

# Variable Coordination Modes of $\text{NO}_2^-$ in a Series of $\text{Ag(I)}$ Complexes Containing Triorganophosphines, -arsines, and -stibines. Syntheses, Spectroscopic Characterization (IR, $^1\text{H}$ and $^{31}\text{P}$ NMR, Electrospray Ionization Mass), and Structures of $[\text{AgNO}_2(\text{R}_3\text{E})_x]$ Adducts ( $\text{E} = \text{P}, \text{As}, \text{Sb}$ , $x = 1-3$ )

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Received May 30, 2002

Adducts of triorganophosphine, triphenylarsine, and triphenylstibine with silver(I) nitrite have been synthesized and characterized both in solution ( $^1\text{H}$ ,  $^{31}\text{P}$  NMR) and in the solid state (IR, single-crystal X-ray structure analysis). In addition aggregates of  $\text{AgNO}_2$  and  $\text{ER}_3$  ( $\text{E} = \text{P}, \text{As}, \text{Sb}$ ) have been identified in solution by electrospray ionization mass spectrometry (ESI-MS). The topology of the structures in the solid state was found to depend on the nature of  $\text{ER}_3$  and on the stoichiometric ratio  $\text{AgNO}_2:\text{ER}_3$ . The adducts  $\text{AgNO}_2:\text{EPh}_3$  (1:1) ( $\text{E} = \text{P}$  or  $\text{Sb}$ ) are one-dimensional polymers, the role of  $\text{NO}_2^-$  being to bridge successive metal atoms by coordination of the two oxygens to one silver atom and the nitrogen lone pair to a successive Ag. The adduct  $\text{AgNO}_2:\text{P}(o\text{-tolyl})_3$  (1:1) is mononuclear, due to steric hindrance of the phosphine, the nitrite being  $O,O'$ -bidentate, a rare example of a quasi-linear  $\text{P}-\text{Ag}-\text{X}$  array.  $\text{AgNO}_2:\text{P}(p\text{-F}-\text{C}_6\text{H}_4)_3$  (1:1) is a dimer, the nitrite being coordinated through both oxygens, the first unidentate, the second bridging bidentate.  $\text{P}(o\text{-tolyl})_3$  and  $\text{Pcy}_3$  form 1:2 adducts, also mononuclear, the nitrite still an  $O,O'$ -chelate. In contrast, the adduct  $\text{AgNO}_2:\text{AsPh}_3$  (1:2) is a centrosymmetric dimer, essentially an aggregate of a pair of  $[\text{Ag}(\text{O}_2\text{N})(\text{AsPh}_3)_2]$  arrays with one nitrite oxygen being the bridging atom. The adducts  $\text{AgNO}_2:\text{EPh}_3$  (1:3) ( $\text{E} = \text{As}, \text{Sb}$ ) are mononuclear, the nitrite behaving as a consistently strong  $O,O'$ -chelate. The  $\text{E} = \text{As}$  adduct is a triclinic solvated form, whereas the unsolvated  $\text{E} = \text{Sb}$  species is monoclinic. ESI-MS spectra of acetonitrile solutions of these complexes show the existence of  $[\text{Ag}(\text{ER}_3)]^+$ ,  $[\text{Ag}(\text{CH}_3\text{CN})]^+$ ,  $[\text{Ag}(\text{CH}_3\text{CN})_2]^+$ ,  $[\text{AgCl}_2]^-$ ,  $[\text{Ag}(\text{NO}_2)_2]^-$ ,  $[\text{Ag}(\text{ER}_3)(\text{CH}_3\text{CN})]^+$ , and  $[\text{Ag}(\text{ER}_3)_2]^+$  as well as higher aggregates  $[\text{Ag}_2(\text{NO}_2)(\text{ER}_3)_2]^+$ ,  $[\text{Ag}_2(\text{NO}_2)_3]^-$  and  $[\text{Ag}_2\text{Cl}_2(\text{NO}_2)]^-$ , which are less prevalent.

## Introduction

$\text{NO}_2^-$ -containing coordination compounds have been extensively studied, being of interest because of the ability of  $\text{NO}_2^-$  to coordinate a metal in a number of different bonding modes (Figure 1), e.g. yielding nitro compounds  $\text{M}-\text{NO}_2$  as N-donor or nitrito derivatives  $\text{M}-\text{O}-\text{NO}$  as O-donor.<sup>1</sup> Each  $\text{NO}_2$  coordination mode leads to different properties for the compound.

Coordination of  $\text{NO}_2^-$  to a metal can also provide important information for the understanding of chemical reactions in the atmosphere involving pollutants such as nitrogen oxides ( $\text{NO}_x$ ,  $x = 1$  or  $2$ ) and of corrosion processes.

The interaction of the  $\text{NO}_2^-$  ligand with alkaline,<sup>2-6</sup> alkaline earth,<sup>7-10</sup> and transition metal species<sup>11-15</sup> has been widely studied by several authors both theoretically and experimentally, whereas only a few examples of nitrite coordination to silver centers have been reported.

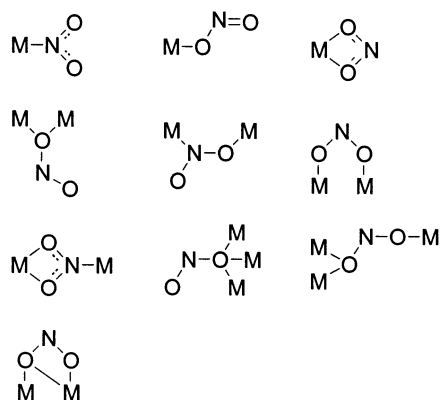
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(1) See for example: (a) Veillard, A. *Chem. Rev.* **1991**, *91*, 743–766. (b) *Organometallic Ion Chemistry*; Freiser, B. S., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1996.



**Figure 1.** Some possible coordination modes for the  $\text{NO}_2^-$  ligand.

A silver(I) nitrite (di-2-pyridyl ketone) complex, stabilized by intramolecular  $\pi$  stacking interactions and aligned into chains through the intermolecular  $\pi$  stacking interactions in a zipper-like fashion, has been recorded by Yang and co-workers.<sup>16</sup>  $\text{AgNO}_2$  reacts with hexamethylenetetramine in  $\text{MeCN}-\text{H}_2\text{O}$  to yield a two-dimensional coordination polymer with square cavities.<sup>17</sup> The reaction of Ag(I) salts with 1,4-dithiane has produced several interesting coordination polymers, the structures of which vary significantly with the anion. In particular, when  $\text{NO}_2^-$  acts as the anion, the interlinked chains give a 3-D diamondoid network.<sup>18</sup>

In this paper we describe a series of  $\text{AgNO}_2$  adducts with unidentate triorganophosphines, -arsines, and -stibines  $\text{EPh}_3$  ( $\text{E} = \text{P}, \text{As}, \text{Sb}$ ),  $\text{P}(o\text{-tolyl})_3$ ,  $\text{P}(m\text{-tolyl})_3$ ,  $\text{P}(p\text{-tolyl})_3$ ,  $\text{P}(p\text{-F-C}_6\text{H}_4)_3$ , and  $\text{Pcy}_3$ . The coordination chemistry of tertiary phosphine adducts provides a well-established basis permitting systematic investigation of the possible coordination modes of oxanions such as  $\text{NO}_3^-$  and  $\text{ClO}_4^-$  to Ag(I)<sup>19–21</sup> and Cu(I) ions,<sup>22</sup> with interesting structural variations within the series  $\text{MX}:(\text{PR}_3)_n$  resulting from the different coordination

modes of the anions. By comparison the chemistry of tertiary stibines and arsines has only been investigated sparsely, though again there has been increased interest recently.<sup>23,24</sup>

Here we report the synthesis and spectroscopic characterization of 16 novel  $\text{AgNO}_2:\text{ER}_3$  adducts supported by 10 single-crystal X-ray studies to assist in understanding the relationships between molecular packing, coordinating ability of  $\text{NO}_2^-$ , donor capacity, and the Tolman cone angle of the ancillary ligand. Our results demonstrate that remarkably stable neutral silver complexes showing different silver(I) coordination environments and  $\text{NO}_2^-$  coordination modes can be easily synthesized: oxygen-bridged one-dimensional polymers, mononuclear forms with nitrite  $O,O'$ -bidentate containing one, two, or three ancillary donors, and binuclear and polymeric aggregates in which nitrite oxygen atoms are the bridging atoms.

Recent advances in electrospray ionization mass spectrometry (ESI-MS) have provided an especially powerful tool for observing in the gas phase the solution composition of charged species.<sup>25</sup> The (ESI-MS) technique has been very successfully applied to problems in biochemistry<sup>26</sup> and in the speciation of inorganic and organometallic complexes of various metals, including Ag, Pd, Zn, and others.<sup>27</sup> The existence in solution of our complexes has been probed by (ESI-MS) in acetonitrile and in some cases also in acetone. Aggregates of the phosphine, arsine, and stibine ligands and  $\text{Ag(I)NO}_2$  are observed in both solvents, but the aggregation is diminished in acetonitrile due to predominance of solvent coordination to silver(I).

## Experimental Section

**Materials and Methods.** All reactions were carried out under an atmosphere of dry oxygen-free dinitrogen, using 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.  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for  $^1\text{H}$ , and 121.4 MHz for  $^{31}\text{P}$ ). Proton chemical shifts are reported in parts per million vs  $\text{Me}_4\text{Si}$ , while phosphorus chemical

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shifts are reported in parts per million vs 85%  $\text{H}_3\text{PO}_4$ . The electrical conductances of the  $\text{CH}_2\text{Cl}_2$  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 MSI detector HP spectrometer, using an acetonitrile mobile phase. Solutions (3 mg/mL) for electrospray ionization mass spectrometry (ESI-MS) were prepared using reagent grade acetone or acetonitrile. For the ESI-MS data, mass and intensities were compared to those calculated using IsoPro Isotopic Abundance Simulator vers. 2.1.<sup>28</sup> Peaks containing silver(I) ions are identified as the center of an isotopic cluster.

**[AgNO<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] (1).** Silver(I) nitrite (0.154 g, 1 mmol) was added to an ethanol solution (30 mL) of PPh<sub>3</sub> (0.262 g, 1 mmol) at 60 °C. After the addition, the solution was stirred for 24 h at 60 °C. A colorless precipitate was formed which was filtered off and washed with ethanol (3 × 5 mL). Recrystallization from ethanol gave complex **1** as a microcrystalline solid in 59% yield. Mp: 162–165 °C. IR (Nujol,  $\text{cm}^{-1}$ ) data: 3170w,  $\nu(\text{C}-\text{H})$ ; 1435s, 1336vw, 1217br,  $\nu(\text{NO}_2)$ ; 838w,  $\delta(\text{ONO})$ ; 523s, 501m, 489s, 437m,  $\delta(\text{PPh}_3)$ . <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 293 K):  $\delta$  7.35–7.55 (m, 15H,  $\text{C}_6\text{H}_5$ ). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ , 293 K):  $\delta$  16.5 (d br,  $^1J(^{31}\text{P}-\text{Ag}) = 621$  Hz). <sup>31</sup>P-{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ , 218 K):  $\delta$  16.1 (dd,  $^1J(^{31}\text{P}-^{107}\text{Ag}) = 666$  Hz,  $^1J(^{31}\text{P}-^{109}\text{Ag}) = 769$  Hz).  $\Lambda_{\text{mol}}$  ( $\text{CH}_2\text{Cl}_2$ , concn =  $1.00 \times 10^{-3}$  M):  $0.1 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . ESI MS (MeCN): (+) 189 (5) [Ag-(MeCN)<sub>2</sub>]<sup>+</sup>, 411 (80) [Ag(MeCN)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 632 (100) [Ag(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 786 (30) [Ag<sub>2</sub>(NO<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>; (–) 178 (18) [AgCl<sub>2</sub>]<sup>–</sup>, 199 (100) [Ag(NO<sub>2</sub>)<sub>2</sub>]<sup>–</sup>, 332 (65) [Ag<sub>2</sub>Cl<sub>2</sub>NO<sub>2</sub>]<sup>–</sup>. Anal. Calcd for C<sub>18</sub>H<sub>15</sub>AgNO<sub>2</sub>P: C, 51.95; H, 3.63; N, 3.37. Found: C, 51.78; H, 3.72; N, 3.40.

**[AgNO<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (2).** Compound **2** has been synthesized similarly to **1**, by using AgNO<sub>2</sub> (0.154 g, 1 mmol) and PPh<sub>3</sub> (0.525 g, 2 mmol). Compound **2** was recrystallized from ethanol. Yield: 80%. Mp: 203–205 °C. IR (Nujol,  $\text{cm}^{-1}$ ) data: 3068vw,  $\nu(\text{C}-\text{H})$ ; 1433s, 1326vw, 1225br,  $\nu(\text{NO}_2)$ ; 832w,  $\delta(\text{ONO})$ ; 511sh, 495s, 438m, 422w,  $\delta(\text{Ph}_3\text{P})$ . <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 293 K):  $\delta$  7.20–7.42 (m, 30H,  $\text{C}_6\text{H}_5$ ). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ , 293 K):  $\delta$  9.3 (s). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ , 218 K):  $\delta$  8.95 (dd,  $^1J(^{31}\text{P}-^{107}\text{Ag}) = 413$  Hz,  $^1J(^{31}\text{P}-^{109}\text{Ag}) = 476$  Hz).  $\Lambda_{\text{mol}}$  ( $\text{CH}_2\text{Cl}_2$ , concn =  $1.05 \times 10^{-3}$  M):  $0.2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . ESI MS (MeCN): (+) 411 (10) [Ag(MeCN)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 632 (100) [Ag(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 786 (5) [Ag<sub>2</sub>(NO<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Anal. Calcd for C<sub>36</sub>H<sub>30</sub>AgNO<sub>2</sub>P<sub>2</sub>: C, 63.73; H, 4.46; N, 2.06. Found: C, 64.03; H, 4.64; N, 2.01.

**[AgNO<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] (3).** Compound **3** was prepared similarly to compound **1**, by using AgNO<sub>2</sub> (0.154 g, 1 mmol) and PPh<sub>3</sub> (0.787 g, 3 mmol). Compound **3** was recrystallized from ethanol. Yield: 85%. Mp: 216–220 °C. IR (Nujol,  $\text{cm}^{-1}$ ) data: 3167vw,  $\nu(\text{C}-\text{H})$ ; 1434s, 1377w, 1183br,  $\nu(\text{NO}_2)$ ; 848vw,  $\delta(\text{ONO})$ ; 501s, 492s, 438m, 419m,  $\delta(\text{Ph}_3\text{P})$ . <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 293 K):  $\delta$  7.20–7.40 (m, 45H,  $\text{C}_6\text{H}_5$ ). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ , 293 K):  $\delta$  5.2 (s). <sup>31</sup>P-{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ , 218 K):  $\delta$  5.6 (d,  $^1J(^{31}\text{P}-\text{Ag}) = 228$  Hz), 32.2 (s).  $\Lambda_{\text{mol}}$  ( $\text{CH}_2\text{Cl}_2$ , concn =  $1.20 \times 10^{-3}$  M):  $\Lambda$   $1.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . ESI MS (MeCN): (+) 632 (100) [Ag(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 786 (5) [Ag<sub>2</sub>(NO<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Anal. Calcd for C<sub>54</sub>H<sub>45</sub>AgNO<sub>2</sub>P<sub>3</sub>: C, 68.94; H, 4.82; N, 1.49. Found: C, 68.68; H, 5.01; N, 1.56.

**[AgNO<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] (4).** Compound **4** was prepared similarly to compound **1**, by using AgNO<sub>2</sub> (0.154 g, 1 mmol) and PPh<sub>3</sub> (1.311 g, 3 mmol) and recrystallized from ethanol (yield 56%). Mp: 166–167 °C. IR (Nujol,  $\text{cm}^{-1}$ ) data: 3052w,  $\nu(\text{C}-\text{H})$ ; 1434s, 1309vw, 1184br,  $\nu(\text{NO}_2)$ ; 819vw,  $\delta(\text{ONO})$ ; 512s, 503s, 494s, 438m,  $\delta(\text{Ph}_3\text{P})$ .

<sup>1</sup>H NMR ( $\text{CDCl}_3$ , 293 K):  $\delta$  7.25–7.41 (m, 60H,  $\text{C}_6\text{H}_5$ ). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ , 293 K):  $\delta$  4.7 (s). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ , 218 K):  $\delta$  5.6 (d,  $^1J(^{31}\text{P}-\text{Ag}) = 228$  Hz), 32.2 (s).  $\Lambda_{\text{mol}}$  ( $\text{CH}_2\text{Cl}_2$ , concn =  $1.00 \times 10^{-3}$  M):  $1.1 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . ESI MS (MeCN): (+) 632 (100) [Ag(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 786 (2) [Ag<sub>2</sub>(NO<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Anal. Calcd for C<sub>72</sub>H<sub>60</sub>AgNO<sub>2</sub>P<sub>4</sub>: C, 71.88; H, 5.03; N, 1.16. Found: C, 71.65; H, 5.22; N, 1.24.

**[AgNO<sub>2</sub>{P(*o*-tolyl)<sub>3</sub>}] (5).** AgNO<sub>2</sub> (0.154 g, 1 mmol) was added to an ethanol solution (30 mL) of P(*o*-tolyl)<sub>3</sub> (0.304 g, 1 mmol) at 60 °C. After the addition, the solution was stirred for 24 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 filtered off and washed with ethanol (3 × 5 mL) and shown to be compound **5** and recrystallized from ethanol. Yield: 60%. Mp: 189–190 °C. IR (Nujol,  $\text{cm}^{-1}$ ) data: 3048w,  $\nu(\text{C}-\text{H})$ ; 1456s, 1306br,  $\nu(\text{NO}_2)$ ; 850vw,  $\delta(\text{ONO})$ ; 565m, 560sh, 524w, 515sh, 467s, 446sh,  $\delta(\text{PAR}_3)$ . <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 293 K):  $\delta$  2.50 (s, 9H,  $\text{CH}_3$ ), 6.81, 7.17, 7.33, 7.43 (t, 12H,  $\text{C}_6\text{H}_4$ ). <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 293 K):  $\delta$  2.50 (s, 9H,  $\text{CH}_3$ ), 6.74, 7.18, 7.34, 7.45 (tbr, 12H,  $\text{C}_6\text{H}_4$ ). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ , 293 K):  $\delta$  –17.7 (d br). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ , 223 K):  $\delta$  –19.2 (d,  $^1J(^{31}\text{P}-\text{Ag}) = 695$  Hz).  $\Lambda_{\text{mol}}$  ( $\text{CH}_2\text{Cl}_2$ , concn =  $1.10 \times 10^{-3}$  M):  $0.05 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . ESI MS (MeCN): (+) 452 (30) [Ag(MeCN)(P(*o*-tolyl)<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 716 (100) [Ag(P(*o*-tolyl)<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 870 (30) [Ag<sub>2</sub>(NO<sub>2</sub>)(P(*o*-tolyl)<sub>3</sub>)<sub>2</sub>]<sup>+</sup>; (–) 178 (15) [AgCl<sub>2</sub>]<sup>–</sup>, 199 (100) [Ag(NO<sub>2</sub>)<sub>2</sub>]<sup>–</sup>, 332 (60) [Ag<sub>2</sub>Cl<sub>2</sub>NO<sub>2</sub>]<sup>–</sup>. Anal. Calcd for C<sub>21</sub>H<sub>21</sub>AgNO<sub>2</sub>P: C, 55.04; H, 4.62; N, 3.06. Found: C, 55.13; H, 4.82; N, 3.20.

**[AgNO<sub>2</sub>{P(*o*-tolyl)<sub>3</sub>}<sub>2</sub>] (6).** Compound **6** was prepared similarly to **5**, by using AgNO<sub>2</sub> (0.154 g, 1 mmol) and P(*o*-tolyl)<sub>3</sub> (0.609 g, 2 mmol). Compound **6** was recrystallized from ethanol. Yield: 42%. Mp: 193–195 °C. IR (Nujol,  $\text{cm}^{-1}$ ) data: 3050w,  $\nu(\text{C}-\text{H})$ ; 1226w,  $\nu(\text{NO}_2)$ ; 828w,  $\delta(\text{ONO})$ ; 564sh, 558s, 552sh, 529s, 475s, 459s,  $\delta(\text{Ph}_3\text{P})$ . <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 293 K):  $\delta$  2.34 (s, 18H,  $\text{CH}_3$ ), 6.81, 7.10, 7.24, 7.34 (pt, 24H,  $\text{C}_6\text{H}_4$ ). <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 223 K):  $\delta$  2.11 (s, 18H,  $\text{CH}_3$ ), 6.84, 7.07, 7.20, 7.35 (pt br, 24H,  $\text{C}_6\text{H}_4$ ). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ , 293 K):  $\delta$  –19.0 (s). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ , 223 K):  $\delta$  –11.0 (br).  $\Lambda_{\text{mol}}$  ( $\text{CH}_2\text{Cl}_2$ , concn =  $1.00 \times 10^{-3}$  M):  $0.2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . ESI MS (MeCN): (+) 716 (100) [Ag(P(*o*-tolyl)<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 870 (5) [Ag<sub>2</sub>(NO<sub>2</sub>)(P(*o*-tolyl)<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Anal. Calcd for C<sub>42</sub>H<sub>42</sub>AgNO<sub>2</sub>P<sub>2</sub>: C, 66.15; H, 5.55; N, 1.84. Found: C, 66.11; H, 5.68; N, 1.92.

**[AgNO<sub>2</sub>{P(*m*-tolyl)<sub>3</sub>}] (7).** Compound **7** was prepared similarly to **5**, by using AgNO<sub>2</sub> (0.154 g, 1 mmol) and P(*m*-tolyl)<sub>3</sub> (0.304 g, 1 mmol). Compound **7** was recrystallized from ethanol. Yield: 46%. Mp: 140–145 °C. IR (Nujol,  $\text{cm}^{-1}$ ) data: 3169w,  $\nu(\text{C}-\text{H})$ ; 1225w,  $\nu(\text{NO}_2)$ ; 832m,  $\delta(\text{ONO})$ ; 544m, 558s, 521vw, 462s, 446m, 430vw,  $\delta(\text{Ph}_3\text{P})$ . <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 293 K):  $\delta$  2.19 (s, 9H,  $\text{CH}_3$ ), 7.08 (br, 3H,  $\text{C}_6\text{H}_4$ ), 7.17 (pd, 9H,  $\text{C}_6\text{H}_4$ ). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ , 293 K):  $\delta$  10.5 (br). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ , 218 K):  $\delta$  10.0 (d,  $^1J(^{31}\text{P}-\text{Ag}) = 660$  Hz).  $\Lambda_{\text{mol}}$  ( $\text{CH}_2\text{Cl}_2$ , concn =  $1.05 \times 10^{-3}$  M):  $1.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . ESI MS (MeCN): (+) 716 (100) [Ag(P(*m*-tolyl)<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 870 (3) [Ag<sub>2</sub>(NO<sub>2</sub>)(P(*m*-tolyl)<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Anal. Calcd for C<sub>21</sub>H<sub>21</sub>AgNO<sub>2</sub>P: C, 55.04; H, 4.62; N, 3.06. Found: C, 55.14; H, 4.51; N, 3.12.

**[AgNO<sub>2</sub>{P(*m*-tolyl)<sub>3</sub>}<sub>2</sub>] (8).** Compound **8** was prepared similarly to **5**, by using AgNO<sub>2</sub> (0.154 g, 1 mmol) and P(*m*-tolyl)<sub>3</sub> (0.609 g, 2 mmol), and recrystallized from ethanol. Yield: 52%. Mp: 180–183 °C. IR (Nujol,  $\text{cm}^{-1}$ ) data: 3047w,  $\nu(\text{C}-\text{H})$ ; 1401m, 1276vw, 1124s,  $\nu(\text{NO}_2)$ ; 830w,  $\delta(\text{ONO})$ ; 544m, 521vw, 462s, 446m, 430vw,  $\delta(\text{Ph}_3\text{P})$ . <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 293 K):  $\delta$  2.16 (s, 18H,  $\text{CH}_3$ ), 7.04 (br, 6H,  $\text{C}_6\text{H}_4$ ), 7.15 (pd, 18H,  $\text{C}_6\text{H}_4$ ). <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 218 K):  $\delta$  2.12 (s, 18H,  $\text{CH}_3$ ), 6.97, 7.07 (br, 12H,  $\text{C}_6\text{H}_4$ ), 7.17 (pd, 12H,  $\text{C}_6\text{H}_4$ ). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ , 293 K):  $\delta$  9.5 (sbr), 29.9 (s). <sup>31</sup>P-

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{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 218 K): 8.8 (dd, <sup>1</sup>J(<sup>31</sup>P, <sup>107</sup>Ag) = 411 Hz, <sup>1</sup>J(<sup>31</sup>P, <sup>109</sup>Ag) = 475 Hz), 32.2 (s).  $\Lambda_{\text{mol}}$  (CH<sub>2</sub>Cl<sub>2</sub>, concn = 1.20 × 10<sup>-3</sup> M): 0.6 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. ESI MS (MeCN): (+) 716 (100) [Ag(P(*m*-tolyl)<sub>3</sub>)<sub>2</sub>]<sup>+</sup>; (-) 178 (10) [AgCl<sub>2</sub>]<sup>-</sup>, 199 (100) [Ag(NO<sub>2</sub>)<sub>2</sub>]<sup>-</sup>. Anal. Calcd for C<sub>42</sub>H<sub>42</sub>AgNO<sub>2</sub>P<sub>2</sub>: C, 66.15; H, 5.55; N, 1.84. Found: C, 65.84; H, 5.74; N, 1.81.

[AgNO<sub>2</sub>(P(*m*-tolyl)<sub>3</sub>)<sub>3</sub>] (9). Compound **9** was prepared similarly to **5**, by using AgNO<sub>2</sub> (0.154 g, 1 mmol) and P(*m*-tolyl)<sub>3</sub> (0.913 g, 3 mmol), and recrystallized from ethanol. Yield: 64%. Mp: 121–124 °C. IR (Nujol, cm<sup>-1</sup>) data: 3338w, 3156w, ν(C–H); 1170m, 1104m, ν(NO<sub>2</sub>); 887m, 770s, δ(ONO); 543s, 534s, 518m, 446s, 423m, δ(Ph<sub>3</sub>P). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K): δ 2.19 (s, 27H, CH<sub>3</sub>), 7.04 (m, 9H, C<sub>6</sub>H<sub>4</sub>), 7.15 (m, 27H, C<sub>6</sub>H<sub>4</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 218 K): δ 1.85, 2.03 (sbr, 27H, CH<sub>3</sub>), 6.58, 6.68, 6.91, 7.07 (sbr, 36H, C<sub>6</sub>H<sub>4</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 293 K): δ 4.9 (s), 29.9 (s). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 218 K): 5.1 (d, <sup>1</sup>J(<sup>31</sup>P, Ag) = 239 Hz), 10.4 (sbr), 32.3 (s).  $\Lambda_{\text{mol}}$  (CH<sub>2</sub>Cl<sub>2</sub>, concn = 1.10 × 10<sup>-3</sup> M): 1.1 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. ESI MS (MeCN): (+) 716 (100) [Ag(P(*m*-tolyl)<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Anal. Calcd for C<sub>63</sub>H<sub>63</sub>AgNO<sub>2</sub>P<sub>3</sub>: C, 70.92; H, 5.95; N, 1.31. Found: C, 70.65; H, 6.25; N, 1.34.

[AgNO<sub>2</sub>(P(*p*-tolyl)<sub>3</sub>)<sub>3</sub>] (10). Compound **10** was prepared similarly to **5**, by using AgNO<sub>2</sub> (0.154 g, 1 mmol) and P(*p*-tolyl)<sub>3</sub> (0.913 g, 3 mmol), and recrystallized from ethanol. Yield: 46%. Mp: 180–183 °C. IR (Nujol, cm<sup>-1</sup>) data: 3173w, ν(C–H); 1392w, 1203m, 1189m, ν(NO<sub>2</sub>); 807s, δ(ONO); 516s, 509s, 490m, 429m, δ(PPh<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K): δ 2.31 (s, 27H, CH<sub>3</sub>), 7.06 (m, 18H, C<sub>6</sub>H<sub>4</sub>), 7.17 (m, 18H, C<sub>6</sub>H<sub>4</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 218 K): δ 2.29 (s, 27H, CH<sub>3</sub>), 6.83 (sbr, 36H, C<sub>6</sub>H<sub>4</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 293 K): δ 2.9 (s), 29.7 (s). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 218 K): 3.7 (dbr, <sup>1</sup>J(<sup>31</sup>P–Ag) = 193 Hz).  $\Lambda_{\text{mol}}$  (CH<sub>2</sub>Cl<sub>2</sub>, concn = 1.00 × 10<sup>-3</sup> M): 1.9 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. ESI MS (MeCN): (+) 716 (100) [Ag(P(*p*-tolyl)<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Anal. Calcd for C<sub>63</sub>H<sub>63</sub>AgNO<sub>2</sub>P<sub>3</sub>: C, 70.92; H, 5.95; N, 1.31. Found: C, 70.58; H, 6.21; N, 1.26.

[AgNO<sub>2</sub>(P(*p*-F–C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>) (11). Compound **11** was prepared similarly to **5**, by using AgNO<sub>2</sub> (0.154 g, 1 mmol) and P(*p*-F–C<sub>6</sub>H<sub>4</sub>)<sub>3</sub> (0.316 g, 1 mmol), and recrystallized from ethanol. Yield: 66%. Mp: 160 °C. IR (Nujol, cm<sup>-1</sup>) data: 3160w, ν(C–H); 1576s, 1461s, 1366br, 1219br, 1152br, ν(NO<sub>2</sub>); 823s, δ(ONO); 523s, 476s, 434s, 415s, 404s δ(PPh<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K): δ 7.1 (m, 9H, C<sub>6</sub>H<sub>4</sub>), 7.4 (m, 6H, C<sub>6</sub>H<sub>4</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 293 K): δ 12.8 (d, <sup>1</sup>J(<sup>31</sup>P–Ag) = 643 Hz).  $\Lambda_{\text{mol}}$  (CH<sub>2</sub>Cl<sub>2</sub>, concn = 1.00 × 10<sup>-3</sup> M): 3.5 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. ESI MS (MeCN): (+) 424 (15) [Ag(P(*p*-F–C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sup>+</sup>, 740 (100) [Ag(P(*p*-F–C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Anal. Calcd for C<sub>18</sub>H<sub>12</sub>AgF<sub>3</sub>NO<sub>2</sub>P: C, 45.99; H, 2.57; N, 2.98. Found: C, 45.87; H, 2.64; N, 2.76.

[AgNO<sub>2</sub>(Pcy<sub>3</sub>)<sub>2</sub>] (12). Compound **12** was prepared similarly to compound **5**, by using AgNO<sub>2</sub> (0.154 g, 1 mmol) and Pcy<sub>3</sub> (0.561 g, 2 mmol). Compound **12** was recrystallized from ethanol. Yield: 56%. Mp: 205–210 °C. IR (Nujol, cm<sup>-1</sup>) data: 3159w ν(C–H); 1346m, 1225m, ν(NO<sub>2</sub>); 886s, 850s, δ(ONO); 512s, 487m, 465s, 400w, δ(Ph<sub>3</sub>P). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K): δ 1.23 (mbr, 30H, C<sub>6</sub>H<sub>11</sub>), 1.65 (sbr, 6H, C<sub>6</sub>H<sub>11</sub>), 1.78 (mbr, 30H, C<sub>6</sub>H<sub>11</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 218 K): δ 1.18 (br, 30H, C<sub>6</sub>H<sub>11</sub>), 1.60 (br, 6H, C<sub>6</sub>H<sub>11</sub>), 1.73 (br, 30H, C<sub>6</sub>H<sub>11</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 293 K): δ 28.9 (d, <sup>1</sup>J(<sup>31</sup>P–Ag) = 435 Hz), 50.6 (s). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 218 K): δ 28.4 (dd, <sup>1</sup>J(<sup>31</sup>P–<sup>107</sup>Ag) = 425 Hz, <sup>1</sup>J(<sup>31</sup>P–<sup>109</sup>Ag) = 491 Hz).  $\Lambda_{\text{mol}}$  (CH<sub>2</sub>Cl<sub>2</sub>, concn = 1.40 × 10<sup>-3</sup> M): 4.5 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. ESI MS (MeCN): (+) 430 (55) [Ag(Pcy<sub>3</sub>)<sup>+</sup>, 668 (100) [Ag(Pcy<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 822 (100) [Ag<sub>2</sub>(NO<sub>2</sub>)(Pcy<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Anal. Calcd for C<sub>36</sub>H<sub>66</sub>AgNO<sub>2</sub>P<sub>2</sub>: C, 60.50; H, 9.31; N, 1.96. Found: C, 60.22; H, 9.53; N, 2.05.

[AgNO<sub>2</sub>(AsPh<sub>3</sub>)<sub>2</sub>] (13). Compound **13** was prepared similarly to compound **1**, by using AgNO<sub>2</sub> (0.154 g, 1 mmol) and AsPh<sub>3</sub> (0.612 g, 2 mmol), and recrystallized from ethanol. Yield: 65%.

Mp: 166–167 °C. IR (Nujol, cm<sup>-1</sup>) data: 3050w, ν(C–H); 1481m, 1255br, 1182vw, ν(NO<sub>2</sub>); 842w, δ(ONO); 473s, 463s, 326s, δ(Ph<sub>3</sub>–As). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K): δ 7.24–7.73 (mc, 35H, C<sub>6</sub>H<sub>5</sub>).  $\Lambda_{\text{mol}}$  (CH<sub>2</sub>Cl<sub>2</sub>, concn = 1.00 × 10<sup>-3</sup> M): 0.02 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. ESI MS (MeCN): (+) 189 (5) [Ag(MeCN)<sub>2</sub>]<sup>+</sup>, 455 (60) [Ag–(MeCN)(AsPh<sub>3</sub>)<sup>+</sup>, 719 (100) [Ag(AsPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 874 (80) [Ag<sub>2</sub>(NO<sub>2</sub>–(AsPh<sub>3</sub>)<sub>2</sub>)<sup>+</sup>; (-) 178 (5) [AgCl<sub>2</sub>]<sup>-</sup>, 199 (100) [Ag(NO<sub>2</sub>)<sub>2</sub>]<sup>-</sup>, 332 (55) [Ag<sub>2</sub>Cl<sub>2</sub>NO<sub>2</sub>]<sup>-</sup>. Anal. Calcd for C<sub>36</sub>H<sub>30</sub>AgAs<sub>2</sub>NO<sub>2</sub>: C, 56.42; H, 3.95; N, 1.83. Found: C, 56.71; H, 3.86; N, 2.01.

[AgNO<sub>2</sub>(AsPh<sub>3</sub>)<sub>3</sub>] (14). Compound **14** was prepared similarly to **1**, by using AgNO<sub>2</sub> (0.154 g, 1 mmol) and AsPh<sub>3</sub> (0.919 g, 3.0 mmol), and recrystallized from ethanol. Yield: 97%. Mp: 182–184 °C. IR (Nujol, cm<sup>-1</sup>) data: 3147w, ν(C–H); 1434s, 1214br, 1182w, ν(NO<sub>2</sub>); 848w, δ(ONO); 478m, 462m, 322s, 312s, δ(Ph<sub>3</sub>–As). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K): δ 7.24–7.42 (mc, 45H, C<sub>6</sub>H<sub>5</sub>).  $\Lambda_{\text{mol}}$  (CH<sub>2</sub>Cl<sub>2</sub>, concn = 1.00 × 10<sup>-3</sup> M): 0.4 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. ESI MS (MeCN): (+) 719 (100) [Ag(AsPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 874 (80) [Ag<sub>2</sub>(NO<sub>2</sub>–(AsPh<sub>3</sub>)<sub>2</sub>)<sup>+</sup>. Anal. Calcd for C<sub>54</sub>H<sub>45</sub>AgAs<sub>3</sub>NO<sub>2</sub>: C, 60.47; H, 4.23; N, 1.31. Found: C, 60.32; H, 4.34; N, 1.38.

[AgNO<sub>2</sub>(SbPh<sub>3</sub>) (15). Compound **15** was prepared similarly to compound **1**, by using AgNO<sub>2</sub> (0.154 g, 1 mmol) and SbPh<sub>3</sub> (0.353 g, 1 mmol), and recrystallized from ethanol. X-ray-quality crystals were grown at 4 °C from MeCN. Yield: 60%. Mp: 147–148 °C. IR (Nujol, cm<sup>-1</sup>) data: 3152vw, ν(C–H); 1430s, 1303w, 1180w, ν(NO<sub>2</sub>); 847w, δ(ONO); 453s, 446sh, 268s, δ(Ph<sub>3</sub>Sb). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K): δ 7.25–7.48 (mc, 15H, C<sub>6</sub>H<sub>5</sub>).  $\Lambda_{\text{mol}}$  (CH<sub>2</sub>Cl<sub>2</sub>, concn = 1.00 × 10<sup>-3</sup> M): 0.4 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. ESI MS (MeCN): (+) 189 (5) [Ag(MeCN)<sub>2</sub>]<sup>+</sup>, 502 (70) [Ag(MeCN)(SbPh<sub>3</sub>)<sup>+</sup>, 813 (100) [Ag(SbPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 968 (60) [Ag<sub>2</sub>(NO<sub>2</sub>)(SbPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>; (-) 178 (10) [AgCl<sub>2</sub>]<sup>-</sup>, 199 (100) [Ag(NO<sub>2</sub>)<sub>2</sub>]<sup>-</sup>, 332 (40) [Ag<sub>2</sub>Cl<sub>2</sub>(NO<sub>2</sub>)<sup>-</sup>, 353 (20) [Ag<sub>2</sub>(NO<sub>2</sub>)<sub>3</sub>]<sup>-</sup>. Anal. Calcd for C<sub>18</sub>H<sub>15</sub>AgNO<sub>2</sub>Sb: C, 42.65; H, 2.98; N, 2.76. Found: C, 42.61; H, 3.14; N, 2.71.

[AgNO<sub>2</sub>(SbPh<sub>3</sub>)<sub>3</sub>] (16). Compound **16** was prepared similarly to **1**, by using AgNO<sub>2</sub> (0.154 g, 1 mmol) and SbPh<sub>3</sub> (1.059 g, 3 mmol). Compound **16** was recrystallized from ethanol. X-ray-quality crystals were grown at 4 °C from ethanol. Yield: 60%. Mp: 182–183 °C. IR (Nujol, cm<sup>-1</sup>) data: 3062w, 3046w, ν(C–H); 1429s, 130br, 1200w, ν(NO<sub>2</sub>); 847w, δ(ONO); 453s, 446sh, 273s, 262s, δ(Ph<sub>3</sub>Sb). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K): δ 7.22–7.40 (mc, 45H, C<sub>6</sub>H<sub>5</sub>).  $\Lambda_{\text{mol}}$  (CH<sub>2</sub>Cl<sub>2</sub>, concn = 1.20 × 10<sup>-3</sup> M): 0.4 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. ESI MS (MeCN): (+) 502 (30) [Ag(MeCN)(SbPh<sub>3</sub>)<sup>+</sup>, 813 (100) [Ag(SbPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 968 (30) [Ag<sub>2</sub>(NO<sub>2</sub>)(SbPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Anal. Calcd for C<sub>54</sub>H<sub>45</sub>AgNO<sub>2</sub>Sb<sub>3</sub>: C, 53.47; H, 3.74; N, 1.15. Found: C, 53.42; H, 3.83; N, 1.10.

**Crystal Structure Determinations.** Crystals for the X-ray work were obtained in all cases (exception: **15** (MeCN, 4 °C)) from ethanol, **13–16** at 4 °C. For compounds **5**, **12**, and **16**, unique room temperature data sets were measured using a single counter instrument (*T*, ca. 295 K; 2θ/θ scan mode; monochromatic Mo Kα radiation; λ = 0.71073 Å), yielding *N* reflections, *N*<sub>o</sub> with *I* > 3σ(*I*) being considered “observed” and used in the full matrix least squares refinement after Gaussian absorption correction; for the remainder, full spheres of low-temperature CCD area detector data were measured (*T*, ca. 153 K; Bruker AXS instrument; ω-scans) *N*<sub>i(total)</sub> reflections merging to *N* unique after “empirical”/multiscan absorption correction (proprietary software), *N*<sub>o</sub> with *F* > 4σ(*F*), considered “observed”. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, (*x*, *y*, *z*, *U*<sub>iso</sub>)<sub>H</sub> constrained at estimates (295 K data) or refined (153 K data) unless otherwise noted. Conventional residuals *R* (=ΣΔ/Σ|*F*<sub>o</sub>|), *R*<sub>w</sub> (= [Σ*w*Δ<sup>2</sup>/Σ*wF*<sub>o</sub><sup>2</sup>]<sup>1/2</sup>) on |*F*| at convergence are cited (weights: (σ<sup>2</sup>(*F*) + 0.0004*F*<sup>2</sup>)<sup>-1</sup>). Neutral atom complex scattering factors were employed, within the context of various versions of the Xtal program

system.<sup>29</sup> Pertinent results are given below and in the tables and figures (displacement ellipsoid amplitudes, 20% (295 K) and 50% (153 K); hydrogen atom radii, 0.1 Å). Individual variations in procedure (etc.) are cited as “*variata*”.

**(a) Compound 1.**  $[\text{Ag}(\text{O}_2\text{N})(\text{PPh}_3)]_{(\infty)} \equiv \text{C}_{18}\text{H}_{15}\text{AgNO}_2\text{P}$ ,  $M = 416.2$ . Monoclinic, space group  $P2_1/c$  ( $C_{2h}^5$ , No. 14),  $a = 10.191(1)$  Å,  $b = 8.906(2)$  Å,  $c = 18.086(2)$  Å,  $\beta = 88.281(3)^\circ$ ,  $V = 1641$  Å<sup>3</sup>.  $D_c(Z=4) = 1.684$  g cm<sup>-3</sup>.  $\mu_{\text{Mo}} = 13.3$  cm<sup>-1</sup>; specimen,  $0.50 \times 0.25 \times 0.20$  mm; “ $T$ ”<sub>min,max</sub> = 0.60, 0.83.  $2\theta_{\text{max}} = 75^\circ$ ;  $N_t = 33\,205$ ,  $N = 8571$  ( $R_{\text{int}} = 0.026$ ),  $N_o = 7722$ ;  $R = 0.029$ ,  $R_w = 0.042$ ;  $|\Delta\rho_{\text{max}}| = 2.76(4)$  e Å<sup>-3</sup>.

*Variata.* Compound **15** below is isomorphous and was refined in the same cell and coordinate setting, with  $\beta$  conventionally obtuse, requiring  $\beta$  acute in the present.

**(b) Compound 2.**  $[\text{Ag}(\text{O}_2\text{N})(\text{PPh}_3)_2] \equiv \text{C}_{36}\text{H}_{30}\text{AgNO}_2\text{P}_2$ ,  $M = 678.5$ . Monoclinic, space group  $P2_1/c$ ,  $a = 11.908(2)$  Å,  $b = 18.364(2)$  Å,  $c = 14.761(2)$  Å,  $\beta = 101.121(2)^\circ$ ,  $V = 3167$  Å<sup>3</sup>.  $D_c(Z=4) = 1.423$  g cm<sup>-3</sup>.  $\mu_{\text{Mo}} = 7.7$  cm<sup>-1</sup>; specimen,  $0.4 \times 0.3 \times 0.1$  mm; “ $T$ ”<sub>min,max</sub> = 0.79, 0.89.  $2\theta_{\text{max}} = 58^\circ$ ;  $N_t = 30\,943$ ,  $N = 7988$  ( $R_{\text{int}} = 0.025$ ),  $N_o = 6648$ ;  $R = 0.030$ ,  $R_w = 0.037$ ;  $|\Delta\rho_{\text{max}}| = 0.55(4)$  e Å<sup>-3</sup>.

*Variata.* Cell and coordinate settings follow those of a previous room temperature determination.<sup>30</sup>

**(c) Compound 5.**  $[\text{Ag}(\text{O}_2\text{N})\{\text{P}(o\text{-tolyl})_3\}] \equiv \text{C}_{21}\text{H}_{21}\text{AgNO}_2\text{P}$ ,  $M = 458.3$ . Orthorhombic, space group  $Pbcn$  ( $D_{2h}^{14}$ , No. 60),  $a = 13.467(6)$  Å,  $b = 14.127(7)$  Å,  $c = 20.298(5)$  Å,  $V = 3862$  Å<sup>3</sup>.  $D_c(Z=8) = 1.576$  g cm<sup>-3</sup>.  $\mu_{\text{Mo}} = 11.4$  cm<sup>-1</sup>; specimen,  $0.34 \times 0.58 \times 0.67$  mm; “ $T$ ”<sub>min,max</sub> = 0.60, 0.72.  $2\theta_{\text{max}} = 60^\circ$ ;  $N_t = 11\,973$ ,  $N = 5628$  ( $R_{\text{int}} = 0.018$ ),  $N_o = 3556$ ;  $R = 0.036$ ,  $R_w = 0.044$ ;  $|\Delta\rho_{\text{max}}| = 0.6(1)$  e Å<sup>-3</sup>.

*Variata.* A quadrant of data was measured.

**(d) Compound 6.**  $[\text{Ag}(\text{O}_2\text{N})\{\text{P}(o\text{-tolyl})_3\}_2] \equiv \text{C}_{42}\text{H}_{42}\text{AgNO}_2\text{P}_2$ ,  $M = 762.6$ . Monoclinic, space group  $P2_1/n$  ( $C_{2h}^5$ , No. 14 (variant)),  $a = 12.516(2)$  Å,  $b = 22.409(4)$  Å,  $c = 13.020(2)$  Å,  $\beta = 92.183(4)^\circ$ ,  $V = 3649$  Å<sup>3</sup>.  $D_c(Z=4) = 1.388$  g cm<sup>-3</sup>.  $\mu_{\text{Mo}} = 6.8$  cm<sup>-1</sup>; specimen,  $0.35 \times 0.28 \times 0.18$  mm; “ $T$ ”<sub>min,max</sub> = 0.73, 0.86.  $2\theta_{\text{max}} = 75^\circ$ ;  $N_t = 69\,781$ ,  $N = 18\,310$  ( $R_{\text{int}} = 0.036$ ),  $N_o = 12\,855$ ;  $R = 0.036$ ,  $R_w = 0.040$ ;  $|\Delta\rho_{\text{max}}| = 1.30(7)$  e Å<sup>-3</sup>. ( $x, y, z, U_{\text{iso}}/H$ ) constrained at estimates.

**(e) Compound 11.**  $[\text{Ag}(\text{O}_2\text{N})\{\text{P}(p\text{-F-C}_6\text{H}_4)_3\}] \equiv \text{C}_{36}\text{H}_{24}\text{Ag}_2\text{F}_6\text{N}_2\text{O}_4\text{P}_2$ ,  $M = 470.1$ . Monoclinic, space group  $C2/c$  ( $C_{2h}^6$ , No. 15),  $a = 13.333(2)$  Å,  $b = 11.599(4)$  Å,  $c = 22.787(3)$  Å,  $\beta = 99.748(3)^\circ$ ,  $V = 3473$  Å<sup>3</sup>.  $D_c(Z=4 \text{ dimers}) = 1.798$  g cm<sup>-3</sup>.  $\mu_{\text{Mo}} = 13.0$  cm<sup>-1</sup>; specimen,  $0.20 \times 0.20 \times 0.11$  mm; “ $T$ ”<sub>min,max</sub> = 0.72, 0.86.  $2\theta_{\text{max}} = 75^\circ$ ;  $N_t = 29\,249$ ,  $N = 8982$  ( $R_{\text{int}} = 0.027$ ),  $N_o = 6697$ ;  $R = 0.030$ ,  $R_w = 0.044$ ;  $|\Delta\rho_{\text{max}}| = 1.17(6)$  e Å<sup>-3</sup>.

**(f) Compound 12.**  $[\text{Ag}(\text{O}_2\text{N})(\text{Pcy}_3)_2] \equiv \text{C}_{36}\text{H}_{66}\text{AgNO}_2\text{P}_2$ ,  $M = 714.8$ . Triclinic, space group  $P\bar{1}$  ( $C_i^1$ , No. 2),  $a = 9.105(4)$  Å,  $b = 9.821(2)$  Å,  $c = 23.437(3)$  Å,  $\alpha = 94.53(1)^\circ$ ,  $\beta = 96.67(2)^\circ$ ,  $\gamma = 116.11(2)^\circ$ ,  $V = 1849$  Å<sup>3</sup>.  $D_c(Z=2) = 1.284$  g cm<sup>-3</sup>.  $\mu_{\text{Mo}} = 6.6$  cm<sup>-1</sup>; specimen,  $0.40 \times 0.36 \times 0.16$  mm; “ $T$ ”<sub>min,max</sub> = 0.80, 0.90.  $2\theta_{\text{max}} = 50^\circ$ ;  $N_t = 10\,672$ ,  $N = 6484$  ( $R_{\text{int}} = 0.033$ ),  $N_o = 5416$ ;  $R = 0.042$ ,  $R_w = 0.049$ ;  $|\Delta\rho_{\text{max}}| = 0.89(3)$  e Å<sup>-3</sup>.

*Variata.* A second hemisphere of data was measured to  $2\theta_{\text{max}} = 40^\circ$  and merged. The cell and coordinate setting follows that of the parent nitrate counterpart,<sup>31</sup> similar disorder being observed in one of the substituent rings.

**(g) Compound 13.**  $[\text{Ag}(\mu\text{-ONO})(\text{AsPh}_3)_2]_2 \equiv \text{C}_{72}\text{H}_{60}\text{Ag}_2\text{As}_4\text{N}_2\text{O}_4$ ,  $M = 1532.7$ . Triclinic, space group  $P\bar{1}$ ,  $a = 18.5301(7)$  Å,  $b = 14.0840(5)$  Å,  $c = 14.1379(5)$  Å,  $\alpha = 61.087(1)^\circ$ ,  $\beta = 79.547(1)^\circ$ ,  $\gamma = 77.195(1)^\circ$ ,  $V = 3138$  Å<sup>3</sup>.  $D_c(Z=1 \text{ dimer}) = 1.622$  g cm<sup>-3</sup>.  $\mu_{\text{Mo}} = 27.7$  cm<sup>-1</sup>; specimen,  $0.15 \times 0.15 \times 0.12$  mm; “ $T$ ”<sub>min,max</sub> = 0.69, 0.83.  $2\theta_{\text{max}} = 75^\circ$ ;  $N_t = 65\,568$ ,  $N = 32\,417$  ( $R_{\text{int}} = 0.030$ ),  $N_o = 21\,311$ ;  $R = 0.030$ ,  $R_w = 0.027$ ;  $|\Delta\rho_{\text{max}}| = 1.8(1)$  e Å<sup>-3</sup>. ( $x, y, z, U_{\text{iso}}/H$ ) constrained at estimates.

*Variata.* The complex is isomorphous with its  $\text{Ph}_3\text{Sb}/\text{AgCl}$ ,  $\text{Br}$ , and  $\text{I}$  counterparts and is presented in that cell and coordinate setting,<sup>32</sup> the numbering of ligands 1 and 2 of molecule 2 being interchanged.

**(h) Compound 14.**  $[\text{Ag}(\text{O}_2\text{N})(\text{AsPh}_3)_3] \cdot 2\text{MeCN} \equiv \text{C}_{58}\text{H}_{51}\text{AgAs}_3\text{N}_3\text{O}_2$ ,  $M = 1154.7$ . Triclinic, space group  $P\bar{1}$ ,  $a = 13.391(3)$  Å,  $b = 13.839(3)$  Å,  $c = 14.119(3)$  Å,  $\alpha = 84.994(4)^\circ$ ,  $\beta = 89.131(4)^\circ$ ,  $\gamma = 77.364(4)^\circ$ ,  $V = 2453$  Å<sup>3</sup>.  $D_c(Z=2) = 1.508$  g cm<sup>-3</sup>.  $\mu_{\text{Mo}} = 23.8$  cm<sup>-1</sup>; specimen,  $0.27 \times 0.03 \times 0.03$  mm; “ $T$ ”<sub>min,max</sub> = 0.74, 0.91.  $2\theta_{\text{max}} = 58^\circ$ ;  $N_t = 24\,593$ ,  $N = 12\,458$  ( $R_{\text{int}} = 0.054$ ),  $N_o = 6605$ ;  $R = 0.055$ ,  $R_w = 0.051$ ;  $|\Delta\rho_{\text{max}}| = 1.2(1)$  e Å<sup>-3</sup>. ( $x, y, z, U_{\text{iso}}/H$ ) constrained at estimates.

*Variata.* C and N of the solvent residues were refined with isotropic displacement parameter forms. The cell and coordinate setting follows that of the  $\text{CuCl}:\text{SbPh}_3$  (1:3) chloroform solvate<sup>33</sup> (see below).

**(i) Compound 15.**  $[\text{Ag}(\text{O}_2\text{N})(\text{SbPh}_3)]_{(\infty)} \equiv \text{C}_{18}\text{H}_{15}\text{AgNO}_2\text{Sb}$ ,  $M = 506.9$ . Monoclinic, space group  $P2_1/c$ ,  $a = 9.939(1)$  Å,  $b = 9.2233(9)$  Å,  $c = 18.983(2)$  Å,  $\beta = 90.064(2)^\circ$ ,  $V = 1740$  Å<sup>3</sup>.  $D_c(Z=4) = 1.935$  g cm<sup>-3</sup>.  $\mu_{\text{Mo}} = 26.9$  cm<sup>-1</sup>; specimen,  $0.35 \times 0.15 \times 0.10$  mm; “ $T$ ”<sub>min,max</sub> = 0.63, 0.83.  $2\theta_{\text{max}} = 75^\circ$ ;  $N_t = 36\,047$ ,  $N = 9091$  ( $R_{\text{int}} = 0.037$ ),  $N_o = 7048$ ;  $R = 0.028$ ,  $R_w = 0.033$ ;  $|\Delta\rho_{\text{max}}| = 1.9(1)$  e Å<sup>-3</sup>.

**(j) Compound 16.**  $[\text{Ag}(\text{O}_2\text{N})(\text{SbPh}_3)_3] \equiv \text{C}_{54}\text{H}_{45}\text{AgNO}_2\text{Sb}_3$ ,  $M = 1213.1$ . Monoclinic, space group  $P2_1/c$ ,  $a = 19.1405(9)$  Å,  $b = 14.2688(7)$  Å,  $c = 17.7907(9)$  Å,  $\beta = 100.050(2)^\circ$ ,  $V = 4784$  Å<sup>3</sup>.  $D_c(Z=4) = 1.684$  g cm<sup>-3</sup>.  $\mu_{\text{Mo}} = 21.2$  cm<sup>-1</sup>; specimen,  $0.35 \times 0.14 \times 0.11$  mm; “ $T$ ”<sub>min,max</sub> = 0.55, 0.88.  $2\theta_{\text{max}} = 75^\circ$ ;  $N_t = 98\,748$ ,  $N = 25\,089$  ( $R_{\text{int}} = 0.048$ ),  $N_o = 16\,028$ ;  $R = 0.032$ ,  $R_w = 0.030$ ;  $|\Delta\rho_{\text{max}}| = 1.0(1)$  e Å<sup>-3</sup>.

*Variata.* The cell and coordinate setting follow those of isomorphous unsolvated  $[\text{AgI}(\text{PPh}_3)_3]$ <sup>34</sup> (see below); for a preliminary determination carried out at ca. 295 K on a single counter instrument,  $a = 19.356(7)$  Å,  $b = 14.236(3)$  Å,  $c = 17.919(4)$  Å,  $\beta = 99.90(2)^\circ$ ,  $V = 4895$  Å<sup>3</sup>.

## Results and Discussion

**Syntheses.** From the interaction of 1 equiv of  $\text{AgNO}_2$  and 1, 2, 3, or 4 equiv of tertiary monophosphine  $\text{PPh}_3$ ,  $\text{P}(o\text{-tolyl})_3$ ,  $\text{P}(m\text{-tolyl})_3$ ,  $\text{P}(p\text{-tolyl})_3$ ,  $\text{P}(p\text{-F-C}_6\text{H}_4)_3$ , or  $\text{Pcy}_3$  in ethanol at 60 °C, complexes **1–12** have been respectively obtained in high yield (eq 1):



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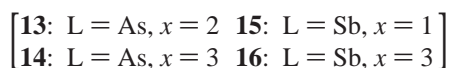
(33) Rheingold, A. L.; Fountain, M. E. *J. Cryst. Spectrosc. Res.* **1984**, 14, 549–557.

(34) Engelhardt, L. M.; Healy, P. C.; Patrick, V. A.; White, A. H. *Aust. J. Chem.* **1987**, 40, 1873–1880.

<b>1</b> : R = Ph, $x = 1$	<b>5</b> : R = <i>o</i> -tolyl, $x = 1$	<b>9</b> : R = <i>m</i> -tolyl, $x = 3$
<b>2</b> : R = Ph, $x = 2$	<b>6</b> : R = <i>o</i> -tolyl, $x = 2$	<b>10</b> : R = <i>p</i> -tolyl, $x = 3$
<b>3</b> : R = Ph, $x = 3$	<b>7</b> : R = <i>m</i> -tolyl, $x = 1$	<b>11</b> : R = <i>p</i> -F-C <sub>6</sub> H <sub>4</sub> , $x = 1$
<b>4</b> : R = Ph, $x = 4$	<b>8</b> : R = <i>m</i> -tolyl, $x = 2$	<b>12</b> : R = cy, $x = 2$

The 1:2 and 1:3 adducts **6** and **9**, respectively, have been obtained also when this reaction was conducted in excess of the P-donor (>4 equiv), whereas when equimolar quantities of AgNO<sub>2</sub> and P(*p*-tolyl)<sub>3</sub> or Pcy<sub>3</sub> were employed, no 1:1 adduct was obtained, deposition of metallic silver rapidly occurring, even if the reaction was carried out in the dark. The same behavior, which does not seem to correlate with any property of the P-donor, has been previously described in the literature.<sup>22</sup> The reaction between P(*p*-F-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub> and AgNO<sub>2</sub> afforded the 1:1 adduct **11** also in excess of phosphine.

From the interaction of AgNO<sub>2</sub> with 2 mol of AsPh<sub>3</sub> or 1 mol of SbPh<sub>3</sub>, in ethanol at 60 °C, complexes **13** and **15** have been obtained respectively in high yield (eq 2):



From the interaction of 1 equiv of AgNO<sub>2</sub> with 3 equiv of AsPh<sub>3</sub> or SbPh<sub>3</sub>, in ethanol at room temperature, complexes **14** and **16** have been obtained respectively in high yield (eq 2). These compounds were obtained also when excesses of the phosphorus donors were employed (>3 equiv).

All derivatives **1–16** show good solubility in chlorinated solvents, acetonitrile, acetone, and dimethyl sulfoxide (DMSO), but they are insoluble in diethyl ether, alcohols, aromatics, and aliphatic hydrocarbons. They are nonelectrolytes in CH<sub>2</sub>-Cl<sub>2</sub> solution, the  $\Lambda_{\text{mol}}$  values being always lower than 4.5  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . In the case of the 1:4 adduct **4** this could be due to formation in solution of a solvated ion pair or, alternatively, to dissociation of PPh<sub>3</sub> ligands from the silver with consequent reassociation of the counterion (see below).

**Spectroscopy.** The infrared spectra of derivatives **1–16** (see Experimental Section) are consistent with the formulations proposed, showing all of the bands required by the presence of the nitrito group and of the phosphorus donor,<sup>35,36</sup> the phosphine ligand absorptions being only slightly shifted with respect to those of the free donors. In the far-IR spectra of all derivatives **1–12** we assigned, on the basis of a previous report on phosphino copper(I) derivatives,<sup>22</sup> the broad absorptions near 500 cm<sup>-1</sup> and those at 400–450 cm<sup>-1</sup> to Whiffen's  $\gamma$  and  $t$  vibrations, respectively, whereas some bands in the region 300–400 cm<sup>-1</sup>, similar to those described in the literature for some silver(I) nitrate derivatives,<sup>22b</sup> can be tentatively assigned to  $\nu(\text{Ag}-\text{O})$  vibrations.

**Table 1.** <sup>31</sup>P{<sup>1</sup>H} NMR Data for R<sub>3</sub>P Containing Complexes

compd	$\delta(^{31}\text{P})$ , 293 K, ppm	$^1J(^{31}\text{P}-\text{Ag})$ , Hz	$\delta(^{31}\text{P})$ , ppm	$^1J(^{31}\text{P}-^x\text{Ag})$ , Hz
<b>1</b>	16.5 d br	621	16.1 dd <sup>a</sup>	666 ( $x = 107$ ); 769 ( $x = 109$ )
<b>2</b>	9.3 s		8.95 dd <sup>a</sup>	413 ( $x = 107$ ); 476 ( $x = 109$ )
<b>3</b>	5.2 s		5.6 d <sup>a</sup>	228
			32.2 s	
<b>4</b>	4.7 br		5.6 d <sup>a</sup>	228
			32.2 s	
<b>5</b>	-17.7 d br		-19.2 <sup>b</sup>	695
<b>6</b>	-19.0 br		-11.0 br <sup>b</sup>	
<b>7</b>	10.5 br		10.0 d <sup>a</sup>	660
<b>8</b>	9.5 s br, 29.9 s		8.8 dd <sup>a</sup>	411 ( $x = 107$ ); 475 ( $x = 109$ )
			32.2 s	
<b>9</b>	4.9 s 29.9 s		5.1 d <sup>a</sup>	239
			10.4 s br	
			32.3 s	
<b>10</b>	2.9 s 29.7 s		3.7 d br <sup>a</sup>	193
<b>11</b>	12.8 d	643		
<b>12</b>	28.9 d 50.6 s	435	28.4 <sup>a</sup>	425 ( $x = 107$ ); 491 ( $x = 109$ )

<sup>a</sup>  $T = 218 \text{ K}$ . <sup>b</sup>  $T = 223 \text{ K}$ .

In the <sup>1</sup>H NMR spectra of **1–16** in CDCl<sub>3</sub> (see Experimental Section), the signals due to the triorganophosphines, -arsines, and -stibines are in the range of 6.80–7.80 ppm, showing a different pattern of signals with respect to those found for the free donors, confirming the existence, at least partial, of the complexes in solution. The room temperature <sup>1</sup>H NMR spectra of derivatives **5–9** exhibit only one set of signals for the methyl protons of the P-donor. On cooling the CDCl<sub>3</sub> solutions of **5–9** to 223 K, some weak additional signals appeared, typical of the free donor, suggesting partial dissociation of the complexes.

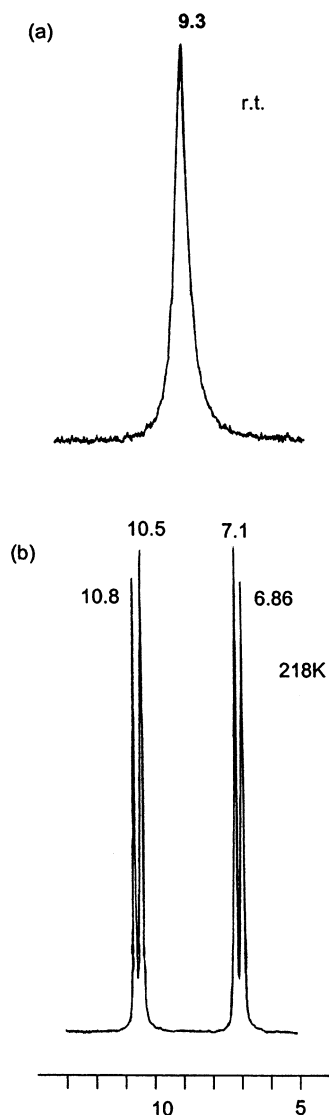
<sup>31</sup>P chemical shifts (CDCl<sub>3</sub> solution) and <sup>31</sup>P–Ag coupling constants for derivatives **1–12**, are reported in Table 1. They have been found to be dependent on the dilution of the solutions. Our experiments have been carried out at a concentration of 0.02 mol/L.

The <sup>31</sup>P NMR spectrum at room temperature of complex **6** consists of a broad singlet, presumably due to rapid exchange equilibria, also unresolved in the spectrum recorded at 218 K. Whereas for derivatives **2–4** and **7–10**, for which at room temperature only a broad singlet was found, exchange is quenched at lower temperature, and one and/or two unresolved doublets or resolved pairs of doublets, arising from coupling between the phosphorus and silver atom, are observed in the accessible temperature range. In particular in the spectra of derivatives **1**, **2**, **8**, and **12** typical pairs of doublets, due to  $^1J(^{31}\text{P}-^{107}\text{Ag})$  and  $^1J(^{31}\text{P}-^{109}\text{Ag})$  coupling, are resolved at 218 K and the observed  $^1J(^{107}\text{Ag})/^1J(^{109}\text{Ag})$  ratio is in good agreement with that calculated from the gyromagnetic ratio of the Ag nuclei  $\gamma(^{107}\text{Ag})/\gamma(^{109}\text{Ag})$  (Figure 2).<sup>37</sup> For derivatives **1**, **5**, **11**, and **12** such doublets were also observed at room temperature, suggesting that rapid exchange equilibria are not operative in the cases of 1:1 adducts or sterically hindered phosphines. The signal due to

(35) (a) Shobatake, K.; Postmus, C.; Ferraro, J. F.; Nakamoto, K. *Appl. Spectrosc.* **1969**, *23*, 12–16. (b) Bradbury, J.; Forest, K. P.; Nuttall, R. H.; Sharp, D. W. A. *Spectrochim. Acta* **1967**, *23*, 2701–2704.  
(36) (a) Deacon, G. B.; Jones, R. A. *Aust. J. Chem.* **1963**, *16*, 499–503. (b) Perreault, D.; Drouin, M.; Michel, A.; Miskowski, V. M.; Schaefer, W. P.; Harvey, P. D. *Inorg. Chem.* **1992**, *31*, 695–702.

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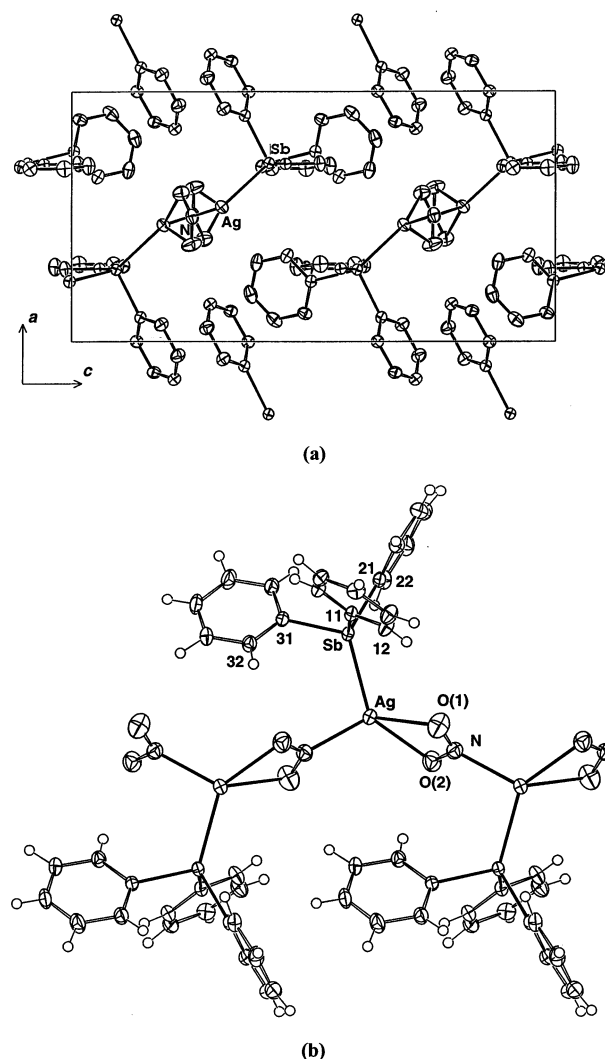


**Figure 2.**  $^{31}\text{P}$  NMR spectra of derivative **2** at room temperature (a) and 218 K (b).

each free phosphine is upfield with respect to the corresponding silver(I) complex. The magnitudes of  $\Delta$  ( $\Delta = \delta^{31}\text{P}_{\text{complex}} - \delta^{31}\text{P}_{\text{free ligand}}$ ) and the coupling constants decrease with the decreasing basicity, also correlating with steric bulk of the ligands.

The chemical shifts and  $^1J(\text{Ag}-^{31}\text{P})$  coupling constants are strongly dependent on the stoichiometric ratio  $\text{Ag}/\text{P}$  ( $\text{P} = \text{triorganophosphine}$ ). The higher  $^1J(\text{Ag}-^{31}\text{P})$  values found for derivatives **1**, **5**, **7**, and **11**, typical of monophosphine adducts, may be rationalized in terms of formation of a mononuclear  $[\text{Ag}(\text{NO}_2)\text{PR}_3]$  fragment, containing an  $\text{sp}$  hybridized silver, arising from the dissociation of the poly- and dinuclear species, respectively.<sup>38</sup> The derivatives **2**, **8**, and **12** exhibit  $^1J(\text{Ag}-^{31}\text{P})$  values, consistent with the presence of two phosphines on a two- or three-coordinate silver atom. The derivatives **3**, **4**, and **9** present identical low-temperature  $^{31}\text{P}$  spectra with  $^1J(\text{Ag}-^{31}\text{P})$  values in the range of 228–240 Hz, typical of compounds with an  $\text{AgP}_3$  or  $\text{AgP}_4$  central core.<sup>39</sup>

The positive electrospray mass spectra of complexes **1–16** (the most relevant data are reported in the Experimental



**Figure 3.** (a) Unit cell contents of  $\text{AgNO}_2:\text{SbPh}_3$  (1:1)<sub>(\infty)</sub> (**15**), down  $b$  (the polymer axis) (cf. refs 19 and 20 (see text)). (b) Single strand of the polymer. (The  $\text{PPh}_3$  adduct (**1**) is isomorphous).

Section) indicate that these derivatives undergo loss of the anionic  $\text{NO}_2^-$  ligand. The isotopic distribution of these species is in accord with the calculated composition.

The aggregation behavior is strongly dependent on the stoichiometry of the adducts and the solvent employed: for

- (38) (a) Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1970**, *92*, 4114–4115. (b) Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 6386–6391. (c) van der Ploeg, A. F. M. J.; van Koten, G.; Spek, A. L. *Inorg. Chem.* **1979**, *18*, 1052–1060. (d) van der Ploeg, A. F. M. J.; van Koten, G. *Inorg. Chim. Acta* **1981**, *51*, 225–239. (e) Barrow, M.; Bürgi, H.-B.; Camalli, M.; Caruso, F.; Fischer, E.; Venanzi, L. M.; Zambonelli, L. *Inorg. Chem.* **1983**, *22*, 2356–2362. (f) Socol, S. M.; Verdake, R. A. *Inorg. Chem.* **1984**, *23*, 3487–3493. (g) Socol, S. M.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* **1984**, *23*, 88–94. (h) Barron, P. F.; Dyason, J. C.; Healy, P. C.; Engelhardt, L. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1986**, 1965–1970. (i) Camalli, M.; Caruso, F. *Inorg. Chim. Acta* **1987**, *127*, 209–213. (j) Dean, P. A.; W. Vittal, J. J.; Srivastava, R. S. *Can. J. Chem.* **1987**, *65*, 2628–2633. (k) Camalli, M.; Caruso, F. *Inorg. Chim. Acta* **1988**, *144*, 205–211. (l) Obendorf, D.; Probst, M.; Peringer, P.; Falk, A.; Müller, N. *J. Chem. Soc., Dalton Trans.* **1988**, 1709–1711. (m) Bowmaker, G. A.; Effendy; Harvey, P. J.; Healy, P. C.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1996**, 2459–2466.
- (39) (a) Di Bernardo, P.; Dolcetti, G.; Portauova, R.; Tolazzi, M.; Tomat, G.; Zanonato P. *Inorg. Chem.* **1990**, *29*, 2859–2862. (b) Harker, C. S. W.; Tiekink, E. R. T. *J. Coord. Chem.* **1990**, *21*, 287–293.

**Table 2.** Selected Geometries: AgNO<sub>2</sub>:EPh<sub>3</sub> (1:1) (E = P, Sb (**1**, **11**, **15**))

(a) AgNO <sub>2</sub> :EPh <sub>3</sub> (1:1) <sub>(∞)</sub> (E = P, Sb) ( <b>1</b> , <b>15</b> ) <sup>a</sup>			
Distances (Å)			
Ag–E	2.3918(4), 2.6423(3)	Ag–O(1)	2.610(1), 2.498(2)
Ag–N'	2.563(1), 2.365(2)	Ag–O(2)	2.298(1), 2.392(2)
N–O(1)	1.231(2), 1.209(3)	N–O(2)	1.267(2), 1.245(3)
Angles (deg)			
E–Ag–O(1)	119.06(3), 108.75(5)	O(1)–Ag–O(2)	114.71(4), 123.54(7)
E–Ag–O(2)	152.75(3), 139.64(5)	N'–Ag–O(1)	99.87(4), 116.67(7)
E–Ag–N'	106.90(3), 103.60(5)	N'–Ag–O(2)	50.45(4), 50.74(6)
O(1)–N–O(2)	115.4(1), 117.4(2)	O(1)–N–Ag''	116.1(1), 120.3(2)
Ag–O(1)–N	89.88(9), 93.8(1)	O(2)–N–Ag''	128.34(9), 121.5(2)
Ag–O(2)–N	104.26(9), 98.0(1)		
(b) AgNO <sub>2</sub> :( <i>p</i> -F-C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> P (1:1) <sub>2</sub> ( <b>11</b> ) <sup>b</sup>			
Distances (Å)			
Ag–P	2.3571(4)	Ag–O(1')	2.636(2)
Ag–O(1)	2.399(1)	N–O(1)	1.258(2)
Ag–O(2)	2.342(1)	N–O(2)	1.251(3)
Ag...Ag'	3.9821(6)		
Angles (deg)			
P–Ag–O(1)	147.07(4)	O(1)–Pg–O(2)	52.73(6)
P–Ag–O(2)	148.21(5)	O(1)–Ag–O(1')	75.56(5)
P–Ag–O(1')	111.58(3)	O(2)–Ag–O(1')	95.92(6)
O(1)–N–O(2)	114.2(2)	Ag–O(1)–N	95.1(1)
Ag–O(1)–Ag'	104.44(6)	Ag–O(2)–N	98.0(1)
		Ag–O(1')–N	107.0(1)

<sup>a</sup> Primed and doubly primed atoms are glide related (by  $1 - x, y - 1/2, 1/2 + z$ ;  $1 - x, 1/2 + y, 1/2 + z$ ). Ag, Ag'' lie out of the NO<sub>2</sub> plane by 0.103(6), –0.169(7) Å (E = P), 0.10(1), –0.36(1) Å (E = Sb).  $\tau(\text{Ag} - \text{P} - \text{C}(n1) - \text{C}(\text{ortho}), n = 1 - 3)$  are 41.2(1), 57.0(1), 51.8(1)° (**1**); 44.0(2), 60.5(2), 44.8(2)° (**15**).  
<sup>b</sup> Primed atoms are inversion related. The Ag<sub>2</sub>O(1)<sub>2</sub>/NO<sub>2</sub> interplanar dihedral angle is 109.0(1)°.  $\tau(\text{Ag} - \text{P} - \text{C}(n1) - \text{C}(n6), n = 1 - 3)$  are 52.8(1), 27.2(1), 32.2(2)°.

most of the systems investigated aggregation of phosphine, stibine, and arsine donors with Ag cations is significantly present in acetonitrile, also at concentrations of 10<sup>–3</sup> M. Aggregates containing a single silver(I) ion dominate significantly over adducts containing two silver atoms.

Under our conditions in acetonitrile also a species is noted at *m/z* 147.9, which corresponds to a 1:1 adduct of Ag(I) with the solvent. Although far less abundant, the higher adduct [Ag(MeCN)<sub>2</sub>]<sup>+</sup> is also observed at *m/z* 188.9. The predominant peaks corresponding to ions containing silver(I) are those that originate from the successive addition of ER<sub>3</sub> ligands and formation of [Ag(ER<sub>3</sub>)<sub>*n*</sub>]<sup>+</sup> ions (*n* = 1 or 2). Other relevant peaks present in the spectra of **1–7** and **12–16** are attributed to the formation of the bimetallic species [Ag<sub>2</sub>(NO<sub>2</sub>)(ER<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. These ions undoubtedly contain bridging nitrito groups. A careful inspection of the data reveals that the species [Ag(ER<sub>3</sub>)<sub>2</sub>]<sup>+</sup> is always the more abundant species in the gas phase.

Acetonitrile itself behaves as ligand toward silver(I) ions, and this is manifest in evidence for the formation of the ions [Ag(MeCN)]<sup>+</sup>, [Ag(MeCN)<sub>2</sub>]<sup>+</sup>, and [Ag(MeCN)(ER<sub>3</sub>)]<sup>+</sup>. However, for the various species with coordination numbers of two or three, evidence for species containing coordinated acetonitrile ligands was insignificant, suggesting that MeCN cannot compete in coordinating ability with ER<sub>3</sub> donors.

The negative electrospray mass spectra are always dominated by the presence of molecular peaks due to [AgCl<sub>2</sub>]<sup>–</sup>, [Ag(NO<sub>2</sub>)<sub>2</sub>]<sup>–</sup>, [Ag<sub>2</sub>Cl<sub>2</sub>(NO<sub>2</sub>)]<sup>–</sup>, and [Ag<sub>2</sub>(NO<sub>2</sub>)<sub>3</sub>]<sup>–</sup>. The absence of [Ag<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> and the abundance of [Ag(NO<sub>2</sub>)<sub>2</sub>]<sup>–</sup> species can be understood as a consequence of the ion distribution between both positive and negative ion ensembles.

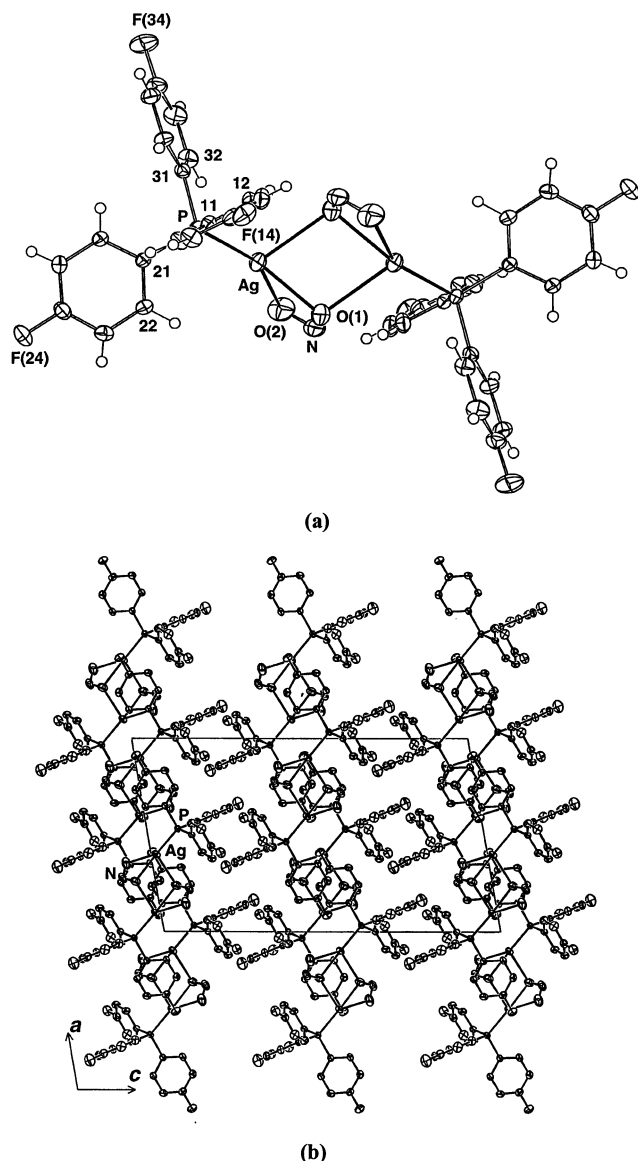
It is likely that quantitative ESI-MS does not represent the relative distribution of species in solution, charged species present in the gas phase being only detected; however, systematic studies of solution aggregation by ESI-MS should yield important information regarding nucleation prior to crystallization such that the process of self-assembly may be better understood.

**X-ray Discussion.** The present array of structural studies requires consideration alongside a series of analogues previously structurally defined, most notably (a) other AgNO<sub>2</sub>:ER<sub>3</sub> adducts and (b) other AgX:R<sub>3</sub>E adducts of similar form. Complexes pertinent to (a) are few in number; more generally, an appreciable proportion of nitrite complexes presents difficulties with respect to the description of the anion, which is often ill-defined, exhibiting displacement envelopes of unreasonably large amplitude, even at low temperature, indicative of high “thermal” motion and/or disordered components contained within the envelopes, possibly indicative of some presence of alternative diverse coordination modes. Whatever the explanation, derivative associated geometrical parameters should in such circumstances be considered circumspectly. Unsurprisingly, in a number of cases, their crystals are isomorphous with various nitrate counterparts and, not infrequently, beyond (see below). Pertinent to the present work, we note the structure determination of AgNO<sub>2</sub>:PPh<sub>3</sub> (1:2) (unsolvated)<sup>30</sup> and its dichloromethane solvate,<sup>40</sup> the latter isomorphous with CuX·(Ph<sub>3</sub>P)<sub>2</sub>·1/2S (X = Cl, Br/S = C<sub>6</sub>H<sub>6</sub>; X = BH<sub>4</sub>/S = py).<sup>32</sup>

Among the AgX:R<sub>3</sub>E analogues extensive surveys are recently available for Ph<sub>3</sub>E adducts of 1:1,<sup>23,41</sup> 1:2,<sup>32</sup> 1:3,<sup>42</sup>

(40) Belaj, F.; Trnoska, A.; Nachbaur, E., *Acta Crystallogr., Sect C* **1998**, *54*, 727–728.

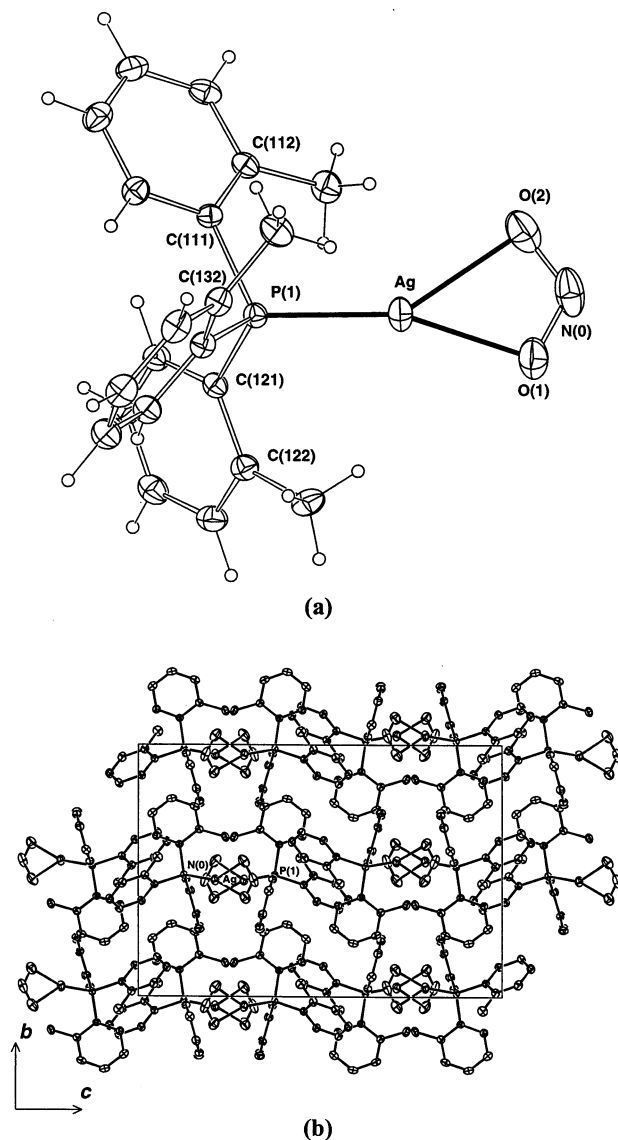




**Figure 4.** (a) Dimer of  $\text{AgNO}_2 \cdot \text{P}(p\text{-C}_6\text{H}_4\text{F})_3$  (1:1)<sub>2</sub> (11) projected normal to the central  $\text{Ag}_2\text{O}_2$  plane. (b) Unit cell contents projected down  $b$ .

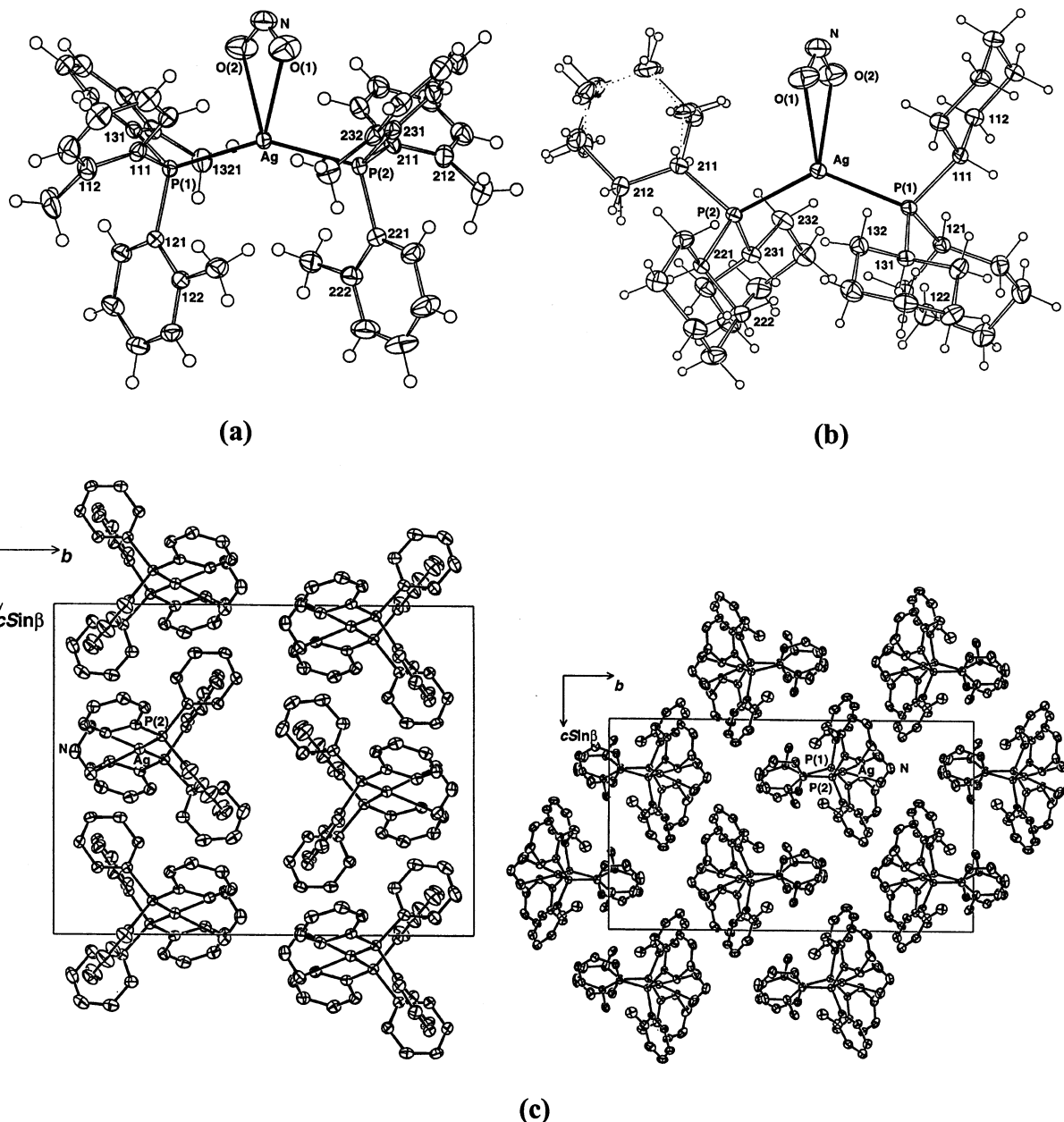
1:4<sup>43</sup> stoichiometry. Among the 1:1 complexes, relative to the remainder, the  $\text{X} = \text{halide}$  adducts are more clearly demarcated from the structural types associated with the oxyanions, the former adopting tetrameric “cubane” or “step” structures<sup>23</sup> and the latter oxygen-bridged one-dimensional polymers for, in particular, the nitrates.<sup>41</sup> Adducts  $\text{AgNO}_3 \cdot \text{EPh}_3$  (1:1)<sub>( $\infty$ )</sub> have been defined for all  $\text{E} = \text{P}$ ,<sup>19</sup>  $\text{As}$ ,<sup>44</sup> and  $\text{Sb}$ ,<sup>41</sup> the  $\text{E} = \text{P}$  and  $\text{As}$  adducts being isomorphous and the  $\text{E} = \text{Sb}$  not so; although the polymer is of similar form, the role of the nitrate is to bridge successive silver atoms by coordination through one oxygen, commonly bridging, and

- (41) Effendy; Kildea, J. D.; White, A. H. *Aust. J. Chem.* **1997**, *50*, 671–674.  
 (42) Effendy; Kildea, J. D.; White, A. H. *Aust. J. Chem.* **1997**, *50*, 587–604 (corrigendum: Effendy; Kildea, J. D.; White, A. H. *Aust. J. Chem.* **1998**, *51*, 90).  
 (43) 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*, 539–552.  
 (44) Baker, L.-J.; Bowmaker, G. A.; Camp, D.; Effendy; Healy, P. C.; Schmidbaur, H.; Stieglmann, O.; White, A. H. *Inorg. Chem.* **1992**, *31*, 3656–3662.



**Figure 5.** (a) Single molecule of  $\text{AgNO}_2 \cdot \text{P}(o\text{-tolyl})_3$  (1:1) (5). (b) Unit cell contents, projected down  $a$ .

the others completing chelates to either side ( $\text{E} = \text{P}$ ,  $\text{As}$ ) or, with a pair of oxygens chelating one silver atom, the remaining oxygen bridging to a successive one. The latter form, with the nitrogen lone pair replacing the third oxygen, is found in the arrays herein described for the 1:1 silver(I) nitrite adducts with  $\text{EPh}_3$  ( $\text{E} = \text{P}$  (1) and  $\text{Sb}$  (15) (we have been unable to obtain satisfactorily crystalline the  $\text{E} = \text{As}$  analogue), the two adducts being isomorphous in a cell (Figure 3), which is very similar in proportions to that found for  $\text{AgNO}_3 \cdot \text{P}$ ,  $\text{AsPh}_3$  (1:1)<sub>( $\infty$ )</sub> (monoclinic,  $P2_1/c$ ,  $a \sim 10.7$  Å,  $b \sim 18.6$  Å,  $c \sim 9.1$  Å,  $\beta \sim 100^\circ$ ,  $Z = 4$ ),<sup>19,20</sup> except that  $b$  and  $c$  are interchanged (a not infrequent occurrence in  $P2_1/c$  pairs of polymorphs); the propagator of the polymer in the latter is a 2-fold screw (as in the present pair), cf. a glide plane in the stibine adduct. In all cases, one formula unit, devoid of crystallographic symmetry comprises the asymmetric unit of the structure. While it might reasonably be surmised that the missing arsine analogue of the present should also be isomorphous, history has shown the need to



**Figure 6.** (a) Single molecule of  $\text{AgNO}_2 \cdot \text{P}\{\text{o-tolyl}\}_3$  (1:2) (**6**). (b) Single molecule of  $\text{AgNO}_2 \cdot \text{Pcy}_3$  (**12**) (1:2) (unit cell contents are depicted in ref 44). (c) Unit cell contents of  $\text{AgNO}_2 \cdot \text{PR}_3$  (1:2),  $\text{PR}_3 =$  (i)  $\text{P}\{\text{o-tolyl}\}_3$  (**6**) and (ii)  $\text{PPh}_3$ , (**2**), projected down  $a$  in both cases.

treat such comparative/extrapolative prognostications circumspectly. The geometries of the two present adducts are compared in Table 2, the increased Ag–E distance in the stibine adduct offset by shortened Ag–N', with concomitant effects on the N–O distances; the mean Ag–O distance remains remarkably constant (2.45 Å, E = P, Sb (both)), although the two distances are much more nearly equivalent in the stibine adduct. In the nitrates, Ag–P, Sb are 2.369–(6), 2.6453(9) Å. By the above standards, the 1:1 adduct of  $\text{AgNO}_2$  with  $(p\text{-F-C}_6\text{H}_4)_3\text{P}$ , **11**, is unusual, being binuclear; the nitrite chelates the  $(\text{R}_3\text{E})\text{Ag}$  array somewhat unsymmetrically (Table 2; Figure 4a), the oxygen associated with the longer of the two Ag–O bonds, O(1), interacting with the silver atom of an inversion related moiety to form a dimer, with the planar components of the structure pertinent to crystal packing (Figure 4b).

*o*-Tolyl<sub>3</sub>P is a sterically more hindered base than  $\text{PPh}_3$ , and we find that in its 1:1 adduct with  $\text{AgNO}_2$ , **5**, a mononuclear form, one  $[\text{Ag}(\text{O}_2\text{N})\text{P}(\text{o-tolyl})_3]$  molecule, Figure 5a, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure, the aromatic substituents disposed umbrella-like about the Ag–P bond and the nitrite *O,O'*-bidentate a rare example of a *quasi*-linear P–Ag–X array, the only other examples described also being with the bulky phosphine  $\text{P}(2,4,6\text{-MeO})_3\text{C}_6\text{H}_2$  and with X = Cl, Br<sup>44</sup> genuinely unidentate, wherein Ag–P are 2.342(1), 2.379(1) Å, respectively. In the present, Ag–P is 2.3616(9) and Ag–O(1,2) are 2.268(3), 2.401(4) Å, P–Ag–O(1,2) are 160.42(9), 146.34(9), with O(1)–Ag–O(2) 52.5(1) and Ag–O(1,2)–N 100.1(3), 93.3(3)°; N–O(1,2) are 1.231(6), 1.236–(6) Å. Ag lies 0.04(2) Å out of the  $\text{NO}_2$  plane. However, the molecules pack in a manner not dissimilar to those

**Table 3.** Selected Geometries: Mononuclear AgNO<sub>2</sub>:PR<sub>3</sub> (1:2) (**2**, **6**, **12**)<sup>a</sup>

Distances (Å)	
Ag–P(1)	2.412(1); 2.4421(7), 2.4325(6); 2.459(1); 2.4416(5)
Ag–P(2)	2.440(1); 2.4372(7), 2.4303(6); 2.461(1); 2.4437(5)
Ag–O(1)	2.481(3); 2.440(2), 2.433(2); 2.448(6); 2.471(2)
Ag–O(2)	2.386(3); 2.433(2), 2.434(1); 2.532(4); 2.495(2)
N–O(1)	1.253(4); 1.244(5), 1.257(2); 1.223(6); 1.247(3)
N–O(2)	1.259(4); 1.236(5), 1.234(2); 1.215(9); 1.241(2)
Angles (deg)	
P(1)–Ag–P(2)	128.67(4); 129.26(3), 129.57(2); 132.03(5); 148.04(2)
P(1)–Ag–O(1)	120.81(8); 110.67(6), 110.81(4); 110.5(1); 117.77(4)
P(1)–Ag–O(2)	118.35(8); 110.96(6), 111.83(4); 108.5(1); 92.96(4)
P(2)–Ag–O(1)	102.06(5); 114.27(6), 113.91(4); 115.5(1); 91.86(5)
P(2)–Ag–O(2)	109.99(6); 115.23(6), 113.77(4); 112.0(4); 116.73(4)
O(1)–Ag–O(2)	51.3(1); 50.6(1), 51.30(5); 47.9(1); 49.59(6)
O(1)–N–O(2)	114.1(3); 114.1(3), 115.1(2); 112.1(6); 113.6(2)
Torsion Angles (deg) (Carbon Atoms Denoted by Number Only)	
Ag–P(1)–C(111)–C(112)	−64.5(4); 50.78(3), 50.6(2); −62.4(4); <sup>b</sup> −170.5(1)
Ag–P(1)–C(121)–C(122)	−29.3(3); 34.4(3), 34.5(2); −56.9(3); <sup>b</sup> 54.3(1)
Ag–P(1)–C(131)–C(132)	−35.8(4); 28.0(3), 26.6(2); −33.0(4); <sup>b</sup> 53.8(1)
Ag–P(2)–C(211)–C(212)	−30.3(4); 49.8(3), 49.0(2); −161.2(4); <sup>b</sup> 56.5(1)
Ag–P(2)–C(221)–C(222)	−22.8(3); 20.0(3), 20.3(2); −62.4(4); <sup>b</sup> 51.4(2)
Ag–P(2)–C(231)–C(232)	−47.5(3); 31.4(3), 30.4(2); −52.6(3); <sup>b</sup> −172.0(1)
Out of NO <sub>2</sub> -Plane Distances (Å)	
δAg	0.06(2), 0.02(2); 0.005(8); 0.01(3); 0.067(9)

<sup>a</sup> The values in each entry are for R = Ph (CH<sub>2</sub>Cl<sub>2</sub> solvate<sup>40</sup>); unsolvated room temperature,<sup>30</sup> low temperature (the present, **2**); Cy, **12**; *o*-tolyl, **6**.

<sup>b</sup> Ag–P(*n*)–C(*nm*1)–C(*nm*6) are 60.7(3), 174.0(3), −160.9(4), 33.8(11), 60.1(3), 176.9(3)°.

**Table 4.** Selected Geometries: AgNO<sub>2</sub>:AsPh<sub>3</sub> (1:2) (**13**)<sup>a</sup>

Distances (Å)			
Ag( <i>n</i> )–As( <i>n</i> 1)	2.5236(2), 2.5432(2)	Ag–O( <i>n</i> 1)	2.374(2), 2.368(2)
Ag( <i>n</i> )–As( <i>n</i> 2)	2.5352(2), 2.5520(2)	Ag–O( <i>n</i> 2)	2.611(2), 2.735(2)
N( <i>n</i> )–O( <i>n</i> 1)	1.258(2), 1.262(2)	Ag–O( <i>n</i> 1)	2.619(1), 2.566(1)
N( <i>n</i> )–O( <i>n</i> 2)	1.233(3), 1.240(3)	Ag( <i>n</i> )...Ag( <i>n</i> )	4.1482(3)
		O( <i>n</i> 1) ... O( <i>n</i> 1)	2.789(2), 2.775(2)
Angles (deg)			
As( <i>n</i> 1)–Ag( <i>n</i> 1)–As( <i>n</i> 2)	127.17(1), 130.26(1)	As( <i>n</i> 2)–Ag( <i>n</i> )–O( <i>n</i> 1)	121.17(3), 115.49(3)
As( <i>n</i> 1)–Ag( <i>n</i> )–O( <i>n</i> 1)	110.03(3), 110.61(3)	As( <i>n</i> 2)–Ag( <i>n</i> )–O( <i>n</i> 2)	103.80(3), 98.26(3)
As( <i>n</i> 1)–Ag( <i>n</i> )–O( <i>n</i> 2)	99.47(3), 98.87(3)	As( <i>n</i> 2)–Ag( <i>n</i> )–O( <i>n</i> 1)	92.78(4), 94.41(4)
As( <i>n</i> 1)–Ag( <i>n</i> )–O( <i>n</i> 1)	119.23(3), 119.71(3)	O( <i>n</i> 1)–Ag( <i>n</i> )–O( <i>n</i> 2)	49.24(6), 47.91(5)
O( <i>n</i> 2)–Ag( <i>n</i> )–O( <i>n</i> 1)	114.37(5), 114.06(5)	O( <i>n</i> 1)–Ag( <i>n</i> )–O( <i>n</i> 1)	67.71(5), 68.31(5)
Ag( <i>n</i> )–O( <i>n</i> 1)–Ag( <i>n</i> )	112.29(5), 111.69(5)	Ag( <i>n</i> )–O( <i>n</i> 1)–N( <i>n</i> )	104.0(1), 107.9(2)
O( <i>n</i> 1)–N( <i>n</i> )–O( <i>n</i> 2)	113.9(2), 114.0(2)	Ag( <i>n</i> )–O( <i>n</i> 2)–N( <i>n</i> )	92.9(1), 90.2(1)
N( <i>n</i> )–O( <i>n</i> 1)–Ag( <i>n</i> )	139.4(2), 136.7(1)		
Torsion Angles (deg) (Carbon Atoms Denoted by Number Only)			
Ag( <i>n</i> )–As( <i>n</i> 1)–n111–n112	40.7(1), 51.3(1)	Ag( <i>n</i> )–As( <i>n</i> 2)–n211–n212	45.0(1), 21.6(2)
Ag( <i>n</i> )–As( <i>n</i> 1)–n121–n122	27.7(2), 36.0(2)	Ag( <i>n</i> )–As( <i>n</i> 2)–n221–n222	29.9(2), 30.8(2)
Ag( <i>n</i> )–As( <i>n</i> 1)–n131–n132	58.7(2), −6.1(2)	Ag( <i>n</i> )–As( <i>n</i> 2)–n231–n232	45.3(2), 92.6(2)

<sup>a</sup> The two values in each entry are for dimers *n* = 1, 2, each being centrosymmetric; centrosymmetrically related atoms are *italicized*. The nitrite NO<sub>2</sub> planes make dihedral angles of 31.2(2), 39.9(2)° with the central AgO<sub>2</sub>Ag plane; silver atom deviations Ag(*n*), Ag(*n*) from their respective nitrite planes are 0.11(1), −1.076(6); 0.02(1), −1.048(5) Å.

generating the polymer with EPh<sub>3</sub> (Figure 5b), although the closest Ag...anion distance Ag...N (1 − *x*, *y*, 1/2 − *z*) is 3.955(4) Å.

The same ligand also forms an adduct of 1:2 stoichiometry, also mononuclear, [Ag(O<sub>2</sub>N){P(*o*-tolyl)<sub>3</sub>}<sub>2</sub>], **6**, the nitrite still an *O*,*O'*-chelate, and the molecule having *quasi*-2-symmetry (Figure 6a). A mononuclear 1:2 complex, **12**, is also formed with the other common sterically bulky PR<sub>3</sub> entity, namely, Pcy<sub>3</sub> (Figure 6b). A considerable array of mononuclear AgX: Ecy<sub>3</sub> (1:2) complexes have been defined for both E = P<sup>31</sup> and As,<sup>45</sup> wherein two common crystalline forms are found, one monoclinic *C*2/*c* and the other a derivative *P*1̄. Both AgNO<sub>3</sub>:Ecy<sub>3</sub> (1:2) (E = P, As) are triclinic, the molecule of

the form [Ag(O<sub>2</sub>NO)(Pcy<sub>3</sub>)<sub>2</sub>], wherein the chelate is unsymmetrical (Ag–O, 2.47(1), 2.79(1) Å; Ag–P, 2.440(2), 2.451(2) Å; P–Ag–P, 139.14(9)°); the present E = P, nitrite analogue is similar, Ag–O more symmetrical, with P–Ag–P considerably diminished. The same form is also found in [Ag(O<sub>2</sub>N)(PPh<sub>3</sub>)<sub>2</sub>], **2**, previously recorded in a room temperature study<sup>30</sup> and redetermined at low temperature here for the sake of comparability with the Pcy<sub>3</sub> and P(*o*-tolyl)<sub>3</sub> counterparts (Table 3). Perhaps the most remarkable variation across the array is found in the P–Ag–P angle, where the disparity between the value for the P(*o*-tolyl)<sub>3</sub> array vis-à-vis the remainder is considerable. It is unlikely to be a consequence of “lattice forces”, but whether the implication is that P(*o*-tolyl)<sub>3</sub> is a markedly “bulkier” ligand than Pcy<sub>3</sub> or whether the difference is electronic is debatable. Interest-

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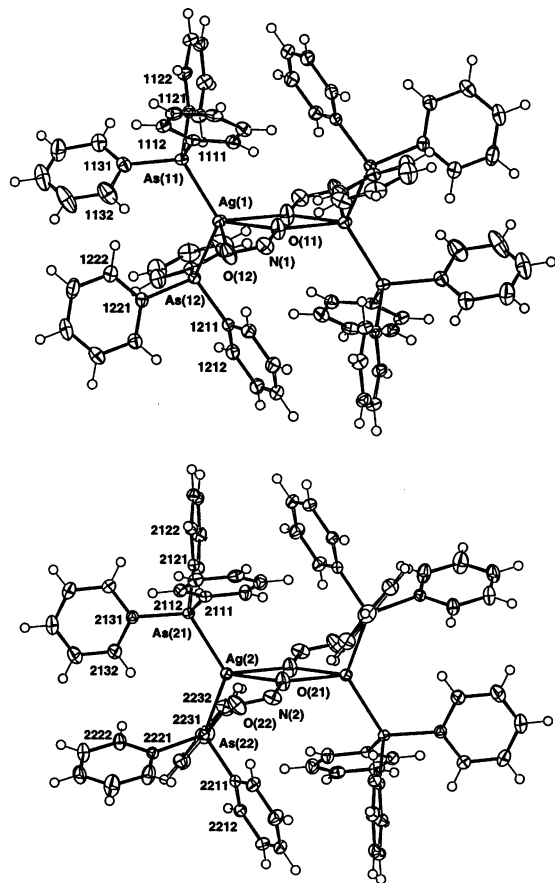


Figure 7. Dimers of  $\text{AgNO}_2\text{:AsPh}_3$  (1:2) (**13**).

ingly, this increase in angle is not accompanied by any noticeable shortening in Ag–P, which are remarkably constant regardless of R, as also are parameters involving the nitrite groups which are twisted about the *quasi*-2-axis passing through Ag, N, and the P–Ag–P bisector, so that the (Ag)NO<sub>2</sub> plane is far removed from coplanarity with the AgP<sub>2</sub> plane. In both PPh<sub>3</sub> and P(*o*-tolyl)<sub>3</sub> arrays, the crystal packing is of interest (Figure 6c); the PPh<sub>3</sub> adduct is a new AgX:EPh<sub>3</sub> (1:2) unsolvated mononuclear type (cf. Table 3 of ref 39).

In contrast to the preceding, the 1:2 adduct of silver(I) nitrate with triphenylarsine, **13**, is binuclear, essentially an aggregate of a pair of [Ag(O<sub>2</sub>N)(AsPh<sub>3</sub>)<sub>2</sub>] arrays with one of the nitrite oxygen atoms; interestingly the one with the shorter of the two chelate interactions (which are unsymmetrical) is the bridging atom. The dimer is centrosymmetric, one-half of each of two independent dimers, of similar geometries and conformations (Table 4, Figure 7) making up the asymmetric unit of the structure. Other unsolvated binuclear 1:2 coinage metal(I) oxyanion salt/EPh<sub>3</sub> adducts have been described for the combinations AgNO<sub>3</sub>/PPh<sub>3</sub>,<sup>46,47</sup> AgNO<sub>3</sub>/AsPh<sub>3</sub>,<sup>20</sup> and CuNO<sub>3</sub>/AsPh<sub>3</sub>,<sup>47</sup> none of which are isomorphous with the present, which, curiously, however, *is* isomorphous with the AgX/SbPh<sub>3</sub> (X = Cl, Br, I)<sup>32</sup> form and is presented here in that cell and coordinate setting, with

Table 5. Selected Geometries: AgNO<sub>2</sub>:EPh<sub>3</sub> (1:2) (**14**, **16**)<sup>a</sup>

Distances (Å)	
Ag–E(1)	2.593(1); 2.7816(2), 2.7434(5)
Ag–E(2)	2.6347(9); 2.7464(2), 2.7185(6)
Ag–E(3)	2.635(1); 2.7168(2), 2.6890(8)
Ag–O(1)	2.516(6); 2.679(3), 2.861(9)
Ag–O(2)	2.529(8); 2.371(2), 2.375(7)
N–O(1)	1.21(1); 1.240(3), 1.115(9)
N–O(2)	1.24(1); 1.231(3), 1.121(8)
Angles (deg)	
E(1)–Ag–E(2)	112.76(3); 110.286(7), 114.23(2)
E(1)–Ag–E(3)	112.55(3); 107.210(7), 110.69(2)
E(1)–Ag–O(1)	107.6(1); 86.78(6), 85.6(2)
E(1)–Ag–O(2)	113.2(1); 111.85(6), 109.1(2)
E(2)–Ag–E(3)	113.28(3); 111.221(7), 113.93(2)
E(2)–Ag–O(1)	122.3(2); 140.11(5), 131.6(2)
E(2)–Ag–O(2)	78.7(2); 92.88(5), 92.3(2)
E(3)–Ag–O(1)	85.6(2); 96.47(6), 96.9(2)
E(3)–Ag–O(2)	121.9(2); 122.49(6), 115.5(2)
O(1)–Ag–O(2)	47.5(2); 47.36(7), 39.6(2)
O(1)–N–O(2)	111.9(8); 111.9(2), 110.0(7)
Ag–O(1)–N	101.0(5); 92.1(2), 90.8(6)
Ag–O(2)–N	99.3(6); 108.2(2), 119.5(5)
Torsion Angles (deg)	
(Carbon Atoms Denoted by Number Only)	
Ag–E(1)–111–112	13.7(6); 34.7(2), 23.3(5)
Ag–E(1)–121–122	54.9(6); 19.4(3), 39.0(7)
Ag–E(1)–131–132	41.2(6); 48.9(2), 41.4(5)
Ag–E(2)–211–212	20.4(6); 26.4(2), 34.4(5)
Ag–E(2)–221–222	50.4(6); 40.9(2), 38.1(5)
Ag–E(2)–231–232	24.4(6); 24.3(2), 24.0(6)
Ag–E(3)–311–312	46.1(6); –0.7(2), 3.8(5)
Ag–E(3)–321–322	4.5(6); 48.3(2), 54.6(5)
Ag–E(3)–331–332	51.5(6); 65.2(2), 59.2(5)

<sup>a</sup> Values in each entry correspond to (a) E = As (bis(acetonitrile) solvate); E = Sb [cf. the present room-temperature study; Ag–Sb(1,2,3)–O(1,2), 2.8137(7), 2.7461(8), 2.726(1), 2.53(1), 2.391(7) Å; Sb(1)–Ag–Sb(2,3), 108.89(2), 106.59(2)°; Sb(2)–Ag–Sb(3), 111.62(2)°], followed by those of its isomorphous nitrate counterpart (ref 52, a room temperature study).

a more rational atom numbering. These MNO<sub>2</sub>:EPh<sub>3</sub> (1:2) arrays are interesting in their diversity: CuNO<sub>3</sub>:PPh<sub>3</sub> (1:2)<sup>48</sup> and CuNO<sub>2</sub>:PPh<sub>3</sub> (1:2)<sup>49</sup> are mononuclear and isomorphous, while AgNO<sub>3</sub>:PPh<sub>3</sub> (1:2) (benzene<sup>50</sup> and toluene<sup>51</sup> solvates) are mononuclear and isomorphous, but of a different crystal-line form. All are of the form [M(O<sub>2</sub>N(O))(PPh<sub>3</sub>)<sub>2</sub>], the oxyanion chelating. AgNO<sub>3</sub>:PPh<sub>3</sub> (1:2) also exists in two different binuclear forms, one triclinic,<sup>46</sup> with an isomorphous E = As analogue,<sup>20</sup> and the other orthorhombic,<sup>47</sup> while CuNO<sub>3</sub>:AsPh<sub>3</sub> (1:2) (binuclear) is of a different monoclinic type,<sup>52</sup> all of these being unsolvated. These binuclear types again exhibit different forms: in the orthorhombic phase,<sup>47</sup> the dimer is bound by a four-membered ring, the oxyanions bridging the two metal atoms cleanly through a single oxygen each, [(Ph<sub>3</sub>E)<sub>2</sub>M(*μ*-ONO<sub>2</sub>)M(EPh<sub>3</sub>)<sub>2</sub>] (although the other

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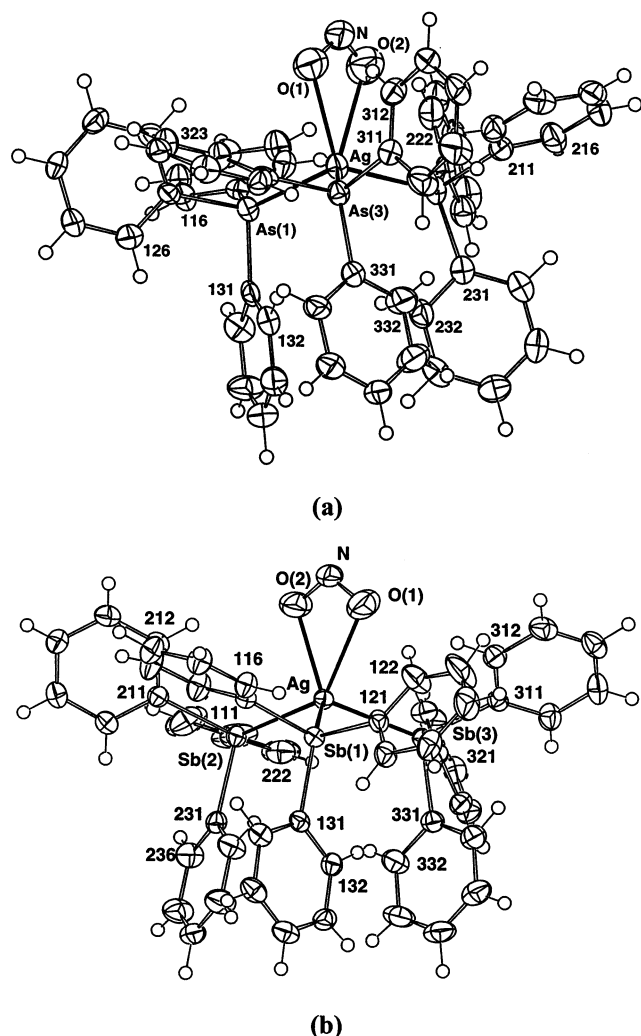
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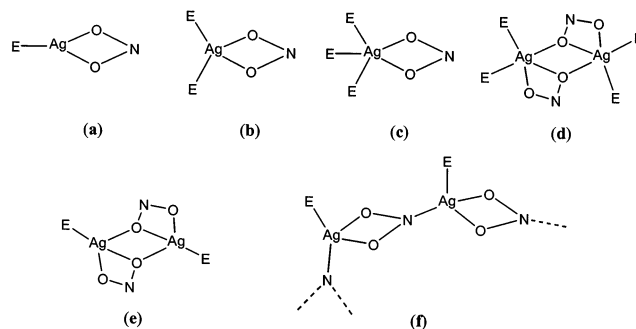
**Figure 8.** Projections of single molecules of (a)  $\text{AgNO}_2\text{:AsPh}_3$  (1:3) (**14**) (in its bis(acetonitrile) solvate). (b)  $\text{AgNO}_2\text{:SbPh}_3$  (1:3) (**16**).

oxygens may be viewed as distant chelates interacting symmetrically to either side), as also is the monoclinic phase,<sup>52</sup> but, in the examples of the triclinic form,<sup>42,46</sup> a second oxygen atom of each anion chelates the metal, as is also the case in the present, its isomorphous parallels<sup>32</sup> being irrelevant since the bridges are single atoms (halides).

Adducts of the form  $\text{AgNO}_2\text{:EPh}_3$  (1:3) are defined herein for  $\text{E} = \text{As}$ ,  $\text{Sb}$ , the  $\text{E} = \text{P}$  adduct, regrettably, not yet being accessed. The two arrays described herein are of types already described. The  $\text{E} = \text{As}$  adduct, **14**, is of the common triclinic solvated form<sup>43</sup> (this time as a bis(acetonitrile) solvate) for which the cell and coordinate setting of  $\text{CuCl}\text{:SbPh}_3$  (1:3).  $\text{CHCl}_3$ <sup>33</sup> has been adopted by us as archetypical; other oxanion arrays have also been defined for this form: nitrates as unidentates<sup>42,53</sup> and an acetate<sup>51</sup> as a bidentate. The  $\text{E} = \text{Sb}$  adduct<sup>42</sup> is unsolvated and corresponds to the common monoclinic  $P2_1/n$  form, the cell and coordinate settings of the  $\text{AgI}\text{:PPh}_3$  (1:3) array<sup>54</sup> taken as archetypical.

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**Figure 9.** Topologies found for the  $\text{AgNO}_2\text{:ER}_3$  adducts: (a) compound **5**; (b) compounds **2**, **6**, and **12**; (c) compounds **14** and **16**; (d) compound **13**; (e) compound **11**; (f) compounds **1** and **15**.

In both forms, one molecule (with solvent, as appropriate), devoid of crystallographic symmetry, comprises the asymmetric unit of each structure; relevant geometries of the substrates are given in Table 5 and the molecules depicted in Figure 8. Of particular interest is the close comparison possible between the unsolvated isomorphous  $\text{AgX}\text{:SbPh}_3$  (1:3) arrays; cf. that for  $\text{AgX}\text{:Pcy}_3$  (1:2) above,  $\text{X} = \text{O}, \text{O}'\text{-NO}_2, \text{NO}_3$ , in both cases, wherein, consistently, the nitrite behaves as a consistently stronger  $\text{O}, \text{O}'$ -chelate. Despite similar  $\text{O}-\text{N}-\text{O}$  angles in each pair,  $\text{Ag}-\text{O}$  are shorter in the nitrite complexes, with corresponding lengthening of  $\text{Ag}-\text{E}$  and conspicuous diminution of the  $\text{E}-\text{Ag}-\text{E}$  angles.

## Conclusion

Aggregation of triorganophosphines, -arsines, and -stibines with silver(I) nitrite has been investigated in the solid state by single-crystal X-ray diffraction and in solution by electrospray ionization mass spectrometry (ESI-MS). In the solid state, topology (Figure 9) is found to depend on the reaction conditions (mainly ligand-to-metal ratio) and on the electronic and steric features of the P-donor ligand. For example sterically hindered ligands such as  $\text{P}(o\text{-tolyl})_3$  and  $\text{Pcy}_3$  yield only mononuclear 1:1 or 1:2  $\text{Ag}\text{:PR}_3$  adducts, whereas  $\text{EPh}_3$  donors ( $\text{E} = \text{P}$ ,  $\text{As}$ , or  $\text{Sb}$ ) form also 1:4  $\text{Ag}\text{:PR}_3$  adducts or di- or polynuclear complexes in which silver atoms are bridged by  $\text{NO}_2^-$  ligands. Significant deformation of the silver(I) coordination environments are observed as a function of the Tolman cone angle. The aggregation behavior is most strongly dependent on the ligand-to-metal ratio and the solvent employed and to a lesser degree on the counterion. For the 1:3 and 1:4 adducts investigated, aggregation of the P-donor ligand is significantly disrupted in acetonitrile at concentrations of approximately  $10^{-3}$  M. Aggregates containing a single silver atom dominate significantly over adducts of higher nuclearity. On the basis of the negative ESI-MS spectra, it is proposed that in solution the  $\text{NO}_2^-$  also coordinates to a silver(I) ion.

**Acknowledgment.** We thank the University of Camerino and CARIMA Foundation for financial help.

**Supporting Information Available:** X-ray crystallographic files, in CIF format, for the structure determinations of **1**, **2**, **5**, **6**, and **11–16**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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