

## 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 $\text{AgOTf}$

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### Supplementary data

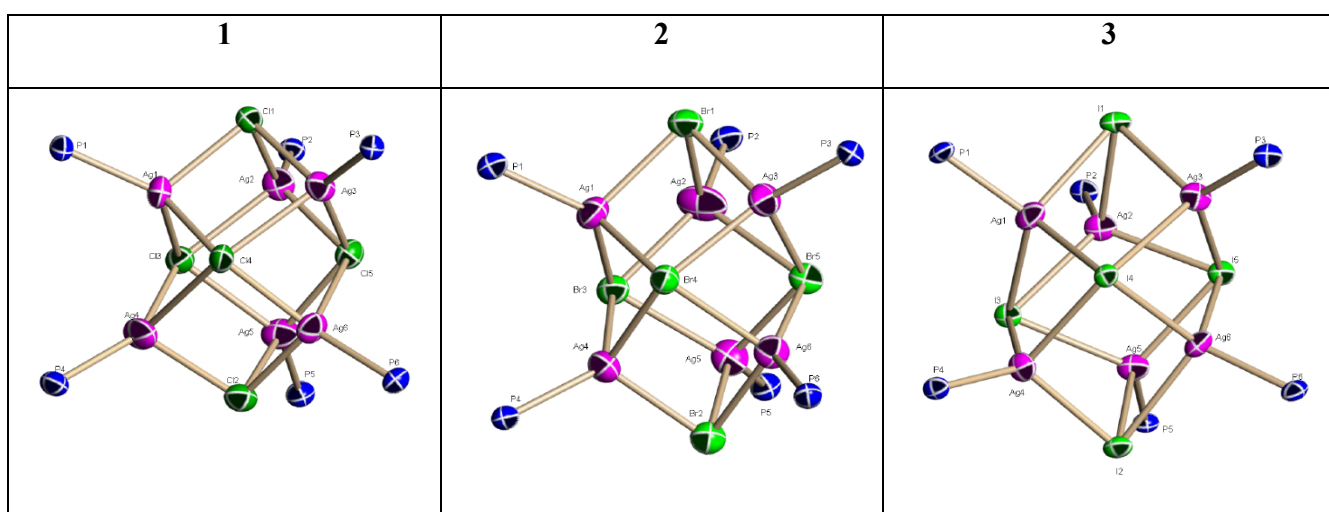


Fig 1: The skeletal structure of **1-3**, showing the  $[\text{Ag}_6\text{X}_5\text{P}_6]^+$  core.

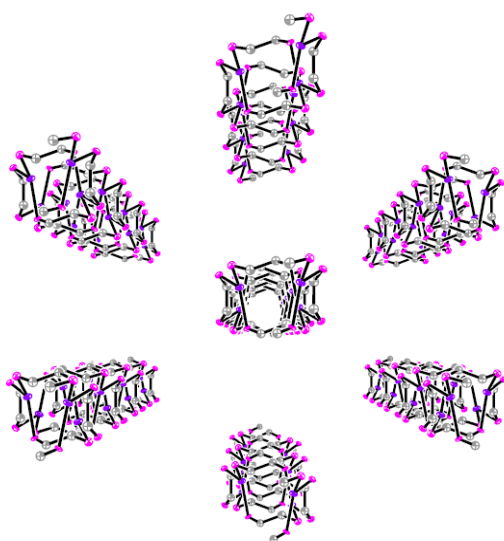


Fig 2: Crystal packing diagram of **4**, showing a columnar structure for each coordination polymer chain.

## Experimental

### General procedures

All reactions were performed under pre-purified dry nitrogen using standard Schlenk techniques. The products are air-stable and hence recrystallizations were performed in air. All reagents used were of reagent grade quality obtained from commercial sources and were used as received. Commercial reagents MeCN, CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> were distilled from CaH<sub>2</sub>. NidppRX<sub>2</sub> are prepared according to literature procedures.<sup>11</sup>

All <sup>1</sup>H NMR(δ (TMS)=0.0ppm) and <sup>31</sup>P {<sup>1</sup>H} NMR(δ(85% H<sub>3</sub>PO<sub>4</sub>) = 0.0 ppm) were recorded at *ca.* 300K at operating frequencies of 500.13 and 202.45 MHz respectively on a Bruker AVANCE 500MHz. ESIMS were obtained with a Finnigan / MAT LCQ mass spectrometer coupled with TSP4000 HPLC system and the crystal 310 CE systems. Samples were injected via a Rheodyne valve fitted with a 5 μL sample loop. The capillary temperature was 100°C for obtaining of the spectra of all complexes. The capillary voltage was 17V. Peaks were assigned from the m/z values and from the isotopic distribution patterns. The m/z values given are for the most intense peak in the envelopment in each case. Samples used for elemental analyses were generally those from the bulk whereas crystals for X-Ray diffraction studies were single-crystals grown from the bulk sample.

### Syntheses

**General synthesis to complexes 1, 2, 4-7.** AgOTf (0.0385g, 0.15mmol) was dissolved in MeCN, followed by the addition of CH<sub>2</sub>Cl<sub>2</sub>. NidppRX<sub>2</sub> (0.075mmol) was added. For **1** and **2**, yellow product precipitates out soon after mixing of reagents so the mixture was filtered and recrystallized. For **4-7**, the reaction mixture was stirred for 1h and filtered. The resultant mixture was filtered to give a colourless filtrate. The filtrate was concentrated and ether was added to precipitate out the white product. The mixture was then filtered and dried under vacuum.

[Ag<sub>6</sub>(dppf)<sub>3</sub>Cl<sub>5</sub>]OTf, **1**. <sup>1</sup>H NMR: δ= 7.26-2.5 (m) (phenyl); 4.1-4.5 (br) (Cp). <sup>31</sup>P NMR: δ= -0.04 (m), 3.4 (m). ESIMS: m/z= 661.2 ([Agdppf]<sup>+</sup>) (100%); 804.8 ([Ag<sub>2</sub>(dppf)Cl]<sup>+</sup>) (95%); 1359.4 ([Ag<sub>2</sub>(dppf)<sub>2</sub>Cl]<sup>+</sup>) (25%); 1502.3 ([Ag<sub>3</sub>(dppf)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>) (10%); 1646.3 ([Ag<sub>4</sub>(dppf)<sub>2</sub>Cl<sub>3</sub>]<sup>+</sup>) (15%). Anal. Cal. For 1.2CHCl<sub>3</sub>: C, 43.86; H, 3.01. Found: C, 43.54; H, 2.76.

[Ag<sub>6</sub>(dppf)<sub>3</sub>Br<sub>5</sub>]OTf, **2**. <sup>1</sup>H NMR: δ= 7.25, 7.26, 7.33, 7.61 (Phenyl); 3.89, 4.58 (Cp). <sup>31</sup>P NMR: δ= -2.7, 0.4. ESIMS: m/z= 661.2 ([Agdppf]<sup>+</sup>) (100%); 1358.7 ([Ag<sub>2</sub>(dppf)<sub>2</sub>Cl]<sup>+</sup>) (70%); 1403.6 ([Ag<sub>2</sub>(dppf)<sub>2</sub>Br]<sup>+</sup>) (20%). ESIMS was carried out in CH<sub>2</sub>Cl<sub>2</sub>, resulting in decomposition of complex in solvent to abstract Cl<sup>-</sup>. Anal. Cal. For 2.3CHCl<sub>3</sub>: C, 39.57; H, 2.73. Found: C, 39.13; H, 2.06.

Synthesis of [Ag<sub>6</sub>(dppf)<sub>3</sub>I<sub>5</sub>]OTf, **3**. DPPF (0.1109g, 0.2mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, followed by the addition of AgI (0.0234.8g, 0.1mmol) and NaPF<sub>6</sub> (0.0168g, 0.1mmol). The mixture was stirred overnight to give a yellow precipitate. The mixture

was filtered, redissolved in  $\text{CHCl}_3$ , and then precipitated with ether.  $^1\text{H}$  NMR:  $\delta = 7.25, 7.26, 7.33, 7.61$  (Phenyl);  $3.89, 4.58$  (Cp).  $^{31}\text{P}$  NMR:  $\delta = -11.5, -8.9$ . Anal. Cal. For  $3.12\text{CHCl}_3$ : C, 30.51; H, 2.14. Found: C, 30.64; H, 1.72. The high insolubility of this complex has made solution studies very difficult. A large amount of  $\text{CHCl}_3$  is trapped in the sample as a lot of  $\text{CHCl}_3$  had to be used to dissolve the complex for purification.

$[\text{Ag}_2(\text{dppe})_3]_n(\text{OTf})_{2n}$ , **4**.  $^1\text{H}$  NMR:  $\delta = 7.21-7.74$  (m) (phenyl);  $2.46, 2.78$  (s) (et).  $^{31}\text{P}$  NMR:  $\delta = 3.3, 4.5$  (d);  $^2J_{\text{P-P}} = 17.4\text{Hz}$ . ESIMS:  $m/z = 1099.8$  (100%) ( $[\text{Ag}_2(\text{dppe})_2\text{Cl}_2 + \text{Na}^+]^+$ ). Anal. Cal. For  $4.\text{CH}_2\text{Cl}_2$ : C, 54.23; H, 4.16. Found: C, 54.21; H, 3.83.

$[\text{Ag}_2(\text{dppe})_3(\text{OTf})]_n(\text{OTf})_n$ , **5**.  $^1\text{H}$  NMR:  $7.26-7.52$  (m) (phenyl);  $3.95$  (m) (et).  $^{31}\text{P}$  NMR:  $11.4$  (d) (min),  $8.8$  (d) (min),  $4.6$  (d) (maj),  $3.2$  (d) (maj);  $^2J_{\text{P-P}} = 17.4\text{Hz}$ . ESIMS:  $m/z = 905.1$  (100%) ( $[\text{Ag}(\text{dppe})_2]^+$ ). Anal. Cal. For  $5.3\text{CH}_2\text{Cl}_2$ : C, 50.76; H, 4.00. Found: C, 51.17; H, 2.84. **5** may exist as a mixture of coordination isomers which we are unable to separate, leading to the slight impurity of sample.

$[\text{Ag}_2(\text{dppe})_3\text{Cl}_2]_n$ , **6, 7**.  $^1\text{H}$  NMR:  $7.26-7.52$  (m) (phenyl);  $3.95$  (m) (et).  $^{31}\text{P}$  NMR:  $4.9$  (d),  $6.2$  (d);  $^2J_{\text{P-P}} = 17.4\text{Hz}$ . ESIMS:  $m/z = 1099.8$  (100%) ( $[\text{Ag}_2(\text{dppe})_2\text{Cl}_2 + \text{Na}^+]^+$ ). As **6** and **7** coexist in the sample mixture in unknown proportions, no elemental analysis data can be calculated.

### Crystal Structure determinations

The diffraction experiments were carried out on a Bruker SMART CCD diffractometer with a Mo-K $\alpha$  sealed tube at -50°C. The program SMART<sup>12</sup> was used for collecting frames of data, indexing reflections and determination of lattice parameters, SAINT for integration of the intensity of reflections and scaling, SADABS<sup>13</sup> for absorption correction and SHELXTL<sup>14</sup> for space group and structure determination and least-squares refinements on F<sup>2</sup>. The relevant crystallographic data and refinement details are shown in table 2. For complex **1**, the crystal is triclinic, space group P-1. In the asymmetric unit, there is one complex cation which has an Ag<sub>6</sub>Cl<sub>5</sub> cluster centre, one anion CF<sub>3</sub>SO<sub>3</sub>, one dichloromethane and one disordered solvent (which appeared to be a mixture of dichloromethane and chloroform). Restraints in bond lengths and thermal parameters were applied to the disordered CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> pair to prevent excessive shifting in final refinement. The final R values for 2-theta max at 50 degrees are: R1= 0.0502 and wR2=0.121. For complex **2**, the crystal is triclinic, space group P-1. The intensity data was bad. T<sub>int</sub>=0.20 at two theta max of 50 degrees. However structure solution showed the cation and anion clearly with a number of solvent molecules of chloroform, some of which were disordered. In the asymmetric unit, there is one cation, one anion OTf and 3.5 chloroform (refined as CHCl<sub>3</sub>). Two of the CHCl<sub>3</sub> were normal, another one at general were disordered into two parts. The third CHCl<sub>3</sub> at a symmetry centre (therefore counted as half) was also disordered. The C atoms and H atoms of the disordered chloroform were not located. The cation has a centre of Ag<sub>6</sub>Br<sub>5</sub> and has structure same as that of **1**. Since the data were bad, final refinement was performed with two max of 45 degrees. C atoms

and disordered Cl atoms were not refined anisotropically. The data to parameter ratio was then kept to 20 to 1. Final R values were  $R_1=0.0753$ ,  $wR_2=0.1432$ . For complex **3**, the crystal is triclinic, space group P-1. The data set was bad, due to the small size of the crystal. Complex **3** is poorly soluble, resulting in great difficulties in crystallization. Although the positions of the heavier atoms (I and Ag) showed up easily, the lighter atoms did not behave well during refinement. The general background was high. This had resulted in weak  $F_o$  values for the weak reflections to be higher than the  $F_c$ 's as shown in the  $F_o/F_c$  list. The asymmetric unit contains one complex cation  $[Ag_6I_5(dppf)_3]^+$ . One anion  $PF_6^-$  is expected, but only half (at special position) could be located. There are a number of residual peaks which could be the remaining half but we could only fit them as disordered solvent  $CHCl_3$  and  $CH_2Cl_2$ . Refinement was done with anisotropic thermal parameters for the heavier atoms and isotropic thermal parameters for the lighter ones. Restraints were applied to C-F and C-Cl distances to keep the values in normal ranges. For complex **4**, the crystal is monoclinic, space group  $C_2/C$ . the data were poor, probably due to small size of the sample. The  $R_{int}$  at 2-theta max of 45 degrees was 0.185. However the structure could be determined despite the high R value of  $R_1=0.152$  and  $wR_2=0.295$ . The C atoms did not respond well to anisotropic refinement, they were left isotropic. The phenyl rings were refined as fixed hexagon. The asymmetric unit contains one cation of the formula  $Ag[(P(Ph))_2(CH_2)]^{3+}$  one OTf and half dichloromethane. The cations form an infinite linear chain through  $CH_2-CH_2$  linkages. For complex **5**, the crystal is triclinic, space group P-1. The structure is that of the complex  $[Ag_2(dppe)_3(OTf)_2]$ . Final R values are  $R_1 = 0.0769$  and  $wR_2=0.1410$ . The cations form a linear chain with alternating  $Ag(dppe)_2Ag$  and  $Ag(dppe)Ag$  linkages. The two OTf's are

linked to the two Ag at two different distances (2.54Å and 2.85Å). One of the phenyl ring (C1L- C6L) had large thermal motion, ISOR restraint was used to contain the thermal parameters. For complex **6**, the crystal is triclinic, space group P-1. The data were poor with  $R_{\text{int}} = 0.1623$ , probably due to decomposition of crystal during data collection. We capped the 2-theta max at 48 degrees and maintained a reflections/parameters ratio of 15:1. The final R values are  $R1=0.115$  and  $wR2=0.265$ . The crystal contains two types of linear chains of the complex chloride. In the asymmetric unit, there are two kinds of Ag complex. One is one half of  $\text{Ag}_2(\text{dppe})_3\text{Cl}_2$ . This forms a linear chain similar to that of complex **5**, with Cl instead of OTf and with all Ag-Cl bond equivalent. The other is a  $\text{Ag}_2(\text{dppe})_2\text{Cl}_2$  chain. The two Ag are bridged by two Cl (Ag-Ag= 3.36Å) and a dppe. The other dppe serves as a link to another  $\text{Ag}_2$ , thus forming a zig-zag linear chain. There are also three  $\text{CH}_2\text{Cl}_2$  solvent molecules in the asymmetric unit. C-Cl bond distances of the solvent dichloromethane were restrained in final refinement to prevent excessive shifting from normal values using DFIX instruction.

<sup>11</sup> J. A. S. Bonfim, F. P. De Souza, C. A. L. Filgueiras, A. G. De Sousa, M. T. P. Gabardella, *Polyhedron*, **2003**, 22, 1567; b. J. A. Rahn, A. Delian, J. H. Nelson, *Inorg. Chem.*, **1989**, 28, 215.

<sup>12</sup> SMART and SAINT Software Reference Manuals, Version 5.611, Bruker Analytical X-Ray Systems, Inc., Madison, WI, **2000**.

<sup>13</sup> Sheldrick, G. M., SADABS, software for empirical absorption correction, University of Göttingen, **2000**.

<sup>14</sup> SHELXTL Reference Manual, Version 5.1, Bruker Analytical X-Ray Systems, Inc., Madison, WI, **1997**.

**Table 1:** Selected bond lengths (Å) for complexes 4-6.

	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>
Ag(1)-P(2)	2.473(5)	2.487 (3)	2.505 (3)	-
Ag(1)-P(1)	2.480(5)	2.514 (3)	2.483 (4)	-
Ag(1)-P(3)	2.494(6)	2.476 (2)	2.484 (4)	-
Ag(2)-P(5)	-	2.460 (3)	2.441 (4)	-
Ag(2)-P(4)	-	2.471 (3)	2.441 (4)	-
Ag(2)-P(6)	-	2.515 (3)	-	-
Ag(2)-O(1)	-	2.554 (8)	-	-
Ag(1)-Cl(1)	-	-	2.624 (4)	-
Ag(2)-Cl(2)	-	-	-	2.590 (4)
Ag(2)-Cl(3)	-	-	-	2.726 (4)
Ag(2)-Ag(3)	-	-	-	3.3618 (16)
Ag(3)-P(7)	-	-	-	2.398 (4)
Ag(3)-P(6)	-	-	-	2.471 (4)
Ag(3)-Cl(3)	-	-	-	2.617 (4)
Ag(3)-Cl(2)	-	-	-	2.724 (4)



Table 2: Crystallographic data for complexes 1-6/7.

	1	2	3	4	5	6
<b>Empirical formula</b>	$C_{105}H_{87.50}Ag_6Cl_{6.5}F_3$ $Fe_3O_3P_6S$	$C_{105}H_{86}Ag_6Br_5Cl_{10.5}F_3$ $Fe_3O_3P_6S$	$C_{104.5}H_{87}Ag_6Cl_7F_{1.5}Fe_3I_5$ $O_{0.5}P_{6.5}$	$C_{40.50}H_{37}AgCl$ $F_3O_3P_3S$	$C_{80}H_{72}Ag_2F_6O_6P_6S_2$	$C_{94}H_{90}Ag_3Cl_9P_7$
<b>Temperature (K)</b>	293(2)	223(2)	223(2)	223(2)	223(2)	223(2)
<b>Formula weight</b>	2823.68	3257.16	3277.97	896.99	1709.06	2079.11
<b>Crystal system</b>	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
<b>Space group</b>	P-1	P-1	P-1	C2/c	P-1	P-1
<b>Unit cell dimensions</b>						
<b>a (Å)</b>	14.3332 (9)	14.886(2)	14.0043(14)	12.920(3)	13.5327(13)	14.6609(12)
<b>b (Å)</b>	16.8136 (10)	20.303(3)	14.5664(15)	24.327(6)	15.8115(14)	17.1020(14)
<b>c (Å)</b>	22.5538 (13)	20.947(3)	28.009(3)	25.854(7)	18.3558(17)	19.2916(15)
<b><math>\alpha</math> (°)</b>	82.9690 (10)	84.359(4)	80.220(2)	90	95.741(3)	100.800(2)
<b><math>\beta</math> (°)</b>	79.3730 (10)	82.480(5)	89.298(2)	96.581(6)	90.455(3)	92.932(2)
<b><math>\gamma</math> (°)</b>	85.157 (2)	70.901(4)	78.533(2)	90	91.385(3)	93.317(2)
<b>V (Å<sup>3</sup>)</b>	5291.2(5)	5920.8(15)	5516.8(10)	8072(4)	3906.6(6)	4733.9(7)
<b>Z</b>	2	2	2	8	2	2
<b>D<sub>calc</sub> (mg/m<sup>3</sup>)</b>	1.772	1.827	1.973	1.476	1.453	1.459
<b>Absorbition coefficient (mm<sup>-1</sup>)</b>	1.889	3.400	3.134	0.787	0.743	1.030
<b>F (000)</b>	2792	3173	3146	3648	1740	2106
<b>Crystal size (mm<sup>3</sup>)</b>	0.28 X 0.20 X 0.10	0.10 X 0.06 X 0.04	0.34 X 0.10 X 0.04	0.10 X 0.10 X 0.04	0.12 X 0.10 X 0.03	0.30 X 0.16 X 0.10
<b>Index ranges</b>	-17 ≤ h ≤ 17, -19 ≤ k ≤ 19, -26 ≤ l ≤ 26	-16 ≤ h ≤ 16, -21 ≤ k ≤ 21, -22 ≤ l ≤ 12	-16 ≤ h ≤ 15, -16 ≤ k ≤ 17, -30 ≤ l ≤ 33	-13 ≤ h ≤ 13, -26 ≤ k ≤ 21, -27 ≤ l ≤ 21	-16 ≤ h ≤ 15, -18 ≤ k ≤ 18, -21 ≤ l ≤ 16	-16 ≤ h ≤ 16, -19 ≤ k ≤ 19, -22 ≤ l ≤ 22
<b>R, wR<sup>2</sup> (all data)</b>	0.0681, 0.1182	0.1883, 0.1809	0.1684, 0.3292	0.2038, 0.2993	0.1770, 0.1958	0.1972, 0.2556
<b>Final R, wR<sup>2</sup></b>	0.0502, 0.1104	0.0753, 0.1432	0.1484, 0.3204	0.1548, 0.2765	0.0926, 0.1613	0.1148, 0.2202

Supplementary Material (ESI) for Chemical Communications  
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**Largest diff peak and hole (eÅ<sup>-3</sup>)**    1.297 and -0.958    1.636 and -0.758    3.247 and -2.436    1.200 and -2.262    1.021 and -0.806    1.122 and -0.951

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