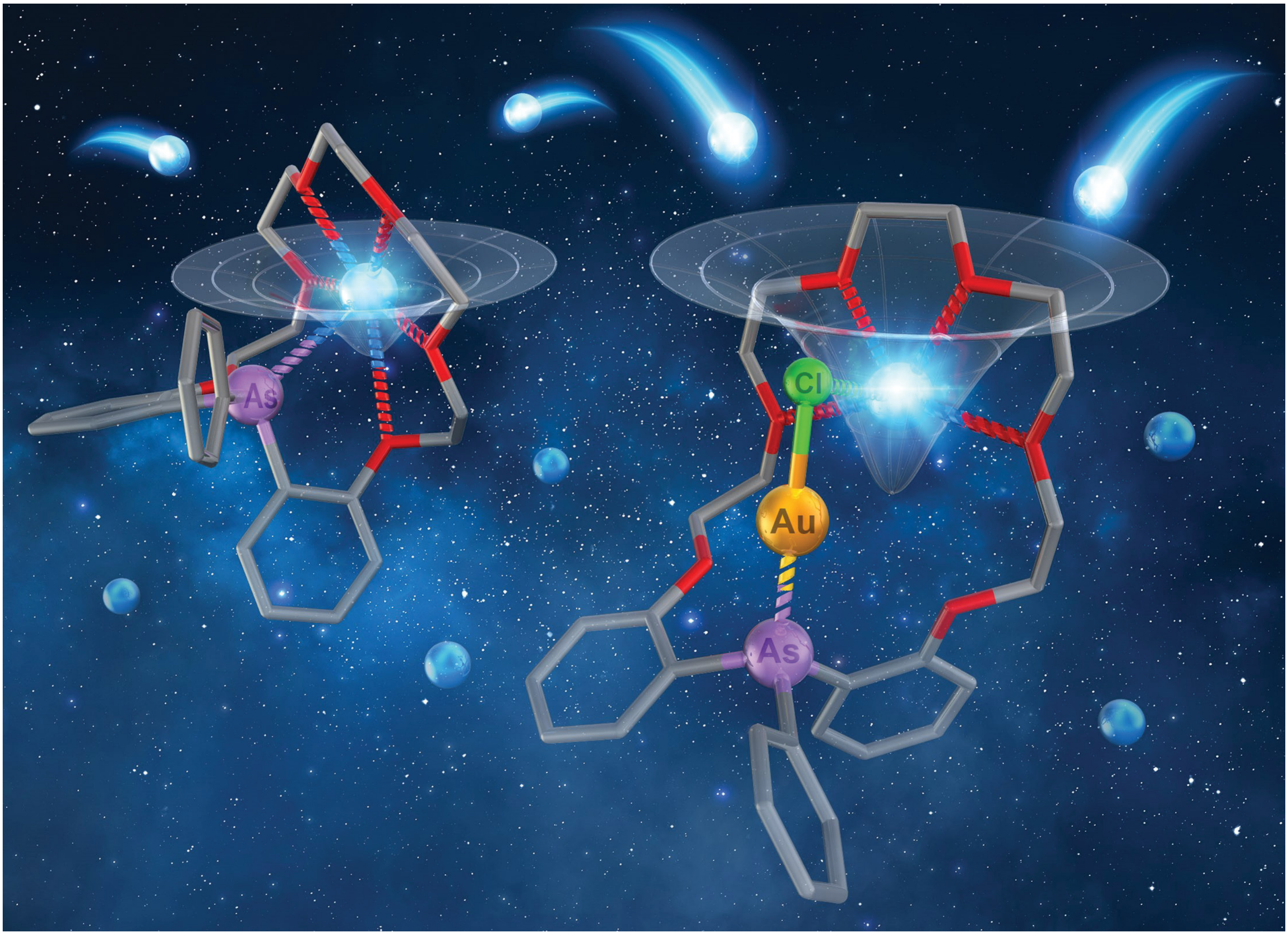

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Dibenzoarsacrowns: an experimental and computational study on the coordination behaviors

Dibenzoarsacrowns have been developed as a novel class of host molecules. The arsenic atom preferentially coordinates to gold(I) chloride to enhance the association constant for binding sodium cation at the ethylene oxide loop.

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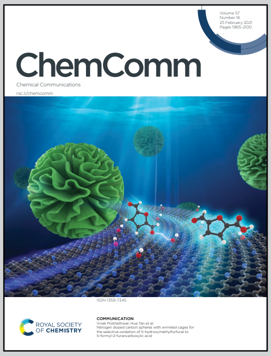

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Dibenzoarsacrowns: an experimental and computational study on the coordination behaviors†

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Dibenzoarsacrowns have been synthesized as a novel class of heteroatom-fused crown ethers. The dibenzoarsacrowns can size-selectively capture alkali metal cations, and the arsenic atoms chemoselectively coordinated to gold(I) chloride (AuCl) due to the soft Lewis acid–base interaction. It is notable that the AuCl complex of 21-dibenzoarsacrown-7 further encapsulated Na^+ with the enhanced association constant from bare 21-dibenzoarsacrown-7. The positive allosteric effect was studied computationally.

Crown ethers have played central roles in supramolecular chemistry.[1,2] Pedersen's discovery of 18-dibenzocrown-6 in 1967 is an important point of departure from conventional naturally-occurring host molecules.[1] Since the artificial inclusion space can be precisely designed according to the purpose, highly functional crown ethers have been developed to date. Among the functionalities, inclusion-driven conformational switching of crown rings has attracted considerable attention as a mimic of enzymes with allosteric regulation; the first binding event transforms the ring conformation to promote the second.[3–5] For allosterically-cooperative crown ethers, a molecular design is required to selectively recognize the first and second guest molecule at separate sites. Pnictogen-fused crown ethers are beneficial for selective guest binding because pnictogen atom and ether ring are soft and hard Lewis bases, respectively. As pioneering work in this field, 2,2′-bipyridine containing crown ethers (Fig. 1a) drastically affected the affinity of the ether ring to alkali metal or ammonium cations by coordination of the 2,2′-bipyridine unit to transition metals.[4] Phosphine-tethered azacrown (Fig. 1b) can bind a cation to change conformation around the transition metal coordinated by the phosphine moiety.[5] Catalytic functions due to the transition metal can be altered in response to the guest inclusion to the crown ring.[6]

In this context, phosphacrown,[7,8] in which some oxygen atoms of a crown ether are substituted by phosphorus, would be a suitable motif to attain cation-induced conformational change around the transition metal center based on a simple structure. Actually, a part of the authors previously reported platinum(II) dichloride and palladium(II) dichloride complexes with diphosphacrowns (Fig. 1c).[8a,b] However, phosphacrown architectures forming bimetallic complex of transition and alkali metals are limited to examples featuring the metallo-crown motif shown in Fig. 1d.[9] A serious drawback to study phosphacrown is air-sensitivity of the trivalent phosphorus

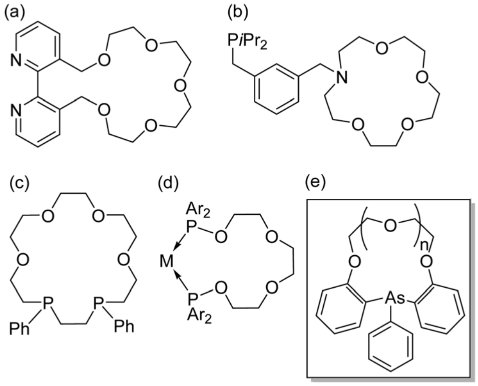

Fig. 1 Heteroatom-fused crown ethers: (a) 2,2′-bipyridine-containing crown ether, (b) phosphine ligand-tethered azacrown, (c) diphosphacrown, (d) metalla-phosphacrown, and (e) dibenzoarsacrown (this work).

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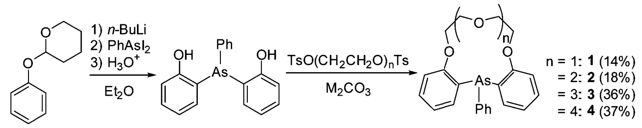
† Electronic supplementary information (ESI) available: Experimental details, X-ray crystallography, NMR spectra, and results of computational calculations. Supplementary crystallographic data: no. 2034462 (**1**), 2034457 (**2**), 2034459 (bis(*o*-anisyl)phenylarsine) 2034458 (**4-Li**), 2034460 (**4-Na**), 2034463 (**4-K**), 2034461 (**4-Rb**), 2034880 ([AuCl(**1**)]), 2034881 ([AuCl(**2**)]), 2034455 ([AuCl(**4**)]), and 2034456 ([AuCl(**4-Na**)]). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0cc07191a

atom; diphosphacrowns should be handled under inert gas after deprotection of the phosphorus atoms.[8] An alternative element for coordination site is desired for practical use. Herein, we focused on arsenic because the trivalent arsenic atom has remarkably higher air-stability than phosphorus.[10] There is no report on arsacrowns despite their promising air-stability, probably due to a lack of synthetic methodologies for organoarsenic compounds. Recently, we have been working on practical synthesis of organoarsenic compounds.[11] In this work, we designed dibenzoarsacrowns, in which a triphenylarsine unit is introduced (Fig. 1e). Gold(I) chloride (AuCl) and alkali metal cations were coordinated to arsenic and oxygen atoms, respectively. Eventually, drastic conformational change has been attained in the bimetallic system.

The synthesis of arsacrowns are shown in Scheme 1. A diethyl ether (Et_2O) solution of $PhAsI_2$ was added to *o*-lithiated phenyoxytetrahydropyran.[12] After deprotection of the tetrahydropyranyl group under acidic conditions, Williamson ether synthesis with oligo(ethylene glycol) ditosylates was carried out in the presence of metal carbonates to give 12-dibenzoarsacrown-4 (**1**), 15-dibenzoarsacrown-5 (**2**), 18-dibenzoarsacrown-6 (**3**), and 21-dibenzoarsacrown-7 (**4**). NMR spectroscopy and high-resolution mass analysis revealed the successful synthesis of the target arsacrowns.

Single crystals of **1** and **2** suitable for X-ray diffraction analysis were grown due to the relatively rigid structures (Fig. 2). The arsenic atoms adopted trigonal pyramidal geometries. Considering that the average C–As–C bond angle of bis(*o*-anisyl)phenylarsine[13] is 98.9°, the endocyclic C–As–C bond angle of **1** (94.7(1)°) was narrowed by the relatively small size of the ring. On the other hand, that of **2** (99.08(8)°) was similar to the average C–As–C bond angle of bis(*o*-anisyl)phenylarsine, meaning that the 15 membered-ring is of sufficient size to circumvent the strain due to ring structure. The phenyl groups of the arsenic atoms were substituted to exocyclic direction because of the steric repulsion against the ring, and thus guest molecules can access to the cavity of the arsacrowns. The lengths between coordination sites (As and O atoms) and their centroids were 1.91–2.13 Å (**1**) and 2.37–2.91 Å (**2**). Considering the van der Waals radii of arsenic (1.85 Å) and oxygen (1.52 Å),[14] there are vacant spaces in the crown rings.



Scheme 1 Synthesis of arsacrowns **1–4**. M_2CO_3: Na_2CO_3 (**1** and **2**), K_2CO_3 (**3**), Cs_2CO_3 (**4**).

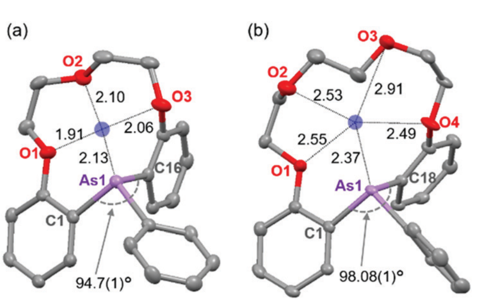


Fig. 2 ORTEP of (a) **1** and (b) **2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Blue dots indicate centroids for all the As and O atoms in the ring. The lengths between the centroids and atoms (Å) and C–As–C bond angle (°) are displayed.

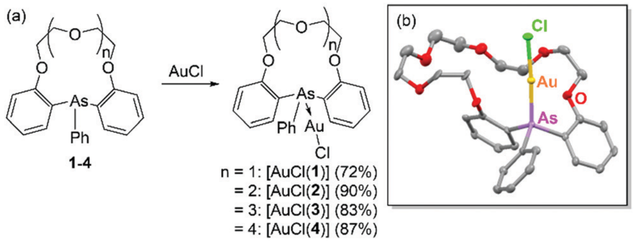
The alkali metal coordination chemistry was explored with hexafluorophosphate (PF_6) salts. The association behaviors of **1–4** with alkali metal cations were evaluated by the chemical shifts of the ^1H-NMR spectra. A 1 : 1 mixed solvent of deuterated chloroform ($CDCl_3$) and acetonitrile (CD_3CN) was used because the former and the latter were good solvents for the arsacrowns and alkali metal cations, respectively, in reference to the previous literature on phosphacrowns.[8d] The Job plots suggested that **1–4** formed 1 : 1 complexes with alkali metal cations when significant changes of the chemical shifts were observed (Fig. S20–S28, ESI†). The association constants were estimated by ^1H-NMR titration (Fig. S29–S46, ESI†) and summarized in Table 1. Arsacrowns **2**, **3**, and **4** had the highest affinities to Na^+, Na^+, and K^+, respectively, and arsacrown **1** showed quite low affinity to even Li^+. The association tendency of the arsacrowns is different from conventional crown ethers; 15-crown-5, 18-crown-6, 21-crown-7 strongly bind Na^+, K^+, and Cs^+, respectively.[15] This is probably because the rigid benzo linkers prohibited induced-fit of the host cavity. The complex structures of **4** with alkali metal cations Li^+, Na^+, K^+, and Rb^+ were analyzed by X-ray crystallography (for detail, see ESI†). It was confirmed that the ethylene oxide loops and the arsenic atoms interacted to the included alkali cations. The oxygen atoms of the phenoxy moieties more weakly coordinated to the cations when compared with those of the ethylene oxide loops, indicating that the rigid benzo linkers inhibited the induced-fit for the cation guests.

Our interest then shifted to complexation of arsacrowns **1–4** with a transition metal. Herein we selected gold(I) chloride (AuCl) because simple mono-coordination structures can be constructed. Complexes [AuCl(arsacrown)] (arsacrown = **1–4**) were synthesized by mixing **1–4** with AuCl (Scheme 2a). The structures of [AuCl(**1**)], [AuCl(**2**)], and [AuCl(**4**)] were successfully analyzed by X-ray crystallography. It was revealed that only the arsenic atoms coordinated to the Au(I) cations due to the soft Lewis acid–base interactions (Scheme 2b). In addition, the

Table 1 Association constants for the 1 : 1 complexations of arsacrowns **1–4** with alkali metal cations.[a]

	Log K^b ($\Delta G°$/kJ mol^{-1})				
	Li^+	Na^+	K^+	Rb^+	Cs^+
1	—[c]	—[c]	—[c]	—[c]	—[c]
2	—[c]	2.04 (−11.5)	—[c]	—[c]	—[c]
3	2.85 (−16.0)	3.15 (−17.7)	2.00 (−11.3)	—[c]	—[c]
4	2.70 (−15.2)	3.20 (−18.1)	4.27 (−24.0)	3.95 (−22.3)	3.46 (−19.5)

[a] Estimated by ^1H-NMR titration in $CDCl_3/CD_3CN$ (v/v = 1/1) at 25 °C. [b] Standard free energy change. [c] Data not obtained because of negligible changes of the chemical shifts.



Scheme 2 (a) Complexation of **1–4** with AuCl, and (b) ORTEP of [AuCl(**4**)]. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

phenyl groups of the arsenic atoms were still substituted to the exocyclic direction likely to the bare arsacrowns **1–4**. Therefore, free ethylene oxide loops can be utilized for further complexation, unlike known platinum(II) dihalide complexes with diphosphacrowns, in which sufficient size of cavity was lost by conformational change by the coordination.[8a]

We thus tried many combinations of [AuCl(arsacrowns)] and alkali metal cations to analyze the complexation structure by X-ray crystallography. Finally, the structure of the complex of [AuCl(**4**)] with Na$^+$ ([AuCl(**4-Na**)]) was successfully analyzed (Fig. 3). As expected, the Na$^+$ was encapsulated by the ethylene oxide loop. Interestingly, the Na$^+$ interacted to the chloride ligand in addition to the oxygen atoms. On the other hand, negligible change from [AuCl(**4**)] was observed for the coordination structures around the Au(I). The insertion of the Na$^+$ did not affected the bond lengths of the Au–Cl ([AuCl(**4**)]: 2.282(2) Å, [AuCl(**4-Na**)]: 2.278(1) Å) and Au–As ([AuCl(**4**)]: 2.329(1) Å, [AuCl(**4-Na**)]: 2.329(1) Å), and the bond angle of the Cl–Au–As ([AuCl(**4**)]: 175.81(4)°, [AuCl(**4-Na**)]: 178.40(3)°). The Na$^+$-captured ethylene oxide loop approached the fixed triphenylarsine–AuCl complex moiety through the formation of the Na–Cl interaction, resulting in the drastic conformational change in the crown ring.

The ^{1}H-NMR titration revealed that the association constant for the 1 : 1 complex of [AuCl(**4**)] with Na$^+$ ($\log K = 3.90$) was significantly higher than that of **4** and Na$^+$ ($\log K = 3.20$), implying minor positive allosteric regulation. To understand this phenomenon, the complexation behavior between [AuCl(**4**)] and Na$^+$ was investigated by dispersion-corrected DFT calculations (B3LYP-D2).[16] On the basis of the X-ray crystallography, suggesting the Cl–Na bond in [AuCl(**4-Na**)], we initially assumed that the positive allosteric effect is attributed to the Cl–Na interaction. To check this hypothesis, the structures of [AuCl(**4-Na**)] and **4-Na** were optimized (Fig. S49, ESI†). The binding energies due to electrostatic interactions between Na$^+$ and negatively charged oxygen atoms of the crown in [AuCl(**4-Na**)] and **4-Na** were estimated to be 100.4 kcal mol^{-1} and 101.1 kcal mol^{-1}, respectively. Even when considering the solvation of acetonitrile (MeCN) to [AuCl(**4-Na**)] and **4-Na** (Fig. S49, ESI†), their binding energies did not change significantly (95.1 kcal mol^{-1} and 90.7 kcal mol^{-1}, respectively). These results cannot support the experimental findings, indicating that the Cl–Na interaction had a negligible effect on the enhancement of the binding constant.

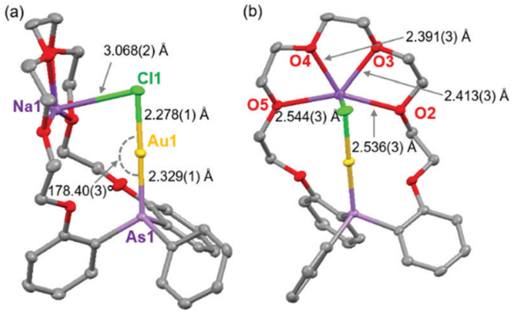


Fig. 3 ORTEP of [AuCl(**4-Na**)]: (a) side few, (b) top view. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and PF$_6$ are omitted for clarity. Bond lengths and angles (bare) are displayed.

Instead of the initial assumption, we considered as another assumption that processes for the complexation of Na$^+$ to the host molecules in the presence of MeCN solvents played pivotal roles here. As initial states, [AuCl(**4**)] and **4** attached by a MeCN molecule ([AuCl(**4-MeCN**)] and **4-MeCN**, respectively) were optimized as shown in Fig. 4a-i and b-i. In [AuCl(**4-MeCN**)] and **4-MeCN**, positively charged hydrogens of MeCN interacted to negatively charged oxygen atoms of **4**. In the case of [AuCl(**4-MeCN**)], the Na$^+$ insertion can preferentially proceed in an exothermic manner (66.6 kcal mol^{-1}) to obtain [AuCl(**4-MeCN-Na**)], as shown in Fig. 4a-ii. This exothermic insertion is due to cation-π interactions in addition to the aforementioned electrostatic interactions. Note that the Na$^+$ insertion to [AuCl(**4-MeCN**)] occurs, keeping the MeCN solvation whose nitrogen location was changed.

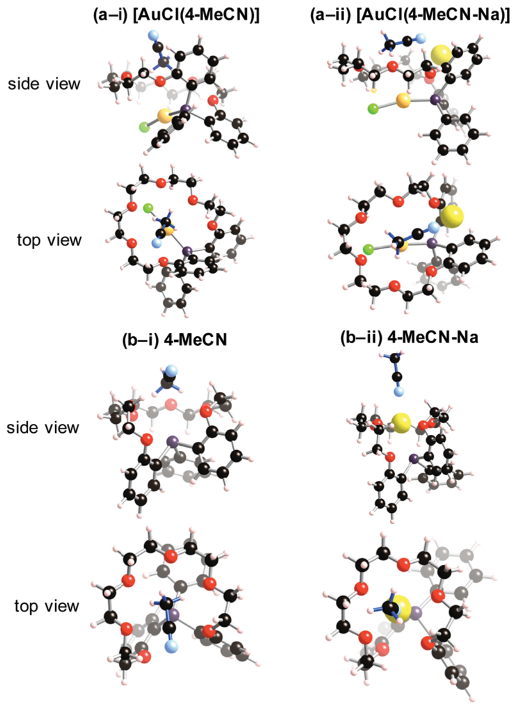


Fig. 4 Optimized structures for (a-i) [AuCl(**4-MeCN**)] and (b-i) **4-MeCN**, where one attached MeCN is involved, on the basis of B3LYP-D2/SDD+6-31G** calculations. Optimized structures for (a-ii) [AuCl(**4-MeCN-Na**)] and (b-ii) **4-MeCN-Na**. Black, red, purple, cyan, and yellow balls represent carbon, oxygen, arsenic, nitrogen, and sodium atoms, respectively.

On the other hand, **4-MeCN** does not have a site suitable for trapping a Na^+ cation to form **4-MeCN-Na.** In fact, the optimization of an initial structure where the Na^+ binds into a nitrogen atom in **4-MeCN** (the separation: 2.4 Å) resulted in the structure for **4-MeCN-Na** in Fig. 4b-ii, equivalent to that in Fig. S49a-ii (ESI†). To generate the structure for **4-MeCN-Na** (Fig. 4b-ii) from **4-MeCN** (Fig. 4b-i) and Na^+, desolvation of the MeCN from **4-MeCN** is necessary to allow negatively charged oxygen atoms to capture the Na^+ cation. After encapsulation of Na^+ into **4**, the MeCN is again solvated to the captured the Na^+, resulting in the optimized **4-Na** solvated by MeCN. This complicated process can proceed, only when MeCN can be desolvated from **4-MeCN** by overcoming the binding energy between **4** and MeCN, calculated to be 12.7 kcal mol^{-1}. Therefore, the experimental findings on the positive allosteric effect can be qualitatively understood from the DFT calculations. While MeCN was fully encapsulated in **4** *via* induced-fit, the flexibility of ethylene oxide chain was reduced by the coordination to AuCl in [AuCl(**4-MeCN**)], resulting in less structural change after the Na^+ insertion where MeCN rotates 90° in a counterclockwise fashion (Fig. 4a-i and a-ii).

In the present study, 12-dibenzoarsacrown-4, 15-dibenzoarsacrown-5, 18-dibenzocrown-6, and 21-dibenzoarsacrown-7 were synthesized as the first examples of arsacrowns. It has been demonstrated that the arsenic and oxygen atoms can effectively interact with soft and hard metals, respectively. Bimetallic complex of 21-dibenzoarsacrown-7 with gold(I) chloride and $NaPF_6$ caused drastic conformational change from the monometallic complexes. The metal-coordination-driven transformation will lead to enzyme-mimic catalytic systems with allosteric regulation. We are now investigating the synthesis of more diverse arsacrown derivatives, and development of bimetallic catalytic reactions. The results will be reported in future publications.

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Conflicts of interest

There are no conflicts to declare.

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