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Golden crowns: cation binding by macrocyclic gold(I) crown ether derivatives

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Abstract

The polyether bis(alkynes) α,ω-bis(*O*-propargyl)triethylene glycol and α,ω-bis(*O*-4-propargyloxyphenoxy)triethylene glycol reacted with [AuCl(SMe$_2$)] in the presence of base to form the corresponding oligomeric gold(I) acetylide complexes (AuC-CCH$_2$O(CH$_2$CH$_2$O)$_3$CH$_2$CCAu)$_n$ and (AuCCCH$_2$OC$_6$H$_4$O(CH$_2$CH$_2$O)$_3$C$_6$H$_4$OCH$_2$CCAu)$_n$. These digold(I) diacetylide complexes reacted with diphosphine ligands to give macrocyclic digold(I) complexes of the type [Au$_2$(μ-CC)(μ-PP)], where CC is the diacetylide and PP is a diphosphine ligand. These digold(I) complexes bind the cations Li$^+$, Na$^+$, K$^+$ and Cs$^+$, as studied by electrospray mass spectrometry.

Keywords: Gold(I); Macrocycle; Crown ether; Cation binding

1. Introduction

The design of supramolecular systems containing macrocycles or mechanically interlocked components is of current interest, since such compounds have potential applications in nanoscale devices [1–8]. Most known catenanes are based on organic or inorganic molecules, and organometallic catenanes have only been known for ten years [9]. Entropy effects do not favour catenane formation from simple macrocycles and so, if a catenane is to be formed by self-assembly, the macrocycle must incorporate functional groups to give favourable enthalpy effects through π–π interactions, dipole–dipole attractions or hydrogen bonding in the catenane product [1,4]. Linear, two-coordinate gold(I) units are useful for the assembly of organometallic macrocycles, and supramolecular association through aurophilic attractions can then occur to give more complex assemblies [10–12]. Some of the known gold(I) acetylide macrocycles are illustrated in Chart 1.

Rigid linear diacetylides give tetragold(I) complexes containing 26- or 34-membered rings **I** (Ar = 1,4-C$_6$H$_4$ or 4,4′-C$_6$H$_4$C$_6$H$_4$), while angular diacetylides formed 24-membered rings **II** [13,14]. Using the diacetylides derived from *o*-, *m*- and *p*-bis(propargyloxy)benzene and the diphosphines Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 1–6) macrocycles of type **III** containing 15–22-membered rings were prepared [15]. Similarly, a more flexible ligand, based on the linker group 3,3-(ethylenedioxy)diphenol, gave 23–28-membered ring structures **IV**, which form interpenetrated dimers in the solid state [16]. Complexes of the type **V**, where X = O, S and OC, also form macrocyclic structures with diphosphine ligands but, when X = Me$_2$C, H$_2$C, O$_2$S and n = 3–6, the complexes undergo self-assembly to give the [2]catenanes **VI** [17–20]. When X = C$_6$H$_{10}$ and n = 4, a rare doubly braided [2]catenane was obtained [21]. A huge variety of structurally diverse crown ethers with high affinities and selectivities for all kinds of cations have been reported [22–26] and there is recent interest in crown ethers incorporating inorganic or organometallic fragments [27,28]. This paper reports digold(I) diacetylide macrocycles that incorporate a flexible polyether chain to form a "gilded" crown ether. It was anticipated that the large cavity of such a macrocycle might allow catenation to occur or that the polyether chain might enable encapsulation of cations.

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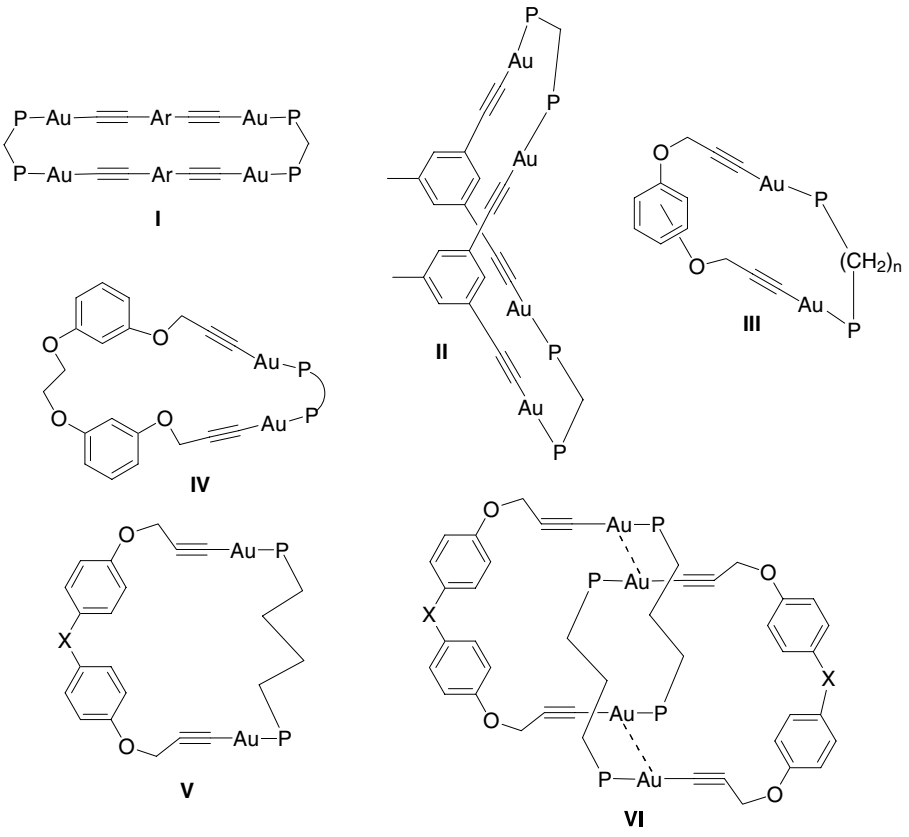
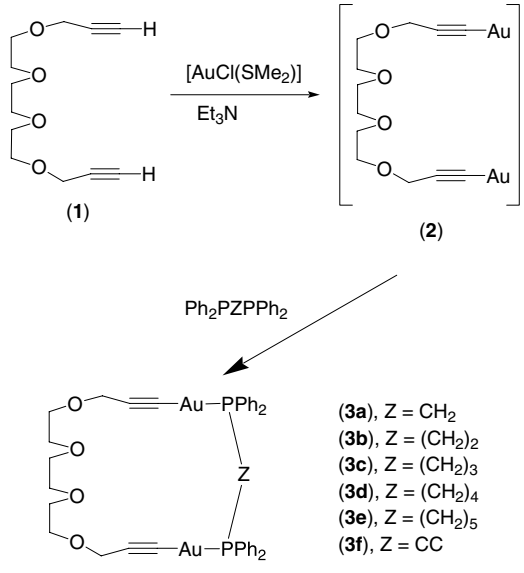


Chart 1. Some known gold(I) macrocycles.

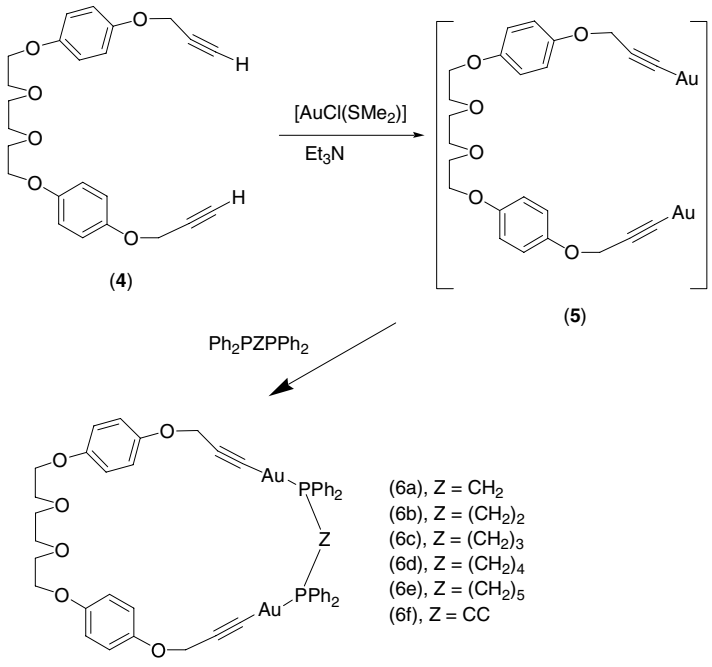
2. Results and discussion

2.1. Ligand and gold(I) macrocycle syntheses

The bis(alkyne) with an oligoether spacer group, α,ω-bis(*O*-propargyl)triethylene glycol, $HCCCH_2O(CH_2CH_2O)_3CH_2CCH$, **1**, was prepared by the literature method [29], and the related bis(alkyne) $HCCCH_2OC_6H_4O(CH_2CH_2O)_3C_6H_4OCH_2CCH$, **4**, having two extra oxyphenylene spacer groups, was prepared by reacting 4,4′-{ethylenebis(oxyethyleneoxy)} diphenol with propargyl bromide in the presence of potassium carbonate. The new bis(alkyne) was characterized by its ^1H, ^{13}C NMR and IR spectra and by the high resolution mass spectrum (see Section 3). Treatment of these bis(alkynes) with two equivalents of $[AuCl(SMe_2)]$ and Et_3N gave the yellow solid products $(AuCCCH_2O(CH_2CH_2O)_3CH_2CCAu)_n$, **2**, and $(AuCCCH_2OC_6H_4O(CH_2CH_2O)_3C_6H_4OCH_2CCAu)_n$, **5**, which were insoluble in common organic solvents. These compounds, like other gold(I) acetylide complexes, are oligomeric or polymeric, and are characterized in the IR spectra by ν(CC) values [1993 cm^{-1} in **2** and 2003 cm^{-1} in **5**] that are lower by ca. 100 cm^{-1} than in the parent bis(alkyne), as a result of π-bonding between gold and the alkynyl groups [30]. The digold(I) oligomers **2** and **5** react with the diphosphine ligands Ph_2PZPPh_2 [$Z = (CH_2)_n$, $n = 1$–5; CC] to form the beige or pale yellow gold(I) macrocyclic complexes (**3a**–**3f** and **6a**–**6f**) as shown in Schemes 1 and 2.



Scheme 1.



Scheme 2.

The new gold complexes did not form crystals suitable for X-ray structure determination, so they were characterized spectroscopically. For example, complex **3a** gave a singlet in the ^{31}P NMR spectrum at δ 32.89 and, in the ^{1}H NMR spectrum, there was a single resonance for the PCH_2P protons at δ 3.63 (t, $^{2}J_{PH} = 11$ Hz) and for the OCH_2C protons of the propargyl group at δ 4.36, indicating the presence of a single complex. However, these data do not distinguish between ring and [2]catenane structures. The ES-MS, obtained from a solution containing CsCl to aid ionization, gave a peak at $m/z = 1134$ $[M + Cs]^+$ for the simple macrocycle with no peak corresponding to the [2]catenane. Thus, the spectroscopic evidence is consistent with the complex having the simple 21-membered macrocyclic structure **3a**, as shown in Scheme 1. The other complexes were characterized similarly. The ring sizes of the macrocycles range from 21 in **3a** to 35 in **6e**.

2.2. Cation binding studies

The observation of intense peaks in the electrospray mass spectra due to Cs^+ adducts of the macrocycles prompted an examination of the cation binding ability of these complexes in more detail. Samples of the gold(I) macrocycles (complexes **3a**, **3c**, **3e** and **6a**, **6c**, **6e**) were treated with solutions containing equimolar amounts of cation pairs (Li^+/Na^+; Na^+/K^+; K^+/Cs^+), the ES mass spectra were recorded, and the relative amounts of the macrocycle-cation adducts in the gas phase were determined from the relative abundance of each in the ES-MS. The results are shown in Table 1. It is most useful to examine trends since the gas phase abundances will not generally be the same as those in solution, due to solvation and ionization effects [31].

It is clear from the competition between Li^+ and Na^+ that complexes **3a**, **3c** and **3e** do not discriminate greatly between these cations, but that the larger ring complexes

Table 1
Cation binding for selected gold(I) macrocycles

Complex	Ring size	Mass[a]	Li/Na[b]	Na/K[b]	K/Cs[b]
		P + Li, Na, K, Cs			
3a	21	1009, 1025, 1041, 1135	0.73	0.87	128
3c	23	1037, 1053, 1069, 1163	1.74	0.59	96
3e	25	1065, 1081, 1097, 1191	1.02	0.87	11.9
6a	31	1193, 1209, 1225, 1319	0.03	0.87	18.9
6c	33	1221, 1237, 1253, 1347	0.19	1.00	6.17
6e	35	1249, 1265, 1281, 1375	0.04	0.75	1.85

[a] Masses of $[P + cation]^+$ ion peaks; P = parent mass for macrocycle.
[b] Ratio of intensities $[P + M_1]^+/[P + M_2]^+$ for pairs of alkali metal cations.

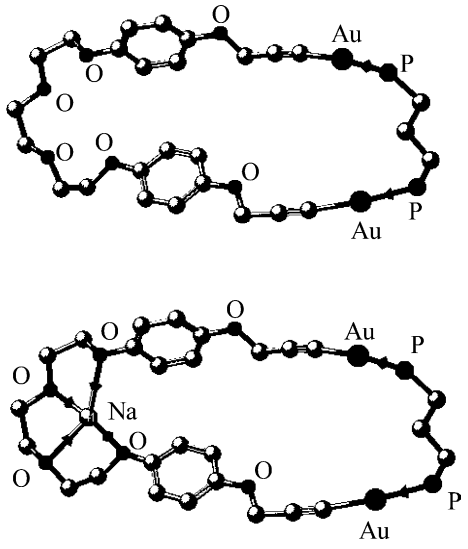


Fig. 1. The macrocyclic structures of complex **6c** (above) and its complex with Na^+ (below), as predicted by molecular mechanics. Hydrogen atoms and phenyl substituents of the diphosphine are omitted for clarity.

6a, **6c** and **6e** bind sodium cations more strongly. None of the complexes discriminate greatly between Na^+ and K^+, and all bind K^+ in preference to Cs^+. For each series **3a**, **3c**, **3e** and **6a**, **6c**, **6e** the selectivity for potassium over cesium decreases as the ring size increases, and the smaller ring complexes **3** discriminate more than the larger ring complexes **6** (Table 1). Fig. 1 shows a structure for the macrocycle **6c** and for its complex with a sodium ion, as predicted by molecular mechanics calculations. It is clear from such structures that the diphosphine digold(I) unit serves to make the macrocycle wider, with longer spacer groups in the diphosphine, or narrower, with shorter spacer groups, but that the effect at the polyether unit is attenuated by the flexibility of the connecting propargyl groups. Overall these results show that the gold(I) macrocycles **3** and **6** show selectivity for binding of alkali metal cations based on size, and that the selectivity can be tuned by changing the length of the spacer group of the diphosphine ligands used.

3. Experimental

NMR spectra were measured using a Varian Mercury 400 MHz spectrometer. ^1H and ^{13}C NMR chemical shifts are reported relative to TMS, while ^{31}P chemical shifts are reported relative to 85% H_3PO_4 as an external standard. IR spectra were recorded using a Perkin–Elmer 2000 FT-IR instrument. Electrospray mass spectra were recorded using a Micromass LCT instrument in positive ion mode. Samples were dissolved in CH_2Cl_2, diluted with MeCN and treated with 10 μl of a solution of CsI in $MeCN/H_2O$ to aid ionization. High-resolution mass spectra were measured using a Finnigan MAT 8200 spectrometer. $[AuCl(SMe_2)]$ [32], α,ω-bis(*O*-propargyl)triethylene glycol [29] and 4,4′-{ethylenebis(oxyethyleneoxy)}diphenol [33] were prepared by literature procedures. All reactions involving gold complexes were carried out in reaction vessels shielded from light.

3.1. Gold(I) oligomer, 2

A solution of α,ω-bis(*O*-propargyl)triethylene glycol **1** (0.138 g, 0.610 mmol) and Et_3N (0.3 ml) in THF was added to a solution of $[AuCl(SMe_2)]$ (0.359 g, 1.22 mmol) in THF (40 ml) and MeOH (30 ml). After stirring for 0.5 h, the solid was isolated by filtration and was washed with THF, MeOH, Et_2O and pentane to give 0.297 g (79%) yellow solid. The compound was stored cold and protected from light. IR (KBr disk, cm^{-1}) 1993 [w, *ν*(CC)]; *Anal.* Calc. for $C_{12}H_{16}Au_2O_4$: C, 23.31; H, 2.61. Found: C, 23.47; H, 2.48%.

3.2. Macrocycle, 3a

A mixture of **2** (0.050 g, 0.081 mmol) and $Ph_2P(CH_2)PPh_2$ (0.026 g, 0.068 mmol) in CH_2Cl_2 (10 ml) was stirred at room temperature for 3 h. The mixture was filtered through Celite and concentrated in vacuum. Addition of pentane gave a colourless solid, which was isolated by filtration, washed with Et_2O and pentane and dried. Yield: 0.057 g, 69% cream coloured solid. ^{31}P NMR (CD_2Cl_2) δ 32.89; ^1H NMR (CD_2Cl_2) δ 3.63 (t, $^2J_{PH} = 11$ Hz, 2H, PCH_2P) 3.64–3.75 (m, 12H, OCH_2CH_2O), 4.36 (s, 4H, OCH_2CO), 7.32–7.47 (m, 12H, PPh_2), 7.58–7.65 (m, 8H, PPh_2); ES-MS (*m*/*z*): 1135 $[M + Cs]^+$; *Anal.* Calc. for $C_{37}H_{38}Au_2O_4P_2$: C, 44.33; H, 3.82. Found: C, 44.35; H, 3.72%.

Similarly were prepared from **2** and the appropriate diphosphine ligand: **3b**: Yield: 57% beige solid. ^{31}P NMR (CD_2Cl_2) δ 40.08; ^1H NMR (CD_2Cl_2) δ 2.64 (s br, 4H, CH_2P), 3.59–3.79 (m, 12H, OCH_2CH_2O), 4.25 (s, 4H, OCH_2CO), 7.44–7.66 (m, 20H, PPh_2); ES-MS (*m*/*z*) 1149 $[M + Cs]^+$; *Anal.* Calc. For $C_{38}H_{40}Au_2O_4P_2$: C, 44.90; H, 3.97. Found: C, 44.63, H, 3.87%. **3c**: Yield: 75% beige solid. ^{31}P NMR (CD_2Cl_2) δ 34.76; ^1H NMR (CD_2Cl_2) δ 1.87 (s br, 2H, CH_2CH_2P), 2.66 (s br, 4H, CH_2P), 3.59–3.77 (m, 12H, OCH_2CH_2O), 4.28 (s, 4H, OCH_2C), 7.42–7.55 (m, 12H, PPh_2), 7.64–7.75 (m, 8H, PPh_2); ES-MS (*m*/*z*) 1163 $[M + Cs]^+$; *Anal.* Calc. for $C_{39}H_{42}Au_2O_4P_2$: C, 45.45; H, 4.11. Found: C, 45.74; H, 4.22%. **3d**: Yield: 69% beige solid. ^{31}P NMR (CD_2Cl_2) δ 38.59; ^1H NMR (CD_2Cl_2) δ 1.79 (s br, 4H, CH_2CH_2P), 2.42 (s br, 4H, CH_2P), 3.59–3.76 (m, 12H, OCH_2CH_2O), 4.26 (s, 4H, OCH_2CO), 7.43–7.54 (m, 12H, PPh_2), 7.61–7.70 (m, 8H, PPh_2); ES-MS (*m*/*z*) 1177 $[M + Cs]^+$; *Anal.* Calc. for $C_{40}H_{44}Au_2O_4P_2$: C, 45.99; H, 4.25. Found: C,

45.70; H, 4.25%. **3e**: Yield: 81% beige solid. ^{31}P NMR (CD_2Cl_2) δ 37.87; ^{1}H NMR (CD_2Cl_2) δ 1.62 (s br, 6H, CH_2CH$_2$P), 2.40 (s br, 4H, CH$_2$P), 3.59–3.73 (m, 12H, OCH$_2$CH$_2$O), 4.25 (s, 4H, OCH$_2$CO), 7.43–7.54 (m, 12H, PPh$_2$), 7.63–7.72 (m, 8H, PPh$_2$); ES-MS (m/z) 1191 [M + Cs]$^+$; *Anal*. Calc. for $C_{41}H_{46}Au_2O_4P_2$: C, 46.51; H, 4.38. Found: C, 46.33; H, 4.46%. **3f**: Yield: 70%. ^{31}P NMR (CD_2Cl_2) δ 21.51; ^{1}H NMR (CD_2Cl_2) δ 3.60–3.75 (m, 12H, OCH$_2$CH$_2$O), 4.26 (s, 4H, OCH$_2$CO), 7.47–7.61 (m, 12H, PPh$_2$), 7.72–7.81 (m, 8H, PPh$_2$); ES-MS (m/z) 1145 [M + Cs]$^+$; *Anal*. Calc. for $C_{38}H_{36}Au_2O_4P_2$: C, 44.44; H, 3.56. Found: C, 44.36; H, 3.47%.

3.3. Bis(alkyne), 4

A mixture of 4,4′-{ethylenebis(oxyethyleneoxy)}diphenol (1.0 g, 2.99 mmol), K_2CO_3 (1.2 g, 8.69 mmol) and propargyl bromide (0.8 ml, 7.48 mmol) in acetone (60 ml) was heated to reflux for ca. 18 h. The suspension was filtered and the filtrate was evaporated to dryness to give 0.66 g, 54% pale yellow solid. ^{1}H NMR ($CDCl_3$) δ 2.50 (t, $J = 2$ Hz, 2H, OCH), 3.74 (t, $J = 5$ Hz, 4H, OCH$_2$CH$_2$O), 3.83 (s, 4H, OCH$_2$CH$_2$O), 4.07 (t, $J = 5$ Hz, 4H, OCH$_2$CH$_2$O), 4.62 (d, $J = 2$ Hz, 4H, OCH2-CO), 6.85 (d, $J = 9$ Hz, 4H, C$_6$H$_4$), 6.89 (d, $J = 9$ Hz, 4H, C$_6$H$_4$); ^{13}C NMR ($CDCl_3$) δ 56.8 (O*C*H2CO), 68.2, 70.1, 71.1 (OCH$_2$CH$_2$O), 75.6 (CO*C*H), 79.1 (*C*OCH), 115.8, 116.3, 152.0, 153.9 (C$_6$H$_4$); IR (KBr disk, cm^{-1}) 3251 (s, OCH), 2115 [w, ν(CC)]; HR-MS found m/z 410.1725, calculated for $C_{24}H_{26}O_6$ m/z 410.1729.

3.4. Gold(I) oligomer, 5

This was prepared from (**4**) (0.25g, 0.61 mmol) and [AuCl(SMe$_2$)] (0.35 g, 1.19 mmol) as described for **2**. Yield: 0.37 g, 76% pale yellow solid. IR (KBr disk, cm^{-1}) 2003 [w, ν(CC)]; *Anal*. Calc. for $C_{24}H_{24}Au_2O_6$: C, 35.93; H, 3.01. Found: C, 36.15; H, 3.02%.

3.5. Gold(I) macrocycles, 6a–6f

The following gold(I) macrocycles were prepared from **5** and the appropriate diphosphine as described above for complex **3a**:**6a**: Yield: 75%. ^{31}P NMR (CD_2Cl_2) δ 32.85; ^{1}H NMR (CD_2Cl_2) δ 3.61 (t, $^2J_{PH} = 10$ Hz, 2H, PCH$_2$P), 3.67 (s, 4H, OCH$_2$CH$_2$O), 3.76 (t, $J = 5$ Hz, 4H, OCH$_2$CH$_2$O), 3.99 (t, $J = 5$ Hz, 4H, OCH$_2$CH$_2$O), 4.69 (s, 4H, OCH$_2$CO), 6.77 (d, $J = 9$ Hz, 4H, C$_6$H$_4$), 6.83 (d, $J = 9$ Hz, 4H, C$_6$H$_4$), 7.29–7.47 (m, 12H, PPh$_2$), 7.55–7.64 (m, 12H, PPh$_2$); ES-MS (m/z) 1319 [M + Cs]$^+$; *Anal*. Calc. for $C_{49}H_{46}Au_2O_6P_2$: C, 49.59; H, 3.91. Found: C, 49.34; H, 3.91. **6b**: Yield: 97%. ^{31}P NMR (CD_2Cl_2) δ 38.79; ^{1}H NMR (CD_2Cl_2) δ 2.60 (s br, 4H, CH$_2$P), 3.69 (s, 4H, OCH$_2$CH$_2$O), 3.79 (t, $J = 5$ Hz, 4H, OCH$_2$CH$_2$O), 4.04 (t, $J = 5$ Hz, 4H, OCH$_2$CH$_2$O), 4.77 (s, 4H, OCH$_2$ CO), 6.86 (d, $J = 9$ Hz, 4H, C$_6$H$_4$), 7.01 (d, $J = 9$ Hz, 4H, C$_6$H$_4$), 7.38–7.65 (m, 20H, PPh$_2$); ES-MS (m/z) 1333 [M + Cs]$^+$; *Anal*. Calc. for $C_{50}H_{48}Au_2O_6P_2$: C, 50.01; H, 4.03. Found: C, 50.02; H, 3.94%. **6c**: Yield: 0.052 g, 81%. ^{31}P NMR (CD_2Cl_2) δ 34.88; ^{1}H NMR (CD_2Cl_2) δ 1.85 (s br, 2H, CH_2CH$_2$P), 2.75 (s br, 4H, CH$_2$P), 3.67 (s, 4H, OCH$_2$CH$_2$O), 3.77 (t, $J = 5$ Hz, 4H, OCH$_2$CH$_2$O), 4.01 (t, $J = 5$ Hz, 4H, OCH$_2$CH$_2$O), 4.76 (s, 4H, OCH$_2$CO), 6.83 (d, $J = 9$ Hz, 4H, C$_6$H$_4$), 6.96 (d, $J = 9$ Hz, 4H, C$_6$H$_4$), 7.39–7.53 (m, 12H, PPh$_2$), 7.61–7.71 (m, 8H, PPh$_2$); ES-MS (m/z) 1347 [M + Cs]$^+$; *Anal*. Calc. for $C_{51}H_{50}Au_2O_6P_2$: C, 50.42; H, 4.15. Found: C, 50.16; H, 4.15%. **6d**: Yield: 80%. ^{31}P NMR (CD_2Cl_2) δ 37.74; ^{1}H NMR (CD_2Cl_2) δ 1.71 (s br, 4H, CH_2CH$_2$P), 2.37 (s br, 4H, CH$_2$P), 3.69 (s, 4H, OCH$_2$CH$_2$O), 3.79 (t, $J = 5$ Hz, 4H, OCH$_2$CH$_2$O), 4.05 (t, $J = 5$ Hz, 4H, OCH$_2$CH$_2$O), 4.75 (s, 4H, OCH$_2$CO), 6.85 (d, $J = 9$ Hz, 4H, C$_6$H$_4$), 6.94 (d, $J = 9$ Hz, 4H, C$_6$H$_4$), 7.41–7.53 (m, 12H, PPh$_2$), 7.57–7.66 (m, 8H, PPh$_2$); ES-MS (m/z) 1361 [M+Cs]$^+$; *Anal*. Calc. for $C_{52}H_{52}Au_2O_6P_2$: C, 50.82; H, 4.27. Found: C, 50.52; H, 4.25%. **6e**: Yield: 89%. ^{31}P NMR (CD_2Cl_2) δ 37.96; ^{1}H NMR (CD_2Cl_2) δ 1.59 (s br, 6H, CH_2CH_2CH$_2$P), 2.36 (s br, 4H, CH$_2$P), 3.69 (s, 4H, OCH$_2$CH$_2$O), 3.79 (t, $J = 5$ Hz, 4H, OCH$_2$CH$_2$O), 4.05 (t, $J = 5$ Hz, 4H, OCH$_2$CH$_2$O), 4.72 (s, 4H, OCH$_2$CO), 6.84 (d, $J = 9$ Hz, 4H, C$_6$H$_4$), 6.89 (d, $J = 9$ Hz, 4H, C$_6$H$_4$), 7.42–7.52 (m, 12H, PPh$_2$), 7.61–7.69 (m, 8H, PPh$_2$); ES-MS (m/z) 1375 [M + Cs]$^+$; *Anal*. Calc. for $C_{53}H_{54}Au_2O_6P_2$: C, 51.22; H, 4.38. Found: C, 51.19; H, 4.24%. **6f**: Yield: 92%. ^{31}P NMR (CD_2Cl_2) δ 18.26; ^{1}H NMR (CD_2Cl_2) δ 3.69 (s, 4H, OCH$_2$CH$_2$O), 3.79 (t, $J = 5$ Hz, 4H, OCH$_2$CH$_2$O), 4.05 (t, $J = 5$ Hz, 4H, OCH$_2$CH$_2$O), 4.76 (s, 4H, OCH$_2$CO), 6.85 (d, $J = 9$ Hz, 4H, C$_6$H$_4$), 6.96 (d, $J = 9$ Hz, 4H, C$_6$H$_4$), 7.44–7.59 (m, 12H, PPh$_2$), 7.69–7.78 (m, 8H, PPh$_2$); ES-MS (m/z) 1329 [M+Cs]$^+$; *Anal*. Calc. for $C_{50}H_{44}Au_2O_6P_2$: C, 50.18; H, 3.71. Found: C, 49.91; H, 3.77%.

3.6. ES-MS cation binding studies

Samples of the gold(I) macrocycles were dissolved in CH_2Cl_2, diluted with MeCN and treated with 20 μl of a solution of the cation pair under investigation (5 mM Cs/K, K/Na and Na/Li as iodide salts in H_2O/MeCN). Relative proportions of the gold(I) complex/cation adducts were estimated from the intensities of the [M + cat]$^+$ peaks corrected, when necessary, for the natural abundance of the isotope of the alkali metal.

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