A metallocavitand functioning as a container for anions. Formation of non-covalent, linear assemblies mediated by a cyclodextrin-entrapped NO$_3^-$ anion.

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General Methods

All commercial reagents were used as supplied. The syntheses involving diphosphine 1 were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. CDCl$_3$ was passed down a 5 cm-thick alumina column and stored under nitrogen over molecular sieves (4 Å). Routine $^1$H, $^{13}$C{$^1$H}, $^{19}$F{$^1$H} and $^{31}$P{$^1$H} NMR spectra were recorded on FT Bruker AVANCE 300 ($^1$H: 300.1 MHz, $^{13}$C: 75.5 MHz, $^{19}$F: 282.4 MHz, $^{31}$P: 121.5 MHz) and AVANCE 500 ($^1$H: 500.1 MHz, $^{13}$C: 125.8 MHz) instruments at 25°C. $^1$H NMR spectral data were referenced to residual protiated solvents [7.26 ppm for CDCl$_3$, 2.05 ppm for (CD$_3$)$_2$CO], $^{13}$C chemical shifts are reported relative to deuterated solvents [77.0 ppm for CDCl$_3$, 29.84 ppm for (CD$_3$)$_2$CO], and the $^{31}$P NMR data are given relative to external H$_3$PO$_4$. The $^{19}$F spectrum of complex 2 was measured relative to neat CFCl$_3$. Mass spectra were recorded either on a Bruker MicroTOF spectrometer (ESI-TOF) using CH$_2$Cl$_2$, CH$_3$CN or CH$_3$OH as solvent, or on a Bruker MaldiTOF spectrometer (MALDI-TOF) using α-cyano-4-hydroxycinnamic acid as matrix. Elemental analysis were performed by the Service de Microanalyse, Institut de Chimie (CNRS), Strasbourg. Melting points were determined with a Büchi 535 capillary melting-point apparatus.

Assignment of the stereochemistry of the asymmetric P atoms was made by giving arbitrarily priority to glucose units A and D over glucose units B and E, respectively. The numbering of the atoms within a glucose unit is the usual one (see below).
General Procedure for the Synthesis of the Silver(I) Complexes

To a stirred solution of 1 (0.160 g, 0.12 mmol) in CH$_2$Cl$_2$ (10 mL) was added a suspension of AgX (X = BF$_4$, Cl, Br, I, AcO, NO$_3$, BPh$_4$) (1 equiv.) in THF (3 mL). After 0.25 h the solvent was evaporated. The residue was dissolved in CH$_2$Cl$_2$ (5 mL). Addition of pentane (100 mL) precipitated the corresponding complex [Ag.1]X (2-8, respectively), which was recovered by filtration and dried in vacuo.

General Procedure for the Anion Exchange Reactions

A complex of the type [Ag.1]X (X = BF$_4$, Cl, Br, I, NO$_3$, BPh$_4$) (0.10 mmol) was added as a powder to a saturated aqueous solution of NaX’ or KX’ (X’ = BF$_4$, BPh$_4$, Cl, Br, I, NO$_3$). After sonication for ca. 1 h, the silver(I) complex was extracted with CH$_2$Cl$_2$ (4 × 10 mL). The organic solution was washed with water (15 mL), then dried over MgSO$_4$ before being evaporated to dryness to afford pure [Ag.1]X’. The exchange reactions which were found to be effective are summarised hereafter:
Beige solid (yield 0.180 g, 98%). \( R_f \) (SiO\(_2\), CH\(_2\)Cl\(_2\)/MeOH, 90:10, \( v/v \)) = 0.34; Mp 228°C dec. 

\(^1\)H NMR (300.1 MHz, CDCl\(_3\), 25°C): \( \delta \) (assignment by COSY) = 2.04 (m, 2 H, H-6a\(^{A,D}\) or B,E), 2.27 (m, 2 H, H-6a\(^{B,E}\) or A,D), 2.72 (s, 6 H, 6-OMe), 3.10-3.63 (24 H, H-2, H-3, H-4, H-6b\(^{A,B,D,E}\), H-6a\(^{C,F}\)), 3.46 (s, 6 H, OMe), 3.51 (s, 6 H, OMe), 3.55 (s, 6 H, OMe), 3.62 (s, 6 H, OMe), 3.65 (s, 12 H, OMe), 3.95 (m, 2 H, H-5\(^{A,F}\)), 4.19-4.28 (4 H, H-5\(^{B,E}\) or A,D, H-6b\(^{C,F}\)), 4.36 (m, 2 H, H-5\(^{A,D}\) or B,E), 4.82 (d, 2 H, \(^3\)J\(_{H-1,H-2}\) = 3.3 Hz, H-1\(^{A,D}\) or B,E), 5.04 (two overlapping d, 4 H, H-1\(^{B,E}\) or A,D, H-1\(^{C,F}\)), 7.36-7.41 (4 H, H\(_{arom}\)), 7.49-7.55 (6 H, H\(_{arom}\)) ppm; \(^{13}\)C\(^{1}\)H NMR (75.5 MHz, CDCl\(_3\), 25°C): \( \delta \) (assignment by HMQC) = 26.3 (m, C-6\(^{B,E}\) or A,D), 35.8 (m, C-6\(^{A,D}\) or B,E), 57.7, 57.9, 58.0 (2-OC\(_3\)H), 60.3 (6-OC\(_3\)H), 61.7, 61.7, 62.0 (3-OC\(_3\)H), 64.8 (C-5\(^{B,E}\) or A,D), 71.7 (virtual t, \(|^{2}\)J\(_{C,P} + ^{4}\)J\(_{C,P}\)| = 20.5 Hz, C-5\(^{A,D}\) or B,E), 72.7 (C-5\(^{C,F}\)), 73.7 (C-6\(^{C,F}\)), 80.7,
80.8, 81.1, 81.4, 81.5, 82.5, 84.2 (C-2, C-3, C-4), 86.6 (virtual t, $|^3J_{C,P} + ^5J_{C,P'}| = 13.0$ Hz, C-4B,E or A,D), 88.4 (C-4A,D or B,E), 98.6 (C-1B,E or A,D), 99.7 (C-1A,D or B,E), 100.3 (C-1C,F), 129.5 (virtual t, $|^3J_{C,P} + ^5J_{C,P'}| = 9.9$ Hz, m-C), 131.8 (2 virtual t, $^3J_{C,Ag} = 1.9$ Hz, $|^2J_{C,P} + ^4J_{C,P'}| = 14.9$ Hz, o-C) ppm; $^{19}$F$[^1]$H NMR (282.4 MHz, CDCl$_3$, 25°C): $\delta = -152.0$ (s) ppm; $^{31}$P$[^1]$H NMR (121.5 MHz, CDCl$_3$, 25°C): $\delta = 5.8$ [2 d, $^{107}J_{P,Ag} = 505.7$ Hz, $^{109}J_{P,Ag} = 582.5$ Hz] ppm; elemental analysis (%): calcd for C$_{62}$H$_{94}$AgBF$_4$O$_{26}$P$_2$•0.5(CH$_2$Cl)$_2$ (1512.05 + 84.93): C 48.29, H 6.16; found: C 48.08, H 5.91; MS (ESI-TOF): m/z (%): 1425.4 (100) [M – BF$_4$]$^+$, 1535.4 (1) [M + Na]$^+$.


White solid (yield 0.175 g, 99%). $R_f$ (SiO$_2$, CH$_2$Cl$_2$/MeOH, 90:10, v/v) = 0.34; Mp > 250°C. $^1$H NMR (300.1 MHz, CDCl$_3$, 25°C): $\delta$ (assignment by COSY) = 1.93-2.07 (4 H, H-6a$^{A,B,D,E}$), 2.97 (s, 6 H, 6-OMe), 3.09-3.27 (12 H, H-2, H-4$^{A,B,D,E}$, H-6b$^{A,D}$ or B,E), 3.38-3.75 (12 H, H-3, H-4$^{C,F}$, H-6$^{C,F}$), 3.47 (s, 6 H, OMe), 3.49 (s, 6 H, OMe), 3.51 (s, 6 H, OMe), 3.66 (s, 6 H, OMe), 3.67 (s, 6 H, OMe), 3.67 (s, 6 H, OMe), 3.83 (m, 2 H, H-6b$^{B,E}$ or A,D), 4.52 (m, 2 H, H-5$^{C,F}$), 4.70 (m, 2 H, H-5$^{A,D}$ or B,E), 4.87 (d, 2 H, $^3J_{H-1,H-2} = 3.3$ Hz, H-1$^{A,D}$ or B,E), 4.98 (d, 2 H, $^3J_{H-1,H-2} = 4.4$ Hz, H-1$^{B,E}$ or A,D), 5.01 (d, 2 H, $^3J_{H-1,H-2} = 3.3$ Hz, H-1$^{C,F}$), 5.04 (m, 2 H, H-5$^{B,E}$ or A,D), 7.23-7.54 (10 H, aromatic H) ppm; $^{13}$C$[^1]$H NMR (75.5 MHz, CDCl$_3$, 25 °C): $\delta$ (assignment by HMQC) = 27.5 (m, C-6$^{A,D}$ or B,E), 35.6 (m, C-6$^{B,E}$ or A,D), 57.5, 57.6, 57.8, 59.2, 61.8, 62.2, 62.3 (2-OCH$_3$, 3-OCH$_3$, 6-OCH$_3$), 64.5, 70.3 (C-5$^{A,B,D,E}$), 71.0 (C-5$^{C,F}$), 72.2 (C-6$^{C,F}$), 80.6, 80.7, 81.5, 81.7, 82.9, 82.9, 83.1, 87.6, 89.1 (C-2, C-3, C-4), 97.9 (C-1$^{A,D}$ or B,E), 99.7 (C-1B,E or A,D), 100.3 (C-1C,F), 129.5 (virtual t, $|^3J_{C,P} + ^5J_{C,P'}| = 9.9$ Hz, m-C), 131.8 (2 virtual t, $^3J_{C,Ag} = 1.9$ Hz, $|^2J_{C,P} + ^4J_{C,P'}| = 14.9$ Hz, o-C) ppm; $^{19}$F$[^1]$H NMR (282.4 MHz, CDCl$_3$, 25°C): $\delta = -152.0$ (s) ppm; $^{31}$P$[^1]$H NMR (121.5 MHz, CDCl$_3$, 25°C): $\delta = 5.8$ [2 d, $^{107}J_{P,Ag} = 505.7$ Hz, $^{109}J_{P,Ag} = 582.5$ Hz] ppm; elemental analysis (%): calcd for C$_{62}$H$_{94}$AgBF$_4$O$_{26}$P$_2$•0.5(CH$_2$Cl)$_2$ (1512.05 + 84.93): C 48.29, H 6.16; found: C 48.08, H 5.91; MS (ESI-TOF): m/z (%): 1425.4 (100) [M – BF$_4$]$^+$, 1535.4 (1) [M + Na]$^+$.
Pale yellow solid (yield 0.178 g, 97%). \( R_f \) (SiO\(_2\), CH\(_2\)Cl\(_2\)/MeOH, 90:10, \( v/v \)) = 0.34; Mp > 250°C. \(^1\)H NMR (300.1 MHz, CDCl\(_3\), 25°C): \( \delta \) (assignment by COSY) = 1.90-2.05 (4 H, H-6\(a\),6\(b\),6\(d\),6\(e\)), 2.93 (s, 6 H, 6-OMe), 3.06-3.31 (12 H, H-2, H-4\(a\),4\(b\),4\(c\),4\(d\),4\(e\),4\(f\)), 3.41-3.87 (14 H, H-3, H-5\(a\),5\(b\),5\(c\),5\(d\),5\(e\),5\(f\),6\(a\),6\(b\),6\(d\),6\(e\)); 3.46 (s, 6 H, OMe), 3.49 (s, 6 H, OMe), 3.53 (s, 6 H, OMe), 3.67 (s, 6 H, OMe), 3.68 (s, 6 H, OMe), 4.55 (m, 2 H, H-5\(c\),5\(f\)), 4.81 (m, 2 H, H-5\(a\),5\(b\),5\(c\),5\(d\),5\(e\)), 4.87 (d, 2 H, \( 3J_{H-1,H-2} = 3.2 \) Hz, H-1\(a\),1\(b\),1\(c\),1\(d\),1\(e\),1\(f\)), 4.97 (d, 2 H, \( 3J_{H-1,H-2} = 3.9 \) Hz, H-1\(a\),1\(b\),1\(c\),1\(d\),1\(e\),1\(f\)), 5.01 (d, 2 H, \( 3J_{H-1,H-2} = 3.3 \) Hz, H-1\(c\),1\(f\)), 5.13 (m, 2 H, H-5\(a\),5\(b\),5\(c\),5\(d\),5\(e\)), 7.15-7.49 (10 H, aromatic H) ppm; \(^13\)C\{\(^1\)H\} NMR (75.5 MHz, CDCl\(_3\), 25 °C): \( \delta \) (assignment by HMQC) = 27.0 (m, C-6\(a\),6\(b\),6\(c\),6\(d\),6\(e\),6\(f\)), 33.4 (m, C-6\(a\),6\(b\),6\(c\),6\(d\),6\(e\),6\(f\),6\(g\)), 57.6, 57.7, 57.9, 59.2, 61.8, 62.2, 62.3 (2-OCH\(_3\), 3-OCH\(_3\), 6-OCH\(_3\)), 64.5, 70.0 (C-5\(a\),5\(b\),5\(c\),5\(d\),5\(e\),5\(f\)), 71.1 (C-5\(c\),5\(d\)), 72.1 (C-6\(c\),6\(d\),6\(e\),6\(f\)), 80.7, 80.8, 81.6, 81.8, 82.9, 83.0, 83.2, 87.4, 90.0 (C-2, C-3, C-4), 97.9 (C-1\(c\),1\(f\)), 99.0 (C-1\(a\),1\(b\),1\(c\),1\(d\),1\(e\)), 106.6 (C-1\(a\),1\(b\),1\(c\),1\(d\),1\(e\)), 128.2-131.8 (aromatic C) ppm; \(^31\)P\{\(^1\)H\} NMR (121.5 MHz, CDCl\(_3\), 25°C): \( \delta = -5.2 \) [2 d, \( 10^3J_{P,Ag} = 401.0 \) Hz, \( 10^3J_{P,Ag} = 463.4 \) Hz] ppm; elemental analysis (%): calcd for C\(_{62}\)H\(_{94}\)AgBrO\(_{26}\)P\(_2\).
Pale yellow solid (yield 0.185 g, 98%). $R_f$ (SiO$_2$, CH$_2$Cl$_2$/MeOH, 90:10, v/v) = 0.34; Mp $> 250^\circ$C. $^1$H NMR (300.1 MHz, CDCl$_3$, 25°C): $\delta$ (assignment by COSY) = 1.93-2.12 (4 H, H-6a$^{A,B,D,E}$), 2.98 (s, 6 H, 6-OMe), 3.09-3.28 (12 H, H-2, H-4$^{A,B,D,E}$, H-6b$^{A,D}$ or $^{B,E}$), 3.42-3.83 (14 H, H-3, H-4$^{C,F}$, H-6$^{C,F}$, H-6b$^{B,E}$ or $^{A,D}$), 3.47 (s, 6 H, OMe), 3.50 (s, 6 H, OMe), 3.52 (s, 6 H, OMe), 3.69 (s, 6 H, OMe), 3.69 (s, 6 H, OMe), 3.70 (s, 6 H, OMe), 4.58 (m, 2 H, H-5$^{C,F}$), 4.86 (d, 2 H, $^3$J$_{H-1,H-2}$ = 3.3 Hz, H-1$^{A,D}$ or $^{B,E}$), 4.94 (m, 2 H, H-5$^{A,D}$ or $^{B,E}$), 4.97 (d, 2 H, $^3$J$_{H-1,H-2}$ = 4.2 Hz, H-1$^{B,E}$ or $^{A,D}$), 5.01 (d, 2 H, $^3$J$_{H-1,H-2}$ = 3.4 Hz, H-1$^{C,F}$), 5.36 (m, 2 H, H-5$^{B,E}$ or $^{A,D}$), 7.19-7.43 (10 H, aromatic H) ppm; $^{13}$C($^1$H) NMR (75.5 MHz, CDCl$_3$, 25°C): $\delta$ (assignment by HMQC) = 27.9 (m, C-6$^{A,D}$ or $^{B,E}$), 34.1 (m, C-6$^{B,E}$ or $^{A,D}$), 57.4, 57.5, 57.6, 59.2, 61.8, 62.2, 62.4 (2-OCH$_3$, 3-OCH$_3$, 6-OCH$_3$), 64.8, 70.5 (C-5$^{A,B,D,E}$), 71.3 (C-5$^{C,F}$), 72.2 (C-6$^{C,F}$), 80.4, 80.6, 81.5, 81.7, 82.8, 82.9, 83.2, 87.6, 89.2 (C-2, C-3, C-4), 97.8 (C-1$^{A,D}$ or $^{B,E}$), 99.1 (C-1$^{C,F}$), 100.5 (C-1$^{B,E}$ or $^{A,D}$), 128.6-131.6 (aromatic C) ppm; $^{31}$P($^1$H) NMR (121.5 MHz, CDCl$_3$, 25°C): $\delta$ = -7.5 [2 d, $^{107}$J$_{P,Ag}$ = 378.7 Hz, $^{109}$J$_{P,Ag}$ = 437.7 Hz] ppm; elemental analysis (%): calcd for C$_{62}$H$_{94}$AgI$_2$O$_{26}$P$_2$·CH$_2$Cl$_2$ (1552.14 + 84.93): C 46.22, H 5.91; found: C 46.05, H 5.73; MS (ESI-TOF): $m/z$ (%): 1425.5 (100) $[M - I]^+$. 

$P,P'$-{(6$^A$,6$^B$,6$^D$,6$^E$)-tetradeoxy-6$^A$,6$^B$·6$^D$,6$^E$-bis[(S)-phenylphosphinidene]-2$^A$,2$^B$,2$^C$,2$^D$,2$^E$,2$^F$,3$^A$,3$^B$,3$^C$,3$^D$,3$^E$,3$^F$,6$^C$,6$^F$-tetradeca-O-methyl-\(\alpha\)-cyclodextrin}silver(I) iodide (5)
$P,P'-(6^A,6^B,6^D,6^E.-\text{Tetradeoxy-}6^A,6^B,6^D,6^E.-\text{bis[(S)-phenylphosphinidene]-}$

$2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^C,6^E.-\text{tetradeca-}O\text{-methyl-}\alpha\text{-cyclodextrin)silver(I)}$ acetate (6)

White solid (yield 0.173 g, 97%). $R_f$ (SiO$_2$, CH$_2$Cl$_2$/MeOH, 90:10, v/v) = 0.34; $^1$H NMR (300.1 MHz, CDCl$_3$, 25°C): $\delta$ (assignment by COSY and ROESY) = 1.95 (m, 4 H, H-6a$_{A,B,D,E}$), 2.11 (broad s, 3 H, CH$_3$CO$_2$), 3.00 (s, 6 H, OMe), 3.05-3.28 (12 H, H-2, H-4$_{A,B,D,E}$, H-6b$_{A,D}$ or $B,E$), 3.31-3.82 (12 H, H-3, H-4$_C,F$, H-6a$_{C,F}$, H-6b$_{B,E}$ or $A,D$), 3.46 (s, 6 H, OMe), 3.49 (s, 6 H, OMe), 3.53 (s, 6 H, OMe), 3.67 (s, 6 H, OMe), 3.69 (s, 6 H, OMe), 3.71 (s, 6 H, OMe), 3.89 (m, 2 H, H-5$_{A,D}$ or $B,E$), 4.41 (m, 2 H, H-5$_{C,F}$), 4.85 (m, 2 H, H-5$_{C,F}$), 4.88 (d, 2 H, $^3$J$_{H-1,H-2}$ = 3.2 Hz, H-1$_{B,E}$ or $A,D$), 4.96 (d, 2 H, $^3$J$_{H-1,H-2}$ = 4.4 Hz, H-1$_{A,D}$ or $B,E$), 5.01 (d, 2 H, $^3$J$_{H-1,H-2}$ = 3.2 Hz, H-1$_{C,F}$), 5.05 (2 H, H-5$_{B,E}$ or $A,D$) tentative assignment), 7.15-7.46 (10 H, aromatic H) ppm; $^{13}$C{$_^1$H} NMR (125.8 MHz, CDCl$_3$, 25°C): $\delta$ = 27.4 (m, C-6$_{A,D}$ or $B,E$), 35.7 (m, C-6$_B$ or $E$), 57.4, 57.6, 57.7 (2-OCH$_3$), 59.0 (6-OCH$_3$), 61.6, 62.1, 62.2 (3-OCH$_3$), 64.6 (C-5$_A,D$ or $B,E$), 70.4 (C-5$_{C,F}$), 70.5 (virtual t, $|^3$J$_{C,P}$ + $^4$J$_{C,P'}$| = 24.3 Hz, C-5$_{B,E}$ or $A,D$), 72.2 (C-6$_{C,F}$), 81.0, 81.0, 81.8, 82.8, 82.9, 83.6 (C-2, C-3, C-4$_{C,F}$), 87.3 (virtual t, $|^3$J$_{C,P}$ + $^5$J$_{C,P'}$| = 10.8 Hz, C-4$_A,D$ or $B,E$), 89.2 (broad virtual t, C-4$_{B,E}$ or $A,D$), 98.2 (C-1$_{A,D}$ or $B,E$), 98.6 (C-1$_B$ or $E$ or $A,D$), 100.4 (C-1$_{C,F}$), 128.7 (virtual t, $|^3$J$_{C,P}$ + $^5$J$_{C,P'}$| = 9.0 Hz, m-C), 129.8 (p-C), 131.6 (2 virtual t, $^3$J$_{C,Ag}$ = 1.8 Hz, $|^3$J$_{C,P}$ + $^4$J$_{C,P'}$| = 16.2 Hz, o-C) ppm; $^{31}$P{$_^1$H} NMR (121.5 MHz, CDCl$_3$, 25°C): $\delta$ = -1.76 [2 d, $^{107}$J$_{P,Ag}$ = 421.0 Hz, $^{109}$J$_{P,Ag}$ = 485.6 Hz] ppm.

White solid (yield 0.177 g, 98%). R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, v/v) = 0.34; Mp 196°C dec. 

^1H NMR (300.1 MHz, CDCl_3, 25°C): δ (assignment by COSY) = 1.95 (m, 2 H, H-6_6^A,D or B,E), 2.04 (m, 2 H, H-6_6^B,E or A,D), 2.92 (s, 6 H, OMe), 3.08-3.27 (12 H, H-2_2^A,B,D,E, H-4_4^A,B,D,E), 3.34-3.49 (4 H, H-4_4^C,F, H-6_6^B,E or A,D), 3.46 (s, 6 H, OMe), 3.50 (s, 6 H, OMe), 3.62-3.93 (10 H, H-3_3^C,F, H-6_6^C,F), 3.69 (s, 6 H, OMe), 3.70 (s, 6 H, OMe), 3.71 (s, 6 H, OMe), 4.30 (m, 2 H, H-5_5^B,E or A,D), 4.44 (m, 2 H, H-5_5^C,F), 4.71 (2 H, H-5_5^A,D or B,E), 4.84 (d, 2 H, 3_JH_1_1,H-2 = 3.2 Hz, H-1_1^A,D or B,E), 4.96 (d, 2 H, 3_JH_1_1,H-2 = 4.4 Hz, H-1_1^B,E or A,D), 5.02 (d, 2 H, 3_JH_1_1,H-2 = 3.3 Hz, H-1_1^C,F), 7.21-7.48 (10 H, aromatic H) ppm; ^13C{1H} NMR (75.5 MHz, CDCl_3, 25°C): δ (assignment by HMQC) = 26.7 (m, C-6_6^B,E or A,D), 35.6 (m, C-6_6^A,D or B,E), 57.5, 57.6, 57.8 (2-OCH_3), 59.2 (6-OCH_3), 61.7, 62.2, 62.3 (3-OCH_3), 64.4 (C-5_5^B,E or A,D), 70.9 (virtual t, 3_JC,P + 4_JC,P = 22.3 Hz, C-5_5^A,D or B,E), 70.9 (C-5_5^C,F), 72.6 (C-6_6^C,F), 80.5 (C-3_3^C,F), 80.6 (C-3_3^A,D or B,E), 81.8, 81.8 (C-2_2^A,D or B,E, C-2_2^C,F), 82.8 [×2] (C-2_2^B,E or A,D, C-3_3^B,E or A,D), 83.4 (C-4_4^C,F), 87.3 (virtual t, 3_JC,P + 4_JC,P = 11.2 Hz, C-4_4^B,E or A,D), 88.9 (virtual t, 3_JC,P + 4_JC,P = 5.0 Hz, C-4_4^A,D or B,E), 98.2 (C-1_1^B,E or A,D), 98.9 (C-1_1^A,D or B,E), 100.5 (C-1_1^C,F), 128.8 (virtual t, 3_JC,P + 4_JC,P = 15.5 Hz, m-C), 130.2 (p-C), 132.9 (2 virtual t, 3_JC,Ag = 1.7 Hz, 3_JC,P + 4_JC,P = 9.5 Hz, o-C) ppm; ^31P{1H} NMR (121.5 MHz, CDCl_3, 25°C): δ = 0.5 [2 d, 107_JP,Ag = 458.9 Hz, 109_JP,Ag = 529.1 Hz] ppm; elemental analysis (%): calcd for C_62H_94AgNO_3P_2 (1487.25): C 50.07, H 6.37, N 0.94; found: C 49.89, H 6.41, N 0.81; MS (MALDI-TOF): m/z (%): 1425.4 (100) [M – NO_3]^+. 
$P,P'$-{6$^A$,6$^B$,6$^D$,6$^F$-Tetradeoxy-6$^A$,6$^B$,6$^D$,6$^F$-bis[(S)-phenylphosphinidene]-2$^A$,2$^B$,2$^C$,2$^D$,2$^E$,2$^F$,3$^A$,3$^B$,3$^C$,3$^D$,3$^E$,3$^F$,6$^C$,6$^F$-tetradeca-O-methyl-α-cyclodextrin}silver(I) tetraphenylborate (8)

White solid (yield 0.206 g, 97%). Complex 8 decomposes on silica (SiO$_2$). Mp 243°C dec. $^1$H NMR (500.1 MHz, (CD$_3$)$_2$CO, 25°C): $\delta$ (assignment by COSY) = 2.00 (m, 2 H, H-6$^A$ or H-6$^D$), 2.28 (m, 2 H, H-6$^B$ or H-6$^E$), 2.68 (s, 6 H, 6-OMe), 3.09-3.15 (s, 6 H, H-2$^A$, H-2$^B$, H-2$^C$, H-2$^D$, H-2$^E$, H-2$^F$), 3.30-3.64 (s, 18 H, H-2$^C$, H-2$^F$, H-3$^A$, H-3$^B$, H-3$^C$, H-3$^D$, H-3$^E$, H-3$^F$), 3.43 (s, 6 H, OMe), 3.48 (s, 6 H, OMe), 3.53 (s, 6 H, OMe), 3.57 (s, 6 H, OMe), 3.58 (s, 6 H, OMe), 3.62 (s, 6 H, OMe), 3.87 (m, 2 H, H-5$^B$, H-5$^E$ or H-5$^A$, H-5$^D$), 4.15 (m, 2 H, H-5$^C$, H-5$^F$), 4.35-4.39 (m, 4 H, H-5$^A$, H-5$^B$, H-5$^C$, H-5$^D$, H-5$^E$, H-5$^F$), 5.09 (d, 2 H, $^3$J$_{H-1,H-2}$ = 3.2 Hz, H-1$^B$, H-1$^D$), 5.13 (d, 2 H, $^3$J$_{H-1,H-2}$ = 4.8 Hz, H-1$^C$, H-1$^F$), 5.22 (d, 2 H, $^3$J$_{H-1,H-2}$ = 3.2 Hz, H-1$^A$, H-1$^D$), 6.77 (m, 4 H, p-H of BPh$_4$), 6.92 (m, 8 H, m-H of BPh$_4$), 7.33 (m, 8 H, o-H of BPh$_4$), 7.53 (m, 4 H, m-H of PPh), 7.61 (m, 2 H, p-H of PPh), 7.69 (m, 4 H, o-H of PPh) ppm; $^{13}$C{$^1$H} NMR (125.8 MHz, (CD$_3$)$_2$CO, 25 °C): $\delta$ (assignment by HMQC) = 26.8 (m, C-6$^B$, C-6$^A$), 37.0 (m, C-6$^D$, C-6$^E$), 57.5, 57.9, 58.2 (2-OCH$_3$), 60.4 (6-OCH$_3$), 61.8, 62.1, 62.2 (3-OCH$_3$), 65.6 (C-5$^B$, C-5$^E$), 72.5 (virtual t, $^1$J$_{C,P}$ + $^4$J$_{C,P}$ = 17.6 Hz, C-5$^A$, C-5$^D$), 73.6 (C-5$^F$), 74.8 (C-6$^C$), 82.0, 82.1, 82.3, 82.5, 83.1, 84.8, 84.9 (C-2, C-3, C-4), 87.5 (virtual t, $^1$J$_{C,P}$ + $^4$J$_{C,P}$ = 11.2 Hz, C-4$^B$, C-4$^D$), 89.0 (C-4$^A$, C-4$^E$), 99.4 (C-1$^F$), 100.2 (C-1$^B$, C-1$^D$), 100.9 (C-1$^A$, C-1$^E$), 122.2 (p-C of BPh$_4$), 126.0 (q, $^2$J$_{C,B}$ = 2.8 Hz, m-C of BPh$_4$), 130.2 (virtual t, $^1$J$_{C,P}$ + $^5$J$_{C,P}$ = 10.0 Hz, m-C of PPh), 132.2 (p-C of PPh), 133.3 (2 virtual t, $^3$J$_{C,Ag}$ = 2.4 Hz, $^1$J$_{C,P}$ + $^4$J$_{C,P}$ = 15.2 Hz, o-C of PPh), 137.1 (o-C of BPh$_4$), 165.0 (q, $^1$J$_{C,B}$ = 49.4 Hz, ipso-C of BPh$_4$) ppm; $^{31}$P{$^1$H} NMR (121.5 MHz, CD$_3$D$_6$, 25°C): $\delta$ = 7.8 [2 d, $^{107}$J$_{Ag,P}$ = 504.6 Hz, $^{109}$J$_{Ag,P}$ = 582.5 Hz] ppm; $^{31}$P{$^1$H} NMR (121.5 MHz, CDCl$_3$, 25°C): $\delta$ = 8.0 [2 d,
\[ J_{Ag,P} = 504.6 \text{ Hz}, \quad J_{Ag,P} = 582.5 \text{ Hz} \] ppm; elemental analysis (%): calcd for C\(_{86}\)H\(_{114}\)AgBO\(_2\)P\(_2\) • 2(CH\(_2\)Cl\(_2\)) (1744.48 + 169.87): C 55.21, H 6.21; found: C 55.29, H 6.07; MS (ESI-TOF): \( m/z \) (%): 1425.5 (100) \([M – BPh_4]^{+}\).

**X-ray Structure Analyses**

Crystal structure of complex 2: 2AgP\(_2\)C\(_{62}\)H\(_{94}\)O\(_2\)BF\(_4\) • 5.5C\(_2\)H\(_2\)Cl\(_4\), \( Mr = 4116.93 \), triclinic, \( P1 \), \( a = 14.1642(3), b = 18.7043(3), c = 19.4619(3) \) Å, \( \alpha = 92.390(1), \beta = 106.382(1), \gamma = 105.321(1)°, \) \( V = 4733.2(2) \) Å\(^3\), \( Z = 1, D_X = 1.444 \) Mg m\(^{-3}\), \( \lambda(MoK\alpha) = 0.71073 \) Å, \( \mu = 6.89 \) cm\(^{-1}\), \( F(000) = 2119, T = 120 \) K. Data were collected on a NONIUS Kappa CCD diffractometer (graphite MoK\( \alpha \) radiation, \( \lambda = 0.71073 \) Å). The structure was solved with SIR-97\(^1\), which revealed the non hydrogen atoms of the molecule. The structure was refined with SHELXL97\(^2\) using a riding model for H atoms; 2181 variables and 33966 observations with \( I > 2.0 \sigma(I) \). \( R = 0.079, R_W = 0.211 \) and \( S_W = 1.054, \Delta \rho < 3.2 \) eÅ\(^{-3}\), Flack parameter -0.01(2).

The structure consists of two molecules of \([Ag•1]BF_4\) crystallising with six molecules of C\(_2\)H\(_2\)Cl\(_4\), one at a partially occupied site, all lying outside the CD cavity. There are also two molecules of CH\(_2\)Cl\(_2\) inside the CD that are both disordered over two sites. One methoxy group of the secondary face is also disordered.

Crystal structure of complex 3: AgP\(_2\)C\(_{62}\)H\(_{94}\)ClO\(_2\)BF\(_4\) • 4C\(_2\)H\(_2\)Cl\(_4\), \( Mr = 2131.98 \), triclinic, \( P1 \), \( a = 14.1004(11), b = 18.6373(12), c = 19.4885(14) \) Å, \( \alpha = 92.123(4), \beta = 105.562(4)°, \gamma = 106.027(4)°, \) \( V = 4707.6(6) \) Å\(^3\), \( Z = 2, D_X = 1.504 \) Mg m\(^{-3}\), \( \lambda(MoK\alpha) = 0.71073 \) Å, \( \mu = 8.00 \) cm\(^{-1}\), \( F(000) = 2192, T = 133 \) K. The data were collected on aBruker SMART 1000 CCD diffractometer with graphite monochromatized MoK\( \alpha \) radiation. The structure was solved as above for complex 2. 2034 variables and 44547 observations with \( I > 2.0 \sigma(I) \). \( R = 0.070, R_W = 0.188 \) and \( S_W = 1.02, \Delta \rho < 2.0 \) eÅ\(^{-3}\), Flack parameter -0.04(2). The asymmetric unit consists of two molecules of 3 and eight of C\(_2\)H\(_2\)Cl\(_4\). Because of pronounced pseudosymmetry (the molecules of 3 are related by a pseudo-inversion centre), structure determination involved the resolution of a double image. The refinement was stabilised by the use of 2230 restraints.

Crystal structure of complex 7: AgP\(_2\)C\(_{62}\)H\(_{94}\)NO\(_2\)BF\(_4\) • CHCl\(_3\), \( Mr = 1606.56 \), monoclinic, \( P2_1 \), \( a = 11.6970(6), b = 16.3644(7), c = 19.3652(8) \) Å, \( \beta = 93.007(5)°, V = 3701.7(3) \) Å\(^3\), \( Z = 2, D_X = 1.441 \) Mg m\(^{-3}\), \( \lambda(MoK\alpha) = 0.71073 \) Å, \( \mu = 5.06 \) cm\(^{-1}\), \( F(000) = 1680, T = 100 \) K. The data were collected on an Oxford Diffraction Xcalibur Saphir 3 diffractometer with graphite...
monochromatized MoKα radiation. The structure was solved as above for complex 2. 892 variables and 7111 observations with \( I > 2.0 \sigma(I) \). \( R = 0.049 \), \( R_W = 0.078 \) and \( S_W = 0.744 \), \( \Delta \rho < 1.1 \text{ eÅ}^{-3} \), Flack parameter -0.053 (19).

CCDC 272302, 625926, and 601087 contain the supplementary crystallographic data for 2, 3 and 7, respectively. Crystallographic data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB 11EZ, UK; ax: (internat.) 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

References
