Lewis Base Adducts of Group 11 † Metal Compounds. Part 24.‡ Co-ordination of Triphenylphosphine with Silver Nitrate. A Solid-state Cross-polarization Magic Angle Spinning ^{31}P Nuclear Magnetic Resonance, Crystal Structure, and Infrared Spectroscopic Study of Ag(PPh$_3$)$_n$NO$_3$ (n = 1—4) §

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Solid-state cross-polarization magic angle spinning ^{31}P n.m.r. spectroscopy, single-crystal X-ray structure determination, and i.r. spectroscopy have been used to investigate the properties of the adducts of triphenylphosphine with silver(I) nitrate: Ag(PPh$_3$)NO$_3$, (**1**); Ag(PPh$_3$)$_2$NO$_3$, (**2**); Ag(PPh$_3$)$_3$NO$_3$, (**3**); and Ag(PPh$_3$)$_4$NO$_3$, (**4**). The value of ^1J(Ag–P) decreases with increasing co-ordination number: (**1**), 780; (**2**), 470; (**3**), 310; and (**4**), 190 Hz, paralleling solution results. Single-crystal X-ray structure determinations of compounds (**2**)—(**4**) have been performed: (**2**), triclinic, space group $P\bar{1}$, a = 11.821(3), b = 11.990(3), c = 13.660(3) Å, α = 102.05(2), β = 112.80(2), and γ = 105.30(2)°, yielding R = 0.036 for 4 090 'observed' reflections; Ag–P 2.443(1) and 2.440(1) Å, P–Ag–P 138.21(5)°; (**3**), monoclinic, space group $P2_1/n$, a = 18.984(5), b = 13.710(3), c = 17.900(4) Å, and β = 94.94(2)°, yielding R = 0.053 for 5 126 reflections; Ag–P 2.630(2), 2.525(1), and 2.545(2) Å, P–Ag–P 118.37(5), 112.07(4), and 116.44(5)°; (**4**), trigonal, space group $R\bar{3}$, a = 19.07(2) Å, and α = 43.77(5)°, yielding R = 0.060 for 1 903 observed reflections; Ag–P 2.643(3) and 2.671(4) Å, P–Ag–P 109.49(12) and 109.45(10)°. Structures (**2**) and (**3**) [and (**1**)] are isomorphous with the analogous triphenylarsine compounds. In all cases the nitrate group is only weakly co-ordinated [and is ionic in (**4**)]: Ag–O 2.464(4) and 2.649(4) in (**2**), 2.684(6) and 2.775(6) Å in (**3**). These weak interactions are reflected in the small splitting observed for the asymmetric N–O stretching vibrational mode compared to the analogous copper(I) compounds.

The reaction of silver nitrate with tertiary organophosphorus ligands gives rise to adducts in which the ligand to silver ratio can vary from one to four depending on the nature of the ligand and the stoicheiometric ratios used. The nature of the solution interaction of these adducts has been analysed principally through the use of ^{31}P n.m.r. data.[1—4] Solid-state single-crystal X-ray diffraction studies have been reported for the 1:1 complex of triphenylphosphine, with AgNO$_3$,[5] and for the mixed-metal 3:1 complex Au$_{0.67}$Ag$_{0.33}$(PPh$_3$)$_3$NO$_3$.[6] Structural data available on related compounds include Ag[P(NMe$_2$)$_3$]$_2$BPh$_4$[3] and Ag[P(C$_6$H$_2$Me$_3$(2,4,6))$_3$]$_2$PF$_6$[7] and the adducts of the bidentate ligand 2,11-bis(diphenylphosphinomethyl)benzo[c]-phenanthrene, dpbp, with AgNO$_3$ and AgClO$_4$.[4] Recently, it has become technically feasible to obtain high-resolution solid-state ^{31}P cross-polarization magic angle-spinning (c.p.m.a.s.) n.m.r. data which, in conjunction with solution n.m.r. data and X-ray diffraction results, provides important links between the structural characteristics of molecules in both the solid and solution states. In this paper we report the results of our study of the solid-state ^{31}P n.m.r. spectrum of Ag(PPh$_3$)NO$_3$, (**1**), and the solid-state ^{31}P n.m.r. spectra and crystal structure

characterization of Ag(PPh$_3$)$_2$NO$_3$, (**2**), Ag(PPh$_3$)$_3$NO$_3$, (**3**), and Ag(PPh$_3$)$_4$NO$_3$, (**4**).

Experimental

Preparation of Complexes.—All four compounds were prepared in a similar manner. Typically, silver nitrate (0.425 g, 0.0025 mol) dissolved in hot acetonitrile (2—3 cm^3) was added to a warm solution of stoicheiometric quantities of triphenylphosphine dissolved in warm ethanol (50—80 cm^3). The warm, clear solutions were allowed to cool slowly in the dark to give well formed crystals of the desired compounds. Excessive heating of the solutions often lead to decomposition problems. Bulk samples were characterized by comparison of X-ray powder diffraction data with powder patterns calculated from single-crystal X-ray data[8] and subsequently by solid-state ^{31}P n.m.r. spectroscopy. Satisfactory results were obtained for 1:1, 3:1, and 4:1 samples. Samples of the 2:1 compound, however, always revealed some contamination due to the presence of other adducts, and possibly, photodecomposition products.

Structure Determinations.—Unique data sets were measured to the specified $2\theta_{max}$ limits (Table 1) using a Syntex $P\bar{1}$ four-circle diffractometer (monochromatic Mo-K_α radiation source, λ = 0.7106$_9$ Å) in conventional 2θ—θ scan mode. N Independent reflections were measured, N_0 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement with statistical weights after solution of the structures by the heavy-atom method. Data were corrected for absorption (analytical correction); $(x, y, z, U_{iso})_H$ were included at idealized values. Residuals on $|F|$ at convergence were R, R'.

Table 1. Crystal data

Compound	Ag(PPh$_3$)$_2$NO$_3$ (2)	Ag(PPh$_3$)$_3$NO$_3$ (3)	Ag(PPh$_3$)$_4$NO$_3$ (4)
Formula	C$_{36}$H$_{30}$AgNO$_3$P$_2$	C$_{54}$H$_{45}$AgNO$_3$P$_3$	C$_{72}$H$_{60}$AgNO$_3$P$_4$
M	694.5	956.7	1 219.0
Crystal system	Triclinic	Monoclinic	Trigonal
Space group	$P\bar{1}$ (C_i no. 2)	$P2_1/n$ (C_{2h}^5, no. 14)	$R\bar{3}$ (C_{3i}^2, no. 148)
a/Å	11.821(3)	18.984(5)	19.07(2)
b/Å	11.990(3)	13.710(3)	
c/Å	13.660(3)	17.900(4)	
α/°	102.05(2)		
β/°	112.80(2)	94.94(2)	43.77(5)
γ/°	105.30(2)		
U/Å^3	1 612.8(7)	4 641(2)	3 014(4)
D_m/ g cm^{-3}	1.42(2)	1.36(2)	1.32(2)
D_c/g cm^{-3}	1.43	1.37	1.34
Z	2	4	2
$F(000)$	708	1 968	1 260
μ_{Mo}/cm^{-1}	7.5	5.8	4.9
Specimen (mm)	0.25 × 0.25 × 0.8	cuboid, 0.15	rhomboid, 0.2
$T_{min.,max.}$	No correction	0.90, 0.92	0.90, 0.94
$2\theta_{max.}$/°	50	50	45
N	5 691	8 182	2 641
N_o	4 090	5 126	1 903
R	0 036	0.053	0.060
R'	0.036	0.040	0.048

Table 2. Non-hydrogen-atom co-ordinates for compound (2)

Atom	x	y	z	Atom	x	y	z
Ag	0.088 79(4)	−0.004 13(3)	0.183 57(3)	Ligand 2			
				P(2)	−0.074 57(10)	−0.173 43(10)	0.188 84(10)
Nitrate				C(19)	−0.235 1(4)	−0.163 7(4)	0.158 7(4)
N	0.178 6(3)	−0.116 0(3)	0.028 2(3)	C(20)	−0.249 7(5)	−0.055 5(4)	0.151 3(4)
O(1)	0.093 8(3)	−0.067 0(3)	0.002 1(2)	C(21)	−0.370 4(6)	−0.045 1(6)	0.130 0(5)
O(2)	0.231 2(3)	−0.116 3(3)	0.126 9(3)	C(22)	−0.474 4(5)	−0.141 6(7)	0.115 4(4)
O(3)	0.206 7(3)	−0.164 1(3)	−0.043 5(3)	C(23)	−0.460 1(5)	−0.247 8(6)	0.122 7(5)
				C(24)	−0.342 3(5)	−0.260 7(5)	0.142 5(5)
Ligand 1				C(25)	−0.009 1(4)	−0.183 1(4)	0.330 3(4)
P	0.262 66(11)	0.197 58(10)	0.312 65(9)	C(26)	0.107 5(4)	−0.202 2(4)	0.371 7(4)
C(1)	0.196 1(4)	0.307 9(4)	0.356 2(4)	C(27)	0.167 9(5)	−0.202 6(5)	0.480 2(4)
C(2)	0.260 2(5)	0.398 8(4)	0.462 0(4)	C(28)	0.112 2(5)	−0.184 3(5)	0.549 4(4)
C(3)	0.201 7(5)	0.479 8(5)	0.487 6(5)	C(29)	−0.003 9(6)	−0.164 7(5)	0.510 5(5)
C(4)	0.080 8(6)	0.469 3(5)	0.409 5(5)	C(30)	−0.066 0(5)	−0.164 4(5)	0.401 6(4)
C(5)	0.015 4(5)	0.379 0(5)	0.304 7(4)	C(31)	−0.113 9(4)	−0.327 0(4)	0.096 7(3)
C(6)	0.071 9(5)	0.297 9(4)	0.278 1(4)	C(32)	−0.142 9(5)	−0.432 6(4)	0.124 9(4)
C(7)	0.370 0(4)	0.276 3(4)	0.261 1(3)	C(33)	−0.175 9(5)	−0.546 3(4)	0.048 7(4)
C(8)	0.404 3(5)	0.400 0(4)	0.275 5(4)	C(34)	−0.177 9(5)	−0.556 6(4)	−0.052 8(4)
C(9)	0.488 0(5)	0.454 0(5)	0.233 8(5)	C(35)	−0.148 9(5)	−0.453 6(4)	−0.080 9(4)
C(10)	0.535 9(6)	0.385 3(5)	0.180 2(5)	C(36)	−0.117 3(4)	−0.339 6(4)	−0.007 5(4)
C(11)	0.503 4(6)	0.262 2(5)	0.166 0(5)				
C(12)	0.418 9(5)	0.207 7(4)	0.206 2(5)				
C(13)	0.380 7(4)	0.195 1(4)	0.445 4(3)				
C(14)	0.337 8(5)	0.109 1(5)	0.488 4(4)				
C(15)	0.423 3(6)	0.105 0(6)	0.589 4(5)				
C(16)	0.551 3(5)	0.186 1(5)	0.648 3(4)				
C(17)	0.596 1(4)	0.272 4(4)	0.608 1(4)				
C(18)	0.510 8(4)	0.278 0(4)	0.506 4(4)				

300 spectrometer at 121.4 MHz using ^{1}H–^{31}P cross-polarization with radiofrequency fields of 8 and 20 G respectively.[11] Single contact times of 1 ms were used with temperature alternation and recycle times of 20 s. Samples were packed in Delrin rotors and spun at speeds of between 3.0 and 4.0 kHz at the magic angle. A sweep width of 20 kHz with a total acquisition time of 12.8 ms was used. Chemical shift data were referenced to 85% H$_3$PO$_4$ *via* solid triphenylphosphine [δ(PPh$_3$) = −9.9 p.p.m.]. Infrared spectra in the range 4 000—400 cm^{-1} were recorded as KBr disks at room temperature using a Perkin-Elmer 377 spectrometer.

Results and Discussion

Structure Determinations.—The structure determination of compound (2) is consistent with the stoicheiometry Ag(PPh$_3$)$_2$-NO$_3$, the asymmetric unit comprising a full formula unit of the complex. Whereas it is common to find isomorphism amongst isostoicheiometric adducts of triphenylphosphine with complexes of copper(I), silver (I), and gold(I), this is not the case here. The copper complex is reported to be monoclinic, space group $I2/a$, $Z = 4$, with crystallographic 2 symmetry imposed on the formula unit so that the nitrate group is symmetrically bidentate with respect to the copper:[12] Cu–P–O 2.256(3), 2.22(1) Å respectively, with P–Cu–P 131.2(1) and O–Cu–O 57.5(3)°. In the present silver(I) analogue, the formula unit is devoid of crystallographically imposed symmetry, in keeping with the

Neutral complex scattering factors were used.[9] Computation involved the XTAL83 program system[10] implemented by S. R. Hall on a Perkin-Elmer 3240 computer, and the APPLECRYST program package, written by C. H. L. Kennard for an APPLE IIe microcomputer.

Spectroscopy.—Solid-state ^{31}P n.m.r. spectra of the compounds were obtained at room temperature on a Bruker CXP-

presence of a nitrate group which is now quite unsymmetrically co-ordinated; the compound is isostructural with the arsine analogue, for which the structure determination has been recently reported,[13] and the cell setting and numbering scheme of the present derivative is presented in conformity with that complex, to enable convenient comparison between the two. In the present compound Ag–P differ only trivially [2.443(1) and 2.440(1) Å], being some 0.18$_5$ Å longer than the corresponding

Table 3. Non-hydrogen-atom co-ordinates, for compound (3)

Atom	x	y	z	Atom	x	y	z
Ag	0.007 04(2)	0.186 87(3)	0.234 35(2)	C(25)	−0.038 4(3)	−0.084 3(4)	0.193 4(3)
N	−0.104 9(3)	0.269 7(4)	0.103 8(4)	C(26)	0.020 3(3)	−0.096 3(4)	0.153 7(3)
O(1)	−0.063 9(3)	0.205 5(5)	0.092 9(4)	C(27)	0.023 9(3)	−0.171 1(4)	0.103 2(3)
O(2)	−0.098 6(3)	0.293 8(5)	0.167 1(3)	C(28)	−0.031 6(3)	−0.236 8(4)	0.091 5(3)
O(3)	−0.148 4(3)	0.296 6(4)	0.057 6(3)	C(29)	−0.089 9(3)	−0.225 3(4)	0.130 6(3)
P(1)	0.119 28(6)	0.201 01(10)	0.168 96(7)	C(30)	−0.094 1(3)	−0.150 3(4)	0.182 0(3)
C(1)	0.142 5(3)	0.102 1(3)	0.107 1(3)	C(31)	0.015 1(3)	−0.029 3(4)	0.341 1(3)
C(2)	0.204 5(3)	0.048 3(4)	0.117 0(3)	C(32)	0.038 2(4)	−0.121 3(5)	0.349 7(4)
C(3)	0.216 8(3)	−0.027 4(4)	0.068 4(3)	C(33)	0.083 4(5)	−0.149 3(6)	0.412 3(5)
C(4)	0.168 4(3)	−0.048 8(4)	0.008 7(3)	C(34)	0.106 6(4)	−0.083 4(7)	0.464 5(4)
C(5)	0.106 8(3)	0.005 0(4)	−0.001 9(3)	C(35)	0.084 1(5)	0.007 7(6)	0.456 3(4)
C(6)	0.093 1(3)	0.079 3(4)	0.047 7(3)	C(36)	0.038 0(4)	0.036 3(5)	0.395 4(4)
C(7)	0.194 8(2)	0.202 1(4)	0.239 4(3)	P(3)	0.001 99(6)	0.315 71(11)	0.342 63(7)
C(8)	0.243 0(3)	0.277 8(4)	0.248 1(3)	C(37)	−0.086 3(3)	0.334 5(4)	0.374 1(3)
C(9)	0.297 5(3)	0.272 6(5)	0.306 0(4)	C(38)	−0.105 2(3)	0.421 8(4)	0.407 1(3)
C(10)	0.303 7(3)	0.193 6(6)	0.353 4(3)	C(39)	−0.173 2(3)	0.432 8(5)	0.430 9(4)
C(11)	0.255 9(4)	0.119 7(5)	0.345 0(3)	C(40)	−0.221 7(3)	0.359 4(5)	0.420 7(4)
C(12)	0.200 9(3)	0.124 9(4)	0.289 3(3)	C(41)	−0.204 1(3)	0.275 9(5)	0.386 2(4)
C(13)	0.128 1(2)	0.307 6(4)	0.110 2(3)	C(42)	−0.135 9(3)	0.263 2(4)	0.362 8(3)
C(14)	0.181 9(3)	0.316 0(4)	0.061 4(3)	C(43)	0.024 7(3)	0.438 9(4)	0.313 7(3)
C(15)	0.184 4(3)	0.396 8(5)	0.015 8(3)	C(44)	0.080 2(3)	0.493 2(5)	0.344 2(5)
C(16)	0.135 6(4)	0.469 9(5)	0.017 4(3)	C(45)	0.092 8(4)	0.586 1(6)	0.315 1(6)
C(17)	0.082 5(3)	0.462 4(4)	0.065 0(4)	C(46)	0.049 4(4)	0.622 4(5)	0.257 9(5)
C(18)	0.078 9(3)	0.380 1(4)	0.110 7(3)	C(47)	−0.007 0(5)	0.570 3(6)	0.228 1(4)
P(2)	−0.039 72(7)	0.017 25(10)	0.260 01(7)	C(48)	−0.019 1(4)	0.477 6(4)	0.255 9(4)
C(19)	−0.130 8(3)	0.013 1(4)	0.284 9(3)	C(49)	0.057 8(3)	0.300 2(4)	0.429 7(3)
C(20)	−0.180 9(3)	0.065 0(5)	0.240 2(3)	C(50)	0.128 1(3)	0.272 2(4)	0.426 9(3)
C(21)	−0.252 6(4)	0.058 9(6)	0.252 8(4)	C(51)	0.174 0(3)	0.263 3(5)	0.490 3(4)
C(22)	−0.273 6(3)	0.002 3(5)	0.310 6(4)	C(52)	0.151 8(4)	0.279 9(5)	0.559 3(4)
C(23)	−0.224 1(3)	−0.047 0(5)	0.355 3(3)	C(53)	0.082 6(4)	0.305 5(6)	0.565 0(3)
C(24)	−0.153 1(3)	−0.042 8(5)	0.343 0(3)	C(54)	0.035 5(3)	0.316 4(5)	0.500 7(3)

distances in the copper(I) analogue, with P–Ag–P increased, relative to the copper complex, to 138.21(5)°. These values can be compared to those found for other molecules containing the $[Ag(PPh_3)_2]^+$ molecular fragment: $[Ag(PPh_3)_2SCN]_2$,[14] 2.455(3), 2.503(5) Å, 124.9(2)°; $[Ag(PPh_3)_2]_2[Ni\{S_2C_2-(CN)_2\}_2]$,[15] 2.465(3), 2.504(3) Å, 118.5(1)°; $[Ag(PPh_3)_2]_2-[Ni\{S_2C=C(CN)_2\}_2]$,[15] 2.463(5), 2.519(5) Å, 116.9(2)°; 2.488(5), 2.451(5) Å, 122.1(2)°; $[Ag(PPh_3)_2]_3[Al(O_2C_2S_2)_3]$,[16] 2.465(5), 2.492(3) Å, 113.4(2)°; $[Ag(PPh_3)_2]_3[Fe(O_2C_2S_2)_3]$,[16] 2.455(2), 2.480(2) Å, 115.2(1)°. The range of values of Ag–P distances in these compounds (2.440—2.519 Å) is surprisingly small, despite the wide variation in P–Ag–P angles (113.4—138.26°). The Ag–P distances also do not differ significantly from that reported for the compound $Ag[P(C_6H_2Me_3-2,4,6)_3]_2PF_6$,[7] 2.461(6) Å, although the steric bulk of that ligand and the lower associated co-ordination number increases the P–Ag–P angle to 179.4°; or for the complex $Ag(dpbp)NO_3$,[4] Ag–P 2.424(2) and 2.410(2) Å, P–Ag–P 148.6(1)°. As might be expected, these bond lengths are significantly longer than the distance [2.369(6) Å] found for the 1:1 compound $Ag(PPh_3)NO_3$[5] (Table 5). Whereas in the copper complex the Cu–O distances are shorter than the Cu–P distances, here the shorter of the two Ag–O distances is longer [2.464(4) Å] than Ag–P, while the other is very long [2.649(4) Å]. Recently, the structures of bis(2,6-dimethylpyridine)silver(I) nitrate, $Ag(2,6Me_2-py)_2NO_3$, and bis(benzotriazole)silver(I) nitrate, $Ag(C_6H_5N_3)_2NO_3$, have been reported[17,18] in which there are likewise a pair of strongly bound unidentate base molecules, with a weakly co-ordinated bidentate group. In $Ag(2,6Me_2-py)_2NO_3$, Ag–N are 2.192(6) and 2.182(6) Å, N–Ag–N is 169.3(2)°, and Ag–O are 2.716(6) and 2.663(6) Å. In $Ag(C_6H_5N_3)_2NO_3$, Ag–N are 2.151(3) and 2.146(3) Å (cation 1), 2.206(3) and 2.186(3) Å (cation 2), N–Ag–N are 158.4(1) (cation 1) and 151.3(3)° (cation 2), and Ag–O are 2.630(3), 2.679(3), and 2.752(3) Å.

The structure determination of compound (3) confirms the 3:1 stoicheiometry of the $[Ag(PPh_3)_3]^+$ fragment, with the nitrate group acting as a weakly co-ordinating ligand; this compound also is isostructural with its arsine analogue,[13] and again presentation is made with the same cell setting and numbering scheme. In the present compound the Ag–O distances [2.684(6) and 2.775(6) Å] are similar to those found for the bis(unidentate nitrogen base) systems mentioned above. The Ag–P bond lengths in this compound [2.630(2), 2.525(1), and 2.545(2) Å] are ca. 0.10—0.17 Å longer than those found for the 2:1 compound (2). The P–Ag–P angles [118.37(5), 116.44(5), and 112.07(4)°] are irregular and considerably greater than the tetrahedral value of 109.58°, the larger angle being opposite the longer Ag–P bond. In the analogous, but not isomorphous, copper compound, $Cu(PPh_3)_3NO_3 \cdot EtOH$,[19] the Cu–P distances are 0.2 and 0.3 Å shorter at 2.312(2), 2.337(2), and 2.339(2) Å although the P–M–P angles are similar [113.42(6), 114.15(7), and 121.37(6)°]. In the copper compound the nitrate group acts as a strongly co-ordinated unidentate ligand with Cu–O 2.174(2) Å, consistent with the fact that the tetrakis compound, $Cu(PPh_3)_4NO_3$, has not been isolated.[20] In the mixed-metal compound $Au_{0.67}Ag_{0.33}(PPh_3)_3NO_3$[5] the metal–phosphorus distances [2.435(21), 2.382(26), and 2.391(29) Å] are considerably shorter than reported here and there are significant differences in the P–M–P angles [129.7(8), 115.0(9), and 113.4(8)°]. These parameters, however, are more consistent with those of other 'pure' $[Au(PPh_3)_3]^+$ cations[21,22] and suggest that the isomorphous replacement of the gold by silver has not significantly influenced the overall lattice geometry.

By contrast to the above, the structure determination of compound (4) shows that it is isomorphous with both $Cu(PPh_3)_4ClO_4$ and $Ag(PPh_3)_4ClO_4$.[23] The Ag–P distances [2.643(3) and 2.671(4) Å] do not differ significantly from those

Table 4. Non-hydrogen-atom co-ordinates, for compound (4)

Atom	x	y	z	Atom	x	y	z
Ag	0.252 02(2)	a	a	C(24)	−0.121 7(7)	0.097 4(7)	0.732 8(8)
				C(25)	−0.068 6(8)	0.088 5(7)	0.762 3(7)
Nitrate				C(26)	0.033 6(7)	0.100 2(6)	0.682 7(6)
N(1)	$\frac{1}{2}$	a	a	C(31)	0.239 8(6)	0.155 5(7)	0.519 2(6)
N(2)	0	a	a	C(32)	0.206 6(7)	0.264 8(7)	0.483 7(6)
O(1)[b]	0.439(3)	0.462(5)	0.553(2)	C(33)	0.215 4(8)	0.293 5(8)	0.524 0(9)
O(2)[b]	−0.051(16)	0.003(11)	0.088(7)	C(34)	0.254 0(10)	0.214 5(12)	0.602 5(11)
				C(35)	0.288 4(11)	0.102 4(11)	0.640 6(12)
Triphenylphosphine (off-axis)				C(36)	0.282 4(9)	0.071 9(8)	0.597 9(9)
P_{oa}	0.214 8(2)	0.125 9(2)	0.467 2(1)				
C(11)	0.306 4(6)	−0.022 1(6)	0.494 4(6)	Triphenylphosphine (axial)			
C(12)	0.271 9(6)	−0.106 9(6)	0.582 2(6)	P_{ax}	0.200 85(6)	a	a
C(13)	0.346 6(8)	−0.214 8(6)	0.591 9(7)	C(1)	0.218 4(6)	0.281 9(6)	0.056 8(6)
C(14)	0.455 5(7)	−0.241 2(6)	0.517 2(8)	C(2)	0.315 3(7)	0.299 3(7)	−0.027 6(7)
C(15)	0.491 5(7)	−0.156 5(7)	0.430 3(7)	C(3)	0.334 1(7)	0.356 0(7)	−0.137 8(7)
C(16)	0.418 7(7)	−0.048 8(6)	0.420 0(6)	C(4)	0.258 8(9)	0.396 5(8)	−0.165 0(8)
C(21)	0.076 8(5)	0.122 0(5)	0.574 0(5)	C(5)	0.161 9(8)	0.381 5(8)	−0.082 1(8)
C(22)	0.018 1(6)	0.132 8(6)	0.548 1(6)	C(6)	0.141 1(7)	0.325 4(7)	0.028 8(6)
C(23)	−0.080 1(7)	0.119 6(7)	0.626 0(8)				

^{a} $x = y = z$. ^{b} Population: 0.5.

Table 5. Molecular geometry of compound (1); distances in Å, angles in °. Square brackets are for the isomorphous arsine analogue; atom numbering follows that given for the latter[13]

Ag–P(As)	2.369(6) [2.471(2)]
Ag–O(1)	2.628(7) [2.560(6)]
Ag–O(3)	2.438(7) [2.618(8)]
Ag–O(1^1)	2.916(7) [2.829(6)]
Ag–O(2^1)	2.363(7) [2.355(6)]
(As)P–Ag–O(1)	117.2(2) [116.4(2)]
(As)P–Ag–O(3)	136.5(2) [118.3(2)]
(As)P–Ag–O(1^1)	95.7(2) [95.3(2)]
(As)P–Ag–O(2^1)	141.3(2) [141.9(2)]
O(1)–Ag–O(3)	49.7(2) [49.3(2)]
O(1)–Ag–O(1^1)	110.0(2) [116.6(4)]
O(1)–Ag–O(2^1)	89.7(2) [80.6(2)]
O(3)–Ag–O(1^1)	127.6(2) [146.5(4)]
O(3)–Ag–O(2^1)	82.0(2) [98.9(2)]
O(1^1)–Ag–O(2^1)	46.9(2) [48.0(2)]

Transformations of the asymmetric unit: I ($x, \frac{1}{2} - y, z - \frac{1}{2}$); Ag–O–Ag ($x, \frac{1}{2} - y, \frac{1}{2} + z$) is 168.4(3) [171.6(2)]°.

Table 6. Molecular geometry of compound (2). Details in Table 5

Ag–P(1)	2.443(1) [2.535(5)]
Ag–P(2)	2.440(1) [2.521(3)]
Ag–O(1)	2.464(4) [2.409(6)]
Ag–O(2)	2.649(4) [2.684(7)]
Ag–O(1^1)	3.075(3) [2.737(6)]
P(1)–Ag–P(2)	138.21(5) [134.2(1)]
P(1)–Ag–O(1)	111.81(7) [113.7(3)]
P(1)–Ag–O(2)	100.24(7) [96.6(3)]
P(2)–Ag–O(1)	109.54(7) [110.1(3)]
P(2)–Ag–O(2)	101.56(8) [101.7(3)]
O(1)–Ag–O(2)	49.86(11) [49.5(2)]

Transformation of the asymmetric unit: I ($\bar{x}, \bar{y}, \bar{z}$). Nitrate geometry: N–O(1,2,3) 1.264(5), 1.248(5), and 1.233(6) Å. Angles opposite O(1,2,3): 121.0(4), 120.2(4), and 118.8(4)°. Deviation of Ag from nitrate plane: 0.082(6) Å. Ag–O(1)–Ag^1 is 114.2(1)°. For the complex di-μ-nitrato-tetrakis(trimethyl phosphite)disilver(I),[24] a centrosymmetric dimer, with one of the nitrate oxygen atoms performing a bridging function, Ag–P are 2.441(3) and 2.412(3) and Ag–O 2.455(8) and 2.454(8) Å, P–Ag–P is 133.7(1)°, while P–Ag–O range from 106.4(2) to 133.7(2)°, and O–Ag–O is 67.0(3)°. Note that in the present complex (and its arsine analogue) the angle sum P(1)–Ag–P(2) + P(1,2)–Ag–O(1) is 359.56° (358.0° for the arsine[13]), perhaps indicative that a dominant trigonal planar description of the co-ordination environment is to be preferred to one in terms of any more complex irregular array.

found for the perchlorate salt [2.668(5) and 2.650(2) Å]. As in the perchlorate salts, the steric crowding of the four ligands around the central metal atom leads to a regular tetrahedral angular geometry, and the anion is disordered.

As well as enabling comparison with their copper(I) analogues, the present results may also be compared with those of the arsine analogues in the cases of (1)—(3); although not available in an isomorphous system, the tetrakis(ligand) cation may be profitably compared with its arsenic counterpart in its salts with the [SnPh$_2$(NO$_3$)$_3$]$^-$ and [SnPh$_2$(NO$_3$)$_2$Cl]$^-$ counter ions.[13] Initial consideration of Ag–P,As distances by consideration of the weighted mean values for each species is given in Table 9, where it is seen that the difference in bond lengths between comparable arsenic and phosphorus compounds diminishes from *ca.* 0.10 Å to almost zero on passing from $n = 1$ to $n = 4$. Among the other ligands more subtle changes are observed. In compound (1) the rather short Ag–O(3) distance increases rather inexplicably on passing to the arsine analogue by almost 0.2 Å, with associated large changes in the angles subtended at the silver atom which involve O(3).

Atom O(1) of the nitrate lies almost equidistant between silver atoms; both of these distances shorten slightly on passing to the arsine analogue, with O(1)–Ag–O(1^1) changing from 110.0(2) to 116.6(4)°. Since Ag–O(2) remains relatively unchanged, the lengthening of Ag–O(3) suggests a twist of the nitrate group about O(1) · · · O(2), which is reflected in substantial variation in the deviation of the two silver atoms from the plane of the nitrate group: deviations of Ag and Ag($x, \frac{1}{2} - y, \frac{1}{2} + z$) are 0.23(1) and 0.26(1) Å in the phosphine, and 0.26(1) and 0.11(1) Å in the arsine complex. The Ag · · · Ag distance changes from 5.515(2) to 5.375(3) Å, and Ag–O(1)–Ag from 168.4(3) to 171.6(2)°.

In considering the arsenic analogue of compound (2), attention has been drawn to its similarity to di-μ-nitrato-tetrakis(trimethyl phosphite)disilver(I)[24] (Table 6); it might reasonably be expected that in (2) the analogy might be closer.
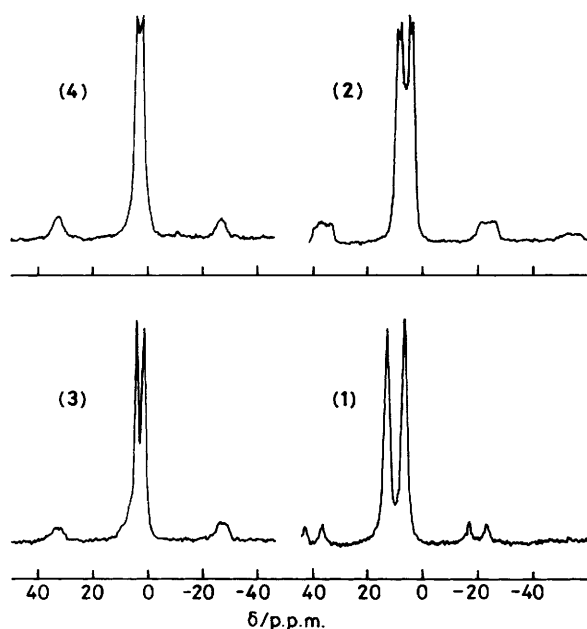
Figure. C.p.m.a.s. ^{31}P n.m.r. spectra of (1)—(4). The spinning side bands observed on either side of the main signal indicate the existence of ^{31}P chemical shift anisotropy. The broadness of the bands does not permit the resolution of individual ^{107}Ag and ^{109}Ag isotope peaks

Table 7. Molecular geometry of compound (3). Details as in Table 5

Ag–P(1)	2.525(1) [2.608(3)]
Ag–P(2)	2.545(2) [2.617(2)]
Ag–P(3)	2.630(2) [2.678(2)]
Ag–O(2)	2.684(6) [2.61(2)]
Ag–O(1)	2.775(6) [2.54(1)]
P(1)–Ag–P(2)	118.37(5) [116.3(1)]
P(1)–Ag–P(3)	112.07(4) [110.9(1)]
P(1)–Ag–O(2)	112.2(1) [112.2(1)]
P(1)–Ag–O(1)	86.1(1) [88.1(4)]
P(2)–Ag–P(3)	116.44(5) [114.9(1)]
P(2)–Ag–O(2)	108.7(1) [114.4(3)]
P(2)–Ag–O(1)	95.7(1) [98.1(4)]
P(3)–Ag–O(2)	83.7(1) [82.9(3)]
P(3)–Ag–O(1)	124.4(1) [126.0(4)]

Nitrate geometry: N–O(1,2,3) 1.202(9), 1.176(9), and 1.178(8) Å. Angles opposite O(1,2,3): 126.5(7), 122.8(7), and 110.4(6)°. Deviation of silver from nitrate plane: −0.07 Å.

Table 8. Molecular geometry of compound (4)

Distances (Å)		Angles (°)	
The silver environment			
Ag–P$_{ax}$	2.643(3)	P$_{ax}$–Ag–P$_{oa}$	109.49(12)
Ag–P$_{oa}$	2.671(4)	P$_{oa}$–Ag–P$_{oa}$	109.45(10)
Nitrate 1			
N–O	1.17(1)	O–N–O	101(4)
Nitrate 2			
N–O	1.22(2)	O–N–O	90(4)

Surprisingly, it is not. In spite of the fact that Ag–P in (2) are *ca.* 0.03 Å longer than in the trimethyl phosphite analogue, P–Ag–P is larger [138.21(5), *cf.* 133.7(1)°], presumably a

consequence of the different steric characteristics of the two ligands. The Ag–O distances are also longer in compound (2); the high symmetry of the $P_2AgO_2AgP_2$ core of the trimethyl phosphite complex (Table 9), diminished on passing to the arsine, is further diminished on passing to (2), with one of the Ag–O(1) distances becoming very long while Ag–O(2) is somewhat shorter, perhaps indicative of incipient monomer formation with a bidentate nitrate group. Interestingly, in both (2) and its arsenic analogue the $P_2(As_2)AgO(1)$ component of the co-ordination sphere has an angle sum of 359.5 (358.0°), suggesting that the environment of the silver atoms in both is predominantly isosceles trigonal planar, a situation which is not the case in the trimethyl phosphite derivative in which O(1) is replaced by the (μ-O_2) bidentate groups. In the latter, surprisingly, Ag–O is also shorter than in compound (2). The tendency towards increased P–Ag–P angle in (2) relative to the As–Ag–As angle in its analogue, concomitant with shorter metal–ligand distances, is continued in (3). The angle sum of the P_3Ag group in compound (3) is 346.9, *cf.* 342.1° for As_3Ag, and in keeping with this tendency the Ag–O distances are substantially longer. In spite of the relatively weak co-ordination of the nitrate group, in this complex it is most nearly a symmetrical bidentate ligand (*cf.* the copper analogue, above) and a surprisingly large distortion is observed in its angular geometry in regard to diminution of the bidentate angle. However, it seems that this and the associated bond shortening may be largely due to the lack of a libration correction as the thermal parameters associated with all nitrate oxygen atoms are by far the highest in the structure; for the arsenic analogue, O(1)–N–O(2) is reported as 109.5(9)°.

Solid-state ^{31}P N.M.R. Spectroscopy.—The solid-state c.p.m.a.s. ^{31}P n.m.r. spectrum for each complex at room temperatures consists of unresolved doublets arising from ^{107}Ag–^{31}P and ^{109}Ag–^{31}P spin–spin coupling (Figure). Compounds (1)—(4) contain one, two, three, and two independent phosphorus atoms respectively. However, the signals from each phosphorus are resolved only for compound (2). The average chemical shift values move upfield towards the value of free triphenylphosphine with increasing co-ordination number: (1), 11.7: ; (2), 7.8; (3), 4.3; (4), 4.4 p.p.m., with very little difference being observed for (3) and (4). These parameters can be compared with those of the analogous copper compounds:[11,19] $Cu(PPh_3)_2NO_3$, 0.3; $Cu(PPh_3)_3NO_3\cdot EtOH$, −2.9; and $Cu(PPh_3)_4ClO_4$, −5.0 p.p.m., the substitution of silver for copper producing a small, but significant 'deshielding' effect on the ^{31}P nuclei. The values of $^1J(Ag–P)$ for compounds (2)—(4) are in remarkable agreement with parallel low-temperature *solution* data on $Ag[P(C_6H_4Me-p)_3]_nNO_3$ systems:[1] (2) 470 (av.), $Ag[P(C_6H_4Me-p)_3]_2NO_3$, 470; (3), 310, $Ag[P(C_6H_4Me-p)_3]_3NO_3$, 312; (4) 190, $Ag[P(C_6H_4Me-p)_3]_4NO_3$, 224 Hz, suggesting similar solution and solid-state structural characteristics. Spin–spin coupling values in solution for $Ag(PBu^t_3)_2NO_3$, 480 Hz (av.),[2] and $Ag(dpbp)NO_3$, 461 Hz [Ag–P 2.417(7) Å],[4] are strikingly similar to the values reported for the present compounds. The value of 780 Hz observed for (1), however, is significantly larger than solution values reported for $Ag(PBu^t_3)NO_3$, 683 Hz;[2] whether this is a consequence of differing Ag–P distances and/or other steric or electronic factors is unknown at this stage in the absence of structural data for the latter complex.

Infrared Spectroscopy.—The weak interactions between the silver cation and the nitrate groups in compounds (1)—(3) are reflected in the small magnitude of the splitting of the asymmetric N–O stretching mode (v_1) (Table 10). For (2), the splitting of v_1 is slightly greater than that reported for $Ag(PBu^t_3)_2NO_3$ (105 *vs.* 75 cm^{-1}), but still much less than that

Table 9. Comparative Ag–P,As distances (Å)

Compound	$\langle Ag-P_n \rangle$		$\langle Ag-As_n \rangle$		δ
(1)	2.36_9		2.47_1		0.10_2
		0.07_3		0.05_7	
(2)	2.442_2		2.52_8		0.08_6
		$0.09_3, 0.18_8$ ($\equiv 0.12_4$)		$0.085_5, 0.15_0$ ($\equiv 0.10_6$)	
(3)[a]	$2.53_5, 2.63_0$ ($\equiv 2.56_6$)		$2.61_3, 2.67_8$ ($\equiv 2.63_4$)		$0.07_8, 0.04_8$ ($\equiv 0.06_3$)
		$0.12_8, 0.03_3$ ($\equiv 0.09_7$)		$0.060, -0.00_5$ ($\equiv 0.03_9$)	
(4)	2.66_3		$2.67_3{}^{b}$		0.01_0

[a] Distances here are grossly disparate, comprising two short and one long; separate and merged values are given. [b] Mean value for all distances observed in the $[SnPh_2(NO_3)_3]^-$ and $[SnPh_2(NO_3)_2Cl]^-$ salts.[12]

Table 10. Infrared bands (cm^{-1}) for nitrate vibrational modes for compounds (1)—(4) (s = strong, m = medium, and w = weak). Bending modes were obscured by bands assignable to PPh_3 vibrations

Assignment	(1)	(2)	(3)	(4)
Asym N–O str. (v_1)	1 375s	1 400s	1 385s	1 340s
	1 310s	1 295s	1 310s	
Sym N–O str. (v_3)	1 040w	1 030m	1 040m	
Out-of-plane def. (v_2)	815m	820m	825m	830w

found for the analogous copper compound $Cu(PPh_3)_2NO_3$ [20] (200 cm^{-1}). Similarly the strongly co-ordinated unidentate nitrate in $Cu(PPh_3)_3NO_3\cdot EtOH$ [25] shows greater splitting of v_1 than in compound (3) (120 vs. 75 cm^{-1}). The multiple bridging mode of the nitrate group in (1) is similarly reflected in the small, but distinct splitting of v_1 (and the appearance of the symmetric N–O stretching mode v_3 which is i.r.-inactive in nitrate groups adopting D_{3h} symmetry). As expected, and previously reported,[20] the values reported for compound (4) indicate the presence of ionic nitrate. The decrease in energy of the out-of-plane deformation mode, v_2, in passing from (4) to (1) is consistent with increasing co-ordination of the nitrate oxygens.[26]

Acknowledgements

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