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Two-Coordinate Complexes of Univalent Coinage Metals with Group 5B Ligands and the Crystal Structures of $[Ag\{As(C_5H_9)_3\}_2][ClO_4]$ and $[Ag\{PPh_2(C_5H_9)\}_2][ClO_4]$

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Twelve complexes of general formula $[M(ZR_2R')_2]X$ (M = Ag, Cu, Au; X = BF_4, ClO_4; Z = As, P) have been isolated and characterized. The stoichiometry is principally determined by the steric properties of the ZR_2R' ligands. For a majority of the complexes, their infrared spectra are indicative of free anions. However, the structural studies detailed below indicate a weak association of the metals with the anions, and demonstrate that neither $[Ag\{As(C_5H_9)_3\}_2][ClO_4]$ nor $[Ag\{PPh_2(C_5H_9)\}_2][ClO_4]$ contain a linear Z–Ag–Z cation. This substantiates the rarity of the linear ML_2 geometry. Crystals of $[Ag\{As(C_5H_9)_3\}_2][ClO_4]$ belong to the monoclinic space group $P2_1/n$, with $a = 10.162$ (4) Å, $b = 23.211$ (6) Å, $c = 14.351$ (3) Å, $\beta = 98.37$ (2)°, and $Z = 4$. Anisotropic refinement of all non-hydrogen atoms gave a final, weighed R value of 0.0501. Silver–arsenic bond lengths are 2.480 (2) and 2.482 (2) Å. Ionic interactions give rise to short contacts between the Ag^+ ions and ClO_4^- anions, with the shortest oxygen–silver distance of 2.644 (5) Å. These interactions lead to a nonlinear geometry for the $AgAs_2$ moiety with the As–Ag–As angle bent to 151.2 (1)°. The tertiary phosphine complex crystallizes in the monoclinic space group Pn, with $a = 10.574$ (6) Å, $b = 17.142$ (11) Å, $c = 18.812$ (13) Å, $\beta = 104.34$ (5)°, and $Z = 4$. Anisotropic refinement of all atoms with $Z \geq 6$ gave a final weighted R value of 0.0484. The unit cell contains two independent cations. Anion–cation interactions again lead to nonlinear coordination, with P–Ag–P angles of 145.1 (1) or 153.0 (1)°. The Ag–P bonds in the two ions are 2.432 (2) and 2.415 (2) Å and 2.419 (2) and 2.397 (2) Å, respectively. An evaluation of the effect that the change in coordination number has on the radius of the Ag(I) ion is given.

Introduction

Coinage metals form very stable univalent complexes with π-acid ligands. These can be two-, three-, or four-coordinate depending upon the size and ligation capabilities of the ligands.[1-5] In general, only very large tertiary phosphines form linear two-coordinate complexes,[3,4] while large but less bulky tertiary phosphines or arsines tend to form nonlinear two-coordinate species.[1,5] With Cu(I), tertiary phosphines with large R substituents, such as cyclohexyl groups, have been shown to form complexes of stoichiometry $[CuL_2]X$,[1] while medium-size tertiary phosphine ligands form four-coordinate complexes such as $[Cu(PPh_3)_4][ClO_4]$[2] when the anion is of low coordinating power. For M(I), two-coordinate complexes are more common with several complexes known to contain linear silver(I) cations,[3,4] presumably due to the more favorable hybridization energy of the silver(I) ion. Significantly, however, examples of nonlinear two-coordinate Ag(I) species have also been reported. Thus, $[Cu\{P(C_6H_{11})_3\}_2][ClO_4]$ has a P–Cu–P angle of 144.5°[1] and $[Ag\{P(NMe_2)_3\}_2][BPh_4]$ has a P–Ag–P angle of 166.9°.[5] These bent species may be viewed as precursors of three-coordinate complexes which can form if the organo groups of the ligands mesh properly when coordinated. Hence $PPh_2(C_5H_9)$ forms $[Ag\{PPh_2(C_5H_9)\}_3][BF_4]$ when the ligand to metal ratio is three or more in the preparative reaction. Here the cation core is slightly distorted from a planar trigonal geometry due to interaction with the anion.[6] For this reason it was decided to investigate the steric limits of two-coordination, and the geometry of the cations formed, in more detail. Thus a series of copper(I) and silver(I) complexes of general formula $[ML_n]X$ (n = 2, 3, 4; X = ClO_4, BF_4) were prepared, where L was a ligand intermediate in size between $P(C_6H_{11})_3$ and PPh_3.[6] The results of the investigation of the n = 2 compounds are reported here, while the n = 3 and n = 4 series will be the subject of subsequent papers.

Results

Spectra and Conductivity. The white, diamagnetic complexes were prepared by allowing an ethanolic solution of the ligand to react with a copper(II) or silver(I) salt or with $[H_3O][Au(NO_3)_4]$. It is convenient to make a preliminary assignment of the structures of these compounds based on the conductivity and IR measurements reported in Table I. On the basis of the absence of splitting of the anion ν_4 vibrational band at ~1100 cm^{-1} in the IR spectra, the majority of the complexes would appear to contain $[ML_2]^+$ cations and free tetrahedral anions and, by implication, a linear Z–M–Z core. The splitting of the ν_4 band, observed for the $[M\{As(C_5H_9)_3\}_2][ClO_4]$ complexes and $[Cu(FBF_3)\{P(C_6H_{11})_2Ph\}_2]$, is indicative that some interaction does occur in these complexes and thus, presumably, for a nonlinear core. That the latter compound appears to be a tetrafluoroborato complex is not surprising since such behavior has been found in the structure of $[Cu(FBF_3)(PPh_3)_3]$.[7] However, the absence of splitting of this ν_4 band is, at best, a poor indication of possible cation–anion interaction. In particular, most of the salts show solution conductivities that are slightly suppressed from the theoretical value (28 S) expected for a 1:1 electrolyte. While extrapolation from solution to solid-state behavior is, at best, tenuous, it makes the assumption of a linear Z–M–Z core suspect for the majority of these salts.

Table I. Physical Properties of $[M(ZR_3)_2]X$ Complexes

complex	conductivity/ S^a	anion $\nu_4/cm^{-1\,b}$	anion sym
$[Ag\{P(C_5H_9)_2Ph\}_2][BF_4]$	22.4	1055	T_d
$[Ag\{P(C_5H_9)_2Ph\}_2][ClO_4]$	23.0	1100	T_d
$[Ag\{P(C_5H_9)Ph_2\}_2][ClO_4]$	26.6	1105	T_d
$[Ag\{P(C_6H_{11})_2Ph\}_2][ClO_4]$	26.4	1090, 615	T_d
$[Ag\{As(C_5H_9)_3\}_2][ClO_4]$	23.6	1125, 1025, 620	C_{3v}
$[Cu\{P(C_5H_9)_2Ph\}_2][BF_4]$	28.7	1100	T_d
$[Cu\{P(C_5H_9)_2Ph\}_2][ClO_4]$	28.0	1105	T_d
$[Cu\{P(C_6H_{11})_2Ph\}_2][ClO_4]$	27.0	1100, 600	T_d
$[Cu(FBF_3)\{P(C_6H_{11})_2Ph\}_2]$	20.6	1080, 1035	C_{3v}
$[Cu\{As(C_5H_9)_3\}_2][ClO_4]$	24.7	1130, 1030	C_{3v}
$[Au\{P(C_6H_{11})Ph_2\}_2][ClO_4]$		1100	T_d
$[Au\{P(C_6H_{11})_2Ph\}_2][ClO_4]$		1093	T_d

[a] Determined on millimolar nitrobenzene solutions. [b] Nujol mull spectra.

Silver(I) Coordination. Crystal structure analyses were thus undertaken on two of the salts prepared in this study. [Ag{As-

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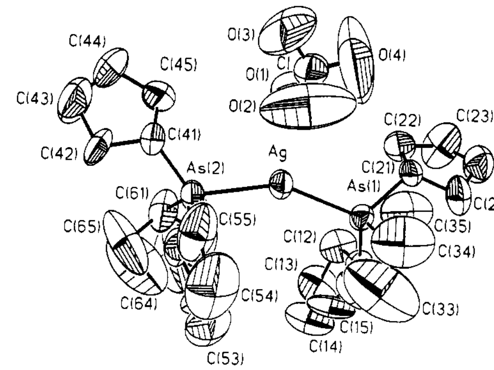

Figure 1. Illustration of the cation in $[Ag\{As(C_5H_9)_3\}_2][ClO_4]$.

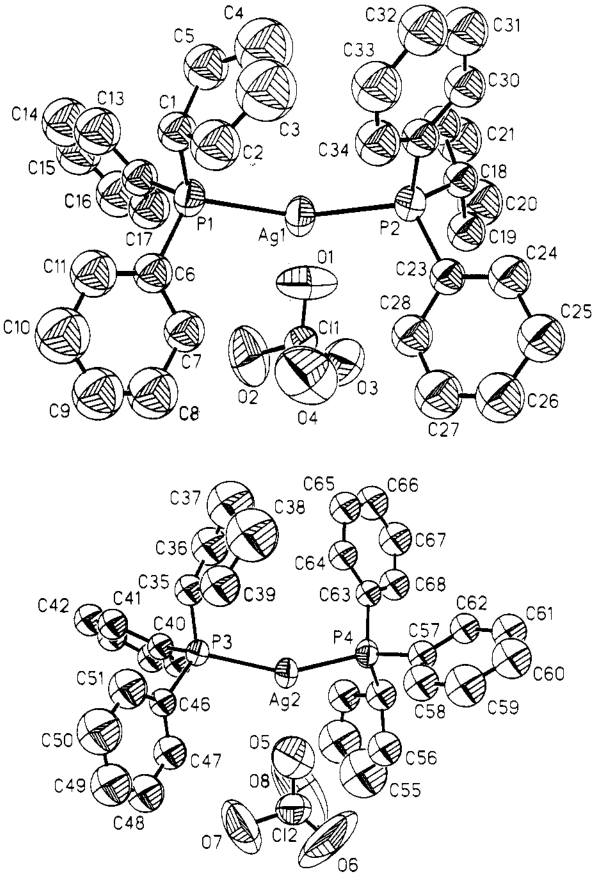

Figure 2. Illustration of the two cations in $[Ag\{P(C_5H_9)Ph_2\}][ClO_4]$.

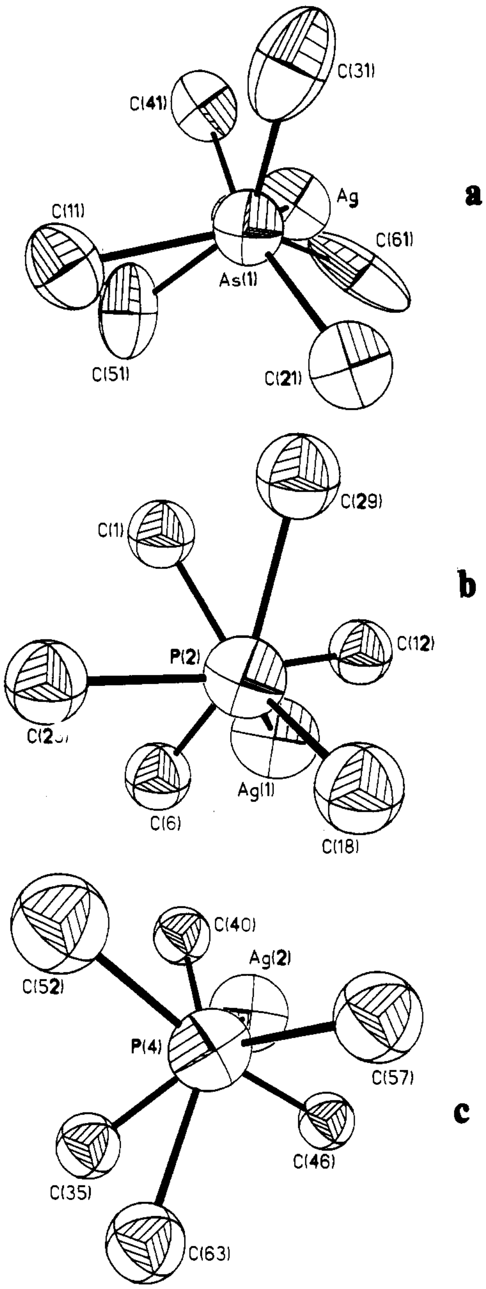

Figure 3. Illustrations of the conformations of the $Ag(ZC_3)_2$ moieties, as viewed parallel to the Z···Z direction: (a) $[Ag\{As(C_5H_9)_3\}_2][ClO_4]$; (b and c) $[Ag\{P(C_5H_9)Ph_2\}][ClO_4]$.

$(C_5H_9)_3\}_2][ClO_4]$ was chosen since the IR data indicated interactions occurred with the perchlorate anion. For comparative purposes, the structure of a complex with a normal IR spectrum, but a slightly reduced conductivity, $[Ag\{P(C_5H_9)Ph_2\}_2][ClO_4]$, was also determined.

These structure determinations show that both of these perchlorate salts contain nonlinear AgZ_2^+ coordination spheres with very similar distortions from linearity. The distortions arise from weak electrostatic interactions with the perchlorate counterions as seen in Figures 1 and 2. In the As complex the ionic interaction between silver ion and the perchlorate group leads to a Ag–O distance of 2.644 Å. The $[Ag\{PPh_2(C_5H_9)\}_2][ClO_4]$ salt contains two crystallographically independent formula units, for which the shortest Ag–O distances are 2.662 and 2.709 Å. It is the ionic interactions between the perchlorate groups and the cations that are primarily responsible for the latter's nonlinearity, with the As–Ag–As angle distorted to 151.2° while the P–Ag–P angles are 145.1° for Ag(1) and 153.0° for Ag(2). These variations in angles appear to be related to the relative conformations of the pair of ZR_3 groups coordinated to the silver(I) ion (vide infra). These compare with the P–Cu–P angle of 144.5° in the $[Cu(PCy_3)_2][ClO_4]$ cation.[1]

On the basis of these structural results, it seems unlikely that any of the $[M(ZR_3)_2]X$ salts ($X = ClO_4^-$, BF_4^-) reported here contain linear $Z{-}M{-}Z^+$ moieties in the solid state. The observed geometries can be viewed as precursors for $[M(ZR_3)_3]^+$ species, formed when an excess of the ZR_3 ligands are present in solution. The role of R group size and of the ligating ability of the ZR_3 ligands will be most evident in these latter complexes.[6]

The formation of $[ML_2][ClO_4]$ complexes by $PPh_2(C_5H_9)$ complexes is exceptional since they also form $[ML_3]X$ complexes, and species of the latter stoichiometry are also formed by the larger homologous ligands containing cyclohexyl or cycloheptyl groups. Nevertheless, the reverse behavior is noted for ligands in the PPh(cycloalkyl)$_2$ series; these always form $[ML_2]^+$ complexes and only exceptionally $[ML_3]^+$ species. Tricyclopentylamine always gives $[ML_2]X$ products irrespective of the quantities used in the preparative reactions.

The only difference in behavior between silver and copper was with PPh(cyclohexyl)$_2$, where an $[AgL_3]^+$ cation was isolated in

Table II. Analytical Data and Melting Points for Ligands and Complexes

		anal./%					
		found			calcd		
compound	mp/°C	C	H	Z	C	H	Z
$P(C_5H_9)_2Ph$	<20	79.7	7.8		78.0	9.4	
$P(C_5H_9)Ph_2$	<20	80.3	7.52		80.3	7.5	
$P(C_6H_{11})Ph_2$	45–50	78.0	7.8		80.6	7.9	
$P(C_6H_{11})_2Ph$	55–58	78.8	8.2		78.8	9.9	
$As(C_5H_9)_3$	<20	63.4	9.4		63.8	9.6	
$[Ag\{P(C_5H_9)_2Ph\}_2][BF_4]$	202–204	55.2	7.1		55.9	6.7	
$[Ag\{P(C_5H_9)_2Ph\}_2][ClO_4]$	134–140	54.6	6.8		54.9	6.6	
$[Ag\{P(C_5H_9)Ph_2\}_2][ClO_4]$	175–177	57.1	5.5	8.9	57.0	5.4	8.7
$[Ag\{P(C_6H_{11})_2Ph\}_2][ClO_4]$	151–152	57.3	7.4	8.0	57.2	7.2	8.2
$[Ag\{As(C_5H_9)_3\}_2][ClO_4]$	145–146	46.7	7.4	19.6	46.7	7.1	19.4
$[Cu\{P(C_5H_9)_2Ph\}_2][BF_4]$	164–166	59.0	7.4		59.8	7.2	
$[Cu\{P(C_5H_9)_2Ph\}_2][ClO_4]$	158–160	59.3	7.1		58.6	7.1	
$[Cu\{P(C_6H_{11})_2Ph\}_2][ClO_4]$	176–178	60.8	7.9	9.0	60.8	7.7	8.7
$[Cu(FBF_3)\{P(C_6H_{11})_2Ph\}_2]$	176–177	61.3	8.2		61.9	7.8	
$[Cu\{As(C_5H_9)_3\}_2][ClO_4]$	129–130	49.5	7.8	20.7	49.3	7.5	20.6
$[Au\{P(C_6H_{11})Ph_2\}_2][ClO_4]$	176–177	52.4	5.2	7.4	52.0	5.0	7.3
$[Au\{P(C_6H_{11})_2Ph\}_2][ClO_4]$	205	51.6	6.7	7.5	51.2	6.4	7.4

Table III. Crystallographic Data

	$[Ag\{As(C_5H_9)_3\}_2]$-$[ClO_4]$	$[Ag\{P(C_5H_9)Ph_2\}_2]$-$[ClO_4]$
empirical formula	$C_{30}H_{54}AgAs_2ClO_4$	$C_{34}H_{38}AgClO_4P_2$
fw	1544	716
a/Å	10.162 (4)	10.574 (6)
b/Å	23.211 (6)	17.142 (11)
c/Å	14.351 (3)	18.812 (13)
β/deg	98.37 (2)	104.34 (5)
V/Å^3	3349 (2)	3273 (3)
T/°C	22	22
space group	$P2_1/n$	Pn
radiation (λ/Å)	Mo Kα (0.71069)	Mo Kα (0.71069)
μ/cm^{-1}	26.63	8.2
ρ/g cm^{-3}	1.53 (Z = 4)	1.46 (Z = 4)
R	0.0730	0.0430
R_w	0.0501	0.0484

Table IV. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $[Ag\{As(C_5H_9)_3\}_2][ClO_4]$

	x	y	z	U^a
Ag	3313 (1)	6047 (1)	6532 (1)	67 (1)
As(1)	3663 (1)	7042 (1)	7155 (1)	57 (1)
C(11)	5026 (11)	7079 (5)	8269 (7)	71 (5)
C(12)	6336 (11)	6823 (6)	8094 (8)	104 (7)
C(13)	6907 (16)	6583 (8)	9029 (11)	139 (10)
C(14)	5882 (17)	6467 (8)	9552 (12)	152 (10)
C(15)	4670 (12)	6735 (6)	9085 (8)	125 (8)
C(21)	4123 (11)	7638 (4)	6293 (8)	65 (5)
C(22)	5389 (12)	7532 (5)	5868 (9)	98 (7)
C(23)	6056 (17)	8087 (6)	5880 (14)	183 (12)
C(24)	5257 (15)	8541 (6)	6145 (10)	116 (8)
C(25)	4280 (13)	8252 (4)	6703 (9)	101 (7)
C(31)	2038 (13)	7392 (6)	7519 (12)	98 (8)
C(32)	1412 (15)	7048 (8)	8178 (11)	153 (10)
C(33)	24 (24)	7169 (14)	7899 (20)	374 (31)
C(34)	−326 (22)	7407 (10)	7116 (16)	211 (17)
C(35)	926 (18)	7464 (8)	6712 (11)	157 (11)
As(2)	2982 (1)	5002 (1)	6766 (1)	68 (1)
C(41)	2273 (12)	4547 (5)	5636 (8)	77 (6)
C(42)	2038 (15)	3911 (6)	5805 (10)	115 (8)
C(43)	2156 (22)	3632 (7)	4918 (13)	194 (13)
C(44)	2893 (18)	3993 (6)	4367 (11)	147 (10)
C(45)	3155 (14)	4574 (5)	4882 (8)	108 (7)
C(51)	1618 (16)	4885 (5)	7573 (10)	97 (8)
C(52)	2017 (23)	5165 (7)	8571 (12)	168 (13)
C(53)	624 (36)	5306 (13)	8782 (18)	227 (24)
C(54)	−350 (18)	5348 (9)	7942 (14)	271 (17)
C(55)	330 (18)	5160 (7)	7112 (14)	152 (12)
C(61)	4743 (18)	4565 (6)	7258 (10)	145 (9)
C(62)	5663 (21)	4982 (9)	7751 (15)	247 (15)
C(63)	6274 (31)	4692 (9)	8686 (24)	255 (17)
C(64)	6078 (21)	4208 (10)	8420 (21)	267 (20)
C(65)	4618 (19)	4238 (12)	8005 (17)	345 (23)
Cl	2298 (5)	6356 (2)	4267 (3)	101 (2)
O(1)	3482 (11)	6171 (5)	4707 (7)	149 (6)
O(2)	1543 (12)	6331 (10)	4899 (9)	336 (14)
O(3)	1728 (14)	6057 (6)	3552 (8)	241 (9)
O(4)	2344 (20)	6851 (6)	3996 (15)	392 (15)

[a] The equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

addition to an $[ML_2]^+$ cation. It is possible that the more favorable hybridization energy for two-coordinate silver(I) inhibits the formation of $[AgL_3]^+$ species that might be expected to be isolated on the basis of the larger size of the Ag^+ ion.

That there is not a definite change in behavior on varying the ligand size and that the homologous series of complexes are not isomorphous both indicate the importance of meshing between the organo groups of ligands on the same metal atom.

Silver–Oxygen Bonds. In silver perchlorate, the silver–oxygen distance is 2.51 Å,[8] while in the two-coordinate *O*-carbonato silver complex $K_2[Ag_2(CO_3)_2]$ the silver–oxygen distance is 2.09 Å.[9] Therefore, it may be concluded that, in silver perchlorate itself as well as in this series of complexes, there are only weak ionic interactions between silver and an oxygen atom of the perchlorate group. The large apparent thermal motion of the perchlorate ions in all of these structures prevents firm conclusions from being drawn, but generally the longest chlorine–oxygen bonds are those for that atom nearest silver and the thermal motion of these oxygen atoms are the least.

Silver–Group 5B Bonds. The length of silver(I)–group 5B element bonds depends not only upon the coordination number of silver but also upon the number of π-acid ligands present in the coordination sphere. The σ-bond radii for the various coordination numbers may be deduced by subtracting standard σ-bond radii of sundry elements from the known lengths of their bonds to silver. Thus subtraction of 0.66 Å (the covalent radius of oxygen) from the Ag–O distance in $K_2[Ag_2(CO_3)_2]$[9] gives a value of 1.43 Å for two-coordinate silver. The bond between three-coordinate silver and iodine in $[AgI(PPh_3)]_4$ is 2.724 Å long,[10] whence by subtracting 1.33 Å (the covalent radius of iodine) the covalent radius of tricoordinate silver is 1.49 Å. Similarly subtraction of the covalent radii of the halide ion (Cl = 0.99 Å, Br = 1.14 Å) from the length of the halide–silver bonds in $[AgX(PEt_3)]_4$ (X = Cl, Br,[11] I[12]) gives a mean σ-bond covalent radius for four-coordinate silver of 1.61 Å.

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Table V. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[Ag\{P(C_6H_5)_2(C_5H_9)\}_2][ClO_4]$

	x	*y*	*z*	U^a
Ag(1)	5182	4140 (1)	4655	67 (1)
Ag(2)	5640 (1)	9171 (1)	2947 (1)	58 (1)
P(1)	4770 (2)	4980 (1)	5615 (1)	59 (1)
P(2)	6678 (2)	3216 (1)	4339 (1)	54 (1)
P(3)	4132 (2)	8340 (1)	3374 (1)	46 (1)
P(4)	6153 (2)	10202 (1)	2204 (1)	53 (1)
C(1)	6125 (7)	5656 (5)	5954 (4)	67 (3)
C(2)	7423 (8)	5236 (6)	6238 (5)	96 (4)
C(3)	8257 (10)	5467 (10)	5762 (8)	147 (7)
C(4)	7632 (15)	5971 (8)	5240 (9)	148 (8)
C(5)	6304 (8)	6193 (5)	5317 (5)	85 (3)
C(6)	4644 (7)	4393 (4)	6397 (5)	67 (3)
C(7)	4367 (8)	3604 (5)	6295 (5)	80 (3)
C(8)	4269 (10)	3160 (6)	6918 (7)	108 (5)
C(9)	4438 (10)	3479 (6)	7558 (6)	106 (4)
C(10)	4750 (15)	4246 (7)	7678 (7)	126 (6)
C(11)	4844 (10)	4701 (5)	7094 (5)	91 (4)
C(12)	3299 (7)	5566 (4)	5406 (4)	62 (2)
C(13)	3260 (12)	6343 (6)	5574 (8)	125 (6)
C(14)	2140 (14)	6731 (7)	5408 (10)	143 (7)
C(15)	1016 (11)	6428 (7)	5020 (7)	122 (6)
C(16)	1032 (11)	5669 (9)	4830 (7)	128 (6)
C(17)	2175 (9)	5244 (6)	5025 (5)	96 (4)
C(18)	7072 (7)	3324 (4)	3457 (4)	62 (2)
C(19)	5899 (9)	3137 (5)	2820 (4)	81 (3)
C(20)	6120 (13)	3554 (8)	2184 (6)	141 (6)
C(21)	6996 (16)	4231 (7)	2466 (6)	130 (6)
C(22)	7497 (8)	4145 (4)	3293 (5)	75 (3)
C(23)	6178 (7)	2204 (4)	4385 (4)	57 (2)
C(24)	6997 (8)	1599 (4)	4368 (5)	76 (3)
C(25)	6614 (12)	839 (5)	4446 (5)	101 (4)
C(26)	5344 (12)	698 (6)	4526 (5)	108 (5)
C(27)	4547 (12)	1297 (6)	4514 (5)	106 (5)
C(28)	4925 (8)	2055 (5)	4456 (4)	72 (3)
C(29)	8230 (7)	3261 (4)	5033 (4)	61 (2)
C(30)	9418 (7)	3326 (5)	4877 (5)	74 (3)
C(31)	10521 (8)	3398 (6)	5440 (5)	92 (4)
C(32)	10455 (9)	3409 (5)	6157 (5)	96 (4)
C(33)	9288 (11)	3313 (6)	6308 (5)	101 (4)
C(34)	8186 (8)	3250 (6)	5744 (4)	81 (3)
C(35)	2480 (7)	8483 (4)	2820 (4)	65 (3)
C(36)	2293 (11)	8249 (8)	2043 (5)	115 (5)
C(37)	1324 (13)	8784 (9)	1604 (8)	178 (7)
C(38)	1635 (17)	9499 (8)	1951 (10)	211 (9)
C(39)	2060 (8)	9376 (5)	2801 (8)	115 (5)
C(40)	4372 (6)	7296 (4)	3354 (3)	51 (2)
C(41)	3383 (7)	6779 (4)	3420 (5)	73 (3)
C(42)	3567 (10)	5986 (5)	3387 (6)	88 (4)
C(43)	4712 (9)	5705 (4)	3285 (5)	75 (3)
C(44)	5690 (8)	6185 (4)	3248 (5)	76 (3)
C(45)	5511 (7)	6998 (4)	3277 (4)	61 (2)
C(46)	4144 (6)	8532 (3)	4324 (4)	51 (2)
C(47)	5259 (9)	8598 (5)	4832 (4)	79 (3)
C(48)	5300 (11)	8772 (6)	5544 (5)	99 (4)
C(49)	4176 (15)	8900 (6)	5755 (6)	115 (5)
C(50)	3044 (12)	8816 (9)	5252 (8)	140 (6)
C(51)	2994 (9)	8654 (7)	4532 (6)	102 (4)
C(52)	6298 (8)	9840 (4)	1327 (5)	75 (3)
C(53)	5086 (10)	9408 (6)	897 (5)	92 (4)
C(54)	5511 (15)	8722 (8)	581 (9)	165 (8)
C(55)	6850 (16)	8652 (10)	832 (13)	226 (11)
C(56)	7392 (10)	9220 (5)	1395 (6)	93 (4)
C(57)	7668 (7)	10751 (4)	2570 (4)	60 (2)
C(58)	8622 (8)	10411 (5)	3101 (5)	86 (3)
C(59)	9777 (10)	10806 (6)	3410 (8)	113 (5)
C(60)	9949 (10)	11548 (6)	3146 (7)	111 (5)
C(61)	9010 (9)	11868 (5)	2634 (6)	90 (4)
C(62)	7842 (8)	11495 (4)	2334 (5)	74 (3)
C(63)	4889 (7)	10941 (4)	1995 (4)	56 (2)
C(64)	4256 (7)	11136 (4)	2523 (4)	67 (3)
C(65)	3322 (7)	11726 (5)	2417 (5)	78 (3)
C(66)	3042 (9)	12130 (6)	1776 (5)	90 (3)
C(67)	3639 (10)	11947 (5)	1241 (5)	93 (4)
C(68)	4590 (9)	11349 (5)	1344 (4)	77 (3)
Cl(1)	1976 (2)	3640 (1)	3448 (1)	67 (1)
Cl(2)	8789 (2)	8397 (1)	4008 (1)	83 (1)
O(1)	3108 (8)	4066 (4)	3517 (6)	130 (4)
O(2)	913 (8)	4099 (5)	3505 (6)	138 (4)
O(3)	1591 (10)	3301 (5)	2768 (5)	150 (4)
O(4)	2183 (11)	3057 (6)	3991 (7)	180 (6)
O(5)	7756 (10)	8874 (7)	4061 (9)	195 (7)
O(6)	9850 (11)	8624 (14)	4164 (14)	380 (13)
O(7)	8550 (11)	7692 (5)	4332 (5)	162 (5)
O(8)	8354 (20)	8393 (6)	3315 (6)	250 (10)

[a] The equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The latter effect is well exemplified by the series of triphenylarsine complexes investigated by Nardelli et al.[13] All the complexes in their series contain four-coordinate silver, but the Ag–As distances increase with the number of triphenylarsine ligands in the coordination sphere. When only one $AsPh_3$ ligand is present, Ag–As = 2.471 Å; when two are coordinated, the mean bond length is 2.528 Å, whereas the ranges found with three or four $AsPh_3$ ligands present are 2.61–2.68 and 2.66–2.70 Å, respectively. These increases are caused by a lowering of the double-bond character of each individual bond with the increasing number of π-acid ligands present. The apparent effect is an increase in the covalent radius of silver(I) (calculated from the Ag–As bond lengths) from 1.26 to 1.47 Å showing that the degree of π-bonding is inversely proportional to the number of π-acid ligands present.

Bearing the above factors in mind, one observes that the bond lengths between silver and the group 5B elements found here are fairly typical for two-coordinate silver. In the bent $[Ag\{P(NMe_2)_3\}_2]^+$ cation, the mean silver–phosphorus distance is 2.394 Å. The two $[Ag\{PPh_2(C_5H_9)\}_2]^+$ cations have bonds of 2.432, 2.415 Å and 2.419, 2.397 Å, respectively. The mean silver–arsenic bond length of 2.482 Å is about 0.2 Å shorter than the bonds in the $[Ag(AsPh_3)_4]^+$ cation,[12] which is consistent with the decrease in covalent radii with coordination number discussed above.

In all instances, however, the silver–group 5B element bonds are shorter than the sum of the σ-bonded covalent radii. The two-coordinate σ-bond radius of silver(I) can be taken to be 1.43 Å and internally consistent values of the σ-bond radius of the group 5B elements can be derived by subtracting 0.70 Å from the phosphorus sp² carbon bond length or by subtracting 0.77 Å from the mean arsenic–carbon bond length. The sum of the silver group 5B element σ-bond radii thus obtained are Ag–As = 2.62 Å and Ag–P = 2.54. The observed values are some 5.6–5.8% shorter than the calculated σ-bonded radii, indicating a modest degree of π-bonding between silver and the donor atoms.

Organo Groups. The structure of the organo groups bound to the group 5B atoms are essentially unremarkable. The bond angles in the phenyl groups are all close to 120°, and the bond angles in the cyclopentyl groups are all close to tetrahedral angles except that there is some disorder of the third and fourth carbon atoms of each ring. This is probably due to fractional site occupancy of the two sites, each giving a chair conformation to the ring. The mean site shown makes the rings nearly planar and gives rise to large apparent thermal motions for these atoms. It was not considered productive to investigate the fractional site occupancy further.

The configurations of the organo rings are, however, worthy of comment. The six cyclopentyl groups in the $[Ag\{As(C_5H_9)_3\}_2]^+$ cation are nearly eclipsed (Figure 3a) whereas the six rings of the $[Ag\{PPh_2(C_5H_9\}_2]^+$ cations for Ag(1) are in a minimum energy staggered arrangement while for Ag(2) the configuration is closer to eclipsed. This apparently is the reason the P–Ag(2)–P angle is larger than the P–Ag(1)–P angle. In addition, the conformations are different in the two independent phosphine cations. In the first, the cyclopentyl groups are anti (Figure 3b) while in the

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[13] Nardelli, M.; Pelizzi, C.; Pelizzi, G.; Tarasconi, P. *J. Chem. Soc., Dalton Trans.* **1985**, 321.

second, the five-membered rings are syn (Figure 3c).

Experimental Section

Carbon and hydrogen microanalyses (Table II) were carried out by Mr. M. F. Newman of the North East London Polytechnic Analytical Service. Phosphorus and arsenic microanalyses (Table II) were carried out by Analytische Laboratorien, Elbach, Gummersbach, Federal Republic of Germany.

Conductivity measurements were made on millimolar nitrobenzene solutions, thermostated at 25 °C, by using a Wayne Kerr universal bridge, Model B221. The cell constant was determined by using aqueous potassium chloride solutions of known concentration. Nitrobenzene (analytical grade) was further purified by drying it over $CaCl_2$ and redistilling; the fraction distilling in the range 209–211 °C at 760 mmHg was collected and used immediately.

Melting points (Table II) were determined in an Electrothermal melting point apparatus and are uncorrected. All preparative reactions were carried out in dry nitrogen atmospheres. Solvents were deaerated by purging them with dry nitrogen. All silver and gold complexes were prepared in externally blackened flasks to minimize photolysis.

Infrared spectra were obtained in Nujol or hexachlorobuta-1,3-diene mulls between potassium bromide plates using either a Perkin-Elmer 377 or a Perkin-Elmer 781 spectrophotometer, the latter in conjunction with a Perkin-Elmer 3600 data station.

$As(C_5H_9)_3$. Bromocyclopentane (0.50 mol) was dried over anhydrous $CaCl_2$ and dissolved in sodium-dried diethyl ether (150 cm^3). This solution was added dropwise to a suspension of Mg turnings (0.485 mol) in the same solvent. The solution of cyclopentyl magnesium bromide was cooled to −20 °C, stirred, and allowed to react with an ethereal solution of arsenic trichloride (0.161 mol) in dry diethyl ether, which was added dropwise over a period of several hours. After the addition was complete, the reaction mixture was allowed to reach room temperature, and stirring was continued for 2 h. Finally, to ensure complete reaction, the mixture was refluxed for 1 h. The product was decomposed by addition of a deaerated aqueous solution of NH_4Cl (200 cm^3). The ethereal layer was separated and distilled under nitrogen until its volume had been reduced to 500 cm^3. White crystals of the ligand were obtained upon cooling.

PR_2R' Compounds. These were obtained similarly via the bromocycloalkane Grignard reagent (0.50 mol) and either $PPhCl_2$ (0.24 mol) or PPh_2Cl (0.485 mol) in place of $AsCl_3$.

$[CuL_2]X$ Complexes. These were prepared by allowing $[Cu(H_2O)_6]X_2$ ($X = ClO_4^-$, BF_4^-) (10 mmol) to react with the ligand (25 mmol) in ethanol. The solution was heated under reflux until the color of copper(II) species disappeared.

$[AgL_2]X$ Complexes. These were prepared by allowing ethanolic suspensions of silver(I) perchlorate or tetrafluoroborate (1 equiv) to react with the neutral ligand (2 equiv) at reflux temperatures for 1 h. The solutions were allowed to cool and the white complexes filtered off at the pump. The complexes were washed twice with small portions of deuterated ethanol and dried in vacuo.

$[AuL_2]X$ Complexes. These were prepared by allowing $[H_3O][Au(NO_3)_4]$ (1 equiv) to react with the tertiary phosphine (4 equiv) in refluxing ethanol. The white, gold(I) products crystallized out on cooling of the solution. These were filtered off at the pump and dissolved in a fresh portion of ethanol together with a small quantity of the ligand. A hot, ethanolic solution containing excess lithium perchlorate was added to a solution of the gold(I) material. On cooling, white crystals of the gold(I) perchlorate complexes were obtained. These crystals were filtered off at the pump, washed cautiously with small quantities of deaerated ethanol, and dried in vacuo.

Table VI. Selected Bond Distances (Å) and Angles (deg)

	length		angle
	$Ag\{P(C_5H_9)Ph_2\}_2ClO_4$		
Ag(1)–P(1)	2.432 (2)	P(1)–Ag(1)–P(2)	145.1 (1)
Ag(1)–P(2)	2.415 (2)	P(3)–Ag(1)–P(4)	153.0 (1)
Ag(2)–P(3)	2.419 (2)		
Ag(2)–P(4)	2.397 (2)		
Ag(1)–O(1)	2.662 (5)		
Ag(2)–O(5)	2.709 (5)		
Ag(2)–O(8)	3.082 (5)		
	$Ag\{As(C_5H_9)_3\}ClO_4$		
Ag–As(1)	2.482 (2)	As(1)–Ag–As(2)	151.2 (1)
Ag–As(2)	2.480 (2)		
Ag–O(2)	2.644 (5)		

Crystal Structure Analyses. Crystal structures of the colorless monoclinic crystals of $[Ag\{As(C_5H_9)_3\}_2][ClO_4]$ and of $[Ag\{PPh_2(C_5H_9)\}_2][ClO_4]$ were determined by using diffraction data collected on a Syntex $P2_1$ diffractometer system, upgraded to Nicolet P3 specification, utilizing Mo Kα radiation (λ = 0.71069 Å).[14] The structures were solved via the direct-methods program SOLV (the P complex) or through the Patterson search routine (the As complex) in the SHELXTL structure solution package.[15] These yielded heavy-atom positions, and light atoms were located in subsequent rounds of Fourier difference syntheses. A summary of pertinent data collection parameters and refinement results are given in Table III, with a more complete description available. Final positional parameters are given in Tables IV and V, and bond distances and angles involving the Ag atom are listed in Table VI.

The structure determination process for the P complex is worthy of some further comment. The heavy atoms (Ag, P) for the two independent species in the structure are related by an approximate center of inversion. However, attempts to refine the structure in the centrosymmetric space group were not successful. This was due to the different configuration of the phosphine ligands in the two complexes, as discussed above. In particular, it is to be noted that, for Ag(1), both P–C bonds to a C_5H_9 ring, P(1)–C(1) and P(2)–C(18), lie nearly in the AgP_2 plane. In contrast, for the Ag(2) complex, one of the P–C bonds to the C_5H_9 rings lies nearly in the AgP_2 plane (P(3)–C(35)) while the other (P(4)–C(52)) is essentially normal to that plane.

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Supplementary Material Available: Tables of X-ray data collection parameters, hydrogen atom positions, and thermal parameters and a complete listing of bond distances and angles (12 pages); a table of F_o/F_c data (62 pages). Ordering information is given on any current masthead page.

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