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Multidentate Pyridyl-Based Ligands in the Coordination-Driven Self-Assembly of Palladium Metallo-Macrocycles

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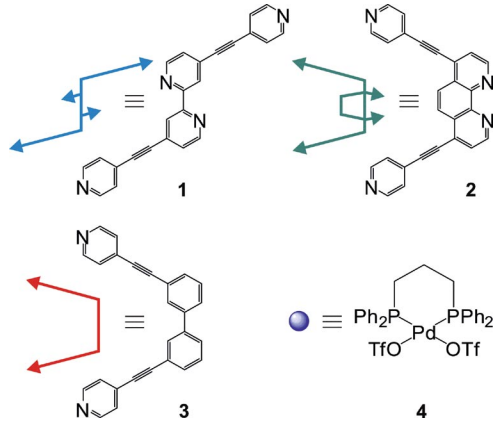
In the current study, a convenient way is presented to synthesize one ditopic and two tetratopic pyridine-based ligands, which are then used to construct metallo-supramolecular polygons. The tetratopic ligands offer two different metal-binding sites, one central 2,2′-bipyridine, which can act as a chelate ligand, and two separate pyridine rings, which mediate assembly formation. The three ligands differ with respect to their conformational flexibility. While a biphenyl core allows the ligand to adjust its conformation as needed, a bipyridine core strongly prefers a divergent arrangement of the additional pyridine binding sites, but can be fixed in a *cisoid* conformation by metal complexation to the bipyridine. Instead, a phenanthroline core already fixes the pyridinylethynyl substituents in a *cisoid* structure without any metal coordinated to it. Upon mixing each one of the ligands separately with the appropriate amount of dpppPd^{II} triflate, discrete self-assembled metallo-macrocycles are formed which are characterized by ^{1}H and ^{31}P NMR spectroscopy and mass spectrometry. Mixing all three ligands simultaneously with the metal complex leads to the formation of a statistical dynamic combinatorial library (DCL) of all possible homo- and heterodimeric metallo-supramolecular assemblies. This underlines the conformational differences between the three ligands not to impact significantly on the self-assembly process.

Introduction

Metallo-supramolecular chemistry[1] has evolved to a high degree of sophistication and provides access to a broad variety of supramolecular architecture such as grids,[2] helicates,[3] polygons,[4] polyhedra and cages,[5] or interlocked structures,[6] just to name a few. They exhibit remarkable features when they for example undergo highly selective self-sorting[7] or when they perform function[8] such as catalyzing reactions in their cavities.[9] Interesting are also architectures, in which different metal binding sites are incorporated.[10] Earlier reports introduced 2,2′:4,4′′;4′,4′′′-quaterpyridine ligands to generate heterometallic macrocycles by applying the "complex-as-ligand" approach. This strategy is based on the formation of a kinetically inert complex of a ligand with the first metal ion followed by the formation of metallo-supramolecular macrocycles through coordination of the remaining binding sites to a kinetically labile metal ion.[11] In these quaterpyridine-based macrocycles, the inner cavities are rather small, even though extraction studies have shown small aromatic molecules to bind inside the cavities in water by the hydrophobic effect.[12]

The aim of the present study is to extend the cavity size by inserting ethynylene spacers between the pyridine rings. Therefore, the three ligands **1**–**3** (Scheme 1) have been synthesized, two of which (**1** and **2**) bear an additional chelating 2,2′-bipyridine or phenanthroline binding site, respectively, for metal complexation. The biphenyl ligand may serve as a control compound. These three ligands differ with respect to their conformational flexibility: ligand **3** bears a dihedral angle around the central aryl–aryl bond of about 140° and can easily adjust to the requirements of metallo-supramolecular assembly formation. Ligand **2** fixes the two pyridylethynyl substituents in a *cisoid* arrangement. Ligand **1**, however, prefers the *transoid* coplanar structure as shown in Scheme 1, but can rotate into the energetically



Scheme 1. Ligands and metal centre used in the studies.

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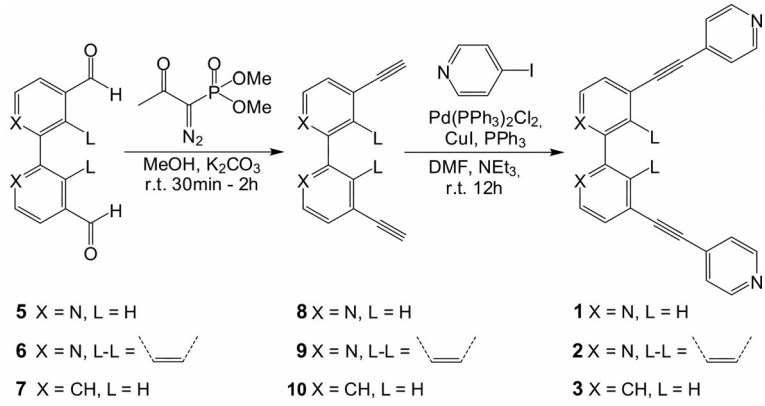

Scheme 2. Preparation of ligands **1**, **2** and **3**.

less favorable *cisoid* structure, if induced by the assembly formation. Upon metal-ion binding to its 2,2′-bipyridine site, this orientation is again fixed.

Herein, we report the synthesis of the three ligands **1**–**3** (Scheme 2) and their self-assembly features when complexed to the (dppp)Pd^{II} triflate **4**. The ancillary dppp Ligand [dppp = 1,3-bis(diphenylphosphanyl)propane] protects two coordination sites at the square-planar metal centers and thus dictates the two remaining binding sites to complex two ligands in a 90° arrangement. In order to assess potential conformational differences influencing the outcome of the assemblies, different ligand mixtures were subjected to self-assembly experiments. The resulting library compositions indicate, whether certain isomers are energetically unfavorable.

Results and Discussion

Synthesis and Molecular Modeling of Ligands 1–3

The synthesis of the two tetratopic ligands **1** and **2** and the ditopic analogue **3** is shown in Scheme 2. The key step is the transformation of the dicarbaldehydes **5**–**7** to the corresponding acetylene moieties using Bestmann–Ohira[13] conditions. This reaction step works with good to excellent yields and simplifies the syntheses of the ethynyl-substituted intermediates significantly, in particular in comparison to an earlier literature-known route[14] describing bipyridine **8**. A second Pd-catalyzed Sonogashira cross-coupling step concludes the ligand synthesis by attaching the pyridine rings to the terminal alkynes.

Molecular modeling (MM2 force-field as implemented in the CaCHE 5.0 program package)[15] was used to obtain insight into the geometric features of the three ligands **1**–**3** (Figure 1). In ligand **1**, the bipyridine site adopts an almost coplanar *transoid*[16] conformation with the two pyridyl sites pointing away from each other (N–N distance: 18.94 Å). The corresponding *cisoid* conformation is predicted by the simple force field calculation to be higher in energy by 8.4 kJ/mol. Likely, this value is somewhat too low and deviates from the literature value (23.8 kJ/mol).[17] Nevertheless, the trend is in line with the literature data. The additional bridge between the two pyridine rings in phenanthroline ligand **2** necessarily implies a fixed *cisoid* conformation instead. The two pyridyl binding sites are consequently oriented to the same site of the phenanthroline core with an N–N distance of the pyridyl nitrogens of 13.19 Å. While **2** is fixed, bipyridine ligand **1** can be converted into a *cisoid* conformation by metal complexation to the bipyridine site. Finally, two conformations exist for ligand **3**. In one of them, the aryl-aryl bond dihedral angle amounts to approximately 139° (conformer **3a**). The second conformer **3b** bears a smaller dihedral angle of ca. 40°. Both conformers are calculated to be energetically very close to each other (ΔE = 0.13 kJ/mol). Likely, the barrier for their mutual interconversion is not very high. Ligand **3** is thus quite flexible with respect to the relative orientation of the two terminal pyridine binding sites and can adapt to different structural requirements resulting from assembly formation.

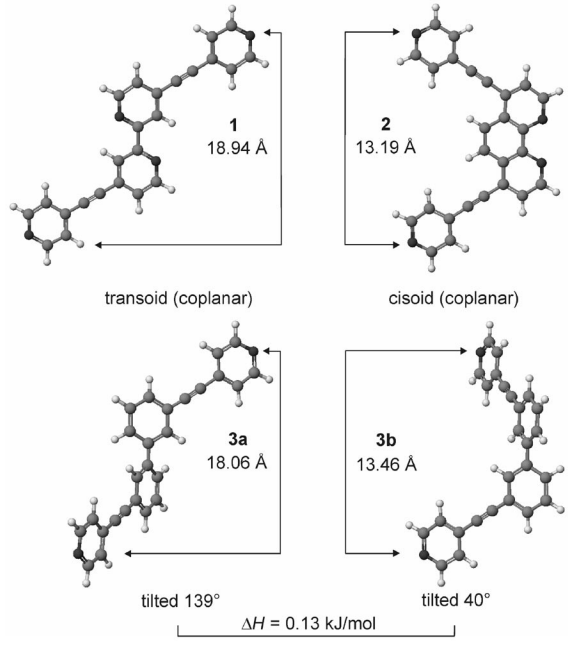

Figure 1. MM2-optimized[15] geometries of ligands **1**, **2** and **3** shown in ball and stick representation. Lengths give the N–N distances between the terminal pyridine nitrogen atoms.

Self-Assembly of Metallo-Supramolecular Macrocycles

In order to test whether the three ligands **1**–**3** assemble with metal complex **4** into the expected well-defined metallo-supramolecular macrocycles **11**, **12** and **13** (Figure 2), each of them was stirred with the appropriate amount of **4** (1:2 ratio for **1** and **2**, 1:1 ratio for **3**) in CD_2Cl_2 for 30 min at room temperature. Since (dppp)Pd^{II} pyridine complexes equilibrates quite quickly,[18] the thermodynamic equilibrium is reached after this time interval. No changes in the NMR spectra have been observed after longer reaction times.

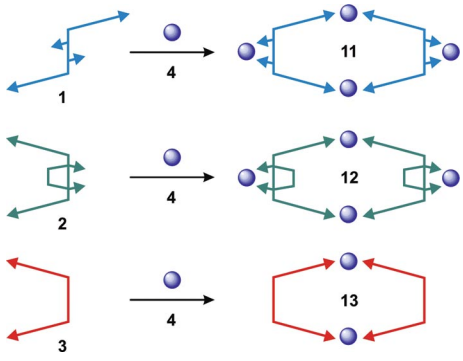

Figure 2. Cartoon illustration of the formation of three different metallo-macrocycles **11**, **12** and **13** after reacting two tetratopic ligands **1**, **2** and one ditopic ligand **3** separately with Pd metal centre **4**. In all three cases, a ligand concentration of 4.9 mM was used.

In all three cases, the formation of discrete assemblies as the only products is indeed confirmed by ^1H and ^{31}P NMR spectroscopy and ESI mass spectrometry (Figure 3). In the ^1H NMR spectra, only one set of signals is observed which can be assigned unambiguously by ^1H,^1H COSY NMR spectra. The pyH_α protons show the expected small downfield shifts relative to the free ligand, which are indicative of the coordination to the Pd metal centers. The pyH_β, $bipyH_\alpha$, $phenH_\alpha$, $bipyH_\beta$ and $phenH_\beta$ signals, however, shift to higher field upon coordination to the Pd complex. These signal shifts can be explained by the shielding effect of the dppp phenyl groups, in whose anisotropy these protons are located. In the ^{31}P NMR, two quite sharp signals are observed for each of the assemblies **11** and **12**. Both are shifted to higher field as compared to the free Pd metal complex **4**. The signals at 14.89 (for **11**) and 15.51 ppm (for **12**) can be assigned to the P atoms of the (dppp)Pd^{II} centers complexed to the bidentate bipyridine or phenanthroline sites, respectively. The other signals at δ = 7.27 ppm for **11** and 7.48 ppm for **12** correspond to the (dppp)Pd^{II} coordinated to the terminal pyridine nitrogen atoms. The fact that singlets are observed for all phosphorus atoms in the ^{31}P NMR spectra indicates both P atoms in each metal complex to be symmetry equivalent so that we can safely conclude highly symmetrical assemblies to form. For **13**, only one signal at δ = 7.04 ppm appears in the ^{31}P NMR spectrum, supporting the assignments of the ^{31}P NMR signals of the other assemblies as discussed above. Electrospray ionization mass spectrometric analyses unambiguously confirm the existence of the three assemblies. For **11** and **12**, doubly (*m*/*z* = 1843, 1866) and triply charged (*m*/*z* = 1179, 1195) ions are observed, **13** appears in the mass spectra as a singly charged quasimolecular ion (*m*/*z* = 2197). The isotope patterns agree well with those calculated based on natural abundances. Larger oligomers have not been found in the ESI mass spectra. Some minor signals correspond to fragments and are typical for many metallo-supramolecular assemblies.

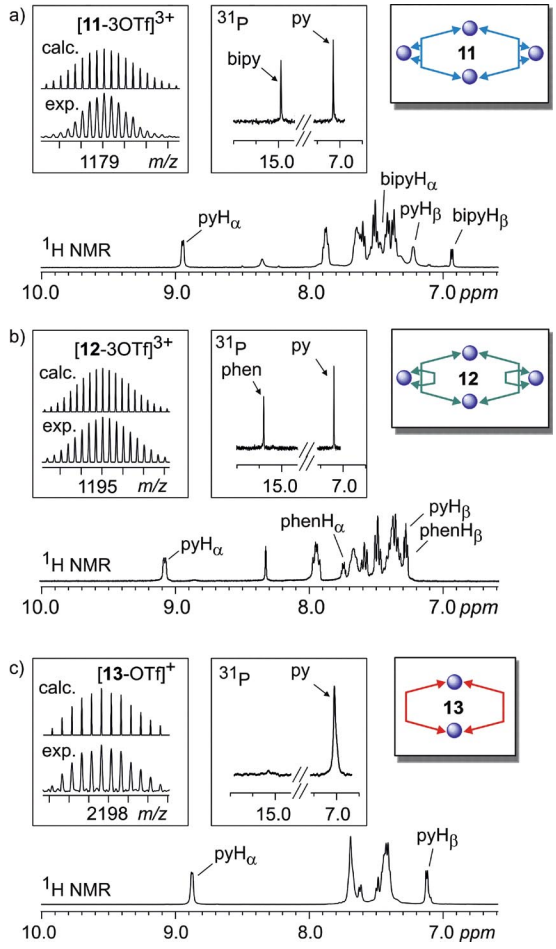

Figure 3. Partial ^1H and ^{31}P NMR spectra of **11** (a), **12** (b) and **13** (c). ^1H NMR signals were assigned by ^1H,^1H COSY NMR experiments. Insets on the left show the experimental and calculated isotope patterns obtained from ESI-MS experiments.

The above-mentioned studies on quaterpyridine complexes[11,12] reported that the 2,2′-bipyridine site is the first one to complex to a given metal center. Afterwards, a second metal ion mediated the formation of the metallo-macrocycles. Ligands **1** and **2** in the present study offer similar binding sites and based on the quaterpyridine studies, the coordination of the first (dppp)Pd^{II} metal complex to ligand **1** or **2** would be expected to occur at the bipyridine. Recent studies by Besenyei et al.[10] employing less closely related Schiff-base-type ligands however revealed the metal to first coordinate at the terminal pyridyl group and only in a second step to the chelating bis-imine binding site. This prompted us to titrate ligand **1** with metal complex **4** to examine the sequence of binding events for **1** (Figure 4). Upon mixing ligand **1** with **4** in a 1:1 ratio in CD_2Cl_2 and

stirring for 30 min at room temperature, the most significant signal shifts in the ^{1}H NMR spectra (again assigned with the help of COSY NMR spectra) are observed for the pyH_α and pyH_β protons, while the protons of the bipyridine binding site do not shift much. Similarly, in the ^{31}P NMR spectrum, a signal appears at the position which was assigned to a (dppp)Pd^{II} complexed to two pyridines. The second signal for the bipyridine-coordinated metal complex is missing completely. Again, the signals in the ^{31}P NMR spectra indicate a high symmetry of the complex which is presumably the 2:2 metallo-macrocycle **14**. Upon addition of a second equivalent of **4**, also the bipyridine protons undergo significant shifts and the second signal in the ^{31}P NMR assigned to the bipyridine-coordinated metal center becomes visible. From these NMR results, we can conclude that the (dppp)Pd^{II} metal center first complexes to the pyridines and only in a second step forms complexes with the bipyridine site.

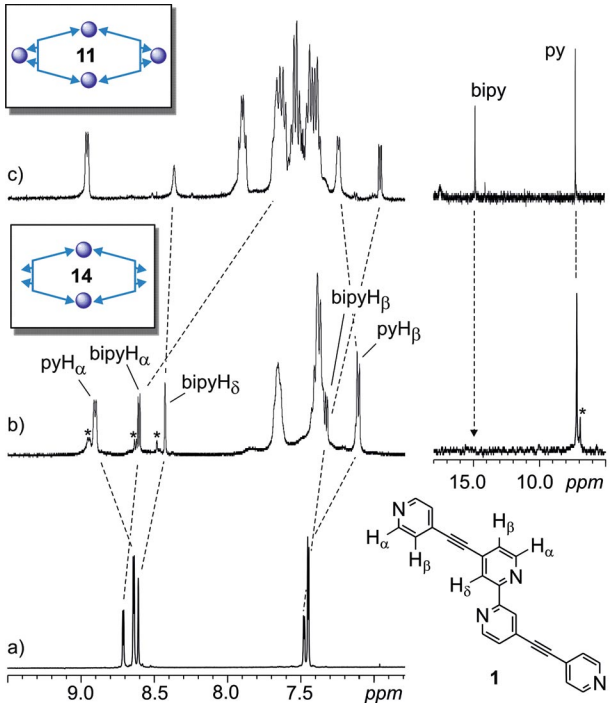

Figure 4. Partial ^{1}H and ^{31}P NMR spectra of a) ligand **1**, b) **1** (4.9 mM) mixed with **4** in a 1:1 ratio, and c) **1** (4.9 mM) and **4** mixed in a 1:2 ratio (asterisks * indicate the formation of a 3:3 metallo-macrocycle).

ESI mass spectra of **14** obtained under conditions that were also used for the characterization of macrocycles **11**–**13** only exhibit signals for 1:1 complexes, whose symmetry is not in agreement with the NMR spectroscopic data. Consequently, we ascribe these signals to fragments. The apparent higher tendency of **14** to fragment upon ionization may be rationalized as follows: Ligand **1** prefers a coplanar *transoid* conformation. Upon assembly formation, it must fold into a less favorable bent conformation higher in energy. While this is easily accomplished for ligand **3**, which thus forms more stable ESI-MS-detectable metallo-macrocycles **13**, assembly **14** suffers from some strain. After transfer into the gas phase, charge repulsion adds to the lower stability and fragmentation occurs. As soon as a second metal has bound to the bipyridine site, the conformation of **1** is fixed in a *cisoid* structure which can again nicely assemble. Consequently, **11** can easily be ionized as intact macrocycle.

The fact that the first coordination occurs at the pyridine site implies that a 2:2 metallo-supramolecular macrocycle can be generated which can be switched in conformation by metal coordination to the two bipyridine sites: Molecular modeling predicts a chair-like conformation as the most stable structure for **14** as well as its biphenyl analogue **13** (Figure 5, top). In this analogy to a cyclohexane ring, the cyclohexane carbon atoms are identified with the two metal centers and the two aromatic rings of the two bipyridine/biphenyl aromatic rings. In this chair-like conformation, minimal torsional strain builds up along the aryl-aryl bonds for the biphenyl ligands **3**. Ligand **1** however has already undergone a conformational change from the coplanar *transoid* structure to a structure with a NCCN dihedral angle of 143°. Upon coordination of metal centers to the two bipyridine sites in **14**, a second conformational change occurs. The bipyridine needs to convert into the *cisoid* form and the conformation of the assembly must thus change into a boat-like conformation as realized also for the phenanthroline complex **12** (Figure 5, bottom).

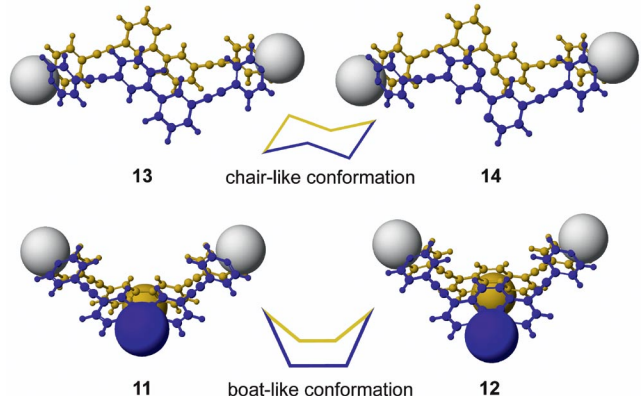

Figure 5. A comparison of geometry-optimized structures (MM2 force field)[15] of **13** and **14** in their chair-like conformations (top) and of **11** and **12** in their boat-like conformations. For clarity, the dppp ligands were removed after geometry optimization. The metal ions are depicted in space-filling representation.

In order to investigate, whether the conformational preferences of the ligands would affect the formation of the macrocycles, we mixed ligands **1**–**3** in all possible binary combinations with the appropriate amount of **4** in CD_2Cl_2. In a first experiment, **1**, **3** and **4** were thus mixed in a 1:1:3 ratio. The ^{1}H and ^{31}P NMR spectra are shown in Figure 6 (bottom trace). Similarly, **2**, **3** and **4** (1:1:3) and **1**, **2** and **4** (1:1:4) were mixed in a second and third experiment (Figure 6, two center traces). Finally, all ligands **1**, **2**, and **3** were treated with **4** in a 1:1:1:5 ratio (Figure 6, top trace). Parts of the ESI mass spectra obtained from the last experiment are shown in Figure 7. Our idea was that no significant deviations from statistical mixtures of the homo- and hetero-

dimeric macrocycles would be observed when all ligands can adapt to the geometric requirements of the assemblies. Instead, if strain would build during the assembly formation due to the conformational preferences of any one of the ligands, one would expect certain heterodimers to be energetically disfavored. Consequently, the formation of small dynamic libraries would provide some insight into the importance of conformational aspects for the assembly formation.

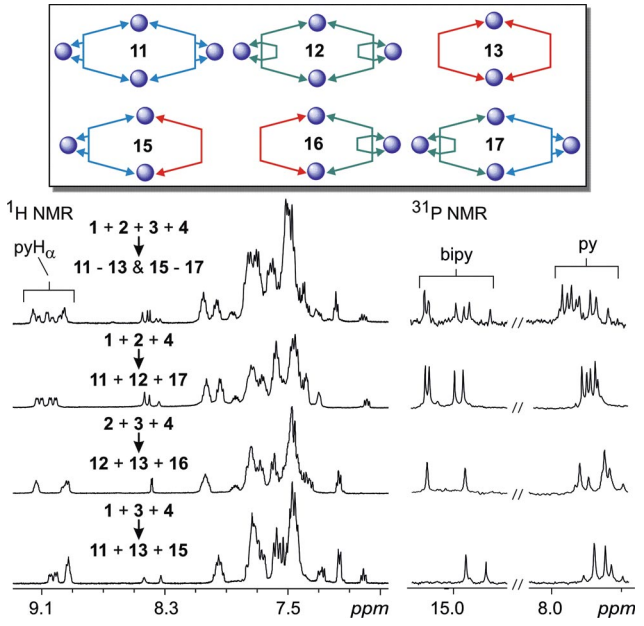

Figure 6. Partial ^{1}H and ^{31}P NMR spectra of a small DCL of three to six discrete metallo-supramolecular assemblies **11**, **12**, **13**, **15**, **16** and **17** ([**4**] = 7.4 mM).

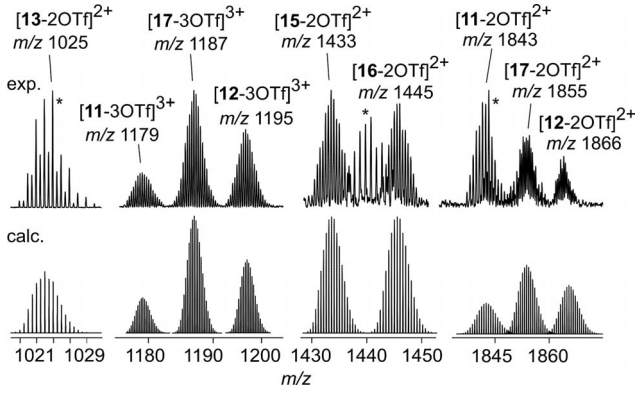

Figure 7. Partial ESI mass spectra (top) and calculated isotopic distributions (bottom) of a mixture of all three ligands **1**, **2** and **3** with Pd complex **4** (1:1:1:5) sprayed from a DCM/acetone (1:1); [**4**] = 98 μM. The spectrum contains signals for all expected metallo-macrocycles **11**, **12**, **13**, **15**, **16** and **17** (asterisks * denote differences between experimental and calculated patterns can be explained by superposition with typical singly-charged fragment ions).

With the help of $^{1}H,^{1}H$ COSY NMR spectra, the pyH_{α} signals of all macrocycles can be assigned (Supporting Information). Similarly, all ^{31}P NMR signals for the (dppp)-Pd^{II} complexed to the bipyridine binding site can be unambiguously assigned. The ^{1}H and ^{31}P NMR spectra thus reveal the formation of statistically distributed small dynamic libraries of discrete metallo-macrocycles to form. All possible homo- and heterodimers are present in the mixtures. Mass spectrometric experiments with the most complex mixture containing all three ligands and complex **4** also supports the formation of a statistical mixture of **11**, **12**, **13**, **15**, **16**, and **17** (Figure 7). Consequently, we can conclude that the ligands **1** and **3** can adapt to structural requirements occurring during the assembly process. Ligand **2** of course is fixed in its conformation, but since the other ligands can adjust their geometry this does not pose any problems for the assembly process.

Conclusions

Besides making use of the quite efficiently working Bestmann–Ohira reaction as a key step in the synthesis of the ligands under study here, the data obtained shows discrete 2:2 and 2:4 metallo-macrocycles to form from **1**–**3** when assembled with metal complex **4**. A remarkable finding is the order of coordination steps of **4** to ligand **1**, which follows a reversed order than the literature data published on very similar ligands. With the ethynylene spacers incorporated, the first two (dppp)Pd^{II} complexes coordinate to the pyridine binding sites forming a 2:2 macrocycle. In the second step, the bipyridine sites are occupied, when a second equivalent of (dppp)Pd^{II} triflate is added. These two steps proceed well separated from each other as becomes clear from the NMR spectra, which hardly show any coordination to the bipyridine site after the addition of the first equivalent of **4**. Mixing experiments lead to the formation of statistical mixtures of all possible assemblies and thus underline the different conformational preferences of the ligands not to have visible effects on the self-assembly process.

The interesting coordination sequence can be used to construct heterometallic complexes in the future, maybe even with metals which do not form kinetically inert complexes. It will certainly be interesting to study a heterometallic self-sorting during the assembly of metallo-supramolecular macrocycles from the ligands presented here. Furthermore, the macrocycles under study have somewhat larger cavities which may be useful for host-guest chemistry. Through the different conformational features and the possibility to attach additional metal complexes to the bipyridine sites, it should be feasible to tune the host properties to some extent and thus to influence the host-guest properties.

Experimental Section

General Remarks: All chemicals were of reagent grade quality and used as obtained from commercial suppliers without further purification. Solvents were used as received or – if necessary – dried with 4 Å molecular sieve. 2,2′-Bipyridine-4,4′-dicarbaldehyde (**5**) is commercially available at HetCat Product List. Pd(dppp)OTf_2,[19]

1,1′-(1,10-phenanthroline-4,7-diyl)diethanone (**6**),[20] biphenyl-3,3′-dicarbaldehyde (**7**),[21] were prepared as described in the literature. ^{1}H, ^{13}C NMR spectra of ligands **1**–**3**, ^{1}H,^{1}H COSY NMR spectra of metallo-macrocycles **11**–**13** and the DCL of **11**–**13** and **15**–**17** are provided in the Supporting Information

Instrumentation and Methods: ^{1}H,^{31}P and ^{1}H,^{1}H COSY NMR spectra were recorded with Jeol ECX-400, Bruker AMX 500 or AV 700 instruments. All chemical shifts are reported in ppm with solvent signals taken as internal standards; coupling constants are in Hz. Silica gel for flash chromatography was Fluka Analytic 60. The electrospray-ionization Fourier-transform ion-cyclotron-resonance (ESI-FTICR) mass spectrometric experiments were performed with a Varian/IonSpec QFT-7 FTICR mass spectrometer equipped with a superconducting 7 Tesla magnet and a micromass Z-spray ESI ion source utilizing a stainless steel capillary with a 0.65 mm inner diameter. The sample solutions were introduced into the source with a syringe pump (Harvard Apparatus) at a flow rate of ca. 4.0 μL min^{-1}. Parameters were adjusted as follows: source temperature: 45 °C; temperature of desolvation gas: 45 °C; parameters for capillary voltage, sample and extractor cone voltages are optimized for maximum intensities and minimal fragmentation. No nebulizer gas was used for the experiments. The ions were accumulated in the instrument's hexapole for 2.5 to 4 s. Next, the ions were transferred into the FTICR analyzer cell by a quadrupole ion guide. The FTICR cell was operated at pressures below 10^{-9} mbar, and the ions detected by a standard excitation and detection sequence. For each measurement, 2 to 4 scans were averaged to improve the signal-to-noise ratio.

4,4′-Diethynyl-2,2′-bipyridine (8):[22] 2,2′-Bipyridine-4,4′-dicarbaldehyde (200 mg, 0.94 mmol) and K_2CO_3 (520 mg, 1.88 mmol) were dissolved in 15 mL MeOH. After the addition of dimethyl (1-diazo-2-oxopropyl)phosphonate (434 mg, 2.26 mol) the reaction mixture was stirred for 30 min at room temp. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (silica gel, mobile phase: CH_2Cl_2/MeOH = 97:3); yield 180.0 mg, 94%. ^{1}H NMR (400 MHz, [D$_6$]THF): δ = 3.99 (s, 2 H, C≡H^1), 7.40 (dd, ^3J = 6.5, ^4J = 1.5 Hz, 2 H, Ar-H^2), 8.51 (d, ^4J = 1.3 Hz, 2 H, ArH^4), 8.63 (d, ^3J = 5.79 Hz, 2 H, ArH^3) ppm. ^{13}C NMR (100 MHz, [D$_6$]THF): δ = 82.14, 83.93 (C≡CH), 124.46, 127.12, 150.47 (CH), 132.48, 156.63 (Cq) ppm. ESI-MS: *m/z* (%) = 205.1 (100) [M + H]$^+$. HRMS (ESI) calculated mass 205.0760 ($C_{14}H_8N_2$ [M + H]$^+$); found 205.0776.

4,7-Diethynyl-1,10-phenanthroline (9): 1,10-Phenanthroline-4,7-dicarbaldehyde (98.2 mg, 0.42 mmol) and K_2CO_3 (231.2 mg, 1.68 mmol) were dissolved in 15 mL MeOH. After the addition of dimethyl (1-diazo-2-oxopropyl)phosphonate (193.7 mg, 1.10 mmol) the reaction mixture was stirred for 2 h at room temp. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (silica gel, mobile phase: CH_2Cl_2/MeOH = 97:3); yield 56 mg, 58%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.74 (s, 2 H, C≡H^1), 7.78 (d, ^3J = 7.2 Hz, 2 H, ArH^2), 7.51 (s, 2 H, ArH^4), 9.17 (d, ^3J = 7.2 Hz, 2 H, ArH^3) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 79.11, 86.96 (C≡CH), 124.96, 149.73 (CH), 126.36, 128.57, 128.74, 146.90 (Cq) ppm. ESI-MS: *m/z* (%) = 229.0 (100) [M + H]$^+$. HRMS (ESI) calculated mass 229.0760 ($C_{16}H_9N_2$ [M + H]$^+$); found 229.0760.

3,3′-Diethylnylbiphenyl (10): Biphenyl-3,3′-dicarbaldehyde (100 mg, 0.48 mmol) and K_2CO_3 (138 mg, 1.90 mmol) were dissolved in 15 mL MeOH. After the addition of dimethyl (1-diazo-2-oxopropyl)phosphonate (219 mg, 1.14 mmol) the reaction mixture was stirred for 2 h at room temp. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (silica gel, mobile phase: hexane); yield 60 mg, 63%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 3.16 (s, 2 H, C≡H^1), 7.43 (t, ^3J = 7.7 Hz, 2 H, ArH^3), 7.51 (dt, ^3J = 7.7, ^4J = 1.4 Hz, 2 H, ArH^4), 7.59 (dt, ^3J = 7.8, ^4J = 1.3 Hz, 2 H, ArH^3), 7.74 (t, ^4J = 1.4 Hz, 2 H, ArH^5) ppm. ^{13}C NMR (175 MHz, CD_2Cl_2): δ = 78.00, 83.84 (C≡CH), 128.15, 129.54, 131.26, 131.26 (CH), 123.25, 140.90 (Cq) ppm. MS (EI, 80 eV, 200 °C): *m/z* (%) = 202.1 (100) [M + H]$^+$, 99.8 (8) [M – C_8H_6]$^+$, 72.1 (3) [M – $C_{10}H_{10}$]$^+$, 46.1 (1) [M – $C_{12}H_{12}$]$^+$.

4,4′-Bis(pyridine-4-ylethynyl)-2,2′-bipyridine (1): 4,4′-Diethynyl-2,2′-bipyridine (80 mg, 0.38 mmol) and 4-iodopyridine (176 mg, 0.86 mmol) were dissolved under argon atmosphere in 4 mL DMF. After the addition of triethylamine (2 mL), PPh_3 (19.8 mg, 0.08 mmol), CuI (7.2 mg, 0.04 mmol) and $Pd(PPh_3)_2Cl_2$ (27.48 mg, 0.04 mmol), the reaction mixture was stirred for 12 h at room temp. KCN (1.2 mg, 0.02 mmol) was added to the reactions mixture and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, mobile phase: CH_2Cl_2/MeOH = 100:4); yield 83 mg, 58%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.43 (AA′*XX*′, *J* = 6.0 Hz, 4 H, pyH$_\beta$), 7.46 (dd, ^3J = 6.5, ^4J = 1.6 Hz, 2 H, bipyH$_\beta$), 8.59–8.58 (br., 2 H, bipyH$_\delta$), 8.62 (*AA*′XX′, *J* = 6.0 Hz, 4 H, pyH$_\alpha$) 8.69 (d, ^3J = 5.0 Hz, 2 H, bipyH$_\alpha$) ppm. ^{13}C NMR (176 MHz, CD_2Cl_2): δ = 91.15, 91.20 (C≡C), 123.66, 126.13, 126.30, 150.02, 150.59 (CH), 130.66, 131.18, 156.28 (Cq) ppm. ESI-MS: *m/z* (%) = 359.1 (100) [M + H$^+$]. HRMS (ESI) calculated mass 359.1291 ($C_{24}H_{14}N_4$ [M + H]$^+$); found 359.1279.

4,7-Bis(pyridin-4-ylethynyl)-1,10-phenanthroline (2): 4,7-Diethynyl-1,10-phenanthroline (45 mg, 0.20 mmol) and 4-iodopyridine (93 mg, 0.45 mmol) were dissolved under argon atmosphere in 5 mL DMF. After the addition of triethylamine (2 mL), PPh_3 (5.6 mg, 0.06 mmol), CuI (10.4 mg, 0.04 mmol) and $Pd(PPh_3)_2Cl_2$ (13.9 mg, 0.02 mmol), the reaction mixture was stirred for 12 h at room temp. KCN (0.65 mg, 0.01 mmol) was added to the reactions mixture and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, mobile phase: CH_2Cl_2/MeOH = 100:4); yield 24 mg, 32%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.56 (AA′*XX*′, *J* = 6.0 Hz, 4 H, pyH$_\beta$), 7.85 (d, ^3J = 4.2 Hz, 2 H, phenH$_\beta$), 8.46 (s, 2 H, ArH$_5$), 8.70 (*AA*′XX′, *J* = 6.0 Hz, 4 H, pyH$_\beta$) 9.16–9.17 (br. s, 2 H, phenH$_\alpha$) ppm. ^{13}C NMR (175 MHz, CD_2Cl_2): δ = 89.16, 96.22 (C≡CH), 125.62, 126.10, 126.47, 150.41, 150.70 (CH), 128.79, 129.12, 130.48, 146.91 (Cq) ppm. ESI-MS: *m/z* (%) = 383.1 (100) [M + H$^+$]. HRMS (ESI) calculated mass 383.1291 ($C_{26}H_{15}N_4$ [M + H]$^+$); found 383.1305.

3,3′-Bis(pyridin-4-ylethynyl)biphenyl (3): 3,3′-Diethylnylbiphenyl (60 mg, 0.30 mmol) and 4-iodopyridine (139.8 mg, 0.68 mmol) were dissolved under argon atmosphere in 5 mL DMF. After the addition of triethylamine (2 mL), PPh_3 (15.6 mg, 0.06 mmol), CuI (8.5 mg, 0.04 mmol) and $Pd(PPh_3)_2Cl_2$ (20.8 mg, 0.03 mmol), the reaction mixture was stirred for 12 h at r.t and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, mobile phase: CH_2Cl_2 → CH_2Cl_2/EE = 1:1); yield 48 mg, 45%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.42 (AA′*XX*′, *J* = 4.4 Hz, 4 H, pyH$_\beta$), 7.51 (t, ^3J = 7.6 Hz, 2 H, ArH$_4$), 7.59 (br. t, ^3J = 7.6 Hz, 2 H, ArH$_5$), 7.63 (br. t, ^3J = 7.8 Hz, 2 H, ArH$_3$), 7.84 (s, ArH$_6$), 8.60 (*AA*′XX′, *J* = 4.4 Hz, 4 H, pyH$_\alpha$) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 87.37, 93.95 (C≡CH), 125.81, 128.39, 129.61, 130.87, 131.62 150.46 (CH), 130.87 123.22, 141.03 (Cq) ppm. ESI-MS: *m/z* (%) = 357.1 (100) [M + H]$^+$. HRMS (ESI) calculated mass 357.1386 ($C_{26}H_{17}N_2$ [M + H]$^+$); found 357.1385.

Metallo-Macrocycle 11: Ligand **1** (0.44 mg, 0.0012 mmol) in CD_2Cl_2 (0.25 mL) was added to a suspension of Pd(dppp)OTf_2 **4** (2.00 mg, 0.0024 mmol) in CD_2Cl_2 (0.25 mL). The mixture was stirred at room temp. for 30 min. The yellowish solution was transferred into an NMR tube for analysis. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 2.25–2.29 (m, 8 H, H_{dppp}), 2.67–2.70 (br. s, 8 H, H_{dppp}), 3.18–3.20 (br. s, 8 H, H_{dppp}), 6.94 (dd, ^3J = 7.5, ^4J = 1.5 Hz, 4 H, bipyH_β), 7.21 (d, ^3J = 5.5 Hz, 8 H, pyH_β), 7.34–7.70 (m, 64H + 4 H, H_{dppp}, bipyH_α), 7.88 (m, 16 H, H_{dppp}), 8.33–8.36 (br., 4 H, bipyH_δ), 8.94 (d, ^3J = 5.6 Hz, 8 H, pyH_α) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 7.27 (s), 14.89 (s) ppm. ESI-MS: *m*/*z* = 1843.0 (100) [**11** – 2OTf]$^{2+}$, 1179.0 (55) [**11** – 3OTf]$^{3+}$.

Metallo-Macrocycle 12: Ligand **2** (0.44 mg, 0.0012 mmol) in CD_2Cl_2 (0.25 mL) was added to a suspension of Pd(dppp)OTf_2 **4** (2.00 mg, 0.0024 mmol) in CD_2Cl_2 (0.25 mL). The mixture was stirred at room temp. for 30 min. The yellowish solution was transferred into an NMR tube for analysis. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 2.26–2.33 (m, 8 H, H_{dppp}), 2.68–2.71 (br. s, 8 H, H_{dppp}), 3.22–3.24 (br. s, 8 H, H_{dppp}), 7.32–7.80 (m, 8 H, 4H, 64 H, pyH_β, phenH_β, H_{dppp}), 7.77–7.79 (m, 4 H, phenH_α) 7.98 (m, 16 H, H_{dppp}), 8.35 (s, 4 H, ArH_5), 9.08 (d, ^3J = 5.2 Hz, 8 H, pyH_α) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 7.48 (s), 15.51 (s) ppm. ESI-MS: *m*/*z* = 1866.0 (100) [**12** – 2OTf]$^{2+}$, 1195.0 (20) [**12** – 3OTf]$^{3+}$.

Metallo-Supramolecular Assembly 13: Ligand **3** (0.87 mg, 0.0024 mmol) in CD_2Cl_2 (0.25 mL) was added to a suspension of Pd(dppp)OTf_2 **4** (2.00 mg, 0.0024 mmol) in CD_2Cl_2 (0.25 mL). The mixture was stirred at room temp. for 30 min. The yellowish solution was transferred into an NMR tube for analysis. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 2.25–2.34 (m, 4 H, H_{dppp}), 3.21–3.23 (br. s, 8 H, H_{dppp}), 7.12 (d, ^3J = 6.4 Hz, 8 H, pyH_β), 7.34–7.70 (m, 20 H, 4H, 4 H, H_{dppp}, ArH_4, ArH_5), 7.68–7.70 (m, 20 H, 4 H, H_{dppp}, ArH_6), 8.87 (d, ^3J = 8.1 Hz, 8 H, pyH_α) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 7.04 (s) ppm. ESI-MS: *m*/*z* = 2197.2 (100) [**13**-OTf]$^+$.

Synthesis of a Dynamic Combinatorial Library (DCL) of 2-D Metallo-Supramolecular Assemblies: Ligand **1** (0.44 mg, 0.0012 mmol), ligand **2** (0.47 mg, 0.0012 mmol) were dissolved in CD_2Cl_2 (0.25 mL) and simultaneously added to a suspension of Pd(dppp)OTf_2 **4** (4.00 mg, 0.0049 mmol) in CD_2Cl_2 (0.25 mL). The mixture was stirred at room temp. for 24 h. The yellowish-green solution was transferred into an NMR tube for analysis. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 2.32–2.36 (m, 28 H, H_{dppp}), 2.73–2.75 (m, 20 H, H_{dppp}), 3.23–3.25 (m, 24 H, H_{dppp}), 6.93–6.96 [m, 6 H, bipy$H_{\beta(11)(17)}$], 7.21–7.25 [m, 12 H, $py_1H_{\beta(11)(17)}$], 7.34–7.70 [m, 12 H, 192H, 6 H, $py_2H_{\beta(11)(17)}$, H_{dppp}, phen$H_{\beta(12)(17)}$], 7.78–7.82 [m, 6 H, phen$H_{\alpha(12)(17)}$], 7.88–7-92 (m, 24 H, H_{dppp}) 7.93–7.98 (m, 24 H, H_{dppp}), 8.26–8.30 [br., 2 H, bipy$H_{\delta(17)}$], 8.36 [s, 4 H, $ArH_{5(17)}$], 8.37–8.39 [br., 4 H, 4 H, $ArH_{5(12)}$, bipy$H_{\delta(11)}$], 8.97–9.00 [m, 8 H, 4 H, $py_1H_{\alpha(11)}$, $py_1H_{\alpha(17)}$], 9.05 [m, 8 H, 4 H, $py_2H_{\alpha(11)}$, $py_2H_{\alpha(17)}$] ppm. ^{31}P NMR (202 MHz, CD_2Cl_2): δ = 7.38 (s), 7.42 (s), 7.49 (s), 7.54 (s), 7.61 (s) ppm. ESI-MS: *m*/*z* = 1842.6 (18) [**11** – 2OTf]$^{2+}$, 1855.0 (100) [**17** – 2OTf]$^{2+}$, 1866.5 (25) [**12** – 2OTf]$^{2+}$.

Ligand **2** (0.44 mg, 0.0012 mmol), ligand **3** (0.47 mg, 0.0012 mmol) were dissolved in CD_2Cl_2 (0.25 mL) and simultaneously added to a suspension of Pd(dppp)OTf_2 **4** (3.00 mg, 0.0037 mmol) in CD_2Cl_2 (0.25 mL). The mixture was stirred at room temp. for 24 h. The yellowish-green solution was transferred into an NMR tube for analysis. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 2.28–2.31 (m, 18 H, H_{dppp}), 2.75–2.77 (m, 16 H, H_{dppp}), 3.21–3.24 (m, 24 H, H_{dppp}), 7.12–7.14 [m, 12 H, $py_3H_{\beta\ (13)(16)}$], 7.30–7.70 [m, 12 H, 156H, 6H, 6H, 6H, 6 H, $py_2H_{\beta(12)(16)}$, H_{dppp}, $ArH_{3(13)(16)}$, $ArH_{4(13)(16)}$, $ArH_{5biaryl(13)(16)}$, $ArH_{6(13)(16)}$], 7.78–7.82 [m, 6 H, phen$H_{\alpha(12)(16)}$], 7.89–7.98 (m, 24 H, H_{dppp}), 8.33 [s, 2 H, $ArH_{5phen(16)}$], 8.34 [s, 4 H, $ArH_{5phen(12)}$], 8.86–8.92 [m, 12 H, $py_3H_{\alpha(13)(16)}$], 8.95–9.10 [m, 12 H, $py_2H_{\alpha(12)(16)}$] ppm. ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 6.78 (s), 6.99 (s), 7.06 (s), 7.30 (s) 7.43 (s) 14.83 (s), 15.51 (s) ppm. ESI-MS: *m*/*z* (%) = 1024.1 (100) [**13** – 2OTf]$^{2+}$, 1195.0 (80) [**12** – 3OTf]$^{3+}$, 1445.6 (10) [**16** – 2OTf]$^{2+}$, 2197.2 (5) [**13** – OTf]$^+$.

Ligand **1** (0.44 mg, 0.0012 mmol), ligand **3** (0.44 mg, 0.0012 mmol) were dissolved in CD_2Cl_2 (0.25 mL) and simultaneously added to a suspension of Pd(dppp)OTf_2 **4** (3.00 mg, 0.0037 mmol) in CD_2Cl_2 (0.25 mL). The mixture was stirred at room temp. for 24 h. The yellowish solution was transferred into an NMR tube for analysis. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 2.28–2.32 (m, 18 H, H_{dppp}), 2.78–2.81 (m, 16 H, H_{dppp}), 3.21–3.24 (m, 24 H, H_{dppp}), 6.96 [two overlapped dd, ^3J = 6.0, ^4J = 1.6 Hz, 6 H, bipy$H_{\beta\ (11)(15)}$], 7.10–7.13 [br. d, 12 H, $py_3H_{\beta(13)(15)}$], 7.21–7.24 [m, 12 H, $py_1H_{\beta(11)(15)}$], 7.35–7.70 [m, 156 H, 6H, 6H, 6H, 6H, 6 H, H_{dppp}, bipy$H_{\alpha(11)(15)}$, $ArH_{3(13)(15)}$, $ArH_{4(13)(15)}$, $ArH_{5(13)(15)}$, $ArH_{6(13)(15)}$], 7.88–7.94 (m, 24 H, H_{dppp}), 8.26–8.28 [br. s, 2 H, bipy$H_{\delta(15)}$], 8.37–8.39 [br. s, 4 H, bipy$H_{\delta(11)}$], 8.86–8.89 [m, 12 H, $py_3H_{\alpha(13)(15)}$], 8.95–8.98 [m, 8 H, 4 H, $py_1H_{\alpha(11)}$, $py_1H_{\alpha(15)}$] ppm. ^{31}P NMR (202 MHz, CD_2Cl_2): δ = 7.01 (s), 7.17 (s), 7. 26 (s), 7.42 (s), 7.56 (s), 14.53 (s), 14.88 (s) ppm. ESI-MS: *m*/*z* (%) = 1843.1 (100) [**11** – 2OTf^{2+}], 1179.0 (25) [**11** – 3OTf^{3+}], 1433.6 (10) [**15** – 2OTf^{2+}]. 2197.2 (5) [**13** – OTf$^+$].

Ligand **1** (0.26 mg, 0.00073 mmol), ligand **2** (0.26 mg, 0.00073 mmol) and ligand **3** (0.28 mg, 0.0073 mmol) were dissolved in CD_2Cl_2 (0.25 mL) and simultaneously added to a suspension of Pd(dppp)OTf_2 **4** (3.00 mg, 0.0037 mmol) in CD_2Cl_2 (0.25 mL). The mixture was stirred at room temp. for 24 h. The yellowish-green solution was transferred into an NMR tube for analysis. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 2.31–2.34 (m, 46 H, H_{dppp}), 2.73–2.76 (m, 34 H, H_{dppp}), 3.22–3.25 (m, 40 H, H_{dppp}), 6.93–6.96 [m, 8 H, bipy$H_{\beta(11)(15)(17)}$], 7.11–7.15 [m, 16 H, $py_3H_{\beta(13)(15)(16)}$], 7.21–7.26 [m, 16 H, $py_1H_{\beta(11)(15)(17)}$], 7.34–7.75 [m, 16 H, 270H, 10H, 8H, 8H, 8 H, $py_2H_{\beta(12)(16)(17)}$, H_{dppp}, $ArH_{3(13)(15)(16)}$, $ArH_{4(13)(15)(16)}$, $ArH_{5(13)(15)(16)}$, $ArH_{6(13)(15)(16)}$], 7.78–7.82 [m, 8 H, phen$H_{\alpha(12)(16)(17)}$], 7.88–7-92 (m, 30 H, H_{dppp}), 7.96–8.00 (m, 30 H, H_{dppp}), 8.26–8.28 [br. s, 2 H, bipy$H_{\delta(15)}$], 8.29–8.30 [br. s, 2 H, bipy$H_{\delta(17)}$], 8.33 [s, 2 H, phen$H_{5(16)}$], 8.35 [s, 2 H, phen$H_{5(17)}$], 8.37–8.39 [br. s, 4 H, 4 H, phen$H_{5(12)}$, bipy$H_{\delta(11)}$], 8.89–9.10 [m, 48 H, $py_1py_2py_3H_{\alpha(11)(12)(13)}$] ppm. ^{31}P NMR (202 MHz, CD_2Cl_2): δ = 6.96 (s), 7.12 (s) 7.20 (s), 7.34 (s), 7.39 (s), 7.45 (s), 7.51 (s), 7.57(s), 14.48 (s), 14.80 (s), 14.88 (s), 15.01 (s), 15.43 (s), 15.50 (s) ppm. ESI-MS: *m*/*z* (%) = 1024.1 (100) [**13** – 2OTf^{2+}], 1179.0 (10) [**11** – 3OTf^{3+}],1187.0 (80) [**17** – 3OTf^{3+}], 1195.0 (25) [**12** – 3OTf^{3+}], 1433.6 (5) [**15** – 2OTf^{2+}], 1445.6 (5) [**16** – 2OTf^{2+}], 1842.6 (8) [**11** – 2OTf^{2+}], 1855.0 (5) [**17** – 2OTf^{2+}], 1866.5 (3) [**12** – 2OTf^{2+}].

Supporting Information (see also the footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of ligands **1**–**3** and H,H-COSY NMR spectra of the metallo-macrocycles.

Acknowledgments

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