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Non-Templated Assembly of D_{5h}-Symmetric Pd_5L_{10} Rings by Precise Ligand Angle Adjustment

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We report a series of $Pd(II)_nL_{2n}$ coordination rings for which nuclearity is controlled by the binding angle of the corresponding bis-monodentate bridging ligands. Judicious choice of the angle within a family of rather rigid ligands allowed for the first-time to synthesize a homoleptic five-membered Pd_5L_{10} ring that does not require any template to form. We demonstrate that control over the ring size is maintained both in the solid-, solution-, and gas-phase. Two X-ray structures of five-membered rings from ligands with ideal angles (yielding a perfect pentagonal ring) *vs.* suboptimal angles (resulting in a highly distorted structure) illustrate the importance of the correct ligand geometry. A mathematical model for estimating the expected ring size based on the ligand angle was derived and DFT computations show that ring-strain is the major factor determining the assembly outcome.

Introduction

Discrete metallo-supramolecular structures such as spheres, cages, and rings, self-assembled from organic bridging ligands and metal ions, have experienced growing interest since the field was pioneered by Fujita,[1] Nitschke,[2] Saalfrank,[3] Stang,[4] Steel,[5] and others.[6] Applications in sensor technology,[7,8] catalysis,[9,10] drug delivery,[11,12] and other areas[13,14] often exploit the cavity of the assemblies for encapsulating guest molecules. For binding guests with high affinity, complementarity in terms of size,[15,16] shape,[17,18] and electronic situation[19,20] between cavity and guest is of pivotal importance. Hence, gaining control over defined assembly sizes and shapes belongs to the key tasks of the supramolecular chemist.

While artificial intelligence and machine learning approaches recently promise to predict self-assembly outcomes prior to their synthetic realization in the laboratory, this so far only works for limited sub-classes of compounds.[21–23] Rational design approaches, together with screening of ligands, metals, counter ions, solvents, and additives (and a grain of serendipity) are thus still the major routes that lead to the discovery of rare or unexpected assembly topologies and properties. Serving as examples from the popular class of Pd_nL_{2n} assemblies, we reported a mechanically-bonded Pd_2L_4 dimer of lemniscates,[24] a chiral, self-penetrating Pd_2L_4 ravel[25] (both differing from the expected lantern-shaped or helicate structure[26]) a Pd_3L_6 double trefoil knot,[27] several Pd_4L_8 alternatives (catenated dimers,[28] pseudo-tetrahedra,[29] and with Severin a bridged dimer of bowls[30]) and – with Lützen – a Pd_6L_{12} cage-in-ring assembly[31] (contrasting the expected Platonic geometry). With a focus on the more common, less intricate geometries, as a rule-of-thumb, the larger the binding angle α[32] of rigid bent ligands, the higher is the nuclearity of the assemblies.[33] Whilst ligands with angles close to 0° (i.e. colinear bonding vectors) self-assemble into lantern-shaped Pd_2L_4 cages,[34] a binding angle approaching 90° leads to the formation of Pd_6L_{12} face-centred cubes.[35–37] Ligands featuring even larger angles ($90 < \alpha < 180°$) assemble into spheres.[33,38] The dependence of the nuclearity of these spheres on the ligand angle was thoroughly investigated by Fujita and coworkers.[39] Rigid ligands with angles between 0° and 90° usually form Pd_nL_{2n} rings ($n = 3, 4$).[40–42] As an example, phenanthrene-based ligand $\mathbf{L^3}$ with an angle of 63° assembles to tetranuclear rings.[17] Numerous examples of Pd_nL_{2n} assemblies with $n = 2$, 3, 4, and 6 have been reported over the years and the field shifts towards the implementation of specific functionalities, often tightly associated with high structural complexity.[43] However, despite this progress, it is astonishing to realize that the non-templated formation of a simple homoleptic five-membered ring with Pd_5L_{10} stoichiometry has not been reported yet.

Chemical compounds with a five-fold symmetry often receive significant attention, in particular concerning their 2D surface coverage and solid-state packing.[44] In terms of heteroleptic structures, Chand and coworkers described a $Pd_5L_5L'_5$ pentanuclear ring in which a linear bipyridine ligand occupies positions on the inner and a flexible phenylene bis(methylene)-based ligand positions on the outer perimeter.[45] A single report on a homoleptic pentagonal Pd_5L_{10} ring was published by Sun and coworkers, however, based on a rather small and highly flexible ligand that forms rings of various nuclearities ($n = 3–7$), strictly depending on the size of an obligatory templating anion present during the self-assembly process.[46] Noteworthy, some other five-membered architectures such as Lehn's pentanuclear circular helicates,[47,48] Leigh's pentafoil knots,[49] a metal-organic ring,[50] and a

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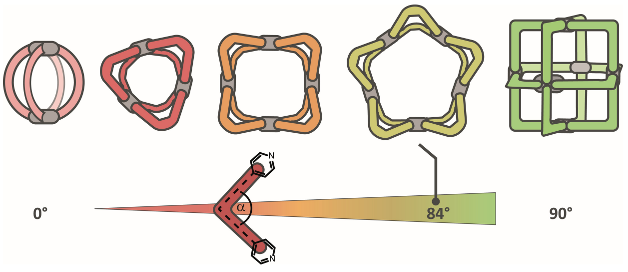
pentagonal grid[51,52] were realized based on other metal-ligand combinations.

Herein, we report on a series of Pd(II)-based three- to five-membered rings assembled from rigid bent ligands with varying binding angles between 28° to 90° (Scheme 1). We show that five-membered rings can be cleanly accessed in the solid and solution state with a ligand angle of 84°, not requiring any template, and that a variation from this angle by only a few degrees results in the formation of ring mixtures containing different nuclearities.

Results and Discussion

Rigid bis-monodentate ligands $\mathbf{L^1}$, $\mathbf{L^2}$, and $\mathbf{L^4}$ were synthesized via Suzuki cross-coupling reaction starting from commercially available dibromo precursors based on fluorenone, dibenzothiophene, and dithienothiophene ($\mathbf{L^3}$, based on phenanthrene, was reported by us before[17]). First, we investigated cage formation with $\mathbf{L^1}$ and $\mathbf{L^4}$, having binding angles of 84° and 28°, respectively. For this, the ligands were combined with $[Pd(CH_3CN)_4](BF_4)_2$ in $[D_6]$DMSO and the reaction mixture was heated at 70 °C for 5 h. The ^{1}H NMR spectrum of each reaction mixture shows a downfield shift of the pyridyl proton signals a and b, which is indicative for the coordination to the Pd(II) ions (Figures 1, S22). The lack of signal splitting discloses that the ligands maintain their two-fold symmetry in the assemblies. Furthermore, the ^{1}H NMR signals of the assembly of $\mathbf{L^1}$, but not the ones of the assembly of $\mathbf{L^4}$, are slightly broadened, suggesting that the former forms a relatively large assembly. DOSY NMR confirmed the formation of single species in both cases with hydrodynamic radii of 16.8 Å and 12.5 Å (Figures S11, S25). High-resolution electrospray ionization mass spectrometry (HR ESI-MS) revealed the formulae $Pd_5\mathbf{L^1}_{10}$ and $Pd_3\mathbf{L^4}_6$ with prominent peaks for $[Pd_5\mathbf{L^1}_{10}+nBF_4]^{(10-n)+}$ (n = 2–5) and $[Pd_3\mathbf{L^4}_6+nBF_4]^{(6-n)+}$ (n = 0–2), respectively (Figures 1c, S27). The spectral data of $Pd_3\mathbf{L^4}_6$ indicate that it has a triangular shape in which the Pd(II) corners are bridged by pairs of ligands, similar to trinuclear rings reported by us before.[25,29] A DFT geometry-optimized model of the ring $Pd_3\mathbf{L^4}_6$ is shown in Figure S45.



Scheme 1. Pd_nL_{2n} coordination assemblies of different topologies and nuclearities formed by rigid bent ligands L with binding angles $0 \leq \alpha \leq 90°$.

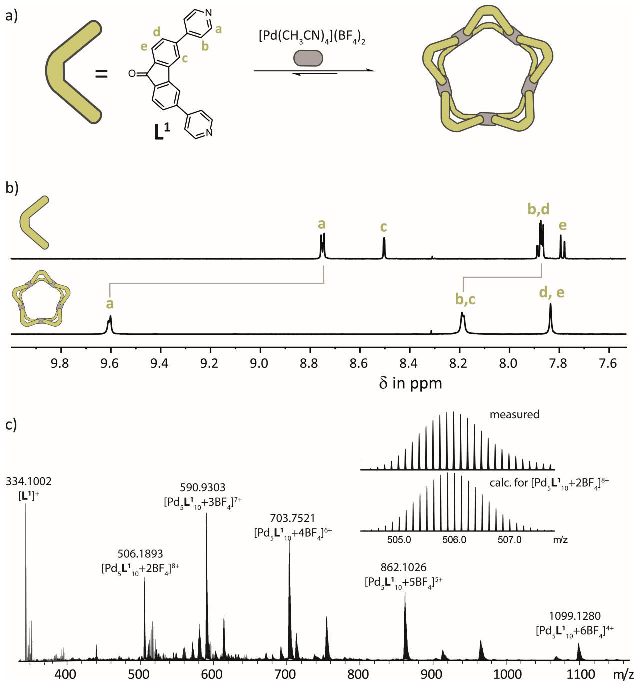


Figure 1. (a) Self-assembly of ring $Pd_5\mathbf{L^1}_{10}$; (b) ^{1}H NMR spectra (500 and 700 MHz, 298 K, $[D_6]$DMSO) of $\mathbf{L^1}$ (top) and $Pd_5\mathbf{L^1}_{10}$ (bottom); (c) HR ESI-MS of $Pd_5\mathbf{L^1}_{10}$, the inset shows the isotopic pattern of $[Pd_5\mathbf{L^1}_{10}+2BF_4]^{8+}$.

Slow vapor diffusion of toluene into an acetonitrile solution of assemblies of $\mathbf{L^1}$ allowed us to obtain yellow block-shaped single crystals, but their volume of 40×30×10 μm^3 required synchrotron radiation to push experimental resolution to 1.4 Å. In accordance with the mass spectrometric results, the diffraction experiment revealed a five-membered ring in orthorhombic space group *P*nma with the asymmetric unit containing half of the assembly and a mirror plane going through the five Pd atoms (Figure 2a,b). The five-membered rings are arranged in zig-zag chains that are separated by rhombic gaps (Figures 2c, S43,44). The latter enable the periodic ordering of the pentagon-shaped molecules.[53]

The only discrete homoleptic assembly of the formula Pd_5L_{10} published so far was formed by ring-to-ring transformation upon addition of heptamolybdate anions, while rings of different sizes were obtained from the same ligand in the presence of other anions.[46] Hence, we were curious whether the formation of $Pd_5\mathbf{L^1}_{10}$ is restricted to the specific self-assembly conditions or is intrinsic to the geometry of the ligand. Thus, for examining the reliability of the Pd_5L_{10} ring formation, we investigated the self-assembly of $\mathbf{L^1}$ at different concentrations, with different counter anions, as well as in different solvents.

The self-assembly of $\mathbf{L^1}$ with $[Pd(CH_3CN)_4](BF_4)_2$ was investigated at ligand concentrations ranging from 0.6 to 11.1 mM. At each of the tested concentrations, the five-membered ring $Pd_5\mathbf{L^1}_{10}$ was obtained as the sole assembly product according to ^{1}H NMR analysis (Figure S28). Furthermore, self-assembly of $\mathbf{L^1}$ with triflate salt $[Pd(CH_3CN)_4](CF_3SO_3)_2$ as well as with hexafluorophosphate salt $[Pd(CH_3CN)_4](PF_6)_2$ also resulted in the quantitative formation of $Pd_5\mathbf{L^1}_{10}$, as evidenced by ^{1}H NMR spectroscopy and HR ESI-MS (Figures S29–32). These results exclude a templation effect of the counter anions as origin of the formation of the five-fold symmetrical ring. However, the self-assembly displayed a solvent-dependency: reaction of $\mathbf{L^1}$ with $[Pd(CH_3CN)_4](BF_4)_2$ in CD_3CN and $[D_7]$DMF leads to mixtures containing $Pd_4\mathbf{L^1}_8$, $Pd_5\mathbf{L^1}_{10}$, and $Pd_6\mathbf{L^1}_{12}$ (Figures S33–38). Never-

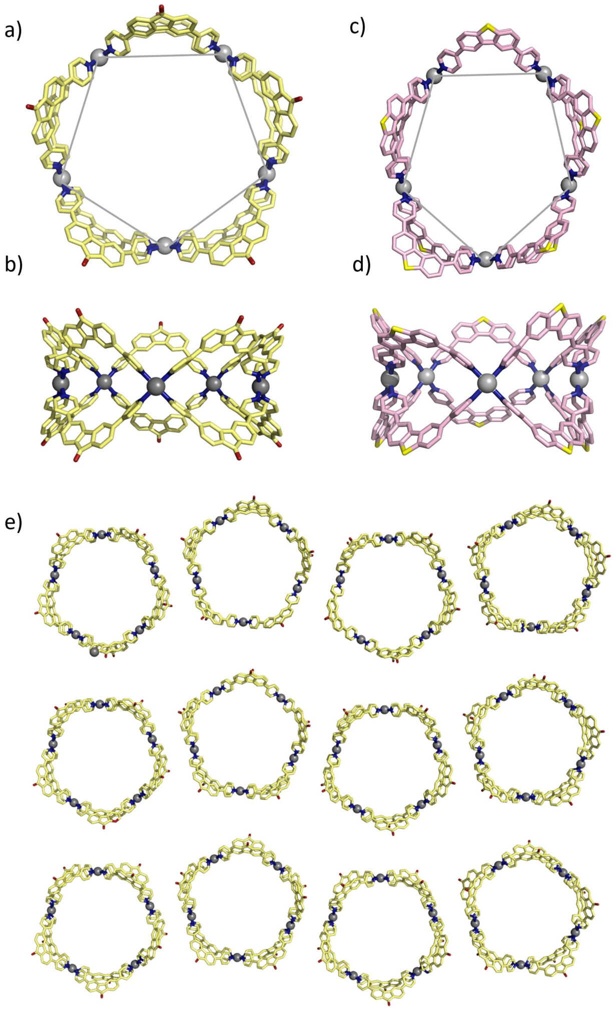


Figure 2. X-ray crystal structures of perfectly pentagonal $Pd_5\mathbf{L}^1_{10}$ in (a) top and (b) side view, and of distorted $Pd_5\mathbf{L}^2_{10}$ in (c) top and (d) side view; (e) solid-state packing of $Pd_5\mathbf{L}^1_{10}$ (counter anions and solvent molecules omitted for clarity).

theless, across all tested conditions, $Pd_5\mathbf{L}^1_{10}$ is a favored species. This behavior contrasts the adaptive nature of the Pd_5L_{10} ring reported by Sun[46] as well as further assemblies based on flexible ligands that show stimuli-induced changes in topology and/or nuclearity.[54–58]

Additionally, we were curious about the self-assembly behavior off stiff ligands whose binding angles lie in between the ones of ligands that form four-membered rings ($\mathbf{L}^4$, 63°) and five-membered rings. Therefore, we investigated the self-assembly of $\mathbf{L}^2$ which possesses an angle of 78°. After ligand $\mathbf{L}^2$ was combined with $[Pd(CH_3CN)_4](BF_4)_2$ in [D$_6$]DMSO and heated for 3 h at 70 °C, the ^{1}H NMR spectrum showed two sets of signals in a ratio of 1.0: 0.2, both shifted compared to the signals of the free ligand (Figures S15, S2). The hydrodynamic radius of the main species is 14.8 Å as determined by DOSY NMR (Figure S18) and lies between the radii of the three-membered ring $Pd_3\mathbf{L}^4_6$ and the five-membered ring $Pd_5\mathbf{L}^1_{10}$. This points toward the formation of a tetranuclear assembly. Indeed, HR ESI-MS revealed the formulae $Pd_4\mathbf{L}^2_8$ and $Pd_5\mathbf{L}^2_{10}$ for the major and minor species, respectively (Figure S20). Thus, a decrease in the binding angle by only 6° leads to a mixture with a main component of lower nuclearity (Figure 3).

In order to correlate the angle of the organic ligands with the nuclearity of the rings Pd_nL_{2n}, we derived a mathematical model based on simple geometrical considerations (Supporting Information section 5). We can indeed show that the model can be used for rationalizing the nuclearity of the rings reported by others[40–42] and by us (Figure S47).[17,29] However, the purely geometrical model cannot be used as sole prediction tool since other factors such as the ligand flexibility,[41] deviation from the ideal square-planar Pd(II) environment, and choice of the solvent[40] affect the outcome.

In general, in tetranuclear Pd_4L_8 assemblies, the metal nodes can be arranged in a cyclic,[17,41] tetrahedral[29,59–61] or linear (interlocked cages)[28,62] fashion. However, the high symmetry of $Pd_4\mathbf{L}^2_8$ as observed by ^{1}H NMR excludes the latter topologies, leaving a ring-shaped assembly the only plausible structure. Colorless block-shaped single crystals of the $\mathbf{L}^2$-based assembly were grown by slow vapor diffusion of benzene into a mixture of $Pd_4\mathbf{L}^2_8$ and $Pd_5\mathbf{L}^2_{10}$ in [D$_7$]DMF solution (for solvent-dependency see Supporting Information section 2.3.3.). Synchrotron-based structure determination revealed that the five-membered ring $Pd_5\mathbf{L}^2_{10}$ had crystallized, showing, similar to $Pd_5\mathbf{L}^1_{10}$, a pentanuclear geometry with Pd(II) vertices that are bridged by two ligands. However, a closer comparison of the crystal

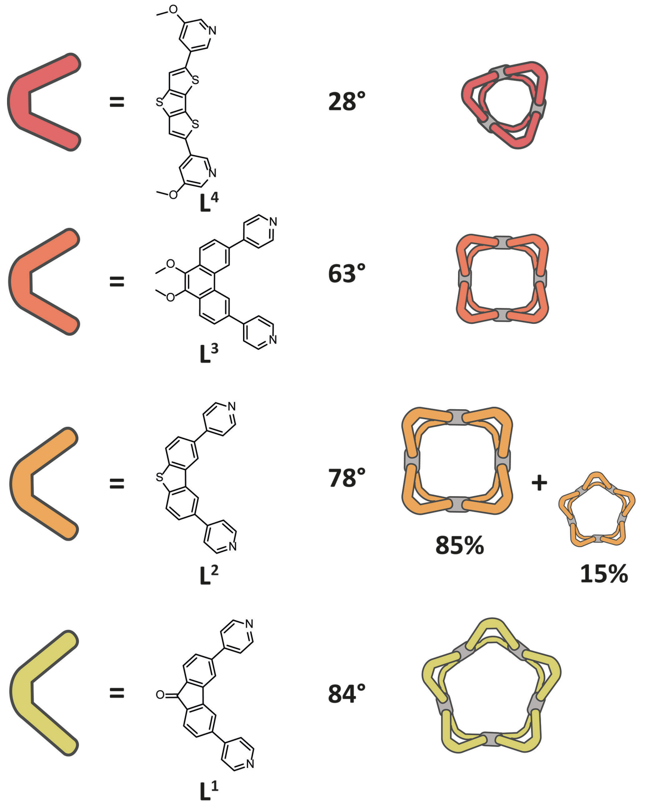


Figure 3. Series of rings of different nuclearity formed by bent bis-monodentate ligands with distinct binding angles. Left column: ligand structures (from bottom to top) of $\mathbf{L}^1$, $\mathbf{L}^2$, $\mathbf{L}^3$, and $\mathbf{L}^4$; central column: ligand binding angles; right column: self-assembled rings.

structures reveals some striking differences: 1) In $Pd_5\mathbf{L}^2_{10}$, the arrangement of the Pd(II) nodes deviates more from the ideal pentagon, in which two adjacent edges enclose an angle of 108° ($Pd_5\mathbf{L}^1_{10}$: 106°–109°, $Pd_5\mathbf{L}^2_{10}$: 102°–119°, Tables S2,S4). 2) The distances between the two backbones sitting on the same edge vary considerably in $Pd_5\mathbf{L}^2_{10}$ ($Pd_5\mathbf{L}^1_{10}$: 12.5–13.8 Å, $Pd_5\mathbf{L}^2_{10}$: 12.4–14.8 Å, Tables S3,S5). 3) Some angles between the Pd–N bonds and pyridine planes deviate significantly from 180° in $Pd_5\mathbf{L}^2_{10}$ ($Pd_5\mathbf{L}^1_{10}$: 172–179°, $Pd_5\mathbf{L}^2_{10}$: 166–180°, Tables S2,4). This suggests a higher conformational strain in $Pd_5\mathbf{L}^2_{10}$ as compared to $Pd_5\mathbf{L}^1_{10}$, which is in accordance with the preference of $\mathbf{L}^2$ for the four-membered ring in solution. To support this conclusion, we studied the difference in ring strain associated with the transformation of the tetranuclear to the pentanuclear ring for both ligands by DFT-calculations (ωb97xd/Def2SVP). Indeed, while the transformation to the five-membered ring is associated with a slight increase in strain for $\mathbf{L}^2$ (+4.6 kJ/mol), it leads to a strong decrease in strain for $\mathbf{L}^1$ (−39.7 kJ/mol, Supporting Information section 4.3.). The small energetic difference between $Pd_4\mathbf{L}^2_8$ and $Pd_5\mathbf{L}^2_{10}$ is also in accordance with our geometrical analysis showing that the binding angle of $\mathbf{L}^2$ lies in between the theoretical binding angles for the four- and five-membered rings.

Conclusions

We introduced the first homoleptic D_{5h}-symmetric Pd(II)-based coordination ring that is reliably formed across different self-assembly conditions as the geometry of the bent bis-monodentate bridging ligand $\mathbf{L}^1$ with a 84° angle intrinsically favors this nuclearity. The size of each self-assembled n-membered ring ($n=3$–5) reported herein can be rationalized by the angle of the organic ligand that was employed via a simplified geometrical model, supported by DFT-based energy calculations. These findings on a rare structural motif within the otherwise large family of Pd_nL_{2n} assemblies is an important step towards rationally designing (and computationally predicting) self-assembled architectures with particular size, shape, and function.[63]

Supporting Information

The authors have cited additional references within the Supporting Information.[64–81]

Deposition Numbers 2297390 (for $Pd_5\mathbf{L}^1_{10}$), 2297391 (for $Pd_5\mathbf{L}^2_{10}$) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Self-assembly · Ligand design · Supramolecular chemistry · Solvent effects · Fivefold symmetry

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