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Variable Coordination Modes of NO_2^- in a Series of Ag(I) Complexes Containing Triorganophosphines, -arsines, and -stibines. Syntheses, Spectroscopic Characterization (IR, ^1H and ^{31}P NMR, Electrospray Ionization Mass), and Structures of $[AgNO_2(R_3E)_x]$ Adducts ($E = P$, As, Sb, $x = 1–3$)

**Augusto Cingolani,[†] Effendy,[‡,§] Maura Pellei,[†] Claudio Pettinari,[*,†] Carlo Santini,[†]
Brian W. Skelton,[§] and Allan H. White[§]**

*Dipartimento di Scienze Chimiche, Università degli Studi di Camerino, via S. Agostino 1,
62032 Camerino MC, Italy; Jurusan Kimia, FMIPA Universitas Negeri Malang,
Jalan Surabaya 6, Malang, Indonesia 65145, and Department of Chemistry, The University of
Western Australia, Crawley, Western Australia 6009*

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Adducts of triorganophosphine, triphenylarsine, and triphenylstibine with silver(I) nitrite have been synthesized and characterized both in solution (^1H, ^{31}P NMR) and in the solid state (IR, single-crystal X-ray structure analysis). In addition aggregates of $AgNO_2$ and ER_3 ($E = P$, As, 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 ER_3 and on the stoichiometric ratio $AgNO_2$:ER_3. The adducts $AgNO_2$:EPh_3 (1:1) ($E = P$ or Sb) are one-dimensional polymers, the role of 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 $AgNO_2$:P(*o*-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 P–Ag–X array. $AgNO_2$:P(*p*-F–C_6H_4)$_3$ (1:1) is a dimer, the nitrite being coordinated through both oxygens, the first unidentate, the second bridging bidentate. P(*o*-tolyl)$_3$ and Pcy_3 form 1:2 adducts, also mononuclear, the nitrite still an *O,O′*-chelate. In contrast, the adduct $AgNO_2$:$AsPh_3$ (1:2) is a centrosymmetric dimer, essentially an aggregate of a pair of $[Ag(O_2N)(AsPh_3)_2]$ arrays with one nitrite oxygen being the bridging atom. The adducts $AgNO_2$:EPh_3 (1:3) ($E =$ As, Sb) are mononuclear, the nitrite behaving as a consistently strong *O,O′*-chelate. The $E =$ As adduct is a triclinic solvated form, whereas the unsolvated $E =$ Sb species is monoclinic. ESI-MS spectra of acetonitrile solutions of these complexes show the existence of $[Ag(ER_3)]^+$, $[Ag(CH_3CN)]^+$, $[Ag(CH_3CN)_2]^+$, $[AgCl_2]^-$, $[Ag(NO_2)_2]^-$, $[Ag(ER_3)(CH_3CN)]^+$, and $[Ag(ER_3)_2]^+$ as well as higher aggregates $[Ag_2(NO_2)(ER_3)_2]^+$, $[Ag_2(NO_2)_3]^-$ and $[Ag_2Cl_2(NO_2)]^-$, which are less prevalent.

Introduction

NO_2^--containing coordination compounds have been extensively studied, being of interest because of the ability of NO_2^- to coordinate a metal in a number of different bonding modes (Figure 1), e.g. yielding nitro compounds $M-NO_2$ as N-donor or nitrito derivatives $M-O-NO$ as O-donor.[1] Each NO_2 coordination mode leads to different properties for the compound.

Coordination of 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 (NO_x, $x = 1$ or 2) and of corrosion processes.

The interaction of the NO_2^- ligand with alkaline,[2−6] alkaline earth,[7−10] and transition metal species[11−15] 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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[*] To whom correspondence should be addressed. Fax: 0039 0737 637345. E-mail: claudio.pettinari@unicam.it.

[†] Università di Camerino.

[‡] FMIPA Universitas Negeri Malang.

[§] University of Western Australia.

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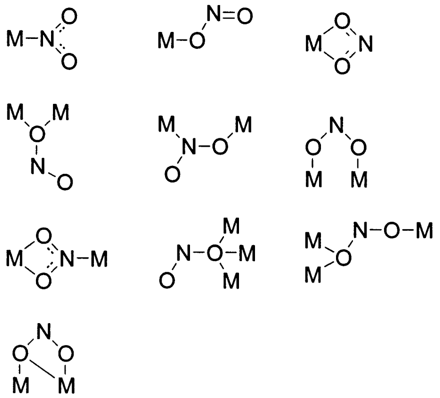

Figure 1. Some possible coordination modes for the NO_2^- ligand.

A silver(I) nitrite (di-2-pyridyl ketone) complex, stabilized by intramolecular π stacking interactions and aligned into chains through the intermolecular π stacking interactions in a zipper-like fashion, has been recorded by Yang and coworkers.[16] $AgNO_2$ reacts with hexamethylenetetramine in $MeCN-H_2O$ to yield a two-dimensional coordination polymer with square cavities.[17] 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 NO_2^- acts as the anion, the interlinked chains give a 3-D diamondoid network.[18]

In this paper we describe a series of $AgNO_2$ adducts with unidentate triorganophosphines, -arsines, and -stibines EPh_3 (E = P, As, Sb), P(*o*-tolyl)$_3$, P(*m*-tolyl)$_3$, P(*p*-tolyl)$_3$, P(*p*-F$-C_6H_4$)$_3$, and Pcy_3. The coordination chemistry of tertiary phosphine adducts provides a well-established basis permitting systematic investigation of the possible coordination modes of oxyanions such as NO_3^- and ClO_4^- to Ag(I)[19-21] and Cu(I) ions,[22] with interesting structural variations within the series $MX:(PR_3)_n$ 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.[23,24]

Here we report the synthesis and spectroscopic characterization of 16 novel $AgNO_2:ER_3$ adducts supported by 10 single-crystal X-ray studies to assist in understanding the relationships between molecular packing, coordinating ability of NO_2^-, donor capacity, and the Tolman cone angle of the ancilliary ligand. Our results demonstrate that remarkably stable neutral silver complexes showing different silver(I) coordination environments and 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.[25] The (ESI-MS) technique has been very successfully applied to problems in biochemistry[26] and in the speciation of inorganic and organometallic complexes of various metals, including Ag, Pd, Zn, and others.[27] 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 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 cm^{-1} with a Perkin-Elmer System 2000 FT-IR instrument. ^1H and ^{31}P NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^1H, and 121.4 MHz for ^{31}P). Proton chemical shifts are reported in parts per million vs Me_4Si, while phosphorus chemical

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shifts are reported in parts per million vs 85% H_3PO_4. 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 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.[28] Peaks containing silver(I) ions are identified as the center of an isotopic cluster.

[AgNO$_2$(PPh$_3$)] (1). Silver(I) nitrite (0.154 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 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, cm^{-1}) data: 3170w, ν(C−H); 1435s, 1336vw, 1217br, ν(NO$_2$); 838w, δ(ONO); 523s, 501m, 489s, 437m, δ(PPh$_3$). ^{1}H NMR (CDCl$_3$, 293 K): δ 7.35−7.55 (m, 15H, C$_6$*H*$_5$). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K): δ 16.5 (d br, $^1J(^{31}P-Ag) = 621$ Hz). ^{31}P{^{1}H} NMR (CDCl$_3$, 218 K): δ 16.1 (dd, $^1J(^{31}P-^{107}Ag) = 666$ Hz, $^1J(^{31}P-^{109}Ag) = 769$ Hz). Λ_{mol} (CH$_2$Cl$_2$, concn = 1.00×10^{-3} M): 0.1 Ω^{-1} cm^2 mol^{-1}. ESI MS (MeCN): (+) 189 (5) [Ag(MeCN)$_2$]$^+$, 411 (80) [Ag(MeCN)(PPh$_3$)]$^+$, 632 (100) [Ag(PPh$_3$)$_2$]$^+$, 786 (30) [Ag$_2$(NO$_2$)(PPh$_3$)$_2$]$^+$; (−) 178 (18) [AgCl$_2$]$^-$, 199 (100) [Ag(NO$_2$)$_2$]$^-$, 332 (65) [Ag$_2$Cl$_2$NO$_2$]$^-$. Anal. Calcd for $C_{18}H_{15}AgNO_2P$: C, 51.95; H, 3.63; N, 3.37. Found: C, 51.78; H, 3.72; N, 3.40.

[AgNO$_2$(PPh$_3$)$_2$] (2). Compound **2** has been synthesized similarly to **1**, by using AgNO$_2$ (0.154 g, 1 mmol) and PPh$_3$ (0.525 g, 2 mmol). Compound **2** was recrystallized from ethanol. Yield: 80%. Mp: 203−205 °C. IR (Nujol, cm^{-1}) data: 3068vw, ν(C−H); 1433s, 1326vw, 1225br, ν(NO$_2$); 832w, δ(ONO); 511sh, 495s, 438m, 422w, δ(Ph$_3$P). ^{1}H NMR (CDCl$_3$, 293 K): 7.20−7.42 (m, 30H, C$_6$*H*$_5$). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K): δ 9.3 (s). ^{31}P{^{1}H} NMR (CDCl$_3$, 218 K): δ 8.95 (dd, $^1J(^{31}P-^{107}Ag) = 413$ Hz, $^1J(^{31}P-^{109}Ag) = 476$ Hz). Λ_{mol} (CH$_2$Cl$_2$, concn = 1.05×10^{-3} M): 0.2 Ω^{-1} cm^2 mol^{-1}. ESI MS (MeCN): (+) 411 (10) [Ag(MeCN)(PPh$_3$)]$^+$, 632 (100) [Ag(PPh$_3$)$_2$]$^+$, 786 (5) [Ag$_2$(NO$_2$)(PPh$_3$)$_2$]$^+$. Anal. Calcd for $C_{36}H_{30}AgNO_2P_2$: C, 63.73; H, 4.46; N, 2.06. Found: C, 64.03; H, 4.64; N, 2.01.

[AgNO$_2$(PPh$_3$)$_3$] (3). Compound **3** was prepared similarly to compound **1**, by using AgNO$_2$ (0.154 g, 1 mmol) and PPh$_3$ (0.787 g, 3 mmol). Compound **3** was recrystallized from ethanol. Yield: 85%. Mp: 216−220 °C. IR (Nujol, cm^{-1}) data: 3167vw, ν(C−H); 1434s, 1377w, 1183br, ν(NO$_2$); 848vw, δ(ONO); 501s, 492s, 438m, 419m, δ(Ph$_3$P). ^{1}H NMR (CDCl$_3$, 293 K): δ 7.20−7.40 (m, 45H, C$_6$*H*$_5$). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K): δ 5.2 (s). ^{31}P{^{1}H} NMR (CDCl$_3$, 218 K): δ 5.6 (d, $^1J(^{31}P-Ag) = 228$ Hz), 32.2 (s). Λ_{mol} (CH$_2$Cl$_2$, concn = 1.20×10^{-3} M): Λ 1.4 Ω^{-1} cm^2 mol^{-1}. ESI MS (MeCN): (+) 632 (100) [Ag(PPh$_3$)$_2$]$^+$, 786 (5) [Ag$_2$(NO$_2$)(PPh$_3$)$_2$]$^+$. Anal. Calcd for $C_{54}H_{45}AgNO_2P_3$: C, 68.94; H, 4.82; N, 1.49. Found: C, 68.68; H, 5.01; N, 1.56.

[AgNO$_2$(PPh$_3$)$_4$] (4). Compound **4** was prepared similarly to compound **1**, by using AgNO$_2$ (0.154 g, 1 mmol) and PPh$_3$ (1.311 g, 3 mmol) and recrystallized from ethanol (yield 56%). Mp: 166−167 °C. IR (Nujol, cm^{-1}) data: 3052w, ν(C−H); 1434s, 1309vw, 1184br, ν(NO$_2$); 819vw, δ(ONO); 512s, 503s, 494s, 438m, δ(Ph$_3$P). ^{1}H NMR (CDCl$_3$, 293 K): δ 7.25−7.41 (m, 60H, C$_6$*H*$_5$). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K): δ 4.7 (s). ^{31}P{^{1}H} NMR (CDCl$_3$, 218 K): δ 5.6 (d, $^1J(^{31}P-Ag) = 228$ Hz), 32.2 (s). Λ_{mol} (CH$_2$Cl$_2$, concn = 1.00×10^{-3} M): 1.1 Ω^{-1} cm^2 mol^{-1}. ESI MS (MeCN): (+) 632 (100) [Ag(PPh$_3$)$_2$]$^+$, 786 (2) [Ag$_2$(NO$_2$)(PPh$_3$)$_2$]$^+$. Anal. Calcd for $C_{72}H_{60}AgNO_2P_4$: C, 71.88; H, 5.03; N, 1.16. Found: C, 71.65; H, 5.22; N, 1.24.

[AgNO$_2${P(*o*-tolyl)$_3$}] (5). AgNO$_2$ (0.154 g, 1 mmol) was added to an ethanol solution (30 mL) of P(*o*-tolyl)$_3$ (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, cm^{-1}) data: 3048w, ν(C−H); 1456s, 1306br, ν(NO$_2$); 850vw, δ(ONO); 565m, 560sh, 524w, 515sh, 467s, 446sh, δ(PAr$_3$). ^{1}H NMR (CDCl$_3$, 293 K): δ 2.50 (s, 9H, C*H*$_3$), 6.81, 7.17, 7.33, 7.43 (t, 12H, C$_6$*H*$_4$). ^{1}H NMR (CDCl$_3$, 293 K): δ 2.50 (s, 9H, C*H*$_3$), 6.74, 7.18, 7.34, 7.45 (tbr, 12H, C$_6$*H*$_4$). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K): δ −17.7 (d br). ^{31}P{^{1}H} NMR (CDCl$_3$, 223 K): δ −19.2 (d, $^1J(^{31}P-Ag) = 695$ Hz). Λ_{mol} (CH$_2$Cl$_2$, concn = 1.10×10^{-3} M): 0.05 Ω^{-1} cm^2 mol^{-1}. ESI MS (MeCN): (+) 452 (30) [Ag(MeCN)(P(*o*-tolyl)$_3$)]$^+$, 716 (100) [Ag(P(*o*-tolyl)$_3$)$_2$]$^+$, 870 (30) [Ag$_2$(NO$_2$)(P(*o*-tolyl)$_3$)$_2$]$^+$; (−) 178 (15) [AgCl$_2$]$^-$, 199 (100) [Ag(NO$_2$)$_2$]$^-$, 332 (60) [Ag$_2$Cl$_2$NO$_2$]$^-$. Anal. Calcd for $C_{21}H_{21}AgNO_2P$: C, 55.04; H, 4.62; N, 3.06. Found: C, 55.13; H, 4.82; N, 3.20.

[AgNO$_2${P(*o*-tolyl)$_3$}$_2$] (6). Compound **6** was prepared similarly to **5**, by using AgNO$_2$ (0.154 g, 1 mmol) and P(*o*-tolyl)$_3$ (0.609 g, 2 mmol). Compound **6** was recrystallized from ethanol. Yield: 42%. Mp: 193−195 °C. IR (Nujol, cm^{-1}) data: 3050w, ν(C−H); 1226w, ν(NO$_2$); 828w, δ(ONO); 564sh, 558s, 552sh, 529s, 475s, 459s, δ(Ph$_3$P). ^{1}H NMR (CDCl$_3$, 293 K): δ 2.34 (s, 18H, C*H*$_3$), 6.81, 7.10, 7.24, 7.34 (pt, 24H, C$_6$*H*$_4$). ^{1}H NMR (CDCl$_3$, 223 K): δ 2.11 (s, 18H, C*H*$_3$), 6.84, 7.07, 7.20, 7.35 (pt br, 24H, C$_6$*H*$_4$). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K): δ −19.0 (s). ^{31}P{^{1}H} NMR (CDCl$_3$, 223 K): δ −11.0 (br). Λ_{mol} (CH$_2$Cl$_2$, concn = 1.00×10^{-3} M): 0.2 Ω^{-1} cm^2 mol^{-1}. ESI MS (MeCN): (+) 716 (100) [Ag(P(*o*-tolyl)$_3$)$_2$]$^+$, 870 (5) [Ag$_2$(NO$_2$)(P(*o*-tolyl)$_3$)$_2$]$^+$. Anal. Calcd for $C_{42}H_{42}AgNO_2P_2$: C, 66.15; H, 5.55; N, 1.84. Found: C, 66.11; H, 5.68; N, 1.92.

[AgNO$_2${P(*m*-tolyl)$_3$}] (7). Compound **7** was prepared similarly to **5**, by using AgNO$_2$ (0.154 g, 1 mmol) and P(*m*-tolyl)$_3$ (0.304 g, 1 mmol). Compound **7** was recrystallized from ethanol. Yield: 46%. Mp: 140−145 °C. IR (Nujol, cm^{-1}) data: 3169w, ν(C−H); 1225w, ν(NO$_2$); 832m δ(ONO); 544m, 558s, 521vw, 462s, 446m, 430vw, δ(Ph$_3$P). ^{1}H NMR (CDCl$_3$, 293 K): δ 2.19 (s, 9H, C*H*$_3$), 7.08 (br, 3H, C$_6$*H*$_4$), 7.17 (pd, 9H, C$_6$*H*$_4$). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K): δ 10.5 (br). ^{31}P{^{1}H} NMR (CDCl$_3$, 218 K): δ 10.0 (d, $^1J(^{31}P-Ag) = 660$ Hz). Λ_{mol} (CH$_2$Cl$_2$, concn = 1.05×10^{-3} M): 1.4 Ω^{-1} cm^2 mol^{-1}. ESI MS (MeCN): (+) 716 (100) [Ag(P(*m*-tolyl)$_3$)$_2$]$^+$, 870 (3) [Ag$_2$(NO$_2$)(P(*m*-tolyl)$_3$)$_2$]$^+$. Anal. Calcd for $C_{21}H_{21}AgNO_2P$: C, 55.04; H, 4.62; N, 3.06. Found: C, 55.14; H, 4.51; N, 3.12.

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

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[28] Senko, M. W. *IsoPro Isotopic Abundance Simulator*, v. 2.1; National High Magnetic Field Laboratory, Los Alamos National Laboratory: Los Alamos, NM.

$\{^1H\}$ NMR ($CDCl_3$, 218 K): 8.8 (dd, $^1J(^{31}P,^{107}Ag) = 411$ Hz, $^1J(^{31}P,^{109}Ag) = 475$ Hz), 32.2 (s). Λ_{mol} (CH_2Cl_2, concn = 1.20×10^{-3} M): 0.6 Ω^{-1} cm^2 mol^{-1}. ESI MS (MeCN): (+) 716 (100) $[Ag(P(m\text{-tolyl})_3)_2]^+$; (−) 178 (10) $[AgCl_2]^-$, 199 (100) $[Ag(NO_2)_2]^-$. Anal. Calcd for $C_{42}H_{42}AgNO_2P_2$: C, 66.15; H, 5.55; N, 1.84. Found: C, 65.84; H, 5.74; N, 1.81.

$[AgNO_2\{P(m\text{-tolyl})_3\}_3]$ (9). Compound **9** was prepared similarly to **5**, by using $AgNO_2$ (0.154 g, 1 mmol) and $P(m\text{-tolyl})_3$ (0.913 g, 3 mmol), and recrystallized from ethanol. Yield: 64%. Mp: 121−124 °C. IR (Nujol, cm^{-1}) data: 3338w, 3156w, ν(C−H); 1170m, 1104m, $\nu(NO_2)$; 887m, 770s, δ(ONO); 543s, 534s, 518m, 446s, 423m, $\delta(Ph_3P)$.^{1}H NMR ($CDCl_3$, 293 K): δ 2.19 (s, 27H, CH_3), 7.04 (m, 9H, C_6H_4), 7.15 (m, 27H, C_6H_4). ^{1}H NMR ($CDCl_3$, 218 K): δ 1.85, 2.03 (sbr, 27H, CH_3), 6.58, 6.68, 6.91, 7.07 (sbr, 36H, C_6H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 4.9 (s), 29.9 (s). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 218 K): 5.1 (d, $^1J(^{31}P, Ag) = 239$ Hz), 10.4 (sbr), 32.3 (s). Λ_{mol} (CH_2Cl_2, concn = 1.10×10^{-3} M): 1.1 Ω^{-1} cm^2 mol^{-1}. ESI MS (MeCN): (+) 716 (100) $[Ag(P(m\text{-tolyl})_3)_2]^+$. Anal. Calcd for $C_{63}H_{63}AgNO_2P_3$: C, 70.92; H, 5.95; N, 1.31. Found: C, 70.65; H, 6.25; N, 1.34.

$[AgNO_2\{P(p\text{-tolyl})_3\}_3]$ (10). Compound **10** was prepared similarly to **5**, by using $AgNO_2$ (0.154 g, 1 mmol) and $P(p\text{-tolyl})_3$ (0.913 g, 3 mmol), and recrystallized from ethanol. Yield: 46%. Mp: 180−183 °C. IR (Nujol, cm^{-1}) data: 3173w, ν(C−H); 1392w, 1203m, 1189m, $\nu(NO_2)$; 807s, δ(ONO); 516s, 509s, 490m, 429m, $\delta(PPh_3)$. ^{1}H NMR ($CDCl_3$, 293 K): δ 2.31 (s, 27H, CH_3), 7.06 (m, 18H, C_6H_4), 7.17 (m, 18H, C_6H_4). ^{1}H NMR ($CDCl_3$, 218 K): δ 2.29 (s, 27H, CH_3), 6.83 (sbr, 36H, C_6H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 2.9 (s), 29.7 (s). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 218 K): 3.7 (dbr, $^1J(^{31}P{-}Ag) = 193$ Hz). Λ_{mol} (CH_2Cl_2, concn = 1.00×10^{-3} M): 1.9 Ω^{-1} cm^2 mol^{-1}. ESI MS (MeCN): (+) 716 (100) $[Ag(P(p\text{-tolyl})_3)_2]^+$. Anal. Calcd for $C_{63}H_{63}AgNO_2P_3$: C, 70.92; H, 5.95; N, 1.31. Found: C, 70.58; H, 6.21; N, 1.26.

$[AgNO_2\{P(p\text{-F}{-}C_6H_4)_3\}]$ (11). Compound **11** was prepared similarly to **5**, by using $AgNO_2$ (0.154 g, 1 mmol) and $P(p\text{-F}{-}C_6H_4)_3$ (0.316 g, 1 mmol), and recrystallized from ethanol. Yield: 66%. Mp: 160 °C. IR (Nujol, cm^{-1}) data: 3160w, ν(C−H); 1576s, 1461s, 1366br, 1219br, 1152br, $\nu(NO_2)$; 823s, δ(ONO); 523s, 476s, 434s, 415s, 404s $\delta(PPh_3)$. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.1 (m, 9H, C_6H_4), 7.4 (m, 6H, C_6H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 12.8 (d, $^1J(^{31}P{-}Ag) = 643$ Hz). Λ_{mol} (CH_2Cl_2, concn = 1.00×10^{-3} M): 3.5 Ω^{-1} cm^2 mol^{-1}. ESI MS (MeCN): (+) 424 (15) $[Ag(P(p\text{-F}{-}C_6H_4)_3)]^+$, 740 (100) $[Ag(P(p\text{-F}{-}C_6H_4)_3)_2]^+$. Anal. Calcd for $C_{18}H_{12}AgF_3NO_2P$: C, 45.99; H, 2.57; N, 2.98. Found: C, 45.87; H, 2.64; N, 2.76.

$[AgNO_2(Pcy_3)_2]$ (12). Compound **12** was prepared similarly to compound **5**, by using $AgNO_2$ (0.154 g, 1 mmol) and Pcy_3 (0.561 g, 2 mmol). Compound **12** was recrystallized from ethanol. Yield: 56%. Mp: 205−210 °C. IR (Nujol, cm^{-1}) data: 3159w ν(C−H); 1346m, 1225m, $\nu(NO_2)$; 886s, 850s, δ(ONO); 512s, 487m, 465s, 400w, $\delta(Ph_3P)$. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.23 (mbr, 30H, C_6H_{11}), 1.65 (sbr, 6H, C_6H_{11}), 1.78 (mbr, 30H, C_6H_{11}). ^{1}H NMR ($CDCl_3$, 218 K): δ 1.18 (br, 30H, C_6H_{11}), 1.60 (br, 6H, C_6H_{11}), 1.73 (br, 30H, C_6H_{11}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 28.9 (d, $^1J(^{31}P{-}Ag) = 435$ Hz), 50.6 (s). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 218 K): δ 28.4 (dd, $^1J(^{31}P{-}^{107}Ag) = 425$ Hz, $^1J(^{31}P{-}^{109}Ag) = 491$ Hz). Λ_{mol} (CH_2Cl_2, concn = 1.40×10^{-3} M): 4.5 Ω^{-1} cm^2 mol^{-1}. ESI MS (MeCN): (+) 430 (55) $[Ag(Pcy_3)]^+$, 668 (100) $[Ag(Pcy_3)_2]^+$, 822 (100) $[Ag_2(NO_2)(Pcy_3)_2]^+$. Anal. Calcd for $C_{36}H_{66}AgNO_2P_2$: C, 60.50; H, 9.31; N, 1.96. Found: C, 60.22; H, 9.53; N, 2.05.

$[AgNO_2(AsPh_3)_2]$ (13). Compound **13** was prepared similarly to compound **1**, by using $AgNO_2$ (0.154 g, 1 mmol) and $AsPh_3$ (0.612 g, 2 mmol), and recrystallized from ethanol. Yield: 65%. Mp: 166−167 °C. IR (Nujol, cm^{-1}) data: 3050w, ν(C−H); 1481m, 1255br, 1182vw, $\nu(NO_2)$; 842w, δ(ONO); 473s, 463s, 326s, $\delta(Ph_3As)$. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.24−7.73 (mc, 35H, C_6H_5). Λ_{mol} (CH_2Cl_2, concn = 1.00×10^{-3} M): 0.02 Ω^{-1} cm^2 mol^{-1}. ESI MS (MeCN): (+) 189 (5) $[Ag(MeCN)_2]^+$, 455 (60) $[Ag(MeCN)(AsPh_3)]^+$, 719 (100) $[Ag(AsPh_3)_2]^+$, 874 (80) $[Ag_2(NO_2)(AsPh_3)_2]^+$; (−) 178 (5) $[AgCl_2]^-$, 199 (100) $[Ag(NO_2)_2]^-$, 332 (55) $[Ag_2Cl_2NO_2]^-$. Anal. Calcd for $C_{36}H_{30}AgAs_2NO_2$: C, 56.42; H, 3.95; N, 1.83. Found: C, 56.71; H, 3.86; N, 2.01.

$[AgNO_2(AsPh_3)_3]$ (14). Compound **14** was prepared similarly to **1**, by using $AgNO_2$ (0.154 g, 1 mmol) and $AsPh_3$ (0.919 g, 3.0 mmol), and recrystallized from ethanol. Yield: 97%. Mp: 182−184 °C. IR (Nujol, cm^{-1}) data: 3147w, ν(C−H); 1434s, 1214br, 1182w, $\nu(NO_2)$; 848w, δ(ONO); 478m, 462m, 322s, 312s, $\delta(Ph_3As)$. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.24−7.42 (mc, 45H, C_6H_5). Λ_{mol} (CH_2Cl_2, concn = 1.00×10^{-3} M): 0.4 Ω^{-1} cm^2 mol^{-1}. ESI MS (MeCN): (+) 719 (100) $[Ag(AsPh_3)_2]^+$, 874 (80) $[Ag_2(NO_2)(AsPh_3)_2]^+$. Anal. Calcd for $C_{54}H_{45}AgAs_3NO_2$: C, 60.47; H, 4.23; N, 1.31. Found: C, 60.32; H, 4.34; N, 1.38.

$[AgNO_2(SbPh_3)]$ (15). Compound **15** was prepared similarly to compound **1**, by using $AgNO_2$ (0.154 g, 1 mmol) and $SbPh_3$ (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^{-1}) data: 3152vw, ν(C−H); 1430s, 1303w, 1180w, $\nu(NO_2)$; 847w, δ(ONO); 453s, 446sh, 268s, $\delta(Ph_3Sb)$. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.25−7.48 (mc, 15H, C_6H_5). Λ_{mol} (CH_2Cl_2, concn = 1.00×10^{-3} M): 0.4 Ω^{-1} cm^2 mol^{-1}. ESI MS (MeCN): (+) 189 (5) $[Ag(MeCN)_2]^+$, 502 (70) $[Ag(MeCN)(SbPh_3)]^+$, 813 (100) $[Ag(SbPh_3)_2]^+$, 968 (60) $[Ag_2(NO_2)(SbPh_3)_2]^+$; (−) 178 (10) $[AgCl_2]^-$, 199 (100) $[Ag(NO_2)_2]^-$, 332 (40) $[Ag_2Cl_2(NO_2)]^-$, 353 (20) $[Ag_2(NO_2)_3]^-$. Anal. Calcd for $C_{18}H_{15}AgNO_2Sb$: C, 42.65; H, 2.98; N, 2.76. Found: C, 42.61; H, 3.14; N, 2.71.

$[AgNO_2(SbPh_3)_3]$ (16). Compound **16** was prepared similarly to **1**, by using $AgNO_2$ (0.154 g, 1 mmol) and $SbPh_3$ (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^{-1}) data: 3062w, 3046w, ν(C−H); 1429s, 130br, 1200w, $\nu(NO_2)$; 847w, δ(ONO); 453s, 446sh, 273s, 262s, $\delta(Ph_3Sb)$. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.22−7.40 (mc, 45H, C_6H_5). Λ_{mol} (CH_2Cl_2, concn = 1.20×10^{-3} M): 0.4 Ω^{-1} cm^2 mol^{-1}. ESI MS (MeCN): (+) 502 (30) $[Ag(MeCN)(SbPh_3)]^+$, 813 (100) $[Ag(SbPh_3)_2]^+$, 968 (30) $[Ag_2(NO_2)(SbPh_3)_2]^+$. Anal. Calcd for $C_{54}H_{45}AgNO_2Sb_3$: 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; $2\theta/\theta$ scan mode; monochromatic Mo Kα radiation; $\lambda = 0.7107_3$ Å), yielding N reflections, N_o with $I > 3\sigma(I)$ 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) $N_{t(otal)}$ reflections merging to N unique after "empirical"/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$, considered "observed". Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ constrained at estimates (295 K data) or refined (153 K data) unless otherwise noted. Conventional residuals R $(=\sum\Delta/\sum|F_o|)$, R_w $(= [\sum w\Delta^2/\sum wF_o^2]^{1/2})$ on $|F|$ at convergence are cited (weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$). Neutral atom complex scattering factors were employed, within the context of various versions of the Xtal program system.[29] 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. $[\mathrm{Ag(O_2N)(PPh_3)}]_{(\infty|\infty)} \equiv \mathrm{C_{18}H_{15}AgNO_2P}$, $M = 416.2$. 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, $\beta = 88.281(3)°$, $V = 1641$ Å^3. $D_c(Z=4) = 1.68_4$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 13.3$ cm^{-1}; specimen, 0.50 × 0.25 × 0.20 mm; "T"$_{\mathrm{min,max}} = 0.60, 0.83$. $2\theta_{\mathrm{max}} = 75°$; $N_t = 33\,205$, $N = 8571$ ($R_{\mathrm{int}} = 0.026$), $N_o = 7722$; $R = 0.029$, $R_w = 0.042$; $|\Delta\rho_{\mathrm{max}}| = 2.76(4)$ e Å^{-3}.

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

(b) Compound 2. $[\mathrm{Ag(O_2N)(PPh_3)_2}] \equiv \mathrm{C_{36}H_{30}AgNO_2P_2}$, $M = 678.5$. Monoclinic, space group $P2_1/c$, $a = 11.908(2)$ Å, $b = 18.364(2)$ Å, $c = 14.761(2)$ Å, $\beta = 101.121(2)°$, $V = 3167$ Å^3. $D_c(Z=4) = 1.42_3$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 7.7$ cm^{-1}; specimen, 0.4 × 0.3 × 0.1 mm; "T"$_{\mathrm{min,max}} = 0.79, 0.89$. $2\theta_{\mathrm{max}} = 58°$; $N_t = 30\,943$, $N = 7988$ ($R_{\mathrm{int}} = 0.025$), $N_o = 6648$; $R = 0.030$, $R_w = 0.037$; $|\Delta\rho_{\mathrm{max}}| = 0.55(4)$ e Å^{-3}.

Variata. Cell and coordinate settings follow those of a previous room temperature determination.[30]

(c) Compound 5. $[\mathrm{Ag(O_2N)\{P(\mathit{o}\text{-tolyl}_3)\}}] \equiv \mathrm{C_{21}H_{21}AgNO_2P}$, $M = 458.3$. 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^3. $D_c(Z=8) = 1.57_6$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 11.4$ cm^{-1}; specimen, 0.34 × 0.58 × 0.67 mm; "T"$_{\mathrm{min,max}} = 0.60, 0.72$. $2\theta_{\mathrm{max}} = 60°$; $N_t = 11\,973$, $N = 5628$ ($R_{\mathrm{int}} = 0.018$), $N_o = 3556$; $R = 0.036$, $R_w = 0.044$; $|\Delta\rho_{\mathrm{max}}| = 0.6(1)$ e Å^{-3}.

Variata. A quadrant of data was measured.

(d) Compound 6. $[\mathrm{Ag(O_2N)\{P(\mathit{o}\text{-tolyl}_3)\}_2}] \equiv \mathrm{C_{42}H_{42}AgNO_2P_2}$, $M = 762.6$. 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, $\beta = 92.183(4)°$, $V = 3649$ Å^3. $D_c(Z=4) = 1.38_8$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 6.8$ cm^{-1}; specimen, 0.35 × 0.28 × 0.18 mm; "T"$_{\mathrm{min,max}} = 0.73, 0.86$. $2\theta_{\mathrm{max}} = 75°$; $N_t = 69\,781$, $N = 18\,310$ ($R_{\mathrm{int}} = 0.036$), $N_o = 12\,855$; $R = 0.036$, $R_w = 0.040$; $|\Delta\rho_{\mathrm{max}}| = 1.30(7)$ e Å^{-3}. $(x, y, z, U_{\mathrm{iso}})_{\mathrm{H}}$ constrained at estimates.

(e) Compound 11. $[\mathrm{Ag(O_2N)\{P(\mathit{p}\text{-F-C_6H_4})_3\}}] \equiv \mathrm{C_{36}H_{24}Ag_2F_6N_2O_4P_2}$, $M = 470.1$. 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, $\beta = 99.748(3)°$, $V = 3473$ Å^3. $D_c(Z=4 \text{ dimers}) = 1.79_8$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 13.0$ cm^{-1}; specimen, 0.20 × 0.20 × 0.11 mm; "T"$_{\mathrm{min,max}} = 0.72, 0.86$. $2\theta_{\mathrm{max}} = 75°$; $N_t = 29\,249$, $N = 8982$ ($R_{\mathrm{int}} = 0.027$), $N_o = 6697$; $R = 0.030$, $R_w = 0.044$; $|\Delta\rho_{\mathrm{max}}| = 1.17(6)$ e Å^{-3}.

(f) Compound 12. $[\mathrm{Ag(O_2N)(Pcy_3)_2}] \equiv \mathrm{C_{36}H_{66}AgNO_2P_2}$, $M = 714.8$. 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, $\alpha = 94.53(1)°$, $\beta = 96.67(2)°$, $\gamma = 116.11(2)°$, $V = 1849$ Å^3. $D_c(Z=2) = 1.28_4$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 6.6$ cm^{-1}; specimen, 0.40 × 0.36 × 0.16 mm; "T"$_{\mathrm{min,max}} = 0.80, 0.90$. $2\theta_{\mathrm{max}} = 50°$; $N_t = 10\,672$, $N = 6484$ ($R_{\mathrm{int}} = 0.033$), $N_o = 5416$; $R = 0.042$, $R_w = 0.049$; $|\Delta\rho_{\mathrm{max}}| = 0.89(3)$ e Å^{-3}.

Variata. A second hemisphere of data was measured to $2\theta_{\mathrm{max}} = 40°$ and merged. The cell and coordinate setting follows that of the parent nitrate counterpart,[31] similar disorder being observed in one of the substituent rings.

(g) Compound 13. $[\mathrm{Ag(\mu\text{-}ONO)(AsPh_3)_2}]_2 \equiv \mathrm{C_{72}H_{60}Ag_2As_4N_2O_4}$, $M = 1532.7$. Triclinic, space group $P\bar{1}$, $a = 18.5301(7)$ Å, $b = 14.0840(5)$ Å, $c = 14.1379(5)$ Å, $\alpha = 61.087(1)°$, $\beta = 79.547(1)°$, $\gamma = 77.195(1)°$, $V = 3138$ Å^3. $D_c(Z=1 \text{ dimer}) = 1.62_2$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 27.7$ cm^{-1}; specimen, 0.15 × 0.15 × 0.12 mm; "T"$_{\mathrm{min,max}} = 0.69, 0.83$. $2\theta_{\mathrm{max}} = 75°$; $N_t = 65\,568$, $N = 32\,417$ ($R_{\mathrm{int}} = 0.030$), $N_o = 21\,311$; $R = 0.030$, $R_w = 0.027$; $|\Delta\rho_{\mathrm{max}}| = 1.8(1)$ e Å^{-3}. $(x, y, z, U_{\mathrm{iso}})_{\mathrm{H}}$ constrained at estimates.

Variata. The complex is isomorphous with its $\mathrm{Ph_3Sb/AgCl}$, Br, and I counterparts and is presented in that cell and coordinate setting,[32] the *numbering* of ligands 1 and 2 of molecule 2 being interchanged.

(h) Compound 14. $[\mathrm{Ag(O_2N)(AsPh_3)_3}]\cdot\mathrm{2MeCN} \equiv \mathrm{C_{58}H_{51}AgAs_3N_3O_2}$, $M = 1154.7$. Triclinic, space group $P\bar{1}$, $a = 13.391(3)$ Å, $b = 13.839(3)$ Å, $c = 14.119(3)$ Å, $\alpha = 84.994(4)°$, $\beta = 89.131(4)°$, $\gamma = 77.364(4)°$, $V = 2453$ Å^3. $D_c(Z=2) = 1.50_8$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 23.8$ cm^{-1}; specimen, 0.27 × 0.03 × 0.03 mm; "T"$_{\mathrm{min,max}} = 0.74, 0.91$. $2\theta_{\mathrm{max}} = 58°$; $N_t = 24\,593$, $N = 12\,458$ ($R_{\mathrm{int}} = 0.054$), $N_o = 6605$; $R = 0.055$, $R_w = 0.051$; $|\Delta\rho_{\mathrm{max}}| = 1.2(1)$ e Å^{-3}. $(x, y, z, U_{\mathrm{iso}})_{\mathrm{H}}$ 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 $\mathrm{CuCl{:}SbPh_3}$ (1:3) chloroform solvate[33] (see below).

(i) Compound 15. $[\mathrm{Ag(O_2N)(SbPh_3)}]_{(\infty|\infty)} \equiv \mathrm{C_{18}H_{15}AgNO_2Sb}$, $M = 506.9$. Monoclinic, space group $P2_1/c$, $a = 9.939(1)$ Å, $b = 9.2233(9)$ Å, $c = 18.983(2)$ Å, $\beta = 90.064(2)°$, $V = 1740$ Å^3. $D_c(Z=4) = 1.93_5$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 26.9$ cm^{-1}; specimen, 0.35 × 0.15 × 0.10 mm; "T"$_{\mathrm{min,max}} = 0.63, 0.83$. $2\theta_{\mathrm{max}} = 75°$; $N_t = 36\,047$, $N = 9091$ ($R_{\mathrm{int}} = 0.037$), $N_o = 7048$; $R = 0.028$, $R_w = 0.033$; $|\Delta\rho_{\mathrm{max}}| = 1.9(1)$ e Å^{-3}.

(j) Compound 16. $[\mathrm{Ag(O_2N)(SbPh_3)_3}] \equiv \mathrm{C_{54}H_{45}AgNO_2Sb_3}$, $M = 1213.1$. Monoclinic, space group $P2_1/c$, $a = 19.1405(9)$ Å, $b = 14.2688(7)$ Å, $c = 17.7907(9)$ Å, $\beta = 100.050(2)°$, $V = 4784$ Å^3. $D_c(Z=4) = 1.68_4$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 21.2$ cm^{-1}; specimen, 0.35 × 0.14 × 0.11 mm; "T"$_{\mathrm{min,max}} = 0.55, 0.88$. $2\theta_{\mathrm{max}} = 75°$; $N_t = 98\,748$, $N = 25\,089$ ($R_{\mathrm{int}} = 0.048$), $N_o = 16\,028$; $R = 0.032$, $R_w = 0.030$; $|\Delta\rho_{\mathrm{max}}| = 1.0(1)$ e Å^{-3}.

Variata. The cell and coordinate setting follow those of isomorphous unsolvated $[\mathrm{AgI(PPh_3)_3}]$[34] (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, $\beta = 99.90(2)°$, $V = 4895$ Å^3.

Results and Discussion

Syntheses. From the interaction of 1 equiv of $\mathrm{AgNO_2}$ and 1, 2, 3, or 4 equiv of tertiary monophosphine $\mathrm{PPh_3}$, $\mathrm{P(\mathit{o}\text{-tolyl})_3}$, $\mathrm{P(\mathit{m}\text{-tolyl})_3}$, $\mathrm{P(\mathit{p}\text{-tolyl})_3}$, $\mathrm{P(\mathit{p}\text{-F-C_6H_4})_3}$, or $\mathrm{Pcy_3}$ in ethanol at 60 °C, complexes **1**−**12** have been respectively obtained in high yield (eq 1):

$$\mathrm{AgNO_2} + x\mathrm{PR_3} \rightarrow [\mathrm{AgNO_2(R_3P)}_x] \tag{1}$$

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$$\left[\begin{array}{lll} \mathbf{1}\text{: R = Ph, } x = 1 & \mathbf{5}\text{: R = } o\text{-tolyl, } x = 1 & \mathbf{9}\text{: R = } m\text{-tolyl, } x = 3 \\ \mathbf{2}\text{: R = Ph, } x = 2 & \mathbf{6}\text{: R = } o\text{-tolyl, } x = 2 & \mathbf{10}\text{: R = } p\text{-tolyl, } x = 3 \\ \mathbf{3}\text{: R = Ph, } x = 3 & \mathbf{7}\text{: R = } m\text{-tolyl, } x = 1 & \mathbf{11}\text{: R = } p\text{-F-C}_6\text{H}_4\text{, } x = 1 \\ \mathbf{4}\text{: R = Ph, } x = 4 & \mathbf{8}\text{: R = } m\text{-tolyl, } x = 2 & \mathbf{12}\text{: R = cy, } x = 2 \end{array}\right]$$

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 $AgNO_2$ and P(p-tolyl)$_3$ or Pcy_3 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.[22] The reaction between P(p-F−C_6H_4)$_3$ and $AgNO_2$ afforded the 1:1 adduct **11** also in excess of phosphine.

From the interaction of $AgNO_2$ with 2 mol of $AsPh_3$ or 1 mol of $SbPh_3$, in ethanol at 60 °C, complexes **13** and **15** have been obtained respectively in high yield (eq 2):

$$AgNO_2 + xLPh_3 \rightarrow [AgNO_2(LPh_3)_x] \qquad (2)$$

$$\left[\begin{array}{ll} \mathbf{13}\text{: L = As, } x = 2 & \mathbf{15}\text{: L = Sb, } x = 1 \\ \mathbf{14}\text{: L = As, } x = 3 & \mathbf{16}\text{: L = Sb, } x = 3 \end{array}\right]$$

From the interaction of 1 equiv of $AgNO_2$ with 3 equiv of $AsPh_3$ or $SbPh_3$, 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_2Cl_2 solution, the Λ_{mol} values being always lower than 4.5 Ω^{-1} cm^2 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_3 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,[35,36] 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,[22] the broad absorptions near 500 cm^{-1} and those at 400−450 cm^{-1} to Whiffen's y and t vibrations, respectively, whereas some bands in the region 300−400 cm^{-1}, similar to those described in the literature for some silver(I) nitrato derivatives,[22b] can be tentatively assigned to ν(Ag−O) vibrations.

Table 1. $^{31}P\{^1H\}$ NMR Data for R_3P Containing Complexes

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

^{a} T = 218 K. ^{b} T = 223 K.

In the ^1H NMR spectra of **1**−**16** in $CDCl_3$ (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 ^1H NMR spectra of derivatives **5**−**9** exhibit only one set of signals for the methyl protons of the P-donor. On cooling the $CDCl_3$ solutions of **5**−**9** to 223 K, some weak additional signals appeared, typical of the free donor, suggesting partial dissociation of the complexes.

^{31}P chemical shifts ($CDCl_3$ solution) and ^{31}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 ^{31}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 $^1J(^{31}P-{}^{107}Ag)$ and $^1J(^{31}P-{}^{109}Ag)$ coupling, are resolved at 218 K and the observed $^1J(^{107}Ag)/^1J(^{109}Ag)$ ratio is in good agreement with that calculated from the gyromagnetic ratio of the Ag nuclei $\gamma(^{107}Ag)/\gamma(^{109}Ag)$ (Figure 2).[37] 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

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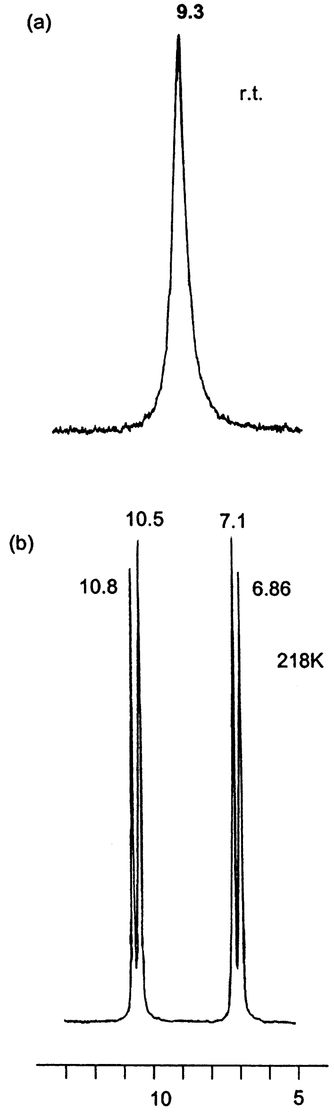

Figure 2. ^{31}P NMR spectra of derivative **2** at room temperature (a) and 218 K (b).

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

The chemical shifts and $^1J(Ag-^{31}P)$ coupling constants are strongly dependent on the stoichiometric ratio Ag/P (P = triorganophosphine). The higher $^1J(Ag-^{31}P)$ values found for derivatives **1**, **5**, **7**, and **11**, typical of monophosphine adducts, may be rationalized in terms of formation of a monuclear $[Ag(NO_2)PR_3]$ fragment, containing an sp hybridized silver, arising from the dissociation of the poly- and dinuclear species, respectively.[38] The derivatives **2**, **8**, and **12** exhibit $^1J(Ag-^{31}P)$ 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}P spectra with $^1J(Ag-^{31}P)$ values in the range of 228−240 Hz, typical of compounds with an AgP_3 or AgP_4 central core.[39]

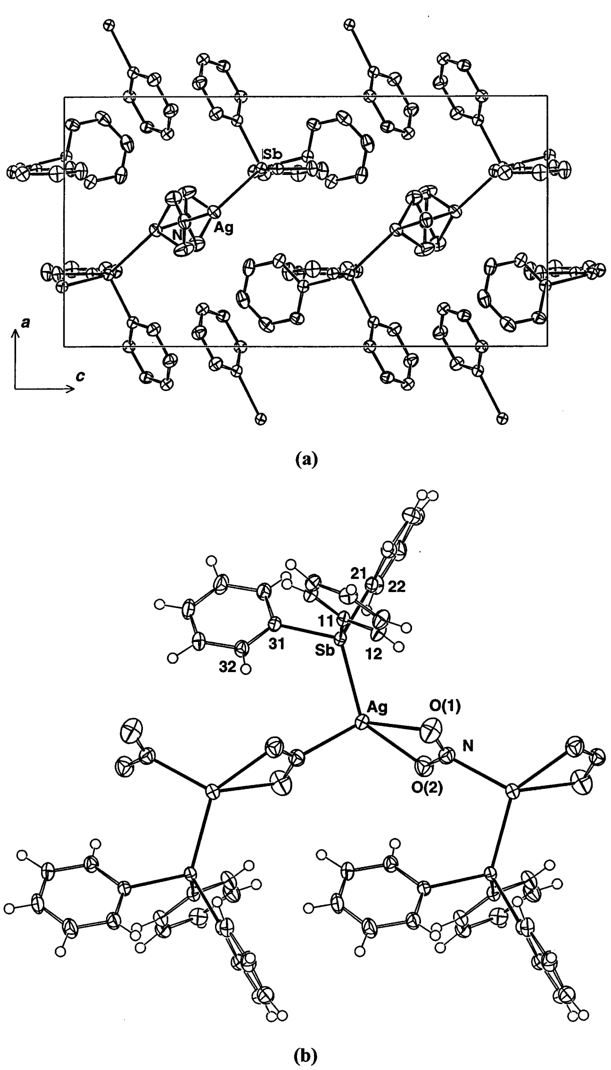

Figure 3. (a) Unit cell contents of $AgNO_2$:$SbPh_3$ (1:1)$_{(\infty|\infty)}$ (**15**), down *b* (the polymer axis) (cf. refs 19 and 20 (see text)). (b) Single strand of the polymer. (The PPh_3 adduct (**1**) is isomorphous).

The positive electrospray mass spectra of complexes **1**−**16** (the most relevant data are reported in the Experimental Section) indicate that these derivatives undergo loss of the anionic 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

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Table 2. Selected Geometries: $AgNO_2$:EPh_3 (1:1) (E = P, Sb (**1**, **11**, **15**))

(a) $AgNO_2$:EPh_3 $(1{:}1)_{(\infty\|\infty)}$ (E = P, Sb) (**1**, **15**)[a]			
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) $AgNO_2$:$(p\text{-F-}C_6H_4)_3P$ $(1{:}1)_2$ (**11**)[b]			
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)

[a] 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_2 plane by 0.103(6), −0.169(7) Å (E = P), 0.10(1), −0.36(1) Å (E = Sb). τ(Ag−P−C(*n*1)−C(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**). [b] Primed atoms are inversion related. The $Ag_2O(1)_2/NO_2$ interplanar dihedral angle is 109.0(1)°. τ(Ag−P−C(*n*1)−C(*n*6), *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^{-3} 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 $[Ag(MeCN)_2]^+$ 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_3 ligands and formation of $[Ag(ER_3)_n]^+$ 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 $[Ag_2(NO_2)(ER_3)_2]^+$. These ions undoubtedly contain bridging nitrito groups. A careful inspection of the data reveals that the species $[Ag(ER_3)_2]^+$ 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 $[Ag(MeCN)]^+$, $[Ag(MeCN)_2]^+$, and $[Ag(MeCN)(ER_3)]^+$. 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_3 donors.

The negative electrospray mass spectra are always dominated by the presence of molecular peaks due to $[AgCl_2]^-$, $[Ag(NO_2)_2]^-$, $[Ag_2Cl_2(NO_2)]^-$, and $[Ag_2(NO_2)_3]^-$. The absence of $[Ag_2(NO_2)]^+$ and the abundance of $[Ag(NO_2)_2]^-$ 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 $AgNO_2$:ER_3 adducts and (b) other AgX:R_3E 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 $AgNO_2$:PPh_3 (1:2) (unsolvated)[30] and its dichloromethane solvate,[40] the latter isomorphous with CuX$(Ph_3P)_2$•1/2S (X = Cl, Br/S = C_6H_6; X = BH_4/S = py).[32]

Among the AgX:R_3E analogues extensive surveys are recently available for Ph_3E adducts of 1:1,[23,41] 1:2,[32] 1:3,[42]

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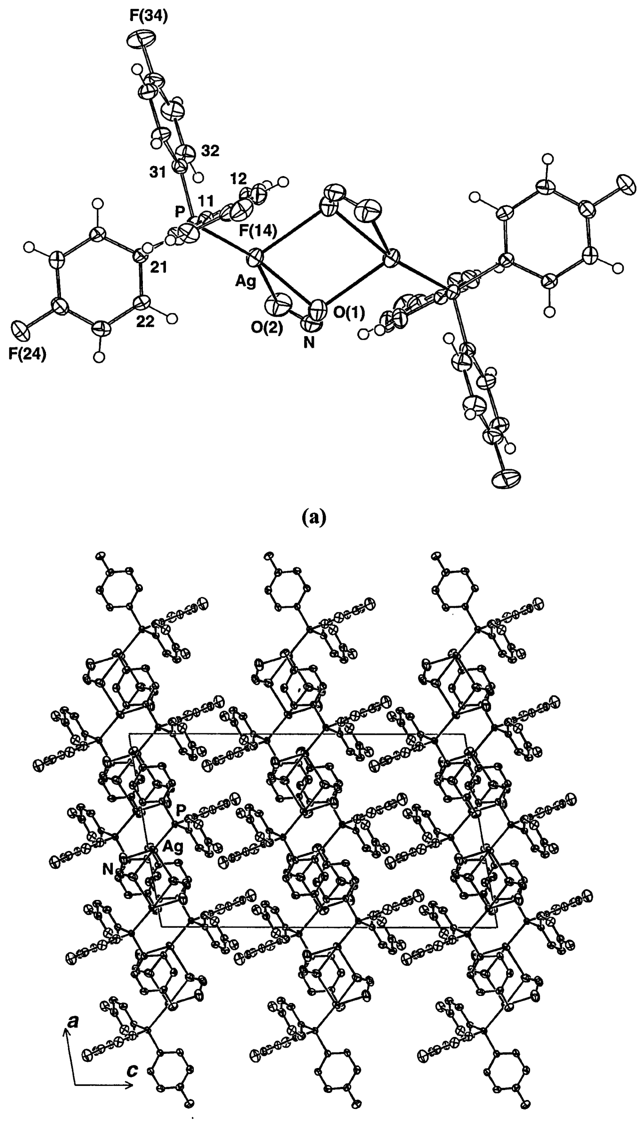
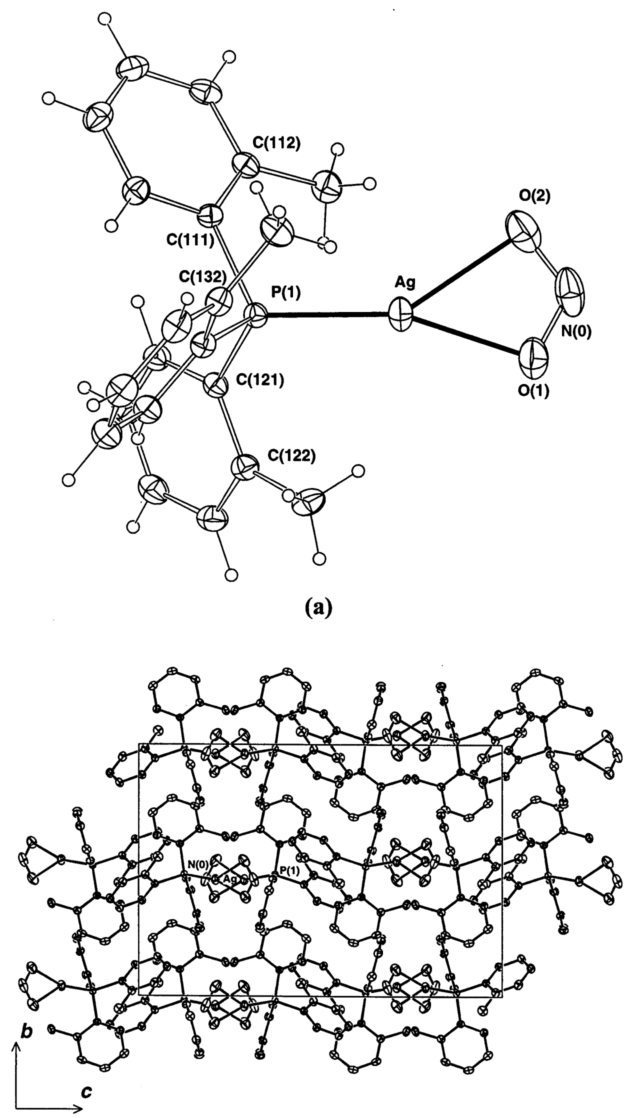


(a)

(b)

Figure 4. (a) Dimer of $AgNO_2$:P(p-C_6H_4F)$_3$ (1:1)$_2$ (**11**) projected normal to the central Ag_2O_2 plane. (b) Unit cell contents projected down *b*.



(a)

(b)

Figure 5. (a) Single molecule of $AgNO_2$:P{o-tolyl$_3$} (1:1) (**5**). (b) Unit cell contents, projected down *a*.

1:4[43] stoichiometry. Among the 1:1 complexes, relative to the remainder, the X = halide adducts are more clearly demarcated from the structural types associated with the oxyanions, the former adopting tetrameric "cubane" or "step" structures[23] and the latter oxygen-bridged one-dimensional polymers for, in particular, the nitrates.[41] Adducts $AgNO_3$:EPh_3 (1:1)$_{(\infty|\infty)}$ have been defined for all E = P,[19] As,[44] and Sb,[41] the E = P and As adducts being isomorphous and the E = 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 the others completing chelates to either side (E = P, 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 EPh_3 (E = P (**1**) and Sb (**15**) (we have been unable to obtain satisfactorily crystalline the E = As analogue), the two adducts being isomorphous in a cell (Figure 3), which is very similar in proportions to that found for $AgNO_3$:P, $AsPh_3$ (1:1)$_{(\infty|\infty)}$ (monoclinic, $P2_1/c$, $a \sim 10.7$ Å, $b \sim 18.6$ Å, $c \sim 9.1$ Å, $\beta \sim 100°$, $Z = 4$),[19,20] 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

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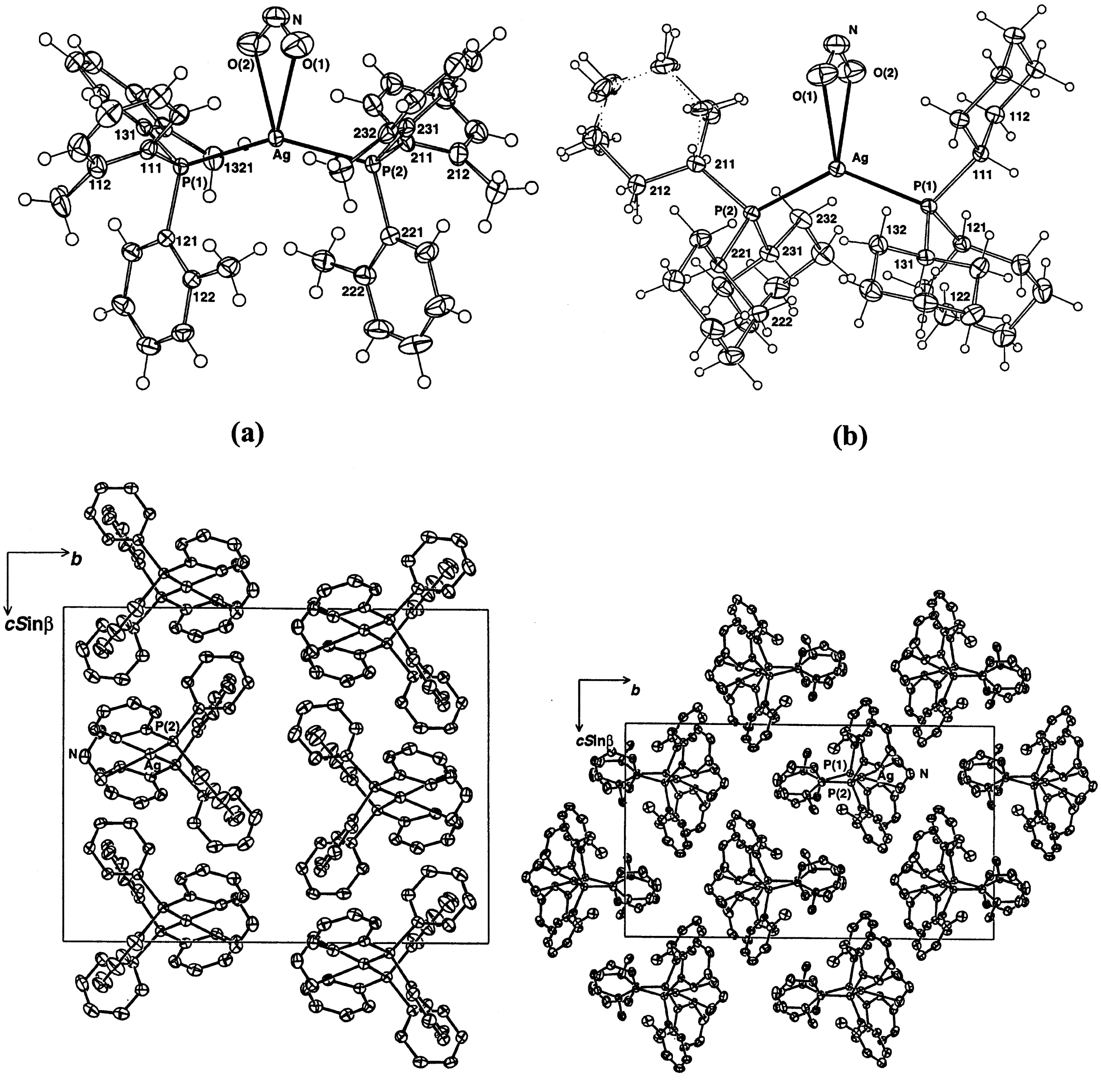

Figure 6. (a) Single molecule of $AgNO_2$:P{*o*-tolyl$_3$} (1:2) (**6**). (b) Single molecule of $AgNO_2$:Pcy_3 (**12**) (1:2) (unit cell contents are depicted in ref 44). (c) Unit cell contents of $AgNO_2$:PR_3 (1:2), PR_3 = (i) P{*o*-tolyl$_3$} (**6**) and (ii) PPh_3, (**2**), projected down *a* in 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 $AgNO_2$ with (p-F-C_6H_4)$_3$P, **11**, is unusual, being binuclear; the nitrite chelates the (R_3E)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$_3$P is a sterically more hindered base than PPh_3, and we find that in its 1:1 adduct with $AgNO_2$, **5**, a mononuclear form, one [Ag(O_2N)P(*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 P(2,4,6-(MeO)$_3$$C_6H_2$)$_3$ and with X = Cl, Br[44] 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 NO_2 plane. However, the molecules pack in a manner not dissimilar to those

Table 3. Selected Geometries: Mononuclear $AgNO_2$:PR_3 (1:2) (**2**, **6**, **12**)[a]

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);[b] −170.5(1)
Ag−P(1)−C(121)−C(122)	−29.3(3); 34.4(3), 34.5(2); −56.9(3);[b] 54.3(1)
Ag−P(1)−C(131)−C(132)	−35.8(4); 28.0(3), 26.6(2); −33.0(4);[b] 53.8(1)
Ag−P(2)−C(211)−C(212)	−30.3(4); 49.8(3), 49.0(2); −161.2(4);[b] 56.5(1)
Ag−P(2)−C(221)−C(222)	−22.8(3); 20.0(3), 20.3(2); −62.4(4);[b] 51.4(2)
Ag−P(2)−C(231)−C(232)	−47.5(3); 31.4(3), 30.4(2); −52.6(3);[b] −172.0(1)
Out of NO_2-Plane Distances (Å)	
δAg	0.06(2), 0.02(2); 0.005(8); 0.01(3); 0.067(9)

[a] The values in each entry are for R = Ph (CH_2Cl_2 solvate[40]); unsolvated room temperature,[30] low temperature (the present, **2**); Cy, **12**; *o*-tolyl, **6**. [b] 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: $AgNO_2$:$AsPh_3$ (1:2) (**13**)[a]

Distances (Å)			
Ag(*n*)−As(*n*1)	2.5236(2), 2.5432(2)	Ag−O(*n*1)	2.374(2), 2.368(2)
Ag(*n*)−As(*n*2)	2.5352(2), 2.5520(2)	Ag−O(*n*2)	2.611(2), 2.735(2)
N(*n*)−O(*n*1)	1.258(2), 1.262(2)	Ag−*O(n1)*	2.619(1), 2.566(1)
N(*n*)−O(*n*2)	1.233(3), 1.240(3)	Ag(*n*)···*Ag(n)*	4.1482(3)
		O(*n*1) ···*O(n1)*	2.789(2), 2.775(2)
Angles (deg)			
As(*n*1)−Ag(*n*1)−As(*n*2)	127.17(1), 130.26(1)	As(*n*2)−Ag(*n*)−O(*n*1)	121.17(3), 115.49(3)
As(*n*1)−Ag(*n*)−O(*n*1)	110.03(3), 110.61(3)	As(*n*2)−Ag(*n*)−O(*n*2)	103.80(3), 98.26(3)
As(*n*1)−Ag(*n*)−O(*n*2)	99.47(3), 98.87(3)	As(*n*2)−Ag(*n*)−*O(n1)*	92.78(4), 94.41(4)
As(*n*1)−Ag(*n*)−*O(n1)*	119.23(3), 119.71(3)	O(*n*1)−Ag(*n*)−O(*n*2)	49.24(6), 47.91(5)
O(*n*2)−Ag(*n*)−*O(n1)*	114.37(5), 114.06(5)	O(*n*1)−Ag(*n*)−*O(n1)*	67.71(5), 68.31(5)
Ag(*n*)−O(*n*1)−*Ag(n)*	112.29(5), 111.69(5)	Ag(*n*)−O(*n*1)−N(*n*)	104.0(1), 107.9(2)
O(*n*1)−N(*n*)−O(12)	113.9(2), 114.0(2)	Ag(*n*)−O(*n*2)−N(*n*)	92.9(1), 90.2(1)
N(*n*)−O(*n*1)−*Ag(n)*	139.4(2), 136.7(1)		
Torsion Angles (deg) (Carbon Atoms Denoted by Number Only)			
Ag(*n*)−As(*n*1)−*n*111−*n*112	40.7(1), 51.3(1)	Ag(*n*)−As(*n*2)−*n*211−*n*212	45.0(1), 21.6(2)
Ag(*n*)−As(*n*1)−*n*121−*n*122	27.7(2), 36.0(2)	Ag(*n*)−As(*n*2)−*n*221−*n*222	29.9(2), 30.8(2)
Ag(*n*)−As(*n*1)−*n*131−*n*132	58.7(2), −6.1(2)	Ag(*n*)−As(*n*2)−*n*231−*n*232	45.3(2), 92.6(2)

[a] The two values in each entry are for dimers *n* = 1,2, each being centrosymmetric; centrosymmetrically related atoms are *italicized*. The nitrite NO_2 planes make dihedral angles of 31.2(2), 39.9(2)° with the central AgO_2Ag 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_3 (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, $[Ag(O_2N)\{P(o\text{-tolyl})_3\}_2]$, **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_3 entity, namely, Pcy_3 (Figure 6b). A considerable array of mononuclear AgX:Ecy_3 (1:2) complexes have been defined for both E = P[31] and As,[45] wherein two common crystalline forms are found, one monoclinic *C*2/*c* and the other a derivative $P\bar{1}$. Both $AgNO_3$:Ecy_3 (1:2) (E = P, As) are triclinic, the molecule of the form $[Ag(O_2NO)(Pcy_3)_2]$, 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 $[Ag(O_2N)(PPh_3)_2]$, **2**, previously recorded in a room temperature study[30] and redetermined at low temperature here for the sake of comparability with the Pcy_3 and $P(o\text{-tolyl})_3$ 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 $P(o\text{-tolyl})_3$ array vis-à-vis the remainder is considerable. It is unlikely to be a consequence of "lattice forces", but whether the implication is that $P(o\text{-tolyl})_3$ is a markedly "bulkier" ligand than Pcy_3 or whether the difference is electronic is debatable. Interest-

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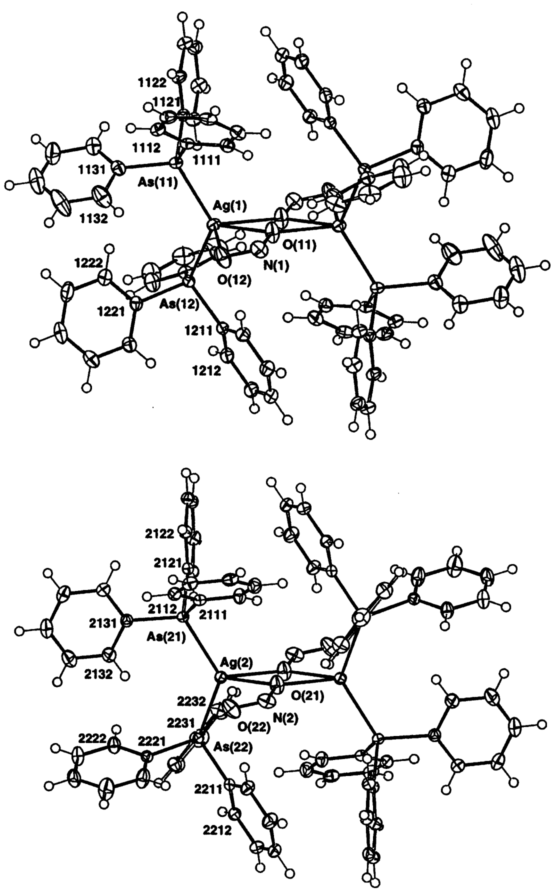

Figure 7. Dimers of $AgNO_2$:$AsPh_3$ (1:2) (**13**).

Table 5. Selected Geometries:$AgNO_2$:EPh_3 (1:2) (**14**, **16**)[a]

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)

[a] 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).

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_2 plane is far removed from coplanarity with the AgP_2 plane. In both PPh_3 and P(*o*-tolyl)$_3$ arrays, the crystal packing is of interest (Figure 6c); the PPh_3 adduct is a new AgX:EPh_3 (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 $[Ag(O_2N)(AsPh_3)_2]$ 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_3 adducts have been described for the combinations $AgNO_3$/PPh_3,[46,47] $AgNO_3$/$AsPh_3$,[20] and $CuNO_3$/$AsPh_3$,[47] none of which are isomorphous with the present, which, curiously, however, *is* isomorphous with the AgX/$SbPh_3$ (X = Cl, Br, I)[32] form and is presented here in that cell and coordinate setting, with a more rational atom numbering. These MNO_2:EPh_3 (1:2) arrays are interesting in their diversity: $CuNO_3$:PPh_3 (1:2)[48] and $CuNO_2$:PPh_3 (1:2)[49] are mononuclear and isomorphous, while $AgNO_3$:PPh_3 (1:2) (benzene[50] and toluene[51] solvates) are mononuclear and isomorphous, but of a different crystalline form. All are of the form $[M(O_2N(O))(PPh_3)_2]$, the oxyanion chelating. $AgNO_3$:PPh_3 (1:2) also exists in two different binuclear forms, one triclinic,[46] with an isomorphous E = As analogue,[20] and the other orthorhombic,[47] while $CuNO_3$:$AsPh_3$ (1:2) (binuclear) is of a different monoclinic type,[52] all of these being unsolvated. These binuclear types again exhibit different forms: in the orthorhombic phase,[47] the dimer is bound by a four-membered ring, the oxyanions bridging the two metal atoms cleanly through a single oxygen each, $[(Ph_3E)_2M(\mu\text{-}ONO_2)M(EPh_3)_2]$ (although the other

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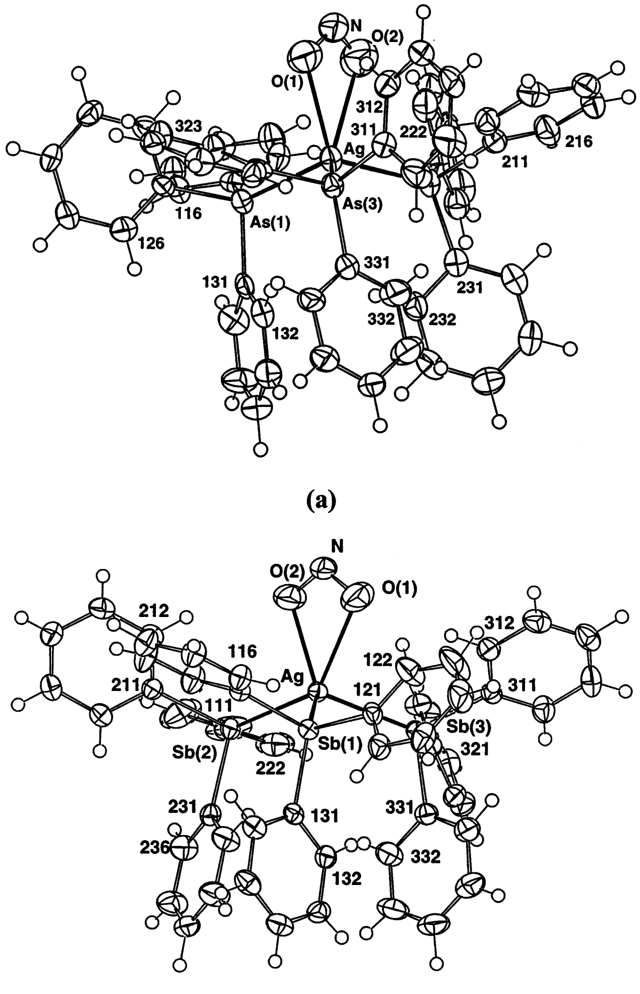

(a)

(b)

Figure 8. Projections of single molecules of (a) $AgNO_2$:$AsPh_3$ (1:3) (**14**) (in its bis(acetonitrile) solvate). (b) $AgNO_2$:$SbPh_3$ (1:3) (**16**).

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

Adducts of the form $AgNO_2$:EPh_3 (1:3) are defined herein for E = As, Sb, the E = P adduct, regrettably, not yet being accessed. The two arrays described herein are of types already described. The E = As adduct, **14**, is of the common triclinic solvated form[43] (this time as a bis(acetonitrile) solvate) for which the cell and coordinate setting of CuCl:$SbPh_3$ (1:3). $CHCl_3$[33] has been adopted by us as archetypical; other oxyanion arrays have also been defined for this form: nitrates as unidentates[42,53] and an acetate[51] as a bidentate. The E = Sb adduct[42] is unsolvated and corresponds to the common monoclinic $P2_1/n$ form, the cell and coordinate settings of the AgI:PPh_3 (1:3) array[54] taken as archetypical.

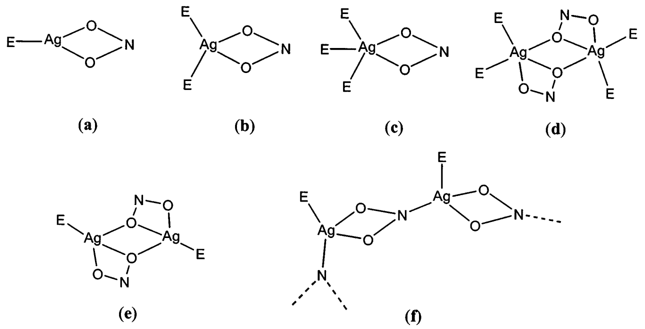

Figure 9. Topologies found for the $AgNO_2$:ER_3 adducts: (a) compound **5**; (b) compounds **2**, **6**, and **12**; (c) compounds **14** and **16**; (d) compound **13**; (e) compound **11**; (f) compounds **1** and **15**.

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 AgX:$SbPh_3$ (1:3) arrays; cf. that for AgX:Pcy_3 (1:2) above, X = *O,O′*-NO_2,NO_3, in both cases, wherein, consistently, the nitrite behaves as a consistently stronger *O,O′*-chelate. Despite similar O−N−O angles in each pair, Ag−O are shorter in the nitrite complexes, with corresponding lengthening of Ag−E and conspicuous diminution of the E−Ag−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 P(*o*-tolyl)$_3$ and Pcy_3 yield only mononuclear 1:1 or 1:2 Ag:PR_3 adducts, whereas EPh_3 donors (E = P, As, or Sb) form also 1:4 Ag:PR_3 adducts or di- or polynuclear complexes in which silver atoms are bridged by 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 acetonotrile 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 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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