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First heterobimetallic complexes of phosphocavitands

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Abstract

The synthesis and characterisation were described for tetranuclear phosphocavitand complexes **4**, where each phosphorus atom is coordinated to the silver atom, and tetranuclear heterobimetallic phosphocavitand complexes **6**, in which only three phosphorus atoms are coordinated to silver and the fourth phosphorus atom is coordinated to molybdenum. Compounds **4** were obtained by the reaction of AgBr with amidophosphitocavitands **1**. Compounds **6** were synthesised by the reaction of AgBr with mononuclear molybdenum complexes of amidophosphocavitands **3**. It was found that, in the presence of diethylammonium cation, **4a** forms anionic complex $[(C_2H_5)_2NH_2][\text{cavitand}\cdot Ag_4(\mu\text{-Br})_4(\mu_4\text{-Br})]$ (**5**), whose structure was supported by X-ray diffraction analysis.

Keywords: Phosphocavitands; Silver bromide; Complexation; Bimetallic complexes

1. Introduction

Amidophosphitocavitands **1** are macrocyclic cavity systems based on calix[4]resorcinarenes containing four amidophosphite fragments in the upper rim of the molecular bowl with equatorial amido groups and axial lone electron pairs oriented inside the cavity.

Compounds **1** are very suitable for further modifications [1,2]. This is due to two factors. First, they are stable to air and water, which decreases the amount of by-products and, hence, increases the yield of target products. Second, these compounds are individual stereoisomers, and their configuration generally does not change during the functionalisation, which favours stereoselective processes. Therefore, amidophosphitocavitands **1** have large potentialities to be used for the creation of complex co-ordination systems [3–6]. Complexes of transition metals with different numbers (1, 2, 4) of metal-containing fragments specifically oriented with respect to one another and to the cavity were obtained on their basis. Note that the complexation selectivity largely depends on the nature and volume of substituents introduced to the phosphorus atoms [3,6]. The successive interaction of amidophosphitocavitands with different complexing agents can result in the formation of polymetallic complexes with different metal-containing fragments fixed on the same macropolycyclic matrix.

With the purpose of creating bimetallic complexes, we studied the reactions of silver bromide with amidophosphitocavitands **1** and their bi- and mono-nuclear Mo(0) complexes (**2** and **3**, respectively).

2. Results and discussion

As complexes **2** and **3** are labile compounds, their complexation should proceed in mild conditions. This

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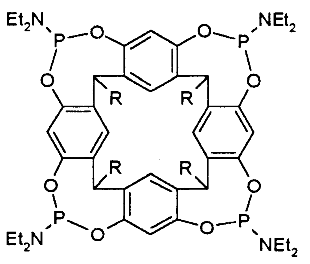
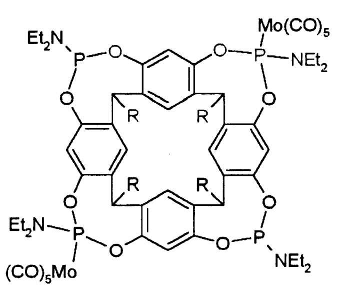
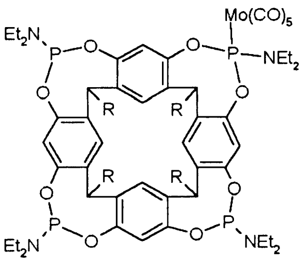


1a-c



2a,b



3a,b

R=CH_3- (1a,2a,3a), C_3H_7-(1b,2b,3b), C_9H_{19}-(1c)

factor was crucial for the selection of complexing agent. Puddephatt and co-workers showed that a phenylphosphonitocavitand reacts with $(AgC{\equiv}CPh)_n$ or $AgNO_3$ in the presence of pyridium chloride in mild conditions to form tetranuclear anionic complexes $[C_5H_5NH][cavitand \cdot Ag_4(\mu\text{-}Cl)_4(\mu_4\text{-}Cl)]$ [7]. We supposed that silver bromide should behave similarly in reactions with phosphocavitands and introduced it into reaction with amidophosphitocavitands **1** and their molybdenum complexes **2**, **3**.

2.1. Reaction of silver bromide with amidophosphitocavitands 1

The reaction of amidophosphitocavitands **1a**–**c** with silver bromide was performed in ethyl bromide at room temperature and the stoichiometric reagent ratio 1:AgBr = 1:4. The reaction was monitored by means of ^{31}P-NMR spectroscopy. After the reaction was completed, no signals from uncoordinated phosphorus atoms (δ 143 ppm) were observed in the ^{31}P-NMR spectra of the reaction mixture. Hence, all phosphorus atoms in the reaction products are co-ordinated to Ag(I).

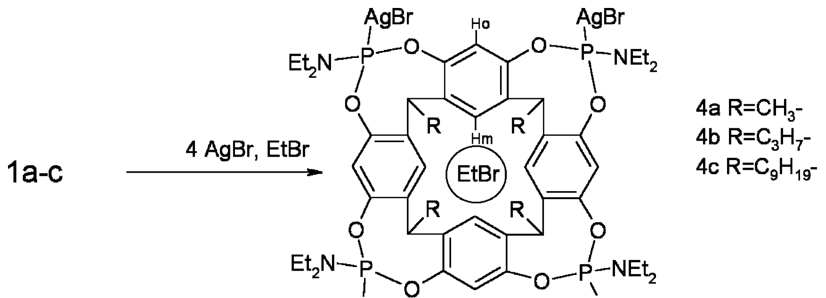
Tetranuclear complexes **4a**–**c** are white fine crystals with high melting points. The composition and structure of compounds **4** were determined by elemental analysis, mass spectrometry and NMR spectroscopy.

The ^{31}P-NMR spectra of complexes **4** displayed two doublets with equal integral intensities and chemical shifts but different coupling constants, which was due to similar amounts of two magnetic silver isotopes Ag^{107} and Ag^{109} (51.8 and 48.2%, respectively).

The ^{1}H-NMR spectra displayed a set of signals for all protons with slightly changed chemical shifts compared to the initial ligand. This indicated the chemical identity of all phosphocin cycles in cavitands **4** and the structural correspondence between ligands and complexes.

Molecular peaks in the mass spectra of compounds **4** corresponded to the calculated molecular weight of the tetranuclear complex solvated with a molecule of ethyl bromide.

In the presence of diethylammonium cations, **4a** forms anionic complex $[(C_2H_5)_2NH_2][cavitand \cdot Ag_4(\mu\text{-}Br)_4(\mu_4\text{-}Br)]$ (**5**), whose monocrystal has been isolated from dioxane. The X-ray analysis revealed that the crystal consists of an anion composed by the complex of phosphocavitand with an $Ag_4Br_5^-$ fragment, a diethyl ammonium cation and 3.5 molecules of dioxane solvate. The formation of complexes with AgBr results in no significant changes in the principal geometrical parameters of phosphocavitand (Fig. 1, Table 1). In the crystalline state, complex **5** is characterised by the approximate C_4 symmetry. Similar to the molecules studied previously, **5** has a bowl shape (Fig. 1), where the top rim diameters (C(2)···C(16) and C(9)···C(23) are



4a-c

Table 1
Selected bond lengths (Å) and angles (°)

Bond lengths			
Ag(1)–Br(1)	2.7657(7)	P(1)–O(1)	1.644(3)
Ag(1)–Br(4)	2.6661(7)	P(1)–O(2)	1.634(3)
Ag(1)–Br(5)	2.7829(7)	P(2)–O(3)	1.644(3)
Ag(2)–Br(1)	2.7551(7)	P(2)–O(4)	1.637(3)
Ag(2)–Br(2)	2.6666(7)	P(3)–O(5)	1.631(3)
Ag(2)–Br(5)	2.7946(7)	P(3)–O(6)	1.634(3)
Ag(3)–Br(2)	2.6504(7)	P(4)–O(7)	1.646(3)
Ag(3)–Br(3)	2.7414(7)	P(4)–O(8)	1.639(3)
Ag(3)–Br(5)	2.8397(7)	P(1)–N(1)	1.630(4)
Ag(4)–Br(3)	2.7353(7)	P(2)–N(2)	1.624(4)
Ag(4)–Br(4)	2.6633(7)	P(3)–N(3)	1.638(4)
Ag(4)–Br(5)	2.8148(7)	P(4)–N(4)	1.632(4)
Ag(1)–P(1)	2.421(1)	O–C	1.391(5)–1.414(5)
Ag(2)–P(2)	2.421(1)	N(1S)–C(3S)	1.488(6)
Ag(3)–P(3)	2.408(1)	N(1S)–C(2S)	1.488(6)
Ag(4)–P(4)	2.418(1)		
Bond angles			
Br(4)–Ag(1)–Br(1)	114.22(2)	O(5)–P(3)–Ag(3)	115.6(2)
Br(2)–Ag(2)–Br(1)	109.27(3)	O(6)–P(3)–Ag(3)	116.5(1)
Br(2)–Ag(3)–Br(3)	109.26(2)	N(3)–P(3)–Ag(3)	120.0(2)
Br(4)–Ag(4)–Br(3)	111.92(2)	N(4)–P(4)–O(8)	99.6(2)
Ag(2)–Br(1)–Ag(1)	75.08(2)	N(4)–P(4)–O(7)	102.6(2)
Ag(3)–Br(2)–Ag(2)	83.41(2)	O(8)–P(4)–O(7)	101.0(2)
Ag(4)–Br(3)–Ag(3)	79.34(2)	N(4)–P(4)–Ag(4)	120.0(2)
Ag(4)–Br(4)–Ag(1)	80.76(2)	O(8)–P(4)–Ag(4)	114.8(1)
N(1)–P(1)–O(2)	99.4(2)	O(7)–P(4)–Ag(4)	115.9(1)
N(1)–P(1)–O(1)	103.1(2)	C(29)–N(1)–C(31)	117.8(4)
O(2)–P(1)–O(1)	100.3(2)	C(29)–N(1)–P(1)	119.8(3)
N(1)–P(1)–Ag(1)	119.7(2)	C(31)–N(1)–P(1)	122.2(4)
O(2)–P(1)–Ag(1)	117.6(1)	C(35)–N(2)–C(33)	116.1(4)
O(1)–P(1)–Ag(1)	113.7(1)	C(35)–N(2)–P(2)	120.1(3)
N(2)–P(2)–O(4)	99.5(2)	C(33)–N(2)–P(2)	123.8(4)
N(2)–P(2)–O(3)	103.8(2)	C(37)–N(3)–C(39)	117.1(4)
O(4)–P(2)–O(3)	99.7(2)	C(37)–N(3)–P(3)	119.4(3)
N(2)–P(2)–Ag(2)	118.2(2)	C(39)–N(3)–P(3)	120.8(3)
O(4)–P(2)–Ag(2)	117.9(1)	C(43)–N(4)–C(41)	115.6(4)
O(3)–P(2)–Ag(2)	115.8(1)	C(43)–N(4)–P(4)	118.8(4)
O(5)–P(3)–O(6)	100.2(2)	C(41)–N(4)–P(4)	123.6(4)
O(5)–P(3)–N(3)	98.7(2)	C(3S)–N(1S)–C(2S)	113.4(4)
O(6)–P(3)–N(3)	102.5(2)		

8.261(5) and 8.149 Å) and the bottom rim diameters (C(5)···C(19) and C(12)···C(26) are 5.277(5) and 5.262(5) Å), respectively; i.e., they are practically equal to the corresponding values in the unsubstituted phosphocavitand (8.27 and 5.21 Å) [8].

The ‘lead’ of the bowl is composed of a crown-shaped eight-membered ring Ag_4Br_4, where all silver atoms are co-ordinated to a phosphorus atom and to the μ_4-Br^- atom located in the centre of the plane formed by the phosphorus atoms. Similar complexes were observed previously in salts of a phenylphosphonitocavitand with silver chlorides [8]. The Ag–(μ_4-Br) bonds are slightly elongated (2.7829(7)–2.8397(7) Å) compared to the Ag–(μ-Br) bonds (2.6633(7)–2.7657(7) Å). The unbound Ag···Ag contacts vary in the range of 3.3642(7)–3.5372(7) Å.

All phosphocin cycles are characterised by the chair–boat conformation with Ag atoms and methyl groups in axial positions and NEt_2 groups in equatorial positions. It is noteworthy that nitrogen atoms in **5**, as in the complexes studied previously [8], are significantly flattened, the sum of the bond angles being in the range of 357.3–360.0°.

The distortions of the $Ag_4Br_5^-$ fragment are apparently due to the crystal packing effects and especially to the anion···cation (Et_2NH_2) hydrogen bonds. The analysis of intermolecular contacts revealed that the diethylammonium cation forms two strong N–H···Br bonds with two μ-Br atoms (Br(1) and Br(3)) and the Br···N distances equal to 3.309(4)–3.328(4) Å. By these contacts, anions are assembled into dimers, which are surrounded by two molecules of dioxane solvate participating in weak N–H···O bonds with diethylammonium (Fig. 2).

Thus, interaction between amidophosphitocavitands **1** and AgBr proceeds in mild conditions and results in the formation of tetranuclear complexes. Hence, AgBr meets the requirements imposed to complexing agents and can be used for further modification of bi- and mono-nuclear metallocomplexes **2**, **3**.

2.2. *Reaction of silver bromide with bi- and mono-nuclear complexes of amidophosphitocavitands*

Binuclear molybdenum complexes of amidophosphitocavitands **2**, whose molecule contains two uncoordinated atoms of trivalent phosphorus, are essentially bidentate ligands. We attempted to realise the complexation of compounds **2a**, **b** with AgBr using different solvents (methylene chloride, chloroform, ethyl chloride) and varying the reagent ratio (**2**:AgBr = 1:2–8), temperature (20–60 °C) and reaction time (50–100 days). No changes were observed in the ^{31}P-NMR spectra of reaction mixtures in all cases.

Two pentacarbonylmolybdenum fragments probably completely shield the trivalent phosphorus atoms in binuclear complexes **2**, which makes their further modification impossible.

A single phosphorus atom is co-ordinated to Mo(0) in the mononuclear complexes of amidophosphitocavitands **3**. The single pentacarbonylmolybdenum fragment shields the trivalent phosphorus atoms to a much lower extent than in binuclear complexes **2**. Therefore, com-

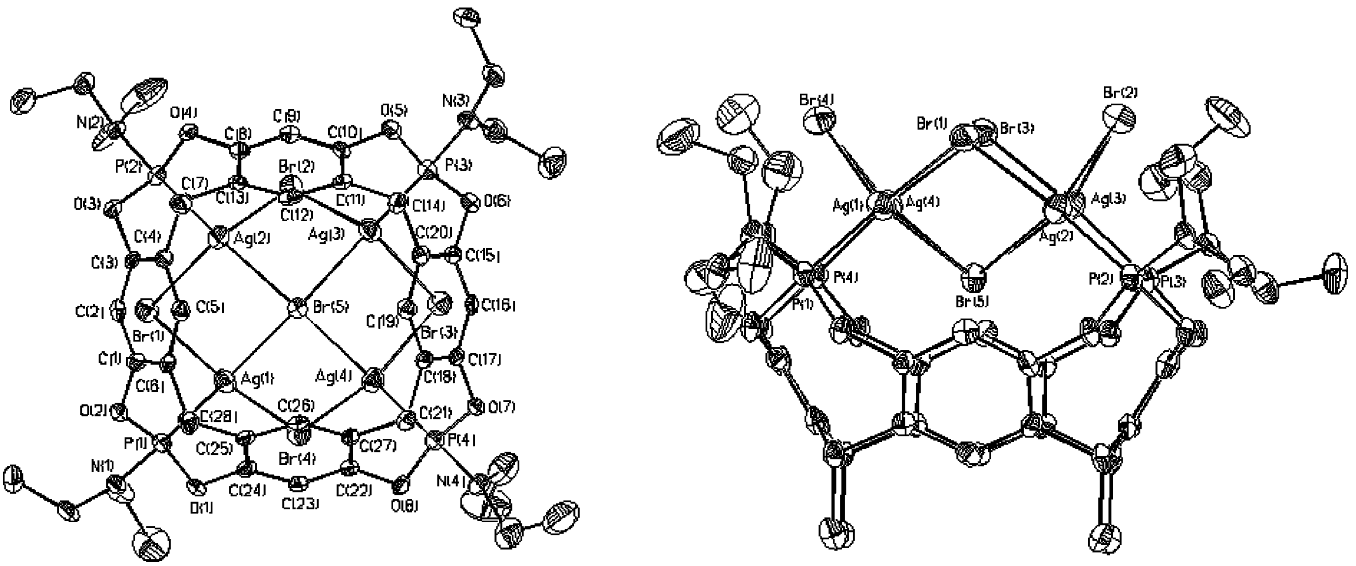
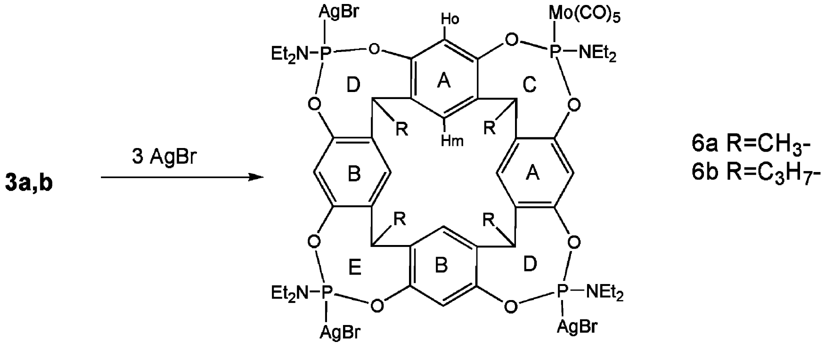


Fig. 1. The general view of anion in complex **4a** and its two projection with the representation of atoms by the thermal ellipsoids at the 50% probability level.

pounds **3** are tridentate ligands and undergo further complexation.

The reaction of complexes **3a**, **b** with AgBr was performed in methylene chloride at room temperature and reagent ratio **3**:AgBr = 1:3. The process continued for 15–18 days. It was shown by NMR spectroscopy that the reaction resulted in the co-ordination of each of three trivalent phosphorus atoms from ligands **3** to Ag(I) and the formation of bimetallic tetranuclear complexes **6a**, **b**.



6a,b

The ^{31}P-NMR spectra of compounds **6** exhibited a singlet at 168 ppm corresponding to the phosphorus atom co-ordinated to Mo(0) and two doublets from the phosphorus atoms co-ordinated to Ag(I). The integral signal ratio was $I_{\mathrm{P}\rightarrow\mathrm{Mo}}:\Sigma I_{\mathrm{P}\rightarrow\mathrm{Ag}} = 1:3$.

Doubling of signals from aromatic protons due to the inequivalence of benzene rings A and B was observed in the ^{1}H-NMR spectra, as well as trebling of signals from methine protons due to the inequivalence of phosphocin cycles C, D and E. The integral signal ratio of methine protons was $I_{\mathrm{CH(C)}}:I_{\mathrm{CH(D)}}:I_{\mathrm{CH(E)}} = 1:2:1$. The overlap of signals from methyl and methylene protons of amide groups of phosphocin cycles D and E resulted in doubling of these signals rather than in their trebling. The ratio of integral signal intensities was $I_{\mathrm{NCH_2}\mathit{CH_3}\mathrm{(C)}}:I_{\mathrm{NCH_2}\mathit{CH_3}\mathrm{(D,E)}} = I_{\mathrm{N}\mathit{CH_2}\mathrm{CH_3(C)}}:I_{\mathrm{N}\mathit{CH_2}\mathrm{CH_3(D,E)}} =$ 1:3. The vicinal coupling constant of diethylamide methylene protons with the phosphorus nucleus co-ordinated to silver ($^3J_{\mathrm{PH}}$) was higher than that observed for the phosphorus nucleus co-ordinated to molybde-

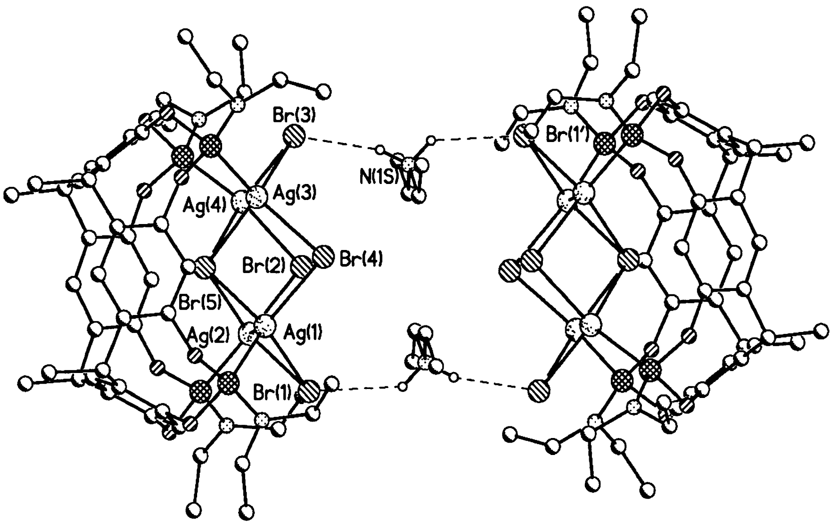


Fig. 2. The scheme illustrating the formation of the dimers in crystal structure **4a**. The N–H· · ·Br and N–H· · ·O contacts a re shown by dashed lines.

num ($\Delta J = 3$ Hz) and comparable to the analogous constant in complexes **4**.

Molecular peaks in the mass spectra of complexes **6a**, **b** corresponded to the calculated molecular weights of these compounds.

3. Experimental

3.1. General

^{1}H-NMR spectra were recorded on a Bruker WM-200 spectrometer with TMS as an internal standard. ^{31}P-NMR spectra (at 32.4 MHz, 85% H_3PO_4 as an external standard) were recorded on a Bruker WP-80 spectrometer. Mass spectra were recorded in a Kratos PC-Kompact MALDI 4 spectrometer.

The crystallographic data for complex **5** are presented in Table 2. The structure was solved by the direct method and refined by full-matrix least squares against F^2 in the anisotropic (H-atoms isotropic) approximation using SHELXTL-97 package. The absorption correction was applied semi-empirically using the SADABS program. All hydrogen atoms in **1** were localised in an electron density difference map and refined in isotropic approximation.

All syntheses were performed in dry solvents under argon. Phosphocavitands **1a**, **1b** and **1c** were synthesised by the procedures described previously ([9], [8] and [10], respectively). Binuclear **2a**, **b** and mononuclear **3a**, **b** complexes were synthesised using the procedures described in Ref. [6].

3.2. Complex *4a*

A solution of cavitand **1a** (0.0894 g, 0.094 mmol) in 1 ml of ethyl bromide was added to AgBr (0.069 g, 0.37 mmol). The reaction mixture was exposed at 20 °C for 40 days. The precipitate was filtered off; the solvent was evaporated from the filtrate, and the residue was dried

Table 2
Crystallographic data for complex **5**

	5
Molecular formula	$C_{66}H_{104}Ag_4Br_5N_5O_{15}P_4$
Formula weight	2162.45
Colour, shape	Colourless, prism
Dimension	$0.35 \times 0.32 \times 0.20$
Diffractometer	SMART 1000 CCD
Temperature (K)	110
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	22.561(4)
b (Å)	14.080(3)
c (Å)	25.860(4)
β (°)	98.233(4)
V (Å^3)	8130(2)
Z	4
$F(0\,0\,0)$	4312
ρ_{calc} (g cm^{-1})	1.767
Radiation, λ (Mo–K$_\alpha$) (Å)	0.71072
Linear absorption, μ (cm^{-1})	35.47
T_{min}/T_{max}	0.894/0.956
Scan type	ω-scan with 0.3° step in ω and 10 s exposure per frame
θ Range (°)	1.91–28.99
Completeness of dataset (%)	98.0
Measured	50 790
Unique	19 290 ($R_{int} = 0.0582$)
With $[I > 2\sigma(I)]$	10 948
Parameters	914
Final R (F_{hkl}): R_1	0.0450
wR_2	0.0941
Goodness-of-fit on F^2	1.085
ρ_{max}/ρ_{min} (e Å^{-3})	1.657/−0.659

under vacuum (1 mmHg) at 20 °C. Yield: 0.0938 g (60%). M.p. 335–337 °C (dec.). ^{1}H-NMR ($\mathrm{CDCl_3}$) δ, ppm: 1.25 (t, 24H, $\mathrm{NCH_2C}H_3$); 1.77 (d, $^3J_{\mathrm{HH}} = 7.7$ Hz, 12H, $\mathrm{CHC}H_3$); 3.42 (m, $^3J_{\mathrm{PH}} = 13.2$ Hz, 16H, $\mathrm{NC}H_2\mathrm{CH_3}$); 4.80 (q, 4H, $\mathrm{C}H\mathrm{CH_3}$); 6.79 (s, 4H, Ho); 7.31 (s, 4H, Hm). ^{31}P-NMR ($\mathrm{CDCl_3}$) δ, ppm: 134.2 (dd, $^1J_{\mathrm{PAg(107)}} = 648.5$ Hz, $^1J_{\mathrm{PAg(109)}} = 745.7$ Hz). Elemental analysis Found (%): C, 33.70; H, 4.20; N, 3.20; P, 6.80. Anal. Calc. (%) for $\mathrm{C_{48}H_{64}Ag_4Br_4N_4O_8P_4 \cdot EtBr}$: C, 33.21; H, 3.85; N, 3.10; P, 6.85. *m/z* (%) = 1806.4 (100) [$\mathrm{M^+ + EtBr}$].

3.3. *Complex* **4b**

Complex **4b** was obtained analogously to **4a** by the reaction of cavitand **1b** (0.078 g, 0.07 mmol) and AgBr (0.056 g, 0.29 mmol) in 1 ml of ethyl bromide for 30 days. Yield: 0.069 g (51%). M.p. 315–317 °C. ^{1}H-NMR ($\mathrm{CD_2Cl_2}$) δ, ppm: 1.01 (t, 12H, $\mathrm{CH_2CH_2C}H_3$); 1.22 (t, 24H, $\mathrm{NCH_2C}H_3$); 1.33 (m, 8H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$); 2.23 (m, 8H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$); 3.39 (m, $^3J_{\mathrm{PH}} = 13.2$ Hz, 16H, $\mathrm{NC}H_2\mathrm{CH_3}$); 4.57 (t, 4H, CH); 6.69 (s, 4H, Ho); 7.22 (s, 4H, Hm). ^{31}P-NMR ($\mathrm{CD_2Cl_2}$) δ, ppm: 134.5 (dd, $^1J_{\mathrm{PAg(107)}} = 653.0$ Hz, $^1J_{\mathrm{PAg(109)}} = 756.6$ Hz). Elemental analysis Found (%): C, 36.74; H, 3.98; N, 2.86; P, 6.60. Anal. Calc. (%) for $\mathrm{C_{56}H_{80}Ag_4Br_4N_4O_8P_4 \cdot EtBr}$: C, 36.26; H, 4.47; N, 2.91; P, 6.45. *m/z* (%) = 1921.6 (100) [$\mathrm{M^+ + EtBr}$].

3.4. *Complex* **4c**

Complex **4c** was obtained analogously to **4a** by the reaction of cavitand **1c** (0.66 g, 0.048 mmol) and AgBr (0.045 g, 0.24 mmol) in 0.8 ml of ethyl bromide for 15 days. Yield: 0.106 g (95%). M.p. 300–302 °C. ^{1}H-NMR ($\mathrm{CD_2Cl_2}$) δ, ppm: 0.81 (t, 12H, $\mathrm{CH_2(CH_2)_7C}H_3$); 1.19 (t, 24H, $\mathrm{NCH_2C}H_3$); 1.22 (br, 56H, $\mathrm{CH_2(C}H_2\mathrm{)_7CH_3}$); 2.17 (m, 8H, $\mathrm{C}H_2\mathrm{(CH_2)_7CH_3}$); 3.32 (m, $^3J_{\mathrm{PH}} = 13.2$ Hz, 16H, $\mathrm{NC}H_2\mathrm{CH_3}$); 4.48 (t, 4H, CH); 6.60 (s, 4H, Ho); 7.15 (s, 4H, Hm). ^{31}P-NMR ($\mathrm{CD_2Cl_2}$) δ, ppm: 134.9 (dd, $^1J_{\mathrm{PAg(107)}} = 663.8$ Hz, $^1J_{\mathrm{PAg(109)}} = 793.4$ Hz). *m/z* (%) = 2263.2 (100) [$\mathrm{M^+ + EtBr}$].

3.5. *Complex* **5**

A suspension of AgBr (0.062 g, 0,34 mmol), cavitand **1a** (0.079 g, 0.0841 mmol) and diethylammonium chloride (0.01 g, 0.0913 mmol) in 1 ml of ethyl bromide was exposed at 20 °C for 47 days. The precipitate was filtered off; the filtrate solvent was evaporated, and the residue was recrystallised from dioxane. All crystals were selected for X-ray structure determination.

3.6. *Complex* **6a**

A solution of complex **3a** (0.0504 g, 0.0425 mmol) in 0.8 ml of methylene chloride was added to AgBr (0.024 g, 0.13 mmol), and the reaction mixture was exposed at 20 °C for 15 days. The solvent was evaporated, and the residue was treated with dioxane. The precipitate was filtered off; dioxane was evaporated, and the residue was dried under vacuum (1 mmHg) at 20 °C. Yield: 0.019 g (25%). M.p. 157–159 °C. ^{1}H-NMR ($\mathrm{CDCl_3}$) δ, ppm: 1.17 (t, 6H, $\mathrm{NCH_2C}H_3$); 1.25 (t, 18H, $\mathrm{NCH_2C}H_3$); 1.78 (d, $^3J_{\mathrm{HH}} = 7.3$ Hz, 12H, $\mathrm{CHC}H_3$); 3.26 (m, $^3J_{\mathrm{PH}} = 10.7$ Hz, 4H, $\mathrm{NC}H_2\mathrm{CH_3}$); 3.42 (m, $^3J_{\mathrm{PH}} = 13.7$ Hz, 12H, $\mathrm{NC}H_2\mathrm{CH_3}$); 4.69 (q, 1H, $\mathrm{C}H\mathrm{CH_3}$); 4.80 (q, 2H, $\mathrm{C}H\mathrm{CH_3}$); 4.91 (q, 1H, $\mathrm{C}H\mathrm{CH_3}$); 6.65 (s, 2H, Ho); 6.75 (s, 2H, Ho); 7.31 (s, 2H, Hm); 7.33 (s, 2H, Hm). ^{31}P-NMR ($\mathrm{CDCl_3}$) δ, ppm: 134.7 (dd, $^1J_{\mathrm{PAg(107)}} = 610.8$ Hz, $^1J_{\mathrm{PAg(109)}} = 727.5$ Hz, 3P, P–Ag); 168.3 (s, 1P, P–Mo). *m/z* (%) = 1809.7 (100) [$\mathrm{M^+ + Na^+ + K^+}$].

3.7. *Complex* **6b**

Complex **6b** was obtained analogously to **6a** by the reaction of mononuclear complex **3b** (0.051g, 0.0393 mmol) with AgBr (0.022 g, 0.118 mmol) in 0.6 ml of methylene chloride for 18 days. Yield: 0.041 g (56%). M.p. 201–204 °C. ^{1}H-NMR ($\mathrm{CDCl_3}$) δ, ppm: 1.02 (t, 12H, $\mathrm{CH_2CH_2C}H_3$); 1.17 (t, 6H, $\mathrm{NCH_2C}H_3$); 1.24 (t, 18H, $\mathrm{NCH_2C}H_3$); 1.27 (m, 8H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$); 2.22 (m, 8H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$); 3.27 (m, $^3J_{\mathrm{PH}} = 10.2$ Hz, 4H, $\mathrm{NC}H_2\mathrm{CH_3}$); 3.40 (m, $^3J_{\mathrm{PH}} = 13.2$ Hz, 12H, $\mathrm{NC}H_2\mathrm{CH_3}$); 4.50 (q, 1H, CH); 4.58 (q, 2H, CH); 4.72 (q, 1H, CH); 6.56 (s, 2H, Ho); 6.76 (s, 2H, Ho); 7.18 (s, 2H, Hm); 7.20 (s, 2H, Hm). ^{31}P-NMR ($\mathrm{CDCl_3}$) δ, ppm: 134.7 (dd, $^1J_{\mathrm{PAg(107)}} = 677.1$ Hz, $^1J_{\mathrm{PAg(109)}} = 774.3$ Hz, 3P, P–Ag); 168.3 (s, 1P, P–Mo). *m/z* (%) = 1927.3 (100) [$\mathrm{M^+ + Na^+ + K^+}$].

4. Supplementary material

Crystallographic data (except for the structural factors) for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary no. CCDC 198732. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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