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Neutral Metallomacrocycles with Four or Ten (PEt₃)Pd(II) Centers

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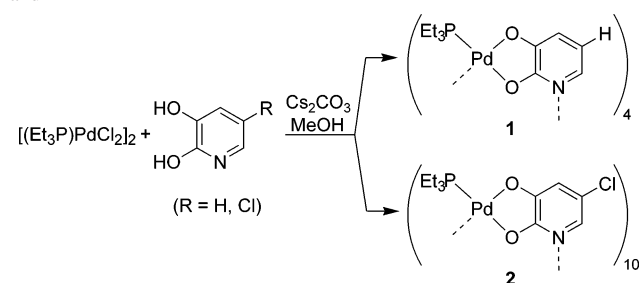
The reaction of $[(Et_3P)PdCl_2]_2$ with 2,3-dihydroxypyridine, 5-chloro-2,3,-dihydroxypyridine, or 2-hydroxynicotinic acid in the presence of base gives neutral, metallomacrocyclic compounds in which the heterocycles act as dianionic, bridging ligands. The macrocycles contain four or ten palladium atoms as evidenced by single crystal X-ray analyses.

For the construction of macrocyclic compounds by transition metal based self-assembly, palladium and platinum complexes have been among the most favorite building blocks.[1] With very few exceptions,[2] these Pd(II)- and Pt(II)-containing macrocycles are highly charged cationic complexes. Evidently, this has severe influence not only on the solubility of the complexes but also on the potential host−guest chemistry (the macrocyclic cavities are filled with anions; reduced affinity to cationic guests). In the following, we demonstrate that neutral metallomacrocycles with ring sizes of 16 and 40 atoms can be obtained by reaction of $[(Et_3P)PdCl_2]_2$ with anionic N,O,O′-chelate ligands.

In previous publications, we have reported that the reaction of 2,3-dihydroxypyridine derivatives with organometallic half-sandwich complexes of ruthenium,[3−6] rhodium,[4,5] and iridium[5−7] allows us to generate tri- and tetranuclear macrocycles.[8] In all cases, the metal complexes display a piano stool type geometry with three facial coordination sites being occupied by the bridging heterocycle. In an extension of this work, we have investigated whether the chloro-bridged

Scheme 1. Synthesis of the Macrocyclic (Et₃P)Pd(II) Complexes **1** and **2**

complex $[(Et_3P)PdCl_2]_2$ can be used as an alternative building block having a square-planar instead of a pseudotetrahedral geometry.

First, we have examined the reaction of $[(Et_3P)PdCl_2]_2$ with 2,3-dihydroxypyridine in methanol using Cs_2CO_3 as the base (Scheme 1). An orange precipitate was formed which was shown to contain predominantly a single complex (**1**) with the stoichiometry $[(Et_3P)Pd(C_5H_3NO_2)]_n$ as evidenced by ¹H and ³¹P NMR spectroscopy (crude yield: 85%). Purification of this complex was possible by crystallization from chloroform/pentane (yield: 50%).

Since NMR spectroscopy is not suited to determine the nuclearity of highly symmetrical metallomacrocycles, we performed a single crystal X-ray analysis of complex **1**.[9] This analysis revealed that a tetranuclear molecular square with a ring size of 16 atoms had formed (Figure 1).

The dianion of the pyridone ligand is coordinated to the palladium atom via the two oxygen atoms to form a five-

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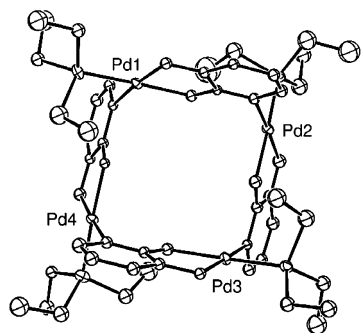(8) For an overview see: Severin, K. *Coord. Chem. Rev.* **2003**, *245*, 3−10.

Figure 1. ORTEP[11] representation of the molecular structure of **1** in the crystal. The hydrogen atoms and the cocrystallized solvent molecules (one pentane and one water) are not shown for clarity.

membered chelate ring. The resulting $(Et_3P)Pd(C_5H_3NO_2)$ units are connected via Pd–N bonds (Pd–N = 2.00 Å).[10] As expected, planar geometry can be found for the palladium centers. The planes of two adjacent N-heterocycles are nearly orthogonal to each other ($\alpha = 89.6°$)[10] resulting in the square-like overall geometry (Pd1···Pd3 = 6.678(2) Å; Pd2···Pd4 = 6.917(2) Å). The cavity of the square is filled with one water molecule which is within hydrogen bond distance to three of the oxygen atoms of the macrocycle (O···O′= 3.03-(3)−3.13(3) Å).

Next, the reaction of $[(Et_3P)PdCl_2]_2$ with 5-chloro-2,3-dihydroxypyridine was investigated using conditions similar to what were described above (MeOH, Cs_2CO_3). Again, an orange precipitate was formed from which after recrystallization the spectroscopically pure (^{1}H, ^{31}P NMR) complex **2** was obtained in 47% yield. Crystallographic analysis of the latter revealed a decameric complex with a ring size of 40 atoms (Figure 2).[12] In order to obtain additional evidence that the decamer is not a side product formed during crystallization, two other crystals from different preparations were investigated by X-ray analysis. Although different amounts of cocrystallized solvent molecules were observed, a decameric macrocycle was found for both crystals indicating that complex **2** has indeed this large macrocyclic structure.

Since metallomacrocycles with high nuclearity are entropically disfavored, it appeared likely that the formation of **2** occurred under kinetic control. This assumption is supported by the observation that if a dilute solution of **2** in CD$_3$OD (1.0 mM) was heated to 50 °C for 3.5 h, new signals in the ^{31}P NMR could be observed. These signals are likely

(9) Crystal data for complex **1**·C$_5$H$_{12}$·H$_2$O: C$_{49}$H$_{86}$N$_4$O$_9$P$_4$Pd$_4$, M = 1424.70, triclinic, a = 12.0311(12) Å, b = 15.1306(16) Å, c = 17.1127(10) Å, α = 83.932(7)°, β = 82.510(7)°, γ = 78.999(9)°, V = 3021.4(5) Å^3, T = 140(2) K, space group $P\bar{1}$, Z = 2, μ(Mo Kα) = 0.71073 mm^{-1}, 18252 reflections collected, 9365 independent reflections, R_{int} = 0.1118, R_1 [I > 2σ(I)] = 0.0668, wR_2 (all data) = 0.1581. Due to the low quality of the crystal, the light atoms were refined isotropically.
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(12) Crystal data for complex **2**·4CHCl$_3$: C$_{114}$H$_{174}$Cl$_{22}$N$_{10}$O$_{20}$P$_{10}$Pd$_{10}$, M = 4158.23, triclinic, a = 14.7501(15) Å, b = 16.9319(17) Å, c = 17.478(2) Å, α = 74.495(10)°, β = 72.735(10)°, γ = 84.043(8)°, V = 4015.4(8) Å^3, T = 140(2) K, space group $P\bar{1}$, Z = 1, μ(Mo Kα) = 0.71073 mm^{-1}, 24229 reflections collected, 12394 independent reflections, R_{int} = 0.0946, R_1 [I > 2σ(I)] = 0.0752, wR_2 (all data) = 0.1969.
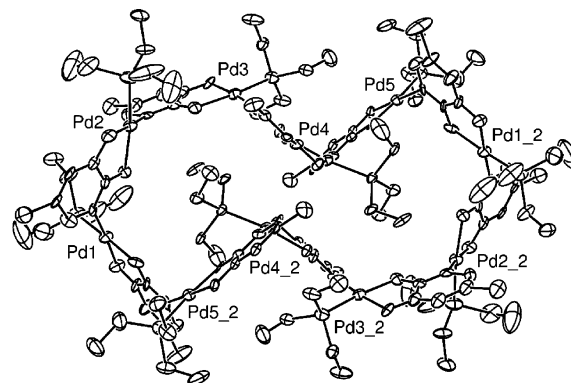
Figure 2. ORTEP[11] representation of the molecular structure of **2** in the crystal. The hydrogen atoms and the cocrystallized solvent molecules (four CHCl$_3$) are not shown for clarity.

to correspond to smaller macrocycles of the formula $[(Et_3P)Pd(C_5H_2ClNO_2)]_n$ (n < 10). Attempts to characterize the palladium complexes by mass spectrometry were unfortunately not successful.

The connectivity of **2** is similar to that of **1**: the dianion of the heterocyclic ligand is coordinated via the two oxygen atoms to one palladium atom and via the nitrogen atom to another palladium atom (Pd–O = 2.05 Å, Pd–N = 2.02 Å).[10] The macrocycle is folded back on itself with the first and the sixth $(Et_3P)Pd(C_5H_2ClNO_2)$ units approaching each other (Pd···Pd = 4.146(2) Å). As a result, two cavities are formed, which are partially occupied by two PEt$_3$ ligands. The overall dimensions of the peanut-shaped molecule are 26 × 17 × 13 Å^3.

Similar to 2,3-dihydroxypyridines, 2-hydroxynicotinic acid can potentially act as a dianionic, bridging ligand.[4a] Indeed, upon reaction with $[(Et_3P)PdCl_2]_2$, a complex of the formula $[(Et_3P)Pd(C_6H_3NO_3)]_n$ (**3**) was obtained (Scheme 2). The crude yield of this reaction was 85%, but in order to remove small amounts of side products, recrystallization form CH$_2$-Cl$_2$/pentane was necessary, which reduced the final yield to 35%.

Scheme 2. Synthesis of the Tetranuclear $(Et_3P)Pd(II)$ Complex **3**
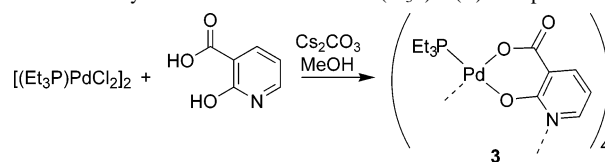
Complex **3** was characterized by a single crystal X-ray analysis.[13] As in the case of **1**, a tetranuclear structure was found (Figure 3). The dianion of the ligand is coordinated via the carboxylate (Pd–O = 2.00 Å)[10] and the oxo group (Pd–O = 2.06 Å)[10] to the palladium atom to form a six-membered O,O′-chelate. The remaining coordination sites at the metal are occupied by the PEt$_3$ spectator ligand and by a pyridine N-atom (Pd–N = 2.01 Å).[10] The planes

(13) Crystal data for complex **3**·5CHCl$_3$: C$_{53}$H$_{77}$Cl$_{15}$N$_4$O$_{12}$P$_4$Pd$_4$, M = 2043.42, monoclinic, a = 18.0936(12) Å, b = 21.3120(12) Å, c = 20.8727(19) Å, β = 96.519(6)°, V = 7996.7(10) Å^3, T = 140(2) K, space group $P2_1/c$, Z = 4, μ(Mo Kα) = 0.71073 mm^{-1}, 45810 reflections collected, 13815 independent reflections, R_{int} = 0.0748, R_1 [I > 2σ(I)] = 0.1041, wR_2 (all data) = 0.3232.
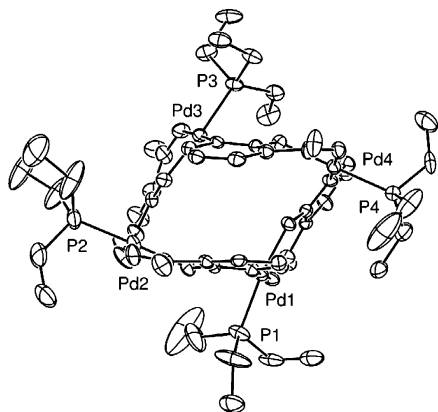
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Figure 3. ORTEP[11] representation of the molecular structure of **3** in the crystal. The hydrogen atoms and the cocrystallized solvent molecules (five CHCl$_3$) are not shown for clarity.

defined by the pyridine rings cross at angles of 63.8°, 68.17°, 123.4°, and 126.8°, respectively, resulting in a rhomboid instead of a square structure (Pd1···Pd3 = 5.404(1) Å; Pd2···Pd4 = 7.406(2) Å).

In summary, we have shown that the chloro-bridged complex [(Et$_3$P)PdCl$_2$]$_2$ can be used as a synthon for the (Et$_3$P)Pd^{2+} fragment having three available coordination sites. In combination with potentially dianionic N,O,O′-ligands such as 2,3-dihydroxypyridine, 5-chloro-2,3-dihydroxypyridine, and 2-hydroxynicotinic acid, metallomacrocyclic complexes can be obtained. These assemblies are neutral in contrast to the highly charged macrocycles that are generally found with (L−L)Pd^{2+} building blocks (L−L = chelating amine or phosphine ligand).

A potential drawback of the reactions described above is that they do not give a single product as it is often observed in transition metal based self-assembly reactions.[1] In order to obtain the clean product, purification steps such as crystallization are thus required. A possible explanation is

Scheme 3. Graphic Representation of the Reaction between the (Et$_3$P)Pd^{2+} Fragment (Ball) and the (N,O,O′)$^{2-}$ Ligand (Line) To Give Neutral Macrocycles of General Formula [(Et$_3$P)Pd(N,O,O′-ligand)]$_{2n}$ ($n \geq 2$)
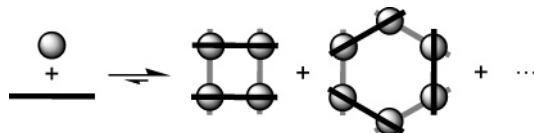
the inherent flexibility of the Pd−N connection. A simple rotation along this bond is sufficient to allow the formation of macrocycles of the general formula [(Et$_3$P)Pd(N,O,O′-ligand)]$_{2n}$ with $n \geq 2$. This is schematically illustrated in Scheme 3.

It should be noted, however, that "fuzzy" assembly reactions of this kind are of interest for investigations in the context of dynamic combinatorial chemistry.[14] Here, the formation of several nearly isoenergetic structures is a prerequisite to perform selection experiments with potential guest molecules. Experiments along these lines are currently being pursued in our laboratory.

Supporting Information Available: X-ray crystallographic files (CIF) and experimental and spectroscopic data for the complexes **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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