

Accepted Manuscript

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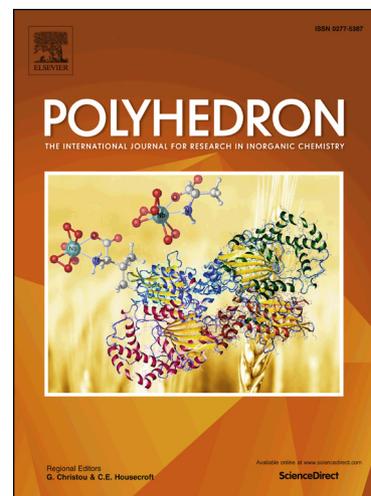
PII: S0277-5387(17)30085-2
DOI: <http://dx.doi.org/10.1016/j.poly.2017.01.048>
Reference: POLY 12452

To appear in: *Polyhedron*

Received Date: 9 December 2016
Revised Date: 27 January 2017
Accepted Date: 28 January 2017

Please cite this article as: G. Besenyei, G. Szalontai, L. Párkányi, Synthesis and structure of dinuclear silver complexes of *N,N*-bis(2-(diphenylphosphanyl)ethyl)phenylamine (REVISED), *Polyhedron* (2017), doi: <http://dx.doi.org/10.1016/j.poly.2017.01.048>

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Synthesis and structure of dinuclear silver complexes of *N,N*-bis(2-(diphenylphosphanyl)ethyl)phenylamine (REVISED)

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Abstract

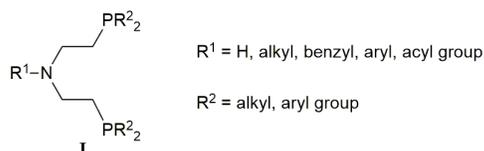
N,N-bis(2-(diphenylphosphanyl)ethyl)phenylamine, (PN^{Ph}P), and AgX compounds (X = OTf, Cl, Br, I) form dimeric complexes of general formula [Ag₂X₂(PN^{Ph}P)₂], **1-4**, in which, as revealed by crystallographic investigations, the two phosphorus donors are bound to different metal centers but the central N-donor remains unbound. NMR studies performed on solutions of any 1:1 mixtures of **2-4** demonstrated that these complexes retain their dimeric structure in solution. To the contrary, a monomer/dimer equilibrium strongly shifted toward dimerization was observed in the solutions of **1**. The distribution of the dimeric species in the halide¹/halide² mixtures compared to that in the OTf/halide systems is remarkably different and reflects the preference of the Ag/halide interaction over the Ag/OTf coordination. Based on the interplay of the AgP₂ planes, the known [Ag₂(μ-X)₂(μ-Ph₂PYPPPh₂)₂] complexes can be arranged into four well-discernible groups (Y stands for a 4-6-membered linkage).

Keywords

PNP ligand, silver complexes, dimers, X-ray structure, Ag-P coupling

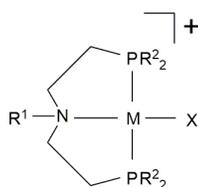
1. Introduction

Nitrogen-containing polyphosphines cover a wide range of chemical compounds whose complexes, due to their exceptional balance of stability *versus* reactivity, have found application in many fields of coordination chemistry [1]. Within this class of compounds, tridentate ligands in which two phosphorus donor groups are connected to the central nitrogen atom by 1,2-ethylene bridges (**I** in Scheme 1) have been intensively studied over the past two decades. The combination of soft and hard donor atoms furnishes a hemilabile nature to these ligands, of which numerous representatives have been successfully applied to stabilize complexes possessing outstanding catalytic activity [2].

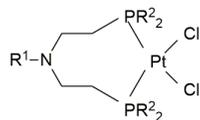


Scheme 1. General formula of compounds **I**

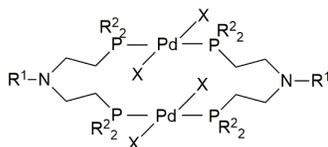
Complexes of aminodiphosphanes **I** excel not only by their remarkable catalytic properties but by their structural variety as well. In cationic square planar complexes, compounds **I** typically act as tridentate ligands [3-5] (structure **A** in Scheme 2) but strong metal-halogen bonds like the Pt-Cl interaction [4, 6] or reduced electron density at the nitrogen atom induced by an acyl moiety [3, 7] result in P,P-coordination mode (structures **B** and **C**). Interestingly, the $R^1 = R^2 = \text{phenyl derivative}$ that gives a monomeric complex cation with PdCl_2 , with PdBr_2 yields the dimeric adduct of type **C** [8]. Moreover, the $1,4\text{-C}_6\text{H}_4\{\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2\}_2$ ligand possessing two sets of donor atoms shows a two-faced behaviour with PdCl_2 , as it binds the metal as a tripodal ligand at one end but establishes only P,P coordination at the other [9]. From a detailed multinuclear NMR study, the formation of a dimeric species from $[\text{Pd}(\text{OTf})(\text{PNP})](\text{OTf})$ was inferred in which the PNP ligand acts both as a chelating and as a bridging agent (Scheme 2, structure **D**) [10].

**A**

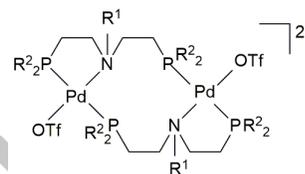
$R^1 = \text{H}, R^2 = \text{phenyl}, \text{M} = \text{Pd}, \text{X} = \text{Cl}, \text{Br}, \text{NO}_3$
 $R^1 = \text{phenyl}, t\text{-butyl}, R^2 = \text{phenyl}, \text{M} = \text{Pd}, \text{X} = \text{Cl}$
 $R^1 = 1\text{-phenylethyl}, R^2 = \text{phenyl}, \text{M} = \text{Pt}, \text{X} = \text{Cl}, \text{I}, \text{CN}$

**B**

$R^1 = 1\text{-phenylethyl}, R^2 = \text{phenyl}$
 $R^1 = \text{benzyl}, R^2 = \text{phenyl}$

**C**

$R^1 = 4\text{-methoxybenzoyl}, R^2 = \text{phenyl}, \text{X} = \text{Cl}$
 $R^1 = \text{phosphoryl}, R^2 = \text{phenyl}, \text{X} = \text{Cl}$
 $R^1 = R^2 = \text{phenyl}, \text{X} = \text{Br}$

**D**

$R^1 = 1\text{-phenylethyl}, R^2 = \text{phenyl},$

Scheme 2. Representative structures of square planar complexes with ligands **I**

In octahedral aminocarbene ruthenium complexes, the PNP ligand was found to occupy three facial coordination sites [11] but meridional arrangement of the aminodiphosphane was observed in the phosphane derivative, $[\text{RuCl}_2(\text{PNP})\text{PPh}_3]$ [12]. The five-coordinate $[\text{FeCl}_2(\text{PNP})]$ complex (PNP denotes $\text{HN}(\text{CH}_2\text{CH}_2\text{P}^i\text{R}_2)_2$) could be isolated in two different geometries. In the square pyramidal species, the PNP ligand coordinates in the expected meridional fashion whereas the phosphorus and nitrogen donor atoms occupy facial coordination sites in the trigonal bipyramidal isomer [13]. A rare example for the structural flexibility of the PNP ligands has been demonstrated recently with the $[\text{CoI}_2(\text{PNP})]$ complex ($R^1 = \text{benzyl}, R^2 = \text{phenyl}$ group) that shows up as a P,P-coordinated tetrahedral adduct and a P,N,P-coordinated square pyramidal variant within a single crystal structure [14].

The structural variety observed with most of the late transition metals can certainly be attributed to the highly flexible ethylenic chains, to the donor set that combines two soft (P) and one hard (N) donor atoms making the PNP ligands inherently hemilabile, and to the

substituents of the phosphorus and nitrogen atoms that can finely tune both the steric and the electronic properties of these ligands.

Most of the studies performed with ligands **I** so far have focused on metals of catalytic importance leaving the chemistry of Group 11 metals largely unexplored [15]. To our knowledge, the only crystallographically characterized silver complex incorporating an *N*-aryl PNP ligand was published by Puddephatt and coworkers [9] who reported a weak Ag...N interaction in the silver complex of the bis(PNP)-donor pincer ligand 1,4-C₆H₄{N(CH₂CH₂PPh₂)₂}₂. In this paper, we report on the synthesis and solution and solid state structural features of four novel dimeric silver complexes incorporating PhN(CH₂CH₂PPh₂)₂ as bridging ligand. In order to gain information on the nuclearity of the complexes in solution, special attention was paid to the ³¹P NMR spectra of mixtures containing different anions.

2. Experimental

General comments: All chemicals were purchased from Aldrich and used without further purification. THF was dried over sodium/benzophenone and distilled before use. Preparation of ligand **I** was carried out under a nitrogen atmosphere by using standard Schlenk techniques. NMR spectra were recorded on a Bruker-Avance II 400 (9.38 T) and Varian 500 (11.75 T) using tetramethylsilane (¹H) as internal standard and 85% H₃PO₄ (³¹P) as external standard, in CDCl₃ or CD₂Cl₂ solutions. Pulse sequences used for the EXSY [16] and DOSY [17] experiments were the standard Bruker sequences without modifications. Abbreviations used in the description of the NMR spectra: s, singlet; d, doublet; m, multiplet; br, broad.

2.1. X-ray structure determination

Intensity data collections were performed on a Rigaku Rapid diffractometer using MoK α radiation ($\lambda = 0.71075 \text{ \AA}$). Absorption corrections were applied to each data set (numerical for **1**, **3**, **4**, **1/3**, multi-scan for **2**). The structures were solved by direct methods using SHELXS [18] (SHELXT [19] for **1/3**) and were refined by anisotropic full matrix least-squares using the SHELXL [18] program. The maximum and average shift/error after the final cycle was 0.0 in all cases. Crystal data and structure determination details are given in Table 1.

Table 1.

Crystal data and details of the structure determination.

Compound	1	2	3
Formula	$C_{70}H_{66}Ag_2F_6N_2O_6P_4S_2$	$C_{68}H_{66}Ag_2Cl_2N_2P_4 \cdot 2 \cdot CHCl_3$	$C_{68}H_{66}Ag_2Br_2N_2P_4 \cdot 2 \cdot CHCl_3$
Formula weight	1549.01	1560.48	824.70
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P-1$ (no. 2)	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)
a, b, c [Å]	10.5844(3), 13.0926(5), 13.4142(4)	14.3385(3), 14.2883(3), 17.5684(4)	19.8975(4), 15.4236(2), 25.2582(5)
α, β, γ [°]	67.9124(9), 82.8519(9), 70.8218(9)	90, 103.9587(7), 90	90, 113.7450(9), 90
V [Å ³]	1626.88(9)	3493.00(13)	7095.3(2)
Z	1	4	8
$D(\text{calc})$ [g/cm ³]	1.581	1.484	1.544
$\mu(\text{MoK}\alpha)$ [mm ⁻¹]	0.837	1.000	2.036
$F(000)$	788	1584	3312
Crystal size [mm]	0.40x0.54x0.66	0.23x0.48x0.66	0.38x0.40x0.45
Temperature [K]	93	93	295

θ min, max [°], completeness	3.1, 29.6, 0.979	3.1, 25.3, 0.996	2.8, 26.4, 0.991
Dataset	-14:13; -18:18 ; -18:18	-17:17; -17:17 ; -21:21	-24:24; -19:19; -31:31
Total, unique data, $R(\text{int})$	33563, 8929, 0.028	97976, 6369, 0.037	78027, 7217, 0.043
Observed data [$I > 2.0 \sigma(I)$]	8541	5895	6700
$N_{\text{ref}}, N_{\text{par}}$	8929, 415	6369, 388	7217, 388
$R, wR2$ [$I > 2\sigma(I)$]	0.0234, 0.0588	0.0593, 0.1663	0.0443, 0.1090
$R, wR2, S$	0.0251, 0.0594, 1.12	0.0626, 0.1689, 1.06	0.0491, 0.1118, 1.07
Min. and max. resd. dens. [$\text{e}/\text{\AA}^3$]	-0.33, 0.57	-1.56, 2.71	-0.70, 0.53

(Table 1, continued)

Compound	4	1/3
Formula	$C_{68}H_{66}Ag_2I_2N_2P_4 \cdot 2 \cdot CHCl_3$	$C_{142}H_{142}Ag_4Br_2F_6N_4O_7P_8S_2$
Formula weight	871.69	3033.78
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)
a, b, c [Å]	20.2010(4), 15.1698(2), 24.6049(4)	12.646(5), 38.650(2), 14.192(5)
α, β, γ [°]	90, 111.6267(7), 90	90.00, 93.45(1), 90.00
V [Å ³]	7009.3(2)	6924(4)
Z	8	2
$D(\text{calc})$ [g/cm ³]	1.652	1.455
$\mu(\text{MoK}\alpha)$ [mm ⁻¹]	1.802	1.321
$F(000)$	3456	3084
Crystal size [mm]	0.46 x 0.55 x 0.60	0.38 x 0.25 x 0.13
Temperature [K]	93	103
θ min, max [°], completeness	2.2, 33.1, 0.996	3.00, 25.4, 0.830

Dataset	-31:29 ; -23:23 ; -37:37	-15:15;-46:46;-16:16
Total, unique data, $R(\text{int})$	67907, 13315, 0.064	67598, 10520, 0.1502
Observed data [$I > 2.0 \sigma(I)$]	12138	6099
N_{ref} , N_{par}	13315, 388	10520, 813
R indices [$I > 2\sigma(I)$]	0.0406, 0.1148	0.0724, 0.1404
R , $wR2$, S (all data)	0.0472, 0.1203, 1.02	0.1400, 0.1695, 1.026
Min. and max. resd. dens. [$\text{e}/\text{\AA}^3$]	-1.722, 2.413	0.55, -0.68

Several attempts were made to obtain suitable crystals for the mixed ligand **1/2**, **1/3**, **1/4** complexes. The structure of **1/4** could be solved but was not refinable. The structure determination and refinement of compound **1/3** was carried out with limited success. The crystal lattice seemed to deteriorate during experiment resulting in high *R* for the agreement between equivalent reflections, low observed/unobserved reflection ratio, low completeness value. Though the experiment was carried out at low temperature, the ADP values look more characteristic for a room temperature measurement, indicating disorder for some phenyl ring atoms and for F2, F3, O2. However, this structure clearly proves that the mixed ligand complex is formed.

Similar unit cell data and identical space group for compounds **3** and **4** indicates possible isostructurality, but no such relationship exists. **3** and **4** form different hydrogen bonding schemes (Table 6). The centroid of the molecule of **4** is shifted by a non-crystallographic operation $\frac{1}{4}$, $\frac{1}{4}$, $-\frac{1}{2}$ with respect to that of **3**.

2.2 Syntheses

Preparation of *N,N*-bis(2-(diphenylphosphanyl)ethyl)phenylamine, PN^{Ph}P

Of the various routes suggested for the preparation of *N*-phenyl PNP type ligands, that suggested in [3] was followed with some modifications. Into an oven-dried (120 °C) Schlenk-tube, 40 mL of dry THF, 370 mg (9.46 mmol) K and 0.85 mL (1.04 g, 4.73 mmol) of Ph₂PCl were charged under N₂. The reaction mixture was gently refluxed and stirred under N₂ for 90 min. The reaction vessel was immersed into melting ice and 1.15 g (2.35 mmol) of PhN(CH₂CH₂OTs)₂ was added under N₂ in small portions. The cooling bath was removed and the viscous reaction mixture was stirred at RT for 2 hours. After addition of 5 mL of deaerated MeOH and 40 mL of dry THF, the slurry was filtered under N₂ and the filtrate was concentrated to an oil under vacuum. The crude product was redissolved in a deaerated mixture of 5 mL CH₂Cl₂ and 15 mL EtOH. Slow evaporation of the more volatile solvent under vacuum resulted in the formation of a white precipitate that was filtered out, washed with chilled ethanol and dried. Yield: 1.01 g (83%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 2.24-2.30 (4H, m, CH₂P), 3.30-3.38 (4H, m, CH₂N), 6.33-6.38 (2H, m), 6.60-6.65 (1H, m), 7.06-7.12 (2H, m) (resonances of the *ortho*, *para* and *meta* protons of the *N*-phenyl group), 7.29-7.35 (12H, m, PPh), 7.37-7.43 (8H, m, PPh); ³¹P NMR (CDCl₃), δ (ppm): -21.1 (s).

Preparation of [Ag₂(OTf)₂(PN^{Ph}P)₂], **1**

233 mg (0.450 mmol) of $\text{PN}^{\text{Ph}}\text{P}$ ligand was added to 118 mg (0.459 mmol) of $[\text{Ag}(\text{OTf})]$ suspended in a mixture of 10 mL of CH_2Cl_2 and 6 mL of diethyl ether. The colourless homogeneous solution was protected from light and was stirred for 30 min under N_2 .

Evaporation to ca. 3 mL and addition of diethyl ether resulted in a white precipitate that was filtered, washed with Et_2O and dried under vacuum. Yield: 293 mg (84%)

^1H NMR (500 MHz, CDCl_3) δ (ppm) (major component): 2.75-2.85 (4H, br, CH_2P), 3.66-3.76 (4H, br, CH_2N), 6.11-6.18 (2H, m), 6.49-6.55 (1H, m), 6.97-7.04 (2H, m) (resonances of the *ortho*, *para* and *meta* protons of the *N*-phenyl group), 7.27-7.34 (8H, m, *PPh*), 7.35-7.41 (4H, m, *PPh*) 7.49-7.56 (8H, m, *PPh*); ^{31}P NMR (CDCl_3 , 161.8 MHz), δ (ppm): 0.46 (two doublets, $^1J(^{107}\text{Ag}-^{31}\text{P}) = 491$ Hz, $^1J(^{109}\text{Ag}-^{31}\text{P}) = 568$ Hz. The resonances of the minor isomer (ca. 9 %) can be observed in the ^1H NMR spectrum at 2.34-2.44, 3.13-3.23 and 7.58-7.71 ppm and in the ^{31}P NMR spectrum at -2.1 and -6.4 ppm as broad signals.

Preparation of $[\text{Ag}_2\text{Cl}_2(\text{PN}^{\text{Ph}}\text{P})_2]$, **2**

85.0 mg (0.109 mmol) of $[\text{Ag}_2(\text{OTf})_2(\text{PN}^{\text{Ph}}\text{P})_2]$ was suspended in 10 mL of CH_2Cl_2 and 41.7 mg (0.107 mmol) of benzyltriphenylphosphonium chloride in 3 mL of CH_2Cl_2 was added dropwise at ambient temperature. A homogeneous solution is formed that was stirred for 15 min. Evaporation to ca. 3 mL and addition of 10 mL of methanol yielded a white precipitate that was filtered out, washed with methanol and dried (63 mg, 89 %). ^1H NMR (400 MHz, CDCl_3) δ (ppm): 2.53-2.81 (4H, br), 3.69-3.96 (4H, br), 6.09-6.29 (2H, m), 6.44-6.59 (1H, m), 6.96-7.09 (2H, m) (resonances of the *ortho*, *para* and *meta* protons of the *N*-phenyl group), 7.09-7.79 (20H, multiplets of the *PPh* hydrogen atoms). ^{31}P NMR (300 K, CDCl_3), δ (ppm): -4.42 (two doublets, $^1J(^{107}\text{Ag}-^{31}\text{P}) = 386$ Hz, $^1J(^{109}\text{Ag}-^{31}\text{P}) = 444$ Hz).

Preparation of $[\text{Ag}_2\text{Br}_2(\text{PN}^{\text{Ph}}\text{P})_2]$, **3** and $[\text{Ag}_2\text{I}_2(\text{PN}^{\text{Ph}}\text{P})_2]$, **4**

By using MePh_3PBr and MePh_3PI in the metathetical reaction, the bromide and iodide analogs of compound **2**, $[\text{Ag}_2\text{Br}_2(\text{PN}^{\text{Ph}}\text{P})_2]$, **3** and $[\text{Ag}_2\text{I}_2(\text{PN}^{\text{Ph}}\text{P})_2]$, **4** could be prepared identically on 0.1 mmol scale delivering **3** in 94% and **4** in 92 % yield. We note that it is advisable to use methanol as precipitating agent in the anion exchange reactions because diethyl ether renders the product contaminated with the phosphonium salt.

$[\text{Ag}_2\text{Br}_2(\text{PN}^{\text{Ph}}\text{P})_2]$, **3**. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 2.68-2.84 (4H, br), 3.73-3.89 (4H, br), 6.17-6.31 (2H, m), 6.46-6.57 (1H, m), 6.99-7.09 (2H, m) (resonances of the *ortho*, *para* and *meta* protons of the *N*-phenyl group), 7.15-7.50 (20H, multiplets of the *PPh* hydrogen atoms). ^{31}P NMR (300 K, CDCl_3), δ (ppm): -8.55 (two doublets $^1J(^{107}\text{Ag}-^{31}\text{P}) = 377$ Hz, $^1J(^{109}\text{Ag}-^{31}\text{P}) = 435$ Hz).

ppm are attributed to *P*-phenyl moieties. Interestingly, a second set of resonances attributed to both aliphatic (2.44 and 3.19 ppm) and aromatic (7.07-7.32 and 7.60-7.71 ppm) hydrogen atoms can also be recognized, indicating the presence of a minor constituent in solution phase. As the proportion of the minor component was dependent on the solvent and the concentration, it could be concluded that it is not a contamination but several molecular entities are formed upon dissolution of the solid **1**. The multicomponent nature of the silver/phosphane complexes in solution is known and has been repeatedly observed by various experimental techniques [20, 21]. In contrast to the pure PNP ligand (Fig. S1), the resonances of the aliphatic hydrogen atoms of **1** are unresolved both at RT and at low temperatures, hampering a deeper analysis of the NMR spectra.

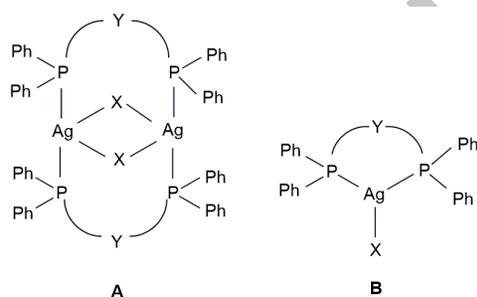
The room temperature ^{31}P NMR spectrum of **1** (major constituent) (Fig. S4) displays two well resolved doublets centered at 0.98 ppm, due to $^1J(^{107}\text{Ag}-^{31}\text{P})$ and $^1J(^{109}\text{Ag}-^{31}\text{P})$ coupling. The magnitude of the coupling constants ($^1J(^{107}\text{Ag}-^{31}\text{P}) = 491$, $^1J(^{109}\text{Ag}-^{31}\text{P}) = 568$) are in the range typical for silver complexes coordinating two tertier phosphane ligands and an oxo anion with strong electron withdrawing properties [20, 22, 23]. The broad resonances of the minor component show up at -3.66 and -6.85 ppm and the average coupling constant (517 Hz) suggests that the environment around the silver atom is similar to that in the main constituent. The striking feature of the ^{31}P NMR spectrum is that the resonances are sharp not only at low temperatures which is characteristic for silver/phosphane complexes but at ambient temperature as well. In contrast to the well resolved ^{31}P NMR spectrum of **1**, the silver complex of the earlier mentioned $1,4\text{-C}_6\text{H}_4\{\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2\}_2$ ligand showed only a broad resonance with no resolved coupling to the metal center [9].

The ^1H and ^{31}P NMR spectra of the halide complexes **2-4** are presented in Figures S5-S10, the ^{31}P NMR spectral data are summarized in Table 2. The spectra show that replacement of the OTf ion by halide ions eliminates the minor constituent. The methylene resonances invariably appear as broad signals at 2.7-2.8 ppm and around 3.8 ppm and the *N*-phenyl and *P*-phenyl hydrogen atoms are also insensitive to the nature of the halide ion. To the contrary, both the chemical shifts and the $^1J(\text{Ag-P})$ coupling constants show a systematic decrease on going from chloride to iodide, in line with the increasing nucleophilicity of the halide anions ($\text{I} > \text{Br} > \text{Cl}$). The trends observed in the ^{31}P NMR features are in coincidence with the behavior of other AgX/phosphane complexes [24-26].

Table 2.

^{31}P NMR data of the isolated (**1-4**) and the mixed ligand complexes in CDCl_3 at the indicated temperatures.

Anion	Comp.	δ/ppm	$^1J(^{107}\text{Ag}-^{31}\text{P})/^1J(^{109}\text{Ag}-^{31}\text{P})$ (absolute values)	T/K
OTf	1	0.46	491/568	300
Cl	2	-4.42	386/444	300
Br	3	-8.55	377/435	296
I	4	-13.70	350/404	298
Cl/Br	2/3	-5.41	381/439	298
Cl/Br	2/3	-4.95	385/445	218
Cl/I	2/4	-8.07	368/425	218
Br/I	3/4	-9.30	370/426	223
OTf/Cl	1/2	-1.04	432/498	298
OTf/Br	1/3	-1.90	427/491	298
OTf/I	1/4	-4.12	416/480	218



Scheme 4. General formula of dimeric and monomeric $[\text{AgX}(\mu\text{-PPh}_2\text{YPPH}_2)]$ complexes.

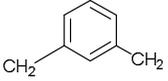
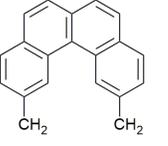
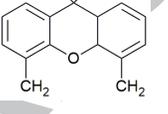
The kinetic lability of silver/phosphane complexes, especially of those incorporating monophosphane ligands, is known and they readily form multicomponent systems in solution [20]. Although bisphosphane ligands may give chelate complexes with enhanced kinetic stability [27] and, due to their double bridged feature (structure **A** in Scheme 4) as determined by X-ray diffraction (see later), one can expect increased stability for **1-4** as well, it is not evident that the dimeric structure is preserved in solution. Surveying our spectra we may say that they are in line with structure **A** but the broad signals of the methylene protons provide no

unequivocal evidence to confirm this hypothesis. Moreover, a search of literature data have shown that coupling constants reported for mononuclear complexes of type **B** may have very close values (Table 3, right column) that reduces the strength of our data to prove the dimeric nature of **1-4** in solution. In order to gain a deeper insight into the solution structure of these complexes, we set up various experiments.

If we assume that the prevailing form of the complexes in solution is dimeric, observation of $^3J(\text{Ag-P})$ coupling transmitted by the bridging halide ions may provide us a direct proof for the binuclear nature of the complexes. Our attempts to detect such couplings was unsuccessful even at $-60\text{ }^\circ\text{C}$ demonstrating that the halide ions exchange rapidly in the coordination sphere and cannot transfer magnetic information from one silver center to the other. To our knowledge, $^3J(\text{Ag-P})$ couplings have been observed at low temperatures for dinuclear silver complexes only if the P-donors are separated by a single methylene bridge (dppm) [29-32]. The lability of the halide complexes excluded the possibility to detect the heteronuclear ^{107}Ag - ^{109}Ag coupling as well.

Table 3

A compilation of $^1J(^{31}\text{P}-^{107}\text{Ag})$ and $^1J(^{31}\text{P}-^{109}\text{Ag})$ coupling constants (absolute values) regarding structures **A** and **B** in Scheme 4.

A			A			B		
X	$^1J(\text{Ag-P})$	T/K	X	$^1J(\text{Ag-P})$	T/K	X	$^1J(\text{Ag-P})$	
Y =		[24]	Y =	$-(\text{CH}_2)_5-$	[23, 25]	Y =		[23,26]
Cl	382/441	RT	Cl	390/450	263-273	Cl	411/474	
Br	377/434	RT	Br	383/442	218	I	378/437	
I	337/388	RT	Y =	$-(\text{CH}_2)_2\text{S}(\text{CH}_2)_2-$	[23]	ClO ₄	507/585	
NO ₃	457/525	RT	Cl	381/438	263-273	Y =		[28]
			Y =	$-(\text{CH}_2)_6-$	[23]	Cl	377/435	
			Br	372/420	218			

As a further attempt to obtain direct experimental evidence for the dimeric nature of our compounds in solution, we studied the NMR spectra of complexes with mixed (halide¹/halide²) anions. It was anticipated that an exchange of halide ions occurring between monomeric $[\text{AgX}^1(\text{PN}^{\text{Ph}}\text{P})]$ and $[\text{AgX}^2(\text{PN}^{\text{Ph}}\text{P})]$ complexes will not modify the spectra. In case of dimeric complexes, however, a distribution of the halide ions should result and complexes with compositions $[\text{Ag}_2\text{X}^1_2(\text{PN}^{\text{Ph}}\text{P})_2]$, $[\text{Ag}_2\text{X}^1\text{X}^2(\text{PN}^{\text{Ph}}\text{P})_2]$ and $[\text{Ag}_2\text{X}^2_2(\text{PN}^{\text{Ph}}\text{P})_2]$ will be formed. The ^{31}P NMR spectrum of a 1:1 molar mixture of $[\text{Ag}_2\text{Cl}_2(\text{PN}^{\text{Ph}}\text{P})_2]$ and $[\text{Ag}_2\text{Br}_2(\text{PN}^{\text{Ph}}\text{P})_2]$ is presented in Fig. 1, the $\delta(\text{P})$ and $^1J(\text{Ag-P})$ data for the possible **2/3**, **2/4** and **3/4** pairs are summarized in Table 2.

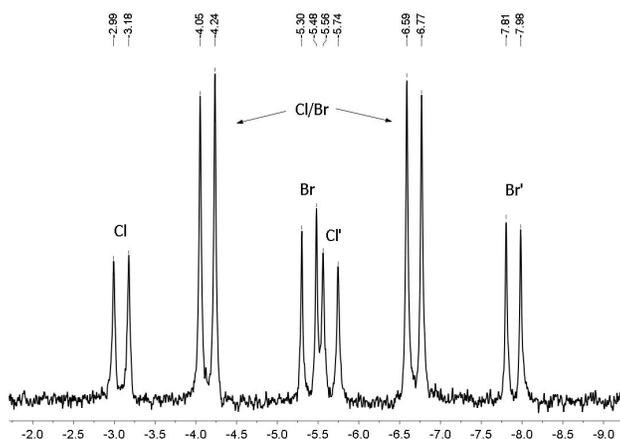


Fig. 1. ^{31}P NMR spectrum of a 1:1 molar mixture of $[\text{Ag}_2\text{Cl}_2(\text{PN}^{\text{Ph}}\text{P})_2]$ and $[\text{Ag}_2\text{Br}_2(\text{PN}^{\text{Ph}}\text{P})_2]$ in CDCl_3 at 298 K. (Cl and Cl', and all analogous designations here and in the Supplement, mark the high- and low-frequency parts of the spin systems ascribed to pure $[\text{Ag}_2\text{X}_2(\text{PN}^{\text{Ph}}\text{P})_2]$ complexes.)

The spectrum in Fig. 1 can be described as a threefold repetition of the pair of doublets characteristic for Ag/P interaction. The sections Cl and Cl' have been ascribed to the bischloro complex, the resonances labeled as Br, Br' to the bisbromo complex while the most intense peaks have been attributed to the mixed ligand chlorobromo derivative, **2/3**. The bischloro and bisbromo constituents of the mixture could be identified by comparing their NMR data with the corresponding values of the pure complexes. The $\delta(\text{P})$ and $^1J(\text{Ag-P})$ data of the mixed ligand dimer take intermediate positions between those of the parent complexes. Because a better separation of the peaks was achieved at 218 K, the integration was carried out on a spectrum recorded at low temperature (Fig. S12). The 1:1.71:0.95 ratio of the components is close to a simple statistical distribution of 1:2:1 and proves directly that the

halide complexes are dimeric in solution. ^{31}P NMR spectra of mixtures **2/4** and **3/4** have an identical appearance and have been assigned according the above considerations.

By recording 2D ^{31}P - ^{31}P exchange spectra using different mixing times we could prove unambiguously that halogen scrambling, slow on the ^{31}P time scale at 9.4 T, is going on between the complexes. As an illustrative example the ^{31}P - ^{31}P exchange spectrum of an $[\text{Ag}_2\text{Cl}_2(\text{PN}^{\text{Ph}}\text{P})_2]:[\text{Ag}_2\text{Br}_2(\text{PN}^{\text{Ph}}\text{P})_2] = 1:1$ molar mixture is shown in Figure 2. The off-diagonal cross peaks identify the exchanging sites clearly already at 50 ms exchange (mixing) time. As expected, the first-order cross-peaks (highlighted in red) connecting the mixed ligand complex (the strongest doublets) with the peaks of **2** or **3** are much stronger than those linking the homogeneous complexes **2** and **3** (highlighted in blue).

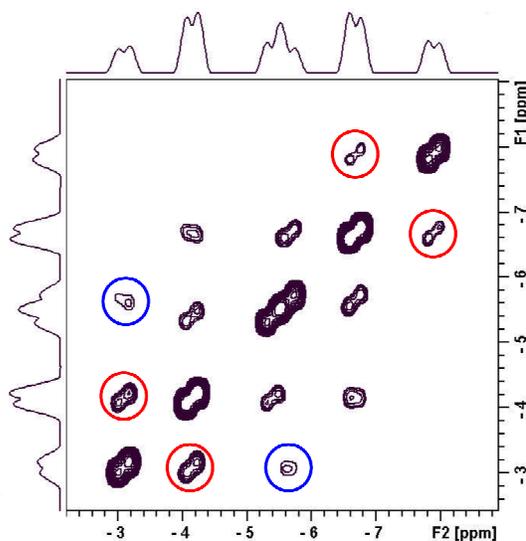


Fig. 2. ^{31}P - ^{31}P exchange (EXSY) spectrum of an $[\text{Ag}_2\text{Cl}_2(\text{PN}^{\text{Ph}}\text{P})_2]:[\text{Ag}_2\text{Br}_2(\text{PN}^{\text{Ph}}\text{P})_2] = 1:1$ molar mixture (**2/3**, exchange time = 50 ms, CDCl_3 , 298 K).

Although the chloride, bromide and iodide ions all form stable complexes with Ag(I), their hard/soft properties are characteristically different and they are classified as hard (Cl^-), intermediate (Br^-) and soft (I^-) bases [33]. In the light of their dissimilar softness, one may expect characteristically different distributions for the Cl/Br, Cl/I and Br/I cases. Therefore it surprised us that the distribution of the dimeric species found for the Cl/Br (1:1.71:0.95), Cl/I (1:1.69:0.84) and Br/I pairs (1:1.83:1.18) practically shows no variance (all measured at 218 K). It should be stressed, however, that these measurements are not suitable (and they were not planned to be) to deliver any kind of thermodynamic data.

The dominance of the halide ions over the OTf ion became visible, however, when we extended our study to OTf/Cl, **1/2**, OTf/Br, **1/3** and OTf/I, **1/4** pairs. Fig. 3 shows the room temperature ^{31}P NMR spectrum of a 1:1 mixture of **1** and **3**. NMR spectra for all of the combinations are added to the Supplementary Material, Table 2 includes the respective $\delta(\text{P})$ and $^1J(\text{Ag-P})$ data.

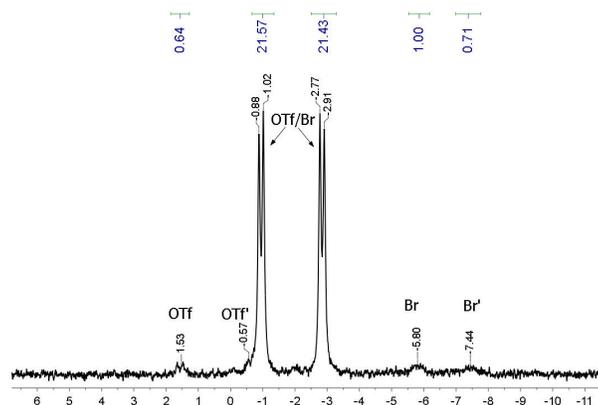


Fig. 3. ^{31}P NMR spectrum of a 1:1 mixture of $[\text{Ag}_2\text{Br}_2(\text{PN}^{\text{Ph}}\text{P})_2]$ and $[\text{Ag}_2(\text{OTf})_2(\text{PN}^{\text{Ph}}\text{P})_2]$ in CDCl_3 at 298 K.

The spectrum in Fig. 3 clearly demonstrates that formation of silver-bromide bonds is much more advantageous than the silver-OTf interaction. The approximate ratio of 1:21:1 witnesses about the dominance of the bromide over the OTf ion in the competition for the available coordination sites. As we have found for the halide pairs, the chemical shifts and the coupling constants of the OTf/halide derivatives occupy intermediate values between those of the parent compounds.

Having strong evidence from the experiments with mixed ligand complexes for the dimeric nature of compounds **1-4** in solution, we turned our attention to the minor constituent of the dissolved $[\text{Ag}_2(\text{OTf})_2(\text{PN}^{\text{Ph}}\text{P})_2]$ complex, which has not been identified. The section of a ^1H DOSY [17] spectrum recorded on a CD_2Cl_2 solution of **1** (Fig. S21) shows that the resonances of the conventional (1D) spectrum are separated according to the diffusion rate of the constituents. As the major component is characterized by the smaller diffusion coefficient, and, consequently, by the larger hydrodynamic radius, this species can be identified as a dimeric aggregate, while resonances of the minor constituent have been ascribed to a monomeric complex.

Based on our investigations carried out with mixed ligand complexes we conclude that compounds **2-4** are dimeric in solution. The different diffusion coefficients detected for the

two constituents in the solutions of **1**, as observed by ^1H DOSY experiments, make a monomer/dimer equilibrium highly probable for the silver triflate/ $\text{PN}^{\text{Ph}}\text{P}$ complex which is, however, strongly shifted toward the dimeric species. The dimeric nature of **1-4** is further supported by the magnitude of the $^1J(\text{Ag-P})$ coupling constants which are in good agreement with couplings found for other dinuclear double bridged diphosphine silver complexes.

3.2 Crystal Structures

Molecular diagrams are shown in Figs. 5 and 6. Atomic displacement parameters are depicted at the 50% probability level (except for **1/3**, where the 40 % probability value is used). As the conformation of **3** and **4** is rather similar as shown in the overlap diagram Fig. 4, only **2** and the low-temperature structure of **4** is presented in the figures. The atomic numbering schemes are identical. Hydrogen atoms and solvent molecules have been omitted for clarity.

Phosphane phenyl ring atoms are drawn as circles with arbitrary radii. Selected parameters are summarized in Tables 4-6 (more detailed description is presented in Tables S1 and S2 (see Supplementary Material)).

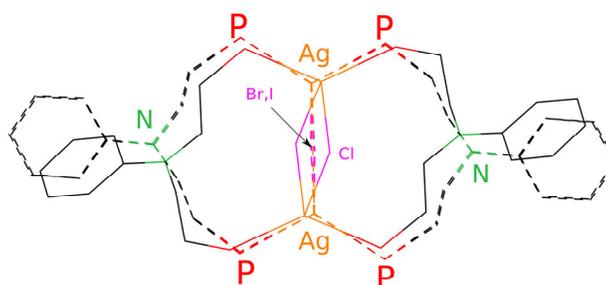


Fig. 4. Least-squares fit of Ag, P and N atoms (solid lines: **2**, dashes: **3** and **4**).

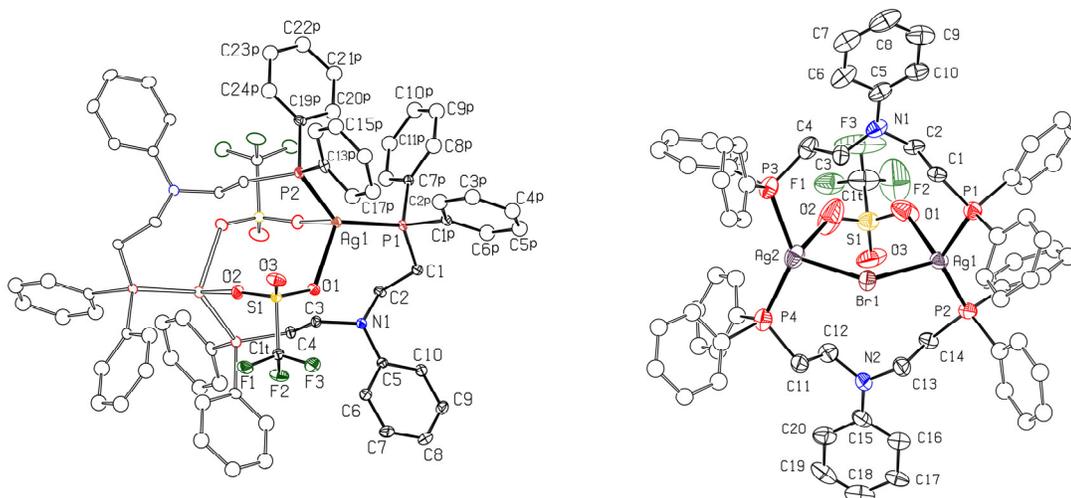


Fig. 5. Molecular diagrams of compounds **1**, (left), and **1/3**, (right).

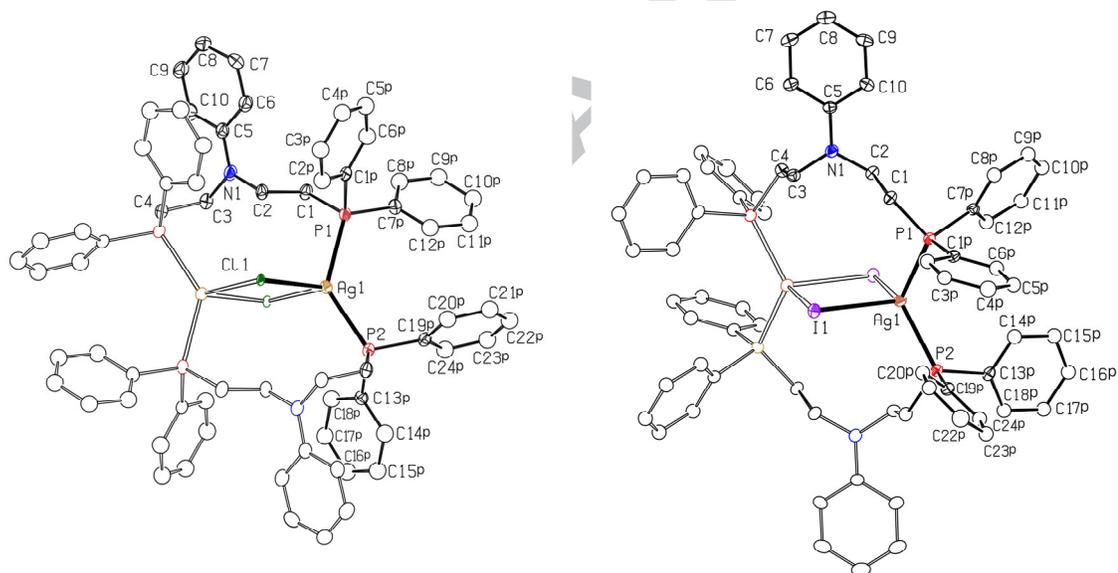


Fig. 6. Molecular diagrams of compounds **2**, (left), and **4**, (right).

The asymmetric unit is half a molecule for complexes **1-4**. The inversion centre generates the whole molecules: **1**: $2-x, -y, 1-z$; **2**: $-x, -y, 1-z$; **3**: $1-x, 1-y, -z$; **4**: $1/2-x, 1/2-y, -z$.

The Ag atoms display distorted tetrahedral configuration. The bulky PPh₂ moieties make wide P-Ag-P angles of 120-135°.

Table 5.Selected bond distances (Å) and angles (°) for **2-4**.

	2 X = Cl; $a = -x, -y, -z$	3 X = Br; $a = -x, -y, 1-z$	4 X = I; $a = 1/2-x, 1/2-y, -z$
Ag1-X1	2.748(1)	2.8292(5)	2.9342(2)
Ag1-P1	2.483(1)	2.471(1)	2.4634(6)
Ag1-P2	2.459(1)	2.474(1)	2.4635(7)
Ag1-X1 _a	2.727(1)	2.7318(5)	2.8707(2)
N1-C5	1.389(7)	1.391(4)	1.384(3)
Ag1-X1-Ag1 _a	93.10(3)	87.88(1)	82.62(1)
C2-N1-C3	116.9(4)	114.0(3)	114.1(2)
C2-N1-C5	120.7(4)	121.7(3)	121.7(2)
C3-N1-C5	122.3(4)	120.9(3)	121.1(2)

Table 6.Hydrogen bonds (Å, °) for compounds **1-4** and **1/3**.

D-H...A	<i>d</i> (D-H)	<i>d</i> (H...A)	<i>d</i> (D...A)	<(D-H...A)
1				
C3-H3a...F2[2-x,-y,1-z]	0.97	2.540	3.493(2)	166.0
C3-H3b...O2	0.97	2.440	3.283(2)	146.0
C10-H10...O3[1-x,-y,1-z]	0.93	2.550	3.380(2)	148.0
1/3				
C14-H14b...O3	0.97	2.420	3.32(1)	154.0
C18-H18...F3[x,y,-1+z]	0.93	2.490	3.36(1)	155.0
C39p-H39p...O1s	0.93	2.340	2.91(3)	119.0
2				
C1s-H1s...Cl1[-x,-y,-z]	1.00	2.40	3.382(11)	168.0
C2-H2b...Cl1	0.93	2.78	3.582(6)	146.0
C2p-H2p...Cl1	0.95	2.79	3.724(6)	169.0
C18p-H18p...Cl1[-x,-y,-z]	0.95	2.80	3.742(6)	169.0
3				
C1s-H1s...Br1[-x,y,1/2-z]	0.98	2.81	3.645(6)	144.0
C21p-H21p...Cl2s[-1/2+x,-1/2+y,z]	0.93	2.77	3.614(8)	151.0
C23p-H23p...Cl3s[[-x,y,1/2-z]	0.93	2.83	3.568(8)	137.0
4				
C1s-H1s...I1[-x,-y,-z]	1.00	2.93	3.744(3)	139.0
C23p-H23p...Cl1s[1/2+x,-1/2-y,1/2+z]	0.95	2.75	3.676(4)	166.0

The Ag...Ag distances across the macrocycle is dependent on the bridging atoms/moieties. The longest separation (5.12 Å) is in **1** where the three-membered O-S-O linkage connects the two Ag atoms. A considerably longer (5.72 Å) Ag...Ag distance is reported for *bis*(μ²-trifluoromethanesulfonato-O,O')-tetrakis(triphenylphosphane)-disilver(I), where the constraint

by the chain linking the pairs of phosphorous atoms is missing [34]. The distance of 4.64 Å in **1/3** indicates that the presence of Br influences the positions of the Ag atoms resulting in an intermediate value. Halogen bridging forces shorter separations that slightly decreases with the atomic number of the halogens (**2**: 3.98, **3**: 3.86 and **4**: 3.83 Å). The Ag-X-Ag bond angles (X = Cl, Br, I) are getting smaller accordingly: 93.1, 87.9 and 82.6° in contrast to the 117° angle of **1/3**. These findings corroborate the similar and more prominent tendency as shown by the series of *bis*((μ²-X)-(μ²-4*R*,5*R*-*trans*-4,5-*bis*((diphenylphosphanyl)methyl)-2,2-dimethyl-1,3-dioxolane-P,P')-silver(I)), (X = Cl, Br, I) where the corresponding Ag...Ag distances and Ag-X-Ag angles are 3.72, 3.59(5)(mean), and 3.07 Å and 88.2(1), 80.3(9). 63.1(4)° [35].

In complexes **1-4**, both the Ag-O and Ag-halogen bond distances (linking to the same Ag atom) are of different length, forming a rhomboid shape. The nitrogen atoms in all structures are planar (*sp*²) showing a considerable interaction with the π electron system of the phenyl ring and contributing to the reduced ability of the nitrogen to form coordinative bonds.

All crystal structures, except **1**, contain solvent molecules that maintain non-classical C-H...A hydrogen bonds (Table 6). **1/3** crystallizes with diethyl-ether and the ether oxygen interacts with a C(*sp*²)-H atom only.

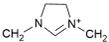
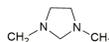
A search for structures of type **A** Scheme 4 in CCDC revealed that disilver complexes incorporating two bridging diphosphine and two bridging halide ligands may have four-, five- and six-membered linkages between the phosphorus atoms. An overview of their structural properties showed that these complexes can be classified according to the relative positions of their AgP₂ planes. In three cases (CPESAG, IPESAG, YAKMON), all the phosphorus atoms and the silver ions lay in the same plane, *i.e.* the two AgP₂ planes are coplanar. In another group of compounds, the two silver atoms are located at the same distance but on the opposite sides of the plane defined by the four phosphorus atoms. This means that the two AgP₂ planes are parallel in these complexes. This structural feature can be observed with a variety of chains linking the donor phosphorus atoms like tetramethylene, hexamethylene and nitrogen-containing five-membered linkages such as that in compounds **1-4**. In the three compounds having 4,5-*bis*((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane as bridging diphosphane ligand (XIDZAL, XIDZEP, XIDZIT), the dispositions of the silver centers from the P₄-plane are different causing thereby the two planes to form a small angle. Finally, the two AgP₂ planes may be twisted around the Ag-Ag axis forming a large (ca. 20-40°) angle. Table 7 summarizes the respective $\psi((\text{AgP}_2)^1/(\text{AgP}_2)^2)$ and $d(\text{P}_4\text{-plane}/\text{Ag})$ data.

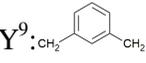
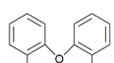
Table 7

Classification of halogen-bridged bis(diphosphine) disilver complexes (structure **A** in Scheme 4) according to the mutual orientation of their AgP₂ planes.

Refcode	X	Y	$\psi((\text{AgP}_2)^1/(\text{AgP}_2)^2)$	$d(\text{P}_4\text{-plane}/\text{Ag})$	References
Coplanar AgP ₂ planes					
CPESAG	Cl	Y ¹	0	0	[36]
IPESAG	I	Y ¹	0	0	[37]
YAKMON	Br	Y ²	0	0	[25]
Parallel AgP ₂ planes					
KAXKOL	Cl	Y ³	0	±0.01	[38]
KAXKUR	Cl	Y ⁴	0	±1.74	[38]
YAKLAY	Br	Y ⁵	0	±0.06	[25]
YAKLEC	I	Y ⁵	0	±0.07	[25]
YAKPEG	Br	Y ⁶	0	±0.12	[25]
YAKPIK	I	Y ⁶	0	±0.11	[25]
1	OTf	Y ⁷	0	±0.28	t. w.
2	Cl	Y ⁷	0	±0.05	t. w.
3	Br	Y ⁷	0	±0.17	t. w.
4	I	Y ⁷	0	±0.15	t. w.
Bent AgP ₂ planes					
XIDZAL	Cl	Y ⁸	0.69	-0.038; 0.040	[35]
XIDZEP(1)	Br	Y ⁸	2.7	-0.01; +0.06	[35]
XIDZEP(2)	Br	Y ⁸	1.0	0; -0.01	[35]
XIDZIT	I	Y ⁸	2.4	-0.05; +0.10	[35]
Twisted AgP ₂ planes					
PPENAG	Cl	Y ²	41.8	n. a.	[39]
YAKMUT(1)	I	Y ²	22.8	n. a.	[25]
YIYMIC	I	Y ⁹	22.7	n. a.	[24]
YIYMOI	Cl	Y ⁹	42.5	n. a.	[24]
OTUGUG	I	Y ¹⁰	18.4	n. a.	[41]
1/3	Br/OTf	Y ⁷	25.7	n. a.	t. w.

t. w. = this work; n.a. = not applicable

Y¹: -CH₂CH₂SCH₂CH₂-; Y²: -(CH₂)₅-; Y³: ; Y⁴: ; Y⁵: -(CH₂)₄-;

Y⁶: -(CH₂)₆-; Y⁷: PhN(CH₂CH₂)₂; Y⁸: ; Y⁹: ; Y¹⁰: 

While searching for explanation why one of the observed conformations is preferred over another, we supposed that intramolecular non-classical hydrogen bonds may be involved. In some cases, indeed, we found relatively strong C–H···O, C–H···F (compound **1**, see Table 6) and C–H···Cl (compound **2**, see Table 6) interactions. However, this type of bonding in other complexes of the same group (e.g. KAXKOL, KAXKUR) seems to be much weaker as almost all the C–H···Cl distances fall outside the limit defined as a criteria for C–H···Cl bonding interactions (2.95 Å) [40]. The compilation in Table 7 also shows that the nature of the halogen bridge is not crucial as Cl, Br and I equally appear in all groups. It seems, however, that the chains linking the phosphorus donor groups have a strong influence on the structural properties as the chloro, bromo and iodo derivatives of a $[\text{Ag}_2\text{X}_2(\text{Ph}_2\text{PYPPH}_2)_2]$ complex tend to behave similarly, although an exception can be identified (see YAKMON vs. PPENAG and YAKMUT). Therefore we believe that intra- and intermolecular steric effects rather than intramolecular secondary bonds are important in determining the conformation of these macrocycles.

4. Conclusions

N,N-bis(2-(diphenylphosphanyl)ethyl)phenylamine, ($\text{PN}^{\text{Ph}}\text{P}$), forms dinuclear $[\text{Ag}_2\text{X}_2(\text{PN}^{\text{Ph}}\text{P})_2]$ complexes with AgX salts (X = OTf, Cl, Br, I), **1-4**, in which both the diphosphane ligands and the halide ions occupy bridging position. Single crystal X-ray diffraction studies on **1-4** showed that this diphosphane can span Ag···Ag distances over a wide range (3.83-5.12 Å), satisfying the requirements of the bridging inorganic ligands, which testifies the remarkable flexibility of the $\text{PN}^{\text{Ph}}\text{P}$ ligand. Solution phase NMR studies on mixed ligand $[\text{Ag}_2\text{X}^1\text{X}^2(\text{PN}^{\text{Ph}}\text{P})_2]$ bis-halide complexes proved in a simply and convincing way that these complexes preserve their dinuclear structure in solution. The analysis of the structural details of the $[\text{Ag}_2(\mu\text{-X})_2(\mu\text{-PN}^{\text{Ph}}\text{P})_2]$ complexes have shown that the linkages between the phosphorus donor atoms rather than intramolecular secondary bonding interactions govern the conformation of the macrocycles.

Acknowledgement

The authors thank the Research Centre for Natural Sciences of HAS and the University of Pannonia for their support and Dr. D. Csányi for recording spectra on Varian-500 instrument.

Appendix A. Supplementary data

Further supplementary data associated with this article are presented in the Supporting Information (Figs. S1–S21 and Tables S1-S2). CCDC 1517416-1517421 contain the supplementary crystallographic data for **1-4**, **1/3** and the unpublished Pd complex (Ref. 28). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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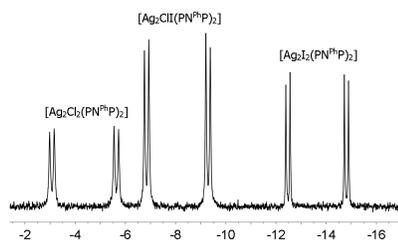
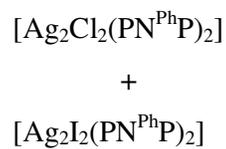
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Table 4Selected bond lengths (Å) and bond angles (°) for **1** and **1/3**.

	1	1/3
	[$a = 2-x, -y, 1-z$]	
Ag1-Br1		2.735(2)
Ag2-Br1		2.710(1)
Ag1-O1	2.484(1)	2.610(7)
Ag1-O2 _a	2.663(1)	
Ag2-O2		2.609(9)
S1-O1	1.450(1)	1.425(7)
S1-O2	1.445(1)	1.409(9)
S1-O3	1.440(1)	1.428(8)
Ag1-Br1-Ag2		116.87(4)

^{31}P NMR spectra of mixtures offer a convenient way to prove the dimeric nature of $[\text{Ag}_2\text{X}_2(\text{PN}^{\text{Ph}}\text{P})_2]$ complexes in solution.



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