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## PAPER

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Diallylaminoarenes: a new class of versatile ligands for silver(ı) that consistently lead to one-dimensional polymeric metallosupramolecular assemblies<sup>†</sup>

Ligands comprised of a diallylamino group attached to a phenyl, 2-pyridyl, 2-pyrimidyl, 2-thiazolyl and 2-quinolyl ring react with silver(i) salts (perchlorate and/or triflate) to faithfully assemble into 1-D coordination polymers,

regardless of variation in the number of additional nitrogen donors, the counterion and the coordination number

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(three to five) of the silver atoms.

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## Introduction

Metallosupramolecular chemistry<sup>1</sup> involves the use of bridging organic ligands and metal atoms to assemble discrete or 1-, 2- or 3-D polymeric species.<sup>2-8</sup> We have long been engaged in the synthesis and study of bridging heterocyclic ligands as synthons for the preparation of a diverse range of metallosupramolecular assemblies, including discrete cages and helicates, as well as coordination polymers of varying dimensionality.<sup>6,9-12</sup> Although alkenes have long been known to bind to silver(1),<sup>13</sup> this interaction has, until recently, been curiously ignored as a synthon for metallosupramolecular chemistry. Following our initial explorations in this area,<sup>14,15</sup> we, and others,<sup>16-24</sup> have shown that the use of bridging ligands containing multiple alkene subunits are indeed useful synthons for the assembly of both discrete and polymeric species.<sup>25</sup> To date, ligands containing vinyl, allyl and allyloxy groups as donors for coordination to silver(1) have been used.<sup>25</sup> We now extend this design concept to the first study of diallylaminoarenes as ligands for silver(1). Four of these contain heterocyclic nitrogen atoms that offer the possibility of additional  $\sigma$ -donation to silver, in concert with the  $\pi$ -donation from the alkene groups.

## **Results and discussion**

The structures of the ligands employed in this study are shown in Fig. 1. They were prepared by reaction of the corresponding aminoarene with two equivalents of allyl bromide in THF in the presence of sodium hydride. The ligands were isolated as yellow oily liquids in 46–97% yield after column chromatography on silica gel and were characterised by <sup>1</sup>H and <sup>13</sup>C NMR, infrared spectroscopy and mass spectrometry. A number of other diallylaminoarenes, which failed to furnish crystalline silver complexes, were also prepared and their preparations and spectral properties are also included in the experimental section.

The ligands were each reacted with two equivalents of a silver salt in acetone or toluene, in the dark. Subsequent diffusion of diethyl ether into the reaction vial provided crystalline products in 36–83% yield. Single crystal X-ray structure determinations showed the consistent formation of 1-D coordination polymers with 1:1 metal:ligand stoichiometry. Attempts to further characterise these complexes using NMR and mass spectrometry, led only to signals for the starting ligands, indicating that the 1-D polymers lost their integrity upon redisolution in solvent such as acetonitrile. This is consistent with our previous studies showing that the silver-alkene interaction is relatively weak.<sup>14,15,25</sup>

The product (6) from the reaction of *N*,*N*-diallylaniline (1) with silver(1) perchlorate crystallises in the orthorhombic space group  $P2_12_12_1$ , with one molecule of (1), a coordinated silver atom and a non-coordinated perchlorate anion in the asymmetric unit. The structure grows into a 1-D zigzag polymeric assembly through the coordination of the two allyl arms in a chelating mode and bridging through the *para* carbon atom of the benzene ring coordinated in a  $\eta^1$ -mode, as shown in Fig. 2. Such  $\eta^1$ -coordination of silver with polycyclic aromatic hydrocarbons has been well studied by Munakata and co-workers.<sup>26</sup> In the present case we believe that the amine group donates electron density into the phenyl ring resulting in a higher electron density at the *para* position, thereby promoting coordination with silver. Such electron delocalisation also explains why the amino nitrogen does not

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Fig. 1 Ligands employed in this study.



Fig. 2 A section of the 1-D zigzag polymer of (6). Hydrogen atoms omitted for clarity.

coordinate to silver in most of the structures described below. A mixed  $\eta^1$ -phenyl/ $\eta^2$ -alkenyl coordination to silver has been reported in the mononuclear complex of 4-phenylbut-1-ene.<sup>27</sup> However, in that case the  $\eta^1$ -coordination was supported by chelation and the  $\eta^1$ -interaction was somewhat weaker than in the present case, with Ag–C bond lengths of 2.547(6) and 2.692(5) Å, compared to 2.454(2) Å in complex (6) (Table 1).

An interesting feature of the structure is that the phenyl ring and both the allyl arms are coordinated from the same face of the ligand, which leads to the zigzag shape of the polymer, with the perchlorate counterions lying in the spaces between the silvers. The silver atom has a slightly distorted trigonal planar geometry with bond angles ranging between 115.1(2) and 125.7(2)°. The bond distances to the alkene groups lie within the normal range for such interactions.<sup>25</sup> Thus, the ligand (1) acts as an ambivergent<sup>28</sup> ligand in both chelating and bridging modes, with adjacent silver atoms separated by 6.304(1) Å.

The packing of the 1-D chains shows various intermolecular interactions involving the anions, the phenyl  $\pi$ -systems and CH groups. All of these are relatively weak and play no obvious role in the self-assembly of the structure. The same applies to the other 1-D polymers described below.

A similar reaction of 2-(diallylamino)-pyridine (2) with silver(1) perchlorate gave a complex (7) that crystallises in the monoclinic space group  $P2_1/n$ . The asymmetric unit contains one molecule of (2), one silver atom and a coordinated perchlorate anion. Once again the structure grows into a 1-D polymeric assembly, involving the coordination of one of the allyl arms and the pyridyl nitrogen in a chelating mode, while the other allyl arm coordinates to a neighbouring silver atom in a bridging mode (Fig. 3). In this case the two allyl arms coordinate from opposite faces of the pyridine ring, leading to an increased separation distance between adjacent silver atoms of 8.219(1) Å.

The silver is four coordinate, being bound to two allyl arms of different ligands, the pyridyl nitrogen and an oxygen atom of the perchlorate anion. The calculated  $\tau_4$  value<sup>29</sup> for silver is 0.76, indicating a seesaw geometry. All the silver–carbon bond distances are within the expected range for silver–olefin  $\eta^2$ -type interactions.<sup>25</sup>

The complex (8) of 2-(diallylamino)-pyrimidine (3) with silver(1) perchlorate crystallises in the orthorhombic space group  $P2_12_12_1$ . The asymmetric unit (Fig. 4a) contains two full molecules of (3), two silver atoms, one non-coordinated perchlorate anion and two half perchlorate anions that lie on a two-fold rotation axis. The diallylamine group of one of the ligand molecules in the asymmetric unit has disorder over two sites with 55% dominant position occupancy.

Once again the complex has 1:1 metal: ligand stoichiometry and extends into a 1-D zigzag polymeric chain, involving the coordination of both nitrogen atoms of the pyrimidine ring and the allyl arms of the ligand with two crystallographically independent silver atoms (Fig. 4b). The two silver atoms are four coordinate, being bound to two allyl groups and two nitrogen atoms from different ligands and have  $\tau_4$  values of 0.74 and 0.68 for Ag1 and Ag2, respectively, indicating seesaw geometries. In this case adjacent silver atoms in the chain are separated by the two independent ligands at distances of 6.662(1) and 6.678(1) Å.

Ligand (3) was also reacted with silver(i) triflate to produce a complex (9) that crystallises in the orthorhombic space group  $P2_12_12_1$ . The asymmetric unit contains two molecules of (3), two silver atoms, a coordinated water molecule and two non-coordinated triflate anions. The structure (Fig. 5) extends into a 1-D polymer with (3) acting as a doubly chelating bridging ligand, as was its role in complex (8). However, due to the coordinated water molecule the two silvers have different coordination numbers; Ag1 is four coordinate, with a seesaw geometry ( $\tau_4 = 0.74$ ), while Ag2 is five coordinate with a  $\tau_5$  value<sup>30</sup> of 0.14, indicating a slightly distorted square pyramidal geometry, with an allyl group occupying the apical position. Because of the higher coordination number of Ag2, the Ag–C bond distances are slightly greater than those seen in the previous structures.

Within this metallopolymer ligand (3) acts in the same ambivergent mode as in the silver perchlorate complex (8). Due to the presence of two independent bridging ligands, there are two different Ag1...Ag2 separation distances, 6.697(1) and 6.865(1) Å. The coordinated water molecule acts as a hydrogen bond donor to two oxygens of the noncoordinated triflate anions, with O...O separations of 2.727(4)and 2.810(4) Å.

2-(Diallylamino)-thiazole (4) failed to furnish a crystalline product from reaction with silver(i) perchlorate, but did do so with silver(i) triflate. This compound (10) crystallised in the triclinic space group  $P\bar{1}$ , the asymmetric unit of which

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Table 1 Selected bo	nd lengths â	and angles. Note: CX/Y rep	presents the r	midpoint of the bond b	etween CX a	and CY					
(9)		(2)		(8)		(6)		(10)		(11)	
Ag1-C8/9	2.331(2)	Ag1-01	2.454(2)	Ag1-N2	2.344(1)	Ag1-C16/17	2.367(3)	Ag1-N1	2.205(3)	Ag1-N1	2.240(4)
Ag1-C11/12	2.354(2)	Ag1-N1	2.402(2)	Ag1-N4	2.417(2)	Ag1-N4	2.379(3)	Ag1-C5/6	2.300(2)	Ag1-N2	2.327(2)
Ag1-C3	2.454(2)	Ag1-C10/11	2.363(2)	Ag1-C11/12	2.319(1)	Ag1-C9/10	2.321(3)	Ag1-C14A/15A	2.221(3)	Ag1-C14/15	2.206(2)
1		Ag1–C7A/8A	2.338(2)	Ag1-C5/6	2.339(2)	Ag1-N2	2.424(2)	Ag2-C8/9	2.260(2)	1	I
I		1	;	Ag2-N5	2.333(2)	Ag2-C19/20	2.373(3)	Ag2-N3	2.235(3)		Ι
I		I		Ag2-C15/16	2.368(1)	Ag2-N5	2.588(2)	Ag2-C17/18	2.301(2)		
I				Ag2-N1	2.424(2)	Ag2-07	2.399(3)				
1		I		Ag2-C1/2	2.328(2)	Ag2-C6/7	2.516(3)				
		1		1		Ag2-N1	2.441(2)	1			
C8/9-Ag1-C11/12	117.4(2)	01-Ag1-N1	99.9(2)	N2-Ag1-N4	104.4(4)	C16/17-Ag1-N4	87.3(2)	N1-Ag1-C5/6	98.1(3)	N1-Ag1-N2	76.8(1)
C8/9-Ag1-C3	125.7(2)	01-Ag1-C10/11	114.4(2)	N2-Ag1-C11/12	122.0(4)	C16/17-Ag1-C9/10	128.5(1)	N1-Ag1-C14A/15A	126.6(2)	N1-Ag1-C14/15	137.6(3)
C11/12-Ag1-C3	115.1(2)	O1-Ag1-C7A/8A	98.6(1)	N2-Ag1-C5/6	90.1(3)	C16/17-Ag1-N2	117.0(1)	C5/6-Ag1-C14A/15A	135.1(4)	N2-Ag1-C14/15	144.6(3)
1		N1-Ag1-C10/11	87.6(1)	N4-Ag1-C11/12	85.9(3)	N4-Ag1-C9/10	137.5(1)	C8/9-Ag2-C17/18	135.7(2)	1	I
1		N1-Ag1-C7A/8A	118.1(1)	N4-Ag1-C5/6	126.5(2)	N4-Ag1-N2	91.6(2)	N3-Ag2-C8/9	125.6(2)	1	I
I		C10/11-Ag1-C7A/8A	134.5(2)	C11/12-Ag1-C5/6	128.8(3)	C9/10-Ag1-N2	90.9(2)	N3-Ag2-C17/18	98.2(2)	1	I
1				N5-Ag2-C15/16	88.9(3)	C19/20-Ag2-N5	82.9(1)			1	
1				N5-Ag2-N1	98.0(3)	C19/20-Ag2-O7	118.2(1)			1	I
I				N5-Ag2-C1/2	117.2(2)	C19/20-Ag2-C6/7	120.4(1)			1	
1				C15/16-Ag2-C1/2	146.1(2)	C19/20-Ag2-N1	109.9(1)			1	
		I		N1-Ag2-C1/2	81.6(3)	N5-Ag2-07	76.7(2)				
1				I		N5-Ag2-C6/7	84.4(2)			1	I
1				I		N5-Ag2-N1	92.9(2)			1	I
1						07-Ag2-C6/7	84.4(1)			1	I
1				1		07-Ag2-N1	128.6(1)				
1	Ι	I	Ι	I	Ι	C6/7-Ag2-N1	86.7(2)	1	Ι		I

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Fig. 3 A section of the 1-D polymer of (7). Hydrogen atoms omitted for clarity.



Fig. 4 (a) The asymmetric unit of complex (8). (b) A section of the 1-D polymer of (8). Hydrogen atoms, counterions and the minor disorder components omitted for clarity.



Fig. 5 A section of the 1-D polymer of (9). Hydrogen atoms (except for the water molecule) and counterions omitted for clarity.

contains two full molecules of (4), two silver atoms and two non-coordinated triflate counterions. One of the triflate anions, the diallylamine of one of the ligand molecules, the thiazole sulfur atom and one of the allyl arms of the second ligand molecule are disordered over two sites. The dominant site occupancy of the diallyl arm, the thiazole sulfur and the allyl arm of the other ligand is 63%, while for the triflate counter anion it is 80%.

The complex (10) again extends into a 1-D coordination polymer (Fig. 6) with, for each ligand, the thiazole nitrogen and one allyl arm chelating to silver, while the other allyl arm acts as a bridge to the next silver. This mode of ligand coordination is similar to that observed for the 2-pyridyl analogue (7). The sulphur atom is not coordinated. The two crystallographically independent ligands bridge silver atoms separated by 8.042(1) and 7.952(1) Å. Both three coordinate silver atoms have distorted trigonal planar geometries, with angles ranging between 98.1(3) and  $135.7(2)^{\circ}$ .

Finally, 8-(diallylamino)-quinoline (5) was reacted with silver(1) perchlorate to produce a complex (11) in the monoclinic space group  $P2_1/n$ . The asymmetric unit contains one full molecule of (5), one silver atom and a non-coordinated perchlorate anion and again extends into a 1-D coordination polymer. However, in this case the mode of coordination by the ligand is somewhat different. For the first time the diallylamino nitrogen atom is found to coordinate to the metal. We believe that this is for two reasons: coordination of silver to the quinoline nitrogen atom would prevent the diallylamino group lying coplanar with the quinoline ring (and hence prevent donation of the lone pair of the amino group into the quinoline ring system), whilst at the same time offering the possibility of the formation of a stable fivemembered chelate ring involving both nitrogens of the ligand. As a consequence the ligand sacrifices one of its allyl arms, which remains non-coordinated, whilst the other arm bridges to an adjacent silver (Fig. 7). The silver atom is again three coordinate but with a highly distorted trigonal geometry, due to the five-membered chelate ring which has a bite angle of 76.8(1)°.



Fig. 6 A section of the 1-D polymer of (10). Hydrogen atoms, the minor disorder component and anions for clarity.



Fig. 7 A section of the 1-D polymer of (11). Hydrogen atoms and counterions omitted for clarity.

### **Experimental section**

#### General

Unless otherwise specified, all reagents and starting materials were reagent grade, purchased from standard suppliers and used as received. Where anhydrous solvents were required, the HPLC-grade solvent was either distilled from standard drying agents or dried by passing over a sealed column of activated alumina. Melting points were recorded on an Electrothermal melting point apparatus and are uncorrected. Elemental analysis was carried out by the Campbell Microanalytical Laboratory, University of Otago.

Infrared spectra were recorded on a PerkinElmer Spectrum One FTIR instrument operating in diffuse reflectance mode with samples prepared as KBr mulls (KBr), or in transmittance mode with liquid samples pressed between KBr discs (neat). NMR spectra were recorded on a Varian INOVA 500 or Varian Unity 300 instrument, operating at 500 and 300 MHz, respectively, for <sup>1</sup>H, and 125 and 75 MHz, respectively, for <sup>13</sup>C. Mass spectra were recorded on either a DIONEX Ultimate 3000 or Bruker MaXis 4G spectrometer, both of which were operated in high resolution positive ion electrospray mode. Samples were dissolved and diluted to the required concentration in HPLC grade acetonitrile or methanol.

#### Preparation of ligands

General procedure (based on Huang's reported<sup>31</sup> preparation of ligand 1). Two equivalents of allylbromide were added to a mixture of one equivalent of the corresponding amine and NaH in 60 ml of dry THF. The resulting solution was refluxed for three days and quenched with 10% ammonium chloride solution. The organic layer was extracted with  $3 \times 50$  ml of diethyl ether and the extracts were washed with water and brine solutions, respectively. The resulting solution was dried over MgSO<sub>4</sub>, filtered and the solvent removed under vacuum. The product was then purified by column chromatography using silica gel (60 mesh, 200–300) and 5:95 ethyl acetate:petroleum ether to give the products as yellow or red oils.

*N*,*N*-Diallylaniline (1). Yield: 97%. <sup>1</sup>H NMR (300 MHZ, CDCl<sub>3</sub>): δ 3.95 (4H, d, J = 4.8 Hz, H5), 5.14–5.21 (4H, m, H7), 5.82–5.94 (2H, m, H6), 6.62 (1H, t, J = 7.2 Hz, H1), 6.69 (2H, d, J = 9.0 Hz, H3), 7.16 (2H, dd, J = 9.0, 7.2 Hz, H2). <sup>13</sup>C NMR (75 MHz): δ 52.85 C5, 112.45 C3, 116.04 C7, 116.38 C1, 129.17 C2, 134.17 C6, 148.83 C4. *IR* (cm<sup>-1</sup>) 3090, 3056, 2956, 1690, 1643, 1599, 1505, 1232, 1181, 989, 919, 745. ESI-MS: found MH<sup>+</sup> = 174.1277; C<sub>12</sub>H<sub>16</sub>N requires MH<sup>+</sup> = 174.1277.



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2-(Diallylamino)-pyridine (2). Yield: 92%. <sup>1</sup>H NMR (300 MHZ, CDCl<sub>3</sub>):  $\delta$  4.11 (4H, d, J = 5.0 Hz, H6), 5.12–5.17 (4H, m, H8), 5.82–5.90 (2H, m, H7), 6.46 (1H, d, J = 8.5 Hz, H4), 6.52 (1H, dd, J = 6.5, 5.5 Hz, H2), 7.39 (1H, dd, J = 8.5, 7.5 Hz, H3), 8.15 (1H, d, J = 6.0 Hz, H1). <sup>13</sup>C NMR (126 MHz):  $\delta$  50.04 C6, 106.04 C4, 111.78 C2, 115.99 C8, 133.96 C7, 137.11 C3, 147.88 C1, 157.97 C5. *IR* (cm<sup>-1</sup>) 3076, 3008, 2918, 2980, 2524, 2376, 2266, 1931, 1846, 1722, 1641, 1595, 1560, 1491, 1436, 1416, 1391, 1359, 1317, 1279, 1244, 1186, 1160, 1130, 1094, 1070, 1055, 1023, 993, 978, 919, 768, 732. ESI-MS: found MH<sup>+</sup> = 175.1229; C<sub>11</sub>H<sub>15</sub>N<sub>2</sub> requires MH<sup>+</sup> = 175.1230.



2-(Diallylamino)-pyrimidine (3). Yield: 46%. <sup>1</sup>H NMR (300 MHZ, CDCl<sub>3</sub>):  $\delta$  4.21 (4H, d, J = 5.4 Hz, H4), 5.09–5.15 (4H, m, H6), 5.78–5.91 (2H, m, H5), 6.44 (1H, t, J = 4.8 Hz, H1), 8.29 (2H, d, J = 4.8 Hz, H2). <sup>13</sup>C NMR (75 MHz):  $\delta$  49.00 C4, 109.81 C1, 116.32 C6, 134.06 C5, 158.05 C2, 161.72 C3. *IR* (cm<sup>-1</sup>) 3078, 3027, 2982, 2924, 2854, 1848, 1766, 1641, 1585, 1547, 1505, 1414, 1387, 1361, 1346, 1315, 1268, 1221, 1180, 1084, 1031, 994, 980, 920, 798, 780, 688. ESI-MS: found MH<sup>+</sup> = 176.1179; C<sub>10</sub>H<sub>14</sub>N<sub>3</sub> requires MH<sup>+</sup> = 176.1182.



2-(Diallylamino)-thiazole (4). Yield 82%. <sup>1</sup>H NMR (300 MHZ, CDCl<sub>3</sub>):  $\delta$  4.06 (4H, d, J = 5.7 Hz, H4), 5.18–5.24 (4H, m, H6), 5.79–5.89 (2H, m, H5), 6.46 (1H, d, J = 3.6 Hz, H2), 7.15 (1H, d, J = 3.6 Hz, H1). <sup>13</sup>C NMR (126 MHz):  $\delta$  53.26 C4, 106.55 C2, 117.96 C6, 132.60 C5, 139.60 C1, C3 not observed. *IR* (cm<sup>-1</sup>) 3475, 3079, 2923, 1717, 1641, 1531, 1417, 1364, 1310, 1225, 1198, 1126, 1055, 992, 925, 749. ESI-MS: found MNa<sup>+</sup> = 203.0622; C<sub>9</sub>H<sub>12</sub>N<sub>2</sub>SNa requires MNa<sup>+</sup> = 203.0613.



8-(Diallylamino)-quinoline (5). Yield: 88%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  4.16 (4H, d, J = 6.3 Hz, H7), 5.13 (2H, dd, J = 10.3, 1.4 Hz, H9), 5.18 (2H, dd, J = 17.5, 1.4 Hz, H9'), 5.86–6.00 (2H, m, H8), 7.10 (1H, dd, J = 6.5, 2.5 Hz, H6), 7.32–7.40 (3H, m, H2, H4, H5), 8.08 (1H, dd, J = 8.4, 1.8 Hz, H3), 8.89 (1H, dd, J = 4.2, 1.8 Hz, H1). <sup>13</sup>C NMR (126 MHz):

δ 55.80 C7, 117.67 C9, 118.78 C4, 121.04 C6, 121.12 C5, 126.53 C2, 129.99 C12, 135.43 C8, 136.70 C3, 143.29 C11, 147.59 C10, 148.11 C1. *IR* (cm<sup>-1</sup>) 3073, 2977, 1841, 1662, 1640, 1607, 1595, 1566, 1499, 1470, 1390, 1242, 1100, 918, 791. ESI-MS: found MNa<sup>+</sup> = 247.1218; C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>Na requires MNa<sup>+</sup> = 247.1206.

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4-(N,N-Diallylamino)azobenzene. Yield: 65%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  4.02 (4H, d, J = 4.5 Hz, H9), 5.17–5.22 (4H, m, H11), 5.84–5.92 (2H, m, H10), 6.76 (2H, d, J = 9.0 Hz, H7), 7.38 (2H, dd, J = 7.0, 7.5 Hz, H2), 7.47 (1H, t, J = 8.0 Hz, H1), 7.83–7.86 (4H, m, H3, H6). <sup>13</sup>C NMR (126 MHz):  $\delta$  53.05 C9, 112.00 C7, 116.70 C11, 122.44 C3, 125.21 C6, 129.17 C2, 129.63 C1, 133.13 C10, 144.11 C5, 151.32 C8, 153.47 C4. *IR* (cm<sup>-1</sup>) 3081, 3008, 2980, 2909, 2642, 1700, 1642, 1600, 1566, 1513, 1461, 1448, 1435, 1414, 1392, 1356, 1334, 1313, 1236, 1177, 1155, 1140, 1069, 1019, 990, 921, 821, 767, 723, 689. ESI-MS: found MNa<sup>+</sup> = 300.1473; C<sub>18</sub>H<sub>19</sub>N<sub>3</sub>Na requires MNa<sup>+</sup> = 300.1471.



1,3-Bis(N,N-diallyamino)benzene. Yield: 53%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  3.91(8H, d, J = 5.0 Hz, H5), 5.16 (4H, dd, J = 10.0, 1.5 Hz, H7), 5.21 (4H, dd, J = 17.0, 1.5 Hz, H7'), 5.84–5.91 (4H, m, H6), 6.10–6.14 (3H, m, H2, H4), 7.05 (1H, t, J = 8.0 Hz, H1). <sup>13</sup>C NMR (126 MHz):  $\delta$  53.25 C5, 97.44 C4, 101.95 C2, 116.12 C7, 129.75 C1, 134.87 C6, 150.14 C3. *IR* (cm<sup>-1</sup>) 3077, 3005, 2924, 2853, 1838, 1641, 1603, 1571, 1505, 1459, 1416, 1357, 1335, 1288, 1248, 1205, 1179, 1128, 1042, 991, 960, 916, 809, 744, 687. ESI-MS: found MH<sup>+</sup> = 269.2018; C<sub>18</sub>H<sub>25</sub>N<sub>2</sub> requires MH<sup>+</sup> = 269.2012.



1,4-Bis(N,N-diallyamino)benzene. Yield: 78%. <sup>1</sup>H NMR

(300 MHz, CDCl<sub>3</sub>):  $\delta$  3.83 (8H, d, J = 3.9 Hz, H3), 5.14 (4H, dd, J = 10.2, 1.5 Hz, H5), 5.20 (4H, dd, J = 17.4, 1.5 Hz, H5'),

5.80-5.91 (4H, m, H4), 6.70 (4H, s, H1). <sup>13</sup>C NMR (75 MHz,

 $CDCl_3$ ):  $\delta$  54.06 C3, 115.42 C1, 116.43 C5, 135.19 C4,

142.00 C2. IR (cm<sup>-1</sup>) 3077, 3005, 2977, 2912, 1842, 1641,

1612, 1517, 1417, 1356, 1333, 1285, 1231, 1182, 1068, 992,

917, 805, 725. ESI-MS: found MNa<sup>+</sup> = 291.1838;  $C_{18}H_{24}N_2Na$  requires MNa<sup>+</sup> = 291.1832.



**1,5-Bis(N,N-diallyamino)naphthalene.** Yield: 70%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  3.79 (8H, d, J = 6.0 Hz, C6), 5.15 (4H, dd, 10.2, 1.5 Hz, H8), 5.25 (4H, dd, 17.1, 1.5 Hz, H8'), 5.82–5.95 (4H, m, H7), 7.08 (2H, d, J = 7.5 Hz, H2), 7.39 (2H, dd, J = 7.5, 8.1 Hz, H3), 8.04 (2H, d, J = 8.4 Hz, H4). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  56.28 C6, 117.10 C8, 117.60 C2, 119.27 C4, 124.70 C3, 131.58 C5, 135.22 C7, 148.06 C1. *IR* (cm<sup>-1</sup>) 3075, 3007, 2978, 2923, 2814, 1847, 1642, 1588, 1505, 1436, 1409, 1357, 1239, 1203, 1174, 1145, 1105, 1034, 992, 919, 785. ESI-MS: found MH<sup>+</sup> = 319.2168; C<sub>22</sub>H<sub>27</sub>N<sub>2</sub> requires MH<sup>+</sup> = 319.2169.



2,7-Bis(N,N-diallyamino)naphthalene. Yield: 45%. <sup>1</sup>H NMR (300 MHz, DMSO):  $\delta$  4.01 (8H, *d*, *J* = 4.8 Hz, H5), 5.16–5.24 (8H, *m*, H7), 5.86–5.98 (4H, *m*, H6), 6.68 (2H, *s*, H4), 6.81 (2H, *d*, *J* = 9.0 Hz, H2), 7.48 (2H, *d*, *J* = 9.0 Hz, H1). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  52.79 C5, 104.69 C4, 112.40 C2, 116.06 C7, 128.35 C1, 134.26 C6, 147.14 C3, C7 and C8 not observed. *IR* (cm<sup>-1</sup>) 3079, 3006, 2978, 2907, 1842, 1738, 1624, 1518, 1475, 1430, 1399, 1358, 1288, 1251, 1217, 1194, 1129, 1022, 991, 951, 917, 846, 813, 748. ESI-MS: found MH<sup>+</sup> = 319.2180; C<sub>22</sub>H<sub>27</sub>N<sub>2</sub> requires MH<sup>+</sup> = 319.2169.



Preparation of complexes

General procedure. A solution of one equivalent of the diallylaminoarene dissolved in acetone was added to an acetone solution of the silver salt. Diffusion of diethyl ether into the mixture at room temperature in the dark led to the formation of colourless crystals of the complexes listed below.

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 $[Ag(1)ClO_4]_n$  (6): Yield: 54%. *M.p.* 123–125 °C. *IR* (cm<sup>-1</sup>) 3056, 2978, 2918, 2868, 2610, 2016, 1642, 1598, 1546, 1505, 1458, 1421, 1340, 1234, 1096, 989, 952, 823, 749, 695, 626. Elem. anal. found: C, 37.99; H, 4.03; N, 3.95. Calc. for  $C_{12}H_{15}NAgClO_4$ : C, 37.87; H, 3.97; N, 3.68.

[Ag(2)ClO<sub>4</sub>]<sub>n</sub> (7): Yield: 74%. *M.p.* 89–91 °C. *IR* (cm<sup>-1</sup>) 3060, 3008, 2918, 2862, 2021, 1648, 1599, 1547, 1490, 1438, 1245, 1094, 979, 941, 768, 734, 627. Elem. anal. found: C, 34.93; H, 3.77; N, 6.78. Calc. for  $C_{11}H_{14}N_2AgClO_4$ : C, 34.63; H, 3.70; N, 7.34.

[Ag(3)ClO<sub>4</sub>]<sub>n</sub> (8): Yield: 42%. *M.p.* 219–221 °C. *IR* (cm<sup>-1</sup>) 3078, 2982, 2913, 2013, 1641, 1586, 1547, 1507, 1415, 1388, 1362, 1269, 1087, 981, 941, 816, 798, 781, 690, 626. Elem. anal. found: C, 30.67; H, 3.24; N, 10.49. Calc. for  $C_{10}H_{13}N_3AgClO_4.0.5H_2O$ : C, 30.67; H, 3.60, N, 10.73.

 $[Ag(3)OTf]_n$  (9): Yield: 83%. *M.p.* 151–153 °C. *IR* (cm<sup>-1</sup>) 3507, 3083, 3009, 2907, 2288, 1643, 1586, 1548, 1508, 1429, 1387, 1364, 1254, 1180, 1113, 1084, 1033, 993, 966, 944, 798, 688, 639, 576, 519. Elem. anal. found: C, 30.60; H, 2.96; N, 9.51. Calc. for  $C_{10}H_{13}N_3AgSO_3CF_3$ : C, 30.57; H, 3.03; N, 9.72.

[Ag(4)OTf]<sub>n</sub> (10): Yield: 36%. *M.p.* 109–111 °C. *IR* (cm<sup>-1</sup>) 3716, 3637, 3079, 3011, 2982, 2905, 1722, 1641, 1623, 1531,

1490, 1434, 1418, 1248, 1174, 1049, 992, 927, 861, 767, 750, 656, 610, 579, 521. Elem. anal. found: C, 27.40; H, 2.68; N, 6.31. Calc. for  $C_9H_{12}N_2SAgSO_3CF_3$ : C, 27.47; H, 2.77; N, 6.41.

 $[Ag(5)ClO_4]_n$  (11): Yield: 59%. *M.p.* 149–151 °C. *IR* (cm<sup>-1</sup>) 3547, 3474, 3413, 3047, 2854, 1716, 1637, 1536, 1485, 1428, 1351, 1265, 1235, 1147, 1110, 1089, 941, 828, 760, 660, 627. Elem. anal. found: C, 41.45; H, 3.78; N, 6.21. Calc. for  $C_{15}H_{16}N_2AgClO_4$ : C, 41.74; H, 3.74; N, 6.49.

#### Crystallography

X-Ray crystallographic data collection was carried out with a Bruker APEXII instrument, using graphite-monochromated Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation All structures were solved using direct methods with SHELXS and refined on *F*2 using all data by full matrix least-squares procedures with SHELXL.<sup>32</sup> Unless otherwise stated all non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 or 1.5 times the isotropic equivalent of their carrier carbon atoms. Experimental details are listed in Table 2.

#### Table 2 X-Ray experimental details

Complex	(6)	(7)	(8)	(9)	(10)	(11)
Empirical formula	C <sub>12</sub> H <sub>15</sub> NO <sub>4</sub> ClAg	C <sub>11</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub> ClAg	C <sub>20</sub> H <sub>26</sub> N <sub>6</sub> O <sub>8</sub> Cl <sub>2</sub> Ag <sub>2</sub>	C <sub>22</sub> H <sub>28</sub> N <sub>6</sub> O <sub>7</sub> F <sub>6</sub> S <sub>2</sub> Ag <sub>2</sub>	C <sub>20</sub> H <sub>24</sub> N <sub>4</sub> O <sub>6</sub> F <sub>6</sub> S <sub>4</sub> Ag <sub>2</sub>	C <sub>15</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> ClAg
Formula weight	380.57	381.56	765.11	882.36	874.41	431.62
Temperature/K	115	114	114	114	117	116
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_{1}2_{1}2_{1}$	$P2_1/n$	P21212	P212121	$P\bar{1}$	$P2_1/n$
Unit cell dimensions:						
a/Å	8.8079(4)	12.6852(4)	15.3229(9)	11.6969(3)	7.8652(3)	12.1378(4)
b/Å	12.2447(4)	8.1924(3)	21.2905(11)	12.9740(3)	14.0587(5)	10.7654(3)
c/Å	12.5250(6)	12.8192(5)	8.0381(4)	20.0150(5)	14.8864(6)	13.2121(4)
$\alpha / ^{\circ}$	90	90	90	90	113.746(2)	90
βl°	90	99.738(2)	90	90	92.329(2)	111.584(2)
y/°	90	90	90	90	90.687(2)	90
Volume/Å <sup>3</sup>	1350.82(10)	1313.00(8)	2622.3(2)	3037.39(13)	1504.73(10)	1605.35(8)
Ζ	4	4	4	4	2	4
Density (calculated)	1.871	1.930	1.938	1.930	1.930	1.786
$Mg m^{-3}$						
Absorption	1.698	1.749	1.754	1.516	1.658	1.443
coefficient mm <sup>-1</sup>						
F(000)	760	760	1520	1752	864	864
Crystal size/mm <sup>3</sup>	0.30  imes 0.18  imes	0.70 imes 0.68 imes	0.29  imes 0.09  imes	$0.36 \times 0.09 \times$	$0.49 \times 0.30 \times$	0.50  imes 0.32  imes
•	0.13	0.33	0.06	0.06	0.10	0.10
Theta range for data collection (°)	5.7 to 55.0°	5.92 to 52.9°	3.82 to 52.8°	4.04 to 50.1°	5.16 to 53.97°	5.22 to 50.1°
Reflections collected	31 161	26 401	14 890	58 870	30 605	28656
Independent	3097[0.0537]	2682[0.0329]	5371[0.0355]	5366[0.0623]	6154[0.0442]	2846[0.0597]
reflections [R(int)]						
Completeness %	100	100	100	100	100	100
Data/restraints/parameters	3097/0/173	2682/0/172	5371/24/399	5366/0/414	6154/0/455	2846/0/218
Goodness-of-fit on $F^2$	1.054	1.105	0.935	0.994	1.250	0.981
Final R <sub>1</sub> indices	$R_1 = 0.0181,$	$R_1 = 0.0216$ ,	$R_1 = 0.0478,$	$R_1 = 0.0210,$	$R_1 = 0.0451,$	$R_1 = 0.0362,$
$[I > 2\sigma(I)]$	$wR_2 = 0.0448$	$wR_2 = 0.0564$	$wR_2 = 0.1080$	$wR_2 = 0.0423$	$wR_2 = 0.1241$	$wR_2 = 0.1012$
Final <i>R</i> indices	$R_1 = 0.0190,$	$R_1 = 0.0236,$	$R_1 = 0.0832,$	$R_1 = 0.0237,$	$R_1 = 0.0578,$	$R_1 = 0.0494,$
[all data]	$wR_2 = 0.0451$	$wR_2 = 0.0580$	$wR_2 = 0.1199$	$wR_2 = 0.0431$	$wR_2 = 0.1297$	$wR_2 = 0.1068$
Largest diff.	0.37/-0.44	0.43/-0.66	0.91/-0.60	0.46/-0.33	1.38/-1.24	0.98 / -0.45
peak/hole/e Å <sup>-3</sup>						
Flack parameter where	-0.04(2)	_	0.05(2)	-0.02(2)	_	_
applicable	. /					



Fig. 8 Coordination modes adopted by the ligands.

## Conclusions

We have shown that ligands containing a diallylamino group attached to a (hetero)aromatic ring represent versatile synthons for silver-based metallosupramolecular synthesis. Despite the fact that the five ligands studied exhibit a variety of coordination modes (Fig. 8), they faithfully assemble into 1-D coordination polymers, regardless of the number of additional nitrogen donors, by adjusting the coordination requirements of the highly flexible d<sup>10</sup> silver atom.

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