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Review

Coordination complexes of silver(I) with tertiary phosphine and related ligands

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This article is dedicated to Professor Allan H. White on the occasion of his retirement.

Contents

Abstract

This paper gives an overview of the structural chemistry of silver(I) coordination complexes. The main discussion is on the halide complexes (F^-, Cl^-, Br^-, I^-) but included are also the pseudo-halides (CN^-, SCN^-) and the classical non-coordinating anions (NO_3^-, ClO_4^-, BF_4^-, PF_6^-) and oxy-anions (NO_3^-, $H_3CCO_2^-$, $F_3CCO_2^-$, $F_3CSO_3^-$, etc.). The main focus is on complexes of these silver(I) salts with phosphine ligands, but where relevant the chemistry of other donor ligands is also reviewed. Coordination complexes of silver(I) halides show a rich variation of structural

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Abbreviations: *c*, cyclo; depe, 1,2-bis(diethylphosphino)ethane; dmpm, bis(dimethylphosphino)methane; dmpe, 1,2-bis(dimethylphosphino)ethane; dppb, 1,4-bis(diphenylphosphino)butane; dppm, bis(diphenylphosphino)methane; dppn, 1,5-bis(diphenylphosphino)pentane; dppe, 1,2-bis(diphenylphosphino)ethane; dppey, *cis*–bis(diphenylphosphino)ethene; dppp, 1,3-bis(diphenylphosphino)propane; d*n*pyppe, 1,2-bis(di-*n*-pyridylphosphino)ethane for $n = 2$, 3 and 4; eppe, 1-(diethylphosphino)-2-(diphenylphosphino)ethane; Fc, ferrocenyl; im, imidazole; L, ligand, typically a Group 15 donor ligand; L^2, bidentate ligand; Py, pyridine; X, halide, pseudo-halide.

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types. The type of structure depends on the stoichiometry of the ligand to silver in the reaction mixture, as well as reaction conditions. Other factors influencing the structure of these complexes include the halide or pseudo-halide ligands used as counterion and the type of solvent.

Keywords: Silver; Phosphine; Ligand; X-ray structure

1. Introduction

Tertiary phosphine complexes of silver(I) of the type $[AgXL_n]$ (L = tertiary phosphine, PR_3 (R = alkyl, aryl or H); $n = 1$–4; X = coordinating or non-coordinating anion) were first prepared in 1937 by Mann et al. [1]. The general method of preparation involves the reaction of appropriate amounts of phosphine ligand with the silver(I) salt in a suitable supporting solvent. Typically, silver(I) halides (Cl^-, Br^-, I^-) and pseudohalides (CN^-, SCN^-) are heated under reflux with 1–3 molar equivalents of the phosphine ligand in acetonitrile, followed by crystallisation from appropriate solvents. Silver(I) complexes of the classical non-coordinating anions (NO_3^-, ClO_4^-, BF_4^-, PF_6^-) are typically prepared by addition of the silver(I) salt to a hot solution of the phosphine in an alcohol (MeOH, EtOH). The desired complex then crystallises out of solution. These coordination complexes of silver(I) salts display a rich diversity of structural types. The interplay of parameters such as the geometrical flexibility of Ag(I), bite angle, electronic properties of the phosphine and the coordination mode of the supporting ligands often renders predictions concerning the structural properties of silver–phosphine complexes, both in solution and in the solid state, difficult.

Previous periodic reviews have reported on the coordination chemistry of silver [2], as well as the design of coordination networks [3] and polymers [4] containing nitrogen-donor ligands. In addition, the chemistry of silver scorpionates [5] and silver carboxylates [6], as well as the increasingly important chemistry of silver carbene complexes [7] was recently reviewed.

This review aims to give a description of the coordination chemistry of AgX salts ($X^- = F^-$, Cl^-, Br^-, I^-, BF_4^-, PF_6^-, NO_3^-, etc.) with Group 15 donor ligands with a main focus on the structural chemistry of simple monodentate tertiary phosphine (PR_3, Section 2) and derivative bidentate ($R_2P(CH_2)_nPR_2$, Section 3) complexes of silver(I) halides. At the end of the descriptions of the various typical structural types, we present the various crystal structures of Ag(I) complexes in tables, as extracted from the Cambridge Structural Database [8]. These tables are comprehensive for phosphine adducts of AgX (X = F^-, Cl^-, Br^-, I^-, BF_4^-, PF_6^-, NO_3^-, ClO_4^-). Also included in the tables, but not extensively discussed, are related adducts of other Group 15 (As, Sb) based donor ligands. For more information on the interesting coordination compounds of these adducts we refer to the original research papers. The tables are complete up to November 2006—an attempt to include structures submitted to the CSD after this date was made, but may not be exhaustive.

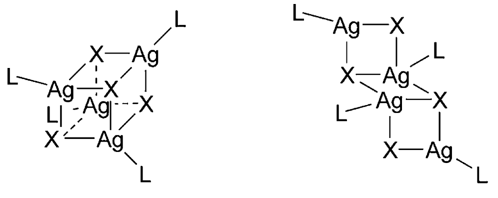
A non-comprehensive description of complexes containing N-donor molecules is also given (Section 4) and this part is included to serve as an introduction to complexes of mixed ligand systems containing both phosphine and nitrogen based donor ligands (Section 5), which in turn are relevant to complexes of pyridylphosphines (Section 6). Silver(I) complexes of bidentate pyridylphosphines are of particular interest to us in their context as potential antitumour agents [9,10]. Not included in this review is any description of silver(I) salts with the various organoborates (e.g. BPh_4^-, pyrazolyl borate [5], etc., although BF_4^- is included) and silver salts of various more complex oxo-ligands such as bidentate acetylacetonato ($acac^-$) and its derivatives.

2. Silver(I) complexes of monodentate phosphines

2.1. Complexes with 1:1 AgX:L stoichiometry

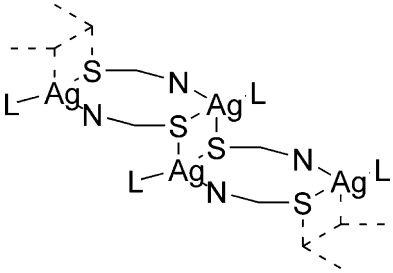
For equimolar stoichiometry (Ag:L = 1) both the tetrameric ‘cubane’ **1** and ‘step’ **2** structures have been characterised, both illustrated in Scheme 1. Noting the difference, it has been argued that control of the isomeric form may be determined by the relative stereochemical parameters of metal, halide and ligand [11,12]. More sterically demanding species tend to relieve strain by forming the step structure **2** rather than the cubane structure **1**, since the three-coordinate metal sites and dibridging halides in the step structure **2** are less crowded. Thus, the trialkylphosphine PEt_3 yields tetrameric cubane clusters $[AgX(PEt_3)]_4$ (X = Cl^-, Br^- [13] and I^- [14]) and the reaction of equimolar ratios of PPh_2Bu with silver(I) halides yields tetrameric cubane structures of type $[AgX(PPh_2Bu)]_4$ (X = Cl^-, Br^- and I^-) [15]. However, the isolation and characterisation of cubane – $[AgI(PPh_3)]_4$ [12,16] from $CHCl_3/Et_2O$ and the step analogue from CH_2Cl_2/Et_2O [11,17], as well as the isolation of the sterically unfavoured cubane complexes $[AgI(PCy_3)]_4$ (Cy = cyclohexyl) [18], $[CuI(PPh_3)]_4$ [19] and $[CuBr(P^tBu_3)]_4$ [20], shows that the nature of the determining factors are not clearly understood. Other factors, such as solvent of crystallisation, may be important determinants of the formation of either cubane, **1**, or step, **2**, structures.

Zigzag polymeric – Ag–SCN–Ag–SCN chains, cross-linked in pairs by Ag–S bonds to form double chains, having a stair-



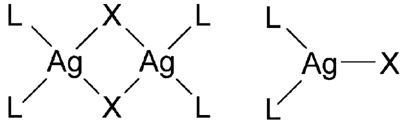
1 **2**

Scheme 1. Tetranuclear ‘cubane’ (**1**) and ‘step’ (**2**) structures (L = phosphine).



Scheme 2. Structure of the [Ag(SCN)(P^nPr_3)] polymer [21]; L = P^nPr_3.

step configuration, with alternating four (Ag(μ-S)$_2$Ag) and eight (Ag(μ-SCN)(μ-NCS)Ag) membered rings (Scheme 2) were found for [Ag(SCN)(P^nPr_3)] [21]. Stable 1:1 complexes of the type [Ag(ClO_4)(PR_3)] have been isolated using bulky phosphines such as P^tBu_3, PCy_3 and P(2-MeC_6H_4)$_3$ as well as the less bulky triphenylphosphine and *para*-substituted triarylphosphines [22]. From molecular weight and IR spectral determinations it was concluded that these compounds were linear two-coordinate monomeric structures in which the perchlorate anion was coordinated to the Ag in both the solid state and dichloromethane solution [22].



3 4

Scheme 3. Dimeric bridged (**3**) and mononuclear trigonal planar (**4**) complexes of 1:2 AgX:L stoichiometry.

Linear monomeric compounds have been isolated and characterised for adducts of the very bulky P(2,4,6-$Me_3C_6H_2$)$_3$ with AgX (X = Cl^-, Br^-). Surprisingly, the PCy_3 [18] and $AsCy_3$ [23] adducts of AgX (X = Cl^-, Br^-) show dimerisation, using the halides as bridging ligands, whereas the AgI adduct is a cubane tetramer. Addition of pyridine to this tetramer resulted in the formation of dimeric [{AgI(PCy_3)}$_2$Py] with

Table 1

Structures of silver complexes with a 1:1 AgX:L stoichiometry

Ligand L	Anion X	References
[AgXL]$_4$ tetranuclear compounds of Type **1** (‘cubane’)		
PEt_3	Cl^-, Br^-	[13]
PEt_3	I^-	[14]
P^tBu_2Cl/$P^tBu_2GeCl_3$	Br^-	[24]
P^iBu_3	Cl^-	[25]
PCy_3	I^-	[18]
$PPh_2{}^nBu$	Cl^-, Br^-, I^-	[15]
PPh_3	Cl^-	[12]
	Br^-	[17,26]
	I^-	[11]
P(4-MeC_6H_4)$_3$	Br^-	[27]
P(4-MeC_6H_4)$_3$	I^-	[28]
P(4-$MeOC_6H_4$)	Br^-	[29]
PPh_2(2-py)	Cl^-	[30]
5-Phenyldibenzophosphole	Cl^-	[31]
$AsCy_3$	Br^-, I^-	[23]
$AsPh_3$	I^-	[17]
[AgXL] linear monomeric compounds		
Tris(cyclohepta-2,4,6-trienyl)phosphine	Cl^-	[32]
P(2,4,6-$MeOC_6H_2$)$_3$	Cl^-, Br^-	[33]
[AgXL]$_2$ dinuclear compounds		
PCy_3	Cl^-, Br^-, I^-	[18]
PPh_3	$CF_3CF_2CO_2{}^-$	[34]
P(4-FC_6H_4)$_3$	$NO_2{}^-$	[35]
P(4-MeC_6H_4)$_3$	$CH_3CO_2{}^-$	[36]
4,6,11,11,12,12-Hexamethyl-10-phenyl-dodecahydro-1,4:6,9-dimethano-phenoxaphosphine	$CF_3SO_3{}^-$	[37]
(dibenzocycloheptatrienyl)diphenylphosphine	$CF_3SO_3{}^-$	[38]
P(N^iPr_2)$_2$(OC = OCF_3)	$CF_3SO_3{}^-$	[39]
$AsCy_3$	Cl^-, $NO_3{}^-$	[23]
[AgXL]$_4$ tetranuclear compounds of Type **2** (‘step’)		
PPh_3	I^-	[11,17]
PPh_3	$BrO_3{}^-$	[40]
PPh_2Me	$CF_3SO_3{}^-$	[41]
μ-dppm (bridging)	Cl^-	[42,43]
μ-dppm (bridging)	Br^-	[43]
μ-dppm (bridging)	I^-	[44]
μ-dppm (bridging)	$CF_3CF_2CO_2{}^-$	[45]

bridging iodides and an unusual bridging pyridine in a 'crevice' co-ordination mode, weakly co-ordinated to both silver atoms [18] (Table 1).

2.2. *Complexes with 1:2 AgX:L stoichiometry*

For the 1:2 complexes [$AgXL_2$], structural determinations have shown that in general the complexes are dimeric (Type **3**, Scheme 3) having halide bridges [$AgXL_2$]$_2$ ($L = PPh_3$, $X = Cl^-$ [46], Br^- [26], I^- [17]; L = 5-phenyldibenzophosphole, $X = Cl^-$ [47]). [$AgBr(PPh_3)_2$]$_2$·$CHCl_3$ is dimeric via bridging bromide [26]. The unsolvated 1:2 AgBr:PPh_3 complex is the first example of a complex with trigonal planar [$AgXL_2$] coordination (Type **4**, Scheme 3) [48] and contains the mononuclear species [$AgBr(PPh_3)_2$]. Recrystallisation of this complex from $CHCl_3$ resulted in the formation of solvates [$Ag_2X_2(PPh_3)_4$]·2$CHCl_3$ which contained almost perfectly symmetrical halide-bridged dimers [$(Ph_3P)_2Ag(\mu\text{-}X)_2Ag(PPh_3)_2$] [48]. In contrast, the structure of the unsolvated 1:2 AgCl:PPh_3 complex reveals the presence of dimers, [$Ag_2Cl_2(PPh_3)_4$], containing bridging chloride and terminal PPh_3 ligands [46]. Additionally, this structure contains unsymmetrical chloride bridging, which has prompted

Table 2
Structures of silver complexes with a 1:2 AgX:L stoichiometry

Ligand L	Anion X	References
[$AgXL_2$] mononuclear compounds		
PCy_3	Cl^-, Br^-, I^- NO_3^-	[50]
PCy_3	ClO_4^-	[55]
PPh_3	Cl^-	[56]
PPh_3	Br^-	[48]
PPh_3	BrO_3^-	[40]
PPh_3	$CF_3CO_2^-$	[57]
PPh_3	$CF_3CF_2CO_2^-$	[58]
PPh_3	NO_2^-	[59]
PPh_3	$(^iPrO)_2PS_2^-$	[60]
PPh_3	$PhNN{=}C(CN)_2^-$	[61]
PPh_2Me	$CF_3SO_3^-$	[41]
$PPh_2(N{=}CPh_2)$	Cl^- ClO_4^-	[62]
$PPhFc_2$	$CF_3SO_3^-$, $Et_2NCS_2^-$	[63]
$AsCy_3$	Cl^- Br^- I^- ClO_4^-, $CF_3CO_2^-$	[64]
$Sb(2\text{-}C_4H_3S)_3$	NO_3^-	[65]
[L_2Ag]X ionic compounds		
PMe_3	PF_6^-	[66]
PPh_2Me	ClO_4^-	[67]
$P\{(CH_2)_2CN\}_3$	NO_3^-	[68]
$P\{c\text{-}CO(CH)_3\}_3$	BF_4^-	[69]
PPh_3	BF_4^-	[70]
$P(2,4,6\text{-}Me_3C_6H_2)$	BF_4^-	[71]
$P(2,4,6\text{-}Me_3C_6H_2)$	PF_6^-	[51]
$PPh_2(c\text{-}C_5H_9)$	ClO_4^-	[54]
(dibenzocycloheptatrienyl)diphenylphosphine	$F_3CSO_3^-$	[38]
$P(c\text{-}C_5H_9)_3$	ClO_4^-	[54]
PCy_2Ph	ClO_4	[72]
$PPh\{2,4,6\text{-}(MeO)_3C_6H_2\}_2$	$F_3CCO_2^-$	[73]
$P\{2,4,6\text{-}(MeO)C_6H_2\}_3$	$Ag_5I_7Py_2^-$, $Ag_5I_6(\text{quinoline})^-$	[74]
$P\{2,4,6\text{-}(MeO)C_6H_2\}_3$	$Ag_5I_7Py_2^-$	[75]
$As(c\text{-}C_5H_9)_3$	ClO_4^-	[54]
[$L_2Ag\text{-}\mu_2\text{-}X$]$_2$ dinuclear compounds		
PPh_3	Cl^-	[46,48]
PPh_3	Br^-	[26a,48]
PPh_3	NO_3^-	[76]
PPh_3	$F_3CSO_3^-$	[41,77]
PPh_3	BrO_3^-	[40]
$P(4\text{-}FC_6H_4)_3$	Cl^-, Br^-, I^-	[29]
$P(4\text{-}MeC_6H_4)_3$	SCN^-	[78]
$P(4\text{-}FC_6H_4)_3$	SCN^-	[29]
$P(4\text{-}ClC_6H_4)_3$	Br^-	[29]
5-Phenyldibenzylphosphole	Cl^-	[47]
$P(OPh)_3$	NO_3^-	[79]
$AsPh_3$	Cl^-, Br^-, I^-	[80]
$AsPh_3$	BrO_3^-	[40]
$SbPh_3$	Cl^-, Br^-, I^-	[81]

the reconsideration of the structure as being an aggregate of two independent $[AgCl(PPh_3)_2]$ units [48]. The complexes $[AgX\{P(4\text{-}MeC_6H_4)_3\}_2]$, where X is halide or CN^-, are thought to exist as monomers, with trigonal geometries [49] in solution, as was inferred by NMR spectroscopy. The complexes $[AgX(PCy_3)_2]$ ($X = Cl^-$, Br^-, I^-) were structurally characterised as monomers [50]. Complexes with a L:Ag stoichiometry of 2:1, containing bulky phosphine ligands and non-coordinating anions, are thought to have linear two-coordinate structures. This has been confirmed for $[Ag\{P(2,4,6\text{-}Me_3C_6H_2)_3\}_2][PF_6]$ [51]. Spectral data and conductance measurements suggested that for $AgX{:}P^tBu_3$ (1:2) with $X = ClO_4^-$, BF_4^-, PF_6^- and NO_3^-, the complexes contained the linear $[P\text{–}Ag\text{–}P]^+$ cation [52].

Structures of nonlinear two-coordinate Ag(I) species have also been reported. Ionic $[Ag\{P(NMe_2)_3\}_2][BPh_4]$ has a P–Ag–P angle of 166.9° [53]. Support for the retention of a two-coordinate structure in solution was implied since the solid-state CP/MAS ^{31}P NMR data coincided with the solution $\delta(^{31}P)$ and $^1J(^{107}Ag\text{–}^{31}P)$ values. With halides, neutral complexes of type $[AgX\{P(NMe_2)_3\}_2]$ ($X = Cl^-$, I^-) are formed by addition of an eightfold excess of $P(NMe_2)_3$ to a suspension of AgX in ether. The complex $[Ag\{PPh_2(c\text{-}C_5H_9)\}_2][ClO_4]$ ($c\text{-}C_5H_9$ = cyclopentyl) contains two crystallographically independent formula units with P–Ag–P angles of 145.1° and 153° [54]. The ionic interactions between the perchlorate groups and the cations are primarily responsible for this non-linearity. These bent species have been viewed as precursors of three-coordinate complexes with the prerequisite that the organic groups of the ligands mesh properly when coordinated [54]. This latter structure is exceptional since $[ML_3]X$ (M = Cu, Ag; $X = ClO_4^-$, BF_4^-) complexes are also formed by the larger homologous ligands containing cyclohexyl or cycloheptyl groups [54]. Nevertheless, $PPhCy_2$ always forms $[ML_2]^+$ complexes and only in exceptional cases $[ML_3]^+$ species [54]. Verification was accomplished by the preparation of 12 complexes of general formula $[M(ZR_2R')_2]X$ (M = Cu, Ag, Au; $X = BF_3^-$, ClO_4^-; Z = P, As; R′ = Ph, R = $c\text{-}C_5H_9$, Cy), a pervasive non-linear ML_2 geometry being inferred from structural data [54] (Table 2).

2.3. Complexes with 1:3 AgX:L stoichiometry

Three-coordinate complexes of type $[Ag(PR_3)_3]^+$ are rare. The coordination number of three in the cation seems to be observed only when steric factors militate against the coordination of two or four ligands. Given that two-coordinate $[M(PCy_3)_2]^+$ (Tolman cone angle = 170° [82]) and $[M(PPhR_2)_2]^+$ (R = $c\text{-}C_5H_9$, Cy) and $[M(PPh_3)_4]^+$ (Tolman cone angle = 145° [82]) are preferred, mixing the $PPhR_2$ (R = $c\text{-}C_5H_9$, Cy) and PPh_3 ligands produced steric requirements that favoured tricoordinate Ag(I) and Au(I) complexes. Thus, by utilising cycloalkyldiphenylphosphines, a series of 18 salts of formula $[M(PPh_2R)_3]X$ (M = Ag, Au; $X = BF_4^-$, ClO_4^-; R = $c\text{-}C_5H_9$, Cy, $c\text{-}C_7H_{13}$) were isolated and characterised [83]. Forty-nine complexes of the type $[M\{ZPh_m(4\text{-}YC_6H_4)_{3-m}\}_n]X$ (M = Cu, Ag; $X = BF_4^-$, ClO_4^-; Z = P, As, Sb; Y = Cl, F, Me, OMe; $n = 3$, 4; $m = 0$–2) were prepared and characterised with the intent of demonstrating the effect of the electronic properties of the ligands on the cation stoichiometry [84]. The behaviour of ligands containing electron withdrawing aryl groups (Y = F, Cl) was the converse of that seen for the electron-rich ligands (Y = Me, OMe). The electron-poor ligands commonly formed $[MXL_3]$ acido complexes with the IR spectra indicative of coordinated anions. The tendency of these electron-poor ligands to efficiently accept π-electrons from the metal, thereby reducing the electron density on the silver(I) centre, favours the formation of acido complexes. The electron-rich ligands formed $[AgL_3][X]$ type complexes only in a few instances—notably with $PPh_2(4\text{-}MeC_6H_4)$ and $PPh(4\text{-}MeC_6H_4)_2$. It is believed that the reason these three-coordinate cations are formed is due to the electron donating properties of the *para*-substituent being transmitted to the Group 15 atom, thus inhibiting its ability to act as a π-acceptor from the metal. This in turn increases the electron density on the metal and renders it incapable of accepting the lone pair from a fourth Group 15 ligand. Evidence for this virtual lack of π-bonding is seen between copper and tri-*para*-anisylphosphine, where the observed Cu–P bond is marginally shorter than the calculated σ-bond value of 2.35 Å [85]. A series of complexes $[Ag\{P(4\text{-}MeC_6H_4)_3\}_3]X$ with a variety of weakly coordinating counter anions has been isolated [49]. However, these generally undergo extensive disproportionation in solution, even at low temperatures, according to Scheme 4.

Complexes of the type $[AgX\{P(4\text{-}MeC_6H_4)_3\}_3]$ (where X is halide or pseudohalide) were assumed to have tetrahedral stereochemistry, and these did not disproportionate in solution (Table 3).

2.4. Complexes with 1:4 AgX:L stoichiometry

Tetrakisphosphine complexes have been isolated with non-coordinating anions e.g. $[Ag(PPh_3)_4]X$, where X is ClO_4^-, BrO_3^- and NO_3^- [101]. Crystallographic structural authentication has been undertaken for $[Ag(PPh_3)_4]X$ ($X = ClO_4^-$ [102] and NO_3^- [103]). To exemplify the subtle influences of steric and electronic factors on the silver(I) complexes once again, the attempted isolation of $[Ag(PCy_3)_4]NO_3$ has been unsuccessful, the bis-phosphine complex only being isolated [104].

Electron-rich ligands of the type $P(4\text{-}YC_6H_4)_3$ where Y is an electron donor, such as methyl or methoxy, most commonly formed $[AgL_4][X]$ type complexes where X is ClO_4^- or BF_4^- [84]. This was attributed to the large volume occupied by the $5sp^3$ orbital on silver, enabling it to accommodate the lone pair from a fourth tertiary phosphine ligand. Attempts to isolate complexes with [Ag]:[L] = 1:4 stoichiometry with a halide have been problematic owing to their instabilities. Isolation of $[Ag(PMe_3)_4]Cl$ was accomplished, but the complex decomposed [105]. The halide anion generally binds with the

$$2\,[Ag(PR_3)_3]X \rightleftharpoons [Ag(PR_3)_4]X + [Ag(PR_3)_2]X \ (\text{or } [Ag(PR_3)_2X])$$

Scheme 4. Disproportionation of $[Ag(PR_3)_3]^+$ complexes.

Table 3
Structures of silver complexes with a 1:3 AgX:L stoichiometry (all are mononuclear)

Ligand L	Anion X	References
[AgXL$_3$] compounds		
PPh$_3$	Cl$^-$	[86,87]
PPh$_3$	Br$^-$	[87]
PPh$_3$	I$^-$	[87–89]
PPh$_3$	BF$_4$$^-$	[88]
PPh$_3$	$^-$O$_2$CCF$_2$CF$_3$	[34]
PPh$_3$	SCN$^-$	[90]
P(4-MeC$_6$H$_4$)$_3$	I$^-$	[91]
P(4-FC$_6$H$_4$)$_3$	PF$_6$$^-$, ClO$_4$$^-$	[29]
AsPh$_3$	Cl$^-$	[92,93]
AsPh$_3$	Br$^-$, I$^-$	[93]
AsPh$_3$	CH$_3$CO$_2$$^-$	[94]
AsPh$_3$	4-MeC$_6$H$_4$SO$_3$$^-$	[95]
SbPh$_3$	Cl$^-$, I$^-$	[96]
P-PPh$_2$(CH$_2$)$_2$AsPh$_2$	Cl$^-$, Br$^-$	[97]
[AgL$_3$]X compounds		
PPh$_3$	NO$_3$$^-$	[98,103]
PPh$_2$(2-NH$_2$C$_6$H$_4$)	NO$_3$$^-$	[99]
PPh$_2$(c-C$_5$H$_9$)	BF$_4$$^-$	[83]
P(4-FC$_6$H$_4$)$_3$	CF$_3$SO$_3$$^-$	[29]
PPh$_2$CH$_2$CpFeCp	CF$_3$SO$_3$$^-$	[100]

Table 4
Structures of silver complexes with a 1:4 AgX:L stoichiometry

Ligand L	Anion X	References
[L$_4$Ag]X complexes		
PPh$_3$	ClO$_4$$^-$	[102]
PPh$_3$	NO$_3$$^-$	[103]
PPh$_3$	PF$_6$$^-$	[107]
PPh$_3$	[Me$_2$Sn(OCOCF$_3$)$_2$O,O′-(OCOCF$_3$)$_2$]$^-$	[108]
PPh$_3$	[Ph$_2$SnCl(O$_2$NO)$_2$]$^-$	[109]
PPh$_3$	BPh$_4$$^-$	[110]
PPh$_3$	Mo$_6$O$_{19}$$^-$	[111]
PPh$_3$	SiF$_6$$^-$	[112]
PPh$_3$	PhNNC(CN)$_2$$^-$	[113]
PPh$_3$	Ph$_3$Sn(OCOCF$_3$)$_2$$^-$	[114]
PPh$_2$(2-py)	ClO$_4$$^-$	[115,116]
P(4-FC$_6$H$_4$)$_3$	PF$_6$$^-$	[29]
P(4-MeC$_6$H$_4$)$_3$	PF$_6$$^-$	[117]
P(OCH$_2$)$_3$CCH$_3$	ClO$_4$$^-$	[118]
P[OC(^{t}Bu)CH]$_2$N	SbF$_6$$^-$	[119]
AsPh$_3$	BF$_4$$^-$	[120]
AsPh$_3$	NO$_3$$^-$, ClO$_4$$^-$	[112]
AsPh$_3$	BrO$_3$$^-$	[40]
AsPh$_3$	PF$_6$$^-$	[121]
AsPh$_3$	[Ph$_2$Sn(NO$_3$)$_3$]$^-$, [Ph$_2$SnCl(NO$_3$)$_2$]$^-$	[122]
AsPh$_3$	[Ph$_2$SnOH(NO$_3$)$_2$]$^-$	[123]
SbPh$_3$	ClO$_4$$^-$, NO$_3$$^-$	[112]
SbPh$_3$	BF$_4$$^-$	[124]
SbPh$_3$	BrO$_3$$^-$	[40]

exclusion of a phosphine group to yield [AgX(PR$_3$)$_3$] type complexes [49]. Nonetheless, owing to the small size and basicity of P(c-NCH$_2$CH$_2$)$_3$, (c = cyclo), complexes of type [Ag{P(c-NCH$_2$CH$_2$)$_3$}$_4$]X, where X = Cl$^-$ or I$^-$ have been isolated, wherein the anion is displaced from the inner sphere [53]. No ligand dissociation is observed for the chloride complex at −95 °C by ^{31}P NMR spectroscopy. However, for the corresponding iodide complex, the equilibrium corresponding to the displacement of the tertiary phosphine by halide was observed (Scheme 5).

Efforts to study the solution behaviour of [AgXL$_n$] complexes were initiated by Muetterties and Alegranti [49]. A series of [AgX{P(4-MeC$_6$H$_4$)$_3$}$_n$] complexes, where n = 2–4 and X included a wide range of counter-anions, was studied by ^{31}P NMR spectroscopy. The ligands were labile in all the complexes studied, so that the first-order P–Ag coupling was not resolved above ca. −70 °C. Rapid ligand exchange reactions have been reported for all ^{31}P NMR investigations of ionic Ag(I) monodentate phosphine complexes, except for the complexes [Ag{P(2,4,6-Me$_3$C$_6$H$_2$)$_3$}$_2$]$^+$ and [Ag(P^{t}Bu$_3$)$_2$]$^+$. These ligands are thought to be too sterically encumbered to participate in the associative process believed to be involved in the exchange [52,106]. Well-resolved first-order P–Ag spin–spin coupling is exhibited by these complexes at ambient temperature (Table 4).

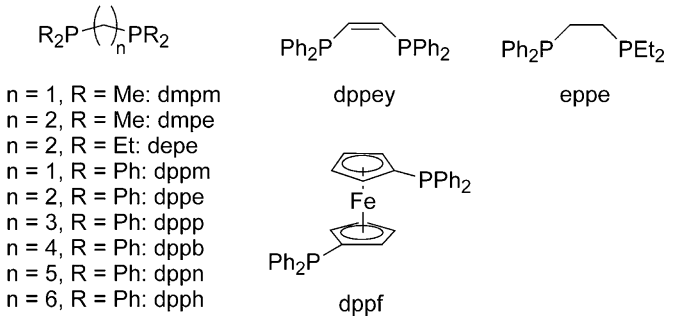
3. Silver(I) complexes of bidentate phosphines

The versatile diphosphine ligands ‘dppx’ are particularly appropriate for the synthesis of low-valent metal complexes. Bis(diphenylphosphino)methane (dppm) and 1,2-bis(diphenylphosphino)ethane (dppe) are widely used in inorganic chemistry, dppm affording dinuclear metal complexes in the μ-dppm form, while dppe affords both chelate and bridged complexes. Complexes containing the M$_2$(dppm)$_2$ structural unit have been intensively investigated. Although a key feature of the chemistry of this class of complexes is the relatively stable and quasi-planar M$_2$P$_4$ framework where two metal atoms are connected by a pair of bridging dppm ligands, it is well known that a variety of structural possibilities can occur when low-valent metals are bonded to a bidentate phosphine and a labile ligand such as nitrate or carboxylate.

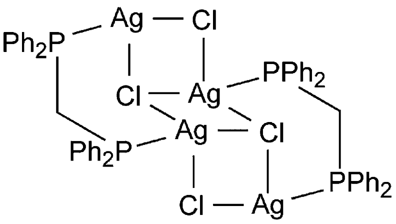
The interaction between bidentate diphosphines R$_2$P(R′)$_n$PR$_2$ and silver salts has attracted a great deal of interest because the resultant complexes have applications in homogeneous catalysis [125] and also as antitumour compounds [126,127]. For example silver(I) carboxylate-(S)Binap (S-Binap = (S)-(−)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) complexes have been reported as highly efficient catalysts for the Mukaiyama aldol reaction using silyl enol ethers or ketene silyl acetals as nucleophiles [128], this kind of catalyst strongly activating nucleophiles to undergo the aldol reaction. Catalytic asymmetric allylation of aldehydes using a chiral silver(I) complex has also been reported [129].

The interplay of parameters such as the geometrical flexibility of Ag(I), bite angle, electronic properties of the phosphine and the coordination mode of the supporting ligands often

Scheme 5. Displacement of a phosphine ligand by a halide in [Ag{P(c-NCH$_2$CH$_2$)$_3$}$_4$]I.



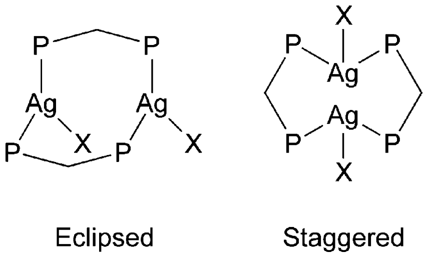
Scheme 6. Structures and abbreviations for diphosphine ligands.



Scheme 7. Tetranuclear structure of $[Ag_4Cl_4(dppm)_2]$.

renders predictions concerning the structural properties of silver–diphosphino complexes difficult [126], both in solution and in the solid state [130]. To date little systematic work has been reported on the interaction between silver salts and diphosphines characterised by different spacers (R′) or substituents R. The purpose of the discussion below is to give an overview of the effect of R and R′ on the coordination mode of the bisphosphine and on the coordination environment of silver(I) (Scheme 6).

Potentiometric measurements and ^{31}P NMR characterisation during titrations involving the addition of the ligands dppm, dppe or dppp to a known concentration of Ag(I) salt have confirmed the prevalent formation of polynuclear complexes when metal to ligand ratios are large [131,132]. $[Ag_2L^2]^{2+}$ forms were common to all the systems studied. Complexes with 2:1 Ag:L^2 stoichiometries include the carboxylate complexes $[Ag_2(O_2CR)_2(dppm)]$ (R = Me [133], Et, ^{i}Pr or Ph [134]), for which the slow-exchange limit ^{31}P NMR spectra were obtained at ca. 223 K in dichloromethane or chloroform solutions. The dppm ligand bridges the two silver atoms and the two carboxylate ligands are also thought to bridge the silver atoms. The compound $[Ag_4Cl_4(dppm)_2]$ (Scheme 7) was the bidentate equivalent of step-tetramer **2**, with the dppm moieties bridging two silver atoms [42,43]. Subsequently, the molecular structure of the related bromine step tetramer has been reported [43].



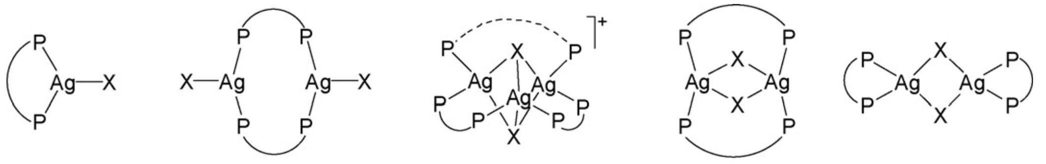
Scheme 9. Eclipsed and staggered structures of dinuclear silver(I) complexes of Type **6** with dppm [142].

Complexes with equimolar Ag:L^2 stoichiometry display a range of structural types (Scheme 8, Table 5), with coordination geometry also depending on the length of the chain between the two donor atoms. Mononuclear complexes of Type **5** (Scheme 8) have been obtained for the ligands 2,11-bis(di-*R*-phosphinomethyl)benzo(*c*)phenanthrene (R = Ph, X = Cl, $SnCl_3$ [135]; R = ^{t}Bu, X = Cl, Br, ClO_4 [136], Et [137]), 3,3′-oxybis[(diphenylphosphino)methyl]benzene [138], bis(diphenylphosphanyl)-*O*-carborane [139] and *R*-$[(4\text{-}MeC_6H_4)_2P(C_{10}H_6)_2]_2$ [(*R*)-Tol-Binap] [140].

Complexes of Type **5** incorporating the ligands dppe or dppp were also inferred as minor species from potentiometric, and calorimetric measurements [131,132]. There was no evidence for the formation of mononuclear species of Ag(I) with dppm [131,132], owing to the presence of only one methylene group between the two donor atoms, whereby the formation of mononuclear species would give rise to a highly strained four-membered chelate ring. This constraint, imposed by the ligand, favours the formation of dinuclear species of Type **6** (Scheme 8). Type **6** structures were also inferred from ^{31}P NMR data for dppe and dppp in DMSO [131] and propylene carbonate [132] and have been structurally characterised for dppp, for the anions Br^-, I^-, $ClO_4{}^-$, $F_3CCO_2{}^-$ and $F_3CSO_3{}^-$ [141].

The reaction of $AgNO_3$ with an equimolar quantity of dppm in methanol afforded the complex $[Ag_2(NO_3)_2(dppm)_2]$ [142]. In this instance, the stable, intrinsic $Ag_2(dppm)_2$ framework as in Type **6** was retained, although, the more unusual eclipsed (or *syn*) geometry was adopted (Scheme 9). Eclipsed geometries have also been reported for the $AgNO_3$ complexes of dppp [143] and dppb [144] of Type **6**.

The di-chloroform solvate of $[Ag_2(NO_3)_2(dppm)_2]$ has been crystallographically characterised and adopts the more usual staggered conformation (Scheme 9) [145]. Metathesis with excess $K[PF_6]$ in methanol of the eclipsed form led to the tetranuclear complex $[Ag_4(NO_3)_2(dppm)_4][PF_6]_2$ [142]. This complex



5 6 7 8 9

Scheme 8. General structures of silver halide complexes with equimolar Ag:L^2 stoichiometry: mononuclear (Type **5**), dinuclear (Type **6**), trimer (Type **7**) and dimers (Type **8** and Type **9**).

Table 5
Structures of AgX:L^2 (1:1) (and related species with other metals)

Ligand	Anion X	References
$[AgX(L^2)]$ mononuclear Type **5**; ((L^2) = bidentate ligand)		
$P(2\text{-}Me_2NCH_2C_6H_4)_3$	Br^-	[157]
3,3′-Oxy-bis(diphenylphosphino)methylbenzene)	Cl^-	[138]
2,11-Bis(diethylphosphinomethyl)benzo(*c*) phenanthrene	ClO_4^-	[137]
2,11-Bis(di-*tert*-butylphosphinomethyl) benzo(*c*)phenanthrene	Cl^-, Br^-, ClO_4^-	[136]
2,11-Bis(diphenylphosphinomethyl) benzo(*c*)phenanthrene	Cl^-, ClO_4^-, $SnCl_3^-$	[135]
2,11-Bis(diphenylphosphinomethyl) benzo(*c*)phenanthrene (dimer)	$\mu_2{-}F^- + BF_4^-$	[158]
R-$[(4\text{-}MeC_6H_4)_2P(C_{10}H_6)_2]_2$	NO_2^-	[140]
2,2′-Bis(diphenylphosphino)-1,1′-biphenyl	$CF_3CO_2^-$	[159]
S-2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl	$CH_3CO_2^-$	[160]
Bi- and trimetallic:		
$(PhCC)_2Pt(Ph_2PCH_2PPh_2)_2$	I^-	[161]
[*trans*-$MeClPt(Ph_2PCH_2PPh_2)_2$]	Cl^-	[162]
[*trans*-$Cl(CO)Rh(PPh_2CH_2)_2AsPh]_2$	Cl^-	[163]
[*trans*-$Cl(CO)Ir(PPh_2CH_2)_2AsPh]_2$	Cl^-	[164]
$[Ag(L^2)]X$ (mononuclear)		
$PPh_2(CH_2CH_2O)_2CH_2CH_2PPh_2$	BF_4^-	[165]
$PPh_2(CH_2CH_2O)_2CH_2CH_2PPh_2$	ClO_4^-, $F_3CSO_3^-$	[166]
9,10-Bis(2-(diphenylphosphino)ethyl)anthracene	ClO_4^-	[167]
9,10-Bis(*N*-diphenylphosphino)propylaminomethyl) anthracene	ClO_4^-	[168]
$[Ag(L^2)]_2X_2$ (dinuclear)		
Dmpm	PF_6^-	[169]
Dppm	ClO_4^-	[146,170,171]
Dppp	BF_4^-	[172,173]
Dppb	BF_4^-	[174]
$PPh_2NMePPh_2$	BF_4^-	[175]
$Cy_2PCH_2PCy_2$	PF_6^-, $F_3CSO_3^-$	[176]
$^tBuP(CH_2)_3P^tBu$	BF_4^-	[177]
$[AgX(L^2)]_2$ dinuclear Type **6**		
Dppm	ClO_4^-, $F_3CCO_2^-$, $F_3CSO_3^-$	[146]
Dppm	NO_2^-	[140]
Dppm	NO_3^-	[142,145]
Dppm	$H_3CCO_2^-$	[178]
Dppe	$Ph_2PS_2^-$	[179]
Dppp	Br^-, I^-, ClO_4^-, $F_3CCO_2^-$, $F_3CSO_3^-$	[141]
Dppp	NO_2^-	[140]
Dppp	NO_3^-	[143]
Dppb	NO_3^-	[144]
Dppf	$MeCO_2^-$	[147]
Dppf	NO_3^-	[180]
$Ph_2AsCH_2AsPh_2$	ClO_4^-, $F_3CCO_2^-$, $F_3CSO_3^-$	[146]
$[Ag_3X_2(L^2)_3]X'$ trinuclear Type **7**		
Dppm	Cl^-, $X' = Cl^-$	[151]
Dppm	Cl^-, $X' = SbF_6^-$	[181]
Dppm	Cl^-, $X' = [SnClPh_2(NO_3)_2]^-$	[150]
Dppm	Br^-, $X' = Br^-$	[149,151]
Dppm	I^-, $X' = I^-$	[151,182]
Dppm	CNO^-, $X' = CNO^-$	[151]
$Ph_2AsCH_2AsPh_2$	Cl^-, $X' = Cl^-$	[151]
$[AgX(L^2)]_2$ dinuclear Type **8**		
Dppp	ClO_4^-, $MeCO_2^-$	[141]
Dppb	Br^-, I^-, CN^-, ClO_4^-, NO_3^-, $F_3CCO_2^-$	[141]
Dppn	Cl^-	[152]
Dppn	Br^-, I^-	[141]
Dpph	Br^-, I^-, NCO^-, NCS^-, NO_3^-	[141]
Dpph	ClO_4^-	[183]
Dppf	Cl^-	[147,184]
Dppf	$F_3CCO_2^-$	[185]
Dppf	Br^-, I^-, CNO^-, CN^-, NO_3^-	[147]

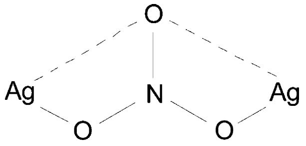
Table 5 (*Continued*)

Ligand	Anion X	References
Bis(2-diphenylphosphinoethyl)sulfide	Cl^-, Br^-	[154]
Bis(2-diphenylphosphinoethyl)sulfide	I^-	[153]
1,3-Bis(diphenylphosphinomethyl)benzene	Cl^-, I^-, $NO_3{}^-$	[155]
$PPh_2CH_2CHEtOPPh_2$	$ClO_4{}^-$	[186]
4*R*,5*R*-*trans*-4,5-bis(diphenylphosphino methyl)-2-dimethyl-1,3-dioxolane	Cl^-, Br^-, I^-	[187]
$[AgX(L^2)]_2$ dinuclear Type **9**		
Dppf	SCN^-	[147]
P^tBu_2(Se-2-py)	Br^-	[188]
1,2-Bis(diphenylphosphinomethyl)benzene	Cl^-, I^-	[155]
$[AgX(L^2)]_\infty$ polymers		
Dppe	$F_3CCO_2{}^-$	[189]
Dppe	$ClO_4{}^-$	[190]
Dppn	Cl^-, SCN^-, NCO^-, $MeCO_2{}^-$	[141]
Dppf	$F_3CSO_3{}^-$	[191]
Dppf	$F_3CCO_2{}^-$	[147]
$Ph_2AsCH_2AsPh_2$	Cl^-, Br^-, I^-, CN^-, SCN^-	[156]
$Ph_2As(CH_2)_2AsPh_2$	Br^-, SCN^-, NCO^-	[156]

consists of two $[Ag_2(dppm)_2]^{2+}$ subunits in the eclipsed conformation bound together by two bridging nitrate anions, in an *anti-anti* bridge-bonding mode (Scheme 10). Reaction of $Ph_2AsCH_2AsPh_2$ with various Ag(I) oxyanions also produced several structures with the basic $Ag_2(Ph_2AsCH_2AsPh_2)_2$ framework of Type **6**. Recently a large number of these structures has been reported [146]. In the same series of papers, the reaction of dppf [1,1′-bis(diphenylphosphino)ferrocene] with various Ag(I) salts was described, resulting in several structures of Type **6**, as well as some structures of Types **8** and **9** (Scheme 8) (see below) [147].

Reaction of equimolar quantities of AgBr and dmpm [bis(dimethylphosphino)methane] in benzene produced an infinite polymeric chain, containing adjacent eight-membered $Ag_2(dmpm)_2$ core components, linked by pairs of bromide anions [148]. A further structural type is found in the trinuclear cations $[Ag_3Br_2(dppm)_3]^+$ [149] and $[Ag_3Cl_2(dppm)_3]^+$ [150] in which each edge of a triangle of Ag atoms is bridged by a dppm ligand; the two coordinated halide atoms each cap a triangular face leading to a coordination polyhedron based on a trigonal bipyramid (Type **7**, Scheme 8). This structure is possibly the most common structure of 1:1 Ag:L^2 stoichiometry, and further examples of compounds containing this structural type have been characterised [151].

Bidentate ligands such as 1,5-bis(diphenylphosphino)-pentane [152], bis[(diphenylphosphino)ethyl]sulfide [153,154] and 1,3-bis[(diphenylphosphino)methyl]benzene [155], containing five atoms between the phosphorus donors, form dimeric complexes of Type **8** (Scheme 8) when reacted with equimolar quantities of silver(I) halide. In these complexes the ligand acts as a bidentate bridging ligand, with the two phosphorus atoms coordinating to different silver atoms.

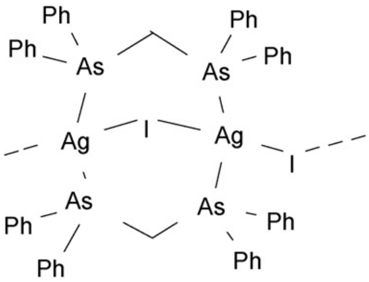


Scheme 10. The *anti–anti*-bonding mode of Ag–O–NO–O–Ag.

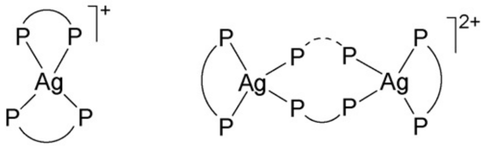
A different structural type with 1:1 Ag:L^2 stoichiometry was crystallographically elucidated [155] for the ligand 1,2-bis[(diphenylphosphino)methyl]benzene, which behaves in a chelating fashion to produce dimeric silver halide complexes of Type **9** (Scheme 8).

Finally, a further class of compounds with a 1:1 ratio of Ag to bidentate ligand is a reported series of polymeric structures with $Ph_2AsCH_2AsPh_2$ as the bidentate ligand [156]. In these complexes, the ligand bridges two silver atoms as in the Type **8** structure (Scheme 8), but instead of two bridging halides (X = Cl^-, Br^-, I^-), only one of the halides is used to bridge the two silver atoms, whereas the other halide is used to bridge towards another 'unit' forming a polymeric structure (Scheme 11).

Complexes containing bidentate phosphines in 3:2 L^2:Ag stoichiometry were, until recently, 'unusual'. A complex of composition $Ag_2(L^2)_3$, where L^2 = dppm, was inferred at high ligand to metal ratios to account for potentiometric and calorimetric measurements obtained in DMSO [131] or propylene carbonate [132] as solvent. This compound was structurally characterised for X = $NO_3{}^-$ [192] and inferred for X = $NO_2{}^-$ based on spectroscopic data [140]. The $Ag_2(L^2)_3$ core was also structurally characterised for L^2 = pmpm [193] as well as for

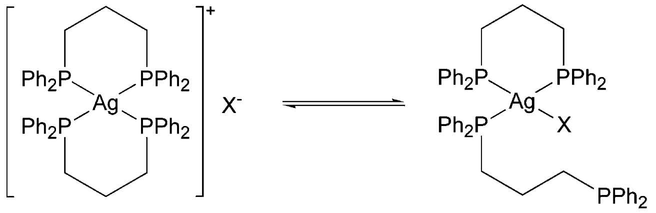


Scheme 11. Polymeric structure of AgI with $PPh_2AsCH_2AsPh_2$ [156].



10 **11**

Scheme 12. General structure of silver(I) diphosphine complexes with 2:1 L^2:Ag stoichiometry: bis-chelated monuclear (Type **10**), dimeric (Type **11**).



Scheme 13. Equilibrium between the ionic ring closed form and neutral ring opened form of $[Ag(dppp)_2]X$ complexes.

$L^2 = PPh_2NPPh_2$ [194]. In addition a different structural type for the 3:2 L^2:Ag stoichiometry was described for the long chain phosphine $PPh_2(CH_2CH_2O)_2CH_2CH_2PPh_2$ [166], two AgL^2 units being linked by the third phosphine. A similar structure was described for L^2 = dppf and silver formate as early as 1992 [180] and for $AgPF_6$ in 1994 [195]. Recently, a large number of structures with 3:2 L^2:Ag stoichiometry have been reported [97].

Complexes of the type $[Ag(L^2)_2]$ with a 2:1 L^2:Ag stoichiometry are also uncommon and exist in two forms (Scheme 12, Table 6). In the mononuclear complexes (Type **10**, Scheme 12), the metal is bis-chelated by two bidentate phosphines to form a four-coordinate tetrahedral silver environment. The rigid bidentate ligand 1,2-$(PEt_2)_2C_6H_4$ is assumed to form a bis-bidentate complex $[Ag(L^2)_2]I$ [196]. The bis-chelated complex $[Ag(dppe)_2][SO_3CH_3]$, prepared from $AgSO_3CH_3$ has also been reported [197], although neither of these studies confirmed the existence of chelated four-coordinated complexes in solution. The first substantiated evidence for the existence of stable bis-chelated complexes of the type $[Ag(L^2)_2]NO_3$ in solution, where L^2 is $Ph_2PCH_2CH_2PPh_2$ (dppe), $Et_2PCH_2CH_2PPh_2$ (eppe), $Et_2PCH_2CH_2PEt_2$ (depe), $Ph_2PCH{=}CHPPh_2$ (dppey) and $Ph_2P(CH_2)_3PPh_2$ (dppp) was accomplished by the application of $^{109}Ag\{^{31}P\}$ INEPT pulse sequences [198]. A tetrahedral AgP_4 core for $[Ag\{Ph_2PCH{=}CHPPh_2\}_2]^+$ in solution was confirmed by ^{109}Ag NMR spectral data, obtained by using a retro-INEPT 2D $^{31}P\{^{109}Ag\}$ pulse sequence [199]. The structures of $[Ag(dppe)_2]NO_3$ and $[Ag(dppey)_2][SnPh_2(NO_3)_2]$ have been confirmed crystallographically [200,201], with the former exhibiting distortions from the ideal tetrahedral geometry owing to the restricted bite distances of the dppe ligands. Whereas dppp forms the bis-chelated $[Ag(dppp)_2]^+$ cation with the non-halide anions NO_3^- and SCN^- [198,202] (in solution and the solid-state), crystallisation of silver(I) halide/pseudo halide:dppp mixtures in a 1:2 stoichiometry from acetonitrile, afforded a novel series of neutral complexes, [AgX(dppp-P,P′)(dppp-P′)] ($X = Cl^-, Br^-, I^-$ or CN^-) containing coordinated anion as well as uni- and bidentate dppp ligands [202]. These complexes were crystallographically characterised in the solid-state and were shown to be isostructural, consistent solid-state ^{31}P NMR data, with the value of $^1J(^{109}Ag–^{31}P)$ decreasing with an increase in donor capacity of the anion. Solution ^{31}P NMR studies indicated that an equilibrium existed between the ionic ring closed form and neutral ring opened form. The proportion of the neutral complex was shown to increase with increasing donor capacity of the anion (Scheme 13).

These complexes, with five- and six-membered chelate rings, exhibit remarkably enhanced kinetic and thermodynamic stability when compared to similar Ag(I) complexes of monodentate phosphines. The rate of Ag–P bond rupture (determined by ^{31}P NMR) in $[Ag\{P(4\text{-}MeC_6H_4)_3\}_4]^+$, for example, has been reported to be >2000 s^{-1} at 40 °C [49], whereas in bis-chelated four coordinate complexes, the rates are ca. 220 s^{-1} [198]. Furthermore, the enthalpies and entropies of formation of the

Table 6
Structures of 1:2 AgX:L^2 complexes (where L^2 is a bidentate ligand)

Ligand	Anion X	References
$[AgX(L^2)_2]$ mononuclear		
Dppp	Cl^-, Br^-, I^-, CN^-	[202]
$[Ag(L^2)_2]X$ mononuclear (Type **10**)		
Dppe	$SnPh_3(O_2CCF_3)_2^-$	[205]
Dppp	$SnPh_2(O_2CCF_3)_2(c{-}C_5H_9)^-$, $SnPh_3(O_2CCF_3)_2^-$	[206]
Dppf	$CF_3SO_3^-$	[191]
Dppf	BF_4^-	[207]
Dppf	ClO_4^-	[208]
1,2-$(PPh_2CH_2)_2C_6H_4$	BF_4^-	[209]
1,2-$(PPh_2C{\equiv}C)_2C_6H_4$	PF_6^-	[210]
2,2′-Bis(diphenylphosphino)-1,1′-biphenyl	SO_4^-	[159]
P,P′-$CH_3C(CH_2PPh_2)_3$	BF_4^-	[211]
$[(L^2)Ag(L^2)]_2X_2$ dinuclear (Type **11**)		
Dmpe	BPh_4^-	[203]
Dppe	NO_3^-	[204]
d2pype	NO_3^-	[9]

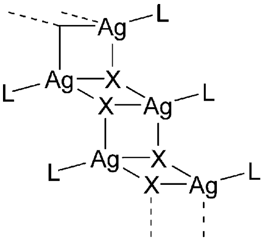
five- and six-membered chelates formed by dppe and dppp respectively, are more exothermic and more negative than the corresponding ΔH° and ΔS° of silver(I) complexes with the unidentate triphenylphosphine ligand [131,132,198]. An increase in stability is also seen for the dppp–silver(I) complex compared to its dppe [131,132,198] counterpart. This has been attributed to some strain within the five-membered chelate ring, formed by dppe, as compared with the six-membered ring formed by dppp as well as the higher basicity of dppp. Mixed four-coordinated silver(I) phosphine complexes containing the ligand bis(diphenylphosphanyl)-*o*-carborane were prepared from three-coordinate $[AgX\{(PPh_2)_2C_2B_{10}H_{10}\}]$ ($X = ClO_4^-$, NO_2^-) [139]. The perchlorate anion is weakly bound to the silver atom and can be displaced by other bidentate (and monodentate) ligands (L^2) to afford cationic four-coordinated $[Ag(L^2)\{(PPh_2)_2C_2B_{10}H_{10}\}][ClO_4]$. The homoleptic complex, where L^2 is $(PPh_2)_2C_2B_{10}H_{10}$, is also obtainable from the reaction of 2 equiv. of L^2 with $AgClO_4$ [139].

A second structural type for complexes with a 2:1 L^2:Ag stoichiometry, (Type **11**, Scheme 12) contains both bridging and chelating modes for the diphosphine ligands in dimeric complexes containing distorted tetrahedral AgP_4 moieties. Crystals of the complex $[Ag_2(dmpe)_4][BPh_4]_2$ [203] were obtained from the interaction of AgO_3SCF_3 with two equivalents of dmpe and sodium tetraphenylborate in acetonitrile. The crystal structure contains dimeric $[Ag(dmpe)_2]_2^{2+}$ cations and BPh_4 anions, with each silver coordinated by two phosphorus atoms from a chelating dmpe ligand and by one phosphorus from each of the two bridging dmpe ligands. This structural type has also been reported for $[Ag(dppe)_2]_2[NO_3]_2$ [204] and the methanol solvate is isomorphous with the analogous complex of 1,2-bis(di-2-pyridylphosphino)ethane (d2pype) [9] (see Section 6).

4. Silver $(AgX)L_n$ complexes (X = halide, L = unidentate nitrogen base)

Recrystallisation of silver(I) halides from neat nitrogen-containing bases produced crystalline products mostly of 1:1 silver(I) halide:nitrogen base stoichiometry. The species formed are often polymeric, being described as a series of AgX_4 tetrahedra which share either faces or edges. Variations in the steric profile of the base have led to a variety of structural types. In order of increasing profile these are: 'stair' polymer, 'cube' 'split-stair' polymer, dimer and monomer [212]. Other structural types exist, such as the 'saddle' and 'tube' polymers but their positions in the steric profile are a matter of conjecture. Here we present merely an introduction to the rich solid-state chemistry of silver complexes with nitrogen donor bases.

In contrast to the 'softer' halide anions, the structures of silver(I) oxyanion (ClO_4^-, NO_3^-, $F_3CCO_2^-$) adducts appear to be mainly of the linear [N–Ag–N]X type [213]. Adducts of the form AgX:L (1:*n*) thus defined represent complexes of salts of silver(I) of 'harder' (BF_4^-, PF_6^-) versus 'softer' (Cl^-, Br^-, I^-) anions universally, correlating broadly with the statistics of lower versus higher coordination numbers about the metal, and with *n* rarely rising above two.



12

Scheme 14. General structure of 'stair' polymer **12** $[AgXL]_n$ with X = halide and L = pyridine derivative.

4.1. 'Stair' (or ribbon) structure

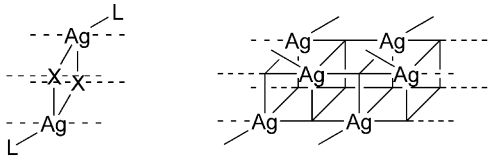
Whereas silver(I) chloride on recrystallisation from pyridine redeposits crystals of silver(I) chloride, the bromide and iodide yield 1:1 base adducts—both of which are 'stair' polymers (**12**, Scheme 14) [212]. 'Stair' polymers have also been assigned to the silver(I) halide complexes of 2,4,6-trimethylpyridine [212] and quinaldine [212] and the silver(I) iodide complexes of 2-methylpyridine [214], 3-methylpyridine [214] and quinoline [214]. Silver(I) bromide forms a 'stair' polymer with 4-methylpyridine [215]. In both the 'stair' polymer and the cubane tetramer, the metal atom is located in a tetrahedral 'hole' formed by the three halides and the ligand coordinating atom.

4.2. Cube structure

Silver(I) iodide forms cube tetramers (**1**, Scheme 1) with triethylamine [214], piperidine [212,216] (as well as silver(I) bromide) and 2,2,6,6-tetramethylpiperidine [212]. Disorders within the piperidine series has been attributed to hydrogen-bonding induced stacking, possibly precursive of the formation of the 'tube' polymer type [212]. Surprisingly, the more sterically demanding tetramethylpiperidine, which forms two-coordinate species with copper(I) [217], here gives the cube tetramer form [212].

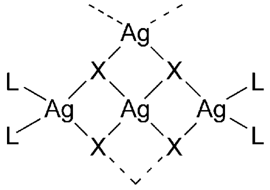
4.3. 'Tube' polymer

Recrystallisation of silver(I) halides with diethylamine produces a formulation of equimolar stoichiometry and a complete halide family of 'tube' polymers (**13**, Scheme 15) [212], a form previously only recorded for $[AgBr(3\text{-}MePy)]_n$ [215]. The tubular nature is generated by an infinite stacking of $Ag_2X_2L_2$ dimers, alternately longitudinally linked so as to make each metal site four-coordinate. Similarly, it may be considered as



13 **13**

Scheme 15. General structure of 'tube polymer' **13**—left, the dimer, and right, the structure of the polymer.



14

Scheme 16. General structure of ‘saddle’ polymer **14** $[AgX(quinoline)]_n$ with $X = Cl^-$ [218] or Br^- [74].

a stack of cubane units [212,215], and like so many of these forms, a solvated fragment of the rock-salt lattice.

4.4. ‘Saddle’ polymer

While quinoline forms a ‘stair’ structure with silver(I) iodide [214], $[AgCl(quinoline)]_\infty$ represented the only structurally characterised equimolar silver(I) chloride:nitrogen base adduct reported in the literature that forms what has been termed a ‘saddle’ polymer (**14**, Scheme 16), although cell dimensions of the bromide analogue indicated it to be isostructural [218]. The saddle effect is obtained by the fact that the repeating unit is not planar, but is curved, rather like a saddle, again, a fragmented, solvated rock-salt motif. A full report confirms the ‘saddle polymer’ form for the adduct of silver(I) bromide and quinoline [74].

Polymeric structures are also formed with pseudo-halides. For example, equimolar silver(I) thiocyanate-base (base = 2- or 3-methylpyridine) complexes are generated by recrystallisation of the silver(I)pseudo-halide from the base. The complexes are infinite 2D polymers with the silver atoms *pseudo*-tetrahedrally four coordinated by the sulfur and nitrogen atoms of the bridging thiocyanate groups and by the nitrogen atom of the base [219]. A 1D polymer containing silver which is coordinated by sulfur and nitrogen atoms of the bridging thiocyanate ligand and 2,6-dimethylpyridine as ligand, was formed when the steric bulk of the monosubstituted pyridine ligand was increased to a disubstituted analogue [219].

4.5. Other stoichiometries

Despite historical predictions, structurally authenticated examples of 1:2 silver(I) halide/pseudo-halide:nitrogen base stoichiometry are remarkably rare. These include $[AgBr(2\text{-}MePy)_2]_2$ [215] and $[Ag(SCN)(quinoline)_2]_n$ [219]. The former is a dimer with a four-coordinate metal atom environment, each metal being surrounded by two ligands and two bridging halides. The latter complex is a 1D polymer, with four-coordinate, pseudo-tetrahedral, silver atoms linked by S,N-bridging thiocyanate groups. The remaining two coordination sites of the silver are filled by quinoline nitrogen atoms in a form reminiscent of the ‘split stair’ polymer. A ‘castellated’ arrangement has been assigned to the product generated by the recrystallisation of silver(I) chloride with piperidine [220] (the surprising structure of $[AgCl(piperidine)_3]$ was reported recently [221]). The resulting polymer is also of a 1:2 AgCl:piperidine stoichiometry, with the asymmetric unit being an $[AgCl(piperidine)_2]$ unit. Ligand groups are alternatively on either side of the 1D Ag. . .Cl. . .Ag. . .Cl polymer string. Instead of halides/pseudo halides, the use of anions of less coordinating propensity such as perchlorate or nitrate can lead to complexes with higher ligand to metal ratios such as the near-linear two coordinate $[Ag(2,6\text{-}Me_2Py)_2][ClO_4]$ [222] and $[Ag(2,6\text{-}Me_2Py)_2][NO_3]$ [222] complexes, the tetrahedral $[Ag(Py)_4][ClO_4]$ [223] complex and the unusual ‘bis(pyridine)silver(I) perchlorate’ complex [224], which X-ray methods show to be of 2.4:1 pyridine:silver(I) perchlorate stoichiometry. The stoichiometry is consequent on the presence of two types of complex cations—$[Ag(Py)_2]^+$ and $[Ag(Py)_4]^+$. These complexes are ionic, having uncoordinated $[ClO_4]^-$ and $[NO_3]^-$ anions. In these $[AgL_n]^+$ complexes, n can be diminished by control of either the steric profile of the ligand or the stoichiometry.

5. Lewis-base adducts of silver(I) compounds containing phosphorus and nitrogen (pyridyl) donors

For silver, although the parent $[Ag(Py)_4]$ and $[AgL_4]$ (L = phosphine) arrays have been structurally characterised, there are only few accounts of mixed base species $[Ag(Py)_m(L)_{4-m}]^+$. Addition of two equivalents of triphenylphosphine to heated pyridine solutions of silver(I) chloride or bromide, produced crystals of $[AgX(Py)(PPh_3)_2]$, $X = Cl^-$ or Br^-, on standing [225]. The structures are isomorphous, with both being mononuclear, and trigonal planar. However, for $X = I^-$, despite the use of a considerable range of triphenylphosphine stoichiometric ratios, a mixed base complex beyond the equimolar complex $[AgI(Py)(PPh_3)]$ was unobtainable. Complexes of $[AgX(Py)_2(PPh_3)]$ stoichiometry are obtainable by the crystallisation of stoichiometric mixtures of silver(I) halides and triphenylphosphine from pyridine [225]. Although the resulting complexes are of overall 1:2:1 $AgX:Py:PPh_3$ stoichiometry, they consist of a 1:1:1 μ,μ'-dihalo-bridged dimer, $[\mu\text{-}XAg(Py)(PPh_3)_2]_2$, solvated with an additional mole of pyridine per silver atom. Thus, in pyridine solution the existence of monomeric $[AgX(Py)_2(PPh_3)]$ is postulated [226]. While the number of structurally characterised silver(I) halide complexes with mixed phosphorus and nitrogen-bases are few, complexes with non-coordinating anions are more extensively known. Oxidation of PPh_2H to diphosphine with the reduction of silver in pyridine, afforded $[(Py)_3AgPPh_2PPh_2Ag(Py)_3][ClO_4]_2$ [227]. The cation consists of two Ag(I) ions, each coordinated in a tetrahedral fashion to three pyridine molecules (via nitrogen) and one phosphorus atom. Each phosphorus atom is surrounded by a tetrahedron comprising a silver atom, the phosphorus atom, and two phenyl rings. The reaction of $[Ag(NO_3)(PPh_3)]$ with bis-imines in methanol and subsequent treatment with salts of the non-coordinating anions X (BF_4^- or PF_6^-) afforded $[Ag(PPh_3)(L)][X]$ where L = bipy, phen, or *trans*-1,2-bis(4-pyridyl)ethylene. Only the bipyridyl complex exhibits resolved ^{31}P NMR spectra $[^1J(^{109}Ag, ^{31}P) = 640\ Hz]$ at room temperature in acetonitrile. A dimeric complex $[Ag_2(PPh_3)_2(\mu\text{-}L)][NO_3]_2$ was also obtained with the *trans*-1,2-bis(4-pyridyl)ethylene lig-

Table 7
Mixed P, N (and S) base complexes

Ligand	Anion X	References
$[L^pL^nAg\text{-}\mu_2\text{-}X]_2$ structures; L^p = phosphine, L^n = nitrogen or sulfur donor		
PPh_3, Py	Cl^-, Br^-, I^-	[226]
PPh_3, 1-Me-im	$MeSO_3^-$	[104]
PPh_3, H-im	NO_2^-	[104]
PPh_3, S-pyrimidine-2-thione	Br^-	[230]
$P(4\text{-}MeC_6H_4)_3$, Py	I^-	[231]
PCy_2Ph, Py	I^-	[232]
PPh_3, 2-aminopyrimidine (polymeric)	Cl^-	[233]
PPh_3, 2-aminopyrimidine (polymeric)	Br^-	[234]
PPh_3, 4,4′-bipy (polymeric)	I^-	[235]
$[L^p_2L^nAgX]$ structures; L^p = phosphine, L^n = nitrogen or sulfur donor		
PPh_3, Py	Cl^-, Br^-	[225,244]
PPh_3, 2-Me-im	NO_3^-	[104]
PPh_3, *S*-pyridine-2-thione	Cl^-	[236]
PPh_3, *S*-ethanedithioamide	Cl^-	[237]
$[L^p_2L^n_2Ag]X$ structures; L^p = phosphine, L^n = nitrogen donor		
PPh_3, H-im	NO_3^-	[104]
PPh_3, 2-Me-im	NO_3^-	[104]
$[L^pL^n_3Ag]X$ structures; L^p = phosphine, L^n = nitrogen donor		
PPh_3, 2-Me-im	$CF_3CO_2^-$	[104]
$[L^p_3L^nAg]X$ structures; L^p = phosphine, L^n = nitrogen donor		
PPh_3, 4-Ph-im	NO_3^-	[104]

and [228]. Five-coordinate $[Ag(PPh_3)_2(terpy)][ClO_4]$ has been prepared by the reaction of terpyridine with $[Ag(PPh_3)_2][ClO_4]$. The metal atom is coordinated to the distal terpyridine pyridyl rings in axial sites. The coordination spheres are completed by the binding of the central pyridyl nitrogen atoms and two phosphorus atoms, which together define the equatorial planes. It was shown by ^1H and ^{13}C NMR spectroscopy that the five-coordinate nature is also retained in solution [229].

Reaction of $[Ag(NO_3)(PCy_3)_2]$ with excess 2-methylimidazole gave the four-coordinate $[Ag(NO_3)(PCy_3)(2\text{-Me-im})_2]$ and reaction with benzimidazole gave the four-coordinated $[Ag(PCy_3)_2(Bz\text{-im})_2]NO_3$. In contrast, the reaction of $[Ag(NO_3)(PCy_3)_2]$ with imidazole, 1-methylimidazole, 4-methylimidazole or 4-phenylimidazole did not give any products. In addition, the reaction of $[Ag(PPh_3)_4]NO_3$ with the above-mentioned imidazoles gave substitution of one or more PPh_3 groups (Table 7).

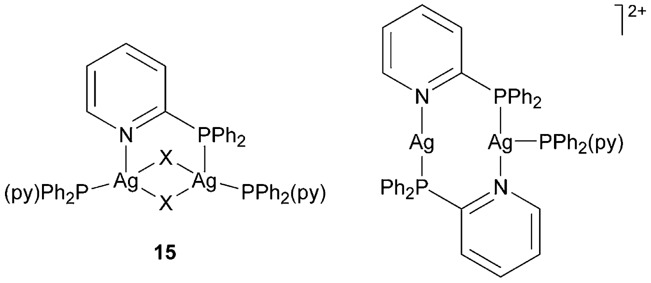
6. Silver(I) complexes of pyridylphosphines

With both a nitrogen donor atom and a phosphorus donor atom present in the same molecule, 2-pyridylphosphines are potentially bidentate chelating ligands. Until relatively recently, the only silver pyridylphosphine complexes that have been structurally authenticated have utilised the ligand diphenyl(2-pyridyl)phosphine. The formation of insoluble microcrystalline materials have precluded structural elucidation of silver(I) complexes of tris(2-pyridyl)phosphine [238,30]. However, these complexes are generally assumed to be of 1:1 stoichiometry.

Nitrogen coordination is usually demonstrated by X-ray crystallography and/or IR spectroscopy. The N-coordination of diphenyl(2-pyridyl)phosphine to a metal ion results in a shift to higher frequencies in the IR absorptions of the pyridine ring by 15–30 cm^{-1} [239,240]. Based on this shift in IR absorptions, early studies [241,242] focused on dividing the metal complexes of diphenyl(2-pyridyl)phosphine into those in which the metal is essentially P-coordinated or N-coordinated. The silver(I) chloride complexes were assigned to the former group, owing to lack of change in the IR absorptions of the pyridine ring.

The first known example of diphenyl(2-pyridyl)phosphine (L) behaving as a bidentate ligand, was the crystallographic elucidation of the complex of composition $[Ag_2Cl_2L_3]$ in 1982 [241]. A schematic illustration of the complex is shown in Scheme 17 (**15**).

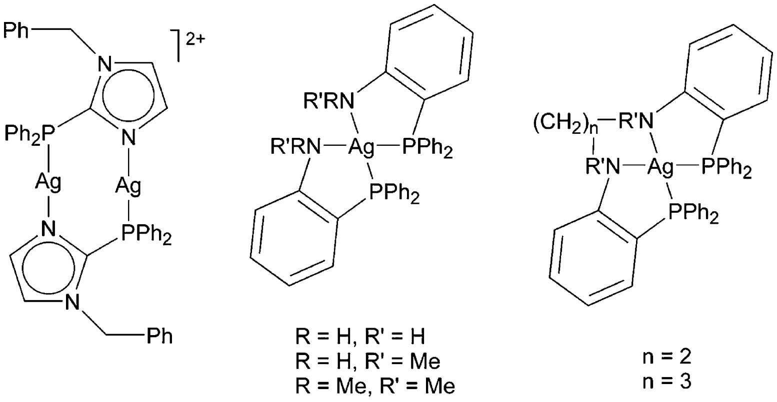
The two silver atoms are held together by two bridging chlorides. One of the silver atoms is bonded to two phosphines through the phosphorus atom, while the other silver atom is bonded to the nitrogen atom of one of the ligands coordinated to the first silver atom. P,N-coordination is



15

16

Scheme 17. Structures of diphenylpyridylphosphine silver(I) complexes **15** and **16**.



17 **18** **19**

Scheme 18. Structures of some Ag(I) complexes with mixed P and N coordination.

always believed to occur when the ligands are used in excess [30,241].

The complex $[AgClPPh_2(2\text{-}Py)]_4$ is a cubanoid tetramer, that is formed on reaction of silver(I) chloride with diphenyl(2-pyridyl)phosphine. The structure determination shows that the silver atoms on the edges of the Ag_4Cl_4 cube are coordinated to one phosphorus atom each, with no interaction with any of the *ortho*-positions on the pyridyl rings. From these structural studies, it has been concluded [30] that pyridine nitrogen atom coordination to silver(I) is only involved when chloro/phosphorus coordination is not sufficient by itself for coordinative saturation. The replacement of halides with weak donor ions like BF_4^-, PF_6^-, etc., facilitates nitrogen coordination. For example, both phosphorus and nitrogen coordinate to the dimeric complex $[Ag_2(\eta^1\text{-L})(\mu^2\text{-L})_2][ClO_4]_2$ [L = PPh_2(2-Py)]. Crystallographic analysis [115], has shown that the two silver atoms are held together by two bridging diphenyl(2-pyridyl)phosphine ligands in a head-to-tail configuration. While one of the metal centres is two-coordinate with a N,P-donor set, the other metal centre is three-coordinate by virtue of a third diphenyl(2-pyridyl)phosphine ligand coordinating in a monodentate fashion through phosphorus exclusively (**16**, Scheme 17).

Addition of excess diphenyl(2-pyridyl)phosphine to a CD_2Cl_2 solution of $[Ag_2(\eta^1\text{-L})(\mu^2\text{-L})_2][ClO_4]_2$ [L = PPh_2(2-Py)] afforded $[Ag(\eta^1\text{-L})_3]ClO_4$, the ^{31}P NMR spectrum of which at 183 K, revealed two sets of doublets, with a first order ^{31}P–^{107}Ag coupling constant ($^1J(^{109}Ag$–$^{31}P) = 324$ Hz) characteristic of three phosphorus atoms bound to the metal centre [115]. Further addition of diphenyl(2-pyridyl)phosphine, showed two sets of doublets by ^{31}P NMR, with a first order ^{31}P–^{107}Ag coupling constant ($^1J(^{109}Ag$–$^{31}P) = 235$ Hz) characteristic of four phosphorus atoms bound to silver(I). Crystallographic elucidation of the product, $[Ag(\eta^1\text{-L})_4]ClO_4$ confirmed a slightly distorted tetrahedral AgL_4 geometry for the cation [115].

Examples of both nitrogen and phosphorus coordination are known for silver(I) complexes containing related aminophosphines, such as $[Ag\{$(l-benzyl-2-imidazolyl)diphenylphosphine$\}_2]^{2+}$ nitrate and tetrafluoroborate [243], and $[Ag\{$1-diphenylphosphino-2-(2-pyridyl)ethane$\}_2]$ $[PF_6]$ [244]. The former complex is either dimeric [243] (**17**, Scheme 18), or polymeric with bridging BF_4 groups [245]. The latter is, however, monomeric and rearranges in solution by inversion of the tetrahedral metal centre.

Monomeric, bis-chelated structures have been assigned to a series of silver(I) (and copper(I)) complexes via either bidentate P,N (**18**, Scheme 18) or tetradentate P_2N_2 (**19**, Scheme 18) coordination of the aminophosphine, as was concluded from spectroscopic (NMR, IR) and mass spectrometry (EI and FAB-MS) analysis [246].

For 1:2 adducts of silver(I) nitrate with the three bidentate ligands 1,2-bis(di-*n*-pyridylphosphino)ethane where $n = 2$, 3 and 4, the structural type is either mononuclear Type **10** or dinuclear Type **11** (Scheme 12), depending on the position of the pyridyl N atom [9]. ^{31}P and [^{31}P–^{109}Ag] HMQC NMR experiments showed that in solution, the 3- and 4-pyridyl exist only as bis-chelated monomeric species $[Ag(dnpype)_2]^+$ (Type **10**), whereas the 2-pyridyl (d2pype) complex forms an equilibrium mixture of monomeric $[[Ag(d2pype)_2]^+$, dimeric $[\{Ag(d2pype)_2\}_2]^{2+}$ and trimeric $[\{Ag(d2pype)_2\}_2]^{3+}$ species in which the d2pype ligands co-ordinate in both bridging and chelated modes via the phosphorus atoms. The complex crystallised as the dimeric species (Type **11**, Scheme 12) in which each silver ion is co-ordinated by one chelated and two bridging d2pype ligands forming a 10-membered ring in a double boat conformation. The pyridyl nitrogen atoms do not co-ordinate to the silver. A similar structure is found for the analogous Ag(I) complex with the hybrid ligand 1-(di-2-pyridylphosphino)-2-(diphenylphosphino)ethane (2-pyppe) from a crystal structure determination of $[Ag_2(2\text{-pyppe})_4][NO_3]_2\cdot H_2O$ [247].

7. Concluding remarks

The rich and varied coordination chemistry of Ag(I) complexes with Group 15 donor ligands is described, with a focus on mono- and bidentate phosphine complexes. An attempt at a comprehensive overview of the structural chemistry is made. The interplay of various parameters such as the geometrical flexibility of Ag(I), the bite angle and electronic properties of the phosphine as well as the coordination mode of the supporting ligands, often renders predictions concerning the structural properties of silver-phosphine complexes difficult. This difficulty is exemplified by the crystallisation of some complexes in more than one polymorph. In general a tetrahedral environment around the silver(I) atom is preferred in the solid state, although many exceptions to this tetrahedral environment have been observed. In general, the observed solution state chemistry shows a rapid equilibrium between various coordination complexes. The difficulty in predicting the structural types of silver(I) complexes warrants more research into which factors govern the formation of particular structural types.

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