Supporting Information

Selective formation of a polar incomplete coordination cage induced by remote ligand substituents

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Experimental section

All reactions requiring anhydrous or inert conditions were carried out under an inert atmosphere of dry nitrogen using standard Schlenk line techniques. Solutions or liquids were introduced in the round bottom flask or in the Schlenk tube using oven dried syringes or cannula through rubber septa. All reactions were stirred magnetically using Teflon-coated stirring bars. In the case heating was required, the reactions were warmed using an electrically heated silicon oil bath, and the stated temperature is the temperature of the bath. Removal of solvents was accomplished using rotary evaporator at water aspirator pressure or under high vacuum.

Tetrahydrofuran and diethyl ether were distilled under nitrogen from sodium benzophenone ketyl.. All other solvents and reagents were used as received from commercial suppliers or purified following standard procedures.

Chemicals were purchased from Sigma-Aldrich Chemical Company, Lancaster or ACROS. Solvents for extractions or chromatography were of technical grade. Flash-chromatography was carried out using Merck Silica (40-60 μ). Analytical TLC was performed with Merck Silica gel 60 F_{254} plates. Visualisation was accomplished by UV-light ($\lambda = 254$ nm) and staining with permanganate solution, followed by heating. All the titrations studies were conducted calculating the equivalency of the titrating solution in respect to the phosphine ligands. Electrospray mass spectra were carried out on the Waters LCT Premier™ XE benchtop orthogonal acceleration time-of-flight (oa-TOF) mass spectrometer.^{1}H, ^{13}C, ^{31}P NMR spectra were all recorded on Bruker AM 300 MHz or AM 500 MHz referenced to the residual 1H or 13C containing solvent or to external 85% H_3PO_4 in the case of ^{31}P-NMR. Chemical shifts (δ) are given in parts per million (ppm) and coupling constants are given in Hertz. Elemental analysis were determined by the Analytical Service Department of the School of Chemistry (ASEP) using a Perkin-Elmer 2400 CHN microanalyser. X-ray crystallography was carried out by the EPSRC Crystallography Service in Southampton and in Daresbury/Newcastle and the structures solved by Prof William Clegg and Dr Ross Harrington, School of Chemistry, Newcastle University, and by Dr Peter Horton, School of Chemistry, University of Southampton.

Scheme S1. Synthetic scheme for ligand **L-NMe$_2$**

Bis-(4-dimethylaminophenyl)phosphine oxide (2)

To a solution of (4-bromophenyl)dimethylamine (15 g, 75.0 mmol) in dry THF (50 ml), Mg (2.370 g, 90.0 mmol) and a crystal of iodine were added at 0°C. After the exothermic reaction had taken place, the mixture was stirred at r.t. for 1 hour. Diethyl phosphite (3.20 ml, 24.7 mmol) was then added at r.t. and the mixture heated to reflux for 2 hours. The reaction was quenched with HCl 0.1 N (100 ml) and the milky mixture was filtered through a short pad of Celite in order to remove the magnesium hydroxide gel. The pad was washed with chloroform.

The water phase was extracted with chloroform (3 x 100 ml) and the collected organic phases dried over $MgSO_4$ and concentrated under reduced pressure. The crude solid obtained was purified by flash-column chromatography (DCM / MeOH = 97/3→95/5). Crystallization from ethyl acetate gave 14.050 g of white crystalline powder.(Yield = 65%).

M.p.= 151°-154°C.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.97 (d, $^1J_{31P-1H}$ = 470 Hz, 1H), 7.50 (dd, J = 8.9 Hz, 13 Hz, 4H), 6.71 (dd, J = 8.9 Hz, 2.2 Hz, 4H), 3.01 (s, 12H).

^{31}P-{^{1}H} NMR (121MHz, $CDCl_3$): δ = 23.39 (s).

Bis-(4-dimethylaminophenyl)phosphine (3)

To a suspension of phosphine oxide (**2**) (1 g, 3.5 mmol) in diethyl ether (150 ml), was added an excess of lithium aluminium hydride (0.530 g, 13.9 mmol) in small portions and the reaction stirred overnight. Distilled degassed water (10 ml) was added slowly, cooling with an ice-bath, to produce a white suspension. The organic layer was transferred to another flask via a canula. The diethyl ether was removed *in vacuo* affording a white powder (0.670 g, Yield = 70%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.69 (m, 4H), 6.63 (d, J = 8.6 Hz, 4H), 5.63 (d, $^1J_{31P-1H}$ = 212 Hz, 1H), 2.55 (s, 12H).

^{31}P-{^{1}H} NMR (121 MHz, $CDCl_3$): δ = -44.30 (s).

1,1,1-tris{bis-(4-dimethylaminophenyl)phosphino-methyl}-ethane (L-NMe_2)[1]

To bis-(4-dimethylamino-phenyl)-phosphine (**3**) (0.670 g, 2.5 mmol) in DMSO (15 ml), KO*t*Bu (0.280 g, 5.2 mmol) was added at room temperature to produce an intense dark-red solution. After stirring for a 15 minutes, 1,3-dichloro-2-(chloromethyl)-2-methylpropane (68 µl, 0.5 mmol) was slowly added and the mixture heated at 130˚-140˚C. When the dark-red colour of the solution had turned to yellow, the mixture was cooling down at room temperature and degassed water was added, producing a white precipitate. The white precipitate was filtered off and washed with water.
Crystallization from acetone/water gave 0.2 g of crystalline product (Yield = 45%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.27 (dd, *J* = 8.5 Hz, 7.4 Hz, 12H), 6.65 (d, *J* = 8.5 Hz, 12H), 2.96 (s, 36H), 2.37 (d, 6H), $^2J_{31P\text{-}1H}$ = 2.6 Hz), 1.01 (s, 3H).

^{31}P-{^{1}H} NMR (121 MHz, $CDCl_3$): δ = -29.84 (s).

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 150.65 (s, C_{ar}), 134.46 (d, $^1J_{31P\text{-}13C}$ = 20.7 Hz, C_{ar}), 127.08 (d, $^3J_{31P\text{-}13C}$ = 6.9 Hz, CH_{ar}), 112.76 (d, $^2J_{31P\text{-}13C}$ = 8.0 Hz, CH_{ar}), 44.6-44.16 (m, CH_2), 40.82 (s, CH_3), 39.17 (q, $^1J_{31P\text{-}13C}$=12.6 Hz, C), 29.76-29.40 (m, CH_3).

ESI-MS (m/z): 883$(M+1)^+$.

CHN analysis for $C_{53}H_{69}N_6P_3$: C 72.09, H 7.88, N 9.52 ; found C 71.70 H 7.60 N 9.25.

$[Ag_6(L\text{-}NMe_2)_4(X)_4][X]_2$

In a typical preparation, a solution of **L** (100 mg, 0.110 mmol) in chloroform (4 ml) was added to a solution of silver(I) salt AgX = (a) NO_3, (b) O_3SCF_3, (c) $O_3SC_6H_4CH_3$, (0.165 mmol) in acetonitrile (1 ml). Crystals of the following complexes were obtained by diffusing hexane or benzene in their solutions and leaving to stand for a period of 3 weeks.

$[Ag_6(L\text{-}NMe_2)_4(O_3SC_6H_4CH_3)_3][O_3SC_6H_4CH_3]_3$

Crystals were obtained after 3 weeks by diffusing benzene in the solution (0.079 mg, Yield = 55%).

^{31}P-{^{1}H} NMR (202 MHz, $CDCl_3/CH_3CN$ = 4/1, -50°C): δ = -9.20 (doublet of pairs of doublets (dpd) 3P, $^1J_{(31P\text{-}109Ag)}$= 572 Hz, $^2J_{(31P\text{-}31P)}$ = 143 Hz), -10.79 (dpd 3P, $^1J_{(31P\text{-}109Ag)}$= 568 Hz, $^2J_{(31P\text{-}31P)}$ = 133 Hz), -12.91 (dpd 3P, $^1J_{(31P\text{-}109Ag)}$= 584 Hz, $^2J_{(31P\text{-}31P)}$ = 133 Hz), -13.64 (dpd 3P, $^1J_{(31P\text{-}109Ag)}$= 550 Hz, $^2J_{(31P\text{-}31P)}$ = 143 Hz).

^{31}P-{^{1}H} NMR (202 MHz, $CDCl_3$/CH_3CN = 4/1, -25^{o}C): δ = -9.00 (doublet of pairs of doublets (dpd) 3P, $^{1}J_{(31P\text{-}109Ag)}$= 571 Hz, $^{2}J_{(31P\text{-}31P)}$ = 145 Hz), -10.86 (dpd 3P, $^{1}J_{(31P\text{-}109Ag)}$= 570 Hz, $^{2}J_{(31P\text{-}31P)}$ = 133 Hz), -12.75 (dpd 3P, $^{1}J_{(31P\text{-}109Ag)}$= 584 Hz, $^{2}J_{(31P\text{-}31P)}$ = 133 Hz), -13.28 (dpd 3P, $^{1}J_{(31P\text{-}109Ag)}$= 550 Hz, $^{2}J_{(31P\text{-}31P)}$ = 145 Hz).

^{31}P-{^{1}H} NMR (202 MHz, $CDCl_3$/CH_3CN = 4/1, 0^{o}C): δ = -8.84 (doublet of pairs of doublets (dpd) 3P, $^{1}J_{(31P\text{-}109Ag)}$= 570 Hz, $^{2}J_{(31P\text{-}31P)}$ = 146 Hz), -10.81 (dpd 3P, $^{1}J_{(31P\text{-}109Ag)}$= 572 Hz, $^{2}J_{(31P\text{-}31P)}$ = 133 Hz), -12.16 (dpd 3P, $^{1}J_{(31P\text{-}109Ag)}$= 584 Hz, $^{2}J_{(31P\text{-}31P)}$ = 133 Hz), -13.00 (dpd 3P, $^{1}J_{(31P\text{-}109Ag)}$= 550 Hz, $^{2}J_{(31P\text{-}31P)}$ = 146 Hz).

^{31}P-{^{1}H} NMR (202 MHz, $CDCl_3$/CH_3CN = 4/1, 25^{o}C): δ = -8.67 (doublet of pairs of doublets (dpd) 3P, $^{1}J_{(31P\text{-}109Ag)}$= 569 Hz, $^{2}J_{(31P\text{-}31P)}$ = 146 Hz), -10.71 (dpd 3P, $^{1}J_{(31P\text{-}109Ag)}$= 572 Hz, $^{2}J_{(31P\text{-}31P)}$ = 133 Hz), -11.83 (dpd 3P, $^{1}J_{(31P\text{-}109Ag)}$= 583 Hz, $^{2}J_{(31P\text{-}31P)}$ = 133 Hz), -12.69 (dpd 3P, $^{1}J_{(31P\text{-}109Ag)}$= 550 Hz, $^{2}J_{(31P\text{-}31P)}$ = 146 Hz),

^{31}P-{^{1}H} NMR (202 MHz, $CDCl_3$/CH_3CN = 4/1, 60^{o}C): δ = -11.5 (pair of doublets, $^{1}J_{(31P\text{-}109Ag)}$= 562 Hz)

CHN analysis for $C_{254}H_{318}Ag_6N_{24}O_{18}P_{12}S_6$: C 58.58, H 6.16, N 6.46 ; found C 58.24, H 6.27, N 6.38.

Crystal data and structure refinement

Identification code	2006src1215/NN4
Chemical formula (moiety)	$C_{233}H_{297}Ag_6N_{24}O_9P_{12}S_3^{3+}\cdot 3C_7H_7O_3S^{-}$
Chemical formula (total)	$C_{254}H_{318}Ag_6N_{24}O_{18}P_{12}S_6$
Formula weight	5206.68
Temperature	120(2) K
Radiation, wavelength	MoKα, 0.71073 Å
Crystal system, space group	cubic, Pa$\bar{3}$

Unit cell parameters	a = 39.4527(8) Å	α = 90°
	b = 39.4527(8) Å	β = 90°
	c = 39.4527(8) Å	γ = 90°
Cell volume	61409(2) Å^3	
Z	8	
Calculated density	1.126 g/cm^3	
Absorption coefficient μ	0.53 mm^{-1}	
F(000)	21696	
Crystal colour and size	Colourless, 0.36 × 0.36 × 0.24 mm^3	
Reflections for cell refinement	12637 (θ range 1.0 to 27.5°)	
Data collection method	Bruker-Nonius KappaCCD	
	ϕ & ω scans	
θ range for data collection	2.9 to 27.5°	
Index ranges	h –51 to 49, k –38 to 29, l –27 to 50	
Completeness to θ = 27.5°	97.4 %	
Reflections collected	149637	
Independent reflections	22890 (R_{int} = 0.1093)	
Reflections with F^2>2σ	6751	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.839 and 0.889	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.2000, 0.0000	
Data / restraints / parameters	22890 / 5610 / 1421	
Final R indices [F^2>2σ]	R1 = 0.1112, wR2 = 0.3148	
R indices (all data)	R1 = 0.2195, wR2 = 0.3610	
Goodness-of-fit on F^2	0.892	
Largest and mean shift/su	0.004 and 0.000	
Largest diff. peak and hole	1.28 and –0.62 e Å^{-3}	

Special details:

All hydrogen atoms were idealized and constrained in a riding model.

There was disorder in most of the 4-(dimethylamino)phenyl groups.

There was some highly disordered solvent in the structure. This was removed from the calculations using the SQUEEZE program, together with the uncoordinated tosylate anions, which could not be located.

$[Ag_6(L\text{-}NMe_2)_4(NO_3)_3][NO_3]_3$

Block crystals were obtained after a week by diffusing hexane in the solution (0.040 g, Yield = 30 %).

$^{31}P\text{-}\{^1H\}$ NMR (202 MHz, $CDCl_3/CH_3CN$= 4/1, 25°C): δ = -8.95 (pair of doublets) $^1J_{109Ag\text{-}31P}$ = 590 Hz.

CHN analysis for $C_{212}H_{276}Ag_6N_{30}O_{18}P_{12}$: C 55.92, H 6.11, N 9.23 ; found C 56.00, H 6.27, N 9.14.

Crystal data and structure refinement

Identification code	2006src1214	
Chemical formula (moiety)	$C_{212}H_{276}Ag_6N_{27}O_9P_{12}^{3+}\cdot 3NO_3^-$	
Chemical formula (total)	$C_{212}H_{276}Ag_6N_{30}O_{18}P_{12}$	
Formula weight	4551.55	
Temperature	120(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	trigonal, $R\bar{3}$	
Unit cell parameters	a = 30.408(2) Å	α = 90°
	b = 30.408(2) Å	β = 90°
	c = 53.007(6) Å	γ = 120°
Cell volume	42445(7) Å^3	

Z	6
Calculated density	1.068 g/cm^3
Absorption coefficient μ	0.53 mm^{-1}
F(000)	14184
Crystal colour and size	Colourless, 0.36 × 0.36 × 0.24 mm^3
Reflections for cell refinement	7899 (θ range 2.9 to 27.5°)
Data collection method	Bruker-Nonius KappaCCD
	ϕ & ω scans
θ range for data collection	2.9 to 27.5°
Index ranges	h –39 to 39, k –39 to 39, l –63 to 62
Completeness to θ = 25.0°	95.5 %
Reflections collected	76905
Independent reflections	19094 (R_{int} = 0.1128)
Reflections with $F^2 > 2\sigma$	7069
Absorption correction	semi-empirical from equivalents
Min. and max. transmission	0.834 and 0.885
Structure solution	direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting parameters a, b	0.2000, 0.0000
Data / restraints / parameters	19094 / 7152 / 1455
Final R indices [$F^2 > 2\sigma$]	R1 = 0.1219, wR2 = 0.3425
R indices (all data)	R1 = 0.2219, wR2 = 0.3760
Goodness-of-fit on F^2	1.006
Largest and mean shift/su	0.001 and 0.000
Largest diff. peak and hole	0.83 and –1.21 e Å^{-3}

Special details:

All hydrogen atoms were idealized and constrained in a riding model.

All the 4-(dimethylamino)phenyl groups were disordered over 2 sites.

There was some highly disordered solvent in the structure. This was removed from the calculations using the SQUEEZE program, together with the uncoordinated nitrate anions, which could not be located.

$[Ag_6(L\text{-}NMe_2)_4(O_3SCF_3)_4][O_3SCF_3]_2$

Crystals were obtained after 3 weeks by diffusing hexane into the solution (0.086 mg, Yield = 62%).

^{31}P-{^1H} NMR (202 MHz, $CDCl_3/CH_3CN$ = 4/1, -50°C): δ = -7.51 (doublet of pairs of doublets (dpd) 3P, $^1J_{(31P\text{-}109Ag)}$= 574 Hz, $^2J_{(31P\text{-}31P)}$ = 149 Hz), -10.20 (pair of doublets 6 P, $^1J_{(31P\text{-}109Ag)}$= 590 Hz), -12.12 (dpd 3P, $^1J_{(31P\text{-}109Ag)}$= 572 Hz, $^2J_{(31P\text{-}31P)}$ = 149 Hz).

^{31}P-{^1H} NMR (202 MHz, $CDCl_3/CH_3CN$ = 4/1, -50°C): δ = -7.70 (doublet of pairs of doublets (dpd) 3P, $^1J_{(31P\text{-}109Ag)}$= 577 Hz, $^2J_{(31P\text{-}31P)}$ = 151 Hz), -10.20 (dpd 3P, $^1J_{(31P\text{-}109Ag)}$= 584 Hz, $^2J_{(31P\text{-}31P)}$ = 140 Hz), -11.09 (dpd 3P, $^1J_{(31P\text{-}109Ag)}$= 589 Hz, $^2J_{(31P\text{-}31P)}$ = 140 Hz), -12.45 (dpd 3P, $^1J_{(31P\text{-}109Ag)}$= 566 Hz, $^2J_{(31P\text{-}31P)}$ = 151 Hz).

^{31}P-{^1H} NMR (202 MHz, $CDCl_3/CH_3CN$ = 4/1, 60°C): δ = -9.35 (pair of doublets, $^1J_{(31P\text{-}109Ag)}$= 590 Hz)

CHN analysis for $[Ag_6(\mathbf{L})_4(O_3SCF_3)_6]$: C 51.60, H 5.48, N 6.63 ; found C 51.24 H 5.27 N 6.34

Crystal data and structure refinement

Identification code	ssg0146
Chemical formula (moiety)	$C_{216}H_{276}Ag_6F_{12}N_{24}O_{12}P_{12}S_4^{2+}\cdot 2CF_3O_3S^-$
Chemical formula (total)	$C_{218}H_{276}Ag_6F_{18}N_{24}O_{18}P_{12}S_2$
Formula weight	5073.94
Temperature	120(2) K
Radiation, wavelength	synchrotron, 0.6926 Å

Crystal system, space group	trigonal, P31c	
Unit cell parameters	a = 26.8708(8) Å	α = 90°
	b = 26.8708(8) Å	β = 90°
	c = 51.831(3) Å	γ = 120°
Cell volume	32410(2) Å^3	
Z	4	
Calculated density	1.040 g/cm^3	
Absorption coefficient μ	0.51 mm^{-1}	
F(000)	10464	
Crystal colour and size	colourless, 0.20 × 0.10 × 0.10 mm^3	
Reflections for cell refinement	9896 (θ range 2.2 to 17.5°)	
Data collection method	Bruker APEX2 CCD diffractometer thin-slice ω scans	
θ range for data collection	2.1 to 18.4°	
Index ranges	h –24 to 20, k –23 to 24, l –47 to 47	
Completeness to θ = 18.4°	98.2 %	
Reflections collected	85791	
Independent reflections	16753 (R_{int} = 0.0551)	
Reflections with $F^2>2\sigma$	14610	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.910 and 0.955	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.1582, 0.0000	
Data / restraints / parameters	16753 / 7688 / 1882	
Final R indices [$F^2>2\sigma$]	R1 = 0.0644, wR2 = 0.1821	
R indices (all data)	R1 = 0.0706, wR2 = 0.1913	
Goodness-of-fit on F^2	1.045	
Absolute structure parameter	0.06(3)	
Extinction coefficient	0.0025(2)	

Largest and mean shift/su	0.056 and 0.002
Largest diff. peak and hole	0.36 and –0.29 e Å^{-3}

Special details:

There are two cations (and associated anions) in the asymmetric unit.

All hydrogen atoms were idealized and constrained in a riding model.

Some of the 4-(dimethylamino)phenyl groups were disordered over 2 sites.

There was some highly disordered solvent in the structure. This was removed from the calculations using the SQUEEZE program, together with the uncoordinated triflate anions, which could not be located.

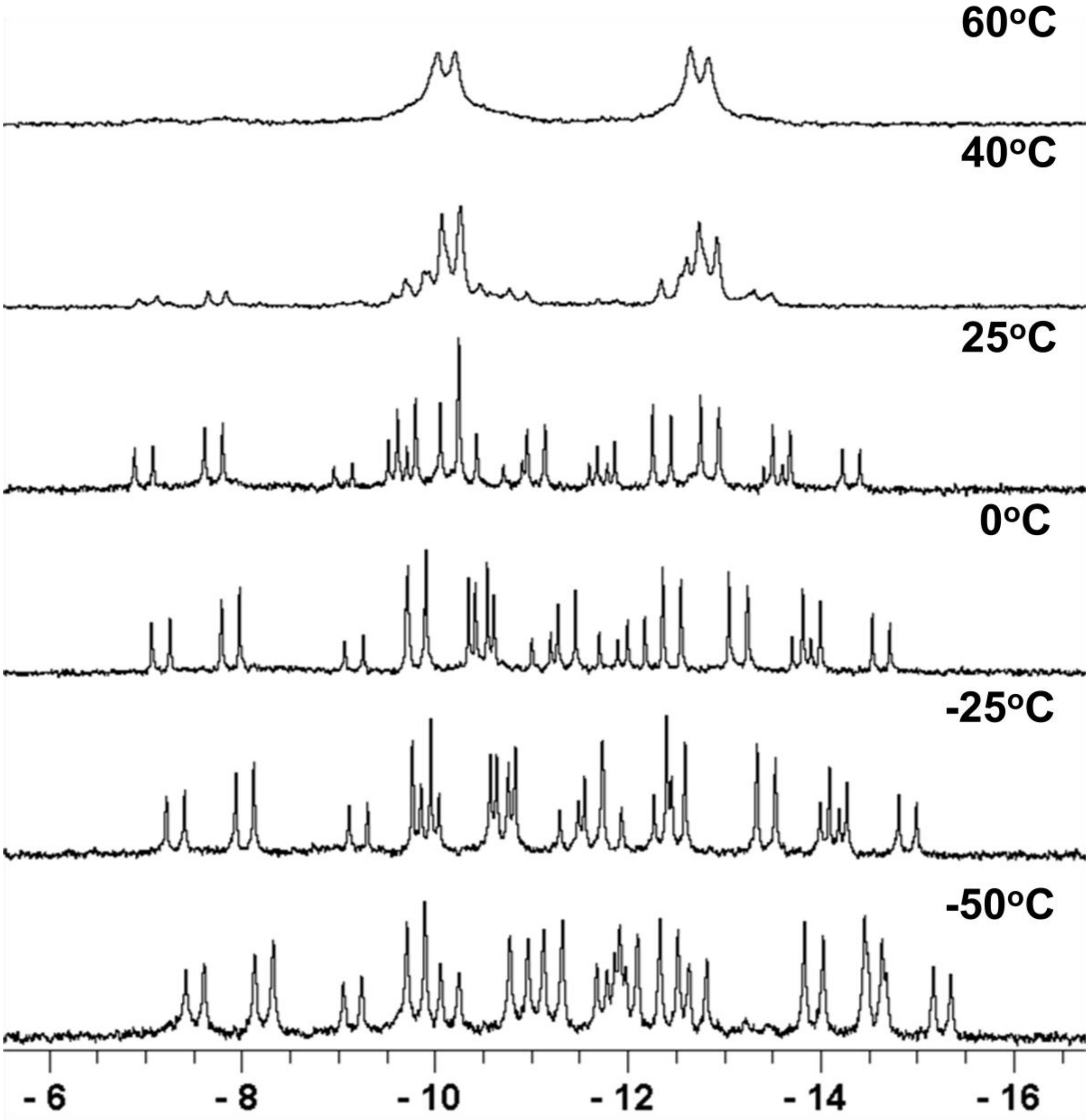

Figure S1. Variable temperature ^{31}P-NMR (202 MHz) spectra in $CDCl_3$-CH_3CN of $[Ag_6(L\text{-}NMe_2)_4(O_3SC_6H_4CH_3)_3][O_3SC_6H_4CH_3]_3$

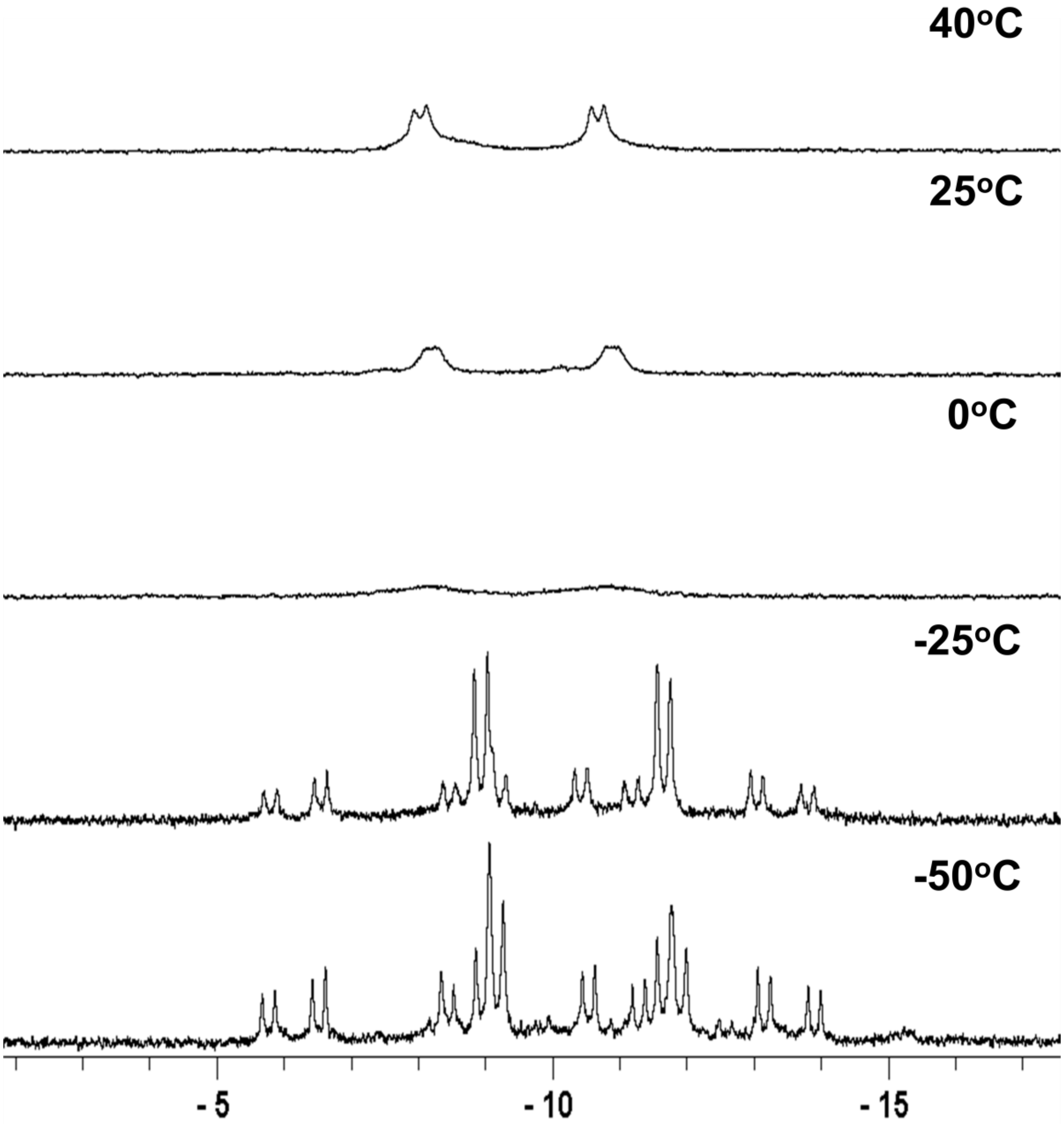

Figure S2. Variable temperature ^{31}P-NMR (202 MHz) spectra in $CDCl_3$-CH_3CN of $[Ag_6(L\text{-}NMe_2)_4(O_3SCF_3)_3][O_3SCF_3]_3$.

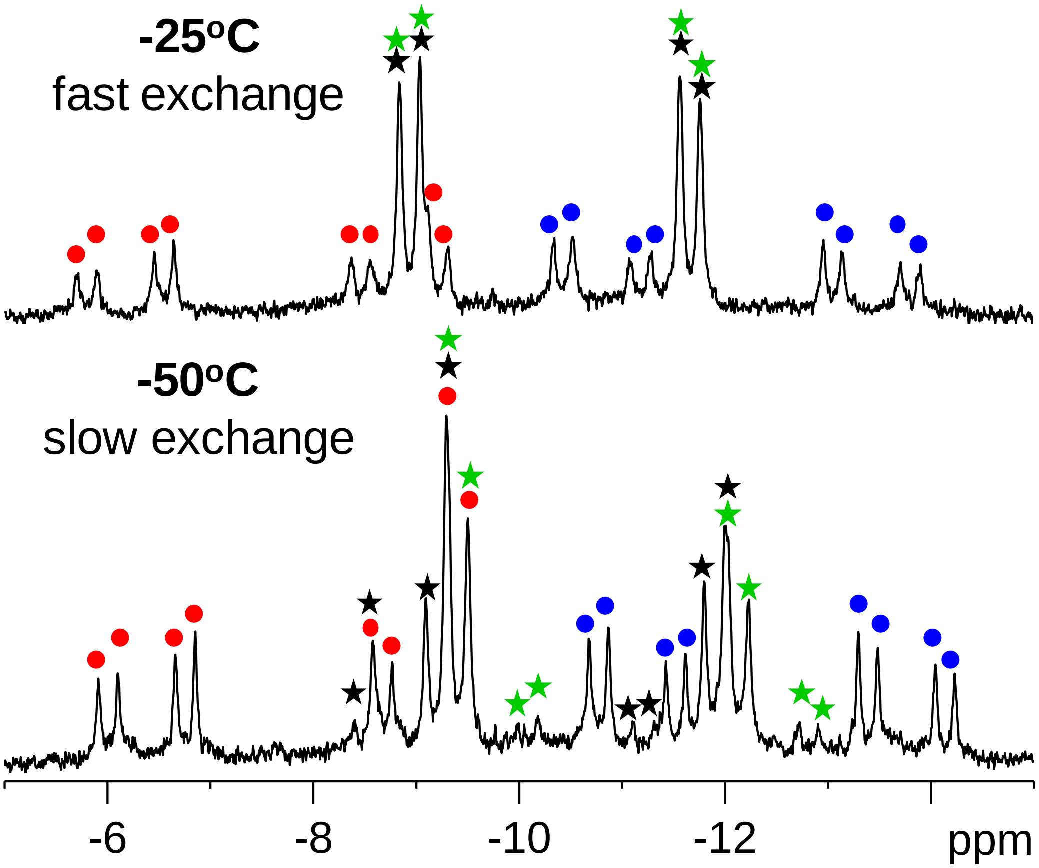

Figure S3. Variable temperature ^{31}P-NMR (202 MHz) spectra in $CDCl_3$-CH_3CN of $[Ag_6(L\text{-}NMe_2)_4(O_3SCF_3)_3][O_3SCF_3]_3$ showing the transition from a cage with C_3 symmetry (at -50^{o}C, four inequivalent P centres observed) to C_{3v} symmetry on the NMR timescale (at -25^{o}C, P_C and P_D become equivalent.

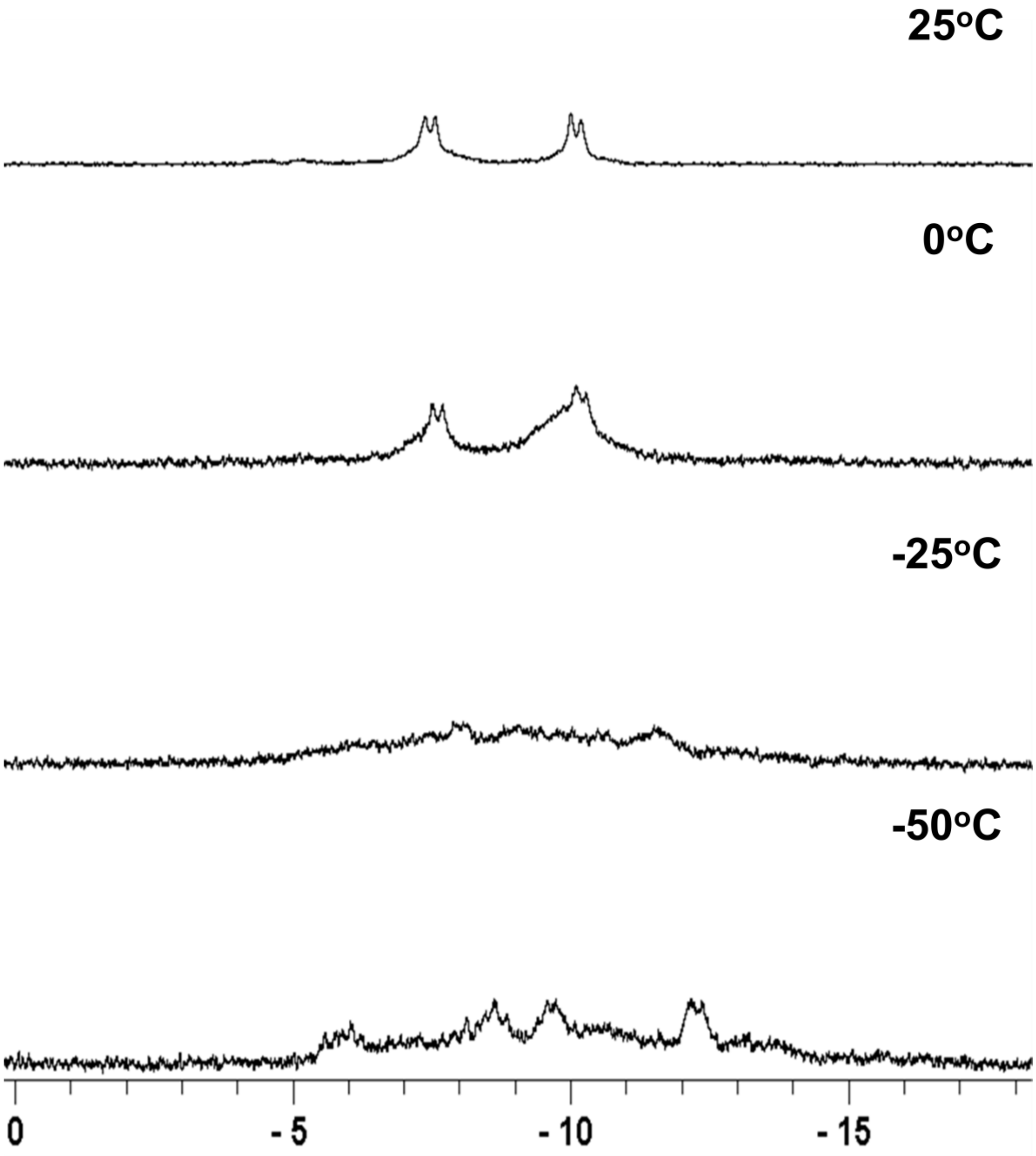

Figure S4. Variable temperature ^{31}P-NMR (202 MHz) spectra in $CDCl_3$-CH_3CN of $[Ag_6(L\text{-}NMe_2)_4(NO_3)_3][NO_3]_3$. At 0^{o}C $[Ag_6(L\text{-}NMe_2)_4(NO_3)_3][NO_3]_3$ started to precipitate resulting in a broad and almost featureless spectra at lower temperatures.

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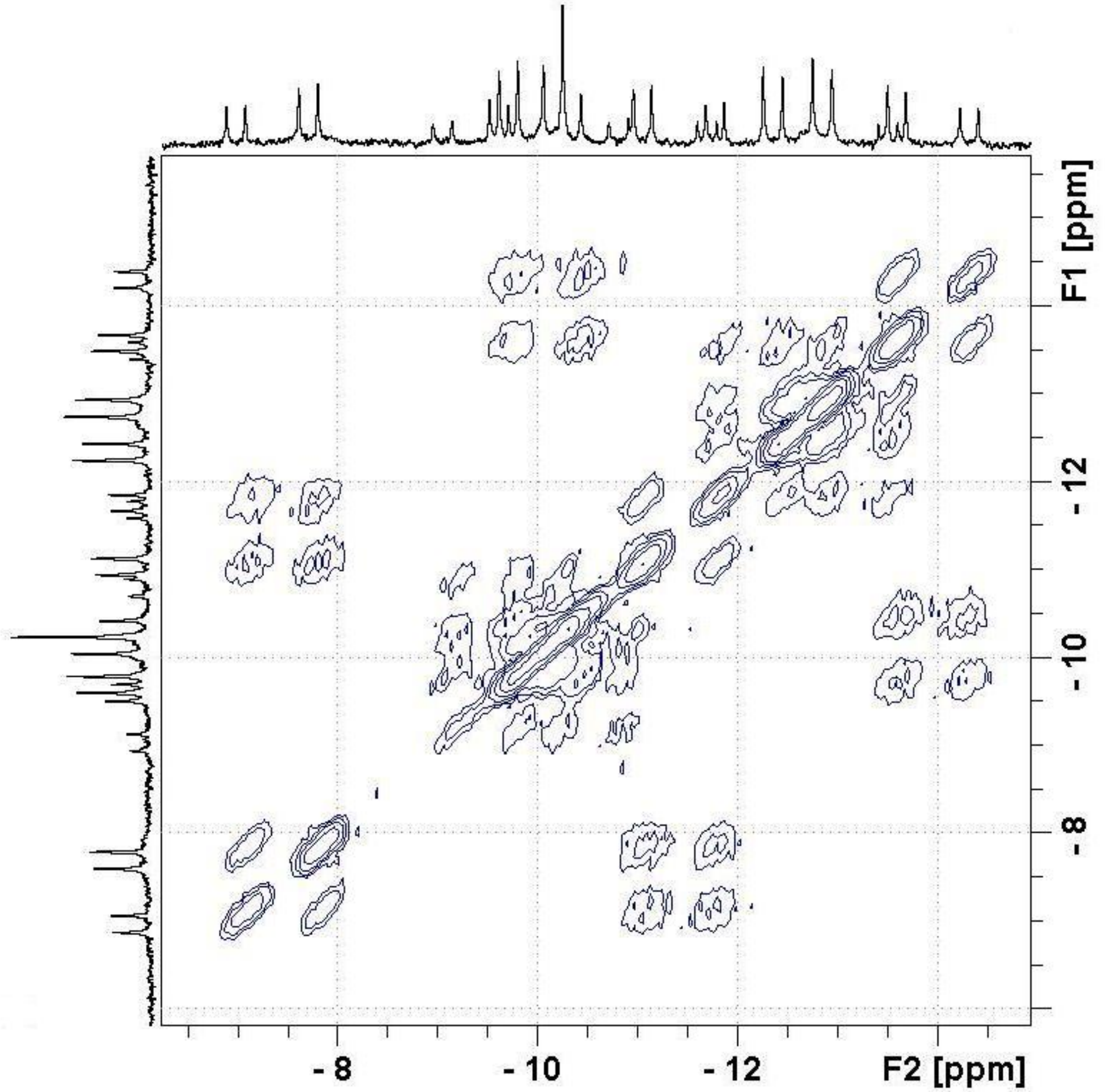

Figure S5. ^{31}P-COSY NMR spectrum in $CDCl_3$-CH_3CN of $[Ag_6(L\text{-}NMe_2)_4(O_3SC_6H_4CH_3)_3][O_3SC_6H_4CH_3]_3$ at 25°C.

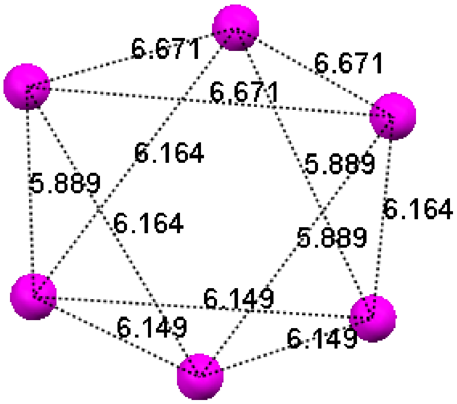

Figure S6. The distorted octahedral core of $[Ag_6(\mathbf{L\text{-}NMe_2})_4(O_3SC_6H_4CH_3)_3]^{3+}$.

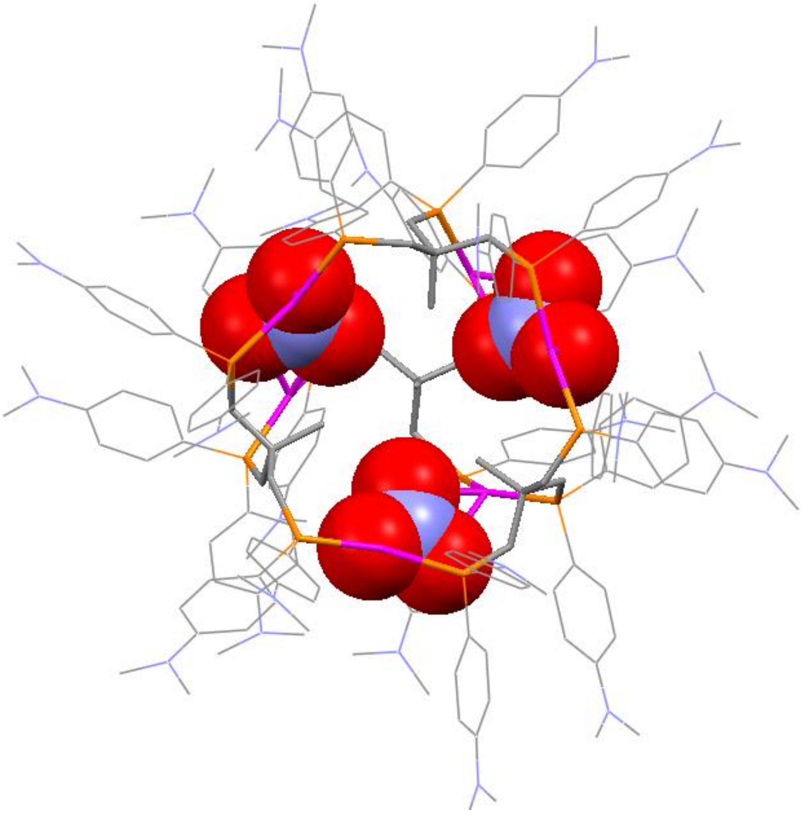

Figure S7. Crystallographically determined structures of incomplete polar cage $[Ag_6(L\text{-}NMe_2)_4(NO_3)_3]^{3+}$.

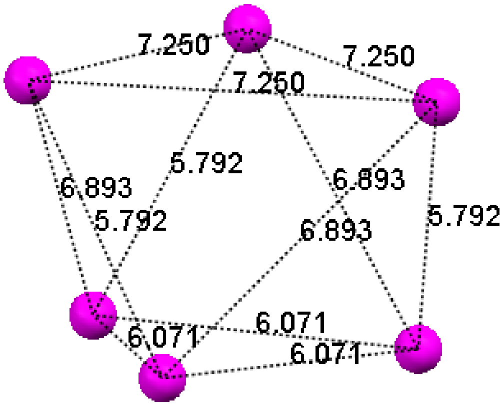

Figure S8. The distorted octahedral core of $[Ag_6(\mathbf{L\text{-}NMe_2})_4(NO_3)_3]^{3+}$

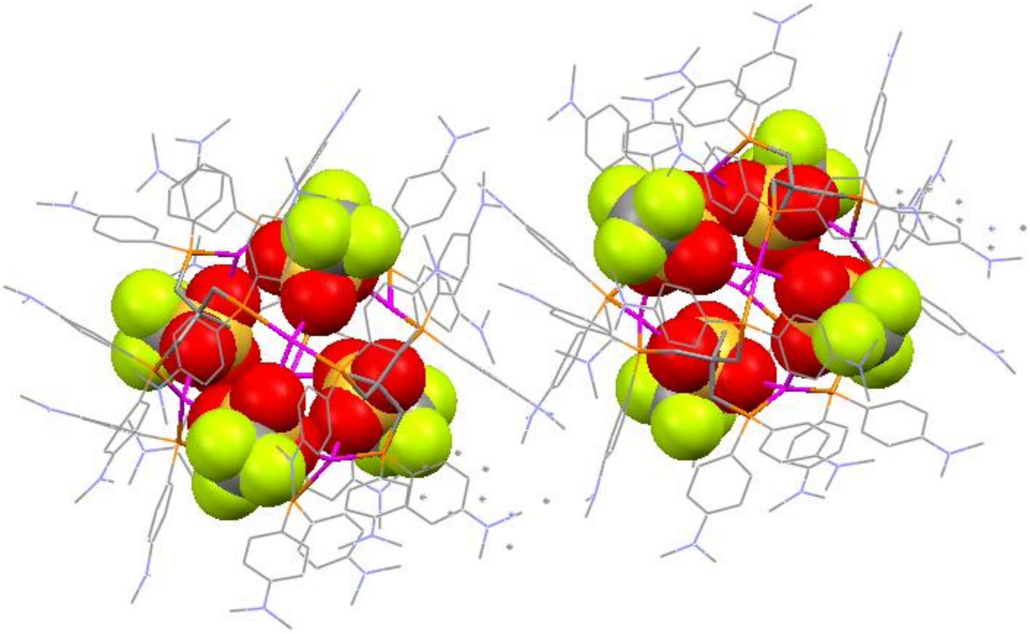

Figure S9. Crystallographically determined structure of $[Ag_6(\mathbf{L\text{-}NMe_2})_4(O_3SCF_3)_4]^{2+}$ emphasizing the cage core. Hydrogen atoms, non-coordinated counter ions and solvent of crystallization have been omitted for clarity.

1. A. Muth, O. Walter, G. Huttner, A. Asam, L. Zsolnai and C. Emmerich *J. Organomet. Chem.* 1994**, 468**, 149-163.