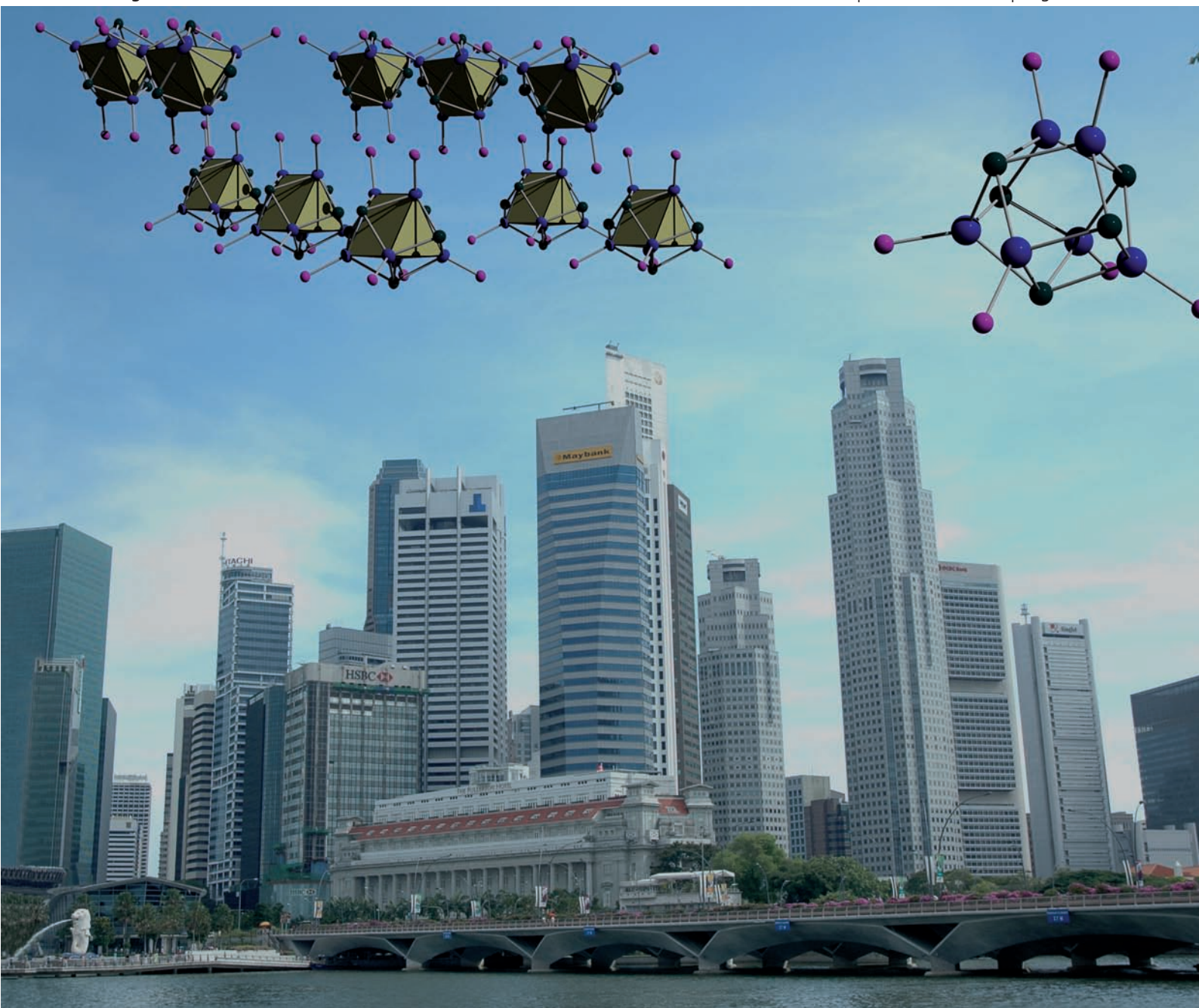


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FEATURE ARTICLE

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T. S. Andy Hor *et al.*
General formation of trigonal-prismatic
 $[Ag_6X_5(dppf)_3]^+$ (X = Cl, Br, I) through
an unusual ligand migration from
 $NiX_2(dppf)$ to AgOTf



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General formation of trigonal-prismatic $[\text{Ag}_6\text{X}_5(\text{dppf})_3]^+$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) through an unusual ligand migration from $\text{NiX}_2(\text{dppf})$ to AgOTf^\dagger

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Use of $\text{NiX}_2(\text{dppf})$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) as a ligand transfer reagent to AgOTf results in the trigonal prismatic $[\text{Ag}_6\text{X}_5(\text{dppf})_3]\text{OTf}$ complexes. Similar reactions with the dppe analogues give at least 4 different types of dppe-bridged coordination polymers.

We have been interested in the coordination¹ and catalytic² chemistry of dppf for two decades. Our earlier work on the coinage metals, especially Ag^+ , revealed a large variety of mono-, di- and polynuclear structures that can be assembled from dppf.³ The structural outcome is generally hard to predict. This is understandable given the numerous permutations arising from the flexible metal geometry (linear \leftrightarrow trigonal planar \leftrightarrow tetrahedral), dppf bonding (unidentate \leftrightarrow bridging \leftrightarrow chelating) and coordination state of the supporting anion (halide, pseudohalide *etc.*) (uncoordinated \leftrightarrow terminal \leftrightarrow bridging \leftrightarrow chelating \leftrightarrow capping). Our current understanding of $[\text{AgX}(\text{dppf})]_n$ complexes is that they generally prefer to give dimeric structures.⁴ Several variations are known within the dinuclear framework, depending on the interplay of the coordination modes of dppf and X^- . These complexes are commonly prepared from direct addition of AgX to dppf (or $\text{Ag}^+ + \text{X}^- + \text{dppf}$) using stoichiometric conditions of 1 : 1.

In this communication, we report a new synthetic route for dppf complexes of silver halides, from which we isolated a general class of Ag_6 trigonal prismatic structures that are unprecedented and unexpected. These compounds are formed under a diphosphine-limiting conditions created by the dppf-carrier of $\text{Ni}(\text{II})$. When the ferrocene-based dppf is replaced by alkyl-chain-based dppe, different types of coordination polymers are isolated. This study hence demonstrated a unique difference between dppf and dppe and their roles in determining the outcome of the $\text{Ag}(\text{I})$ assemblies.

Attempts to carry out a “standard” metathesis reaction between $\text{NiCl}_2(\text{dppf})$ with AgOTf ($\text{OTf} = \text{triflate}, \text{CF}_3\text{SO}_3$) did not result in $\text{Ni}(\text{OTf})_2(\text{dppf})$ or AgCl but an unexpected $[\text{Ag}_6\text{Cl}_5(\text{dppf})_3][\text{OTf}]$, **1**. The formation of this complex supports the high propensity of Ag^+ not just for chloride but also for phosphine. Similar attempts on $\text{RuCl}_2(\text{bpy})$ by AgBF_4 in the presence of dppf also led to the isolation of dimeric $[\text{AgCl}(\text{dppf})]_2$.⁵

The ³¹P NMR spectrum of **1** at 223 K revealed that all phosphines are chemically equivalent with the expected couplings to ^{107/109}Ag. The ESI-MS spectrum shows molecular fragments corresponding to $[\text{Ag}(\text{dppf})]^+$ ($m/z = 661.2$), $[\text{Ag}_2\text{Cl}(\text{dppf})]^+$ ($m/z = 804.8$), $[\text{Ag}_2\text{Cl}(\text{dppf})_2]^+$ ($m/z = 1359.4$), $[\text{Ag}_3\text{Cl}_2(\text{dppf})_2]^+$

($m/z = 1502.3$), $[\text{Ag}_4\text{Cl}_3(\text{dppf})_2]^+$ ($m/z = 1646.3$) *etc.* with matching isotopic patterns.

Single-crystal X-ray crystallographic analysis shows a cage aggregate $[\text{Ag}_6\text{Cl}_5(\text{dppf})_3](\text{OTf})$, **1** of six silver atoms forming a trigonal prismatic core (vol. $\sim 18.6 \text{ \AA}^3$). The prism is longitudinally compressed such that the vertical edges are $\sim 14\%$ shorter than the triangular sides. Each of the two (top and bottom) trigonal faces is capped by a $\mu_3\text{-Cl}$, whereas each rectangular face at the side is capped by $\mu_4\text{-Cl}$ (Fig 1). Each vertical edge of the prism is overheaded by a dppf. These give an overall aggregate framework with an $\sim C_{3h}$ symmetry. Such arrangement enables all the $\text{Ag}(\text{I})$ centers to be chemically identical with each of the $[\text{AgCl}_3\text{P}]$ moiety adopting a stable 18-e tetrahedral configuration. This formulation ignores any active $\text{Ag}\text{-Ag}$ interaction despite the relatively short metal contacts (av. $3.10(7) \text{ \AA}$). As expected, the $\text{Ag}\text{-}\mu_4\text{-Cl}$ bonds (av. 2.6740 \AA) are significantly longer than the $\text{Ag}\text{-}\mu_3\text{-Cl}$ bonds (av. 2.6372 \AA). One other related Ag_6 cage is found in $[\text{Ag}_6(\text{SC}_6\text{H}_5)_6(\text{PPh}_3)_6]$.⁶ Unlike **1**, this electronically neutral aggregate takes up an antiprismatic structure with S_6 symmetry with the thiolato edge-bridging each of the trigonal sides and a significantly longer $\text{Ag}\cdots\text{Ag}$ separation of 3.875 \AA (av.). Other bigger Ag_{12} and Ag_{20} cages assembled by pyrazine-2-carboxamide ligands are known.⁷

Use of $\text{NiBr}_2(\text{dppf})$ as substrate in the above reaction similarly results in $[\text{Ag}_6\text{Br}_5(\text{dppf})_3][\text{OTf}]$, **2**. X-ray crystallographic analysis suggested it to be isostructural to **1**. The volume of the prism expands to $\sim 19.9 \text{ \AA}^3$ in order to accommodate the larger halide.

Attempts to prepare $\text{NiI}_2(\text{dppf})$ were unsuccessful. We therefore used a direct method from the the addition reaction between AgI and dppf (2:1), followed by exchange with triflate or PF_6 . The ³¹P NMR spectrum of the yellow product shows characteristic $\text{Ag}\text{-P}$ resonance peaks at $\delta = -11.5, -8.9$, with $\text{Ag}\text{-P}$ couplings. X-Ray

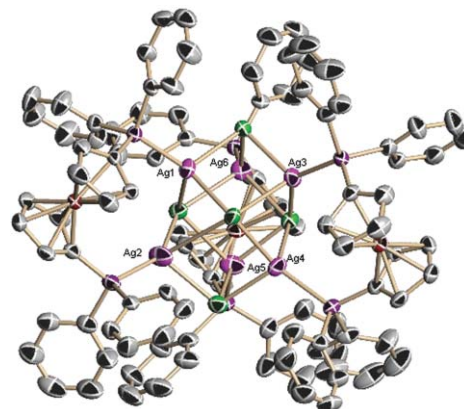


Fig. 1 ORTEP diagram of **1**, showing the cation. (Probability level of thermal ellipsoid 50%.)

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crystallographic analysis of the PF_6^- salt confirmed another isostructural derivative $[\text{Ag}_6\text{I}_5(\text{dppf})_3][\text{PF}_6]$, **3**. The prismatic volume (20.0 \AA^3) is similar to that of the bromide analogue. The Ag_6 core however is more significantly distorted from a regular prism, as evident from the irregular $\text{Ag}\cdots\text{Ag}$ distances. The distortion appears to be needed to accommodate the larger iodide caps, which also create steric conflicts with the bulky dppf. This complex is significantly more insoluble, thus hampering efforts in purification or attempts to produce better crystals for analysis.

The three Ag_6 complexes **1–3** are monocationic and isostructural.[‡] Their general formation suggested that the hexanuclear trigonal prismatic form is the thermodynamically most stable entity under the stoichiometry $[\text{Ag}_2\text{X}_{2n-1}(\text{dppf})]_n$. Attempted synthesis of **1** or **2** directly from AgCl or AgBr with dppf under stoichiometric control did not yield the desired products. Instead, the known dinuclear $[\text{Ag}_2\text{X}_2(\text{dppf})_2]$ complexes were obtained. The high affinity of Ag^+ towards free dppf ligand appears to be overwhelming and drives towards the thermodynamic Ag_2 product, even when dppf is in deficient. Use of $[\text{Ni}^{\text{II}}(\text{dppf})]$ as a diphosphine source overcomes this problem by creating a hurdle for Ag -dppf interaction since the dppf is bound to $\text{Ni}(\text{II})$. There is no inhibition however for $\text{Ag}(\text{I})$ to capture the halide because the latter has free basic lone pairs. Effectively, the transfer agent promotes a slow nucleation process that ensures an effective stoichiometric excess of Ag^+ over dppf throughout the course of reaction, thereby pushing towards the Ag_6 product.

The assembly is expected to be phosphine dependent, although the product outcome is largely unpredictable. This system provides a model to study the influence of a diphosphine. A diphosphine with a much shorter skeletal backbone (*e.g.* dppe) may not be suitable for edge-bridging a prism. Indeed, X-ray crystallographic analysis of the product **4**[‡] from a similar reaction between $\text{NiI}_2(\text{dppe})$ and Ag^+ revealed a coordination polymeric chain with $[\text{Ag}_2(\text{dppe})_3](\text{OTf})_2$ as the stoichiometric unit. This bridge-only assembly comprises two repeating and intercalating entities of doubly-bridging and single-bridging dppe (Fig 3) The nearby triflate is unbound $[\text{Ag}\cdots\text{O} 2.781 \text{ \AA} (\text{av.})]$. Such assembly is rare but its gold analogue has been reported.⁸ The $\text{Ag}\cdots\text{Ag}$ distance [$6.581 \text{ \AA} (\text{av.})$] is too large for any significant argentophilic interactions. The Au analogue shows similar separation ($\text{Au}\cdots\text{Au} 6.596 \text{ \AA}$) and hence no argentophilic bonding. The crystal packing diagram reveals a discrete series of coil-like coordination polymeric chain propagating unidirectionally to create a network of

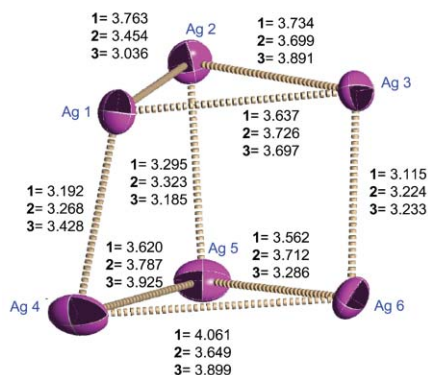


Fig. 2 A schematic sketch of the trigonal prismatic framework of the Ag_6 core of **1–3**, with the $\text{Ag}\cdots\text{Ag}$ separations (\AA) indicated for three complexes.

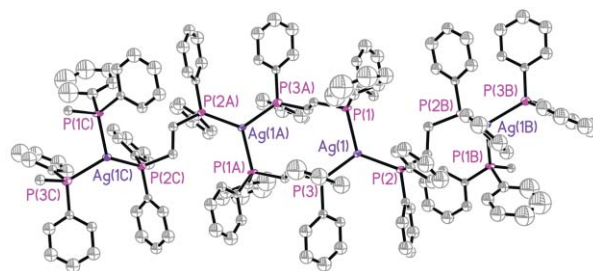
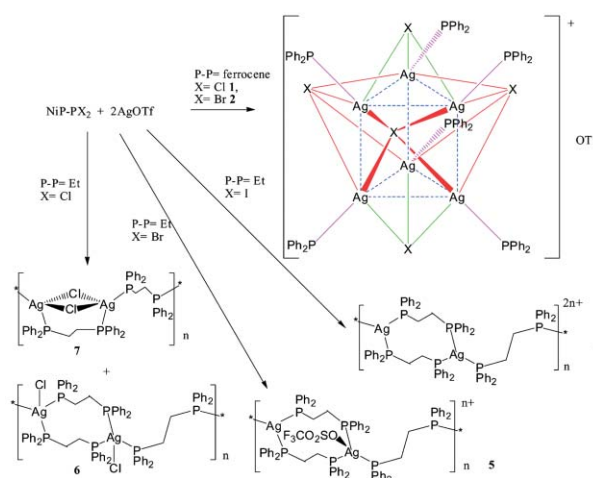


Fig. 3 ORTEP diagram of **4**, showing the polymeric coordination chain (hydrogen atoms omitted for clarity). (Probability level of thermal ellipsoid 50%.)



Scheme 1 A schematic representation of the products formed from the ligand migration reaction from $\text{NiX}_2(\text{P-P})$ ($\text{P-P} = \text{dppf}, \text{dppe}$) to AgOTf .

columnar channels. ^{31}P NMR spectrum of **4** shows the two inequivalent sets of phosphines ($\delta = 3.3$ and 4.5 ppm) in the doubly and singly bridging modes. Two sets of singlet are also recorded in the Au analogue.

The $\text{P} : \text{Ag}$ ratio increases from $0.5 : 1.0$ in **1–3** to $1.5 : 1.0$ in **4** although the synthetic conditions are similar. The $\text{Ag}(\text{I})$ in **4** thus shows a stronger self-selection of dppe over dppf to the extent that it would saturate itself with phosphine donors in dppe and leaves no room for the halides. Another major difference between **1–3** and **4** is that the former complexes are made up of tetrahedral $\text{Ag}(\text{I})$ whereas the latter comprises of trigonal planar $\text{Ag}(\text{I})$.

In our attempts to prepare **4** directly from the addition reaction of AgOTf with dppe under stoichiometric control, *viz.* $\text{Ag} : \text{dppe} 2 : 3$, we succeeded in controlling the stoichiometry but could not yield the same assembly. Instead, it resulted in a similar repeating polymeric chain except that one of the two $\text{Ag}(\text{I})$ atoms coordinated to triflate [$\text{Ag}\cdots\text{O} 2.554(8) \text{ \AA}$] whereas the other was uncoordinated but in proximity ($\text{Ag}\cdots\text{O} 2.819 \text{ \AA}$). This resulted in a polymeric chain of alternating tetrahedral and pyramidally distorted trigonal planar (deviations of $\text{Ag}1, \text{P}1, \text{P}2$ and $\text{P}3$ from the least square plane of $\{\text{AgP}_3\}$ are $+0.3758, -0.1211, -0.1250$, and -0.1298 \AA respectively; P-Ag-P angles range 112.98° – 118.23°) structure, best represented as $[\text{Ag}_2(\text{OTf})(\mu\text{-dppe})_3]_n(\text{OTf})_n$, **5**[‡] (Fig 4). A coordination isomer of **5**, with triflates weakly associated with all $\text{Ag}(\text{I})$ atoms [$2.645(5)$ and $2.653(3) \text{ \AA}$], has been recently reported.⁹

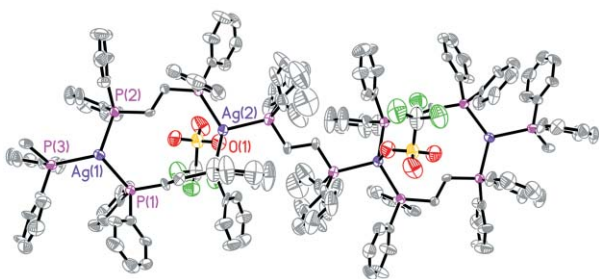


Fig. 4 ORTEP diagram of **5** (hydrogen atoms removed for clarity). (Probability level of thermal ellipsoid 50%.)

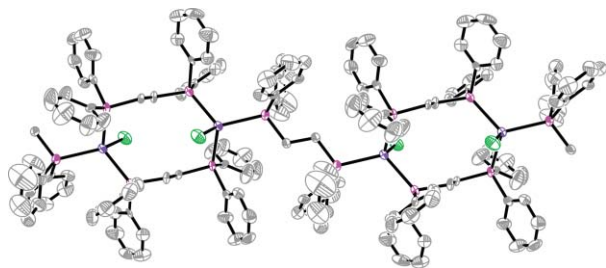


Fig. 5 ORTEP diagram of **6** (hydrogen atoms removed for clarity). (Probability level of thermal ellipsoid 50%.)

The same complex **5** is formed from the reaction between $\text{NiBr}_2(\text{dppe})$ and AgOTf , showing again the higher propensity of Ag(I) for dppe. However, reaction of $\text{NiCl}_2(\text{dppe})$ with AgOTf yields two products $[\text{Ag}_2(\text{dppe})_3\text{Cl}_2]_n$, **6**‡ and $[\text{Ag}_2(\text{dppe})_2(\mu\text{-Cl})_2]_n$, **7**‡ with different stoichiometries and structures. They however co-crystallized in an asymmetric unit of the single crystal, which is unusual but not unprecedented.¹⁰ Unlike **4** and **5**, they show halide coordination, which is not surprising considering that in aprotic solvent chloride is a better nucleophile. Complex **6** is similar to **4**, showing a coordination polymer chain intercalated by doubly- and singly-bridging dppe, except that Cl takes up the 4th site of the metal at the $\{\text{Ag}_2(\text{dppe})_2\}$ ring, thus achieving 18-e tetrahedral Ag(I) (Fig 5). Complex **7**, despite being short of a dppe ligand compared to **6**, also achieves saturation by forming doubly bridging chloride, which also shortens the $\text{Ag}\cdots\text{Ag}$ contact to 3.362(2) Å (Fig 6). These two forms are not strictly constitutional isomers but they are energetically similar. Their comparable chain structure and stability helps them to complement in the crystal packing such that they are aligned parallel to the *a* axis of the unit cell. Their isolation and co-crystallization suggest similar demands between a bridging dppe and doubly-bridging chloride. Complexes **6** and **7** cannot be separated in pure form. They are also likely to be interconverting as a dynamic mixture in solution, since only a pair of broad doublets ($\delta = 4.9, 6.2$) is observed in the ³¹P NMR spectrum at rt. There is no ³¹P-NMR evidence of free dppe in solution.

Complexes **1–3** are trigonal prismatic aggregates whereas complexes **4–7** are dppe-bridging Ag(I) coordination polymers differed by the number of bridging dppe, and secondary association of (weakly) coordinative ligands such as chloride or triflate. This system highlights the complexity and unpredictability of Ag(I) assemblies because of the numerous parameters that could influence the outcome of the aggregates. The different skeletal

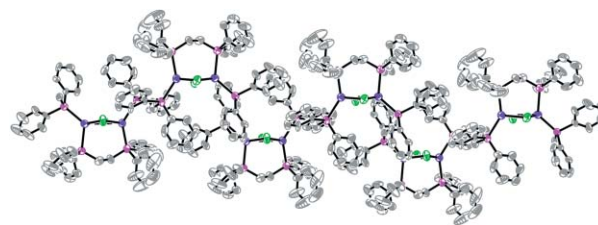


Fig. 6 ORTEP diagram of **7** (hydrogen atoms removed for clarity). (Probability level of thermal ellipsoid 50%.)

properties of dppe and dppe allow them to promote the formation of polyhedral and polymeric Ag(I) respectively. Isolation of the trigonal prismatic aggregates fuels the impetus in our search for new Ag cages and polymers in a functional network. The use of a diphosphine carrier complex such as Ni(II) could lead to a different outcome compared to the use of free phosphines. In this system, there is no evidence for Ni(II) interference in form of the formation of heterometallic $\text{Ni(II)}\text{-Ag(I)}$ complexes.

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Notes and references

‡ Crystals of **1–3** are obtained by slow evaporation of a solution of the compound in CHCl_3 . Crystals for **4–7** are obtained by slow diffusion of hexane into a solution of the compounds in CH_2Cl_2 . CCDC numbers of complexes **1** to **6/7** are 647357–647362 respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b707218j

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