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Supporting Information

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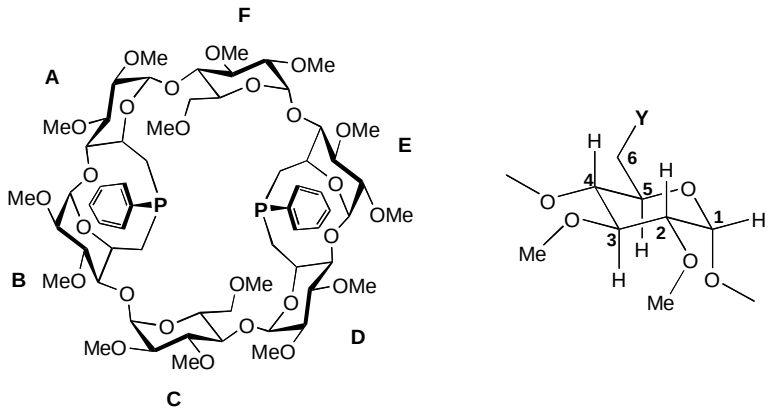
A metallocavitand functioning as a container for anions. Formation of non-covalent, linear assemblies mediated by a cyclodextrin-entrapped NO_3^- anion.

Laurent Poorters, Dominique Armspach, Dominique Matt, Loïc Toupet, Peter G. Jones

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 ^1H, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on FT Bruker AVANCE 300 (^1H: 300.1 MHz, ^{13}C: 75.5 MHz, ^{19}F: 282.4 MHz, ^{31}P: 121.5 MHz) and AVANCE 500 (^1H: 500.1 MHz, ^{13}C: 125.8 MHz) instruments at 25°C. ^1H NMR spectral data were referenced to residual protiated solvents [7.26 ppm for $CDCl_3$, 2.05 ppm for $(CD_3)_2CO$], ^{13}C chemical shifts are reported relative to deuterated solvents [77.0 ppm for $CDCl_3$, 29.84 ppm for $(CD_3)_2CO$], and the ^{31}P NMR data are given relative to external H_3PO_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_2Cl_2, CH_3CN or CH_3OH as solvent, or on a Bruker MaldiTOF spectrometer (MALDI-TOF) using *a*-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).



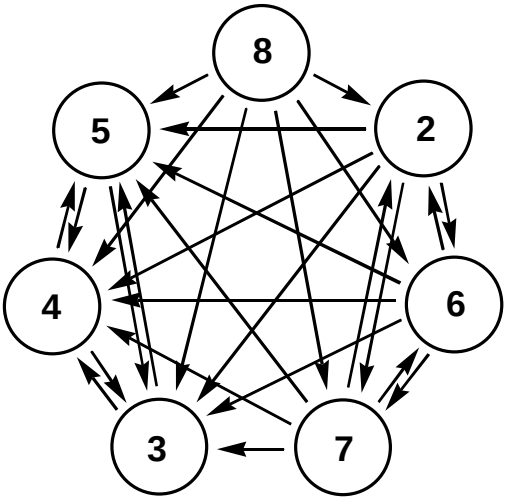
1

General Procedure for the Synthesis of the Silver(I) Complexes

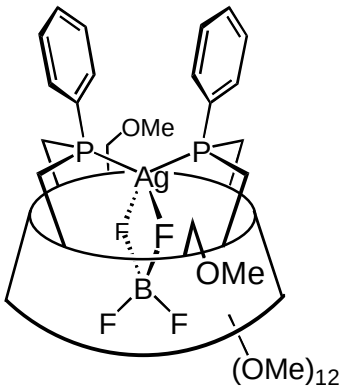
To a stirred solution of **1** (0.160 g, 0.12 mmol) in CH_2Cl_2 (10 mL) was added a suspension of AgX (X = BF_4, Cl, Br, I, AcO, NO_3, BPh_4) (1 equiv.) in THF (3 mL). After 0.25 h the solvent was evaporated. The residue was dissolved in CH_2Cl_2 (5 mL). Addition of pentane (100 mL) precipitated the 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_2Cl_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:



***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-*a*-cyclodextrin}silver(I) tetrafluoroborate (2)**

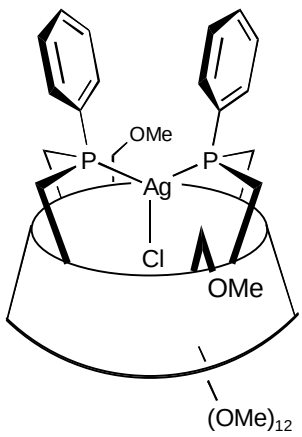


2

Beige solid (yield 0.180 g, 98%). R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v*/*v*) = 0.34; Mp 228°C dec. ^{1}H NMR (300.1 MHz, $CDCl_3$, 25°C): *d* (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^{C,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, $^{3}J_{H\text{-}1,H\text{-}2}$ = 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): *d* (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-OCH_3), 60.3 (6-OCH_3), 61.7, 61.7, 62.0 (3-OCH_3), 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^{C,F}), 86.6 (virtual t, $|^3J_{C,P} + {}^5J_{C,P'}|$ = 13.0 Hz, C-4$^{B,E\ or\ A,D}$), 88.4 (C-4$^{A,D\ or\ B,E}$), 98.6 (C-1$^{B,E\ or\ A,D}$), 99.7 (C-1$^{A,D\ or\ B,E}$), 100.3 (C-1^{C,F}), 129.5 (virtual t, $|^3J_{C,P} + {}^5J_{C,P'}|$ = 9.9 Hz, *m*-C), 131.8 (*p*-C), 132.1 (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): *d* = -152.0 (s) ppm; ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25°C): *d* = 5.8 [2 d, $^{107}J_{P,Ag}$ = 505.7 Hz, $^{109}J_{P,Ag}$ = 582.5 Hz] ppm; elemental analysis (%): calcd for $C_{62}H_{94}AgBF_4O_{26}P_2$•0.5($CH_2Cl_2$) (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]$^+$.

_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-_a_-cyclodextrin}silver(I) chloride (3)

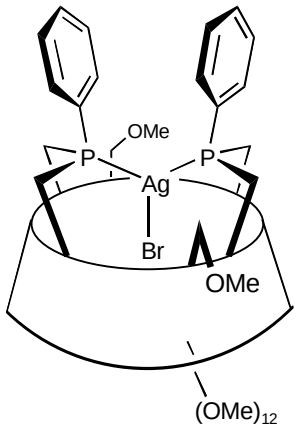


3

White solid (yield 0.175 g, 99%). R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v*/*v*) = 0.34; Mp > 250°C. ^{1}H NMR (300.1 MHz, $CDCl_3$, 25°C): *d* (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): *d* (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$^{A,D\ or\ B,E}$),

99.0 (C-1^{C,F}), 100.6 (C-1$^{B,E\ or\ A,D}$), 128.8 (virtual t, $|^3J_{C,P} + {}^5J_{C,P'}|$ = 9.3 Hz, *m*-C), 130.1 (*p*-C), 131.7 (2 virtual t, $^3J_{C,Ag}$ = 1.9 Hz, $|^2J_{C,P} + {}^4J_{C,P'}|$ = 16.1 Hz, *o*-C) ppm; $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 25°C): *d* = -3.5 [2 d, $^{107}J_{P,Ag}$ = 411.0 Hz, $^{109}J_{P,Ag}$ = 474.5 Hz] ppm; elemental analysis (%): calcd for $C_{62}H_{94}AgClO_{26}P_2$ (1460.69): C 50.98, H 6.49; found: C 50.83, H 6.52; MS (ESI-TOF): *m/z* (%): 1425.4 (30) $[M - Cl]^+$, 1483.4 (100) $[M + Na]^+$.

***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-*a*-cyclodextrin}silver(I) bromide (4)**

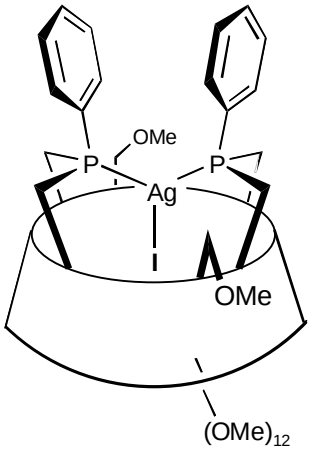


4

Pale yellow solid (yield 0.178 g, 97%). R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v*/*v*) = 0.34; Mp > 250°C. ^1H NMR (300.1 MHz, $CDCl_3$, 25°C): *d* (assignment by COSY) = 1.90-2.05 (4 H, H-6a^{A,B,D,E}), 2.93 (s, 6 H, 6-OMe), 3.06-3.31 (12 H, H-2, H-4^{A,B,D,E}, H-6b$^{A,D\ or\ B,E}$), 3.41-3.87 (14 H, H-3, H-4^{C,F}, H-6b$^{B,E\ or\ A,D}$, H-6^{C,F}), 3.46 (s, 6 H, OMe), 3.49 (s, 6 H, OMe), 3.53 (s, 6 H, OMe), 3.67 (s, 12 H, OMe), 3.68 (s, 6 H, OMe), 4.55 (m, 2 H, H-5^{C,F}), 4.81 (m, 2 H, H-5$^{A,D\ or\ B,E}$), 4.87 (d, 2 H, $^3J_{H-1,H-2}$ = 3.2 Hz, H-1$^{A,D\ or\ B,E}$), 4.97 (d, 2 H, $^3J_{H-1,H-2}$ = 3.9 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}), 5.13 (m, 2 H, H-5$^{B,E\ or\ A,D}$), 7.15-7.49 (10 H, aromatic H) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C): *d* (assignment by HMQC) = 27.0 (m, C-6$^{A,D\ or\ B,E}$), 33.4 (m, C-6$^{B,E\ or\ A,D}$), 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,B,D,E}), 71.1 (C-5^{C,F}), 72.1 (C-6^{C,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,F}), 99.0 (C-1$^{A,D\ or\ B,E}$), 100.6 (C-1$^{B,E\ or\ A,D}$), 128.2-131.8 (aromatic C) ppm; $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 25°C): *d* = -5.2 [2 d, $^{107}J_{P,Ag}$ = 401.0 Hz, $^{109}J_{P,Ag}$ = 463.4 Hz] ppm; elemental analysis (%): calcd for $C_{62}H_{94}AgBrO_{26}P_2$

(1505.14): C 49.48, H 6.30; found: C 49.62, H 6.49; MS (ESI-TOF): *m/z* (%): 1425.5 (100) $[M - \mathrm{Br}]^+$.

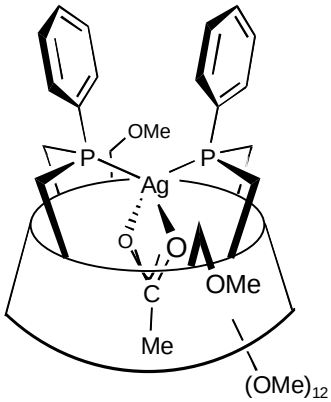
P,P'-{$6^A,6^B,6^D,6^E$-tetradeoxy-$6^A,6^B$:$6^D,6^E$-bis[(*S*)-phenylphosphinidene]-$2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^C,6^F$-tetradeca-*O*-methyl-*a*-cyclodextrin}silver(I) iodide (5)



5

Pale yellow solid (yield 0.185 g, 98%). R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v*/*v*) = 0.34; Mp > 250°C. ^{1}H NMR (300.1 MHz, $CDCl_3$, 25°C): *d* (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, $^3J_{H\text{-}1,H\text{-}2}$ = 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, $^3J_{H\text{-}1,H\text{-}2}$ = 4.2 Hz, H-$1^{B,E\ or\ A,D}$), 5.01 (d, 2 H, $^3J_{H\text{-}1,H\text{-}2}$ = 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): *d* (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): *d* = -7.5 [2 d, $^{107}J_{P,Ag}$ = 378.7 Hz, $^{109}J_{P,Ag}$ = 437.7 Hz] ppm; elemental analysis (%): calcd for $C_{62}H_{94}AgIO_{26}P_2$•CH_2Cl_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) $[M - \mathrm{I}]^+$.

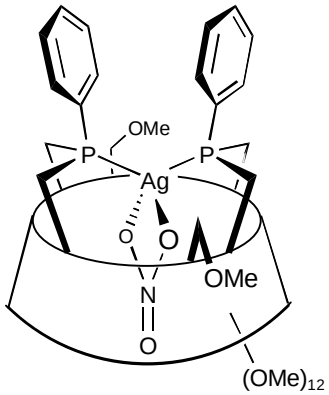
***P,P'*-{6^{A},6^{B},6^{D},6^{E}-Tetradeoxy-6^{A},6^{B}:6^{D},6^{E}-bis[(*S*)-phenylphosphinidene]-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{C},6^{F}-tetradeca-*O*-methyl-*a*-cyclodextrin}silver(I) acetate (6)**



6

White solid (yield 0.173 g, 97%). R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v*/*v*) = 0.34; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25°C): *d* (assignment by COSY and ROESY) = 1.95 (m, 4 H, H-6a^{A,B,D,E}), 2.11 (broad s, 3 H, CH_3CO_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-6b^{C,F}), 4.41 (m, 2 H, H-5$^{A,D\ or\ B,E}$), 4.85 (m, 2 H, H-5^{C,F}), 4.88 (d, 2 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, H-1$^{B,E\ or\ A,D}$), 4.96 (d, 2 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 4.4 Hz, H-1$^{A,D\ or\ B,E}$), 5.01 (d, 2 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 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): *d* = 27.4 (m, C-6$^{A,D\ or\ B,E}$), 35.7 (m, C-6$^{B,E\ or\ A,D}$), 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, $|^{2}J_{C,P} + {}^{4}J_{C,P'}|$ = 24.3 Hz, C-5$^{B,E\ or\ A,D}$), 72.2 (C-6^{C,F}), 81.0, 81.0, 81.8, 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$^{B,E\ or\ A,D}$), 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, $|^{2}J_{C,P} + {}^{4}J_{C,P'}|$ = 16.2 Hz, *o*-C) ppm; ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25°C): *d* = -1.76 [2 d, $^{107}J_{P,Ag}$ = 421.0 Hz, $^{109}J_{P,Ag}$ = 485.6 Hz] ppm.

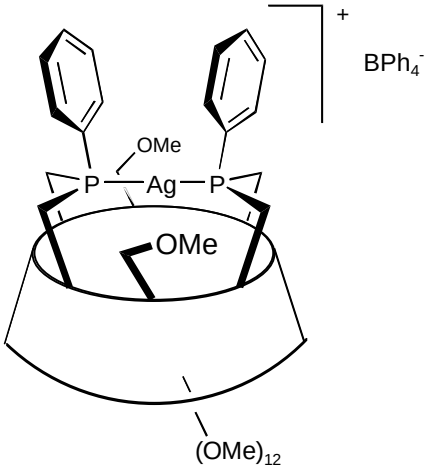
P,P'-{$6^A,6^B,6^D,6^E$-Tetradeoxy-$6^A,6^B$:$6^D,6^E$-bis[(*S*)-phenylphosphinidene]-$2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^C,6^F$-tetradeca-*O*-methyl-*a*-cyclodextrin}silver(I) nitrate (7)



7

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. ^{1}H NMR (300.1 MHz, $CDCl_3$, 25°C): *d* (assignment by COSY) = 1.95 (m, 2 H, H-6a$^{A,D\ or\ B,E}$), 2.04 (m, 2 H, H-6a$^{B,E\ or\ A,D}$), 2.92 (s, 6 H, OMe), 3.08-3.27 (12 H, H-2, H-4^{A,B,D,E}, H-6b$^{B,E\ or\ A,D}$), 3.33-3.49 (4 H, H-4^{C,F}, H-6b$^{A,D\ or\ B,E}$), 3.46 (s, 6 H, OMe), 3.50 (s, 6 H, OMe), 3.51 (s, 6 H, OMe), 3.62-3.93 (10 H, H-3, H-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$^{B,E\ or\ A,D}$), 4.44 (m, 2 H, H-5^{C,F}), 4.71 (2 H, H-5$^{A,D\ or\ B,E}$), 4.84 (d, 2 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, H-1$^{A,D\ or\ B,E}$), 4.96 (d, 2 H, $^3J_{H\text{-}1,H\text{-}2}$ = 4.4 Hz, H-1$^{B,E\ or\ A,D}$), 5.02 (d, 2 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, H-1^{C,F}), 7.21-7.48 (10 H, aromatic H) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25 °C): *d* (assignment by HMQC) = 26.7 (m, C-6$^{B,E\ or\ A,D}$), 35.6 (m, C-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$^{B,E\ or\ A,D}$), 70.9 (virtual t, $|^2J_{C,P} + {}^4J_{C,P'}|$ = 22.3 Hz, C-5$^{A,D\ or\ B,E}$), 70.9 (C-5^{C,F}), 72.6 (C-6^{C,F}), 80.5 (C-3^{C,F}), 80.6 (C-3$^{A,D\ or\ B,E}$), 81.8, 81.8 (C-2$^{A,D\ or\ B,E}$, C-2^{C,F}), 82.8 [×2] (C-2$^{B,E\ or\ A,D}$, C-3$^{B,E\ or\ A,D}$), 83.4 (C-4^{C,F}), 87.3 (virtual t, $|^3J_{C,P} + {}^5J_{C,P'}|$ = 11.2 Hz, C-4$^{B,E\ or\ A,D}$), 88.9 (virtual t, $|^3J_{C,P} + {}^5J_{C,P'}|$ = 5.0 Hz, C-4$^{A,D\ or\ B,E}$), 98.2 (C-1$^{B,E\ or\ A,D}$), 98.9 (C-1$^{A,D\ or\ B,E}$), 100.5 (C-1^{C,F}), 128.8 (virtual t, $|^3J_{C,P} + {}^5J_{C,P'}|$ = 15.5 Hz, *m*-C), 130.2 (*p*-C), 132.9 (2 virtual t, $^3J_{C,Ag}$ = 1.7 Hz, $|^2J_{C,P} + {}^4J_{C,P'}|$ = 9.5 Hz, *o*-C) ppm; ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25°C): *d* = 0.5 [2 d, $^{107}J_{P,Ag}$ = 458.9 Hz, $^{109}J_{P,Ag}$ = 529.1 Hz] ppm; elemental analysis (%): calcd for $C_{62}H_{94}AgNO_{29}P_2$ (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^{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-*a*-cyclodextrin}silver(I) tetraphenylborate (8)**



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, $(CD_3)_2CO$, 25°C): *d* (assignment by COSY) = 2.00 (m, 2 H, H-6a$^{A,D\ or\ B,E}$), 2.28 (m, 2 H, H-6a$^{B,E\ or\ A,D}$), 2.68 (s, 6 H, 6-OMe), 3.09-3.15 (6 H, H-2^{A,B,D,E}, H-3^{C,F}), 3.30-3.64 (18 H, H-2^{C,F}, H-3^{A,B,D,E}, H-4, H-6a^{C,F}, H-6b^{A,D,B,E}), 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$^{B,E\ or\ A,D}$), 4.15 (m, 2 H, H-5^{C,F}), 4.35-4.39 (4 H, H-5$^{A,D\ or\ B,E}$, H-6b^{C,F}), 5.09 (d, 2 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, H-1$^{B,E\ or\ A,D}$), 5.13 (d, 2 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 4.8 Hz, H-1^{C,F}), 5.22 (d, 2 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, H-1$^{A,D\ or\ B,E}$), 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, $(CD_3)_2CO$, 25 °C): *d* (assignment by HMQC) = 26.8 (m, C-6$^{B,E\ or\ A,D}$), 37.0 (m, C-6$^{A,D\ or\ B,E}$), 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$^{B,E\ or\ A,D}$), 72.5 (virtual t, $|^{2}J_{C,P} + {}^{4}J_{C,P'}|$ = 17.6 Hz, C-5$^{A,D\ or\ B,E}$), 73.6 (C-5^{C,F}), 74.8 (C-6^{C,F}), 82.0, 82.1, 82.3, 82.5, 83.1, 84.8, 84.9 (C-2, C-3, C-4^{C,F}), 87.5 (virtual t, $|^{3}J_{C,P} + {}^{5}J_{C,P'}|$ = 11.2 Hz, C-4$^{B,E\ or\ A,D}$), 89.0 (C-4$^{A,D\ or\ B,E}$), 99.4 (C-1^{C,F}), 100.2 (C-1$^{B,E\ or\ A,D}$), 100.9 (C-1$^{A,D\ or\ B,E}$), 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, $|^{3}J_{C,P} + {}^{5}J_{C,P'}|$ = 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, $|^{2}J_{C,P} + {}^{4}J_{C,P'}|$ = 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, C_6D_6, 25°C): *d* = 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): *d* = 8.0 [2 d,

$^{107}J_{Ag,P}$ = 504.6 Hz, $^{109}J_{Ag,P}$ = 582.5 Hz] ppm; elemental analysis (%): calcd for $C_{86}H_{114}AgBO_{26}P_2$•2($CH_2Cl_2$) (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**: $2AgP_2C_{62}H_{94}O_{26}BF_4$•$5.5C_2H_2Cl_4$•$2CH_2Cl_2$, *M*r = 4116.93, triclinic, *P*1, *a* = 14.1642(3), *b* = 18.7043(3), *c* = 19.4619(3)Å, *a* = 92.390(1), *b* = 106.382(1), *g* = 105.321(1)°, *V* = 4733.2(2) Å^3, *Z* = 1, D_X = 1.444 Mg m^{-3}, *l*(MoKα) = 0.71073Å, *m* = 6.89 cm-1, *F*(000) = 2119, *T* = 120 K. Data were collected on a NONIUS Kappa CCD diffractometer (graphite MoKα radiation, *l* = 0.71073 Å). The structure was solved with SIR-97[12] which revealed the non hydrogen atoms of the molecule. The structure was refined with SHELXL97[13] using a riding model for H atoms; 2181 variables and 33966 observations with *I* > 2.0 σ(*I*). *R* = 0.079, R_W = 0.211 and S_W = 1.054, Δ*r* < 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 $C_2H_2Cl_4$, one at a partially occupied site, all lying outside the CD cavity. There are also two molecules of CH_2Cl_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**: $AgP_2C_{62}H_{94}ClO_{26}$•$4C_2H_2Cl_4$, *M*r = 2131.98, triclinic, *P*1, *a* = 14.1004(11), *b* = 18.6373(12), *c* = 19.4885(14) Å, *a* = 92.123(4), *b* = 105.562(4)°, *g* = 106.027(4)°, *V* = 4707.6(6) Å3, *Z* = 2, D_X = 1.504 Mg m-3, *l*(MoKα) = 0.71073Å, *m* = 8.00 cm-1, *F*(000) = 2192, *T* = 133 K. The data were collected on aBruker SMART 1000 CCD diffractometer with graphite monochromatized MoKα radiation. The structure was solved as above for complex **2**. 2034 variables and 44547 observations. *R* = 0.070, R_W = 0.188 and S_W= 1.02 , Δ*r* < 2.0 eÅ^{-3}, Flack parameter -0.04(2). The asymmetric unit consists of two molecules of **3** and eight of $C_2H_2Cl_4$. 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**: $AgP_2C_{62}H_{94}NO_{29}$•$CHCl_3$, *M*r = 1606.56, monoclinic, $P2_1$, *a* = 11.6970(6), *b* = 16.3644(7), *c* = 19.3652(8)Å, *b* = 93.007(5)°, *V* = 3701.7(3) Å3, *Z* = 2, D_X = 1.441 Mg m-3, *l*(MoKα) = 0.71073Å, *m* = 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 $S_W = 0.744$, $\Delta r < 1.1$ 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].

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