The formation of a pentanuclear palladium(II) complex with a phenanthridinonetriazine-based ligand system, which itself is formed by a metal-mediated rearrangement of a triazinephenanthridinium proligand, is described.

Triazine-based compounds are widely used, with applications ranging from medicinal chemistry,1 herbicides,2 catalysis3 and polymer chemistry.4 s-Triazine derivatives have recently shown to be of great interest in supramolecular chemistry, because of the ease with which the successive chloride substitution of 2,4,6-trichloro-1,3,5-triazine can be achieved under controlled conditions, yielding trisubstituted ligands for the construction of multinuclear coordination frameworks.5 We are interested in combining the flexibility of the triazine-based ligand design with a novel heterocyclic system that forms upon reaction between a primary amine6 and (2-bromoethyl)phenanthridinium bromide (PhenBR), which leads to the formation of a dihydroimidazophenantridinium (DIP) heterocyclic cation (Scheme 1).6a

DIPs are interesting because they exhibit tunable structures6b and biological activity and have affinity for DNA as well as resistance to reduction and hydrolysis.7 It has been shown that the cationic nature of the phenanthridinium is vital to its efficacy as a potential anticancer molecule.8 Metal complexes of ligands that contain DNA-intercalating properties/phenantridinium moieties have been used as DNA sensors9 and as possible chemotherapeutic agents.10

Herein, we describe a new ligand design approach that exploits the versatile, “modular” reactivity of 2,4,6-trichloro-1,3,5-triazine to integrate the DIP moiety, producing a ligand that could form multinuclear coordination complexes that integrate pendent-delocalized aromatic frameworks. By using this strategy as a basis, we design complexes that display interesting properties such as supramolecular self-assembly or that act as potential multivalent DNA binding agents;
therefore, a new ligand, compound 3, was designed and synthesized. This compound integrates one DIP moiety along with two bidentate binding sites (Scheme 1). As shown in Scheme 1, 2-chloro[4,6-(dipyridin-2-ylamino)]-1,3,5-triazine11 was coupled with ethylenediaminedihyrimidazo[261x230]phenanthridinium by nucleophilic substitution on the 2 position of the triazine; as a result, compound 3 is obtained with a good yield. The reaction of 2 equiv of palladium(II) acetate with 1 equiv of compound 3 in dichloromethane (DCM) yields light-yellow, needle-shaped single crystals of compound 4 after 2 weeks, whose crystal structure reveals that the initial compound 3 has been hydrolyzed upon coordination to give a new ligand, L (Scheme 2).

The structure of compound 4, which crystallizes in the space group P1, can be formulated as a pentanuclear PdII complex containing two of the new ligands, L, with a formula of [Pd5(L2)(OAc)8](Br)2, and the structure is shown in Figure 1. The structure contains three different PdII ion positions identified as Pd1, Pd2, and Pd3. The coordination geometries around all Pd atoms are square-planar, typical for d8 PdII centers. Pd1 and Pd2 both have a N2O2 donor set resulting from the coordination of two pyridine units and two acetato ligands but with minor deviations. The structure is well-defined, but there is some disorder relating to the position of the two bromide anions that compensate for the charge of the cationic species (Figure 1). In addition, complex 4 crystallizes with water and DCM molecules in the crystal lattice.

The Pd–N and Pd–O bond lengths are in normal ranges, as compared with analogous complexes.12 Pd3 is coordinated by four amine N atoms, belonging to two different L ligands, thus connecting two Pd1/Pd2 entities and generating the title pentapalladium compound (Figure 1). The coordinating ethylenediamine moieties are formed through the alteration of the original compound 3 upon reaction with palladium(II) acetate. The Pd–N bond distances are typical for a square-planar Pd(Namine)4 coordination environment involving bidentate amine ligands.13 The angles around the PdII ion reflect a significant distortion from the ideal square-planar geometry, most likely as the result of the small bite angle of the chelating diethylenediamine group (N4–Pd3–N8: 80.21°), combined with steric hindrance due to the phenanthridine.

The crystal packing of 4 shows interesting supramolecular features. The pentanuclear units are connected to two neighbors via π–π stacking interactions (the distance between the aromatic rings amounts to ca. 3.4 Å), giving rise to a one-dimensional chain (Figure 2). These supramolecular chains are further stabilized through C–H···π binding contacts (dH–arene centroid: 2.694 Å), between phenanthride H atoms and the triazine rings of adjacent pentanuclear complexes. Such C–H···π interactions with the s-triazine ring have been reported.14 It is interesting to note that these electron-deficient arenes appear to be interacting with the


chlorine lone pairs\(^{(15)}\) \((dC−\text{ace}−\text{centeroid} = 3.503 \text{ Å})\) from the DCM solvent (lp), which can be formulated as a type of \(C−H\cdots\pi\cdots\text{lp}\) motif; although this is only a crystallographic observation, a search of CSD indicates that this observation is unique. Furthermore, the interplay between cation−π, π−π, and anion−π interactions\(^{(16)}\) has been clearly demonstrated by density functional theory calculations, which have predicted that such interactions could exist.\(^{(16)}\) Therefore, we tentatively suggest that the present system corresponds to the first crystallographic example of a \(C−H\cdots\pi\cdots\text{lp}\) (which can also be symbolized as a \(\delta^+\cdots\pi\cdots\delta^−\) supramolecular complex, corroborating the recent results of Quinonero et al.\(^{(16)}\)

Solution investigations of 4 show that the \(\text{PdL}_2\) core of compound 4 can be observed using cryospray mass spectrometry as the \([\text{Pd}\{\text{C}_{28}\text{H}_{34}\text{N}_{12}\text{O}_2\}(\text{CH}_3\text{CO}_2\}_5\text{Cl}_6\}−\) anion, where the chloride anions originate from NaCl added to the solvent mixture (see Figure 3).

\(\text{L}\) forms from compound 3 (Scheme 2) via a ring-opening process with the introduction of a carbonyl group to give the ligand observed in the crystal structure upon coordination to \(\text{Pd(OAc)}_2\). While the precise mechanism of this ligand transformation has to await detailed experimental and theoretical investigation, one’s first thought turns to a hydrolitic process during coordination, as shown in Scheme 3.

It is proposed that the Pd\(^{II}\) cation acts as a Lewis acid, which, upon coordination to the DIP N atom, activates the α position of the phenanthridinium moiety to nucleophilic attack from ambient water molecules in the reaction solvents. Elimination of HBr from this intermediate results in the formation of a neutral hydroxydihydroimidazophenanthridinium pseudobase molecule, which then undergoes a ring-opening rearrangement to form the crystallographically observed phenanthridine moiety. This ring opening significantly reduces the steric bulk around the Pd\(^{II}\) coordination environment, which may contribute to the driving force for this reaction. Preliminary NMR experiments (see the Supporting Information) show that the first step of this process is that compound 3 coordinates to Pd\(^{II}\) ion, after which hydrolysis by water completes the transformation.

In conclusion, a new triazine-based building block linked by a phenanthridine molecule through an ethylenediamine unit has been designed and synthesized successfully. A novel pentanuclear Pd\(^{II}\) complex has been obtained by the reaction of compound 3 with \(\text{Pd(OAc)}_2\), in which a Pd\(^{II}\)-mediated ligand transformation from compound 3 to a phenanthridine-based ligand in compound 4 has been observed. This observation represents the potential for the development of a new route to the synthesis of N-derivatized phenanthridine moieties under mild conditions. The possible observation of a \(C−H\cdots\pi\cdots\text{lp}\) interaction is interesting,\(^{(17)}\) and we will investigate this further with both theoretical and other experiments to gather further evidence giving insight into the nature of this interaction.

**Acknowledgment.** We thank the EPSRC and University of Glasgow for funding of this work. Support by the Graduate Research School Combination “NRSC Catalysis”, a joint activity of the graduate research schools NIOK, HRSMC, and PTN is appreciated.

**Supporting Information Available:** Full synthetic information and characterization of compounds 1–3 and complex 4, CIF file of compound 4, along with mass spectra and initial NMR experiments on ligand transformation. This material is available free of charge via the Internet at http://pubs.acs.org.


