In situ recrystallisation of a coordination polymer with hemilabile linkers

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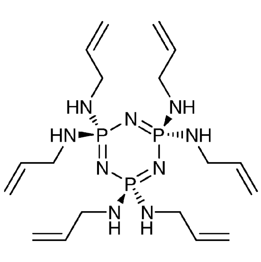
The variable coordination pattern of a hemilabile phosphazene ligand equipped with six pendent olefin groups facilitates the *in situ* recrystallisation of a silver(I) complex from an amorphous precipitate into a 1D coordination polymer and its subsequent isomerisation to a 3D coordination network.

Hemilabile ligands feature at least one labile donor function while the principal donor group remains firmly bound to the metal centre. This concept is well established in the areas of homogeneous catalysis and chemical vapour deposition, where it has led to major advances.[1] We were interested if the concept of hemilability could be extended to multitopic ligands and what effect this would have on the self-assembly of coordination polymers.[2]

Cyclotriphosphazenes $[X_2PN]_3$ are versatile platforms for multifunctional molecules, such as multisite ligands[3] and dendrimers,[4] owing to the ease of equipping the phosphorus centres with a wide range of substituents X.[5] Recently, we have demonstrated that cyclotriphosphazenes $[(RNH)_2PN]_3$ serve as tridentate linkers *via* the three ring nitrogen sites in the presence of silver ions.[6] The affinity of Ag(I) ions for organic π-donors, such as olefins and arenes, is well known and a large number of complexes have been characterised.[7] The allyl derivative **1** features six peripheral olefin groups furnishing a unique hemilabile coordination environment for three ring N bound silver ions. The resulting $[\mathbf{1}Ag_3]^{3+}$ assembly can switch between various modes of connectivity, due to the flexible nature of its donor side arms. Here we show that this behaviour facilitates the *in situ* recrystallisation of an amorphous solid into a 1D coordination polymer and its subsequent isomerisation into a 3D coordination network.



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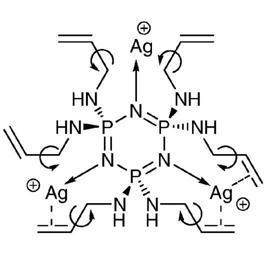

$[\mathbf{1}Ag_3]^{3+}$

The combination of methanol solutions of **1** and $AgClO_4$ leads to the instant formation of a cream coloured precipitate. After a few minutes colourless crystals start to develop on the surface of the amorphous substance. The process did not occur when the freshly precipitated compound was filtered off, dried and covered with methanol. However, the addition of a small amount of $AgClO_4$ to this mixture reinitiated the recrystallisation. In order to monitor the crystal growth, we repeated the latter experiment on an X-ray goniometer. The filtered and dried precipitate was placed into a vertically aligned capillary and dampened with a drop of methanol containing $AgClO_4$. Static X-ray exposures were recorded at intervals using a CCD detector (Fig. 1). The appearances of individual diffraction spots indicate the growth of single crystals.

The crystals obtained from the initial experiment were of sufficient quality for X-ray structure analysis. It showed the formation of the coordination polymer $\mathbf{1}\cdot 3AgClO_4\cdot 4H_2O$ (**2**) comprising a 1D chain assembled from $[\mathbf{1}Ag_3]^{3+}$ units. Two Ag^+ ions are coordinated by two allyl groups in an intramolecular fashion, while the third Ag^+ ion coordinates intermolecularly to two neighbouring $[\mathbf{1}Ag_3]^{3+}$ units *via* Ag–olefin bonds (Fig. 2). Additionally, each intramolecularly coordinated Ag^+ ion binds a water molecule. The $\{[\mathbf{1}Ag_3]^{3+}\}_n$ chains are linked by hydrogen bonds *via* perchlorate ions and water molecules. The compound crystallises in the monoclinic space group *C*2/*c*. The intermolecularly coordinated Ag^+ ion, its adjacent N and the opposite P centre occupy the two-fold axis.

When crystals of **2** were kept in methanol for several weeks, they gradually decomposed giving a black material alongside another crystalline product. Its X-ray structure exhibits the isomeric 3D coordination network $\mathbf{1}\cdot 3AgClO_4$ (**3**) which crystallises in the polar, orthorhombic space group *Fdd*2. Similar to **2**, compound **3** is assembled from $[\mathbf{1}Ag_3]^{3+}$ units, in which silver ions are coordinated by two allyl groups. However, the connectivity pattern of intra- and intermolecular Ag–olefin interactions differs from that of observed in **2**. In **3** only one silver ion of the $[\mathbf{1}Ag_3]^{3+}$ unit is coordinated by two intramolecular allyl groups, while the other two Ag^+ ions form both one intra- and one intermolecular olefin contact. Although the

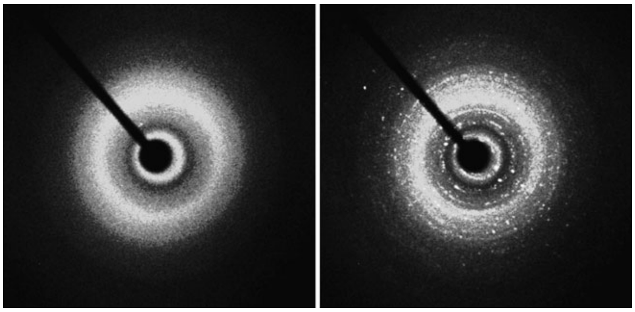

Fig. 1 X-Ray exposures of $\mathbf{1}\cdot 3AgClO_4$; 10 min (left) and 200 min (right) after precipitation.

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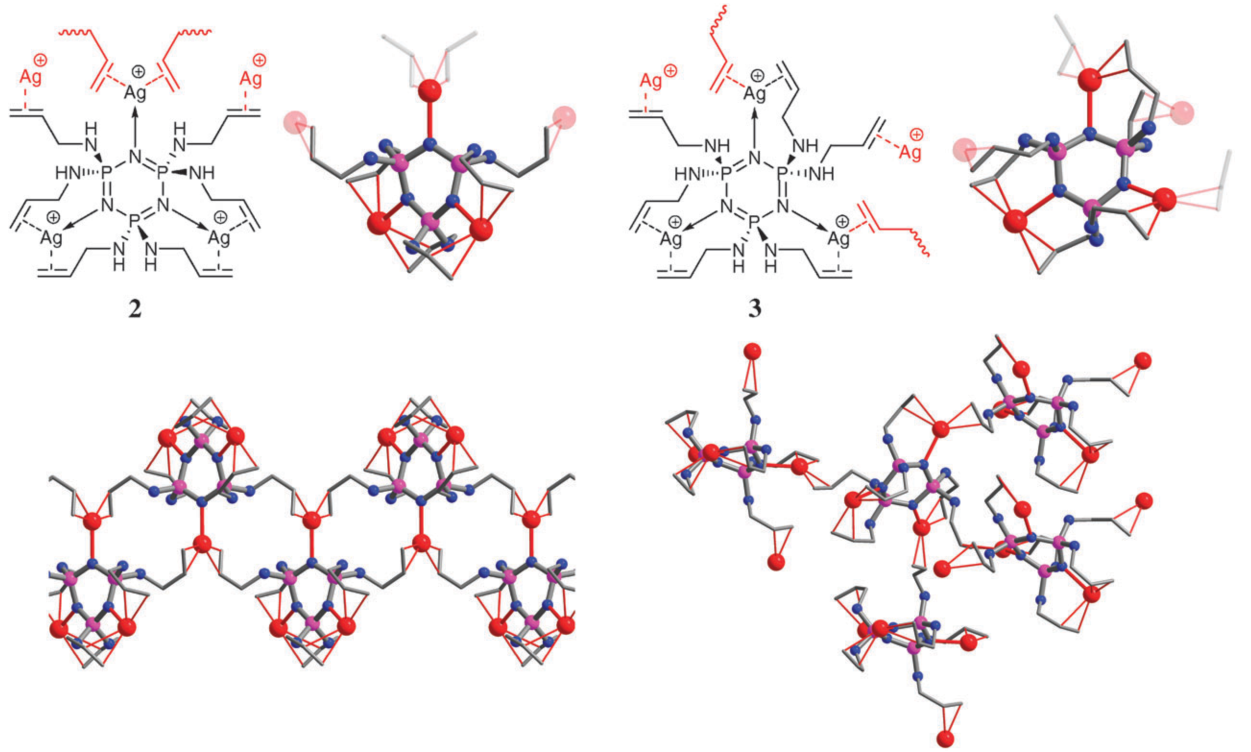


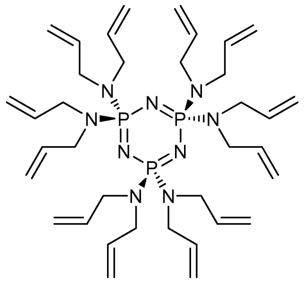
Fig. 2 Crystal structures and connectivity of **2** (left) and **3** (right) showing the monomeric $[\mathbf{1}Ag_3]^{3+}$ units with intermolecular interactions (top) and the polymeric structures (bottom); Ag, red; P, purple; N, blue; allyl groups, grey. The ClO_4^- ions and solvent molecules have been omitted for clarity.

ratio of intra- over intermolecular Ag–olefin contacts in **2** and **3** is equivalent, the distinct connectivity pattern in **3** allows each $[\mathbf{1}Ag_3]^{3+}$ unit to make contacts to four neighbours *via* Ag–olefin interactions resulting in a diamandoid network topology (Fig. 2). In contrast to **2**, crystals of **3** do not contain solvent molecules. This gives a denser network reducing the effective volume V/Z by 14.6%.

It should be noted that the intramolecular coordination of two allyl groups leaves enough space for one extra ligand to coordinate to the Ag centre (a H_2O molecule in **2** and a ClO_4^- ion in **3**, respectively). This additional coordination elongates the Ag–N bonds (av. 2.37 Å) compared to the shorter Ag–N bonds associated with intermolecularly coordinated Ag centres (av. 2.24 Å) that do not carry additional ligands.

The spontaneous recrystallisation of the primary precipitate into single crystals of **2** is controlled by diffusion of $[\mathbf{1}Ag_3]^{3+}$ units through the overlaying methanol solution. As mentioned above, this process is promoted by the presence of excess $AgClO_4$ in solution, which presumably interacts with $[\mathbf{1}Ag_3]^{3+}$ units *via* pendent olefin groups during transport. The flexible coordination behaviour of the $[\mathbf{1}Ag_3]^{3+}$ units, which most likely involves the rapid exchange between intra- and intermolecular coordination modes, facilitates this process. In addition to Ag coordination, the allylamino groups engage in hydrogen bonding to perchlorate ions and solvent molecules. Since both NH and allyl groups are hinged to the same P–N bond, the directionality of both is interdependent, which results in a subtle interplay of metal coordination and hydrogen bonding.

Furthermore, we have synthesised the diallylamino derivative **4** featuring twelve pendent olefin groups to study the effect of surplus donor sites on the hemilabile ligand behaviour. When **4** is treated with excess $AgClO_4$ (eight equivalents) in methanol an amorphous precipitate forms, which, however, does not recrystallise spontaneously. Careful layering of methanol solutions of **4** and $AgClO_4$ gave single crystals of $\mathbf{4}\cdot5AgClO_4\cdot6CH_3OH$ (**5**).†‡



The X-ray structure analysis revealed that the ligand in **5** acts like a 'silver ion sponge': it accommodates a total of five silver ions by employing all of its donor sites (Fig. 3). To our knowledge, there is no structurally characterised example of a single ligand binding such a large number of metal ions *via* olefin–π-interactions. The $[\mathbf{4}Ag_5]^{5+}$ assemblies form separate entities that do not interact intermolecularly *via* Ag–olefin interactions. The five Ag centres are complexed as follows: One is coordinated by a ring N centre *via* a long Ag–bond of 2.647(5) Å, two allyl groups and two ClO_4^- ions. Two Ag centres again are ring-N bound showing Ag–N bond lengths

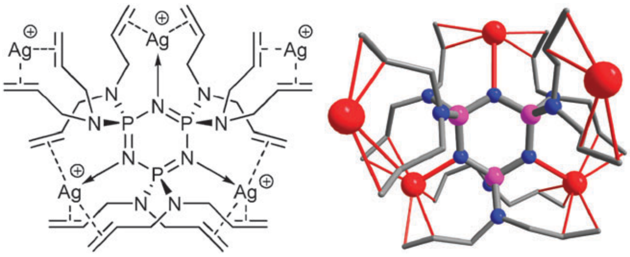


Fig. 3 Crystal structure (perspective view) and connectivity of **5**, showing the $[\mathbf{4}Ag_5]^{5+}$ assembly. The ClO_4^- ions and solvent molecules are omitted for clarity.

of 2.243(5) and 2.328(5) Å. In addition, both are chelated by three allyl groups, but there is no further interaction with anions or solvent molecules. Each of the two remaining silver ions is bonded to two olefins, one methanol molecule and two perchlorate ions. The crystal structure displays a network, in which $[\mathbf{4}Ag_5]^{5+}$ assemblies are interlinked *via* perchlorate ions and methanol molecules.

In summary, cyclotriphosphazenes equipped with six pendent allylamino groups act as multitopic, hemilabile ligands in the presence of Ag(I). The flexibility of the donor side arms and the smooth switch between intra- and intermolecular coordination modes generate highly adaptable linkers that facilitate *in situ* recrystallisation and isomerisation of the coordination network. The provision of twelve pendent olefin groups gives the ligand a 'sponge'-like character, *i.e.*, the capacity to absorb a large number of silver ions.

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Notes and references

† *Synthesis*: **1** was prepared as described previously.[8] **2** + **3**: A solution of **1** (0.10 g) in methanol (3 mL) was combined with a solution of $AgClO_4$ (0.2 g) in methanol (3 mL) resulting in the precipitation of a cream coloured precipitate. Colourless crystals of **2** developed on the surface of the precipitate after a couple of minutes. After 2 h the recrystallisation process ceased, leaving a residual brown substance. Storage of crystalline **2** for several weeks led to decomposition alongside the formation of colourless crystals of **3**. **4**: A mixture of hexachlorocyclotriphosphazene (4.0 g) and diallylamine (25 mL) was refluxed for 7 days. The excess diallylamine was removed under vacuum. The viscous residue was dissolved in 10 mL of pentane and stored at −20 °C yielding colourless crystals after 2 days. The filtrate was concentrated to 3 ml and kept at −20 °C to obtain a further batch of crystals. The crystals were washed with methanol and dried under vacuum. Yield: 3.20 g (40%); mp 46 °C. ^1H NMR ($CDCl_3$, TMS): δ 3.49–3.53 (m, 24H, NCH_2CHCH_2), 4.97–5.00 (m, 24H, NCH_2CHCH_2), 5.66–5.71 (m, 12H, NCH_2CHCH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, TMS): δ 46.8 (NCH_2CHCH_2), 115.4 (NCH_2CHCH_2), 135.7 (NCH_2CHCH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 85% H_3PO_4): δ 22.4. **5**: A solution of **4** (0.1 g) in methanol (3 mL) was layered with a solution of $AgClO_4$ (0.25 g) in methanol (3 mL). Colourless block-like crystals of **5** were obtained after 3 days. Yield: 0.11 g (41%). *Caution should be used when handling perchlorate salts, since these can be explosive when dry*!

‡ *Crystal data* for **2**: $C_{18}H_{36}Ag_3Cl_3N_9O_{12}P_3\cdot4H_2O$, M_r = 1165.49, T = 150 K, monoclinic, $C2/c$, a = 22.012(3), b = 15.727(2), c = 11.781(2) Å, β = 101.206(3)°, V = 4000.6(11) Å^3, Z = 4, $R1$ ($I > 2\sigma(I)$) = 0.043, $wR2$ (all data) = 0.118. **3**: $C_{18}H_{36}Ag_3Cl_3N_9O_{12}P_3$, M_r = 1093.43, T = 150 K, orthorhombic, $Fdd2$, a = 26.306(5), b = 49.555(9), c = 10.710(2) Å, V = 13962(4) Å^3, Z = 16, $R1$ ($I > 2\sigma(I)$) = 0.036, $wR2$ (all data) = 0.087. **5**: $C_{36}H_{60}Ag_5Cl_5N_9O_{20}P_3\cdot6CH_3OH$, M_r = 1940.69, T = 100 K, monoclinic, $P2_1/c$, a = 11.586(3), b = 25.797(5), c = 22.795(5) Å, β = 94.236(4)°, V = 6795(2) Å^3, Z = 4, $R1$ ($I > 2\sigma(I)$) = 0.054, $wR2$ (all data) = 0.136.[9] CCDC 670148–670150. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b718872b

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