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Article

(Bis(1,2,4-triazol-1-yl)methane)silver(I) Phosphino Complexes: Structures and Spectroscopic Properties of Mixed-Ligand Coordination Polymers

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Adducts of the ligand bis(1,2,4-triazol-1-yl)methane ($tz_2(CH_2)$) of the form $AgX:tz_2(CH_2):ER_3:MeCN$ (1:1:1:*x*) (X = NO_3, R = Ph, E = P, As, or Sb, *x* = 1 or 2; X = NO_2, ClO_4, O_3SCF_3, E = P, R = Ph, *x* = 0, 1 or 2; X = NO_3, ClO_4, E = P, R = cy, *x* = 1; X = ClO_4, E = As, R = Ph, *x* = 2) and $AgNO_3:tz_2(CH_2):P(o\text{-tolyl})_3$ (2:2:1) have been synthesized and characterized in the solid state and in solution by analyses, spectral (IR, far-IR, ^1H and ^{13}C NMR, ESI MS data) data, and conductivity measurements. In the one-dimensional polymers (characterized by X-ray studies) $AgNO_3:tz_2(CH_2):PPh_3:CH_3CN$ (1:1:1:1), $AgClO_4:tz_2(CH_2):PPh_3:CH_3CN$ (1:1:1:2), $AgNO_3:tz_2(CH_2):AsPh_3:CH_3CN$ (1:1:1:2), and $AgNO_3:tz_2(CH_2):SbPh_3:CH_3CN$ (1:1:1:2), the silver atom can be regarded as four-coordinate, the $tz_2(CH_2)$ ligands behaving as bridging groups rather than chelates, with no pair of ligands being dominant, quasi-trans, in their interactions. The $AgNO_3:tz_2(CH_2):P(o\text{-tolyl})_3$ (2:2:1) adduct is a two-dimensional polymer containing two independent silver atoms, one four-coordinated unsymmetrically by a pair of triazolyl rings, one $P(o\text{-tolyl})_3$, and a unidentate nitrate and the second by a quasi-symmetrical O_2NO chelate and a pair of equivalent triazolyl rings.

Introduction

The replacement of the pyrazole ring in the poly(pyrazolyl)borates, also known as Trofimenko's ligands,[1] by triazole,[2] imidazole,[3] benzotriazole,[4] or 1-methyl-2-mercaptoimidazole[5] has led to new scorpionates capable of bridging between different metal centers, yielding dimers or coordination polymers exhibiting unusual spectroscopic and structural features. Some of these new ligands offer promise for the synthesis of one-dimensional chain compounds based on metal complexes employed in the development of functional materials as molecular magnets,[6] ferroelectrics,[7] and nonlinear optics materials.[8] Poly(triazolyl)borates, for example, have been shown to yield new possibilities for supramolecular architecture in the solid state, with the incorporation of two-dimensional water layers and linkage isomerism.[9] We have recently reported some interesting single-strand silver(I) coordination polymers containing bridging poly(imidazolyl)borates[10] and some polynuclear copper(I) phosphino species containing bridging poly(triazolyl)borates.[11]

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Table 1. Selected ESI MS Data for Derivatives **1**−**4** and **6**−**10**

compd	(MeCN)Ag$^+$	(MeCN)$_2$Ag$^+$	(ER$_3$)(MeCN)Ag$^+$	(ER$_3$)(tz$_2$CH$_2$)Ag$^+$	(ER$_3$)$_2$Ag$^+$	(ER$_3$)$_2$Ag$_2$(X)$^+$	X$^-$	Ag(X)$_2$$^-$	Ag$_2$(NO$_3$)$_3$$^-$
1	147.9 (8)	188.9 (58)	410.0 (100)	520 (10)	630.8 (45)	801.7 (10)	62.2 (100)	230.9 (30)	401.6 (10)
2		188.9 (20)	501 (100)	611 (10)	814.8 (90)		62.2 (100)	230.9 (30)	401.6 (10)
3			455 (75)		721 (100)	889 (10)	62.2 (100)	230.9 (30)	401.6 (10)
4	147.9 (5)	188.9 (10)	410.0 (100)	520 (15)	630.8 (65)		99 (100)	306.7 (10)	
6					630.8 (100)				
7			429 (100)	538 (10)	668 (90)	838 (10)	62.2 (100)	230.9 (70)	
8			429 (100)	538 (5)	668 (60)	838 (2)	99 (100)	306.7 (5)	
9		189 (10)	454 (100)	565 (10)	721 (90)		99 (100)	306.7 (10)	
10		189 (5)	454 (100)	564 (10)	716 (40)	885 (8)	62.2 (100)	230.9 (30)	

The replacement of pyrazole rings in poly(pyrazolyl)alkanes by 1,2,4-triazole and tetrazole has also been reported,[12] but the coordination chemistry of poly(triazol-1-yl)- or poly(tetrazolyl)alkanes is surprisingly underdeveloped. Li[13] and Reedijk[14] have recently demonstrated that bis(1,2,4-triazol-1-yl)alkanes coordinate with copper atoms through exo-nitrogen atoms on the triazole ring to yield 1-D or 2-D coordination polymers, whereas Tang and co-workers found that (3,5-Me$_2$tz)$_2$CH$_2$ coordinates to tin atoms through exodentate nitrogen atoms at the 4-positions of the triazole rings to form linkage coordination polymers.[15] More recently Tang has reported the synthesis of group 6 metal derivatives of (3,5-Me$_2$tz)$_2$CH$_2$ and their reaction with diorganotin(IV) halides.[16] We have previously reported that tz$_2$(CH$_2$) is able to coordinate silver(I) salts through the nitrogen atoms yielding two- and three-dimensional coordination polymers,[17] and we have now extended this work to the investigation of complexes of tz$_2$(CH$_2$) with AgX in the presence of competitor P-, N-, or S-donor ligands, to build new coordination polymers with different solid-state structures and properties. Here we describe our results showing the nature of the interaction of tz$_2$(CH$_2$) with AgX (X = NO$_3$, NO$_2$, ClO$_4$, O$_3$SCF$_3$) in the presence of tertiary P-donors such as PPh$_3$, Pcy$_3$, or P(o-tolyl)$_3$.

Experimental Section

General Procedures. All reactions were carried out protected from light under an atmosphere of dry oxygen-free dinitrogen, using standard Schlenk techniques. Solvents were used as supplied or distilled by using standard methods. All chemicals were purchased from Aldrich (Milwaukee, WI) and used as received. The donor tz$_2$(CH$_2$) was synthesized by the procedure previously reported[18] and purified by several recrystallizations from chloroform/hexane. Solvents were dried by standard techniques. The samples were dried in vacuo to constant weight (20 °C, ca. 0.1 Torr). 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. ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^{1}H, 121.4 MHz for ^{31}P, and 75 MHz for ^{13}C). H and C chemical shifts are reported in ppm vs SiMe$_4$, and P chemical shifts in ppm vs H$_3$PO$_4$ 85%. The electrical conductances of the acetone and acetonitrile solutions were measured with a Crison CDTM 522 conductimeter at room temperature. 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, masses and intensities were compared to those calculated by using the IsoPro isotopic abundance simulator version 2.1;[19] peaks containing silver(I) ions are identified as the centers of isotopic clusters. Selected ESI-MS data are reported in Table 1.

Syntheses of Complexes. AgNO$_3$:tz$_2$(CH$_2$):PPh$_3$:MeCN (1:1:1:1) (1). To a solution of tz$_2$(CH$_2$) (0.15 g, 1.0 mmol) in acetonitrile (30 mL), were added AgNO$_3$ (0.17 g, 1 mmol) and PPh$_3$ (0.26 g, 1 mmol) simultaneously. The mixture was stirred to reflux for 24 h and then cooled and left at 4 °C until a colorless crystalline solid was formed, which was filtered off and dried to constant weight under reduced pressure (0.44 g, 0.7 mmol, 70% yield). The material is soluble in dmso, acetone, acetonitrile, and chlorinated solvents. Mp: 155−160 °C. Anal. Calcd for C$_{25}$H$_{24}$AgN$_8$O$_3$P: C, 48.17; H, 3.88; N, 17.98. Found: C, 48.12; H, 3.77; N, 17.83. Λ_m (CH$_3$CN, 1.0×10^{-3} M, 298 K): 135 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3130 m, 3078 w, 3054 w, ν(C$_{arom}$−H); 2287 w, 2250 m, ν(CN); 1523 m, 1513 s, ν(C$\overset{...}{-}$N + C$\overset{...}{-}$C); 520 s, 500 vs, 432 m, 404 m, 398 sh, 377 w, 278 w, 254 w, 228 w, 205 w. ^{1}H NMR (CDCl$_3$): δ 2.18 (s, 3H, C*H*$_3$CN), 6.49s (2H, C*H*$_2$), 7.30−7.55m br (15H, PC$_6$*H*$_5$), 7.97s (2H, *H*$_5$), 8.53s (2H, *H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 2.1 (*C*H$_3$CN), 59.8 s (*C*H$_2$), 118.0 s (CH$_3$*C*N), 129.3 d ($^3J_{P-C}$: 9.1 Hz, C$_m$ of PPh$_3$), 130.8 s (C$_p$ of PPh$_3$), 131.4 d ($^1J_{P-C}$: 29.6 Hz, C$_i$ of PPh$_3$), 133.9 d ($^2J_{P-C}$: 16.3 Hz, C$_o$ of PPh$_3$), 144.6 s (*C*$_5$), 153.0 s (*C*$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K): δ 12.5 br, 10.1 br. ^{31}P{^{1}H} NMR (CDCl$_3$, 218 K): δ 12.7 dd (^1J(^{31}P−^{109}Ag), 659.7 Hz; ^1J(^{31}P−^{107}Ag), 575.4 Hz), 10.4 dd (^1J(^{31}P−^{109}Ag), 518.1 Hz; ^1J(^{31}P−^{107}Ag), 451.0 Hz).

AgNO$_3$:tz$_2$(CH$_2$):SbPh$_3$:MeCN (1:1:1:2) (2). Compound **2** was synthesized by the same procedure reported for **1** (0.68 g, 0.9 mmol, 90% yield). It is very soluble in dmso and slightly soluble in acetone and acetonitrile. Mp: 196−203 °C. Anal. Calcd for C$_{27}$H$_{27}$AgN$_9$O$_3$Sb: C, 42.94; H, 3.60; N, 16.69. Found: C, 42.75; H, 3.55;

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N, 16.46. Λ_m (CH$_3$CN, 10^{-3} M, 298 K): 126 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3130 w, 3105 w, ν(C$_\mathrm{arom}$−H); 2290 br, 2250 br, ν(CN); 1573 w, 1514 w, 1505 s, ν(C$\overset{\cdots}{-}$N + C$\overset{\cdots}{-}$C); 454 s, 404 w, 378 s, 365 w, 303 w, 280 m, 262 s, 224 m. ^{1}H NMR (DMSO-d_6): δ 2.05 (s, 6H, CH_3CN), 6.68 s (2H, CH_2), 7.50 m br (15H, SbC$_6H_5$); 8.08 s (2H, H_5); 8.89 s (2H, H_3). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 59.2s (CH$_2$), 129.4 s, 129.9 s, 133.2 s, 135.6 s (SbC_6H$_5$), 145.4 s (C_5), 152.4 s (C_3).

AgNO$_3$:tz$_2$(CH$_2$):AsPh$_3$:MeCN (1:1:1:2) (3). Compound **3** was synthesized by the same procedure reported for **1** in 93% yield (0.65 g, 0.93 mmol). Mp: 202−205 °C. It is soluble in dmso and slightly soluble in acetonitrile. Anal. Calcd for C$_{27}$H$_{27}$AgAsN$_9$O$_3$: C, 45.78; H, 3.84; N, 17.80. Found: C, 45.87; H, 3.68; N, 17.65. Λ_m (CH$_3$CN, 10^{-3} M, 298 K): 123 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3097 w, ν(C$_\mathrm{arom}$−H); 2287 w, 2250 m, ν(CN); 1579 w, 1557 w, 1506 s, ν(C$\overset{\cdots}{-}$N + C$\overset{\cdots}{-}$C); 481 m, 468 vs, 418 w, 397 m, 377 w, 334 m, 320 sh, 316 s, 280 w, 265 w, 253 w, 247 w. ^{1}H NMR (DMSO-d_6): δ 2.06 (s, 6H, CH_3CN), 6.67 s (2H, CH_2), 7.55 m br (15H, AsC$_6H_5$), 8.07 s (2H, H_5), 8.87 s (2H, H_3). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 59.1 s (CH$_2$), 129.5 s, 130.3 s, 133.0 s, 134.2 s (AsC_6H$_5$), 145.4 s (C_5), 152.4 s (C_3).

AgClO$_4$:tz$_2$(CH$_2$):PPh$_3$:MeCN (1:1:1:2) (4). Compound **4** was synthesized by the same procedure reported for **1**. It is soluble in dmso, acetone, acetonitrile, and chlorinated solvents and was recrystallized from MeCN (0.31 g, 0.45 mmol, 45% yield). Mp: 205−210 °C. Anal. Calcd for C$_{27}$H$_{27}$AgClN$_8$O$_4$P: C, 46.29; H, 3.88; N, 15.97. Found: C, 46.43; H, 3.88; N, 16.21. Λ_m (CH$_3$CN, 10^{-3} M, 298 K): 83 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3123 m, 3024 w, ν(C$_\mathrm{arom}$−H); 2252 w, 2177 w (CN); 1585 s, 1570 w, 1555 w, 1514 vs, ν(C$\overset{\cdots}{-}$N + C$\overset{\cdots}{-}$C); 1136 vs, 1085 s br, 1025 s, ν_3(ClO$_4$); 623 vs, ν_4(ClO$_4$); 543 w, 521 s, 503 vs, 492 s, 444 m, 425 s, 394 s, 303 w, 281 w, 257 m, 224 m, 210 s. ^{1}H NMR (CDCl$_3$, 293 K): δ 2.02, 2.18 (2s, 6H, CH_3CN), 6.45 s (2H, CH_2), 7.20−7.50 m br (15H, PC$_6H_5$), 7.92 s (2H, H_5), 8.46 s (2H, H_3). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 2.0 br (CH$_3$CN), 59.9 s (CH$_2$), 114.0 (s, CN), 118.0 (s, CN), 129.1 d ($^3J_\mathrm{P-C}$: 9.7 Hz, *m*-C of PPh$_3$), 130.5 s (*p*-C of PPh$_3$), 132.0 d ($^1J_\mathrm{P-C}$: 29.1 Hz, *i*-C of PPh$_3$), 134.2 d ($^2J_\mathrm{P-C}$: 16.3 Hz, *o*-C of PPh$_3$), 144.4 s (C_5), 153.2 s (C_3). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K): δ 9.3 s. ^{31}P{^{1}H} NMR (CDCl$_3$, 218 K): δ 9.4 dd (^1J(^{31}P−^{109}Ag), 457.1 Hz; ^1J(^{31}P−^{107}Ag), 397.9 Hz) 8.4 d br (^1J(^{31}P−$^{107/109}$Ag), 418.1 Hz), 4.7 s br.

AgO$_3$SCF$_3$:tz$_2$(CH$_2$):PPh$_3$ (1:1:1) (5). Compound **5** was synthesized by the same procedure reported for **1** and was recrystallized from chloroform−diethyl ether (0.49 g, 0.74 mmol, 74% yield). It is soluble in dmso, acetone, acetonitrile, and chlorinated solvents. Mp: 240−246 °C. Anal. Calcd for C$_{24}$H$_{21}$AgF$_3$N$_6$O$_3$PS: C, 43.07; H, 3.16; N, 12.56; S, 4.79. Found: C, 42.82; H, 3.30; N, 12.37; S, 4.68. Λ_m (CH$_3$CN, 10^{-3} M, 298 K): 107 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3128 w, ν(C$_\mathrm{arom}$−H); 1653 w, 1569 w, 1556 w, 1519 m, ν(C$\overset{\cdots}{-}$N + C$\overset{\cdots}{-}$C); 592 w, 579 m, 568 m br, 559 w, 551 w, 543 m, 519 s, 499 s, 491 s, 469 m, 460 w, 449 w, 439 w, 433 m, 422 w, 415 w, 410 w, 397 m. ^{1}H NMR (CDCl$_3$): δ 6.45s (2H, CH_2), 7.30−7.50 m br (15H, PC$_6H_5$), 7.97 s (2H, H_5), 8.45 s (2H, H_3). ^{13}C{^{1}H} NMR (CDCl$_3$, 295 K): δ 59.8 s (CH$_2$), 129.4 d ($^3J_\mathrm{P-C}$: 9.8 Hz, C$_m$ of PPh$_3$), 131.0 s (C$_\mathrm{p}$ of PPh$_3$), 131.3 d ($^1J_\mathrm{P-C}$: 24.6 Hz, C$_i$ of PPh$_3$), 133.7 d ($^2J_\mathrm{P-C}$: 16.3 Hz, C$_o$ of PPh$_3$), 144.9 s (C_5), 152.7 s (C_3). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K): δ 11.4 s. ^{31}P{^{1}H} NMR (CDCl$_3$, 218 K): δ 9.4 d br, 5.9 br, 4.8 br.

AgNO$_2$:tz$_2$(CH$_2$):PPh$_3$ (1:1:1) (6). Compound **6** was synthesized by the same procedure reported for **1**. It was recrystallized from CH$_3$CN (0.37 g, 0.65 mmol, 65% yield). It is soluble in dmso, acetone, acetonitrile, and chlorinated solvents. Mp: 115−121 °C. Anal. Calcd for C$_{23}$H$_{21}$AgN$_7$O$_2$P: C, 48.78; H, 3.74; N, 17.31. Found: C, 48.82; H, 3.87; N, 17.18. Λ_m (CH$_3$CN, 1.0 × 10^{-3} M, 298 K): 15 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3111 w, ν(C$_\mathrm{arom}$−H); 2250 br (CN), 1557 w, 1506 s, ν(C$\overset{\cdots}{-}$N + C$\overset{\cdots}{-}$C); 543 w, 512 s, 502 vs, 492 s, 438 m, 430 w, 424 w, 398 m, 310 w, 271 w, 254 w, 233 w. ^{1}H NMR (CD$_3$CN): δ 2.14 (s, 3H, CH$_3$CN), 6.45 s (2H, CH_2), 7.40−7.50 m br (15H, PC$_6H_5$); 7.91 s (2H, H_5), 8.51 s (2H, H_3). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 3.0 s (CH$_3$CN), 61.3 s (CH$_2$), 119.6 (s, CH$_3C$N), 130.8 d ($^3J_\mathrm{P-C}$: 10.3 Hz, C_m of PPh$_3$), 132.5 d ($^4J_\mathrm{P-C}$: 1.8 Hz, C_p of PPh$_3$), 131.4 d ($^1J_\mathrm{P-C}$: 31.5 Hz, C_i of PPh$_3$), 135.2 d ($^2J_\mathrm{P-C}$: 16.4 Hz, C_o of PPh$_3$), 146.4 s (C_5), 154.2 s (C_3). ^{31}P{^{1}H} NMR (CD$_3$CN, 293 K): δ 10.3 br. ^{31}P{^{1}H} NMR (CDCl$_3$, 238 K): δ 9.1 d br (^1J(^{31}P−$^{107/109}$Ag): 575.5 Hz).

AgNO$_3$:tz$_2$(CH$_2$):Pcy$_3$:MeCN (1:1:1:1) (7). Compound **7** was synthesized by the same procedure reported for **1** and was recrystallized by acetonitrile (0.51 g, 0.80 mmol, 80% yield). It is soluble in dmso, acetone, and acetonitrile and poorly soluble in chlorinated solvents. Mp: 130−132 °C. Anal. Calcd for C$_{25}$H$_{42}$AgN$_8$O$_3$P: C, 46.81; H, 6.60; N, 17.47. Found: C, 46.58; H, 6.50; N, 17.53. Λ_m (CH$_3$CN, 10^{-3} M, 298 K): 140 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3104 w, ν(C$_\mathrm{arom}$−H); 2293 w, 2250 w, 1511 m, ν(C$\overset{\cdots}{-}$N + C$\overset{\cdots}{-}$C); 521 m, 512 m, 488 w, 470 w, 455 w, 439 w, 429 w, 403 w, 387 w, 367 w, 346 w, 318 w, 294 w, 270 w, 261 w, 238 w. ^{1}H NMR (CD$_3$CN): δ 1.3 br (12H, C$_6H_{11}$), 1.8 br (12H, C$_6H_{11}$), 2.11 s (3H, C$_6H_{11}$), 2.19 s (3H, CH_3CN) 6.46 s (2H, CH_2), 7.92 s (2H, H_5), 8.52 s (2H, H_3). ^{13}C{^{1}H} NMR (CD$_3$CN, 295 K): δ 26.8 s (C_6H$_{11}$), 27.85 d (C_6H$_{11}$), 31.7 br (C_6H$_{11}$), 32.4 d (C_6H$_{11}$), 60.8 (CH$_2$), 145.99 s (C_5), 153.7 s (C_3). ^{31}P{^{1}H} NMR (CD$_3$CN, 295 K): 34.89 dd, (^1J(^{31}P−^{109}Ag), 748 Hz; ^1J(^{31}P−^{107}Ag), 648 Hz), 31.83 dd (^1J(^{31}P−^{109}Ag), 529 Hz; ^1J(^{31}P−^{107}Ag), 458 Hz).

AgClO$_4$:tz$_2$(CH$_2$):Pcy$_3$:MeCN (1:1:1:1) (8). Compound **8** was synthesized by the same procedure reported for **1** and was recrystallized from acetonitrile (0.51 g, 0.80 mmol, 80% yield). It is soluble in dmso, acetone, and acetonitrile and poorly soluble in chlorinated solvents. Mp: 179−181 °C. Anal. Calcd for C$_{25}$H$_{42}$AgClN$_7$O$_4$P: C, 44.23; H, 6.24; N, 14.44. Found: C, 44.19; H, 6.50; N, 14.17. Λ_m (CH$_3$CN, 10^{-3} M, 298 K): 142 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3117 w, 3039 w, ν(C$_\mathrm{arom}$−H); 2288 w, 2255 m, ν(CN); 1522 m, 1509 m, ν(C$\overset{\cdots}{-}$N + C$\overset{\cdots}{-}$C); 519 br, 472 m, 459 m, 439 w, 431 w, 399 br, 386 m, 280 w, 235 br. ^{1}H NMR (CD$_3$CN): δ 1.3 br (12H, C$_6H_{11}$), 1.8 br (12H, C$_6H_{11}$), 2.10 s (3H, C$_6H_{11}$), 2.15 s (3H, CH_3CN), 6.46 s (2H, CH_2), 7.94 s (2H, H_5), 8.56 s (2H, H_3). ^{1}H NMR (CDCl$_3$): δ 1.4 br (12H, C$_6H_{11}$), 1.8 br (12H, C$_6H_{11}$), 2.16 s (3H, C$_6H_{11}$), 2.15 s (3H, CH_3CN), 6.58 s (2H, CH_2), 7.96 s (2H, H_5), 8.72 s (2H, H_3). ^{1}H NMR (DMSO-d_6): δ 1.3 br (12H, C$_6H_{11}$), 1.8 br (12H, C$_6H_{11}$), 2.18 s (3H, C$_6H_{11}$), 2.08 s (3H, CH_3CN), 6.65 s (2H, CH_2), 8.05 s (2H, H_5), 8.84 s (2H, H_3). ^{13}C{^{1}H} NMR (CD$_3$CN, 295 K): δ 26.6 s (C_6H$_{11}$), 27.72 d (C_6H$_{11}$), 31.57 m (C_6H$_{11}$), 31.86 br (C_6H$_{11}$), 32.15 d (C_6H$_{11}$), 32.36 d (C_6H$_{11}$), 60.65 (CH$_2$), 145.74 s (C_5), 153.47 s (C_3). ^{31}P{^{1}H} NMR (CD$_3$CN, 295 K): δ 34.3 dd, (^1J(^{31}P−^{109}Ag), 743 Hz; ^1J(^{31}P−^{107}Ag, 643 Hz), 32.1 dd (^1J(^{31}P−^{109}Ag), 529 Hz; ^1J(^{31}P−^{107}Ag), 458 Hz). ^{31}P{^{1}H} NMR (CD$_3$CN, 243 K): δ 33.6 dd, (^1J(^{31}P−^{109}Ag), 734 Hz; ^1J(^{31}P−^{107}Ag), 636 Hz), 31.1 dd (^1J(^{31}P−^{109}Ag, 519 Hz; ^1J(^{31}P−^{107}Ag), 449 Hz).

AgClO$_4$:tz$_2$(CH$_2$):AsPh$_3$:MeCN (1:1:1:2) (9). Compound **9** was synthesized similarly to **1** and was recrystallized by acetonitrile (0.48 g, 0.65 mmol, 65% yield). It is soluble in dmso, acetone, and acetonitrile and poorly soluble in chlorinated solvents. Mp: 264−267 °C. Anal. Calcd for C$_{27}$H$_{27}$AgAsClN$_8$O$_4$: C, 43.48; H, 3.65; N, 15.02. Found: C, 43.19; H, 3.50; N, 15.17. Λ_m (CH$_3$CN, 10^{-3} M, 298 K): 146 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3119 w, 3039 w, ν(C$_\mathrm{arom}$−H); 2288 w, 2255 m, ν(CN); 1578 w, 1513 m ν(C$\overset{\cdots}{-}$N + C$\overset{\cdots}{-}$C); 482 m, 467 m, 395 w, 334 w, 324 w, 314 m,

Table 2. Crystal/Refinement Data

compd	**1**	**2**	**3**	**4**	**10**
formula	$C_{25}H_{24}AgN_8O_3P$	$C_{27}H_{27}AgAsN_9O_3$	$C_{27}H_{27}AgN_9O_3Sb$	$C_{27}H_{27}AgClN_8O_4P$	$C_{31}H_{33}Ag_2N_{14}O_6P$
M_r	623.4	708.4	755.2	701.9	944.4
cryst system	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P1$ (No. 1)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No.2)
a (Å)	8.5328(8)	9.132(2)	9.1565(8)	9.321(3)	10.5051(7)
b (Å)	8.9443(9)	9.311(2)	9.2491(8)	9.590(3)	11.3410(8)
c (Å)	10.562(1)	19.544(2)	20.084(2)	19.689(6)	17.539(1)
α (deg)	75.501(2)	90.064(5)	87.842(2)	80.139(7)	76.802(2)
β (deg)	66.906(2)	89.671(5)	87.911(2)	78.830(7)	77.954(2)
γ (deg)	65.620(2)	61.464(4)	62.131(2)	61.248(7)	62.598(1)
V (Å^3)	671.6	1470	1502	1507	1793
D_c (g cm^{-3})	1.541	1.601	1.669	1.546	1.749
Z (f.u.)	1	2	2	2	2
μ_{Mo} (mm^{-1})	0.85	1.85	1.60	0.86	1.20
specimen (mm)	0.35 × 0.22 × 0.16	0.75 × 0.09 × 0.08	0.60 × 0.09 × 0.06	0.29 × 0.07 × 0.05	0.25 × 0.20 × 0.16
$T_{min/max}$	0.72	0.75	0.83	0.84	0.84
$2\theta_{max}$ (deg)	75	75	75	63	75
N_{total}	13 585	30 311	31 110	21 595	31 385
N_{unique} (R_{int})	5409 (0.028)	15 163 (0.030)	15 439 (0.029)	9811 (0.063)	17 806 (0.024)
N_o	5328	11 334	10 763	5765	11 922
R^a	0.028^b	0.031	0.034	0.046	0.038
$R_w{}^a$	0.034	0.037	0.035	0.040	0.041

^{a} $R = \Sigma\Delta/\Sigma F_o{}^2$; $R_w = (\Sigma w\Delta^2/\Sigma wF^2)^{1/2}$. ^{b} Friedel data preserved distinct, x_{abs} refining to $-0.02(1)$.

279 w, 230 br. ^{1}H NMR (CD_3CN): δ 2.12 s (6H, CH_3CN), 6.46 s (2H, CH_2), 7.4−7.6 m (15H, C_6H_5), 7.94 s (2H, H_5), 8.56 s (2H, H_3). ^{1}H NMR ($CDCl_3$): δ 2.01 s (6H, CH_3CN), 6.48 s (2H, CH_2), 7.2−7.4 m (15H, C_6H_5), 7.92 s (2H, H_5), 8.58 s (2H, H_3). ^{1}H NMR (DMSO-d_6): δ 2.08 s (6H, CH_3CN), 6.62 s (2H, CH_2), 7.3−7.6 m (15H, C_6H_5), 8.03 (2H, H_5), 8.82 s (2H, H_3). ^{13}C{^{1}H} NMR (CD_3CN): δ 60.76 (CH_2), 130.47, 131.34, 134.05, 135.08 (AsC_6H_5), 145.9 s (C_5), 153.3 s (C_3).

$AgNO_3$:tz$_2$(CH_2):P(*o*-tolyl)$_3$ (2:2:1) (10). Compound **10** (0.450 g, 0.47 mmol, 95% yield) was synthesized by the same procedure reported for **1**, by using 0.150 g of tz$_2$(CH_2)$_2$, 0.170 g of $AgNO_3$, and 0.156 g (0.5 mmol) of P(*o*-tolyl)$_3$. It is soluble in dmso, acetone, and acetonitrile and poorly soluble in chlorinated solvents. Mp: 213−214 °C. Anal. Calcd for $C_{31}H_{33}Ag_2N_{14}O_6P$: C, 39.43; H, 3.52; N, 20.76. Found: C, 39.73; H, 3.66; N, 20.59. Λ_m (CH_3CN, 1.0 × 10^{-3} M, 298 K): 203 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3130 w, 3050 w, ν(C_{arom}−H); 1586 m, 1570 w, 1537 m, 1531 m, 1524 m, 1519 m, 1505 m, ν(C$\cdots$N + C$\cdots$C); 562 m, 556 m, 521 w, 511 w, 467 m, 460 m, 439 w, 411 w, 389 m, 373 w, 268 br, 246 w, 227 w, 213 w. ^{1}H NMR ($CDCl_3$): δ 2.54 s (9H, CH_3), 6.45 s (4H, CH_2), 6.82 m (4H, PC_6H_4), 7.44 m br (8H, PC_6H_4), 7.98 s (4H, H_5), 8.43 s (2H, H_3). ^{1}H NMR (CD_3CN): δ 2.43 s (9H, CH_3), 6.48 s (4H, CH_2), 6.85 m br (3H, PC_6H_4), 7.12 pt (3H, PC_6H_4), 7.45 m br (6H, PC_6H_4), 7.93 s (4H, H_5), 8.55 s (2H, H_3). ^{13}C{^{1}H} NMR (CD_3CN): δ 22.14 s, 22.48 s (CH_3), 60.79 s (CH_2), 128.0 d ($^3J_{P-C}$: 6.85 Hz, PC_6H_4), 131.16 s (PC_6H_4), 132.8 d ($^1J_{P-C}$: 7.2 Hz, PC_6H_4), 134.0 d ($^2J_{P-C}$: 6.5 Hz, PC_6H_4), 143.4 s (PC_6H_4), 145.9 s (C_5), 153.6 s (C_3). ^{31}P{^{1}H} NMR (CD_3CN, 293 K): δ −20.6 s. ^{31}P{^{1}H} NMR ($CDCl_3$, 218 K): δ −22.5 dd (^1J(^{31}P−Ag): 663 Hz).

$AgNO_3$:tz$_2$(CH_2):PPh_3:CH_3OH (1:1:1:2) (11). Compound **11** was synthesized by the same procedure reported for **1**, using MeOH as solvent (0.33 g, 0.5 mmol, 50% yield). It is soluble in dmso, acetone, and acetonitrile. Mp: 155−160 °C. Anal. Calcd for $C_{25}H_{29}AgN_7O_5P$: C, 46.45; H, 4.52; N, 15.17. Found: C, 46.32; H, 4.59; N, 15.46. Λ_m (DMSO, 1.0 × 10^{-3} M, 298 K): 40 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3300 br, ν(OH); 3098 m, 3030 w, ν(C_{arom}−H); 1605 br, δ(OH); 1582 wm, 1514 m, ν(C$\cdots$N + C$\cdots$C); 522 s, 505 s, 490 s, 441 m, 426 m, 397 m, 279 w, 253 w, 224 w. ^{1}H NMR (DMSO-d_6): δ 3.3 s (6H, CH_3OH), 4.1 (2H, CH_3OH), 6.64 s (2H, CH_2), 7.30−7.55 m br (15H, PC_6H_5), 8.02 s (2H, H_5), 8.82 s (2H, H_3). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 48.5 s, 48.7 (s, CH_3OH), 59.1 s, 59.2 s (CH_2), 129.4 m, 130.9 s, 131.0 s, 131.5 s, 132.3 m (C_{arom} of PPh_3), 145.3 s, 145.4 s (C_5), 152.4 s, 152.5 s (C_3). ^{31}P{^{1}H} NMR (DMSO-d_6, 293 K): δ 12.5 d (^1J(^{31}P−Ag): 687 Hz).

Structure Determinations. Full spheres of CCD area-detector diffractometer data were measured at ca. 153 K (Bruker AXS instrument; ω-scans; monochromatic Mo Kα radiation, λ = 0.710 73 Å), yielding N_{total} reflections. These merged to N_{unique} (R_{int} quoted) after "empirical"/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being considered "observed" and used in the full-matrix least-squares refinement, refining anisotropic displacement parameter forms for the non-hydrogen atoms, $(x,y,z,U_{iso})_H$, constrained at estimated values. Conventional residuals R and R_w on $|F|$ at convergence are quoted (weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$). Neutral atom complex form factors were employed within the Xtal 3.7 program system.[20] Pertinent results are given below and in Tables 2−4 and figures, the latter showing 50% probability amplitude displacement envelopes for the non-hydrogen atoms, hydrogen atoms, where shown, having arbitrary radii of 0.1 Å. In **4**, the perchlorate was modeled with the oxygen atoms disordered over two sets of sites, occupancies refining to 0.680(7) and complement. Full CIF depositions (excluding structure factor amplitudes) have been made as Supporting Information.

Results and Discussion

Syntheses. Derivatives **1**−**9** were synthesized by the interaction of bis(1,2,4-triazol-1-yl)methane with the appropriate silver salts AgX in the presence of equimolar EPh_3 (E = P, As, or Sb) or Pcy_3 in acetonitrile solution (eq 1). No adducts were afforded under the same conditions when silver(I) halides as acceptors or P(2,4,6-$Me_3C_6H_2$)$_3$ as P-donors were employed. The adduct **10**, ($AgNO_3$):tz$_2$(CH_2):P(o-tolyl)$_3$ (2:2:1), was obtained in high yield when a 2:2:1 molar ratio was employed but also precipitates from the

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

reaction solution when a 1:1:1 molar ratio has been used.

$$n\mathrm{tz_2(CH_2)} + n\mathrm{AgX} + m\mathrm{ER_3} + x\mathrm{MeCN} \rightarrow (\mathrm{AgX}){:}\mathrm{tz_2(CH_2)}{:}\mathrm{ER_3}{:}\mathrm{CH_3CN}\ (n{:}n{:}m{:}x) \quad (1)$$

1, $n = 1$, $m = 1$, $x = 1$, $X = NO_3$, $E = P$, $R = Ph$;
2, $n = 1$, $m = 1$, $x = 2$, $X = NO_3$, $E = Sb$, $R = Ph$

3, $n = 1$, $m = 1$, $x = 2$, $X = NO_3$, $E = As$, $R = Ph$;
4, $n = 1$, $m = 1$, $x = 2$, $X = ClO_4$, $E = P$, $R = Ph$

5, $n = 1$, $m = 1$, $x = 0$, $X = O_3SCF_3$, $E = P$; $R = Ph$;
6, $n = 1$, $m = 1$, $x = 0$, $X = NO_2$, $E = P$, $R = Ph$

7, $n = 1$, $m = 1$, $x = 1$, $X = NO_3$, $E = P$, $R = cy$;
8, $n = 1$, $m = 1$, $x = 1$, $X = ClO_4$, $E = P$, $R = cy$

9, $n = 1$, $m = 1$, $x = 1$, $X = ClO_4$, $E = As$, $R = cy$

It is noteworthy that the stoichiometries found for **1**−**10** are generally independent of the ligand-to-metal ratio employed, although if a large excess of the ER$_3$ donor was used the well-known (ER$_3$)$_x$AgX species were formed. The order of mixing and the reaction times are important: when a solution of the ligand tz$_2$(CH$_2$) was added to a preprepared solution of AgX and EPh$_3$, coordination of the N-donor to the silver appears not to happen, (EPh$_3$)$_x$AgX species always being obtained. By contrast, if the addition of tz$_2$(CH$_2$) to AgX solutions was made simultaneously with that of ER$_3$, derivatives **1**−**10** were formed in quantitative yields. In addition, if the solutions of tz$_2$(CH$_2$), AgX, and ER$_3$ were evaporated 1 h after the mixing, (ER$_3$)$_x$AgX were the only compounds identified. The best way to synthesize **1**−**10** is by slow diffusion of an acetonitrile solution of tz$_2$(CH$_2$) and EPh$_3$ in a solution of AgX, followed by slow evaporation of the solvent. All compounds are prone to absorb molecules of solvent from the CH$_3$CN solution, from which they can be recrystallized.

When the reaction between tz$_2$(CH$_2$), AgNO$_3$, and PPh$_3$ was carried out in methanol, the polynuclear adduct (AgNO$_3$):tz$_2$(CH$_2$):PPh$_3$:CH$_3$OH (1:1:1:2) (**11**) appears to be formed. It is interesting to note that this compound is not immediately soluble in acetonitrile, whereas when **11** is left stand in acetonitrile solution for 2 days, it dissolves and, after evaporation, crystals of **1** are formed.

Most of the derivatives **1**−**10** are poorly soluble in chlorinated solvents, in contrast to previously described polymeric complexes of tz$_2$(CH$_2$), but are more soluble in acetonitrile and in oxygenated solvents such as acetone and DMSO.[17] It is interesting to note that the nitrate complexes **1**−**3** exhibit conductivity values in acetonitrile or DMSO typical of electrolytic species according to eq 2, whereas the nitrite compound **6** is a nonelectrolyte in acetone, suggesting strong coordination of the counteranion also in solution. The perchlorate **4** and the triflate **5** exhibit conductivity values typical of partly ionized species, suggesting partial displacement of the counterion in solution or ion-pair formation. By contrast, the Pcy$_3$ derivatives exhibit the higher conductivity values, suggesting that the sterically hindered phosphine inhibits the nitrate and perchlorate coordination in solution.

$$(\mathrm{AgX}){:}\mathrm{tz_2(CH_2)}{:}\mathrm{ER_3}{:}\mathrm{MeCN}\ (n{:}n{:}m{:}x) + y\mathrm{MeCN} \rightarrow [\mathrm{Ag}_n(\mathrm{ER_3})_m(\mathrm{MeCN})_{x+y}] + n\mathrm{X}^- + n\mathrm{tz_2(CH_2)} \quad (2)$$

The existence of a very weak interaction between the nitrate and silver in **1**−**3** has been confirmed from X-ray studies (see below), which indicated Ag−O$_{\mathrm{nitrate}}$ distances longer than those found in the parent polymeric compounds not containing EPh$_3$. The conductivity measurements suggest that here the Ag−O$_{\mathrm{perchlorate}}$ interaction is stronger than the Ag−O$_{\mathrm{nitrate}}$.

In the IR spectra of all compounds the ring breathing vibrations fall between 1530 and 1510 cm^{-1}. In the IR spectra of **1**−**3**, which can be considered four-coordinate, the absorptions due to NO$_3$ are typical of an ionic group.[21] Also the perchlorate bands are similar to those found in ionic perchlorato species, although the presence of some shoulders may indicate weak interaction between the perchlorate and the metal.[22] The nitrite behavior in **6** is not well defined due to the presence in the solid spectra of several overlapping absorptions in the region 900−1500 cm^{-1},[23] but the existence of Ag−O interactions seems to be supported by the presence of weak to medium absorptions in the range 150−450 cm^{-1}.[24] The ionic CF$_3$SO$_3^-$ group has lower symmetry (C_{3v}), but the absence of splitting of the band at 1261 cm^{-1} is consistent with the presence of a triflate of that form in **5**.[25] The absence of coordinated MeCN, the poor solubility, and the presence of only one P-donor suggest for **5** a cationic polymeric array with the tz$_2$(CH$_2$) perhaps coordinated not only through N(4) but also with the N(2) as previously found.[17]

The strong absorption bands at ca. 1740 and 1270 cm^{-1} assigned to the triazole ring stretching vibrations for the free tz$_2$(CH$_2$) ligand are also present in the spectra of the complexes but are rather weak, these absorption bands being shifted to ca. 1750 and 1279 cm^{-1} in complex **1** and to ca. 1745 and 1275 cm^{-1} in complex **10**.

In the IR spectra of **1**−**4** and **7**−**9** the vibrations of the acetonitrile molecules are always found at ca. 2290 and 2250 cm^{-1}. The lower frequency band is assigned to the C≡N stretching vibration, with that at higher frequency to the $\nu_3 + \nu_4$ combination band, mixed with C≡N stretching.[26] Comparison of the absorptions in **1**−**4** and **7**−**9** with those of free MeCN indicates no significant shift upon coordination. In the far-infrared region of **1**−**11** broad small peaks were found at ca. 270 and 230 cm^{-1} which are comparable with those for Ag−N vibrations as given in the literature.[27]

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Table 3. Selected Geometries of **1**−**4**[a]

	1	**2**	**3**	**4**
Distances (Å)				
Ag−N(14)	2.281(3)	2.310(2)	2.299(2)	2.323(3)
Ag−N(24*)	2.308(3)	2.273(2)	2.269(2)	2.286(3)
Ag−E	2.3807(7)	2.4751(5)	2.5995(4)	2.371(1)
Ag−N(1)	2.729(6)	2.631(2)	2.616(2)	2.585(4)
Ag−O(1)	3.186(4)	2.940(2)	2.914(2)	2.951(4)
Angles (deg)				
N(14)−Ag−N(24*)	100.59(9)	95.99(6)	96.76(7)	96.2(1)
N(14)−Ag−E	133.86(6)	121.92(4)	120.74(5)	131.68(9)
N(14)−Ag−N(1)	95.2(1)	86.31(6)	84.87(6)	85.3(1)
N(14)−Ag−O(1)		85.38(5)	86.27(6)	77.1(6)
N(24*)−Ag−E	125.38(7)	140.84(4)	140.60(4)	131.58(8)
N(24*)−Ag−N(1)	84.9(1)	87.72(6)	88.21(8)	89.7(1)
N(24*)−Ag−O(1)		76.00(6)	78.44(7)	80.1(2)
E−Ag−N(1)	92.8(1)	102.96(4)	105.54(5)	99.52(9)
E−Ag−O(1)		96.11(3)	91.47(4)	101.4(1)
N(1)−Ag−O(1)		160.82(6)	162.99(7)	158.5(1)
Ag−N(1)−C(1)	138.7(3)	154.6(2)	156.0(2)	159.9(4)
Ag−N(14)−C(13)	126.0(2)	131.0(1)	132.2(1)	125.3(2)
Ag−N(14)−C(15)	129.4(3)	125.2(1)	124.4(1)	129.0(3)
Ag*−N(24)−C(23)	130.9(2)	126.0(1)	124.7(2)	134.4(3)
Ag*−N(24)−C(25)	125.9(3)	129.0(1)	129.2(1)	120.6(2)
N(11)−C(0)−N(21)	111.4(2)	111.3(1)	111.1(2)	112.3(3)
C_2N_3/C_2N_3 Interplanar Dihedral Angles (deg)				
$\theta_{1/2}$	70.8(1)	73.08(7)	73.86(9)	68.6(2)
Silver Deviations from the C_2N_3 and NO_3 Planes (Å)				
δ_{tz_1}	0.379(6)	0.150(3)	0.169(4)	0.521(7)
δ_{tz_2}	0.171(6)	0.447(3)	0.548(4)	0.406(6)
δ_{NO_3}	1.33(1)	0.564(6)	0.196(7)	
Torsion Angles (deg)				
N(21)−C(0)−N(11)−N(12)	86.4(3)	83.2(2)	83.1(2)	80.7(4)
N(11)−C(0)−N(21)−N(22)	−62.1(4)	−80.4(2)	−80.1(2)	−77.1(4)

[a] Asterisked atoms are related by a unit translation in the polymer string.

Table 4. Selected Geometries of **10**[a]

atoms	param	atoms	param
Distances (Å)			
Ag(1)−N(114)	2.216(2)	Ag(2)−N(124)	2.134(2)
Ag(1)−N(214)	2.565(3)	Ag(2)−N(224^{i})	2.134(2)
Ag(1)−P	2.3895(6)	Ag(2)−O(11^{ii})	2.731(2)
Ag(1)−O(11)	2.672(2)	Ag(2)−O(12^{ii})	2.755(2)
Angles (deg)			
N(114)−Ag(1)−N(214)	90.09(8)	N(124)−Ag(2)−N(224^{i})	169.21(9)
N(114)−Ag(1)−P	151.97(6)	N(124)−Ag(2)−O(11^{ii})	104.08(9)
N(114)−Ag(1)−O(11)	90.11(6)	N(124)−Ag(2)−O(12^{ii})	79.23(8)
N(214)−Ag(1)−P	109.23(5)	N(224^{i})−Ag(2)−O(11^{ii})	86.25(7)
N(214)−Ag(1)−O(11)	116.75(7)	N(224^{i})−Ag(2)−O(12^{ii})	110.69(7)
P−Ag(1)−O(11)	98.49(5)	O(11^{ii})−Ag(2)−O(12^{ii})	46.54(6)
Ag(1)−N(114)−C(113)	133.7(1)	Ag(2)−N(124)−C(123)	125.2(2)
Ag(1)−N(114)−C(115)	123.0(1)	Ag(2)−N(124)−C(125)	130.8(2)

[a] The interplanar dihedral angles between the two C_2N_3 rings of the ligands are 84.9(1), 80.2(1)° (ligands 1, 2); δ(Ag(1,2)) from the two planes of ligand 1 are 0.070(4) and 0.195(4) Å, and Ag($1,2^{iii}$) from those of ligand 2 are 1.675(4) and 0.085(4) Å. Transformations i−iii of the asymmetric unit are the following: $x - 2, y + 1, z$; $x - 1, y + 1, z$; $x + 2, y - 1, z$. Torsion angle pairs for each ligand (as in Table 2) are 70.9(3), 51.2(3) and −44.8(4), −61.8(3)°.

The ^1H and ^{13}C NMR spectra of the complexes in CD_3CN and DMSO-d_6 show chemical shifts for the protons and carbons of the ligands in the complexes which are not very different from those of the free ligand, presumably due to some partial dissociation of the complexes in solution. A slightly downfield shift was generally found for all carbons and for the H3 and bridging CH_2 protons, whereas H5 are always shifted to high field. These data indicate that extensive dissociation of **1**−**11** occurs in CD_3CN and DMSO-d_6, suggesting weaker interaction between the ligands and the silver(I) acceptors in these solvents. In some cases it has been possible to record the ^1H spectra in $CDCl_3$ solution; in this solvent a greater chemical shift was found with respect to the free tz_2CH_2, suggesting at least partial formation of complexed species in solution. The ^{31}P NMR spectra also indicate that **1**, **3**−**8**, and **10** and **11** dissociate in solution, yielding not only species of formula $PR_3Ag(MeCN)^+$ (the most abundant species in all cases as confirmed also by ESI-MS data; see below) but also $(PR_3)_2Ag^+$ and $(PR_3)_2Ag(MeCN)^+$ as confirmed by the Ag−P coupling constant values. Silver−phosphorus coupling constants have been used by many workers to examine the coordination geometry around the silver center. The two values observed for compound **1** (617 and 484 Hz) agree well with that seen for other two-coordinate species containing one and two unidentate triorganophosphines, respectively.[28]

ESI-MS has proved to be a powerful tool for the analysis of ionic species in solution, several class of chemical compounds having been characterized since its introduction. Useful information regarding stoichiometry has also been achieved for the solution speciation of coordination compounds augmenting that available from spectroscopic techniques. In this context, ESI-MS spectra were recorded for **1**−**4** and **6**−**11** by dissolving small quantities of crystals in acetonitrile to assess the nature of the complexes in solution. The mass spectra of these compounds reveal the presence of a variety of species. For example, in the case of **4**, the following ion peaks were found in the ion positive spectrum: *m*/*z* 147.9 $[(MeCN)Ag]^+$ (5), 188.9 $[(MeCN)_2Ag]^+$ (10), 410.0 $[PPh_3(MeCN)Ag]^+$ (100), 520 $[PPh_3(tz_2(CH_2))Ag]^+$ (15), 632.5 $[(PPh_3)_2Ag]^+$ (65), the isotopic distribution of these species being in accord with the calculated composition. These data indicate that these derivatives mainly undergo loss of the anionic X-group and of the neutral N-donor ligand owing to weak interaction between $tz_2(CH_2)$ with silver in solution, whereas MeCN does itself show ligating properties toward silver(I) ions, as confirmed from the peaks at *m*/*z* 147.9 and 188.9. It is interesting to note that a small peak due to simultaneous coordination of the ER_3 and $tz_2(CH_2)$ was found in the ESI-MS spectra of all PPh_3 derivatives but not in the spectra of compounds containing a more sterically hindered phosphine such as **7**, **8**, and **10** or in the EPh_3 (E = As or Sb) derivatives. No species containing more than two ER_3 ligands were detected, whereas dimeric species of formula $[(ER_3)_2Ag_2X]^+$ were observed only when X = NO_3.

To optimize the conditions for preparation of the polynuclear species **1**−**11**, we have also recorded ESI-MS spectra of mixture containing $tz_2(CH_2)$, ER_3, and AgX in different molar ratio. We have found that the peak due to

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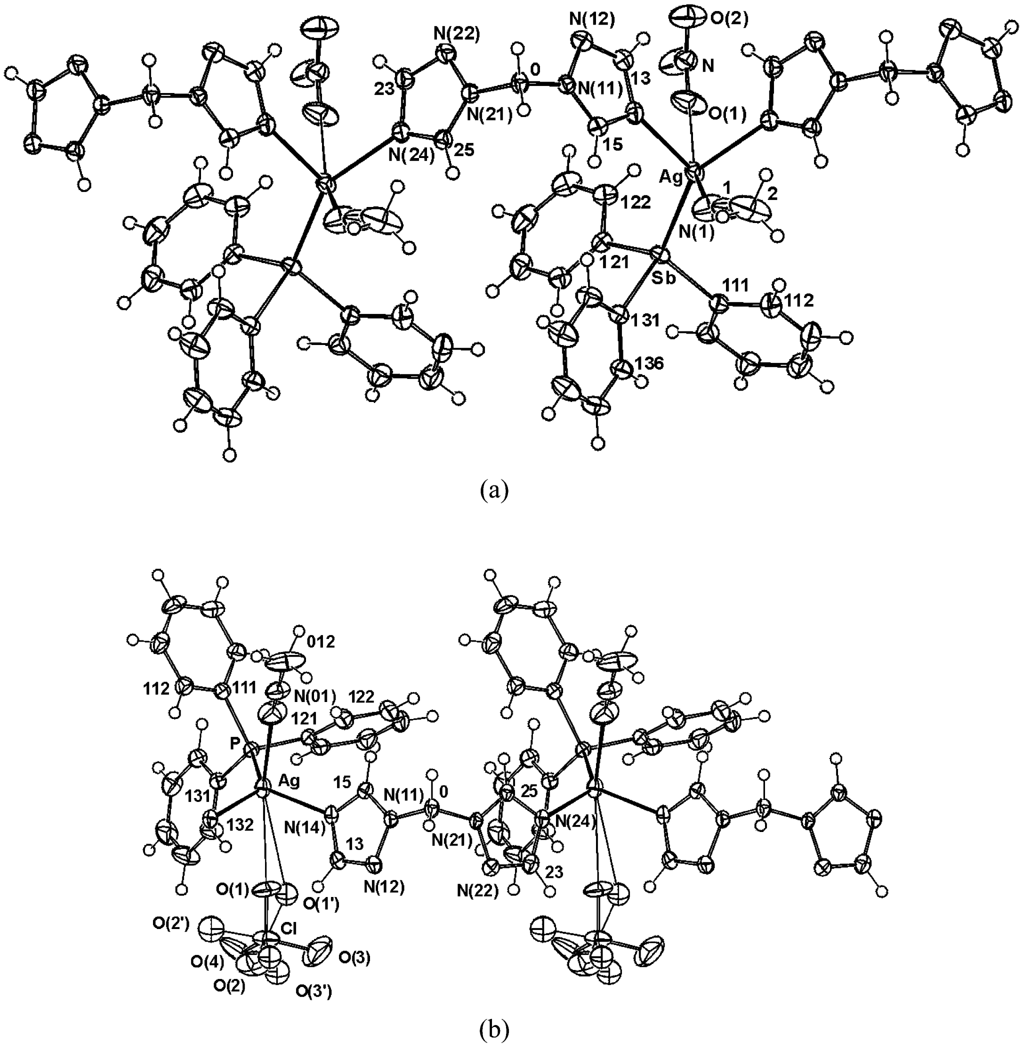


(a)

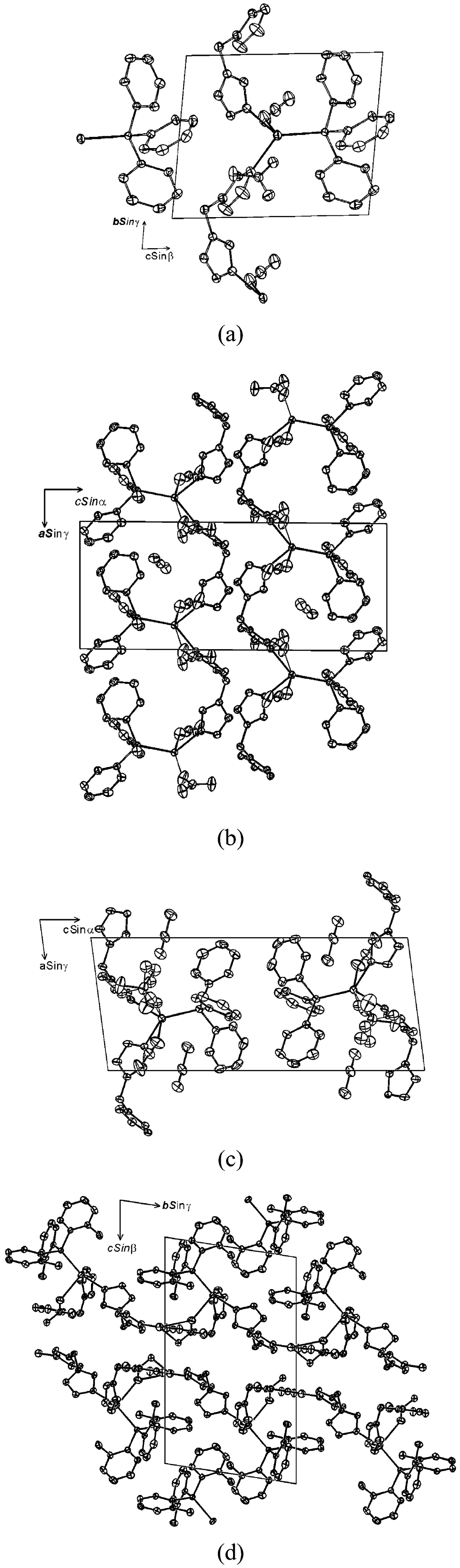
(b)

Figure 1. (a, b) Sections of the one-dimensional polymers of **2** and **4** projected normal to the polymer axis.

$[ER_3(tz_2(CH_2))Ag]^+$ species generally increases with increasing $tz_2(CH_2)$:AgX molar ratio, the maximum intensity being found when the ratio is 8:1. In addition the intensity of the $[ER_3(tz_2(CH_2))Ag]^+$ signal decreases with increasing ER_3:AgX molar ratio, the maximum being detected when the ratio is 1:1.5. If a 1:2 ER_3:AgX ratio was employed, the solutions were not enough stable to be investigated. The peak due to $[ER_3(tz_2(CH_2))Ag]^+$ species generally reaches its maximum intensity when a 16:2:1 $(tz_2)CH_2$:AgX:ER_3 molar ratio was employed.

X-ray Diffraction Studies: Discussion. The results of the "low"-temperature single-crystal X-ray structure determinations of **1**−**4** and **10** are consistent with their formulation as AgX:ER_3:L:MeCN with 1:1:1:1 (**1**), 1:1:1:2 (**2**−**4**), and 2:1:2:0 (**10**) stoichiometries, respectively, those of **2**−**4** being of the form 1:1:1:1(+1) where the acetonitrile molecules are partitioned into coordinated and uncoordinated types respectively. In **1**, the anion approach to the metal is distant, also true of one of the anions in **10**. In the latter, the basis of the structure is a two-dimensional polymer, in the remainder a one-dimensional polymer, the polymers being cationic or neutral, depending in some cases on how their relationships to associated anions are viewed. Geometries are presented in Tables 3 and 4, the polymers being depicted in Figures 1−3. A common feature of all polymers is the linking of successive silver atoms by the tz_2CH_2 ligands, which behave as bridging groups rather than (e.g.) chelates or unidentates, with N(n4) as donors. Torsion angles in the bonds to either side of the central carbon N−C−N−N are of opposite sign (i.e. H(15,25) lie adjacent) in the ligands of all compounds except **10**, where they are the same. In all structures, one of the above formula units as appropriate, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure.

In each of **1**−**4**, the silver atom may be regarded as four-coordinate, without any pair of ligands being dominant, quasi-trans, in their interactions. The Ag−N(tz) distances are closely comparable (range: 2.269(3)−2.323(3) Å) within a particular (MeCN)AgEN(tz)N(tz′) array, the principal variant being Ag−E, short for Ag−P and long for Ag−Sb. In **1**−**3**, this trend is opposed by those in the other bonds, Ag−N(tz) shortening slightly, Ag−N(MeCN) more so, with concomitant straightening of the Ag−N−C angle. These changes are accompanied by the approach of one of the nitrate oxygen atoms. The structures of **1**−**4** are all very similar with respect to lattice dispositions (Figure 2). The structure of **1** is



(a)

(b)

(c)

(d)

Figure 2. (a−d) Unit cell projections of **1**, **3**, **4,** and **10** down *a*, *b*, *b*, and *a*, respectively.

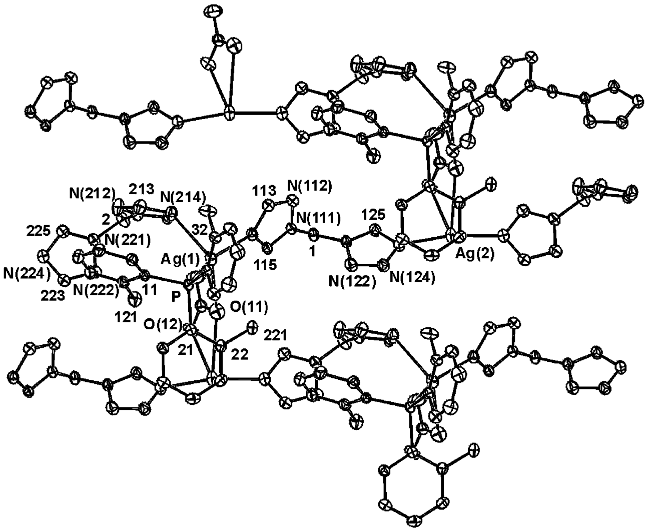


Figure 3. Section of the two-dimensional polymer of **10** projected normal to the plane of the polymer.

unusual, being in space group *P*1, and unsolvated, with parallel polymer strands. In **2**−**4** the lattice is $P\bar{1}$ with the introduction of inversion-related strands between and solvent molecules which, interestingly, appear to lie "within" each strand here—but not in **1**. **2** and **3** are isomorphous; the structure of **4** is very similar. In the latter, the perchlorate approaches the metal at a slightly shorter distance than that found in the analogous nitrate in the principal component of the disordered array; in the minor component Ag−O′ is longer at 3.29(1) Å. In this complex, perhaps because of a different anion profile, Ag−NCMe is straighter with Ag−N correspondingly shorter.

Tris(*o*-tolyl)phosphine is a ligand with a bulkier profile than (P/E)Ph_3, and it comes as no surprise to find the adduct involving it to be of a different form, albeit still polymeric. Here, devoid of solvent, one of the two independent silver atoms has an environment not unlike those of the preceding, except that the acetonitrile may perhaps be regarded as supplanted by a less voluminous quasi-chelate approach of the nitrate (Ag(1)−O(13) 3.126(2) Å); Ag(1)−N(tz) are unsymmetrical. The environment of Ag(2) is quite different and unique among the present arrays, although not unusual in the sense that, devoid of a phosphine donor, it reverts to a classical quasi-linear N−Ag−N system, perturbed by off-axis oxygen contacts, one of the latter serving to link, via a bridging interaction, strands of the form ···Ag(1)(L)Ag(2)-(L)Ag(1)··· in the second dimension (Figure 3).

Conclusions

The compounds presented herein are a first step in the synthesis of new polynuclear coordination compounds. We are currently investigating the use of metal ions other than Ag^I, as well as changing the ancillary ligands and the anions to synthesize materials that can be used as host/guest molecules. This work demonstrates that it is possible to prepare and isolate new coordination polymers which contain a bridging N-donor ligand such as $tz_2(CH_2)$, a triorganophosphine, a solvent molecule (coordinated or solvate), and finally an O-donor counterion. Such coordination compounds, indefinitely stable in the solid state, cannot persist in coordinating solvents such as DMSO or MeCN. It is worth noting that here the ligand $tz_2(CH_2)$, in contrast to those previously described in its organotin(IV) compounds, coordinates always through the N(4) atoms but not the N(4). Sterically hindered P-donors such as $P(o\text{-tolyl})_3$ allow the synthesis of polymers of different stoichiometry or inhibit the counterion coordination (Pcy_3). A different counterion or a different solvent of crystallization can produce polynuclear species having different properties not only in the solid state but also in solution (e.g. conductivity, solubility).

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Supporting Information Available: Four X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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