A Flexible Synthetic Strategy for the Preparation of Heteroleptic Metallacycles of Porphyrins

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ABSTRACT: We present a stepwise synthetic strategy for the preparation of the unprecedented heteroleptic 2+2 neutral metallacycle \([\{\text{t,c,c-RuCl}_2(\text{CO})_2(4'\text{cisDPyP})(3'\text{cisDPyP})\}\] (5), in which two different 5,10-meso-dipyridyloporphyrins, 4'\text{cisDPyP} [i.e., 5,10-bis(4'pyridyl)-15,20-diphenylporphyrin] and 3'\text{cisDPyP} [i.e., 5,10-bis(3'pyridyl)-15,20-diphenylporphyrin], are joined through equal 90°-angular Ru(II) connectors. The synthesis of 5 was accomplished through the preparation of a reactive ditopic intermediate in which one of the two pyridylporphyrins is linked to two neutral ruthenium fragments, each having one residual readily available coordination site (a dmso-O). Thus, compound 5 was obtained under mild conditions through two complementary routes: either by treatment of \([\{\text{t,c,c-RuCl}_2(\text{CO})_2(\text{dmso-O})\}\] (3) with 1 equiv of 3'\text{cisDPyP} or, alternatively, by treatment of \([\{\text{t,c,c-RuCl}_2(\text{CO})_2(\text{dmso-O})\}\] (3) with 1 equiv of 4'\text{cisDPyP}. Heteroleptic metallacycle 5 was isolated in pure form in acceptable yield and fully characterized. Spectroscopic data and a molecular model show that 5 has an L-shaped geometry, with the two porphyrins almost orthogonal to one another. The modular approach that we established is highly flexible and opens the way to several possible exciting developments.

INTRODUCTION

Nature uses sophisticated arrays of tetrapyrrolic macrocycles (e.g., chlorophyll, cytochromes, etc.) to perform precise energy and electron transfer processes. In addition to the specific nature of the macrocycles, their number and relative orientations are of paramount importance for determining the properties of such assemblies. The development of simple procedures for preparing synthetic arrays of tetrapyrole macrocycles with full stereocontrol is one of the challenges of supramolecular chemistry.

The metal-mediated self-assembly approach, which exploits the formation of coordination bonds between peripheral basic site(s) on the porphyrins and suitable metal centers, has afforded a variety of discrete two-dimensional (2D) and three-dimensional (3D) arrays of porphyrins of the type \(\text{M}_{\text{N}}\text{(porp)}_{\text{N}}\) including several 2+2 and 4+4 metallacycles (M can be a naked and inert bonds, are highly symmetric and thus generate no stereoisomers. X-ray structural characterization showed that whereas 1 is perfectly flat in the solid state, 2 has a staggered geometry with the two chromophores rigidly held in a slipped-cofacial arrangement by the Ru(II) fragments (Figure 1). For each porphyrin in 2, (i) the two pyridyl rings are in a syn conformation and (ii) the plane of the heterocycle is almost orthogonal to the equatorial coordination plane (N, N, C, and C) of each Ru linker.

The corresponding zinicated metallacycles 1Zn and 2Zn, in which each embedded metal center is capable of forming an additional axial bond, were exploited by us as two-point molecular panels (Figure 1) for the preparation of molecular sandwiches, boxes, and prisms.

A vast majority of the metal-mediated arrays of porphyrins described in the literature, including metallacycles 1 and 2, are homoleptic systems, as they contain a single type of porphyrin. With few exceptions, they are also homometallic, because most of them contain a single type of metal connector. In the past, we described the stepwise preparation of the heterobimetallic 2+2 metallacycle of porphyrins \(\text{Pd(dpdp)}\{\text{t,c,c-RuCl}_2(\text{CO})_2(4'\text{cisDPyP})\}_2\] (CF\(_3\)SO\(_3\))\(_2\) [dpdp = 1,3-bis-
four angular 4
four T-shaped 4
with the form a dihedral angle of 41.7(1) found to have a folded geometry in which the two porphyrins
thermodynamic product, and the reversibility of the pyridyl adduct, which was not isolated, was believed to be the
selectivity of the preparation. On the contrary, with a similar
Pd(II) bond was apparently a critical feature for the high
 attempted a one-dimensional (1D) and 2D “tapes” of pyridylporphyrins were obtained with much lower selectivities, as mixtures of adducts with different nuclearities.31 The same group later described a mixed porphyrin/porphyrin assembly obtained by postsynthetic modification.32,33 More recently, Schmittel and co-workers, exploiting the HETTAP concept for controlling the coordination equilibrium at the metal ion,34 prepared Cu-mediated assemblies containing two different cofacial metalloporphyrins.35,36 It should be noted that in this case the two porphyrins have very different peripheral binding sites, one being a pyridyl ring and the other a sterically shielded phenanthroline, and the strategy exploits steric and electronic effects originating from the latter.

Given these premises, we aimed to develop a new flexible synthetic strategy that might be used for the construction of ruthenium-mediated heteroleptic systems of meso-pyridylporphyrins containing PyPs that differ in the number of peripheral pyridyl rings (from two to four) and/or in the position of the pyridyl N atom (3′ or 4′). This would open the way to new extended arrays as well as to unprecedented geometries. The formation of Ru-mediated metallacycles of PyPs typically occurs under kinetic control; therefore, a one-pot synthetic approach does not seem to be suitable for our aim. In fact, because all PyPs share the pyridyl ring as a common binding motif, no stereoelectronic discrimination upon coordination to ruthenium can be expected to occur. Thus, we decided to develop a new stepwise modular approach that requires the initial preparation of a reactive polytopic “acceptor”

(diphenylphosphanyl)propane] that features an octahedral neutral Ru(II) complex at one corner and a square planar cationic Pd(II) linker at the other (Figure 2).39 In the solid state, the metallacycle, obtained by treatment of the reactive 90° metal-containing ligand \(t_{\text{c,c}}\text{-RuCl_2(CO)_2}}{(4’\text{cis} \text{DPyP})_2}\) with the cis-protected complex \(\{\text{Pd(dppp)}\text{(CF_3SO}_3\text{)}_2\}\), was found to have a folded geometry in which the two porphyrins form a dihedral angle of 41.7(1)°.

More recently, we described new stereoisomers of homoleptic molecular square 1, in which one or both \(t_{\text{c,c}}\text{-RuCl_2(CO)_2}}\) corners are replaced by the stereoisomeric \(\{c,c,c\text{-RuCl_2(CO)_2}}\) fragment, which can have a C or A configuration, namely, \(\{t_{\text{c,c}}\text{-RuCl_2(CO)_2}}(4’\text{cis} \text{DPyP})_2\}\) and \(\{c,c,c\text{-RuCl_2(CO)_2}}(4’\text{cis} \text{DPyP})_2\}\).30 The examples of metal-mediated assemblies containing different porphyrins are even rarer. In 1998, Drain and co-workers described the high-yield one-pot formation of a nonameric neutral square-shaped grid obtained by addition of 12 equiv of \([\text{PdCl_2(NCPh)}_2]\), a precursor of the linear \{trans-PdCl_2\} linker, to a 1:4:4 mixture of three different meso-4’-pyridylporphyrins:40 one X-shaped 4’-TPyP unit (taking the central position; 4’-TPyP = 5,10,15,20-tetrapyridylporphyrin), four T-shaped 4’-TrPyP units [making the sides of the array; 4’.TrPyP = 5,10,15-tris(4’-pyridyl)-20-phenylporphyrin], and four angular 4’cisDPyP units (making the corners).31 The adduct, which was not isolated, was believed to be the thermodynamic product, and the reversibility of the pyridyl–Pd(II) bond was apparently a critical feature for the high selectivity of the preparation. On the contrary, with a similar

one-pot approach, Pd(II)- or Pt(II)-mediated one-dimensional (1D) and 2D “tapes” of pyridylporphyrins were obtained with much lower selectivities, as mixtures of adducts with different nuclearities.31 The same group later described a mixed porphyrin/porphyrin assembly obtained by postsynthetic modification.32,33 More recently, Schmittel and co-workers, exploiting the HETTAP concept for controlling the coordination equilibrium at the metal ion,34 prepared Cu-mediated assemblies containing two different cofacial metalloporphyrins.35,36 It should be noted that in this case the two porphyrins have very different peripheral binding sites, one being a pyridyl ring and the other a sterically shielded phenanthroline, and the strategy exploits steric and electronic effects originating from the latter.

Figure 1. Homoleptic 2+2 metallacycles 1 (top) and 2 (bottom) with their schematic representations as molecular panels (right). Distances from the X-ray structures.39 Color code: red for 4’cisDPyP, blue for 3’cisDPyP, gray for \(t_{\text{c,c}}\text{-RuCl_2(CO)_2}}\), and gold for the centroid of the porphyrin.

Figure 2. Heterobimetallic 2+2 metallacyle of porphyrins \([\text{Pd(dppp)}\{t_{\text{c,c}}\text{-RuCl_2(CO)_2}}(4’\text{cis} \text{DPyP})_2\}\text{(CF_3SO}_3\text{)}_2\text{) (dppp = 1,3-bis-(diphenylphosphanyl)propane) with its schematic representation shown as a molecular panel (right). Distances from the X-ray structure.29 Color code: red for 4’cisDPyP, gray for \(t_{\text{c,c}}\text{-RuCl_2(CO)_2}}\), green for \{Pd(dppp)}_2^+\), and gold for the centroid of the porphyrin.
intermediate, i.e., a pyridylporphyrin bound to at least two ruthenium fragments, each having one residual readily available coordination site, that is then reacted with the second porphyrin to yield the final heteroleptic assembly. Dimetallic acceptors, not porphyrin-based and typically with a 2+ charge, have been extensively used by several groups for self-assembly purposes. For example, Stang and co-workers exploited di-Pt(II) acceptors of different shapes for the preparation of many metallacycles and metallacages. Dimetallic molecular clips were used as pillars for the preparation of metallacages featuring two equal face-to-face flat organic linkers, including porphyrins. As a proof of concept, this strategy was here first used for the stepwise preparation of the heteroleptic 2+2 neutral metallacycle \[\{t,c,c\text{-RuCl}_2(CO)_2(\text{dmso-O})\}_2(4'\text{cisDPyP})\] (5), in which two different cis-dipyridylporphyrins, 4’ cisDPyP and 3’ cisDPyP, are joined through equal 90°-angular Ru(II) connectors. The synthesis of 5 required the preparation of the reactive ditopic intermediate \[\{t,c,c\text{-RuCl}_2(CO)_2(\text{dmso-O})\}_2(4'\text{MPyP})\] (3), which already contains one of the two porphyrins, that was then treated with 1 equiv of 3’ cisDPyP (Scheme 1). Alternatively, compound 5 was obtained by treatment of the reactive intermediate \[\{t,c,c\text{-RuCl}_2(CO)_2(\text{dmso-O})\}_2(3'\text{cisDPyP})\] (4) with 1 equiv of 4’ cisDPyP (Scheme 1). Heteroleptic metallacycle 5 was isolated in pure form in reasonable yield and fully characterized. Spectroscopic data and the molecular model are consistent with 5 having an unprecedented L-shaped geometry, with the two porphyrins almost orthogonal to one another.

**RESULTS AND DISCUSSION**

**Model Systems.** Because the purification of cisDPyPs is a laborious process, we first ascertained that the two dmso-O ligands in the Ru(II)-dmso carbonyl complex \(t,c,c\)-RuCl\(_2\)(CO\(_2\))(dmso-O)\(_2\)) (6), precursor of the metal corners in 1 and 2, can be indeed replaced in a stepwise manner by pyridyl ligands using 5-(4’-pyridyl)-10,15,20-triphenylporphyrin (4’MPyP) as a model. As described in the Supporting Information, we first isolated \(t,c,c\)-RuCl\(_2\)(CO\(_2\))(dmso-O)- (4’MPyP) \(7\) in good yield and then demonstrated that treatment of 7 at room temperature with 0.5 equiv of linear linkers 4,4’-bpy and 4’ transDPyP afforded the corresponding adducts \(\{t,c,c\text{-RuCl}_2(CO)_2(4'\text{MPyP})\}_2(\mu-4,4'-bpy)\}\) and \(\{t,c,c\text{-RuCl}_2(CO)_2(4'\text{MPyP})\}_2(\mu-4'\text{transDPyP})\}, respectively (Scheme 2).

**Synthesis and Characterization of Reactive Ditopic Intermediate \(\{t,c,c\text{-RuCl}_2(CO)_2(\text{dmso-O})\}_2(4'\text{cisDPyP})\)**

**Scheme 2. Stepwise Preparation of Metal-Mediated Assemblies \(\{t,c,c\text{-RuCl}_2(CO)_2(4'\text{MPyP})\}_2(\mu-L)\}\) (with \(N-L-N = 4,4'\text{-bpy or } 4'\text{transDPyP}\) through Reactive Intermediate \(t,c,c\)-RuCl\(_2\)(CO\(_2\))(dmso-O)(4’MPyP)\) \(7\)**
Treatment of 4′cisDPyP with an excess (typically 6 equiv) of 6 in chloroform at room temperature smoothly afforded ditopic intermediate \([\{t,c,c\text{-}RuCl_2(CO)_2(dmso-O)\}_2(4′\text{cisDPyP})\] (3) in excellent yield (no unreacted 4′cisDPyP detected via TLC within 1 h). After solvent removal, the dark purple solid was washed with water to remove the unreacted ruthenium complex and the released DMSO (the product is soluble in all of the other solvents tested). The washing also removed most of the bound dmso-O, thus affording mainly the aqua species \([\{t,c,c\text{-}RuCl_2(CO)_2(OH_2)\}_2(4′\text{cisDPyP})\] (3H₂O). The ¹H NMR spectrum of the crude reaction product in DMSO-d₆ (Supporting Information) presents only one main set of resonances consistent with 4′cisDPyP being symmetrically coordinated to two equal Ru(II) complexes; for example, the resonances of both pyridyl rings are equally shifted to higher frequencies compared to the free porphyrin. The spectral features of the Ru fragments confirm that the original geometry remained unchanged (Supporting Information).¹⁹

(i) Consistent with being trans to a CO,²⁴ the residual dmso-O resonates as a singlet at 2.97 ppm in the NMR spectrum in CDCl₃; (ii) two clear CO stretching bands are found in the infrared (IR) spectrum at 2072 and 2002 cm⁻¹, as expected for a cis-{Ru(CO)₂} fragment.

Compound 3 can be isolated in almost pure form by dissolving 3H₂O in a chloroform/DMSO mixture followed by precipitation with diethyl ether. Also in this case, the coordinated water is not fully replaced by dmso-O. In fact, the NMR spectrum of this species recorded in CDCl₃ (Figure 3) shows, in addition to the major set resonances of 3, a minor set of partially resolved signals, attributed to the residual aqua species 3H₂O. The equilibrium between these two species is shifted toward 3 by the addition of DMSO-d₆ and the resonances of 3H₂O concomitantly disappear (Figure 3). Because from the point of view of the further reactivity 3H₂O and 3 behave equally, and the influence on the MW and stoichiometric ratio of the reactions is marginal, for the sake of brevity in the following no distinction between them will be made and only 3 will be used.

The corresponding ditopic intermediates with 5,10-bis(4′-pyridyl)-15,20-di-p-(tolyl)porphyrin (4′cisDPyMP, 3Me) and with 3′cisDPyP (4) were prepared with the same procedure (Supporting Information).⁴⁹

Synthesis and Characterization of Heteroleptic 2+2 Metallacycle \([\{t,c,c\text{-}RuCl_2(CO)_2\}_2(4′\text{cisDPyP})(3′\text{cisDPyP})\] (5). Treatment of 3′cisDPyP with a slight excess of 3 at 40 °C in dried CH₂Cl₂ afforded heteroleptic 2+2 metallacycle \([\{t,c,c\text{-}RuCl_2(CO)_2\}_2(4′\text{cisDPyP})(3′\text{cisDPyP})\] (5). The reaction was monitored by TLC and stopped when depletion of 3′cisDPyP was complete (~1 h). The crude was purified by flash chromatography, and a single fraction was collected, with an isolated yield of pure product of 26%. To the best of our knowledge, this is the first example of an isolated heteroleptic metallacycle that features two porphyrins with almost indistinguishable binding sites.
In the reasonable hypothesis that each porphyrin maintains a coordination geometry similar to that found in homoleptic metallacycles 1 and 2,25,26 i.e., either coplanar (4′cisDPyP) or perpendicular (3′cisDPyP) to the equatorial coordination plane (N, N, C, and C) of each Ru linker, 2+2 metallacycle 5 is expected to have a folded, L-shaped geometry in which the planes of the two porphyrins are almost orthogonal to one another. Even though we were unable to grow crystals of 5 suitable for X-ray analysis, its energy-minimized model (Figure 4) is perfectly consistent with this hypothesis. The average planes of the porphyrins form a dihedral angle of 92.6°. The model also shows that the 4′cisDPyP side of the L is significantly longer than the 3′cisDPyP side; in fact, the calculated distance from the intersection between the average planes of the two porphyrins (that falls into a pyrrole ring of 3′cisDPyP) to the centroid of 4′cisDPyP, 9.36 Å, is more than double that to the centroid of 3′cisDPyP, 3.95 Å (Figure 4).

The 1H NMR spectrum of 5 is reported in Figure 5. Assignments were made according to 2D spectra (Supporting Information). The measured dihedral angle (which falls at a frequency significantly lower than those of both 1 and 2) was assigned to 4′cisDPyP. Consistently, in the COSY spectrum (Figure 6) it has a cross peak with the Hβ singlet at 7.47 ppm.

The ultraviolet−visible (UV−vis) spectrum of 5 is similar to those of the component porphyrins, and consistent with the nearly orthogonal orientation between the two porphyrins, no exciton splitting is observed in the Soret band (contrary to what is found in 2).26 In the IR spectrum, the two CO stretching bands (2074 and 2014 cm−1) are similar to those measured for precursor 3.

Heteroleptic metallacycle 5 was also successfully prepared (even though on only a small scale, in an NMR tube) following the complementary synthetic procedure, i.e., upon treating reactive ditopic intermediate 4 with 4′cisDPyP (Supporting Information).

Strictly similar heteroleptic 2+2 metallacycle [[t,ɛ,c-RuCl2(CO)2]2(4′cisDPyMP)(3′cisDPyP)] (8), which contains 4′cisDPyMP in place of 4′cisDPyP, was obtained in 20% isolated yield with the same synthetic approach. Ditopic intermediate [[t,ɛ,c-RuCl2(CO)2(dmso-O)]2(4′cisDPyMP)] (3Me) was treated with a stoichiometric amount of 3′cisDPyP in chloroform at 40 °C, followed by flash chromatography purification of the crude product. The 1H NMR spectrum of 8 (Supporting Information) is similar to that of 5, with the addition of the singlet for the methyl groups at 2.65 ppm and a better resolution of the signals in the crowded aromatic region. Treatment of 8 with an excess of zinc acetate in a CHCl3/MeOH mixture afforded the corresponding fully zinced metallacycle 8Zn. The insertion of zinc involves the expected decrease in the number of Q bands in the UV−vis spectrum from four to two (Supporting Information). Even though, aside from the absence of the NH signals, the 1H NMR spectrum of 8Zn in CDCl3 is very similar to that of 8 (Figure 7), several resonances are better resolved, for example, those of protons H2′ and H6′ of 3′cisDPyP and of the pyrrole protons (see also the Supporting Information).

By virtue of its better resolved 1H NMR spectrum, 8Zn was well suited for a DOSY investigation to obtain more information about the size of these heteroleptic metallacycles (Supporting Information). The measured diffusion coefficient (D⊥) for 8Zn was (6.06 ± 0.10) × 10−6 cm2 s−1, which...
corresponds to a hydrodynamic radius \((r_H)\) for the molecule of 6.7 Å. These data compare well with those of homoleptic \(\text{Zn}^{2+}\) molecular square \(\text{Zn}^{2+}\), measured under the same conditions [\(D_t = (5.55 \pm 0.01) \times 10^{-6}\) cm\(^2\) s\(^{-1}\), and \(r_H = 7.3\) Å].

Finally, we compared the stepwise synthetic approach with the one-pot preparation, which consists of treating a 1:1 mixture of \(4'\text{cisDPyMP}\) and \(3'\text{cisDPyP}\) with 2 equiv of Ru(II) precursor 6. A careful analysis of the TLC spots of the mixture as well as of the low-frequency region (NH resonances) of the otherwise extremely crowded \(^1\text{H}\) NMR spectrum allowed us to establish that the crude product was a mixture of the three possible \(2+2\) metallacycles 8, \([t, c, c\text{-RuCl}_2(\text{CO})_2(4'\text{cisDPyMP})][\text{Me}]\) \(5\), and \([t, c, c\text{-RuCl}_2(\text{CO})_2(3'\text{cisDPyP})][\text{Me}]\) \(2\) in almost equal amounts (in addition to oligomeric species, whose presence is suggested by some broad resonances), as expected for a reaction under kinetic control (Supporting Information). Given the very similar chromatographic mobility of the three metallacycles

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**Figure 5.** \(^1\text{H}\) NMR spectrum (CDCl\(_3\)) of \([t,c,c\text{-RuCl}_2(\text{CO})_2(4'\text{cisDPyP})(3'\text{cisDPyP})]\) \(5\), with the labeling scheme. The protons of \(3'\text{cisDPyP}\) are labeled in blue.

**Figure 6.** \(^1\text{H}\)−\(^1\text{H}\) COSY spectrum of \(5\) (CDCl\(_3\)), with the aromatic region and enlargement showing the cross peaks between \(\beta H\) and NH signals. See Figure 5 for the labeling scheme.
(Experimental Section), this statistical mixture was not easily amenable to separation by column chromatography. In conclusion, even for this relatively simple 2+2 heteroleptic metallacycle, the one-pot approach turned out to be less suitable than the stepwise one.

**CONCLUSIONS**

We described a modular stepwise approach for the preparation of heteroleptic metallacycles of porphyrins linked through neutral 90°-angular Ru(II) fragments. As a proof of concept, the synthetic route was successfully applied to the preparation of unprecedented 2+2 heteroleptic metallacycle [[\(\text{t,c,c-RuCl}_2(\text{CO})_2\)]_2(4’\text{cisDPyP})(3’\text{cisDPyP})] (5). The preparation of 5 was accomplished through the isolation of a reactive ditopic intermediate, in which one of the two porphyrins is linked to two ruthenium fragments, each having one residual readily available coordination site (a dmso-O). Thus, metallacycle 5 was obtained under mild conditions through two complementary routes: by treatment of [[\(\text{t,c,c-RuCl}_2(\text{CO})_2\)]_2(dmso-O)(4’\text{cisDPyP})] (3) with 1 equiv of 3’\text{cisDPyP} or, alternatively, by treatment of [[\(\text{t,c,c-RuCl}_2(\text{CO})_2\)]_2(dmso-O)(3’\text{cisDPyP})] (4) with 1 equiv of 4’\text{cisDPyP}.

Compound 5, which was obtained in pure form in acceptable isolated yield, fills the gap in the series of the corresponding homoleptic metallacycles with 4’\text{cisDPyP} (1) and 3’\text{cisDPyP} (2) (Figure 8). It has an L-shaped geometry, with the 4’\text{cisDPyP} side of the L being more than twice as long as the 3’\text{cisDPyP} side.

![Figure 7. 1H NMR spectrum (CDCl3) of heteroleptic 2+2 metallacycle [[\(\text{t,c,c-RuCl}_2(\text{CO})_2\)]_2(Zn•4’\text{cisDPyMP})(Zn•3’\text{cisDPyP})] (8Zn) with a labeling scheme. The protons of 3’\text{cisDPyP} are labeled in blue.](image-url)

![Figure 8. Schematic representation of the 2+2 metallacycles of porphyrins, homoleptic 1 and 2, and heteroleptic 5. Color code: red for 4’\text{cisDPyP}, blue for 3’\text{cisDPyP}, gray for \{\(\text{t,c,c-RuCl}_2(\text{CO})_2\)\}, and gold for the centroid of the porphyrin.](image-url)

With the same synthetic approach, the strictly similar [[\(\text{t,c,c-RuCl}_2(\text{CO})_2\)]_2(4’\text{cisDPyMP})(3’\text{cisDPyP})] (8), which contains 4’\text{cisDPyMP} in place of 4’\text{cisDPyP}, was obtained. The one-pot approach, tested for this heteroleptic metallacycle, turned out to be unpractical, affording a mixture of 8 with the corresponding homoleptic metallacycles, 1Me and 2, of difficult chromatographic separation.

The modular approach that we established is highly flexible and opens the way to several possible exciting developments, such as the preparation of extended metallacycles. For example, treatment of reactive intermediate 3 with 0.5 equiv of a tetrapyridylporphyrin is expected to lead to the formation of 3+4 extended metallacycles (i.e., three porphyrins and four Ru linkers) featuring two different porphyrins. Combinations of
4′- and 3′PyPs will afford unprecedented geometries that, after metalation, like 1 and 2 might be further exploited as molecular panels for the hierarchical construction of 3D assemblies. In addition, because the porphyrins are introduced in a stepwise manner, it is possible, in principle, to place different metal ions in selected positions inside the metallacycle, thus opening the way to currently unavailable perspectives. For example, it might become possible to investigate how the rate of photoinduced processes (e.g., energy or electron transfer) depends not only on the relative orientation of the porphyrins (orthogonal vs parallel) but also on the specific direction (e.g., center to periphery or vice versa).

Lastly, other reactive intermediates, in which the porphyrin has a different geometry (e.g., 4′transDpyP) or bears reactive metal fragments different from \( \{t,c,c-RuCl_2(CO)\_2(dmso-O)\} \) (or both), might be prepared and used as precursors of new heteroleptic metallacycles.

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### EXPERIMENTAL SECTION

**Materials.** The reference compounds \( \{t,c,c-RuCl_2(CO)\_2(4′cisDpyP)\} \) (1) and \( \{t,c-RuCl_2(CO)\_2(3′cisDpyP)\} \) (2) were prepared as described in refs 25 and 26. \( \{t,c,c-RuCl_2(CO)\_2(4′cisDpyMP)\} \) (1Me) was prepared and purified following the same procedure described in ref 25 for 1. Crystals suitable for X-ray analysis were obtained by layering n-hexane on top of a CHCl₃ solution of 1Me. Elemental analysis for \( \{t,c,c-RuCl_2(CO)\_2(4′cisDpyMP)\} \) 2CHCl₃·7.3H₂O (1Me·2CHCl₃·7.3H₂O) and \( \{C₉H₇Cl₂N₂O₄Ru₂\} \) 2CHCl₃·7.3H₂O (2046.9). CaclC: 55.16; H: 4.07; N: 8.21. Found: C: 54.93; H: 4.16; N: 8.16. H NMR (CDCl₃): \( \delta \) 9.81 (d, 8H, H₂,6), 9.09 (d, 4H, Hj), 9.03 (d, 4H, Hj), 9.03 (s, 4H, Hb), 8.92 (s, 4H, Hb), 8.57 (d, 8H, H3,s), 8.14 (d, 8H, He), 7.63 (d, 8H, Hm), 2.76 (s, 12H, Me), -2.72 (s, 4H, NH).

**Instruments Methods.** Mono- and bidimensional (H¹+H COSY and H¹-¹³C HSQC) NMR spectra were recorded at room temperature, unless stated otherwise, on a Varian 400 or 500 spectrometer (H, 400 or 500 MHz; ¹³C, 100.5 or 125.7 MHz). H DOSY experiments were performed on the Varian 500 spectrometer at -5 °C (CDCl₃), using the Bipolar Pulse Pair Stimulated Echo with Convection Tensorization Sequence implemented in the Vnmrj software. H chemical shifts were referenced to the peak of residual nondeuterated solvent (δ 7.26 for CDCl₃, δ 7.32 for CD₃OD). ESI mass spectra were recorded in positive mode on a Thermo PerkinElmer Fourier-transform IR/Raman 2000 instrument in transmission mode. Elemental analyses were performed of the total energy for isolated systems when simulated with large unit cell, and minimum separation distance of >10 Å between nearest atoms of any two contiguous periodic images. The correction of Makov and Payne to the total energy for isolated systems when simulated with large unit cells, as implemented in the Quantum-Expresso suite, was also applied. Convergence thresholds for geometry relaxation were 1 × 10⁻⁴ Ry for total energy and 1 × 10⁻⁷ Ry/Å for the maximum force component acting on atoms.

**Synthesis of the Complexes.** \( \{t,c,c-RuCl_2(CO)\_2(dmso-O)\} \) (6), dissolved in 20 mL of CHCl₃, was added 50.0 mg (0.081 mmol) of 4′cisDpyP (6:4′cisDpyP ratio of 6). The purple solution was stirred at room temperature for 50 min, and afterward, the solvent was removed under reduced pressure. The recovered purple solid was washed with H₂O to remove the unrelocated complex and the free DMSO and dried under vacuum. The solid was redissolved in chloroform and dried on Na₂SO₄. The solution was recovered, and the solvent was removed by evaporation at reduced pressure and dried under vacuum. Yield: 89.6 mg, 98%. H NMR (DMSO-d₆): δ 9.41 (d, 4H, H2,6), 8.88 (d, 2H, Hj), 8.80 (s, 2H, Hb), 8.77 (d, 2H, Hj), 8.28 (d, 4H, H3,s), 8.12 (d, 4H, Hb), 7.72 (m, 6H, Hm-p), -2.92 (s, 2H, NH).

The dmso compound \( \{t,c,c-RuCl_2(CO)\_2(dmso-O)\} \) (3) was obtained by dissolving 50.0 mg of the product in 10 mL of CHCl₃ in the presence of anhydrous Na₂SO₄. The mixture was stirred for 10 min and filtered, and 500 mL of DMSO was added to the mother liquid. The solution was concentrated to 5 mL, and complex 3 was precipitated by addition of diethyl ether. After crystallization from DMSO, high-resolution mass spectrum (ESI-MS) shows the dmso-O singlet at 2.97 ppm. UV−vis \([\text{CHCl}_3; \lambda_{max} (nm), \text{relative intensity (%)}] = \{425 (100, Soret band), 556 (2.96), 591 (2.39), 647 (1.94)\} \). IR (selected bands in CHCl₃, cm⁻¹): 2072 (νυ(CO)), 1952 (νυ(CO)). [t,c,c-RuCl_2(CO)\_2(OH)(4′cisDpyMP)] (3Me) is similar to that leading to 3. To a 178.8 mg (0.465 mmol) amount of 3Me, \( \{t,c,c-RuCl_2(CO)\_2(dmso-O)\} \) (4′ cisDpyMP) (3 Me) was added, and the mixture was stirred at room temperature for 50 min. The solution was concentrated to 5 mL, and complex 3Me was precipitated by addition of diethyl ether. After crystallization from DMSO, the dmso-O singlet at 2.97 ppm. UV−vis \([\text{CHCl}_3; \lambda_{max} (nm), \text{relative intensity (%)}] = \{425 (100, Soret band), 556 (2.96), 591 (2.39), 647 (1.94)\} \).
Inorganic Chemistry

**One-Pot Synthesis of \([t,c,c-RuCl_2(CO)_2(4\text{-}\text{cisDPyMP})-Zn\text{-}\text{ cisDPyP}](\text{3'cisDPyP})\)**

The reaction was carried out on a small scale in an NMR tube. A 1.2 mg amount (3.1 × 10⁻³ mmol) of 6 was dissolved in 700 µL of CDCl₃ and 1.0 mg of 4'cisDPyMP (1.5 × 10⁻³ mmol) and 0.9 mg of 3'cisDPyP (1.5 × 10⁻³ mmol) (4'cisDPyMP:3'cisDPyP ratio of 1:2) were added. The purple solution was stirred by ¹H NMR during a 24 h period at room temperature. At the end of the reaction, the solvent was removed by evaporation at reduced pressure and the purple solid obtained was thoroughly washed with diethyl ether to remove DMSO (it is partially soluble in the most suitable acetone).

**TLC analysis** (silica gel, CHCl₃) showed the presence of multiple spots, the most intense belonging to 1Me (Rₜ = 0.23), 8 (Rₜ = 0.15), and 2 (Rₜ = 0.13). The presence of the three metallacycles in almost equal amounts was confirmed by the diagnostic signals of the NH protons in the CDCl₃ ¹H NMR spectrum of the mixture: 1Me (δ = 2.70 ppm), 8 (δ = 2.90 – 3.17 ppm), and 2 (δ = 3.00 ppm).

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c01511.

Additional comments on reactive intermediate 7, one- and two-dimensional NMR spectra, and IR and UV-vis spectra for the reported compounds (PDF)

**Accession Codes**

CCDC 2078029 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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PyP, 5,10-bis(3′-pyridyl)-15,20-diphenylporphyrin; 4′TTPyP, 5,10,15-tris(4′-pyridyl)-20-phenylporphyrin; 4′TPyP, 5,10,15,20-tetrapyridylporphyrin. For the sake of brevity, abbreviated versions of the geometrical descriptors for the metal centers are used in the formulas: c for cis and t for trans.
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(46) Compound 6 typically replaces the two adjacent dmso-O ligands without geometrical changes; i.e., it is the precursor of a neutral cis-protected metal fragment. (47) As detailed in the Supporting Information, in a CDCl₃ solution the crude product was actually an equilibrium mixture of 7 and the corresponding aqua species tₜ,c-[RuCl₃(CO)₃(OH)₃(4’MPyP)] (7H₂O), suggesting that the dmso-O is easily replaced by adventitious water in the deuterated solvent.

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(49) Like 3, 3Me and 4 were also obtained mainly as aqua species and could be transformed into the dmso-O species upon recrystallization. The labels 3Me and 4 correspond to mixtures of H₂O and dmso-O species.

(50) Homoleptic metallacycle 1Me was prepared for comparative purposes. We managed to obtain its single-crystal X-ray structure, which is reported in the Supporting Information.

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