Triply-bridged diphos disilver helical complexes [$Ag_2(\mu_2$-dppa-$P,P')_3$(anion)$_2$] [dppa = bis(diphenylphosphino)acetylene]

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Triply-bridged disilver complexes [$Ag_2(\mu_2$-dppa-$P,P')_3$(anion)$_2$] form selectively and are stabilised by many aromatic interactions.

Multimetallic 'coordination clusters' which assemble from metal ions and multidentate bridging ligands currently attract much interest.[1] In most cases, their structures can be predicted from the geometries of the rigid bridging ligand and the metal ion used (*e.g.* square planar or octahedral). By contrast, silver(I)–phosphine complexes exhibit varying coordination numbers, and often dissociative equilibria. Therefore more subtle 'secondary' factors might control product selectivity in the formation of a multisilver complex with bridging phosphines. Some known multisilver and -copper complexes with bridging phosphines[2] are shown in Fig. 1. Some of these have quite unexpected structures, *e.g.* the hexanuclear adamantanoid triphos cages **b**.[2j] With flexible diphosphines $Ph_2P(CH_2)_nPPh_2$, silver(I) or copper(I) salts with oxo-anions selectively form dinuclear (2 : 2) macrocycles, *e.g.* **a**. The larger rings of this type (up to 18-membered) are stabilised by bridging oxo anions. This stabilisation is enabled by the flexibility of the diphosphine, which allows the P lone pairs to point inwards, setting up the metals for anion bridging.

Bis(diphenylphosphino)acetylene ($Ph_2P–C{\equiv}C–PPh_2$, dppa), by contrast, cannot have inwardly pointing lone pairs owing to its rigidity. We were therefore interested to discover what type of stable non-dissociating structure, if any, this ligand would cause to form.

At room temperature, solutions of equimolar mixtures of dppa and AgX (X = SbF_6 or OTf) in $CDCl_3$–$MeNO_2$ (2 : 1) gave ^{31}P NMR spectra (121 MHz) which were broad and did not show Ag–P coupling, suggesting dissociation of the Ag–P bonds on the NMR timescale. At −60 °C, this process is slow on the NMR timescale and only sharp lines characteristic of coupling to ^{107}Ag and ^{109}Ag were seen. 95% of the spectral intensity was due to a mixture of three species, each with distinctly different coupling constants corresponding to AgP (767 Hz), AgP_2 (505 Hz) and AgP_3 (377 Hz) coordination centres.[3] The lowest nuclearity structures which could account for these coordination centres are indicated in Scheme 1. Therefore the rigid dppa ligand does not selectively produce a 2 : 2 macrocycle **2**, but instead favours some disproportionation to the 1 : 2 and 3 : 2 structures **1** and **3**.

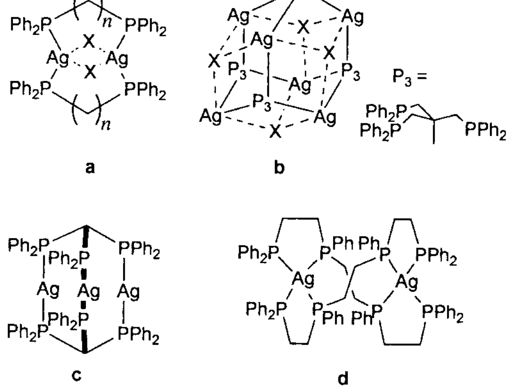
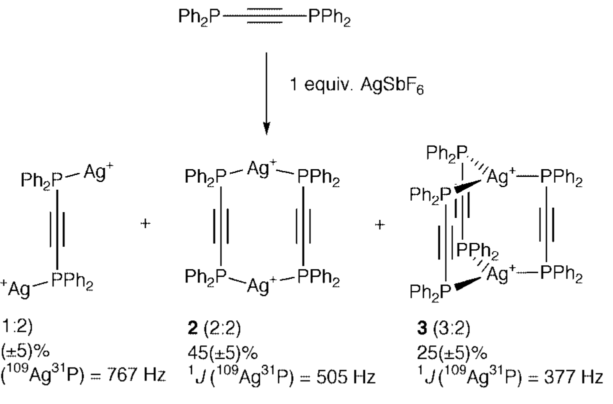


Fig. 1 Multisilver complexes with bridging multidentate phosphines: diphos macrocycles (**a**), triphosphine cages (**b** and **c**), and a tetraphosphine helicate (**d**).

We therefore investigated the selective formation of triply-bridged complex **3**, at the appropriate 3 : 2 ligand to metal ratio. The reaction of 3 equivalents of dppa with 2 equivalents of $AgSbF_6$ did indeed lead quantitatively to this product. This behaviour was further found to be general to the salts AgX (X = BF_4 **3a**, SbF_6 **3b** NO_3 **3c**, OTf **3d**).† Unusually for silver-phosphine complexes, **3a**–**d** show no evidence of Ag–P dissociation at room temperature on the NMR timescale (at 121 MHz). A $^{19}F\{^1H\}$-HOESY spectrum[4] in $CDCl_3$ revealed an interionic contact between the BF_4^- and the dppa *ortho* protons (of < 4.5–5 Å), showing that complex **3** exists as a tight ion-pair in this solvent.

Crystals obtained from chloroform–nitromethane–diethyl ether had the composition [$Ag_2(\mu_2$-dppa-$P,P')_3$-$(BF_4)_2$]·$0.5CHCl_3$·$1.5MeNO_2$ as established by single crystal X-ray crystallography (Fig. 2).‡ Consistent with the NMR data, there is trigonal geometry at silver, although with pyramidal distortion toward the BF_4 anions (distances of Ag1 and Ag2 from their P_3 planes are 0.55 and 0.54 Å, respectively). The two Ag(I) centres are linked by three bridging dppa ligands with outwardly bent P–C≡C–P backbones, and C≡C–P angles lying in the range 171.3(4)–175.1(4)°. This strain results from the mismatch between distorted tetrahedral geometry at phosphorus and pseudo-cofacial silver coordination centres, and is partially alleviated by the pyramidal distortion at silver. There is a helical twist of *ca.* 27°, about the Ag···Ag axis, taken as the average of the torsion angles P(1)–Ag(1)–Ag(2)–P(2), P(3)–Ag(1)–Ag(2)–P(4) and P(5)–Ag(1)–Ag(2)–P(6). The crystalline material is achiral however, each unit cell containing two molecules of each enantiomer. There is small void at the centre (dimensions: Ag to molecular centroid 2.83 Å, typical C≡C centroid to molecular centroid 2.48 Å).

Perhaps importantly, there are sixteen intramolecular aromatic contacts of both stacking and C–H···π types in the range



Scheme 1 The distribution of products from equimolar amounts of dppa and $AgSbF_6$.

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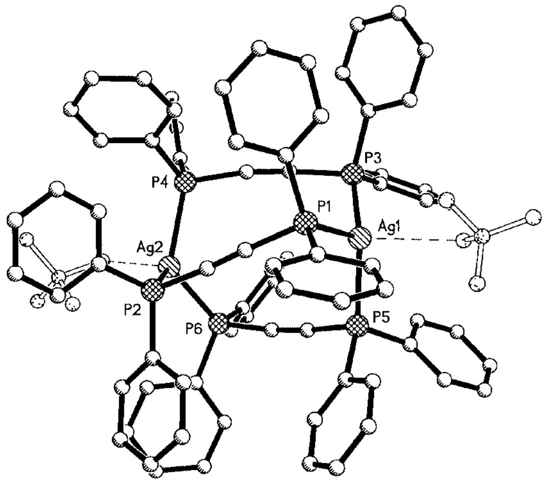

Fig. 2 The structure of complex **3a** in the solid state with H-atoms omitted.

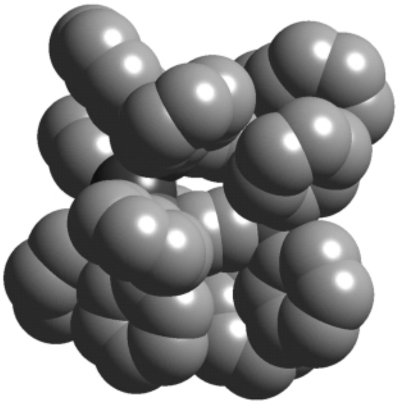

Fig. 3 Space-filling representation of complex **3a** to show the clustering of aromatic groups (H-atoms omitted).

3.5–3.8 Å (C–C distance) between the twelve phenyl groups. An impression of the clustering of aromatic groups can be gained from Fig. 3. Though individually weak, in combination these contacts may contribute significantly to the observed stability of complexes **3** in solution. Multiple aromatic interactions also occur in the triphos cage complexes $[Ag_6(triphos)_4(oxo\text{-}anion)]^{2+}$, and furthermore, may be responsible for their unexpected structure.[2j] The ^1H NMR spectrum of **3a** (−60 °C, 500 MHz) shows only one type of phenyl group suggesting that in solution it is either not helical or rapidly interconverts between enantiomers. Much interest has been shown in triple helicates,[4] and most are based on tris-chelate metal centres. Relevant exceptions are the Cu_3L_3 complex of Potts *et al.*[5a] with trigonal coordination, and the Ag_3L_3 toroidal triple helix with two-coordination at silver reported by Williams *et al.*[5b] We note with interest that the related dppa complexes $[(CO)_3Mo(\mu_2\text{-dppa-}P,P')_3Mo(CO)_3]$[6a] and $[BuTeCu(\mu_2\text{-dppa-}P,P')_3CuTeBu]$[6b] are also helical. In contrast to complex **3a**, as a consequence of their higher coordination numbers and correspondingly smaller P–M–P angles, these complexes have longer, narrower central voids (Mo–Mo distance 7.38 Å, Cu–Cu distance 6.40 Å).

In conclusion, complexes **3a**–**d** are a novel type of stable disilver complex with triply-bridging diphosphines. They assemble selectively from a 3:2 ligand to metal ratio, and unusually their Ag–P bonds do not dissociate on the NMR timescale at room temperature. Interesting structural features are the many intramolecular aromatic interactions, the central void and helical twist. The aromatic interactions may explain their selective assembly and stability in solution. This has implications for coordination-based self-assembly with flexible ligands or where the metal has no clearly preferred coordination number.

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Notes and references

† To a solution of AgX (0.44 mmol) in nitromethane–acetonitrile or acetonitrile (8 ml) was added a solution of dppa (263 mg, 0.66 mmol) in $CHCl_3$ (10 ml). Layering with diethyl ether gave colourless prisms in $>90\%$ yield. **3a** ($X = BF_4$) δ_P 19.4, $^1J(^{109}Ag^{31}P)$ 377 Hz, **3b** ($X = SbF_6$) $^1J(^{109}Ag^{31}P)$ 360 Hz, **3c** ($X = NO_3$) $^1J(^{109}Ag^{31}P)$ 336 Hz, **3d** ($X = OTf$) $^1J(^{109}Ag^{31}P)$ 336 Hz. $\delta_H(CDCl_3)$: **1a** ($X = BF_4$) 7.56 (m, 24H, H_{ortho}), 7.27 (t, 1.8 Hz, 12H, H_{para}), 7.10 (t, 1.8 Hz, 24H, H_{meta}).

‡ *Crystal data* for **3a**. $C_{80}H_{60}Ag_2B_2Cl_{1.50}F_8N_{1.50}O_3P_6$, $M = 1718.65$, monoclinic, space group $P2_1/n$ (no. 14), $a = 22.1929(16)$, $b = 14.8355(18)$, $c = 23.8561(13)$ Å, $\beta = 99.460(6)°$, $V = 7747.6(12)$ Å^3, $Z = 4$, $D_c = 1.473$ g cm^{-3}, $\mu = 0.749$ mm^{-1}. Data collection ($2.21 \leqslant \theta \geqslant 25.00$) was performed at 153 K on a Bruker SMART diffractometer (Mo-Kα, $\lambda = 0.71073$ Å). The structure was solved by direct methods (SHELXS-97)[7] and refined with full matrix least squares to a final R_1 value of 0.0674, for 929 parameters and 13639 unique reflections with $I \geqslant 2\sigma(I)$ and wR_2 of 0.1067 for all 14014 reflections. The BF_4 anions are each disordered over two sites with occupancies of 65 and 60% for the major component of each anion. There are short fluorine contacts to the silver(I) centres and to some *ortho*-hydrogen atoms. For the major components, contacts shorter than the sum of the van der Waals radii (2.67 Å) between fluorine and hydrogen are F11–H62A 2.593, F21–H12B 2.589 and F22–H36B 2.507 Å. To the Ag centres, contacts shorter than the combined van der Waals radii (3.19 Å) are F21–Ag1 2.933(9), F22–Ag1 2.751(7), F11–Ag2 2.861(9) and F12–Ag2 2.656(9) Å. CCDC 182/1549. See http://www.rsc.org/suppdata/cc/a9/a909683c/ for crystallographic files in .cif format.

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