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Self-assembly of Pd_2L_2 Metallacycles Owning Diversely Functionalized Racemic Ligands

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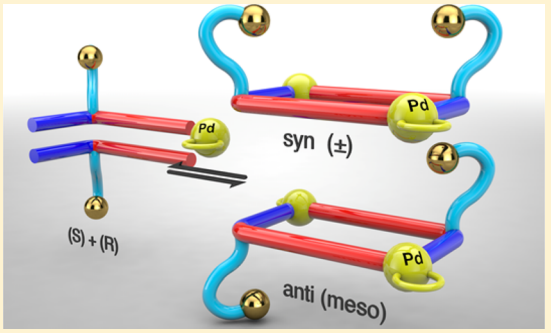
Supporting Information

ABSTRACT: We present herein the efficient palladium(II)-directed self-assembly in water of a series of nine new diversely functionalized metallacycles, owning hydroxy/alkoxycarbonyl/azidoalkyl exo pendant groups attached to ditopic *N*-monoalkyl/aryl-4,4′-bipyridinium/2,7-diazapyrenium ligands. The highly convergent and versatile synthetic route for the ligands uses the Zincke reaction between (dinitrophenyl)-bipyridinium/diazapyrenium salts and racemic amines as the key step. The stereochemical outcome of the self-assembly of the Pd_2L_2 species is discussed on the basis of density functional theory quantum-chemical calculations.



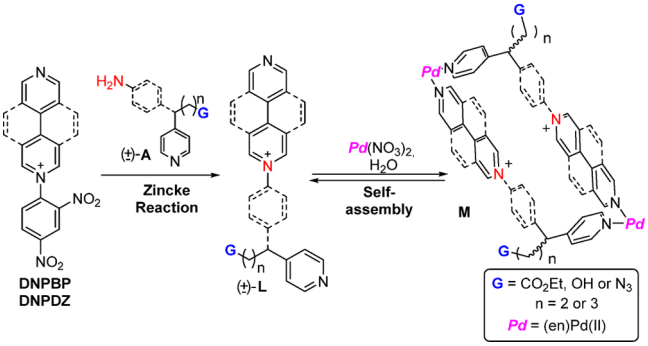
INTRODUCTION

In recent times, coordination-driven self-assembly[1] has been established as an outstanding tool for the preparation of 2D metallacycles and 3D metallacages.[2] The topology of these discrete self-assembled coordination complexes (SCCs) can be easily adjusted by an appropriate selection of ligands and metal centers, resulting in a large number of cases into hollow supramolecular receptors with shapes and sizes modified virtually at will.[2] This modularity of the approach has led to an explosion in the chemistry of SCCs as host molecules[5] and, as a result, in the development of molecular flasks[6] and cavity-controlled catalysis.[7] Furthermore, SCCs can show as well interesting photochemical[2,3] and electronic[2,4] features, opening the door for a vast array of potential applications in electrochemistry,[8] biomedicine,[9] materials science,[10] etc.

Nevertheless, the à la carte synthesis of SCCs, owning completely predesigned and fine-tuned structural and functional features, is still a distant goal;[11] in part because of the potential interference on the self-assembly processes between complexly functionalized ligands with multiple coordination sites. In this context, the exo functionalization of metallacyclic SCCs increases the applicability of self-assembled structures beyond the cavity of the receptor. Several examples of these types of SCCs have recently been reported,[12] showing the benefits of functionalization of these supramolecular receptors in the development of diverse functional systems such as, for example, transmembrane nanopores,[13] metallohydrogels,[14] supramolecular polymers,[15] or vapor sensors.[16]

Following our ongoing interest in the development of new metallacycles[17] and their use as molecular receptors[18] and building blocks for interlocked architectures,[19] we decided to pursue the synthesis of a new series of exo-functionalized Pd_2L_2 metallacyclophanes of type M (Scheme 1), trying to implement

Scheme 1. Planned Self-assembly of Exo-Functionalized Metallocycles of Type M in Water



a flexible derivatization protocol for the future pre- and postassembly modification of the supramolecules. As shown, we intended to self-assemble these metallacycles from palladium(II) metal centers and *N*-monoalkyl/aryl-4,4′-bipyridinium/2,7-diazapyrenium ligands of type (±)-L, owning diverse functionalization in an α position to the quaternized nitrogen atom. To achieve this target, the synthetic plan intended to use

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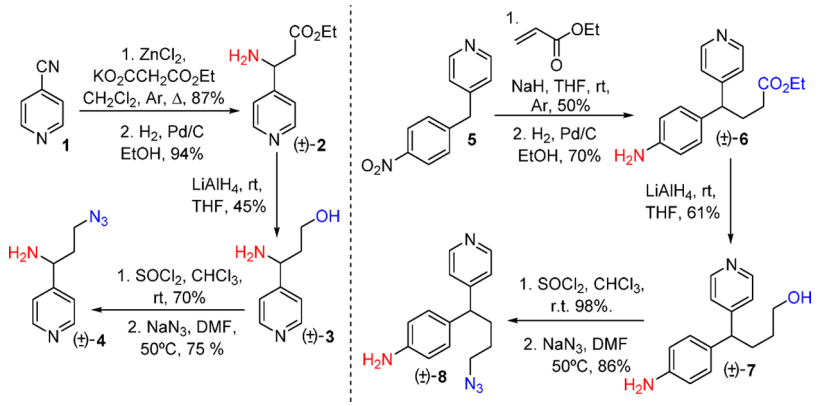
Scheme 2. Synthesis of Racemic Amines of Type A



as the key step the Zincke reaction[20] between the (dinitrophenyl)bipyridinium/diazapyrenium salts DNPBP/DNPDZ[21] and racemic amines of type (±)-A. The utilization of DNPBP or DNPDZ would allow for modification of the π-deficient character of the designed metallacyclic receptors, while the use of different anilines and benzylamines would pave the way for modulation of the length of the supramolecules and their exo functionalization.

It should be noted that our intended synthetic route has been designed to implement two highly desirable objectives: first, the self-assembly of ligands in aqueous media would be guaranteed by the use of appropriate *N*-monoalkylbipyridinium-based nitrates as ligands and, second, the inclusion of pendants with organic functionalities in an sp^3-hybridized carbon opens the door for the introduction of chirality to the self-assembled supramolecules.

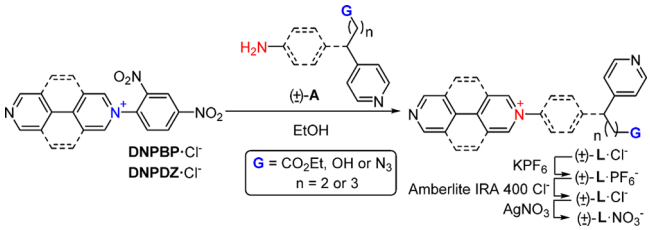
RESULTS AND DISCUSSION

The benzylic amines of type A [(±)-**2**–**4**; Scheme 2] were efficiently synthesized starting from isonicotinonitrile (**1**). By a slight modification of the protocol reported by Fülöp et al.,[22] the racemic aminoester (±)-**2** was prepared by the decarboxylative Blaise reaction of **1** followed by palladium/carbon-catalyzed reduction of the resultant enamine. Reaction of the ester group in (±)-**2** with $LiAlH_4$ yielded the amino alcohol (±)-**3**, which was further transformed into the azide (±)-**4** by treatment with thionyl chloride followed by S_N2 nucleophilic substitution with NaN_3 in *N*,*N*-dimethylformamide (DMF).

In a similar fashion, the synthesis of anilines of type A [(±)-**6**–**8**; Scheme 2] was achieved in good yields starting from 4-(4-nitrobenzyl)pyridine (**5**). Michael addition of **5**, using ethyl acrylate as the acceptor and NaH as the base in dry tetrahydrofuran (THF),[23] followed by reduction of the nitro group by catalytic hydrogenation, yielded the expected racemic aminoester (±)-**6**. The amino alcohol (±)-**7** and the amino-azide (±)-**8** were prepared using the same synthetic protocol as that described for (±)-**2**–**4** (vide supra).

The results regarding the reaction between the DNPBP·Cl^-/DNPDZ·Cl^- salts and amines (±)-**3**, (±)-**4**, and (±)-**6**–**8** are compiled in Table 1.[24] The expected *N*-monoalkyl/aryl-4,4′-bipyridinium/2,7-diazapyrenium ligands **9**–**17** were obtained in good yields as their chloride salts. In general, a slight excess of the amine is required for the reactions to complete, in good agreement with the reversible nature of the reaction proceeding through an ANRORC mechanism.[25] As expected, according to the increased nucleophilicity of the aliphatic amines **2**–**4** compared with the anilines **6**–**8**, ligands **9**–**12** were obtained in shorter times and milder conditions than **13**–**17**.

Table 1. Synthesis of Ligands L by the Zincke Reaction



	(±)-A	(±)-L (G)	reaction conditions[a]	yield[b]	yield[c]
DNPDZ	**3**	**9** (OH)	1.5 equiv, 12 h, rt	70	80
DNPDZ	**4**	**10** (N_3)	1.4 equiv, 12 h, rt	68	50
DNPDZ	**6**	**11** (CO_2Et)	1.3 equiv, 24 h, ref	56	78
DNPDZ	**8**	**12** (N_3)	1.3 equiv, 24 h, ref	72	74
DNPBP	**3**	**13** (OH)	1.5 equiv, 2 h, rt	70	43
DNPBP	**4**	**14** (N_3)	1.4 equiv, 3 h, rt	64	29
DNPBP	**6**	**15** (CO_2Et)	1.3 equiv, 3 h, ref	78	69
DNPBP	**7**	**16** (OH)	1.3 equiv, 3 h, ref	80	57
DNPBP	**8**	**17** (N_3)	1.3 equiv, 3 h, ref	81	54

[a]Equivalents of the amine (±)-A, reaction time, temperature. [b]Yields for the Zincke reaction. [c]Yields for the conversion of (±)-L·Cl into (±)-L·NO_3.

According to our previously reported methodology[17] and in order to avoid the potential coordination of the chloride anions to palladium(II) during the self-assembly of metallacycles of type M, we transformed the ligands into their corresponding noncoordinating water-soluble nitrate salts by anion metathesis. As shown in Table 1, these reaction sequences proceeded in overall moderate to good yields.

Aiming to evaluate the ability of **9**–**17**·NO_3 to form metallacyclic species in water, we proceeded to explore the palladium(II)-directed self-assembly by recording the corresponding ^1H and ^{13}C NMR spectra after mixing stock solutions of the ligands in D_2O with equimolar amounts of (en)Pd(NO_3)$_2$ (see the scheme in Table 2). As shown, the corresponding metallacycles **18**–**26**·6NO_3 appear as the sole products of the self-assembly in the concentration window of 5–0.1 mM,[26] in good agreement with our previous results with nonfunctionalized analogues.[17−19] These results confirm that the extra functional groups installed on the ligands (namely, hydroxyl, alkoxycarbonyl, or azido substituents) do not interfere in the self-assembly process.

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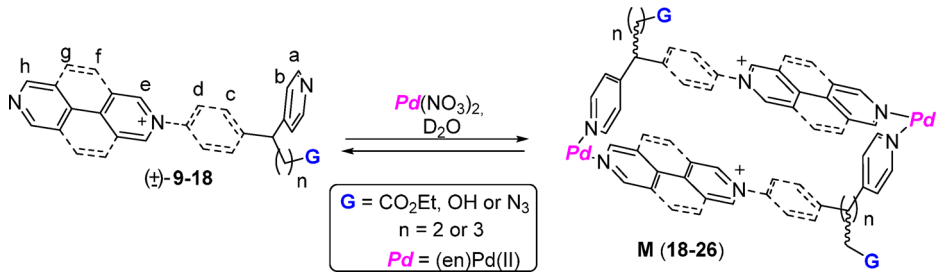
Table 2. ^{1}H Chemical Shifts Induced by the Self-assembly of Metallacycles 18−26 in Water



		Δδ (ppm)[a]							
(±)-L	M (G)	H_a	H_b	H_c	H_d	H_e	H_f	H_g	H_h
9	**18** (OH)	0.35	0.24			−0.11	−0.24	−0.18	0.19
10	**19** (N_3)	0.36	0.24			−0.13	−0.27	−0.19	0.16
11	**20** (CO_2Et)	0.29	−0.04	−0.38	−0.44	−0.22	0.03	0.01	0.38
12	**21** (N_3)	0.33	0.04	−0.38	−0.45	−0.23	−0.02	−0.05	0.31
13	**22** (OH)	0.22	0.22			−0.09	−0.27	−0.09	0.11
14	**23** (N_3)	0.22	0.22			−0.09	−0.27	−0.09	0.1
15	**24** (CO_2Et)	0.12	0.14	−0.14	−0.21	−0.19	−0.15	−0.07	0.13
16	**25** (OH)	0.1	0.11	−0.16	−0.2	−0.19	−0.16	−0.06	0.12
17	**26** (N_3)	0.11	0.12	−0.16	−0.2	−0.19	−0.15	−0.06	0.13

[a] ^{1}H NMR (500 MHz, D_2O) chemical shifts of representative proton nuclei of each metallacycle **18**−**26** compared with the corresponding free ligand (±)-**9**−**17**·NO_3.

1D and 2D NMR experiments allowed us to obtain additional structural information about the supramolecules formed in solution (Table 2). In general, protons in positions α and β with respect to the coordinating nitrogen atoms (i.e., H_a/H_b and H_h) are substantially deshielded upon coordination of the ligands to the metal centers. Conversely, protons on the long side of the rectangular structure are shielded compared with those of the free ligands, which is a typical consequence of the formation of a π-deficient hydrophobic cavity within these types of SSCs. In order to show the potential of the synthetic approach for the construction of other metal-containing supramolecules and in order to characterize more accurately the obtained Pd_2L_2 metallacyclic structures, we decided to use our previously reported microwave-assisted protocol[27] for the synthesis of a platinum(II) analogue of metallacycle **24**. Therefore, the Pt_2L_2 metallacycle **27** was synthesized, isolated, and characterized as the corresponding nitrate and hexafluorophosphate salts. The ^{1}H and ^{13}C NMR spectra of **27** show chemical shifts very similar to those corresponding to the palladium metallacycle. Moreover, mass spectrometry supports the formation of dinuclear species, with characteristic peaks resulting from the loss of between two and five hexafluorophosphate anions.

Figure 1 presents a comparison between the partial ^{1}H NMR spectra (500 MHz, D_2O) obtained for ligand **13** and its corresponding self-assembled metallacycle **22**. Apart from the NMR spectroscopic characteristics commented on above for the aromatic protons of the supramolecule, it is interesting to note the splitting of one of the doublets of the bipyridinium system (H_f) into two doublets of the same intensity. The splitting of certain ^{1}H and ^{13}C NMR signals is also observed for other metallacycles reported in this work (see the Supporting Information). We attribute this effect to the presence of isomeric metallacycles in solution having nearly identical populations and very similar chemical shifts (vide infra).

Indeed, the use of the racemic ligands (±)-**9**−**17** for the self-assembly process has a curious stereochemical outcome. As

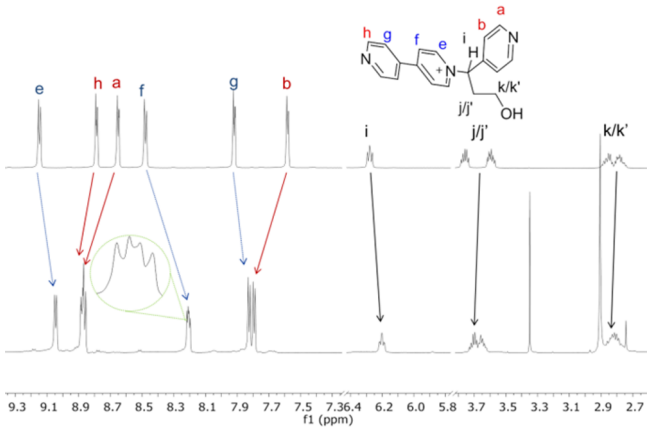


Figure 1. Partial ^{1}H NMR (500 MHz, D_2O) spectra of **13**·NO_3 (top) and **22**·6NO_3 (bottom).

depicted in Scheme 3 for (±)-**13**, the self-assembly around two palladium(II) centers of two ligands owning the same absolute configuration on the asymmetric carbon [(*R*)-**13** + (*R*)-**13** or (*S*)-**13** + (*S*)-**13**] would result in formation of the enantiomeric pair *syn*-(*R*,*R*)-**22**/*syn*-(*S*,*S*)-**22**. On the contrary, if the two ligands involved have different stereochemistries [(*R*)-**14** + (*S*)-**14** or (*S*)-**14** + (*R*)-**14**], these combinations would result in the meso compound *anti*-(*R*,*S*)-**22**.

Because of the dynamic nature of the self-assembly process, the interconversion between isomers *syn*/*anti*-**22** can be easily achieved by reorganization of the constituents, resulting in different populations of the species in solution on the basis of their relative energies. In order to clarify this issue, we performed density functional theory (DFT) calculations in aqueous solution at the M06/6-31G(d,p) level (using the LanL2DZ effective core potential and associated basis set for palladium; see the Supporting Information for details). Full geometry optimization of metallacycle **22** provided the expected *syn* and *anti* isomers as minimum-energy conforma-

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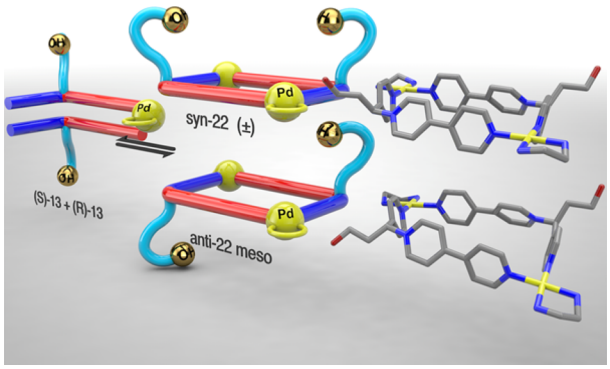
Scheme 3. Representation of the Stereochemical Outcome of the Self-assembly for Metallacycle 22·6NO_3 and Calculated Structures for *Syn* (top) and *Anti* (bottom) Stereoisomers



tions (see the inset in Scheme 3), which possess slightly distorted C_{2v} and C_{2h} symmetries, respectively. The electronic energy difference between the syn and anti isomers is only 0.106 kJ/mol, in good agreement with the NMR data, which show that the isomeric species have virtually identical populations in solution at room temperature. Nonetheless, it should be noted that the similarity in the energies of the isomeric metallacycles has more profound implications on the self-assembly itself: while the two isomers of the enantiomeric pair *syn*-**22** can, in principle, be obtained as the sole products of the self-assembly by using enantiomerically pure ligands, the meso isomer *anti*-**22** cannot.

■ CONCLUSIONS

In summary, we have developed a highly versatile and efficient synthetic route for the preparation of racemic bipyridinium-based ligands and their corresponding Pd_2L_2 metallacycles. This approach allows not only modification of the size and shape of the metallacycles but also modulation of their exo functionalization. Because the derivatization has been implemented in a sp^3-hybridized carbon, the reported synthetic approach implicitly opens the door for the construction of chiral metallacyclic SCCs. Remarkably, the introduction of azide, alcohol, and ester functionalities on the ligands was shown to not interfere with their ability to self-assemble into Pd_2L_2 metallacycles. Furthermore, the self-assembly of the Pt_2L_2 analogue **27** has also been achieved, proving that metal complexes, other than palladium(II), could be employed for the synthesis of functionalized SCCs using our ligands. Crucially, the chameleonic nature of the *N*-monoalkylbipyridinium-based cations used as ligands, with their solubility on aqueous and organic media being controlled by the corresponding counterion, has allowed the self-assembly of the *exo*-functionalized metallacycles in water, amplifying in this manner the potential applications of these SCCs.

Prospectively, the results reported herein open the door for the versatile pre and postassembly modification of Pd_2L_2 and Pt_2L_2 metallacycles by means of, for instance, copper-catalyzed azide alkyne cycloadditions.[28] Ongoing studies in our laboratory along these lines are currently underway and will be reported in due course.

■ EXPERIMENTAL SECTION

General Remarks. Palladium and platinum complexes[29] were prepared according to literature procedures. All other reagents used were commercial-grade chemicals from freshly opened containers. Milli-Q water was purified with a Millipore Gradient A10 apparatus. Merck 60 F254 foils were used for thin-layer chromatography (TLC), and Merck 60 (230−400 mesh) silica gel was used for flash chromatography. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 or a Bruker Avance 500 spectrometer equipped with a dual cryoprobe for ^{1}H and ^{13}C, using the deuterated solvent as a lock and the residual protiated solvent as an internal standard. Mass spectrometry (MS) experiments were carried out in a LCQ-q-TOF Applied Biosystems QSTAR Elite spectrometer for low- and high-resolution electrospray ionization (ESI). Microwave-assisted reactions were carried out in an Anton Paar Monowave 300 reactor in a 30 mL sealed reaction vial. The reaction mixture temperature was monitored via a built-in IR sensor. Microanalyses for carbon, hydrogen, and nitrogen were performed by the elemental analyses general service of Universidade da Coruña.

Synthesis of Amines of Type A. *(±)-Ethyl 3-Amino-3-(pyridin-4-yl)propanoate (**2**).* Compound (*Z*)-**1a** was prepared according to the literature procedure[20] and showed spectroscopic data in good agreement with those reported. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.74 (2H, d, J = 6.2 Hz), 7.49 (2H, d, J = 6.3 Hz), 5.02 (1H, s), 4.19 (2H, q, J = 7.1 Hz), 1.30 (3H, t, J = 7.1 Hz).

Subsequent reduction of the double bond in (*Z*)-**1a** was achieved by a slight modification of the method reported by Fülöp et al.[20] Here, palladium/carbon (1.5 g, 1% w/w) was added to a degassed solution of compound (*Z*)-**1a** (4.5 mmol, 0.865 g) in ethanol (EtOH; 30 mL). The mixture was hydrogenated at atmospheric pressure and room temperature for 24 h. The solution was filtered to remove the catalyst and concentrated under vacuum. The resulting residue was subjected to flash chromatography [SiO_2; 9:1 ethyl acetate (EtOAc)/methanol (MeOH)] to yield (±)-**2** as a yellow oil (94%) and with spectroscopic data coincident with that reported. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.57 (2H, d, J = 4.6 Hz), 7.31 (2H, d, J = 4.6 Hz), 4.41 (1H, dd, J = 8.4 and 5.1 Hz), 4.14 (2H, q, J = 7.1 Hz), 2.74−2.54 (2H, m), 1.23 (3H, t, J = 7.1 Hz). ESI-MS. Calcd for $[M + H]^+$: m/z 195.1128. Found: m/z 195.1146.

*(±)-3-Amino-3-(4-pyridyl)-1-propanol (**3**).* The β-amino ester (±)-**2** (2.5 mmol, 0.49 g) was added to a suspension of $LiAlH_4$ in THF (5 mL) under an argon atmosphere and the mixture stirred for 24 h at room temperature. The reaction was quenched with a mixture of THF/ice, the resulting suspension filtered, and the solvent removed under vacuum to yield a yellow solid residue. This was subjected to flash chromatography (SiO_2; 1:1 EtOAc/MeOH), affording (±)-**2** as a yellow oil (45%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.57 (2H, d, J = 4.6 Hz), 7.24 (2H, d, J = 4.6 Hz), 4.16 (1H, dd, J = 8.3, 4.7 Hz), 3.85−3.76 (2H, m), 1.96−1.81 (2H, m). ESI-MS. Calcd for $[M + H]^+$: m/z 153.1022. Found: m/z 153.1031.

*(±)-3-Azido-1-(pyridin-4-yl)propan-1-amine (**4**).* Compound (±)-**3** (380 mg, 2.49 mmol) was dissolved in a minimum amount of $CHCl_3$ and the solution cooled in an ice bath at 0 °C. $SOCl_2$ (10 equiv) was then added dropwise for 15 min and the reaction monitored by TLC. Once completed, water (15 mL) was added and the pH adjusted to 8−9 by the addition of KOH (50%). The organic layer was separated and the aqueous layer extracted with $CHCl_3$ (2 × 30 mL). The solvent was then evaporated under vacuum to yield (±)-**3a** as a brown oil (70%), which was used without further purification. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.68 (2H, d, J = 4.6 Hz), 7.29 (2H, d, J = 4.6 Hz), 4.21 (1H, t, J = 6.9 Hz), 3.70−3.62 (1H, m), 3.53−3.38 (1H, m), 2.16−2.04 (2H, m). ^{13}C NMR (CD_3OD, 125 MHz): δ 159.55 (CH), 122.38 (CH), 51.97 (CH), 40.15 (CH_2), 38.02 (CH_2).

In order to introduce the azide functional group, (±)-**3a** (265.9 mg, 1.55 mmol) was dissolved in a minimum amount of DMF and NaN_3 (5 equiv) added to the solution, which was heated at 50 °C overnight. Once the reaction was completed (followed by TLC), DMF was removed and EtOAc (20 mL) and water (10 mL) were added. The organic layer was separated and the aqueous layer further extracted with EtOAc (4 × 20 mL). The sum of the organic layers was collected, and the solvents were evaporated under vacuum to yield (±)-**4** as a brown oil (75%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.57 (2H, d, J = 4.6 Hz), 7.26 (2H, d, J = 4.6 Hz), 4.05 (1H, t, J = 6.9 Hz), 3.47−3.38 (1H,

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m), 3.33−3.24 (1H, m), 1.94−1.85 (2H, m). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 154.47 (C), 150.29 (CH), 121.68 (CH), 52.78 (CH), 48.53 (CH_2), 37.89 (CH_2). ESI-MS. Calcd for $[M + H]^+$: *m/z* 178.1090. Found: *m/z* 178.1092.

*(±)-Ethyl 4-(4-Aminophenyl)-4-(pyridin-4-yl)butanoate (**6**).* Compound (±)-**5** was prepared according to the literature procedure[28] showed spectroscopic data in good agreement with those reported. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.54 (2H, d, *J* = 6.1 Hz), 8.17 (2H, d, *J* = 8.8 Hz), 7.39 (2H, d, *J* = 8.8 Hz), 7.14 (2H, d, *J* = 6.3 Hz), 4.18−3.96 (3H, m), 2.48−2.34 (2H, m), 2.26 (2H, t, *J* = 7.2 Hz), 1.23 (3H, t, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 172.49 (C), 151.12 (C), 150.34 (CH), 149.73 (C), 146.98 (C), 128.76 (CH), 124.07 (CH), 123.00 (CH), 60.68 (CH_2), 49.46 (CH), 32.01 (CH_2), 29.53 (CH_2), 14.18 (CH_3). ESI-MS. Calcd for $[M + H]^+$: *m/z* 315.1339. Found: *m/z* 315.1353.

(±)-**5a** (277.3 mg, 0.882 mmol) was dissolved in EtOH (20 mL) and palladium/carbon (100 mg, 5% w/w) added to the degassed solution. The mixture was hydrogenated at atmospheric pressure and room temperature for 24 h. The solution was filtered to remove the catalyst. The resulting filtrate was purified by column chromatography (SiO_2; 8:2 EtOAc/hexane), yielding (±)-**6** as a yellow oil (70%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.46 (2H, d, *J* = 5.6 Hz), 7.19 (2H, d, *J* = 6.0 Hz), 6.97 (2H, d, *J* = 8.3 Hz), 6.63 (2H, d, *J* = 8.5 Hz), 4.10 (2H, q, *J* = 7.1 Hz), 3.83 (1H, t, *J* = 7.5 Hz), 2.35−2.28 (2H, m), 2.28−2.22 (2H, m), 1.23 (3H, t, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 173.36 (C), 155.10 (C), 149.26 (CH), 145.55 (C), 131.77 (CH), 128.96 (CH), 123.42 (CH), 115.58 (CH), 60.62 (CH_2), 49.19 (CH), 32.63 (CH_2), 30.08 (CH_2), 14.34 (CH_3). ESI-MS. Calcd for $[M + H]^+$: *m/z* 285.1597. Found: *m/z* 285.1605.

*(±)-4-(4-Aminophenyl)-4-(pyridin-4-yl)butan-1-ol (**7**).* A solution of (±)-**6** (306.5 mg, 1.08 mmol) in dried THF (40 mL) was added dropwise at 0 °C under an argon atmosphere to a suspension of $LiAlH_4$ (2 equiv) in dried THF (10 mL). The resulting mixture was stirred overnight under an argon atmosphere at room temperature. The reaction was quenched with a mixture of THF/ice mixture and stirred for a few hours. The resulting white suspension was filtered and the obtained solid washed with MeOH. The solvent was removed under vacuum and purified by column chromatography (SiO_2; EtOAc/MeOH) to yield (±)-**7** as a yellow oil (61%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.45 (2H, d, *J* = 6.1 Hz), 7.14 (2H, d, *J* = 6.2 Hz), 6.98 (2H, d, *J* = 8.3 Hz), 6.62 (2H, d, *J* = 8.5 Hz), 3.77 (1H, t, *J* = 7.9 Hz), 3.64 (2H, t, *J* = 6.4 Hz), 2.12−2.01 (2H, m), 1.58−1.45 (2H, m). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 154.85 (C), 149.96 (CH), 145.37 (C), 133.12 (C), 128.92 (CH), 123.38 (CH), 115.61 (CH), 62.75 (CH_2), 49.89 (CH), 31.42 (CH_2), 31.21 (CH_2). ESI-MS. Calcd for $[M + H]^+$: *m/z* 243.1491. Found: *m/z* 243.1501.

*(±)-4-[4-Azido-1-(pyridin-4-yl)butyl]aniline (**8**).* Compound (±)-**7a** was prepared under the same conditions as those described above for (±)-**3a**, yielding (±)-**7a** as a brown oil (98%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.49 (2H, br s), 7.17 (2H, d, *J* = 4.5 Hz), 6.98 (2H, d, *J* = 8.3 Hz), 6.63 (2H, d, *J* = 8.5 Hz), 3.78 (1H, t, *J* = 7.9 Hz), 3.53 (2H, t, *J* = 6.5 Hz), 2.19−2.10 (2H, m), 1.79−1.67 (2H, m).

Compound (±)-**8** was prepared under the same conditions as those described above for (±)-**4**, yielding (±)-**8** as a dark brown oil (86%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.48 (2H, d, *J* = 6.2 Hz), 7.12 (2H, d, *J* = 6.3 Hz), 6.98 (2H, d, *J* = 8.3 Hz), 6.63 (2H, d, *J* = 8.5 Hz), 3.78 (1H, t, *J* = 7.8 Hz), 3.29 (2H, t, *J* = 6.7 Hz), 2.07 (2H, dd, *J* = 15.8 and 7.8 Hz), 1.62−1.48 (2H, m). ^{13}C ($CDCl_3$, 125 MHz): δ 154.38 (C), 150.07 (CH), 145.34 (C), 132.62 (C), 128.85 (CH), 123.17 (CH), 115.58 (CH), 51.44 (CH_2), 49.68 (CH), 32.25 (CH_2), 27.45 (CH_2). ESI-MS. Calcd for $[M + H]^+$: *m/z* 268.1556. Found: *m/z* 268.1556.

Synthesis of Ligands 9−17. *General Synthetic Procedure.* The (dinitrophenyl)pyridinium salt (DNPBZ·Cl or DNPBP·Cl) was dissolved in EtOH, and the corresponding amine of type (±)-A was added in the proper ratio and stirred in the reaction conditions specified in Table 1. After the solution was cooled, the solvent was removed under vacuum to leave a solid residue, which was subjected to flash chromatography [SiO_2; 4:1:1 CH_3CN/NaCl(aq) (0.6 M)/MeOH]. The ligand-containing fractions were combined, and the solvent was removed under vacuum. Water (20 mL) was then added to the obtained a residue and the aqueous phase washed with EtOAc (3 × 10 mL). The aqueous layer was then concentrated under vacuum to yield (±)-L·Cl (yields on Table 1)

In order to modulate the solubility of the salts in aqueous or organic solvents, a series of subsequent metathesis reactions were performed. First the corresponding chloride salt (±)-L·Cl was dissolved in water and then KPF_6 was added into the solution until no further precipitation was observed. The obtained yellow solid was filtered and washed with water to yield (±)-L·PF_6.

In order to obtain the corresponding water-soluble noncoordinating nitrate salt (±)-L·NO_3, a mixture of ligand as hexafluorophosphate salt and Amberlite CG-400 (300 mg) was suspended in water and stirred for 24 h at room temperature. The resin was then removed by filtration and the solvent dried under vacuum to yield (±)-L·Cl. Then, the ligand as chloride salt was dissolved in water and 1 equiv of $AgNO_3$ added, and this solution was stirred at room temperature for 12 h with exclusion of light. Finally, the mixture was filtered to remove the AgCl precipitate formed, and the solvent was evaporated under vacuum to yield (±)-L·NO_3.

*(±)-**9**·NO_3.* Hygroscopic brownish solid. ^{1}H NMR (D_2O, 500 MHz): δ 9.93 (2H, s), 9.65 (2H, s), 8.67 (2H, d, *J* = 6.4 Hz), 8.60 (2H, d, *J* = 9.1 Hz), 8.46 (2H, d, *J* = 9.1 Hz), 7.70 (2H, d, *J* = 6.4 Hz), 6.78−6.60 (1H, m), 3.82−3.78 (1H, m), 3.60−3.55 (1H, m), 3.12−2.99 (2H, m). ^{13}C NMR (D_2O, 125 MHz): δ 149.95 (CH), 146.96 (CH);, 145.90 (C), 137.41 (CH), 131.11 (CH), 129.42 (C), 128.78 (C), 126.28 (C), 125.95 (CH), 124.18 (C), 122.97 (CH), 72.04 (CH), 57.07 (CH_2), 35.16 (CH_2).

*(±)-**9**·PF_6.* Hygroscopic brownish solid. ^{1}H NMR (CD_3CN, 500 MHz): δ 9.86 (2H, s), 9.72 (2H, s), 8.71 (2H, d, *J* = 9.1 Hz), 8.69 (2H, d, *J* = 6.4 Hz), 8.52 (2H, d, *J* = 9.1 Hz), 7.53 (2H, d, *J* = 6.4 Hz), 6.53 (1H, dd, *J* = 8.6 and 6.7 Hz), 3.73−3.64 (1H, m), 3.45−3.35 (1H, m), 2.91−2.84 (2H, m). ^{13}C NMR (CD_3CN, 125 MHz): δ 151.82 (CH), 149.31 (CH), 145.79 (C), 138.59 (CH), 132.25 (CH), 130.40 (C), 130.27 (C), 126.95 (CH), 125.04 (C), 123.65 (CH), 73.35 (CH), 57.87 (CH_2), 36.57 (CH_2). ESI-MS. Calcd for $[M - PF_6]^+$: *m/z* 340.1444. Found: *m/z* 340.1452. Anal. Calcd $C_{22}H_{18}F_6N_3OP$: C, 54.44; H, 3.74; N, 8.66. Found: C, 54.18; H, 3.86; N, 8.35.

*(±)-**10**·NO_3.* Hygroscopic brownish solid. ^{1}H NMR (D_2O, 500 MHz): δ 9.95 (2H, s), 9.66 (2H, s), 8.68 (2H, d, *J* = 5.3 Hz), 8.63 (2H, d, *J* = 9.2 Hz), 8.48 (2H, d, *J* = 9.1 Hz), 7.70 (2H, d, *J* = 5.3 Hz), 6.68 (1H, dd, *J* = 9 and 6.4 Hz), 3.64 (1H, m), 3.43 (1H, m), 5.12 (2H, m). ^{13}C NMR (D_2O, 125 MHz): δ 150.03 (CH), 147.01 (CH), 145.47 (C), 137.28 (CH), 131.21 (CH), 129.50 (C), 128.80 (C), 126.26 (C), 125.92 (CH), 124.10 (C), 122.90 (CH), 72.32 (CH), 47.05 (CH_2), 32.09 (CH_2).

*(±)-**10**·PF_6.* Hygroscopic brownish solid. ^{1}H NMR (CD_3CN, 500 MHz): δ 9.87 (2H, s), 9.71 (2H, s), 8.725 (2H, d, *J* = 9.1 Hz), 8.69 (2H, d, *J* = 6.2 Hz), 8.54 (2H, d, *J* = 9.1 Hz), 7.53 (2H, d, *J* = 6.2 Hz), 6.40 (1H, dd, *J* = 8.6−6.8 Hz), 3.54 (1H, dt, *J* = 13.0−6.2 Hz), 3.40 (1H, dt, *J* = 13.1−6.5 Hz), 3.06−2.94 (2H, m). ^{13}C NMR (CD_3CN, 125 MHz): δ 151.92 (CH), 149.38 (CH), 145.07 (C), 138.33 (CH), 132.39 (CH), 130.59 (C), 130.36 (C), 129.97 (CH), 126.94 (C), 124.95 (C), 123.56 (CH), 73.56 (CH), 48.04 (CH_2), 33.42 (CH_2). ESI-MS. Calcd for $[M - PF_6]^+$: *m/z* 365.1509. Found: *m/z* 365.1508. Anal. Calcd $C_{22}H_{17}F_6N_6P$: C, 51.77; H, 3.36; N, 16.47. Found: C, 51.45; H, 3.00; N, 16.40.

*(±)-**11**·NO_3.* Hygroscopic yellowish solid. ^{1}H NMR (D_2O, 500 MHz): δ 9.89 (2H, s), 9.56 (2H, s), 8.56 (2H, d, *J* = 9.1 Hz), 8.53 (2H, d, *J* = 5.4 Hz), 8.45 (2H, d, *J* = 9.1 Hz), 7.95 (2H, d, *J* = 8.5 Hz), 7.82 (2H, d, *J* = 8.5 Hz), 7.60 (2H, d, *J* = 5.7 Hz),4.37 (1H, t *J* = 7.8 Hz), 4.11 (2H, q, *J* = 7.1 Hz), 2.58 (2H, dd, *J* = 14.7 and 7.3 Hz), 2.47 (2H, t, *J* = 7.2 Hz), 1.25 (3H, t, *J* = 7.1 Hz). ^{13}C NMR (D_2O, 125 MHz): δ 175.90 (C), 155.34 (C), 147.68 (CH), 146.85 (CH), 146.01 (C), 142.37 (C), 138.01 (CH), 131.10 (CH), 130.36 (CH), 128.63 (C), 127.86 (C), 126.08 (C), 126.01 (CH), 125.22 (CH), 124.26 (CH), 123.79 (C), 61.87 (CH_2), 49.17 (CH), 32.32 (CH_2), 28.89 (CH_2), 13.22 (CH_3).

*(±)-**11**·PF_6.* Hygroscopic yellowish solid. ^{1}H NMR (CD_3CN, 500 MHz): δ 9.92 (2H, s), 9.79 (2H, s), 9.78 (2H, d, *J* = 9.1 Hz), 8.65 (2H, d, *J* = 6.9 Hz), 8.61 (2H, d, *J* = 9.0 Hz), 8.00 (2H, d, *J* = 6.9 Hz),

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7.92 (2H, d, J = 8.6 Hz). 7.78 (2H, d, J = 8.6 Hz), 4.59 (1H, t, J = 7.9 Hz), 4.11 (2H, q, J = 7.1 Hz), 2.59−2.50 (2H, m), 2.35 (2H, t, J = 7.4 Hz), 1.23 (3H, t, J = 7.1 Hz). ^{13}C NMR (CD_3CN, 125 MHz): δ 173.14 (C), 149.45 (CH), 145.31 (C), 144.15 (C), 143.10 (CH), 139.28 (CH), 132.67 (CH), 131.50 (CH), 130.04 (C), 129.81 (C), 127.65 (CH), 127.05 (C), 126.90 (CH), 125.06 (C), 61.43 (CH_2), 50.38 (CH), 32.49 (CH_2), 30.16 (CH_2), 14.51 (CH_3). ESI-MS. Calcd for $[M - PF_6]^+$: m/z 472.2019. Found: m/z 472.2023. Anal. Calcd $C_{31}H_{26}F_6N_3O_2P$: C, 60.29; H, 4.24; N, 6.80. Found: C, 60.16; H, 4.20; N, 6.57.

*(±)-**12**·NO$_3$*. Hygroscopic yellowish solid. ^{1}H NMR (D_2O, 500 MHz): δ 9.90 (2H, s), 9.63 (2H, s), 8.61 (2H, d, J = 9.1 Hz), 8.52−8.46 (4H, m), 7.93 (2H, d, J = 8.5 Hz), 7.82 (2H, d, J = 8.6 Hz), 7.52 (2H, d, J = 6.1 Hz), 4.33 (1H, t, J = 8.0 Hz), 3.42 (2H, t, J = 6.7 Hz), 2.32 (2H, dd, J = 15.6 and 7.9 Hz), 1.72−1.60 (2H, m). ^{13}C NMR (D_2O, 125 MHz): δ 154.52 (C), 148.78 (CH), 147.01 (C), 146.91 (CH), 142.35 (C), 138.06 (CH), 131.11 (CH), 130.22 (CH), 128.71 (C), 126.21 (C), 126.06 (CH), 125.13 (CH), 124.01 (C), 123.83 (CH), 50.87 (CH_2), 49.28 (CH), 31.01 (CH_2), 26.39 (CH_2).

*(±)-**12**·PF$_6$*. Hygroscopic beige solid.^{1}H NMR (CD_3CN, 500 MHz): δ 9.91 (2H, s), 9.89 (2H, s), 8.82 (2H, d, J = 9.1 Hz), 8.67 (2H, d, J = 9.1 Hz), 8.64 (2H, br s), 8.03 (2H, d, J = 8.7 Hz), 7.87 (2H, d, J = 8.6 Hz), 7.70 (2H, d, J = 6.4 Hz), 3.47−3.41 (2H, m), 2.43−2.35 (2H, m), 1.75−1.65 (2H, m). ^{13}C NMR (CD_3CN, 125 MHz): δ 149.85 (CH), 148.04 (C), 144.32 (C), 139.33 (CH), 133.06 (CH), 131.70 (CH), 130.59 (C), 130.36 (C), 127.56 (C),127.32 (CH), 126.95 (CH), 125.92 (CH), 125.51 (C), 52.32 (CH_2), 51.37 (CH), 32.80 (CH_2), 28.21 (CH_2). ESI-MS. Calcd for $[M - PF_6]^+$: m/z 455.1978. Found: m/z 455.1985. Anal. Calcd $C_{29}H_{23}F_6N_6P$: C, 58.00; H, 3.86; N, 14.00. Found: C, 58.06; H, 4.01; N, 14.92.

*(±)-**13**·NO$_3$*. Hygroscopic brown solid. ^{1}H NMR (500 MHz, D_2O): δ 9.06 (2H, d, J = 6.9 Hz), 8.70 (2H, d, J = 6.3 Hz), 8.56 (2H, d, J = 6.4 Hz), 8.39 (2H, d, J = 6.9 Hz), 7.83 (2H, d, J = 6.3 Hz), 7.49 (2H, d, J = 6.4 Hz), 6.19 (1H, dd, J = 9.0 and 6.4 Hz), 3.67 (1H, ddd, J = 11.6, 6.3, and 5.1 Hz), 3.50 (1H, ddd, J = 11.9, 7.2, and 4.8 Hz), 2.82−2.63 (2H, m). ^{13}C NMR (125 MHz, D_2O): δ 155.10(C), 150.07 (CH), 149.80 (CH), 145.28 (C), 144.22 (CH), 142.23 (C), 126.59 (CH), 122.83 (CH), 122.47 (CH), 70.57 (CH), 56.99 (CH_2), 34.63 (CH_2).

*(±)-**13**·PF$_6$*. Hygroscopic brown solid. ^{1}H NMR (500 MHz, $CDCN_3$): δ 8.92 (2H, d, J = 7.1 Hz), 8.88 (2H, d, J = 6.2 Hz), 8.72 (2H, d, J = 6.3 Hz), 8.36 (2H, d, J = 7.0 Hz), 7.82 (2H, d, J = 6.2 Hz), 7.48 (2H, d, J = 6.7 Hz), 6.17 (1H, dd, J = 9.3 and 6.0 Hz), 3.69 (1H, m), 3.46 (1H, m), 2.79−2.59 (2H, m). ^{13}C NMR (125 MHz, $CDCN_3$): δ 155.19 (C), 151.10 (CH), 150.83 (CH), 144.72 (C), 144.26 (CH), 141.12 (C), 126.51 (CH), 122.60 (CH), 121.76 (CH), 70.80 (CH), 56.79 (CH_2), 34.96 (CH_2). ESI-MS. Calcd for $[M - PF_6]^+$: m/z 292.1444. Found: m/z 292.1443. Anal. Calcd $C_{18}H_{18}F_6N_3OP$: C, 49.44; H, 4.15; N, 9.61. Found: C, 49.30; H, 4.01; N, 9.73.

*(±)-**14**·NO$_3$*. Hygroscopic yellow solid.^{1}H NMR (D_2O, 500 MHz): δ 9.16 (2H, d, J = 6.8 Hz), 8.79 (2H, d, J = 6.2 Hz), 8.66 (2H, d, J = 6.2 Hz), 8.50 (2H, d, J = 6.6 Hz), 7.92 (2H, d, J = 6.3 Hz), 7.59−7.51 (2H, m), 6.26 (1H, dd, J = 8.6 and 6.7 Hz), 3.63−3.55 (1H, m), 3.50−3.40 (1H, m), 2.97−2.89 (1H, m), 2.88−2.79 (1H, m). ^{13}C NMR (D_2O, 125 MHz): δ 155.27 (C), 150.03 (CH), 149.90 (CH), 144.80 (C), 144.14 (CH), 142.18 (C), 126.74 (CH), 122.81 (CH), 122.48 (CH), 70.85 (CH), 46.92 (CH_2), 31.63 (CH_2), 31.50 (CH_2).

*(±)-**14**·PF$_6$*. Hygroscopic yellow solid.^{1}H NMR (CD_3CN, 500 MHz): δ 8.89 (2H, d, J = 7.0 Hz), 8.85 (2H, d, J = 6.2 Hz), 8.70 (2H, d, J = 6.2 Hz), 8.35 (2H, d, J = 7.0 Hz), 7.78 (2H, d, J = 6.2 Hz), 7.43 (2H, d, J = 6.0 Hz), 6.00 (1H, dd, J = 8.9−6.5 Hz), 3.58−3.47 (1H, m), 3.47−3.33 (1H, m), 2.83−2.65 (2H, m). ^{13}C NMR (CD_3CN, 125 MHz): δ 156.49 (C), 152.20 (CH), 151.98 (CH), 145.14 (CH), 144.56 (C), 141.86 (C), 127.76 (CH),123.38 (CH), 122.86 (CH), 71.93 (CH), 47.96 (CH_2), 32.85 (CH_2). ESI-MS. Calcd for $[M - PF_6]^+$: m/z 317.1509. Found: m/z 317.1518. Anal. Calcd $C_{18}H_{17}F_6N_6P$: C, 46.76; H, 3.71; N, 18.18. Found: C, 46.63; H, 3.84; N, 18.11.

*(±)-**15**·NO$_3$*. Hygroscopic yellow waxy solid. ^{1}H NMR (D_2O, 500 MHz): δ 9.17 (2H, d, J = 7.1 Hz), 8.81 (2H, d, J = 6.3 Hz), 8.56 (2H, d, J = 7.0 Hz), 8.46 (2H, d, J = 6.2 Hz), 7.99 (2H, d, J = 6.3 Hz), 7.76 (2H, d, J = 8.7 Hz), 7.71 (2H, d, J = 8.7 Hz), 7.46 (2H, d, J = 6.2 Hz), 4.26 (1H, t, J = 7.8 Hz), 4.06 (2H, q, J = 7.2 Hz), 2.52 (2H, dd, J = 15.5 and 8.3 Hz), 2.42 (2H, t, J = 7.1 Hz), 1.22 (3H, t, J = 7.2 Hz). ^{13}C NMR (D_2O, 125 MHz): δ 174.94 (C), 154.62 (C), 153.62 (C), 150.02 (CH), 148.88 (CH), 146.37 (C), 144.56 (CH), 142.32 (C), 141.06 (C), 130.07 (CH), 125.95 (CH), 124.32 (CH), 123.74 (CH), 122.52 (CH), 61.74 (CH_2), 48.97 (CH), 32.31 (CH_2), 28.81 (CH), 13.20 (CH_3).

*(±)-**15**·PF$_6$*. Hygroscopic yellow waxy solid. ^{1}H NMR (300 MHz, CD_3CN): δ 9.00 (2H, d, J = 7.2 Hz), 8.90 (2H, d, J = 6.2 Hz), 8.54 (2H d, J = 6.1 Hz), 8.48 (2H, d, J = 7.1 Hz), 7.88 (2H, d, J = 4.5 Hz), 7.70 (4H, d, J = 2.7 Hz), 7.36 (2H, d, J = 5.9 Hz), 4.23 (1H, t, J = 7.8 Hz), 4.10 (2H, q, J = 7.1 Hz), 2.43 (2H, q, J = 7.3 Hz), 2.31 (2H, t, J = 7.2 Hz), 1.26 (3H, t, J = 7.1 Hz). ^{13}C NMR (125 MHz, CD_3CN): δ 172.52 (C), 154.92 (C), 152.26 (C), 151.25 (CH), 150.03 (CH), 147.17 (C), 144.83 (CH), 140.98 (C), 129.91 (CH), 125.95 (CH), 124.75 (CH), 123.17(CH), 121.91 (CH), 60.23 (CH_2), 48.99 (CH), 31.90 (CH_2), 29.33 (CH_2), 13.53 (CH_3). ESI-MS. Calcd for $[M - PF_6]^+$: m/z 424.2020. Found: m/z 424.2019.

*(±)-**16**·NO$_3$*. Hygroscopic yellow waxy solid. ^{1}H NMR (D_2O, 500 MHz): δ 9.17 (2H, d, J = 7.0 Hz), 8.82 (2H, d, J = 4.6 Hz), 8.52 (2H, d, J = 6.9 Hz), 8.47 (2H, s), 7.99 (2H, d, J = 6.3 Hz), 7.75 (2H, d, J = 8.7 Hz), 7.71 (2H, d, J = 8.7 Hz), 7.47 (2H, d, J = 4.4 Hz), 4.26 (1H, t, J = 7.9 Hz), 3.64 (2H, t, J = 6.5 Hz), 2.23 (2H, dd, J = 15.7 and 8.0 Hz), 1.55 (2H, dt, J = 13.4 and 6.5 Hz). ^{13}C NMR (D_2O, 125 MHz): δ 154.60 (C), 154.49 (C), 150.05 (CH), 148.85 (CH), 147.29 (C), 144.62 (CH), 142.36 (C), 140.89 (C), 130.05 (CH), 125.94 (CH), 124.26 (CH), 122.55 (CH), 61.35 (CH_2), 49.35 (CH), 30.15 (CH_2), 29.51 (CH_2).

*(±)-**16**·PF$_6$*. Hygroscopic yellow waxy solid. ^{1}H NMR (CD_3CN, 500 MHz): δ 8.98 (2H, d, J = 7.1 Hz), 8.88 (2H, d, J = 6.2 Hz), 8.51 (2H, d, J = 5.2 Hz), 8.46 (2H, d, J = 7.1 Hz), 7.82 (2H, d, J = 6.2 Hz), 7.69−7.66 (4H, m), 7.36 (2H, d, J = 6.1 Hz), 4.20 (1H, t, J = 7.9 Hz), 3.54 (2H, t, J = 6.3 Hz), 2.24−2.15 (2H, m), 1.52−1.39 (2H, m). ^{13}C NMR (CD_3CN, 125 MHz): δ 155.89 (C), 154.55 (C), 152.30 (CH), 150.68 (CH), 149.01 (C), 145.85 (CH), 141.94 (C), 130.91 (CH), 126.96 (CH), 125.65 (CH), 124.33 (CH), 122.94 (CH), 62.06 (CH_2), 50.69 (CH), 31.72 (CH_2), 31.60 (CH_2). ESI-MS. Calcd for $[M - PF_6]^+$: m/z 382.1913. Found: m/z 382.1919.

*(±)-**17**·NO$_3$*. Hygroscopic yellow waxy solid. ^{1}H NMR (D_2O, 500 MHz): δ 9.17 (2H, d, J = 7.1 Hz), 8.81 (2H, d, J = 6.3 Hz), 8.56 (2H, d, J = 7.0 Hz), 8.46 (2H, d, J = 6.2 Hz), 7.99 (2H, d, J = 6.3 Hz), 7.76 (2H, d, J = 8.8 Hz), 7.72 (2H, d, J = 8.7 Hz), 7.48 (2H, d, J = 6.2 Hz), 4.29 (1H, t, J = 7.9 Hz), 3.38 (2H, t, J = 6.7 Hz), 2.28 (2H, dd, J = 15.7 and 7.9 Hz), 1.61 (2H, dq, J = 12.9 and 6.5 Hz). ^{13}C NMR (D_2O, 125 MHz): δ 154.60 (C), 154.30 (C), 150.03 (CH), 148.89 (CH), 147.10 (C), 144.61 (CH), 142.39 (C), 140.95 (C), 130.02 (CH), 125.96 (CH), 124.32 (CH), 123.76 (CH), 122.54 (CH), 50.83 (CH_2), 49.22 (CH), 30.94 (CH_2), 26.34 (CH_2).

*(±)-**17**·PF$_6$*. Hygroscopic yellow waxy solid. ^{1}H NMR (CD_3CN, 500 MHz): δ 8.97 (2H, d, J = 7.1 Hz), 8.88 (2H, d, J = 6.2 Hz), 8.52 (2H, d, J = 6.1 Hz), 8.46 (2H, d, J = 7.1 Hz), 7.86 (2H, d, J = 6.2 Hz), 7.70−7.65 (4H, m), 7.35 (2H, d, J = 6.2 Hz), 4.19 (1H, t, J = 7.9 Hz), 3.37 (2H, t, J = 6.4 Hz), 2.27−2.18 (2H, m), 1.62−1.48 (2H, m). ^{13}C NMR (CD_3CN, 125 MHz): δ 155.95 (C), 153.76 (C), 152.28 (CH), 150.98 (CH), 148.66 (C), 145.86 (CH), 141.96 (C), 141.90 (C), 130.84 (CH), 126.95 (CH), 125.72 (CH), 124.17 (CH), 122.92 (CH), 51.81 (CH_2), 50.43 (CH), 32.28 (CH_2), 21.84 (CH_2). ESI-MS. Calcd for $[M - PF_6]^+$: m/z 407.1978. Found: m/z 407.1981.

Self-assembly of Metallacycles. *General Synthetic Procedure.* Complex (en)Pd(NO_3)$_2$ was added to a suspension of (±)-L·NO_3 in D_2O. Both compounds were mixed in 1:1 stoichiometry with a final concentration between 5 and 0.1 mM. The product was not isolated; data were taken from measurements on the reaction mixture.

*Metallacycle **18***. ^{1}H NMR (D_2O, 500 MHz): δ 9.38 (8H, d_{ap}), 9.03 (4H, d, J = 6.7 Hz), 8.36 (4H, d, J = 9.2 Hz), 8.28 (4H, d, J = 9.2 Hz), 7.97−7.92 (4H, m), 6.50 (2H, q, J = 7.7 Hz), 3.72 (4H, m), 3.14−3.01

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(4H, m), 3.00−2.92 (8H, m). ^{13}C NMR (D_2O, 125 MHz): δ 152.28 (CH), 148.09 (C), 147.99 (CH), 129.78 (CH), 129.40 (C), 128.12 (C), 127.64 (CH), 127.53−127.50 (C), 125.85 (CH), 124.42−124.40 (C), 72.32 (CH), 57.05 (CH_2), 46.86−46.81 (CH_2), 33.24 (CH_2), 22.18 (CH_2).

Metallacycle ***19***. ^{1}H NMR (D_2O, 500 MHz): δ 9.83 (8H, d_{ap}), 9.04 (4H, d, J = 6.6 Hz), 8.37 (4H, d, J = 9.2 Hz), 8.28 (4H, d, J = 9.2 Hz), 7.99−7.91 (4H, m), 6.49 (2H, q, J = 7.9 Hz), 3.62 (2H, dt, J = 12.4 and 7.5 Hz), 3.54 (2H, dt, J = 13.6 and 7.6 Hz), 3.16 (2H, dt, J = 14.9 and 7.6 Hz), 3.08 (2H, dt, J = 13.8 and 6.7 Hz), 3.02−2.90 (8H, m). ^{13}C NMR (D_2O, 125 MHz): δ 152.35 (CH), 148.05 (CH), 147.67−147.62 (C), 129.86 (CH), 129.48 (C), 128.13 (C), 127.65 (CH), 127.57−127.55 (C), 125.79 (CH), 124.40−124.37 (C), 72.50 (CH), 46.96 (CH_2), 46.87−46.82 (CH_2), 30.20 (CH_2), 30.14 (CH_2).

Metallacycle ***20***. ^{1}H NMR (D_2O, 500 MHz): δ 9.94 (4H, d_{ap}), 9.68 (4H, s), 8.82 (4H, d, J = 5.1 Hz), 8.57 (4H, d, J = 9.2 Hz), 8.47 (4H, d, J = 9.2 Hz), 7.57−7.54 (4H, m), 7.52−7.50 (4H, m), 7.44−7.40 (4H, m), 4.26 (2H, t, J = 7.7 Hz), 4.07 (4H, q, J = 7.1 Hz), 2.95−2.86 (2H, m), 2.83−2.72 (2H, m), 2.60−2.46 (4H, m), 2.47−2.37 (8H, m), 1.20 (6H, t, J = 7.2 Hz). ^{13}C NMR (D_2O, 125 MHz): δ 175.69 (C), 157.52 (C), 151.06 (CH), 148.10 (CH), 145.27 (C), 142.01 (C), 138.90 (CH), 129.87 (CH), 129.79 (CH), 128.81 (C), 128.54 (C), 128.05 (CH), 127.44 (C), 126.09 (CH), 126.06 (CH), 125.09 (C), 124.85 (CH), 61.82 (CH_2), 48.73−48.68 (CH), 46.87−46.80 (CH_2), 32.04 (CH_2), 27.33 (CH_2), 27.27 (CH_2), 13.19 (CH_3).

Metallacycle ***21***. ^{1}H NMR (D_2O, 500 MHz): δ 9.94 (4H, d_{ap}), 9.66 (4H, s), 8.81 (4H, d, J = 5.7 Hz), 8.56 (4H, d, J = 9.2 Hz), 8.46 (4H, d, J = 9.1 Hz), 7.56 (4H, d, J = 5.7 Hz), 7.50 (4H, d, J = 8.6 Hz), 7.44 (4H, d, J = 8.4 Hz), 4.26 (2H, t, J = 7.7 Hz), 3.38 (4H, t, J = 6.6 Hz), 3.02 (8H, s), 2.31−2.54 (4H, m), 1.66−1.53 (4H, m). ^{13}C NMR (D_2O, 125 MHz): δ 158.14 (C), 151.01 (CH), 148.09 (CH), 145.97 (C), 141.84 (C), 138.85 (CH), 129.84 (CH), 129.68 (CH), 128.77 (C), 128.51 (C), 128.01 (CH), 127.39 (C), 126.13 (CH), 125.04 (C), 124.77 (CH), 50.71 (CH_2), 49.04−49.00 (CH), 46.86−46.78 (CH_2), 29.38 (CH_2), 29.33 (CH_2), 26.14 (CH_2).

Metallacycle ***22***. ^{1}H NMR (500 MHz, D_2O): δ 8.96 (4H, d, J = 8.3 Hz), 8.86−8.75 (8H, m), 8.18−8.09 (4H, m), 7.74 (4H, d, J = 6.9 Hz), 7.71 (4H, d, J = 6.9 Hz), 6.12 (4H, t, J = 7.8 Hz), 3.68−3.52 (7H, m), 2.82 (8H, s), 2.82−2.64 (4H, m). ^{13}C NMR (125 MHz, D_2O): δ 152.30 (CH), 152.158 (C), 152.02 (CH), 148.05 (C), 144.28 (C), 143.69 (CH), 126.59 (CH), 125.78 (CH), 124.75 (CH), 70.52 (CH), 56.93 (CH_2), 46.74 (CH_2), 33.11 (CH_2).

Metallacycle ***23***. ^{1}H NMR (D_2O, 500 MHz): δ 9.05 (4H, d, J = 6.1 Hz), 8.92−8.86 (8H, m), 8.22 (4H, d, J = 6.3 Hz), 7.83 (4H, d, J = 6.8 Hz), 7.80 (4H, d, J = 6.8 Hz), 6.19 (2H, t, J = 7.6 Hz), 3.62−3.47 (4H, m), 2.97−2.84 (12H, m). ^{13}C NMR (D_2O, 125 MHz): δ 152.41 (CH), 152.33 (C), 152.05 (CH), 147.61 (C), 144.22−144.20 (C), 143.67 (CH), 126.72 (CH), 125.75 (CH), 124.77 (CH), 70.67 (CH), 46.84 (CH_2), 46.74 (CH_2), 30.12 (CH_2).

Metallacycle ***24***. ^{1}H NMR (500 MHz, D_2O): δ 8.98 (4H, d, J = 7.0 Hz), 8.94 (4H, d, J = 6.8 Hz), 8.68 (4H, d, J = 6.7 Hz), 8.31 (4H, d, J = 7.0 Hz), 7.93 (4H, d, J = 6.9 Hz), 7.59 (4H, d, J = 6.9 Hz), 7.55 (8H, s), 4.27 (2H, t, J = 7.8 Hz), 4.07 (4H, q, J = 7.1 Hz), 2.92 (8H, s), 2.58−2.47 (m, 4H), 2.42 (4H, t, J = 7.1 Hz), 1.20 (6H, t, J = 7.2 Hz). ^{13}C NMR (125 MHz, D_2O): δ 175.68 (C), 157.49 (C), 151.99 (CH), 151.04 (CH), 145.40 (C), 144.89 (C), 144.34 (CH), 140.94 (C), 129.67 (CH), 126.03 (CH), 125.95 (CH), 124.98 (CH), 124.21 (CH), 61.79 (CH_2), 48.94 (CH), 46.66 (CH_2), 32.09 (CH_2), 27.32 (CH_2), 13.19 (CH_3).

Metallacycle ***25***. ^{1}H NMR (D_2O, 500 MHz): δ 8.98 (4H, d, J = 6.9 Hz), 8.94 (4H, d, J = 6.7 Hz), 8.66 (4H, d, J = 6.6 Hz), 8.31 (4H, d, J = 6.9 Hz), 7.93 (4H, d, J = 6.7 Hz), 7.59 (4H, d, J = 6.6 Hz), 7.55 (8H, s), 4.27 (2H, t, J = 7.9 Hz), 3.64 (4H, t, J = 6.4 Hz), 2.92 (8H, s), 2.34−2.16 (4H, m), 1.61−1.46 (4H, m). ^{13}C NMR (D_2O, 125 MHz): δ 158.31 (C), 152.01 (CH), 151.96 (C), 150.95 (CH), 146.32 (C), 144.92 (C), 144.53 (CH), 140.78 (C), 129.58 (CH), 126.03 (CH), 126.01 (CH), 124.99 (CH), 124.16 (CH), 61.18 (CH_2), 49.36 (CH), 46.70−46.62 (CH_2), 29.33 (CH_2), 28.65 (CH_2), 28.61 (CH_2).

Metallacycle ***26***. ^{1}H NMR (D_2O, 500 MHz): δ 8.98 (4H, d, J = 6.9 Hz), 8.94 (4H, d, J = 6.6 Hz), 8.67 (4H, d, J = 6.4 Hz), 8.31 (4H, d, J = 6.8 Hz), 7.93 (4H, d, J = 6.7 Hz), 7.60 (4H, d, J = 6.6 Hz), 7.56 (8H, s), 4.28 (2H, t, J = 7.8 Hz), 3.38 (4H, t, J = 6.6 Hz), 2.92 (8H, s), 2.35−2.24 (4H, m), 1.65−1.55 (4H, m). ^{13}C NMR (D_2O, 125 MHz): δ 158.15 (C), 152.01 (CH), 151.00 (CH), 146.15 (C), 144.93 (C), 144.37 (CH), 140.83 (C), 129.58 (CH), 126.71 (C), 126.05 (CH), 120.01 (CH), 125.01 (CH), 124.21 (CH), 50.70 (CH_2), 49.24 (CH), 46.69−46.63 (CH_2), 29.43 (CH_2), 29.39 (CH_2), 26.17 (CH_2).

Metallacycle ***27***. A suspension of (±)-**L15** (3.2 mg, 0.006 mmol) and (en)Pt(NO_3)$_2$ (5 mg, 0.006 mmol) in water (14 mL) was heated at 150 °C for 3 h using microwave-assisted heating. After removal of the solvent under reduced pressure, the metallacycle **27** was obtained as a solid (7.8 mg, 95%). ^{1}H NMR (500 MHz, D_2O): δ 8.98 (4H, d, J = 7.0 Hz), 8.96 (4H, d, J = 6.9 Hz), 8.71 (4H, d, J = 7.1 Hz), 8.33 (4H, d, J = 6.6 Hz), 7.91 (4H, d, J = 6.9 Hz), 7.58 (4H, d, J = 6.8 Hz), 7.57 (8H, s), 4.30 (2H, q, J = 7.6 Hz), 4.07 (4H, q, J = 7.1 Hz), 2.85 (8H, s), 2.55−2.46 (4H, m), 2.44 (4H, t, J = 7.0 Hz), 1.21 (6H, t, J = 7.1 Hz). ^{13}C NMR (125 MHz, D_2O): δ 175.68 (C), 157.44 (C), 152.83 (CH), 151.78 (CH), 144.93 (C), 144.63 (C), 144.37 (CH), 140.96 (C), 129.69 (CH), 126.27 (CH), 125.98 (CH), 125.41 (CH), 124.23 (CH), 61.80 (CH_2), 48.90 (CH), 47.43 (CH_2), 32.09 (CH_2), 27.38 (CH_2), 13.19 (CH_3). ESI-MS. Calcd for $[M - 2PF_6]^{2+}$: m/z 969.1638. Found: m/z 969.1651. Calcd for $[M - 3PF_6 - H]^{2+}$: m/z 896.1778. Found: m/z 896.1784. Calcd for $[M - 4PF_6 - 2H]^{2+}$: m/z 823.1918. Found: m/z 823.1913. Calcd for $[M - 4PF_6 - H]^{+3}$: m/z 549.1303. Found: m/z 549.1322. Calcd for $[M - 5PF_6 - 2H]^{+3}$: m/z 500.4729. Found: m/z 500.4754.

Computational Methods. Full geometry optimizations of metallacycle **22** were performed in an aqueous solution employing DFT within the hybrid meta-GGA approximation with the M06[30] functional and the *Gaussian 09* package (revision B.01).[31] In these, we used the standard 6-31G(d,p) basis set for carbon, hydrogen, nitrogen, and oxygen atoms, while the palladium atom was treated using the LanL2DZ effective core potential of Wadt and Hay and its associated basis set.[32] No symmetry constraints have been imposed during the optimizations. The stationary points found on the potential energy surfaces as a result of geometry optimizations were tested to represent energy minima rather than saddle points via frequency analysis. The default values for the integration grid (75 radial shells and 302 angular points) and the self-consistent-field energy convergence criteria (10^{-8}) were used in all calculations. Solvent effects were included by using the polarizable continuum model. In particular, we used the integral equation formalism variant, as implemented in *Gaussian 09*.[33]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b02650.

1D and 2D NMR spectra for the compounds studied (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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