

Palladium(II)-Directed Self-Assembly of a Neutral Molecular Triangle as a Heteroditopic Receptor for Ion Pairs

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S Supporting Information

ABSTRACT: A molecular triangle, based on the self-assembly of 4,7-phenanthroline by a neutral palladium complex, has been synthesized and characterized by a combination of techniques: ¹H NMR and UV–vis absorption spectroscopies, mass spectrometry, elemental analysis, and gel permeation chromatography. This new *neutral metallocavitand* has demonstrated the capacity to host *both* anionic and cationic guests, thus acting as an open-shaped heteroditopic receptor. Density functional theory calculations have shown that (i) there is no overtension in the assembly of the discrete triangle, which is more stable than open-chain oligomers, (ii) the adducts formed between the triangle and some salts (modeled in the gas phase) are thermodynamically stable, and (iii) two types of cavities coexist in the triangle, which host ions and ion pairs. This easily accessible triangular unit extends further the rational design of model nanoarchitectures in host–guest chemistry with applications in analytical chemistry and multifunctional molecular materials.

Metallo-supramolecular chemistry is a powerful tool for the construction of multifunctional assemblies, bringing together various subunits for applications in analytical chemistry, catalysis, and material sciences.¹ The overall structure thus obtained is dictated by a combination of the geometrical requirements in the coordination of the metal ions and the binding constraints of the ligands.^{2,3,4} The organic ligand 4,7-phenanthroline (**1**, phen) with a 60° angle between the coordination vectors has demonstrated the ability to form *discrete triangular structures*.^{5–7} For example, Galindo et al. used phen and cationic *cis*-palladium coordination moieties to produce positively charged homochiral trinuclear metallacalix[3]arenes that could host mononucleotides in their conelike cavity, by using the synergy between electrostatic, anion– π , and π – π interactions.^{7a} The development of synthetic receptors that efficiently and selectively bind charged species is actively pursued for applications in environmental science and biology (as salt extracting, solubilizing, or membrane-transfer agents).⁸ Ion-pair recognition by tailor-made receptors has been studied more and more over the past decade.⁹ One favored strategy is the design of ditopic receptors:^{9–11} within a single molecule, two types of recognition sites can simultaneously bind both cationic and anionic guests. So far, most of the heteroditopic systems reported

for ion(-pair) recognition and chemosensing are organic molecules and macrocycles.^{9,10,12} The recognition of anions and cations is mostly based on NH– and CH–anion interactions and cation–dipole/cation– π interactions, respectively.^{13,14} New interaction combinations and geometries are currently explored to expand functional designs.¹⁵ The incorporation of coordination complexes in heteroditopic receptors is of interest because of their tunable structural, redox, and photophysical properties.^{13d,15,16} However, neutral heteroditopic receptors based on heterocyclic building blocks assembled by metals are much more difficult to obtain because of the paucity of suitable starting metal complexes. In addition, gas-phase molecular recognition is a relevant topic of research in order to understand, on a molecular level, the complex principles that govern recognition in solvent-free “simplified” environments.¹⁷ Studies on adduct formation and on molecular recognition mechanisms in the gas phase were successfully conducted using mass spectrometry (see the Supporting Information, SI).

We report herein the synthesis of an original *charge-neutral* molecular triangle, based on the precursor *trans*-PdCl₂(CH₃CN)₂ and on the dinucleating heterocyclic ligand **1**. The use of *trans*-chelated square-planar palladium(II) building blocks is largely underrepresented in supramolecular coordination chemistry compared to their *cis*-chelated analogues.^{18,19} Aside from the known triangle-square equilibrium in solution reported for relatively flexible systems,²⁰ the formation of oligomeric or polymeric species is usually competing with the formation of discrete assemblies, such as triangles. In the case of **1**, its palladium(II)-directed self-assembly should lead to the formation of molecular triangle **2** ([3 + 3] array) over the coordination polymer(s) **3** (or oligomers; Scheme 1). Complex **2** was envisioned to possess a planar structure with a central hydrophobic pocket decorated on each side by a crown of Cl atoms. As shown by density functional theory (DFT) calculations (*vide infra*), the triangle **2** adopts a stable semibowl configuration, with one phen ligand pointing in the opposite direction from the other two (biconvex geometry; Figure 1). This new open-shaped cavitand might, by way of its accommodating conformation, bind *both* cations and anions: through anion–metal and anion–CH interactions (at the inner cavity, formed by the coordinated aromatic ligands) and through electrostatic and cation–dipole

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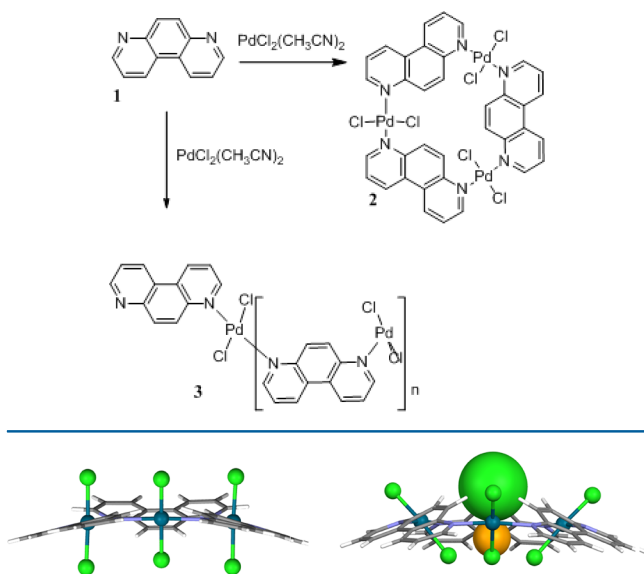
Scheme 1. Palladium(II)-Directed Self-assembly of Ligand 1 into Triangle 2 (top), as Opposed to Polymer 3 (bottom)


Figure 1. DFT-optimized structures for 2: left, semibowl; right, an ion-pair adduct (e.g., $\{\text{CaCl}\}^+$). Flexible 2 can accommodate an anion (green) in the inner cavity and a cation (orange) in the outer cavity.

interactions (at the outer cavity, formed by a crown of Cl atoms), respectively (Figure 1). In such adducts, the hosting triangle would adopt a stable open-bowl configuration, with all phen ligands pointing in the same direction, (concave geometry).

Complexation of 1 with the neutral precursor $\text{trans-PdCl}_2(\text{CH}_3\text{CN})_2$ was investigated under various conditions of concentration, solvent polarity, and temperature (see Table S1 in the SI). The low solubility of the intermediate species probably limits any triangle/square or triangle/higher-nuclearity-oligomers equilibria in solution, thus driving the reaction toward the more stable complexation species. The preferential formation of 2 required a polar media (use of N,N' -dimethylacetamide, DMAc) in order to keep all of the intermediate and final complexation species soluble. Any traces of polymeric species, precipitating in DMAc, were removed by centrifugation. The clear supernatant was further precipitated to isolate the soluble complexation species. The ^1H NMR spectrum of the isolated solid confirmed the formation of one single and symmetric species presenting chemical shifts typical of $\{(1)_2\text{Pd}\}$ moieties^{7a} (Figure S1). In addition, complexation of $\{\text{trans-PdCl}_2\}$ and ligand 1 in a 1:1 ratio was independently confirmed by elemental analysis. However: (i) ^1H NMR spectroscopy only gives information on the local environment of each proton; (ii) elemental analysis confirms the ratio of constitutive elements, but this *does not exclude the formation of regular oligomeric or polymeric species with the same ratios*. We thus set out to confirm the identity of the complex using a combination of gel permeation chromatography (GPC), UV-vis absorption spectroscopy, and high-resolution (HR) time-of-flight (TOF) electrospray ionization mass spectrometry (ESI-MS).

In order to ascertain the presence of a *unique* complexation species, GPC experiments were conducted (Table S1 and Figures S3–S5). The selectivity of the complexation in DMAc was confirmed by the simple chromatogram obtained, with one species eluting at a retention time $t_{\text{ret}} = 31.2$ min (Figure S3). Minor decomplexation (<5%) could not be avoided on the

column and was independently confirmed by (i) control experiments, eluting separately $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ and ligand 1 (see Figure S4) and (ii) the absence of free ligand 1 in the ^1H NMR spectrum of the complex (Figure S1). In addition, the progress of complex formation in solution was monitored over time using absorption spectroscopy. A unique and stable coordination species was obtained in dilute conditions, as evidenced by the existence of isosbestic points and distinct absorption features (see Figure S2 in the SI). The identity of this unique complex was further confirmed by HR ESI-MS. A trimeric species of elemental composition of 2 was identified as its cationic $[\text{M} + \text{Na}]^+$ and its anionic $[\text{M} + \text{Cl}]^-$ adducts (Figure S6). Surprisingly, the ionization mode typically observed for neutral palladium(II) chloropolyridine complexes was not seen: usually, the loss of one chloro ligand leads to the ionized $[\text{M} - \text{Cl}]^+$ species.²¹ Instead, we observed the formation of the Na^+ and Cl^- adducts, resulting from residual trace amounts of ions in commercial solvents. This constitutes qualitative evidence for the heteroditopic binding of ion pairs in the gas phase.¹⁷ In order to further probe the ion-complexation ability of the triangle 2, we conducted a qualitative HR ESI-MS study, using various salts. Detailed analysis showed that the trimeric species was observed in the gas phase (contrary to oligomeric or polymeric species, none of which were seen) and that this species was able to form adducts with both *negatively* and *positively* charged species (see the description and Figures S6–S13 and Table S2). The relatively flexible structure of the open-bowl cavitated 2 seems to be able to accommodate ions of different sizes by conformational changes around the freely rotating coordination bonds.

DFT calculations, performed in order to model the structure of the triangle 2 and to confirm its relative stability, suggested the stabilization of the triangular structure (over other oligomers), as evidenced by its lower single-point energy and no significant overtension of the cycle (see the details in the SI). In addition, sizes for both the inner and outer cavities of the triangle could be estimated (Figure S15): (i) the inner cavity, formed by the coordinating phen ligands, presents a radius of ~ 1.2 Å (volume 7.24 Å³); (ii) the outer cavities, formed on each side of the triangle by the crown of Cl atoms standing nearly orthogonal to the plane of the triangle, present radii of 3.3 – 3.4 Å (volume 150 – 165 Å³). The coexistence of such cavities may explain the recognition of ions of similar sizes by the triangle, as observed in the gas phase by ESI-MS. In order to rationalize the formation of these 2–ion and 2–ion pair adducts, a DFT approach was employed. Preliminary DFT calculations for the triangle hosting different ions or moieties (such as NaCl or $\{\text{CaCl}\}^+$) gave single-point energies and showed stabilization of the various adducts in their bowl-shaped configuration, with respect to the free triangle or to ions in the gas phase (Tables S3 and S4). In such adducts (Figures 1 and S16), cations (e.g., monovalent alkali-metal ions) are hosted in one of the outer cavities and stabilized by electrostatic and ion–dipole interactions, leading to an inward bending of the triangle toward the metal ion. The smaller cations cause more pronounced bending [as shown in Table S3 by the variation of the distance cPd_3 –cation (cPd_3 = centroid of the three Pd atoms) and the angle cPd_3 –Pd–Cl]. In the bent conformation, the steric hindrance between the phen ligands is reduced and the ion–dipole interactions are increased, stabilizing the open-bowl conformation for hosting in 2. For example, the Na^+ adduct is one of the most stabilized species investigated (79 kcal/mol), which is consistent with experimental MS observations. Similarly, 2– NH_4^+ is more stabilized than 2– NMe_4^+ . In the latter case, the hosting triangle needs to become more planar in

order to accommodate a bigger cation and is thus less stabilized. Parameters other than geometrical distortions and size effects (e.g., polarization of ions) take part in the stabilization of adducts (Table S3). On the other hand, anions are stabilized at the inner cavity by anion–CH interactions, with only small distortions of the triangle following the size effects (bigger anions in the halide series gets stabilized farther from the centroid Pd₃, except for F[−], which fits inside the cavity and brings the triangle to a planarized conformation). In light of ion-pair hosting (for example, with NaCl or {CaCl}⁺), two counterbalancing effects influence the stabilization of adducts: (a) electrostatic interactions between the cation and the crowning chloro ligands (further influenced by the overall charge of the guest); (b) the combination of nonclassical Cl⋯H–C hydrogen bonding and of electrostatic Cl[−] anion–CH interactions.

In conclusion, the optimal conditions for the self-assembly of **1** with {*trans*-PdCl₂} into the molecular triangle **2** were identified. ¹H NMR, elemental analysis, HR ESI-MS, and GPC combined to prove the identity and purity of triangle **2** as a [3 + 3] assembly. The key to the metal-directed self-assembly into neutral species lies in the choice of neutral metal precursors able to dictate the self-assembly process. Furthermore, we have shown that these relatively simple self-assembled neutral species can act as hosts for both cations and anions in the gas phase, which is a less explored field for neutral heteroditopic metalloreceptors. This remarkable “encapsulation” capacity by a simple small unit is promising for the cotransport of inorganic salts. We are currently investigating related assemblies with improved solubility and their ion-pair binding properties.

■ ASSOCIATED CONTENT

■ Supporting Information

Synthesis, characterization, and DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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