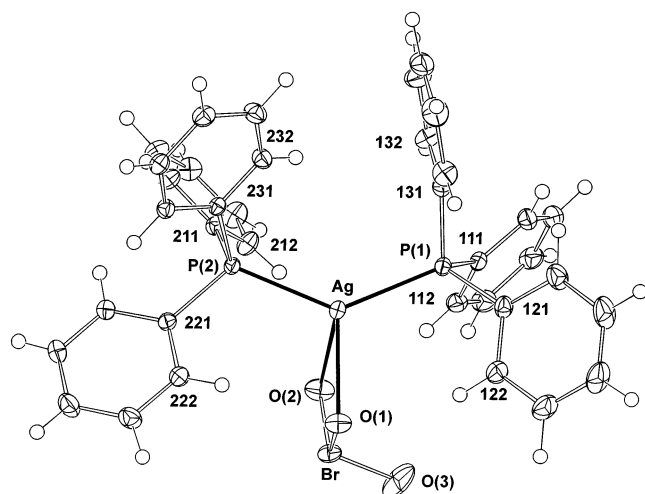


Figure 2. Single molecule of  $[(Ph_3P)_2Ag(O_2BrO)]$  (2).

Table 4. Comparative  $[(Ph_3P)_2Ag\{O_2X(Y)\}]$  Core Geometries

$O_2X(Y)$	Ag—P (Å)	Ag—O (Å)	P—Ag—P (°)	O—Ag—O (°)	O—Ag—P (°)
$O_2BrO^a$	2.4177(5) 2.4339(4)	2.473(1) 2.550(1)	134.80(1)	61.80(3)	97.15(3) −112.93(4)
$O_2N^b$	2.4372(7) 2.4421(7)	2.433(2) 2.440(2)	129.26(3)	50.55(10)	110.67(6) −115.23(6)
$O_2N^c$	2.412(1)	2.386(3)	128.67(4)	51.25(10)	102.06(8)
( $\cdot CH_2Cl_2$ )	2.440(1)	2.481(3)			−120.81(8)
$O_2NO^d$	2.440(1) 2.443(1)	2.464(4) 2.649(4)	138.21(5)	49.86(11)	100.24(7) −111.81(7)
$O_2NO^e$	2.416(1) 2.435(1)	2.463(3) 2.572(2)	139.4(1)	50.4(1)	96.7(1) −114.9(1)
( $\cdot C_6H_6$ )	2.4264(8)	2.379(2)	124.13(3)	52.3(1)	106.03(7)
$O_2CCH_3^f$	−2.4608(8)	−2.510(3)	129.62(3)	53.3(1)	−125.61(8)
$O_2CCH_3^g$	2.404(1)	2.395(3)	128.53(5)	52.5(1)	104.8(1)
(1.5H <sub>2</sub> O; 2 mol)	−2.441(1)	−2.492(4)	129.44(5)	53.7(1)	−119.9(1)
$O_2CCF_3^h$	2.423(1) 2.445(1)	2.526(3) 2.543(3)	142.18(4)	51.6(1)	97.13(9) −112.41(9)

<sup>a</sup> This work. <sup>b</sup> Hanna, J. V.; Ng, S. W. *Acta Crystallogr., Sect. C* **1999**, 55, 9900029. <sup>c</sup> Belaj, F.; Trnoska, A.; Nachbaur, E. *Acta Crystallogr., Sect. C* **1998**, 54, 727. <sup>d</sup> Reference 21 (see text). <sup>e</sup> Harker, C. S. W.; Tiekink, E. R. T. *Acta Crystallogr., Sect. C* **1989**, 45, 1815. <sup>f</sup> Ng, S. W.; Othman, A. H. *Acta Crystallogr., Sect. C* **1997**, 53, 1396. The anhydrous phase was previously recorded by: Femi-Onadenko, B. Z. *Kristallogr.* **1980**, 152, 159. The hydrate was recorded as an isomorphous water/ethanol solvate in: Hanna, J. V.; Ng, S. W. *Acta Crystallogr., Sect. C* **1999**, 55, 9900031. The structure of the formate has been determined also but is of uncertain value; see: Lan-Sun, Z.; Hua-Hui, Y.; Qian-Er, Z. *Jiegou Huaxue* **1991**, 10, 97. Hu, S.-Z. *Jiegou Huaxue* **2000**, 19, 234. Marsh, R. E. *Acta Crystallogr., Sect. B* **1997**, 53, 317 (CCD KIXCAV; KIXCAV01). <sup>g</sup> Ng, S. W. *Acta Crystallogr., Sect. C* **1998**, 54, 743.

related parameters affect the system. For those complexes where alternative crystal forms are available, mean distances and angular parameters generally correlate well, albeit in some instances with considerable scatter, lending confidence to the observation that, for related base pairs ( $O_2N$  cf.  $O_2NO$ ;  $O_2CCH_3$  cf.  $O_2CCF_3$ ), the P—Ag—P angle correlates with base strength within each pair and perhaps even between them, with Ag—O longer for the weaker base anions; remarkably, Ag—P remains little changed. How the bromate donor should be compared with these at this stage is unclear since it is the only example where the central anion atom is other than a first row atom; concomitantly, the anion chelate has a considerably enlarged “bite” angle, although Ag—O lies within the range of the others. Further data is awaited.

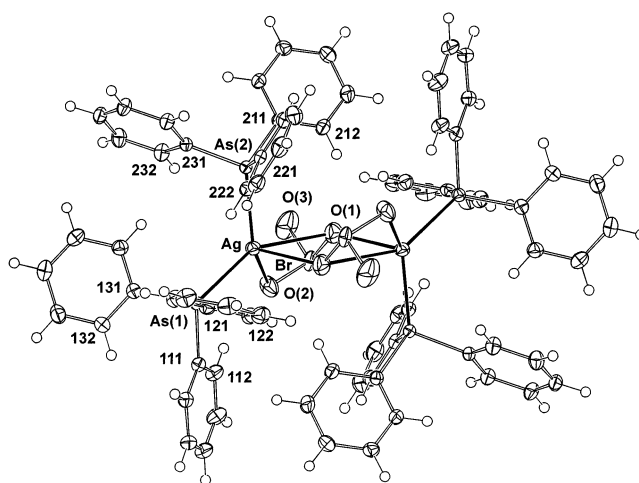


Figure 3. Centrosymmetric dimer of  $AgBrO_3/AsPh_3$  (1:2) (6).

Ligand 1 here is unusual in adopting the less common conformation with internal (quasi) *m* symmetry (Table 3); the possibility that this might be consequent upon interaction with O(3) was considered and rejected since the nearest contacts to O(3) are intermolecular in origin.

It is of interest to note in the present context that  $MX/PPH_3$  (1:2) adducts for  $M = Cu$  are mononuclear, except for anions such as  $N_3$  and  $NCS$ , which, as ambidentates, may bridge the two metal atoms to form eight- rather than four-membered central rings in the dimer form. Binuclear forms with four-membered central rings are found with copper(I) complexes of the present type, but of 2:3 stoichiometry,  $[(Ph_3P)_2Cu(\mu-X)_2Cu(PPH_3)]$ , suggesting that steric interactions may inhibit formation of binuclear 1:2 complexes having four-membered ring cores, an impression reinforced by the observation that, for  $M = Ag$ , both forms may be obtained.<sup>19</sup> Nevertheless, here also it is of interest to note that the  $P_2Ag(\mu-X)_2AgP_2$  form, where  $X$  is a single atom, is only represented for  $X = O$  by a single example, the unsolvated nitrate,<sup>20</sup> which exhibits a symmetrical bridge in one form, and in another a more loosely held species<sup>21</sup> (so much so as to be presented in Table 4 as a “monomer”); the benzene solvate (Table 4) is unambiguously mononuclear.

For  $EPh_3$ ,  $E = As, Sb$ , no monomers are described for simple  $AgX/EPh_3$  (1:2) systems, the binuclear form with the  $E_2Ag(\mu-X)_2AgE_2$  four-membered ring core dominant. Such is also the case here; the only oxyanion adducts thus far described are for nitrate (see preceding description) and nitrite<sup>4</sup> which adopt a form very similar to that found in the present bromate (Figure 3), wherein one oxygen atom of the anion bridges the two metal atoms, a second semichelating (Table 5). Parameters associated with the metal/anion dimer core, centrosymmetric in all cases (one-half of the dimer comprising the asymmetric unit of the structure), are presented comparatively in Table 6. Some curious features

(19) For example, Table 3 of the following: Bowmaker, G. A.; Effendy; de Silva, E. N.; White, A. H. *Aust. J. Chem.* **1997**, 50, 641.

(20) Jones, P. G. *Acta Crystallogr., Sect. C* **1993**, 49, 1148.

(21) Barron, P. F.; Dyason, J. C.; Healy, P. C.; Engelhardt, L. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1986**, 1965. See also: Zheng, L.; Yang, W.; Yang, H. *Xiamen Daxue Xuebao, Ziran Kexueban* **1988**, 27, 437. (CCDC DUSZOG01.)

**Table 5.** Selected Core Geometries [(Ph<sub>3</sub>As)<sub>2</sub>Ag(O<sub>2</sub>BrO)]<sub>2</sub>, (**6**, (**12**))<sup>a</sup>

atoms	parameter	atoms	parameter
Distances (Å)			
Ag–As(1)	2.5960(2) (2.5341(4))	Ag–O(1)	2.600(2) (2.651(5))
Ag–As(2)	2.5356(2) (2.4530(5))	Ag–O(1')	2.934(1) (3.112(3))
Br–O(1)	1.649(2) (1.646(5))	Ag–O(2')	2.355(2) (2.333(4))
Br–O(2)	1.660(1) (1.637(3))	Ag⋯Ag'	4.5338(2) (4.8504(5))
Br–O(3)	1.632(2) (1.609(6))	As–C (range)	1.940(1)–1.949(2) (1.893(4)–1.904(4))
Angles (deg)			
As(1)–Ag–As(2)	118.99(1) (122.65(2))	O(1)–Ag–O(1')	70.13(6) (65.6(1))
As(1)–Ag–O(1)	100.56(3) (100.84(7))	O(1)–Ag–O(2')	102.11(6) (98.9(1))
As(1)–Ag–O(1')	149.08(3) (145.16(5))	O(1')–Ag–O(2')	57.05(6) (54.6(1))
As(1)–Ag–O(2')	98.69(4) (99.73(7))	O(1)–Br–O(2)	102.27(9) (104.3(2))
As(2)–Ag–O(1)	98.85(3) (96.53(7))	O(1)–Br–O(3)	106.9(1) (107.2(3))
As(2)–Ag–O(1')	91.83(3) (91.55(5))	O(2)–Br–O(3)	106.12(9) (105.5(2))
As(2)–Ag–O(2')	132.18(3) (130.83(7))	Br–O(1)–Ag	131.55(7) (135.2(2))
Br–O(2)–Ag'	108.99(9) (112.9(2))	Br–O(1)–Ag'	87.15(7) (82.7(1))
Ag–As(1)–C(111)	117.50(4) (117.99(8))	Ag–O(1)–Ag'	109.87(7) (114.4(1))
Ag–As(1)–C(121)	108.83(5) (109.15(9))	Ag–As(2)–C(211)	124.35(5) (125.11(9))
Ag–As(1)–C(131)	120.99(4) (119.92(8))	Ag–As(2)–C(221)	108.92(4) (109.92(8))
C(111)–As(1)–C(121)	102.99(8) (102.8(2))	Ag–As(2)–C(231)	115.19(5) (112.98(9))
C(111)–As(1)–C(131)	102.29(5) (102.8(2))	C(211)–As(2)–C(221)	102.54(9) (102.4(2))
C(121)–As(1)–C(131)	101.84(8) (101.9(2))	C(211)–As(2)–C(231)	101.58(7) (102.0(1))
		C(221)–As(2)–C(231)	101.34(8) (101.6(1))
Ag–As( <i>n</i> )–C( <i>nm</i> 1)–C(ortho) Torsion Angles (Acute) (deg) (Denoted by <i>nm</i> )			
11	–28.2(2) (–29.0(4))	21	–42.4(2) (–45.8(4))
12	–50.2(1) (–51.9(2))	22	–37.9(1) (–34.7(2))
13	–31.7(2) (–32.0(4))	23	–52.6(1) (–53.6(2))

<sup>a</sup> Primed atoms are related by the intradimer inversion center. As(1,2) lie 1.300(2), –2.505(1) Å (1.385(3), –2.437(1) Å) out of the Ag<sub>2</sub>O<sub>2</sub> (centrosymmetric) core plane.

**Table 6.** Comparative Core Geometries for Binuclear AgO<sub>2</sub>X(Y)/AsPh<sub>3</sub>(1:2)

O <sub>2</sub> X(Y)	O <sub>2</sub> N <sup>a</sup>	O <sub>2</sub> NO <sup>b</sup>	O <sub>2</sub> BrO <sup>c</sup>
Distances (Å)			
Ag–As	2.5237(2)	2.521(3)	2.5356(2)
	2.5354(3)	2.535(5)	2.5960(2)
Ag–O(1)	2.619(1)	2.737(6)	2.600(2)
Ag–O(1')	2.373(2)	2.409(6)	2.934(1)
Ag–O(2')	2.610(2)	2.684(7)	2.355(2)
Angles (deg)			
As–Ag–As	127.17(1)	134.2(1)	118.991(1)
As–Ag–O(1)	119.23(3)	104.7(3)	98.85(3)
	92.78(4)	102.9(2)	100.56(3)
As–Ag–O(1')	110.02(3)	110.1(3)	91.83(3)
	121.17(3)	96.6(3)	149.08(3)
As–Ag–O(2')	99.49(3)	96.6(3)	132.18(3)
	103.76(4)	113.7(3)	98.69(4)
O(1')–Ag–O(2')	49.23(6)	49.5(2)	57.05(6)
Ag–O(1')–Ag'	112.28(6)	111.3(2)	109.87(7)
O <sub>2</sub> X Plane Parameters			
O <sub>2</sub> X/Ag <sub>2</sub> O <sub>2</sub> dihedral (deg)	31.2(2)	54.5(3)	47.92(7)
ΔAg/O <sub>2</sub> X (Å)	1.076(6)	0.31(1)	1.928(4)
ΔAg'/O <sub>2</sub> X (Å)	–0.11(1)	–0.07(1)	–0.831(4)

<sup>a</sup> Reference 4. <sup>b</sup> Reference 2. <sup>c</sup> This work (**6**).

are found; as in the previous (Ph<sub>3</sub>P)Ag(O<sub>2</sub>X) arrays, the Ag–E distances vary little between the various complexes, while the E–Ag–E angle changes quite markedly. In the present E = As examples, however, whereas P–Ag–P for the bromate lies between the values for nitrate and nitrite in the mononuclear complexes, here for E = As, the bromate value lies outside the range spanned by nitrate and nitrite. Of further interest are the Ag–O distances. For the nitrite/nitrate pair, the shortest Ag–O distance is one of the bridging distances: in the nitrite, the one associated with the chelate,

in the nitrate not, but in the bromate the shortest distance is the chelating distance, the two bridging distances being longer, and the longer of those is that which is associated with the chelate.

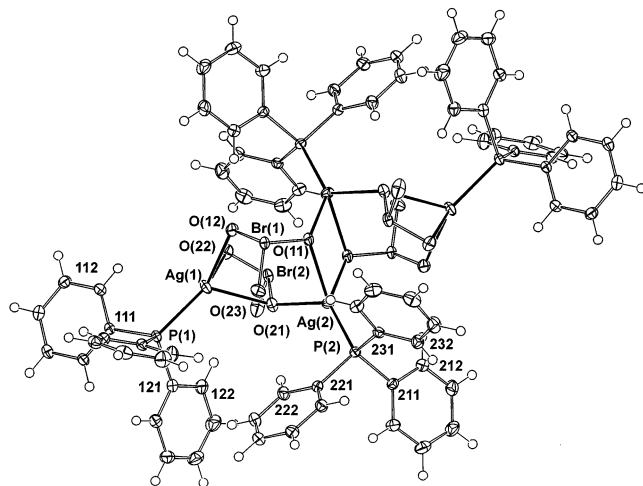
The present adduct of AgBrO<sub>3</sub>/EPh<sub>3</sub> (1:2) stoichiometry is the binuclear E = As adduct, **6** (Figure 3). The central core is relatively well-known for adducts of the more strongly basic anions, of which the carboxylates are probably the most familiar examples, two oxygen atoms chelating one metal atom unsymmetrically, with one oxygen bridging to the other metal; not infrequently, as here, the four membered Ag(μ-O)<sub>2</sub>Ag ring is centrosymmetric. For each metal atom to be associated with two unidentate E donors is less usual, particularly for X = oxyanion; the occurrence of [(Ph<sub>3</sub>E)<sub>2</sub>-Cu(μ-X)<sub>2</sub>Cu(EPh<sub>3</sub>)<sub>2</sub>] for E = As, Sb, where only [(Ph<sub>3</sub>E)-Cu(μ-X)<sub>2</sub>(EPh<sub>3</sub>)<sub>2</sub>] is found for E = P, is believed to be consequent upon the steric crowding inherent in the latter, and that may be a contributing factor toward the current observation that AgBrO<sub>3</sub>/EPh<sub>3</sub> (1:2) is mononuclear for E = P but binuclear for E = (the larger) As. Nevertheless, it is of interest to observe that **6** may be crystallized from solutions containing 1:1 molar ratios of PPh<sub>3</sub>/AsPh<sub>3</sub> ligands to yield material of similar (not significantly different) stoichiometry, **12**, with PPh<sub>3</sub> replacing AsPh<sub>3</sub> in an isomorphous array and with no significant discrimination detected between the two pnictogen sites, which, although generally similar in nature, differ significantly in detail with As(1) lying much closer to the Ag<sub>2</sub>O<sub>2</sub> centrosymmetric core plane than As(2); curiously, Ag–As(1) is longer than Ag–As(2). These distances, as expected, are shorter with the admixture of the phosphorus donor component, with the angle between correspondingly enlarged. The distances to the bridging



**Table 7.** Selected  $Ph_3P/AgBrO_3$  (1:1)<sub>4</sub> Geometries, (1)

atoms	parameter	atoms	parameter
Distances (Å)			
Ag(1)–P(1)	2.3704(7) (2.376(3))	Ag(2)–P(2)	2.3479(8) (2.354(3))
Ag(1)–O(12)	2.350(2) (2.241(8))	Ag(2)–O(11)	2.442(2) (2.320(7))
Ag(1)–O(21)	2.546(2) (3.088(2))	Ag(2)–O(21)	2.392(2) (2.23(1))
Ag(1)–O(22)	2.462(2) (2.26(1))	Ag(2)–O(11')	2.323(2) (2.475(7))
Br(1)–O(11)	1.678(2) (1.24(1))	Br(2)–O(21)	1.683(2) (1.23(2))
Br(1)–O(12)	1.655(2) (1.26(1))	Br(2)–O(22)	1.656(2) (1.23(2))
Br(1)–O(13)	1.637(2) (1.50(2))	Br(2)–O(23)	1.639(2) (1.50(2))
O(11)···O(11')	2.930(2) (3.048(2))	Ag(2)···Ag(2')	3.7601(7) (3.705(2))
Ag(1)···Ag(2)	4.2070(8) (3.122(1))		
Angles (deg)			
P(1)–Ag(1)–O(12)	141.30(5) (128.7(2))	P(2)–Ag(2)–O(11)	119.83(5) (129.2(2))
P(1)–Ag(1)–O(21)	120.53(4) (124.3(2))	P(2)–Ag(2)–O(21)	130.14(4) (127.7(3))
P(1)–Ag(1)–O(22)	130.59(5) (128.6(2))	P(2)–Ag(2)–O(11')	141.06(5) (109.4(2))
O(12)–Ag(1)–O(21)	92.11(6) (103.4(3))	O(11)–Ag(2)–O(21)	92.24(6) (99.8(4))
O(12)–Ag(1)–O(22)	81.42(6) (97.9(3))	O(11)–Ag(2)–O(11')	75.84(6) (78.9(2))
O(21)–Ag(1)–O(22)	61.75(7) (43.8(3))	O(21)–Ag(2)–O(11')	79.64(6) (95.5(3))
O(11)–Br(1)–O(12)	104.41(9) (122(1))	O(21)–Br(2)–O(22)	100.69(10) (122(1))
O(11)–Br(1)–O(13)	103.09(9) (120(1))	O(21)–Br(2)–O(23)	104.28(11) (119(1))
O(12)–Br(1)–O(13)	105.15(10) (117(1))	O(22)–Br(2)–O(23)	106.50(11) (120(1))
Ag(1)–O(12)–Br(1)	108.37(8) (127.2(7))	Ag(1)–O(22)–Br(2)	100.49(10) (118.3(9))
Ag(2)–O(11)–Br(1)	111.58(7) (126.7(7))	Ag(1)–O(21)–Ag(2)	116.80(8) (130(1))
Ag(2)–O(11)–Ag(2')	104.16(7) (101.1(3))	Ag(1)–O(21)–Br(2)	96.54(8) (76.3(9))
Br(1)–O(11)–Ag(2')	127.04(10) (131.8(7))	Ag(2)–O(21)–Br(2)	122.82(8) (130(1))

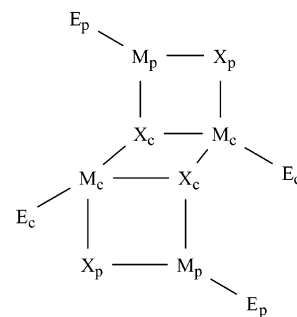
<sup>a</sup> Primed atoms are related by the intratetramer inversion center; counterpart values for the acetate are given in parentheses (Br, O(13) ≡ C). Ag–P(*n*)–C(*nm*1)–C(ortho) (acute) torsion angles for rings 11–13, 21–23, respectively, are  $-23.6(2)$ ,  $-25.0(3)$ ,  $-56.1(2)$ ,  $44.5(2)$ ,  $29.6(2)$ , and  $51.7(2)^\circ$  for the present compound.

**Figure 4.** Centrosymmetric tetramer of  $AgBrO_3/PPH_3$  (1:1) (1).

oxygen are lengthened (as in  $Ag\cdots Ag'$ ), precursive of dissociation to the monomer.

$AgX/EPh_3$  (1:1) ( $X = \text{oxyanion}$ ) complexes are not infrequently polymeric, or binuclear with  $Ag/O$  cores similar to that of 1:2 adduct **6**. The present  $AgBrO_3/PPH_3$  (1:1) complex (**1**) is, unusually, a (centrosymmetric) tetramer (Figure 4; Table 7). This structure may perhaps most usefully be viewed as an oxyanion precursor/analogue of the familiar “step” tetramer frequently observed (as an alternative to the “cubane” form) in  $MX/PPH_3$  (1:1)<sub>4</sub> adducts,  $M = Cu, Ag$ ;  $X = Cl, Br, I$ .

Here, the central silver atoms ( $M_c$ ) are  $Ag(2)$  and the central  $X$  atoms  $O(11)$  ( $=X_c$ ) while the peripheral  $M_p$  are  $Ag(1)$  and the  $X_p$  atoms are  $O(21)$ . In the  $M_4X_4L_4$  “step” structures, the peripheral  $M_p$  are normally trigonal planar although occasionally augmentation of the coordination



number may be found as in  $M_4X_4L_6$ .<sup>22</sup> Such is the case here, where the peripheral  $M_p$  become four-coordinate not by the addition of extra ligands but by chelation of  $O(22)$  as a “fellow traveller” of  $O(21)$ . A further perversion of the peripheral rhomb occurs by the expansion of the  $X_c-M_p$  strut by insertion of  $O(12)$ , so that the ring is six- rather than four-membered. A similar array is found in  $AgX/PPH_3$  (1:1)<sub>4</sub>,  $X = ac = CH_3CO_2$ ,<sup>23</sup> despite the considerable differences in ligand geometry and type, although, as might be expected, there are substantial differences in detail (Table 7). In the acetate,  $O(21)\cdots Ag(1)$  in particular is much longer than in the present, so that the anion behaves more as a second  $AgOCOAg$  strut, with  $Ag(1)\cdots Ag(2)$  correspondingly lengthened.

**Spectroscopy.** The infrared spectra of derivatives **1–14** (Supporting Information) are consistent with the formulations proposed, showing all of the bands required by the presence of the bromate group and of the ancillary donor,<sup>24,25</sup> the phosphine, arsine, or stibine ligand absorptions being only

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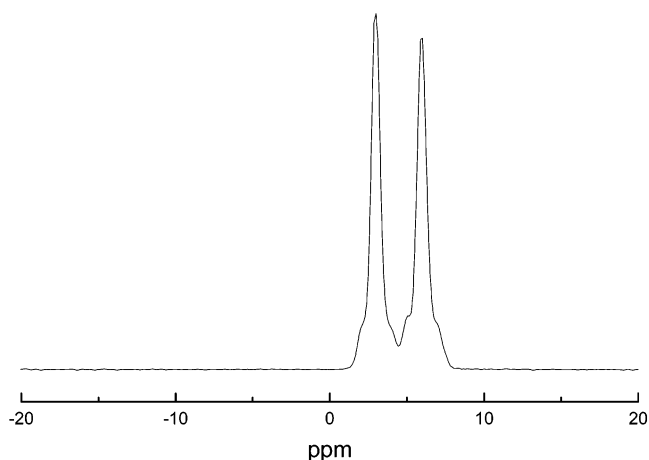
(23) Blues, E. T.; Drew, M. G. B.; Femi-Onadenko, B. *Acta Crystallogr., Sect. B* **1977**, *33*, 3965.



slightly shifted with respect to those of the free donors. In the far-IR spectra of derivatives **1–4**, we have assigned, on the basis of previous reports on phosphino copper(I) and silver(I) derivatives,<sup>4,5</sup> the broad absorptions near  $500\text{ cm}^{-1}$  and those at  $400\text{--}450\text{ cm}^{-1}$  to Whiffen's  $\gamma$  and  $t$  vibrations, respectively, whereas some bands in the region  $250\text{--}400\text{ cm}^{-1}$ , in the spectra of derivatives **1–3**, **5**, **6**, **8–10**, similar to those described in the literature for some silver(I) nitrito<sup>4</sup> and nitrate derivatives,<sup>5</sup> can be tentatively assigned to  $\nu(\text{Ag}=\text{O})$  vibrations. The ionic nature of the bromate group in derivatives **4**, **7**, and **11** is confirmed from the presence of strong absorptions at ca.  $800$ ,  $780$ ,  $740$ ,  $720$ ,  $410$ , and  $340\text{ cm}^{-1}$ , analogous to that reported in the literature for ionic  $\text{XY}_3$  groups, such as  $\text{BrO}_3$ .<sup>26</sup>

In the  $^1\text{H}$  NMR spectra of **1–14** in  $\text{CDCl}_3$  (Supporting Information), the signals due to the triorgano phosphines, arsines, and stibines lie in the ranges  $7.20\text{--}7.70$ ,  $7.15\text{--}7.80$ , and  $7.18\text{--}7.46\text{ ppm}$ , respectively, showing patterns of signals different from those found for the free donors, confirming the existence, at least partially, of the complexes in solution.

$^{31}\text{P}$  chemical shifts ( $\text{CDCl}_3$  solution) for derivatives **1–4** are reported in the Experimental Section. They have been found to be concentration-dependent (our experiments have been carried out at a concentration of ca.  $0.02\text{ mol/L}$ ). The  $^{31}\text{P}$  NMR spectrum in  $\text{CDCl}_3$  at room temperature of complex **1** consists of a signal at ca.  $29.0\text{ ppm}$  due to the formation of  $\text{Ph}_3\text{P}=\text{O}$  and of a broad singlet having the same intensity at ca.  $6.1\text{ ppm}$ , presumably due to rapid exchange equilibrium, resolvable only at low temperature.<sup>27,28</sup> In fact, at  $213\text{ K}$ , exchange is quenched, and one resolved pair of doublets, arising from coupling between the phosphorus and silver atom, is observed, with the  $^1J(^{31}\text{P}\text{--}^{107}\text{Ag})$  and  $^1J(^{31}\text{P}\text{--}^{109}\text{Ag})$  couplings, being, respectively,  $560$  and  $645\text{ Hz}$ , typical of an  $\text{AgP}$  core.<sup>29</sup> In the case of derivatives **2**, **3**, and **4**, broad singlets were observed also at low temperature, in some cases together with the same pairs of doublets found in the spectrum of **1**. The broad signal attributable to the complex is downfield with respect to that of the free ligand  $\text{PPh}_3$ . The magnitudes of  $\Delta$  ( $\Delta = \delta^{31}\text{P}_{\text{complex}} - \delta^{31}\text{P}_{\text{free ligand}}$ ), different from the values previously found for nitrito<sup>4</sup> and nitrate<sup>5</sup> compounds, are not dependent on the number of  $\text{PPh}_3$  moieties originally coordinated to silver, suggesting extensive oxidation of  $\text{PPh}_3$  and consequent breaking of the  $\text{Ag}\text{--}\text{P}$  bond in solution, with the formation of a unique stable species, presumably that containing only a P-donor. The spectra of derivatives **1–4** in  $\text{CD}_3\text{CN}$  solution (Supporting



**Figure 5.**  $^{31}\text{P}$  CPMAS NMR spectrum of  $[(\text{Ph}_3\text{P})_2\text{Ag}(\text{O}_2\text{BrO})]$  (**2**) acquired at a field strength of  $9.4\text{ T}$ .

Information) exhibit different patterns, the most intense signals being those due to free  $\text{Ph}_3\text{P}=\text{O}$  and  $\text{PPh}_3$ . However, a peak of very weak intensity at ca.  $6.0\text{ ppm}$ , due to a species having an  $\text{Ag}\text{--}\text{P}$  core, was generally found in all spectra, suggesting that the only stable complex existent in  $\text{CD}_3\text{CN}$  solution is that derived from **1** or at least that containing only one coordinated  $\text{PPh}_3$ .

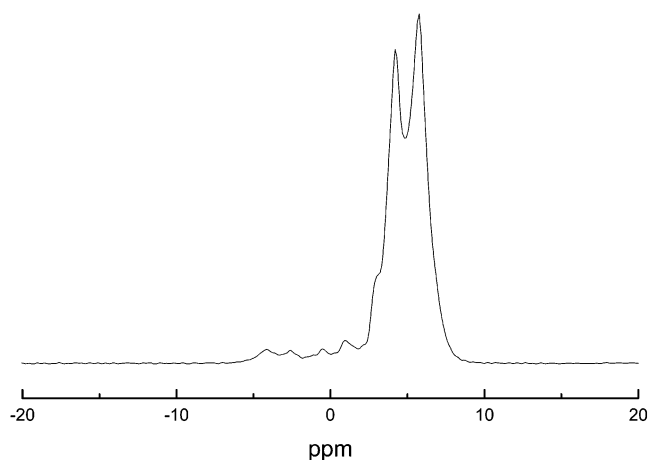
The extensive oxidation of  $\text{PPh}_3$  to  $\text{PPh}_3=\text{O}$  in **1–4** occurs not only in solution (in fact in more than one case we have recovered from the deuterated solution small crystals identified by analysis as  $[(\text{PPh}_3)_4\text{Ag}_4\text{Br}_4]^{15}$ ) but also in the solid state. In fact, when **2** was left in the air for more than  $24\text{ h}$ , its IR spectrum exhibited some peaks previously assigned to  $\text{Ag}\text{--}\text{Br}$  stretching vibrations.<sup>30</sup> Also, the solid state  $^{31}\text{P}$  CPMAS NMR spectra of **1–4**, recorded some weeks after their synthesis, exhibit some broad multiplets assigned to formation of adducts of  $\text{PPh}_3$  with  $\text{AgBr}$ .

The  $^{31}\text{P}$  NMR spectrum of derivative **12** exhibits a broad absorption at room temperature at ca.  $10.8\text{ ppm}$ ; at low temperature, two doublets were found,  $^1J(^{31}\text{P}\text{--}\text{Ag})$  being  $633$  and  $444\text{ Hz}$ , typical of  $\text{AgP}$  and  $\text{AgP}_2$  cores, respectively,<sup>29</sup> in accordance with the existence in solution of both  $[\text{Ag}(\text{AsPh}_3)_n(\text{PPh}_3)\text{BrO}_3]$  ( $n = 0$  or  $1$ ) and  $[\text{Ag}(\text{PPh}_3)_2\text{BrO}_3]$  species. Derivative **13** also exhibits a broad absorption at room temperature, that is resolved in a double doublet at low temperature, the  $^1J(^{31}\text{P}\text{--}\text{Ag})$  coupling constants being typical of an  $\text{AgP}_3$  core.<sup>29</sup> It is interesting to note that in the case of **12** and **13** oxidation of  $\text{PPh}_3$  to  $\text{PPh}_3=\text{O}$  was not evident, also when the sample was exposed to air for  $24\text{ h}$ . On the other hand, the far-IR spectra of **12** and **13** after  $24\text{ h}$  exhibit some peaks due to  $[(\text{PPh}_3)_x\text{AgBr}]$  species, suggesting that in **12** and **13** the oxidation of  $\text{AsPh}_3$  and  $\text{SbPh}_3$  takes precedence over the oxidation of  $\text{PPh}_3$ . On the basis of the  $^{31}\text{P}$  NMR spectra, compounds **12** and **13** can be presumed more stable in solution than derivatives **1–11** and **14**.

From the solid state  $^{31}\text{P}$  CPMAS NMR spectrum of  $[(\text{Ph}_3\text{P})_2\text{AgBrO}_3]$  (**2**) (see Figure 5), a high degree of

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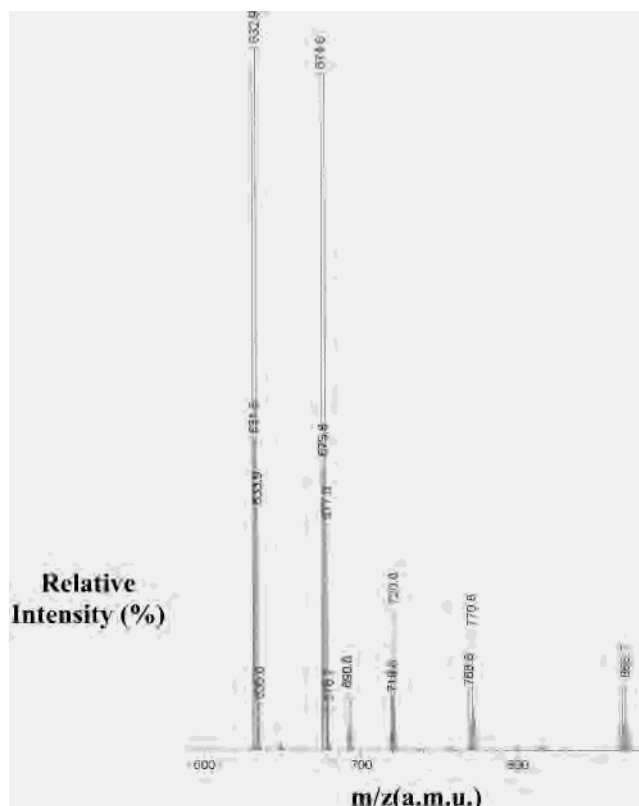
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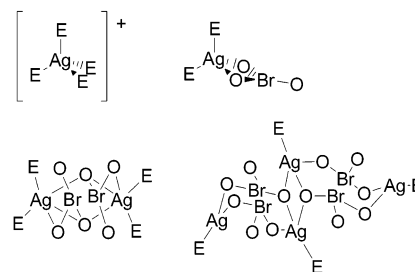
**Figure 6.**  $^{31}\text{P}$  CPMAS NMR spectrum of  $[(\text{Ph}_3\text{P})_3\text{Ag}(\text{BrO}_3)]$  (**3**) acquired at a field strength of 9.4 T.

chemical equivalence between the two P sites is exhibited. The spectrum of **2** is consistent with a very strong AB-type  $^2J(^{31}\text{P}-^{31}\text{P})$  coupling between the multiplets associated with each P site; in effect, this coupling represents the AB portion of a total ABX ( $X = \text{Ag}$ ) spin system. At an external field strength of 9.40 T, the chemical shift difference between these multiplets is so small that the  $^2J(^{31}\text{P}-^{31}\text{P})$  coupling correlating the P sites has virtually collapsed around the base of the main doublet, thus leaving a residual  $^1J(^{31}\text{P}-^{107/109}\text{Ag})$  coupling at a chemical shift of  $\sim 4.6$  ppm to be observed. The  $^1J(^{31}\text{P}-^{107/109}\text{Ag})$  coupling of  $\sim 478$  Hz is consistent with other previously reported  $^1J(^{31}\text{P}-^{107/109}\text{Ag})$  values for  $\text{P}_2\text{AgO}_2$  systems, with 432 and 517 Hz being measured for the  $[(\text{Ph}_3\text{P})_2\text{AgO}_2\text{CH}]$  and  $[(\text{Ph}_3\text{P})_2\text{AgO}_2\text{CH}]\cdot 2\text{HCO}_2\text{H}$  complexes,<sup>30</sup> and values of 352–531 Hz being obtained for the corresponding sulfate, selenate, and phosphate systems.<sup>31</sup> Figure 6 also shows the  $^{31}\text{P}$  CPMAS spectrum of the corresponding  $[(\text{Ph}_3\text{P})_3\text{AgBrO}_3]$  (**3**) complex. This spectrum suggests that a high degree of chemical equivalence is prevalent through the three P sites in accordance with a very strongly coupled ABCX system. The collapsed doublet has a chemical shift of  $\sim 5.2$  ppm and a  $^1J(^{31}\text{P}-^{107/109}\text{Ag})$  coupling constant of  $\sim 244$  Hz, which is markedly smaller than that reported for **2** and is attributed to larger average Ag–P bond lengths experienced in the tris systems. This behavior is consistent with the  $^1J(^{31}\text{P}-^{107/109}\text{Ag})$  coupling constants reported for  $[(\text{Ph}_3\text{P})_3\text{AgO}_2\text{CH}]$  and  $[(\text{Ph}_3\text{P})_3\text{AgO}_2\text{CH}]\cdot 2\text{HCO}_2\text{H}$  which have the range 211–352 Hz.<sup>32</sup>

The positive electrospray mass spectra of complexes<sup>33</sup> (Supporting Information) indicate that these derivatives undergo, as expected, loss of the anionic  $\text{BrO}_3^-$  ligand. Aggregation of phosphine, stibine, and arsine donors with Ag cations is significant in MeOH, also at concentrations of



**Figure 7.** Positive ESI MS spectrum of compound **12**.



**Figure 8.** Topologies found for the  $\text{AgBrO}_3/\text{EPh}_3$  adducts.

$10^{-3}$  M. A careful inspection of the data reveals that the species  $[\text{Ag}(\text{EPh}_3)_2]^+$  is always the more abundant species in the gas phase. In some cases, also a peak due to the dimeric species  $[(\text{EPh}_3)_2\text{Ag}_2\text{Br}]^+$  is present which confirms the reduction of  $\text{AgBrO}_3$  to  $\text{AgBr}$  as suggested. The proposed oxidation of  $\text{EPh}_3$  can be also presumed from the presence of peaks mainly due to  $[(\text{EPh}_3)(\text{EPh}_3\text{O})\text{Ag}]^+$  and  $[(\text{EPh}_3\text{O})(\text{EPh}_3\text{O})\text{Ag}]^+$  species in the case of  $\text{E} = \text{Sb}$  or  $\text{As}$ . The spectra of **12** and **14** are complex for the presence in solution of more than one species due to redistribution of the different  $\text{EPh}_3$  ligands between the Ag(I) centers. As an example, in the ESI MS spectrum of **12**, peaks due to  $[(\text{PPh}_3)_2\text{Ag}]^+$ ,  $[(\text{PPh}_3)(\text{AsPh}_3)\text{Ag}]^+$ ,  $[(\text{PPh}_3)(\text{AsPh}_3)\text{Ag} + \text{O}]^+$ ,  $[(\text{AsPh}_3)_2\text{Ag}]^+$ , and  $[(\text{PPh}_3)(\text{AsPh}_3)\text{Ag}_2\text{Br}]^+$  can be easily detected (Figure 7).

The negative electrospray mass spectra are always dominated by the presence of molecular peaks due to  $[\text{BrO}_3]^-$ ,  $[\text{Ag}(\text{BrO}_3)_2]^-$ , and  $[\text{Na}(\text{BrO}_3)_2]^-$ , the abundance of which can be understood as a consequence of the ion distribution between both positive and negative ion ensembles.

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## Conclusion

Aggregation of triphenyl phosphine, arsine, and stibine with silver(I) bromate has been investigated in the solid state by single crystal X-ray diffraction and IR and in solution by electrospray ionization mass spectroscopy. In the solid state, topology (Figure 8) is found to depend on the reaction conditions (ligand-to-metal ratio) and on the electronic features of the  $EPh_3$  ligand. Oxidation of  $EPh_3$  to  $Ph_3E=O$  by  $AgBrO_3$  can occur when the compounds were left in solution for more than 1 h or when the samples were exposed to light and air. Disruption of the complexes in chlorinated solvents has been confirmed by NMR investigation. Synthesis of mixed-ligand complexes such as  $[AgBrO_3(As-$

$Ph_3)(PPh_3)]$  is also possible, in methanol and  $CHCl_3$  solution as confirmed by  $^{31}P$  NMR solution data.

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**Supporting Information Available:** X-ray crystallographic files, in CIF format, for the structure determinations of **1**, **2**, **6**, **7**, and **12**. IR,  $^1H$  NMR ( $CDCl_3$ ),  $^{31}P$  NMR ( $CD_3CN$ ), and ESI MS data in PDF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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