Metallosupramolecular Chemistry

DOI: 10.1002/anie.201308651

Enantiomerically Pure $[M_6L_{12}]$ or $[M_{12}L_{24}]$ Polyhedra from Flexible Bis(Pyridine) Ligands**

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Dedicated to Professor Karl Heinz Dötz on the occasion of his 70th birthday

Abstract: *Coordination-driven self-assembly is one of the most powerful strategies to prepare nanometer-sized discrete (supra)molecular assemblies. Herein, we report on the use of two constitutionally isomeric BINOL-based bis(pyridine) ligands for this purpose. Upon coordination to Pd^{II} ions these self-assemble into enantiomerically pure endo- and exo-functionalized hexa- and dodecanuclear metallosupramolecular spheres with a chiral skeleton depending on the substitution pattern of the BINOL core. These aggregates were characterized by NMR, MS, DLS, TEM, and EELS as well as ECD. Furthermore, experimental ECD data could be compared to those obtained from theoretical simulations using a simplified Tamm–Dancoff approximation to time-dependent DFT to rationalize the extraordinary high molar circular dichroisms. Despite the rotational freedom around the central aryl–aryl bond of these ligands, the self-assembly process happens completely selective in a "narcissistic" self-recognition manner.*

Coordination-driven self-assembly has proven to be one of the best strategies to prepare discrete (supra)molecular assemblies with dimensions in the 1–10 nm regime.[1] Usually these are highly symmetrical metal–organic polygons or polyhedra that are formed from highly directional bridging organic ligands and geometrically prefixed metal containing nodes. Among the overwhelming number of different combinations of metal centers and ligands that has been used for this purpose to date,[1] the combination of palladium and platinum metal centers and ligands containing pyridine groups has become one of the most successful and popular coordination motifs in supramolecular coordination chemistry.[2] The use of tetravalent Pd^{II} and Pt^{II} acceptors and rigid ditopic bridging N-donor ligands, for instance, has been demonstrated to give rise to three dimensional $[M_nL_{2n}]$ assemblies[3–8] with n ranging from two up to even twenty-four in a relatively reliable manner following the general assumption that the smallest assembly forms in which all the coordination sites on the metal centers and the ligands are occupied (the maximum occupancy rule) that does not experience too much steric strain. According to the beautiful examples of Fujita and co-workers the outcome of the self-assembly process in terms of both composition and size of the closed 3D-assemblies critically depends on the bend angle of the bridging ligand.[6–8] However, this approach is not only interesting from a conceptual point of view but it is also very attractive for a number of applications because functionalized ligands can lead to *endo*- or *exo*-functionalized assemblies with interesting properties.[9,10]

What has not been established yet is the construction of a palladium- or platinum-containing metallosupramolecular assembly with six or more metal atoms and an inherently chiral ligand leading to a chiral spherical metallosupramolecular framework rather than a non-chiral sphere with chiral groups on the *endo*- or *exo*-side of the assembly.[9d,h,j,10a–c] Hence, we decided to prepare two constitutionally isomeric bis(pyridine) ligands **1** and **2** based on a chiral 2,2′-dihydroxy-1,1′-binaphthyl (BINOL) core, both in enantiomerically pure *P*- and *M*-forms and racemic forms, and study their self-assembly to metal–organic $[M_nL_{2n}]$ polyhedra upon coordination to $[Pd(CH_3CN)_4](BF_4)_2$. Knowing that the angle between the two pyridine nitrogen atoms is greater than or equal to 90° we expected the formation of metallosupramolecular assemblies that contain at least six metal atoms. However, BINOL derivatives can adopt several conformations due to the rather unrestricted rotation around the aryl–aryl bond. Thus, another aim of this study was to elucidate

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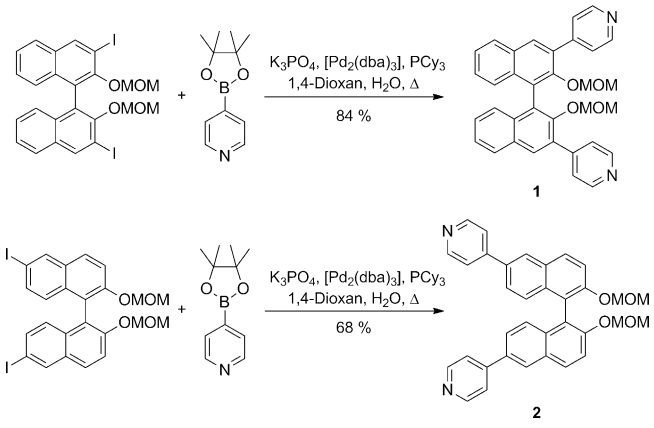
[**] This work was supported by the DFG (SFB 624 and 813) and the Academy of Finland (KR. grant no. 265328 and 263256).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201308651.



Scheme 1. Synthesis of the optically pure ligands **1** and **2**. dba = dibenzylidene acetone, MOM = methoxymethyl, Cy = cyclohexyl.

how this rotational freedom would affect the selectivity of the self-assembly process in terms of the assemblies' composition.

The synthesis of the chiral ligands starts from (*M*)- or (*P*)-3,3′- or -6,6′-diiodo-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl which were prepared according to literature methods.[11] From these compounds the target ligands could be obtained by Suzuki cross coupling in good yield (68–84%) (Scheme 1).[12]

The enantiomerically pure ligands were then mixed with $[Pd(CH_3CN)_4](BF_4)_2$ in a 2:1 ratio in DMSO or acetonitrile and heated for 3 h at 80 °C and the resulting oligonuclear complexes were examined by NMR and electronic circular dichroism (ECD) spectroscopic, mass spectrometric, dynamic light scattering (DLS), and transition electron microscopic means as well as theoretical density functional theory (DFT) methods.

First we measured the ^{1}H NMR spectra (Figure 1) and observed a strongly shifted set of signals for both cases. The signals show the same symmetry as the free ligand indicating the formation of symmetrical coordination compounds. Although, signal broadening was observed in both cases, the broadening was rather small in case of the complex from

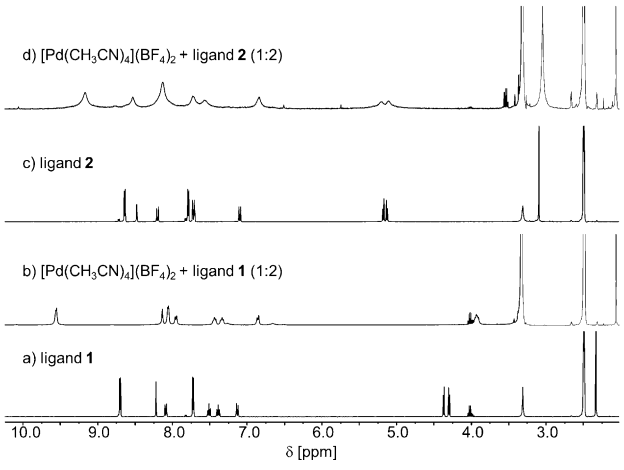


Figure 1. ^{1}H NMR spectra (400.1 MHz in [D$_6$]DMSO at 293 K) of a) **1**, b) a 2:1 mixture of **1** and $[Pd(CH_3CN)_4](BF_4)_2$, c) **2**, and d) a 2:1 mixture of **2** and $[Pd(CH_3CN)_4](BF_4)_2$.

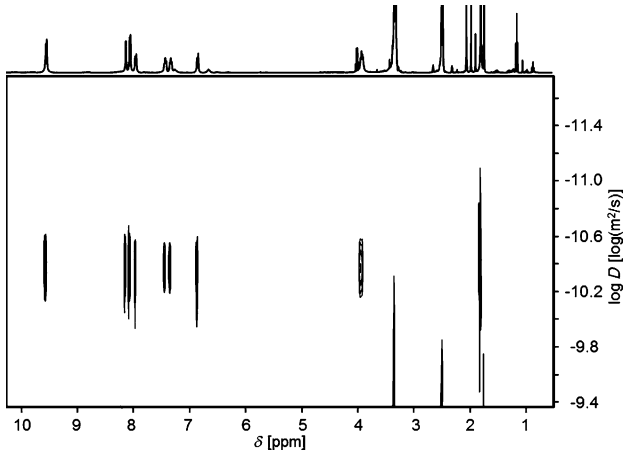


Figure 2. 2D-^{1}H-DOSY-NMR (500.1 MHz in [D$_6$]DMSO at 293 K) of the Pd^{II} complex of ligand **1**.

ligand **1** indicating the formation of a discrete species. On comparison of the data with that of similar $[M_6L_{12}]$ or even larger assemblies, even the more severe signal broadening in the spectrum of ligand **2** complex is still in accordance with a discrete oligonuclear species.

To obtain more evidence for the postulated large assemblies we performed 2D-^{1}H-DOSY measurements and compared the results with the theoretically calculated size of the molecules. For the ligand **1** complex, we obtained diffusion coefficients $D = 6.00 \times 10^{-11}\ m^2 s^{-1}$ in [D$_6$]DMSO (Figure 2) and $D = 4.29 \times 10^{-10}\ m^2 s^{-1}$ in [D$_3$]acetonitrile (Supporting Information) which corresponds to an object with a radius of 13.0–15.1 Å according to the Stokes–Einstein equation. This size fits very well to the calculated dimensions of a truncated cube-shaped structure of a $[Pd_6(\mathbf{1})_{12}](BF_4)_{12}$ aggregate of $10.5 < r_{calcd} < 16.2$ Å.

The DOSY spectra (Supporting Information) of the Pd^{II} complex of ligand **2**, however, gave considerably lower diffusion coefficients of $D = 3.29 \times 10^{-11}\ m^2 s^{-1}$ in [D$_6$]DMSO and $D = 2.04 \times 10^{-10}\ m^2 s^{-1}$ in [D$_3$]acetonitrile which both indicate a considerably larger object with a hydrodynamic radius of $r_H = 27.6$ Å. Such a large size matches the calculated size of an almost spherical $[Pd_{12}(\mathbf{2})_{24}](BF_4)_{24}$ aggregate of ligand **2** ($r_{calcd} = 26.7$ Å) extremely well. These two assemblies are depicted in Figure 3.

Both structures were optimized imposing *O* symmetry at the dispersion- and geometrically counterpoise-corrected DFT level using the PBE functional and the def2-SV(P) basis set.[14] The optimizations were performed with the TURBOMOLE suite[15] and applying the COSMO solvation model ($\varepsilon = 35.7$).[16] We will refer to this level of computation as PBE-D3-gCP/def2-SV(P) (see Supporting Information for details).

To get further support for the composition of our assemblies ESI mass spectra of the two complex solutions were recorded. Unfortunately, we did not succeed in obtaining an ESI mass spectrum under ambient conditions showing an ion of an intact metallosupramolecular assembly of ligand **2** with accurately resolved isotopic pattern.[17]

However for the complex of ligand **1** we were able to get an ESI spectrum that clearly shows the pattern expected for

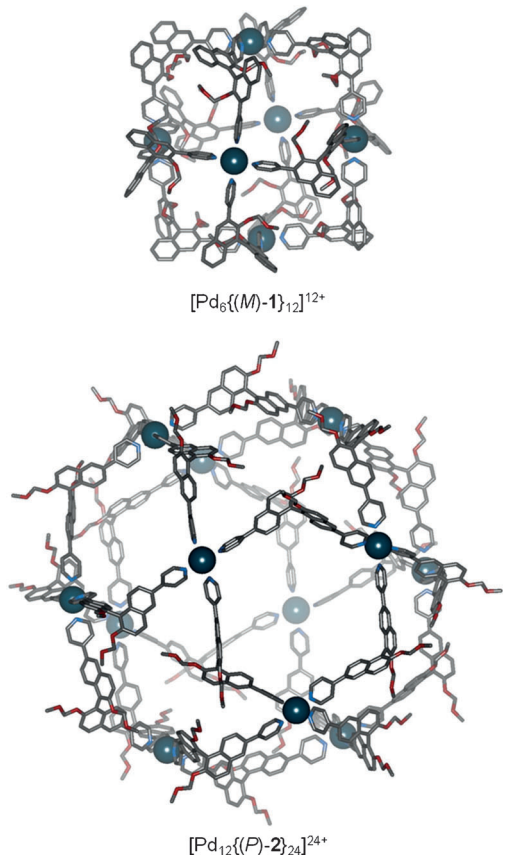


Figure 3. DFT-optimized structures of the *O*-symmetric complexes $[Pd_6\{(M)\text{-}\mathbf{1}\}_{12}]^{12+}$ (top) and $[Pd_{12}\{(P)\text{-}\mathbf{2}\}_{24}]^{24+}$ (top; petrol Pd, red O, blue N, and gray C; hydrogen atoms are omitted for clarity).

a hexanuclear complex in six different charge states with different number of counterions, which confirms our NMR spectroscopic results (Figure 4). In fact, this is one of the very first ESI mass spectra of such a large kind of oligonuclear complexes that could be recorded under ambient conditions without using cold-spray ionization.

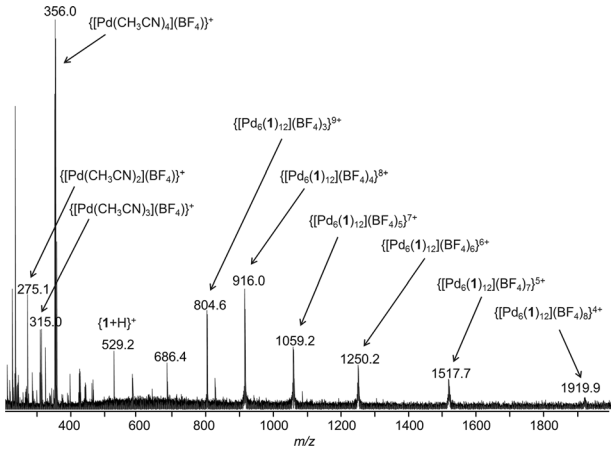


Figure 4. Positive ESI-MS spectrum of the $[Pd_6(\mathbf{1})_{12}](BF_4)_{12}$ complex solution in acetonitrile.

Additional information about the size of nanoscopic objects in solution can be obtained by dynamic light scattering experiments.[18] These DLS experiments confirmed the results of the DOSY NMR and ESI-MS studies for both complexes, and hence provide additional independent support of the size, and therefore, the composition of our assemblies (see Supporting Information), especially because these techniques could also be used to correctly characterize a $[M_{12}L_{24}]$ aggregate from Fujita et al.[19]

We were also able to grow quite well formed crystals from our complexes but owing to the very large voids in the crystal filled with disordered anions and solvent molecules, the X-ray scattering power of the crystals was so weak that not even a unit cell could be obtained.[20]

We also performed transmission electron microscopy (TEM) measurements to visualize the metallosupramolecular spheres. We prepared samples of the metallosupramolecular aggregates on a perforated carbon foil supported by a Cu grid by wetting the grid with solutions of the complexes. Quickly recorded TEM bright field images of the dried samples revealed particles with a weak contrast embedded in the thin film formed by the dried solvent (Figure 5). Given the fact that the metallosupramolecular spheres contain only 6 or 12 palladium atoms, respectively, we expected such low contrasting objects and their size of about 3 or 5 nm fits the size of the hexa- and dodecanuclear $[Pd_6(\mathbf{1})_{12}]$ and $[Pd_{12}(\mathbf{2})_{24}]$ complexes very well.

When the sample is exposed to the electron beam for a longer time the film breaks and does not protect the assemblies anymore. We observe a fast reduction of the palladium(II) complexes to crystalline palladium(0) nanoparticles in a couple of minutes (see Supporting Information). This effect has also been described for other palladium complexes under TEM conditions.[21]

To confirm that these are really the palladium complexes we measured EELS spectra, which showed the characteristic ionization edges for palladium, boron, and fluorine as well as oxygen, nitrogen and omnipresent carbon (see Supporting Information).

All of the results obtained from the different and complementary analytical techniques clearly demonstrate the selective formation of two different types of metallosu-

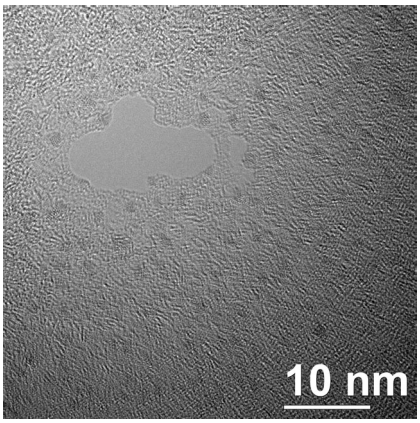


Figure 5. TEM image of $[Pd_6(\mathbf{1})_{12}]$ complexes.

pramolecular spheres by using the constitutional isomeric ligands **1** and **2**. This result is especially interesting because both ligands contain a rather freely rotatable aryl–aryl bond that allows both compounds to markedly change the relative orientation of the two naphthyl groups. Nevertheless, it seems that the 6,6′-disubstituted ligand **2** adopts a conformation with a larger nominal bend angle between the coordinating pyridine moieties than the more concave one of its 3,3′-disubstituted isomer **1**. Clearly, the difference has to be substantial since we observe a completely size-selective assembly in both cases. To study this phenomenon further we studied the behavior of a 1:1:1 mixture of $[Pd(CH_3CN)_4](BF_4)_2$, (*P*)-**1**, and (*P*)-**2**.[22] Interestingly, the ^{1}H NMR spectrum of the equilibrated mixture (3 h at 80 °C in [D$_6$]DMSO) revealed the completely selective formation of the two homoleptic complexes $[Pd_6(\mathbf{1})_{12}](BF_4)_{12}$ and $[Pd_{12}(\mathbf{2})_{24}](BF_4)_{24}$ but no mixed species. Hence, the self-assembly process proceeds with complete self-sorting in a "narcissistic" self-recognition manner.[23]

Finally, we turned our attention to ECD spectroscopy (Figure 6 and Supporting Information) since our assemblies are the first metallosupramolecular spheres of this kind with an enantiomerically pure *O*-symmetric skeleton. Besides some new bands that result from the formation of metal–ligand bonds, the intensities of the bands are considerably larger than the sum of 12 or 24 bands of the pure ligands. To our knowledge, the ECD spectra of these assemblies show the highest $\Delta\varepsilon$ values (up to 4000 L mol^{-1} cm^{-1}) recorded for well-defined molecular entities. Clearly, the relative orientation of the chromophores changes and gets more ordered in the metallosupramolecular complexes which is another excellent indication for the formation of structurally very-well defined assemblies. Interestingly, this effect is more pronounced in the smaller assembly indicating that the conformational change of the binaphthyl core seems to be greater in **1** than in **2**. This assumption is also supported by the comparison of the calculated dihedral angles between the two naphthyl groups in the free ligands **1** and **2** and in their metal complexes (see Supporting Information).

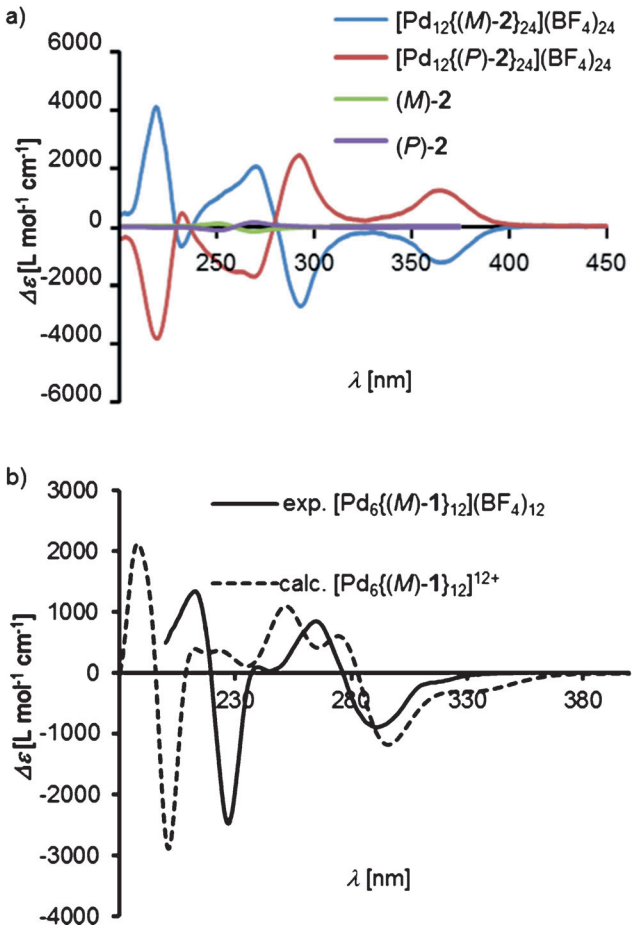


Figure 6. a) ECD spectra of the enantiopure complexes of ligands **2** compared to the ones of (*M*)- and (*P*)-**2** in acetonitrile (for a better view of the ligand spectra see Supporting Information). b) Experimental and calculated ECD spectra of $[Pd_6\{(M)\text{-}\mathbf{1}\}_{12}](BF_4)_{12}$ in acetonitrile.

For further confirmation of our structural assignment, we performed a computational study at the hybrid DFT level to calculate the ECD spectra of the $[Pd_6\{(M)\text{-}\mathbf{1}\}_{12}]^{12+}$ and $[Pd_{12}\{(P)\text{-}\mathbf{2}\}_{24}]^{24+}$ ions. These highly positively charged complexes contain 822 and 1644 atoms, respectively, and hence, represent the largest systems of this kind that have been modeled at a high first-principles level of theory up to date. Even though the huge size of the molecules forced us to make certain approximations in the DFT treatments (see Supporting Information), the spectra calculated using a simplified Tamm–Dancoff approximation to time-dependent DFT (sTDADFT)[24] are in very good agreement both in terms of position and absolute intensity of the individual bands with the experimental ones (see Figure 6b). The observed blue-shift for bands below 250 nm is attributed to various effects (used BHLYP hybrid functional, incomplete basis set and solvation treatment; see Supporting Information for a thorough discussion also of geometry and conformational effects and UV/CD spectra). However, the deviations are systematic and acceptable concerning the size and complexity of the aggregates. These sTDADFT calculations set new standards in the field of theoretical ECD spectroscopy what can be investigated nowadays. They provide further support for the aggregates composition and their structure and the self-assembly of just one enantiomer.

In conclusion we have shown that BINOL-based bis-(pyridine) ligands form hexa- and dodecanuclear enantiomerically pure metallosupramolecular spheres with a chiral skeleton upon coordination to Pd^{II} ions depending on the substitution pattern of the BINOL core. Despite the relatively high rotational freedom around the central aryl–aryl bond of these ligands the self-assembly process happens completely selective in a narcissistic self-recognition manner. In this way we are able to prepare *endo*- and *exo*-functionalized chiral nanoscopic supramolecular objects that show extraordinary high molar circular dichroisms.

Received: October 4, 2013
Published online: January 22, 2014

Keywords: CD spectroscopy · DFT calculations · metallosupramolecular chemistry · self-assembly · self-sorting

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[13] Please note that the truncated cube-like shape of the $[Pd_6(\mathbf{1})_{12}]$ assembly deviates considerably from an ideal sphere. Hence, we gave the calculated distances between two opposite palladium atoms and between the two most-remote hydrogen atoms of opposite naphthyl units as minimum and maximum distances.

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[17] We observed a series of lower molecular-weight fragments of our assembly such as $\{[Pd_6(\mathbf{2})_{11}]F_6\}^{6+}$, $\{[Pd_7(\mathbf{2})_{12}](BF_4)_7\}^{7+}$, $\{[Pd_7(\mathbf{2})_{13}]F_7\}^{7+}$, $\{[Pd_8(\mathbf{2})_{13}]\ F_8\}^{8+}$, $\{[Pd_9(\mathbf{2})_{17}]F_9\}^{9+}$, or $\{[Pd_{11}(\mathbf{2})_{20}]F_{11}\}^{11+}$ (see Supporting Information).

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[19] Note that we referenced our analytical methodology by characterizing one of Fujita's $[M_{12}L_{24}]$ metallosupramolecular assemblies (see ref. [7a]) whose composition has unambiguously been assigned by different analytical tools. In fact our DOSY, ESI MS, and DLS approach perfectly matched these results (see Supporting Information).

[20] Note that the unknown amount of solvent molecules that fill the voids of our spheres also prevented adequate elemental analysis data from being obtained.

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