

Dynamic Self-Assembly of an M_3L_6 Molecular Triangle and an M_4L_8 Tetrahedron from Naked Pd^{II} Ions and Bis(3-pyridyl)-Substituted Arenes

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Abstract: The pyridine-appended non-chelating bidentate ligands 1,4-bis(3-pyridyl)benzene (**1**) and 4,4'-bis(3-pyridyl) biphenyl (**2**) were complexed with a naked Pd^{II} ion for the construction of molecular cage compounds. Prior to these experiments, the complexation of the ligands with *cis*-[Pd(en)(NO₃)₂] was also examined, because self-assemblies from the *cis*-protected Pd^{II} ion were expected to be simple motifs that constitute the assemblies from naked Pd^{II} ion. The structures of the self-assembled compounds resulting from **1** and [Pd(en)(NO₃)₂] depended on the solvent employed. In aqueous solution, an M_2L_2 trenchlike compound was obtained. In dimethyl sulfoxide, however,

a mixture of the M_2L_2 trench and an M_3L_3 macrocycle was found in equilibrium, the dynamic nature of which was confirmed by the concentration-dependent nature of the species. At higher concentration, an M_4L_4 macrocycle was mostly observed. The complexation of **1** with naked Pd^{II} ions was expected to produce novel structures that are combinations of the M_nL_n type frameworks. A peculiar tetrahedral M_4L_8 assembly was obtained quantitatively from **1** and Pd(NO₃)₂, rather than the smallest possible M_3L_6 double-walled triangle. In-

terestingly, the use of Pd(CF₃SO₃)₂ resulted in the sole formation of the latter structure. Thus, the anion is important as a template in the formation of these assemblies. Ligand **2**, which contains an extra *p*-phenylene unit compared to **1**, behaved in a similar manner when treated with [Pd(en)(NO₃)₂], but showed subtle differences with naked Pd^{II} ions. With Pd(NO₃)₂, **2** gave mostly a tetrahedron along with a double-walled triangle. With Pd(CF₃SO₃)₂, this longer ligand formed a double-walled triangle with a negligible amount of tetrahedra. A single discrete assembly of a perfect tetrahedron was obtained from **2** and Pd^{II} ions by choosing *p*-tosylate as a counterion.

Keywords: anions • cage compounds • palladium • self-assembly • template synthesis

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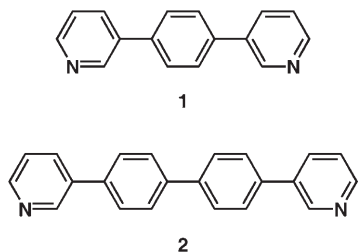
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Introduction

Synthesis of molecular structures from organic ligands and transition-metal ions through self-assembly has received privileged attention during the last decade.^[1] As the coordination geometry around transition-metal ions, the key corners, is usually predictable, the self-assembly structure that would result by the complexation of a metal ion with a designated ligand may be assumed a priori.^[2] However, the mode of arrangement of the participating components depends on many factors: steric requirements, thermodynamic stability, entropy cost of the final assembly, guest molecules if any, solvent, and so on.^[3] Thus, the prediction of a new structure from a designated ligand and a selected metal ion under a particular set of conditions is not always a straightforward task. In solution, two or more isomers or structures may coexist in dynamic equilibrium, depending on the directionality/flexibility of the ligand, especially when the metal–ligand bond of the system is labile.^[4,5] It is also possible in

certain cases to shift the equilibrium towards one of the compounds as a single/major product by suitable control of parameters such as solvent, guest molecules, temperature, time, and so on.^[6]

Herein, we describe the self-assembly of two bidentate nonchelating pyridine-appended ligands **1** and **2** with a



naked Pd^{II} ion. Whereas self-assembly with *cis*-protected Pd^{II} ions has been explored considerably,^[2a] little attention has been paid, to our surprise, to the use of naked Pd^{II} as metal centers^[7] in metal-directed self-assembly. As Pd^{II} ions are easy to handle, owing to their thermo- and photo-stability as well as the moderate lability of Pd^{II}–pyridine bonds, the establishment of very efficient molecular self-assembly systems should not be a problem. The orientation of four pyridyl groups around each Pd^{II} center gives rise to more possibilities for the dynamic self-assembly of two or more structures. In fact, we observed the dynamic self-assembly of two new types of architecture: a molecular double-walled triangle and a peculiar tetrahedron. We show herein that the dynamic equilibrium of the two compounds is controlled by counteranions. The ability of the anion to induce the selective assembly^[8] is also highlighted.

Results and Discussion

Complexation with a *cis*-Protected Pd^{II} Ion

First, we examined the complexation of **1** and **2** with *cis*-[Pd(en)(NO₃)₂]^[2a] because self-assemblies from the *cis*-protected Pd^{II} ion are expected to be simple motifs that constitute the assemblies from a naked Pd^{II} ion. In the following complexation experiments, the solutions obtained from H₂O or dimethyl sulfoxide (DMSO) were subjected to coldspray ionization (CSI)-MS,^[9] and those from D₂O or [D₆]DMSO were used for ¹H and ¹³C NMR spectroscopic measurement.

Abstract in Japanese:

裸のパラジウムイオンと直鎖状の 3-ピリジル二座架橋配位子を自己集合することにより、溝型 M₂L₂、三角形型 M₃L₃ や M₃L₆ および四面体型 M₄L₄ や M₄L₈ などの錯体を合成した。生成物は、使用する溶媒により変化し、水中では M₂L₂ が、DMSO 中では平衡の形で M₂L₂ と M₃L₃ が共存する。より高い濃度では、M₄L₄ が主生成物となる。さらに M₆L₆ と配位子の組み合わせから一部配位子が二重に架橋した四面体型 M₄L₈ が生成する。興味深いことに、カウンターアニオンを NO₃ アニオンから CF₃SO₃ アニオンに変えることにより M₄L₈ ではなく M₃L₆ が生成する。この事実は、錯形成においてアニオンの誘導効果が重要であることを示している。

Ligands **1** and **2** were prepared by Negishi coupling of 3-bromopyridine with 1,4-diiodobenzene or 4,4'-diiodobiphenyl in a single step with a general method. Products that assembled in a pure form in solution were isolated as powders, whereas no effort was made to segregate the assemblies that exist as a dynamic equilibrium of two or more compounds. The NMR spectrum obtained from a solution of the complex matched that of the corresponding isolated complex when redissolved in the deuterated solvent.

A Molecular Trench in an Aqueous Solution

Ligand **1** was mixed with [Pd(en)(NO₃)₂] (1:1) in D₂O (5 mM), and the suspension was stirred at 60°C for 1 h to obtain a clear solution. The proton NMR signals for the resulting complex were shifted downfield relative to those of **1** (Figure 1a), particularly for H_a and H_b (Δδ=0.55 and

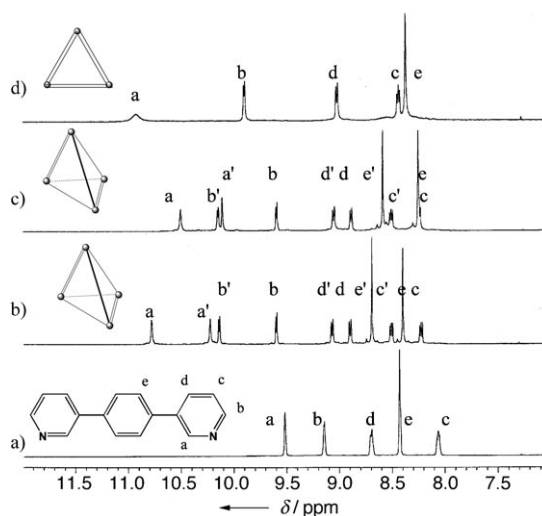


Figure 1. ¹H NMR spectra of a) ligand **1**, b) tetrahedron **7a**, c) tetrahedron **7b**, and d) double-walled triangle **6** (500 MHz, [D₆]DMSO, 25°C, TMS as external standard); a–e: double-walled edges, a'–e': single-walled edges.

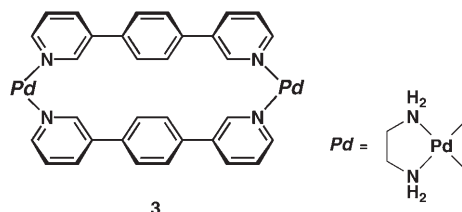
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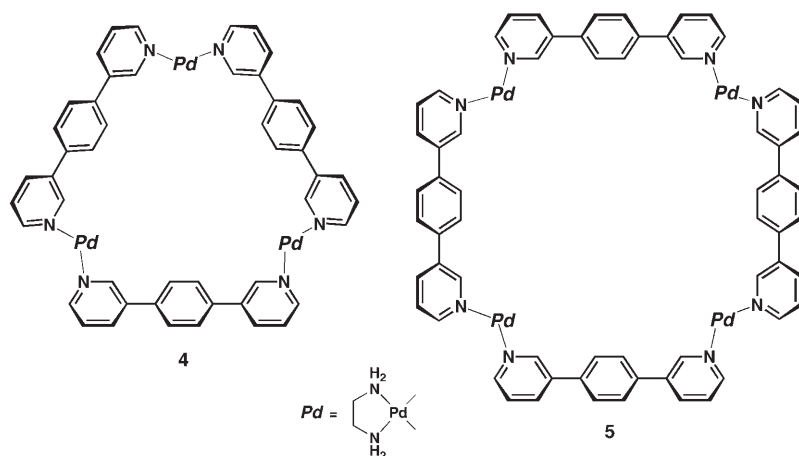
0.26 ppm, respectively); this shift can be ascribed to metal–ligand complexation. The simple pattern of the spectrum suggests the formation of a single species. Interestingly, the signal of H_c is shifted upfield ($\Delta\delta=0.35$ ppm). Considering the rigidity and ability of angular coordination of **1**, the smallest structure assumed for this condition is the M_2L_2 ^[10] trench **3**. CSI-MS measurements of the aqueous solution



(2% *N,N*-dimethylformamide (DMF), ligand concentration = 5 mM) showed the existence of this formulation, which was confirmed from its crystal structure (as discussed later). The upfield shift of the H_c signal above probably resulted from the ring current of adjacent aromatic rings of the complexed ligands held closely in a special position in **3**.

Dynamic Equilibrium of Molecular Trench, Triangle, and Square

The complexation of **1** (5 mM) with $[Pd(en)(NO_3)_2]$ was also performed in $[D_6]DMSO$. A dynamic-equilibrium mixture of two assemblies was observed in the solution as indicated by NMR spectroscopy. However, a single structure out of the two was almost invariably observed at a ligand concentration of 1 mM. All proton signals were shifted down-field except for the C_6H_4 signals, which showed a small upfield shift (also found in the case of **3** in D_2O), thus suggesting the formation of **3** at this concentration. Increasing the ligand concentration (e.g. 5 or 10 mM) resulted in the coexistence of structure **4**, as evident from a new set of signals that developed from the minor peaks seen at a concentration of 1 mM. In this case, the signal of C_6H_4 in **4** was shifted downfield, in contrast to the upfield shift of the signal of



C_6H_4 in the spectrum of **3**. Therefore, the hydrophobic shielding on C_6H_4 for **3** is no longer present in **4**. Thus, the constituent ligands in **4** are expected not to be very close to each other, unlike in **3**. The new signals became intense with increasing concentration and, from entropic considerations, **4** is considered as an M_3L_3 trinuclear molecular triangle.^[11] Because of their high solubility in DMSO, we could prepare the complexes at even higher concentrations. With a ligand concentration of 40 mM, **4** was the major product (Table 1),

Table 1. Percentage ligand distribution for **3**, **4**, and **5** at specified ligand concentrations.

Concentration of 1 [mmol] ^[a]	Ligand distribution [%] ^[b]		
	3	4	5
1	87	13	N ^[c]
5	58	42	N
10	44	56	N
20	29	61	10
40	18	58	24
100	7	36	57
200	N	20	80
400	N	12	88
500	N	8	92

[a] Concentration of **1** was varied (e.g. 1–500 mM) with appropriate amount of metal ion in $[D_6]DMSO$, upon which mixture of **3**, **4**, and **5** was obtained in a concentration-dependent manner. [b] Calculated from the integration of peaks corresponding to H_a in 1H NMR spectra. [c] N = intensity of observed peak is negligible.

along with a small amount of **3** and another new compound **5**, which is a tetranuclear M_4L_4 molecular square.^[12] At a ligand concentration of 500 mM, **5** was almost the only product. CSI-MS measurements strongly supported the NMR spectroscopic result and the formation of **3**, **4**, and **5**. Equilibrium between a molecular triangle and a square are often discussed.^[13] There are also reports on selective crystallization of this kind of species.^[13a,14] Herein is the first time a dinuclear species that is also in equilibrium is reported. Ligand **2** behaved in a similar way to **1**, as observed by 1H NMR spectroscopy.

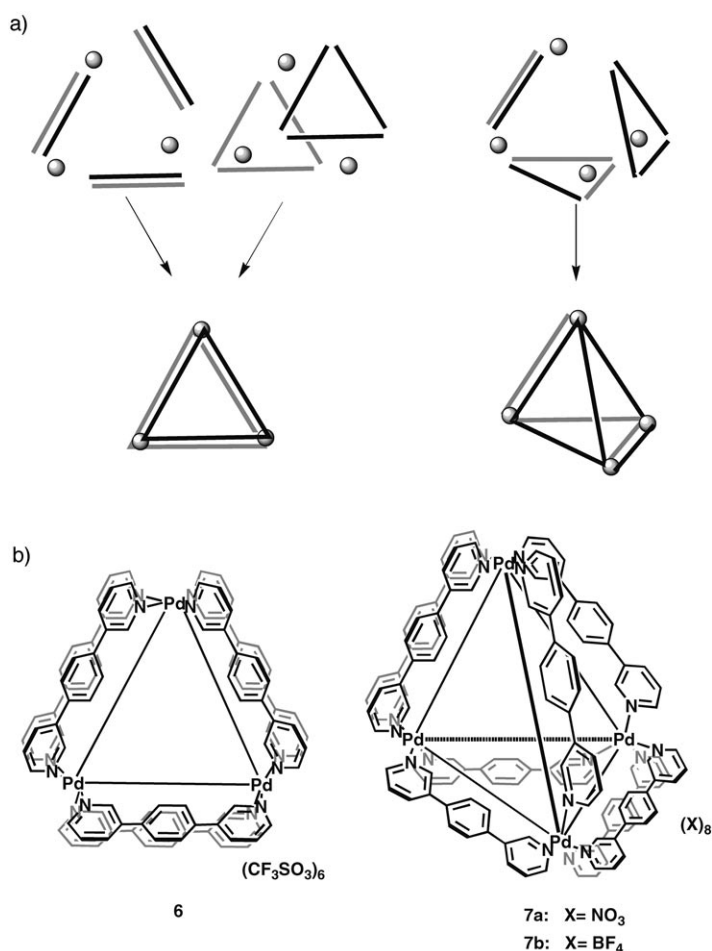
Complexation with a Naked Pd^{II} Ion

It was assumed that complexation of a naked Pd^{II} ion with **1** should result in new assemblies in which both trench and triangle-like moieties (corresponding to the frameworks of **3** and **4**, respectively) exist.

Molecular Tetrahedron from **1**

As described earlier, there is a dynamic equilibrium between **3** and **4** at moderate concentrations in DMSO. In principle, use of a naked Pd^{II} ion in com-

bination with **1** in DMSO should lead to structures that are composed of both the skeletons of M_2L_2 and M_3L_3 cyclic frameworks. The smallest structure logically considered is double-walled triangle **6** (Scheme 1). One can consider that



the backbone of **3** and two units of **4**, thus giving rise to four ligands in one environment and four in another. As shown in Scheme 1, **7a** corresponds to the formulation M₄L₈ and confers to the two sets of signals in the NMR spectrum a ratio of 1:1 for each proton type. Four ligands occupy four edges of the tetrahedron as a single-walled and another four ligands cover the remaining two edges as a double-walled combination. Formation of the double-walled M₄L₈ square was ruled out by consideration of the NMR spectroscopic evidence. All peaks of **7a** were assigned (Figure 1b) by ¹H-¹H COSY and NOESY spectra and by the comparison of its proton NMR spectrum with that of a mixture of **3** and **4**. Notably, cross-peaks were observed from the protons H_a (or H_b) of the two different sets in the NOESY spectrum of **7a** (Figure 2). This observation gives extra evidence that both sets of signals belong to a single compound and are

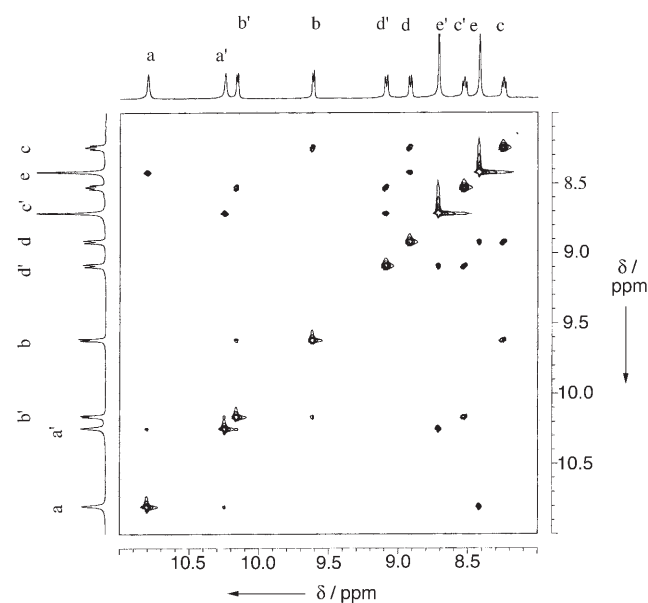


Figure 2. NOESY spectrum of **7a** (500 MHz, [D₆]DMSO, 25 °C, TMS as external standard); a-e: double-walled edges, a'-e': single-walled edges.

positioned close to each other, as the NOESY spectrum of a mixture of **3** and **4** does not exhibit such cross-peaks for H_a or H_b protons. A convincing crystal structure of **7a**, discussed below, provides the final evidence for the assembly.

Anion-Assisted Assembly of Pure Double-Walled Triangle and Tetrahedron from **1**

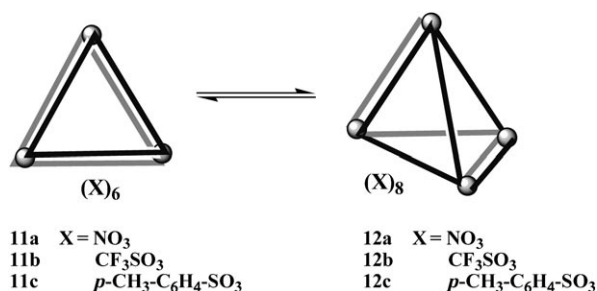
The role of cationic/neutral templates to dictate cage structures has been well-explored.^[15] Recently, there were also examples where anionic templates^[8] direct self-assembly in a selective manner. Various aspects of the role of anions in supramolecular chemistry^[16] are recently gaining importance. However, anion-templated synthesis is still at its infancy and deserves much more study for generalization. Since our cages are cationic, these are expected to encapsulate anionic guests. Therefore, the variation of anions associ-

ated with Pd^{II} centers was carried out in [D₆]DMSO to check the possibility of obtaining structure **6** and to understand their templating nature toward the Pd^{II}-linked cages.

Previous discussion herein describes that **1** and Pd(NO₃)₂ gave a peculiar tetrahedral assembly **7a**. With tetrafluoroborate as the anion, both CSI-MS and NMR spectroscopic studies indicated the sole formation of a tetrahedral structure **7b** (Figure 1c) that is similar to **7a**. However, the signals for protons H_a and H_c were shifted relatively less downfield compared to those for **7a**. This observation preliminarily suggests that a nitrate ion binds strongly to the cavity at the corners. Interestingly, the double-walled triangle structure of the framework of **6** was confirmed when triflate anion was used. A simple concentration-independent pattern of one set of five signals (Figure 1d) was observed, and CSI-MS supported the formulation M₃L₆.

Dynamic Equilibrium Between Double-Walled Triangle and Tetrahedron from **2** and Formation of Pure Tetrahedron

We designed a higher homologue of double-walled triangle/tetrahedron starting from the longer ligand **2**. Ligand **2**, like **1**, formed a mixture of molecular trench **8** and triangle **9** when treated with *cis*-protected Pd^{II} ions. At higher concentrations, square **10** could be also seen (the structures of **8–10** can be defined by replacing ligand **1** with ligand **2** in the structures of **3–5**, respectively). Thus, this system is also expected to give, upon complexation with naked Pd^{II} ions, double-walled triangle **11** and tetrahedron **12**, which are logically composed of the frameworks of **8** and **9**. When **2** was treated with naked Pd^{II} ions, the resulting self-assemblies were again found to be anion-dependent in nature. In this case, dynamic equilibrium between the two products is observed (Scheme 2). With nitrate as the anion, there is a dy-



Scheme 2. Schematic representation of the dynamic equilibrium between double-walled triangle and tetrahedron; the lines stand for ligand **2** and balls for the Pd^{II} ion. The structures **11a** and **12a** exist in dynamic equilibrium, as do **11b** and **12b**. However, only **12c** is formed and no trace of **11c** is observed.

amic equilibrium between **11a** and **12a** with a 1:1 ratio. With triflate, **11b** was predominantly observed along with a negligible proportion of **12b**. Since **2** contains one more *p*-phenylene ring than **1**, it is logical to check whether an aromatic sulfonate can act as a template to readily give a single structure. In fact, the use of *p*-tosylate leads to the formation of pure tetrahedron **12c** of the M₄L₈ framework, and

no trace of a double-walled triangle like **11c** was detected. A concentration study was not performed due to the constraint of solubility of complexes above a ligand concentration of 10 mmol. The formation of all the structures was supported by proton NMR spectroscopy and CSI-MS data. The crystal structure of **12c** was determined; the data showed the framework, but was not good enough for further discussion.

Crystal Structures

3: Single crystals of **3** were grown by slow evaporation of its aqueous-methanolic solution at room temperature. The crystal structure consists of molecules of **3** and water of crystallization. The cationic fragment is shown in Figure 3. The distance between the two metal centers is 11.3 Å, and the Pd–N bond distances are around 2.0 Å. The structure is in line with the spectroscopic evidence. Structure **3** is reminiscent of the tetrahedral assembly **7a** as discussed in next paragraph.

7a: Diffusion of acetone into a solution of **7a** in DMSO gave single crystals suitable for structure determination. The results of the XRD study (Figure 4) agrees with the structure predicted from spectroscopic evidence. The four Pd^{II}

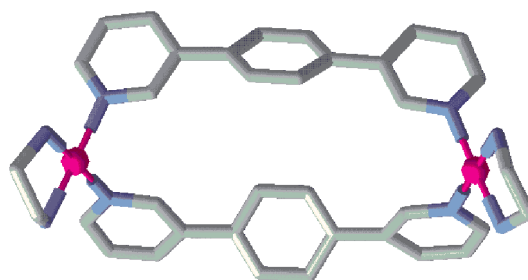


Figure 3. Representation of $[\text{Pd}(\text{en})_2(\mathbf{1})_2]^{4+}$ in the crystal structure of **3**; palladium (magenta), nitrogen (blue), carbon (gray).

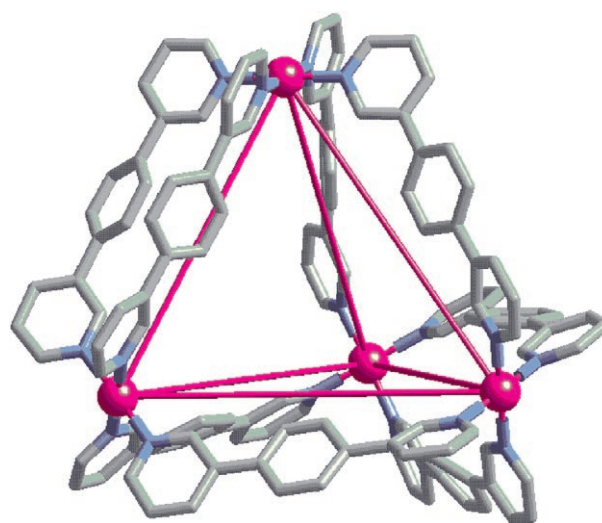


Figure 4. Representation of $[(\text{Pd})_4(\mathbf{1})_8]^{8+}$ in the crystal structure of **7a**; palladium (magenta), nitrogen (blue), carbon (gray).

ions involved in the structure occupy the apices of an imaginary tetrahedral array. All the metal centers have square-planar geometry with Pd–N bond distances of 1.9–2.0 Å. The average distance between terminal metal centers of single-walled edges is 12.2 Å, whereas that of double-walled edges is 11.4 Å. Four of the eight nitrate ions are outside the cavity, one bound axially on each Pd^{II} ion with a Pd–O distance of 3.0 Å. Two nitrate ions are in the cavity, one at an inner corner and the other penetrating one of the four faces of the tetrahedron. One nitrate ion is outside the cavity without any possible interaction, and the last one was not located. The remaining three inner corners of the cavity are occupied one by a water molecule and the other two by unresolved fragments. All four triangular windows of the tetrahedron are also covered, one with a nitrate ion as described above, two each with one DMSO molecule, and the fourth with an unresolved molecule similar to acetone. Thus, at least two nitrate ions interact with the cavity.

The structure **7a** is a unique molecular tetrahedron that deserves particular attention. The other reported structures of edge-capped tetrahedral self-assemblies driven by suitable metal ions consist of six ligand units, one at each edge of the tetrahedron.^[17] Herein, however, we have eight ligand moieties arranged in a typical fashion where two edges are double-walled and the remaining four edges are single-walled.

12c: Similarly, diffusion of acetone into a solution of **12c** in DMSO resulted in single crystals. The results of the XRD study confirmed the tetrahedral framework (Figure 5). However, the data were not good enough for further discussion.

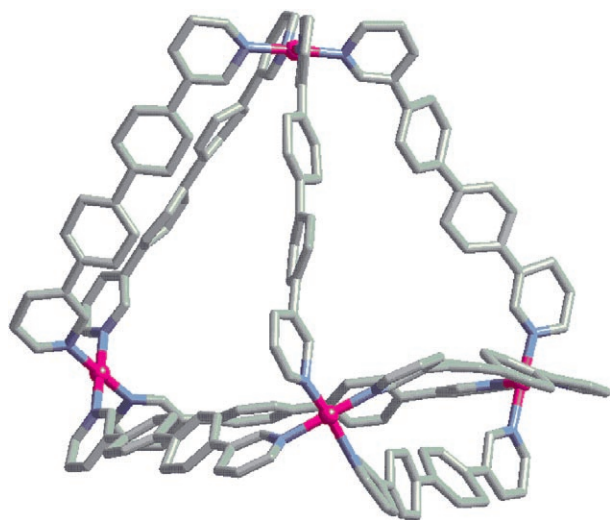


Figure 5. Representation of $[(\text{Pd})_4(\mathbf{2})_8]^{8+}$ in the crystal structure of **12c**; palladium (magenta), nitrogen (blue), carbon (gray).

Conclusions

In conclusion, we have shown the usability of a particular ligand to both *cis*-protected and naked Pd^{II} ions for self-assembly. The results show that metal-directed self-assembly

structures can be quantitatively obtained by proper tuning of the conditions, particularly with respect to the anion. The formation of peculiar molecular tetrahedrons provides a new class of examples to complement the family of tetrahedrons reported earlier.

Experimental Section

Material and Methods

All chemicals were of reagent grade and used without any further purification. Ethylenediamine was used for the *cis*-protection of Pd^{II} ions, as described earlier, to obtain *cis*-[Pd(en)(NO₃)₂]. Melting points were recorded on an electrical micro-melting-point apparatus (Yanaco) and were uncorrected. Deuterated solvents were acquired from Cambridge Isotopic Laboratories, Inc. and used as such for the complexation reactions and NMR spectroscopic measurements. NMR spectral data were recorded with a Bruker DRX 500 spectrometer at ambient temperature, and the chemical shift values reported here are with respect to an external tetramethylsilane (TMS) standard. CSI-MS data were measured with a four-sector (BE/BE) tandem mass spectrometer (JMS-700T, JEOL) equipped with the CSI source.

Crystallography

Single-crystal XRD data for **3** were obtained with a Rigaku AFC5S diffractometer with graphite-monochromated Cu_{Kα} radiation, whereas those of **7a** and **12c** were collected with a Siemens SMART/CCD diffractometer with Mo_{Kα} radiation. For the data of **3**, an empirical absorption correction was applied with the program DIFABS;^[18] structure refinement was performed by utilizing SHELX86.^[19] The data for **7a** and **12c** were corrected for absorption with the SADABS^[20] program; SHELXTL^[21] was used for structure solution and refinement. All nonhydrogen atoms were refined anisotropically. The H atoms were fixed in calculated positions and refined isotropically. Crystal data and structure refinement parameters are shown in Table 2. CCDC-297694, -297695, and -297117 contain the supplementary crystallographic data for **3**, **7a**, and **12c**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

Syntheses

1: Ligand **1** was prepared by the Negishi coupling of 3-bromopyridine with 1,4-diiodobenzene. Dry diethyl ether (100 mL) was placed in a three-necked flask under Ar atmosphere. It was cooled to –78 °C followed by the introduction of *n*BuLi (1.5 M in *n*-hexane, 33.33 mL, 50 mmol) with continuous stirring. 3-bromopyridine (7.27 g, 46 mmol) was then added dropwise, and the solution was stirred for another 30 min. The lithiated pyridine compound was converted into the corresponding organozinc salt by slow introduction of ZnCl₂ (0.5 M in THF, 100 mL, 50 mmol). The mixture was warmed to room temperature and allowed to stir for 1 h. A solution of 1,4-diiodobenzene (6.60 g, 20 mmol) in THF was added slowly followed by transfer of a suspension of the catalyst [Pd(PPh₃)₄] (2.31 g, 2 mmol) in THF through a canula. The mixture was then stirred at room temperature for 12 h. After the usual aqueous workup, the residue was purified by column chromatography over silica gel (CHCl₃/MeOH = 20:1) to obtain **1** as a pale solid (2.60 g, 56%). M.p.: 117–118 °C; ¹H NMR (500 MHz, CDCl₃, TMS): δ = 8.91 (d, *J* = 2.24 Hz, 2H; a), 8.63 (dd, *J* = 1.4, 4.7 Hz, 2H; b), 7.93 (td, *J* = 7.8, 2.0 Hz, 2H; d), 7.72 (s, 4H; e), 7.40 ppm (dd, *J* = 8.0, 5.0 Hz, 2H; c); ¹H NMR (500 MHz, D₂O, TMS): δ = 8.90 (s, 2H; a), 8.57 (d, *J* = 3.1 Hz, 2H; b), 8.23 (d, *J* = 5.9 Hz, 2H; d), 7.89 (s, 4H; e), 7.61 ppm (m, 4H; c); ¹H NMR (500 MHz, [D₆]DMSO, TMS): δ = 9.51 (s, 2H; a), 9.14 (d, *J* = 3.2 Hz, 2H; b), 8.70 (d, *J* = 7.3 Hz, 2H; d), 8.43 (s, 4H; e), 8.06 ppm (dd, *J* = 7.4 and 4.8 Hz, 2H; c); ¹³C NMR (125 MHz, [D₆]DMSO, TMS): δ = 149.7 (b), 148.7 (a), 137.8 (Cq), 135.9 (Cq), 135.1 (d), 128.6 (e), 125.0 ppm (c); elemental analysis: calcd (%) for C₁₆H₁₂N₂: C 82.73, H 5.21, N 12.06; found: C 82.67, H 5.10, N, 12.06.

Table 2. Crystallographic data and summary of data collection and refinement for structures **3**, **7a**, and **12c**.

	3	7a	12c
Empirical formula	C ₃₆ H ₄₄ N ₁₂ O ₁₅ Pd ₂	C ₁₈₂ H ₁₅₆ N ₂₄ O ₃₈ Pd ₄ S ₈	C ₅₁₁ H ₅₈₀ N ₃₁ O ₆₂ Pd ₈ S ₁₆
<i>M_r</i>	1097.61	3993.58	9512.22
<i>T</i> [K]	173(2)	193(2)	113(2)
λ [Å]	1.54178(Cu-K α)	0.71073(Mo-K α)	0.71073(Mo-K α)
Crystal system	monoclinic	triclinic	triclinic
Space group	<i>P</i> ₂ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	22.178(3)	20.705(3)	26.590(8)
<i>b</i> [Å]	12.998(2)	21.151(2)	26.735(8)
<i>c</i> [Å]	30.286(2)	22.278(3)	40.142(12)
α [°]	90.0	91.725(2)	87.676(6)
β [°]	98.138(8)	90.595(2)	79.046(6)
γ [°]	90.0	107.389(2)	85.476(6)
<i>V</i> [Å ³]	8642(1)	9304.0(19)	27920(15)
<i>Z</i>	8	2	2
<i>D_c</i> [g cm ⁻³]	1.687	1.426	1.131
<i>M</i> [mm ⁻¹]	7.428	0.550	0.374
<i>F</i> (000)	4448	4112	9966
Crystal size [mm ³]	0.35 × 0.18 × 0.35	0.20 × 0.15 × 0.15	0.33 × 0.17 × 0.09
θ range [°]	3.0 to 60.1	1.21 to 25.00	2.0 to 20.0
Index ranges	0 ≤ <i>h</i> ≤ 24, 0 ≤ <i>k</i> ≤ 14, -34 ≤ <i>l</i> ≤ 33	-24 ≤ <i>h</i> ≤ 22, -25 ≤ <i>k</i> ≤ 19, -26 ≤ <i>l</i> ≤ 26	-35 ≤ <i>h</i> ≤ 34, -35 ≤ <i>k</i> ≤ 35, -52 ≤ <i>l</i> ≤ 53
Reflections collected	13916	48020	342806
Independent reflections	13521	31665	134310
<i>R</i> _{int}	0.035	0.0519	0.3907
Completeness	100% (θ = 60.1°)	96.6% (θ = 25.0°)	95.6% (θ = 28.5°)
Max. and min. transmission	0.263 and 0.200	0.9220 and 0.8979	0.9671 to 0.8864
Refinement method	full-matrix-least-squares	full-matrix-block-least-squares on <i>F</i> ²	full-matrix-block-least-squares on <i>F</i> ²
Data/restraints/parameters	7942/0/1301	31665/0/2149	134310/4128/2617
Goodness-of-fit on <i>F</i> ²	1.92	1.392	1.097
Final <i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0654, <i>wR</i> ₂ = 0.0932	<i>R</i> ₁ = 0.1094, <i>wR</i> ₂ = 0.3154	<i>R</i> ₁ = 0.2169, <i>wR</i> ₂ = 0.4760
Largest diff. peak/hole [e Å ⁻³]	2.35 and -1.0	3.239 and -2.164	2.011 and -1.029

2: Ligand **2** was prepared by the Negishi coupling of 3-bromopyridine with 4,4'-diiodobiphenyl in a similar manner as described above for the synthesis of **1** (yield 74%). M.p.: 225–226 °C; ¹H NMR (500 MHz, CDCl₃, TMS): δ = 8.92 (d, *J* = 2.4 Hz, 2H; a), 8.62 (dd, *J* = 4.8, 1.6 Hz, 2H; b), 7.93 (td, *J* = 7.8, 2.1 Hz, 2H; d), 7.77 (d, *J* = 8.4 Hz, 4H; e), 7.70 (d, *J* = 8.4 Hz, 4H; f), 7.39 ppm (dd, *J* = 8.0, 4.9 Hz, 2H; c); ¹H NMR (500 MHz, [D₆]DMSO, TMS): δ = 9.51 (s, 2H; a), 9.13 (d, *J* = 3.7 Hz, 2H; b), 8.69 (d, *J* = 7.7 Hz, 2H; d), 8.41 (d-like, *J* = 6.6 Hz, 8H; e and f), 8.02 ppm (t, *J* = 7.0 Hz, 2H; c); ¹³C NMR (125 MHz, [D₆]DMSO, TMS): δ = 149.5 (b), 148.4 (a), 139.9 (Cq), 137.2 (Cq), 135.9 (Cq), 134.9 (d), 128.4 (f), 128.2 (e), 124.8 ppm (c); elemental analysis: calcd (%) for C₂₂H₁₆N₂: C 85.69, H 5.23, N 9.08; found: C 85.87, H 5.11, N 8.89.

3: (Concentration of **1** in solution: 5 mm) [Pd(en)(NO₃)₂] (7.3 mg, 0.025 mmol) was added to a suspension of **1** (5.8 mg, 0.025 mmol) in water (5 mL). The mixture was stirred at 60 °C for 10 min to give a clear solution. Subsequent introduction of diethyl ether resulted in the precipitation of **3** (10.2 mg, 73%). M.p.: decomp. at 240 °C; ¹H NMR (500 MHz, D₂O, TMS): δ = 9.44 (s, 4H; a), 8.83 (d, *J* = 5.4 Hz, 4H; b), 8.152 (d, *J* =

6.4 Hz, 4H; d), 7.579 (t, *J* = 6.5 Hz, 4H; c), 7.54 (s, 8H; e), 2.97 ppm (s, 8H; -CH₂-); ¹³C NMR (125 MHz, D₂O, TMS): δ = 150.4 (b), 149.0 (a), 138.8 (Cq), 138.1 (d), 135.8 (Cq), 128.1 (e), 126.6 (c), 46.8 ppm (-CH₂-); elemental analysis: calcd (%) for C₃₆H₄₀N₁₂O₁₂Pd₂·4H₂O: C 38.69, H 4.33, N 15.04; found: C 38.91, H 4.0, N 15.28; CSI-MS (2% DMF added): *m/z* = 254, 272, 290, 308, 335, 359, 384, and 460, which correspond to [(3-(NO₃)₄+3DMF)⁴⁺], [(3-(NO₃)₄+4DMF)⁴⁺], [(3-(NO₃)₄+5DMF)⁴⁺], [(3-(NO₃)₄+6DMF)⁴⁺], [(3-(NO₃)₃+2DMF)³⁺], [(3-(NO₃)₃+3DMF)³⁺], [(3-(NO₃)₃+4DMF)³⁺], and [(3-(NO₃)₂)²⁺], respectively.

Mixture of **3** and **4:** (Concentration of **1** in solution: 10 mm) [Pd(en)(NO₃)₂] (14.5 mg, 0.050 mmol) was added to a solution of **1** (11.6 mg, 0.050 mmol) in DMSO (5 mL). The mixture was stirred at 60 °C for 10 min to give a clear solution. A control experiment in [D₆]DMSO under the same conditions showed the formation of a mixture of **3** and **4**. ¹H NMR (500 MHz, [D₆]DMSO, TMS): for **3**: δ = 10.40 (s, 4H; a), 9.44 (d, *J* = 5.5 Hz, 4H; b), 9.00 (d, *J* = 8.1 Hz, 4H; d), 8.38 (s, 8H; e), 8.32 (m, 4H; c), 6.27 (s, 8H; -NH₂), 3.30 (s, 8H; -CH₂-); for **4**: 9.86 (s, 6H; a), 9.53 (d, *J* = 5.5 Hz, 6H; b), 9.00 (d, *J* = 8.1 Hz, 6H; d), 8.48 (s, 12H; e), 8.32 (m, 6H and 4H; c), 6.23 (s, 12H; -NH₂), 3.28 ppm (s, 12H; -CH₂-) (the percentage ligand distribution is almost equal for both structures at this concentration, but there exists a negligible amount of **5** (Table 1)); ¹³C NMR (125 MHz, [D₆]DMSO, TMS): δ = 152.2 (b of **3**), 151.5 (b of **4**), 151.1 (a of **4**), 150.1 (a of **3**), 139.1 and 138.7 (d of **3** and **4**), 137.9 (Cq), 137.9 (Cq), 136.4 (Cq), 136.1 (Cq), 129.0 (e of **4**), 128.8 (e of **3**), 127.5 and 127.4 (c of **3** and **4**), 48.0 (-CH₂-), 47.8 ppm (-CH₂-); CSI-MS (concentration of **1** in solution: 20 mm; 20% MeOH added): *m/z* = 297 [(3-(NO₃)₄+5DMSO)⁴⁺], 317 [(3-(NO₃)₄+6DMSO)⁴⁺], 337 [(3-(NO₃)₄+7DMSO)⁴⁺], 364 [(3-(NO₃)₃+3DMSO)³⁺], 390 [(3-(NO₃)₃+4DMSO)³⁺], 500 [(3-(NO₃)₂+DMSO)²⁺]; *m/z* = 486 [(4-(NO₃)₃+1DMSO)³⁺], 512 [(4-(NO₃)₃+2DMSO)³⁺], 694 [(4-(NO₃)₃+9DMSO)³⁺], 721 [(4-(NO₃)₂+DMSO)²⁺]; **5** could also be observed at this concentration (Table 1) at *m/z* = 982 [(5-(NO₃)₂)²⁺].

5: (Concentration of **1** in solution: 500 mm) Structure **5** was observed with 92% ligand sharing at this concentration. ¹H NMR (500 MHz, [D₆]DMSO, TMS): δ = 9.88 (bs, 8H; a), 9.33 (br s, 8H; b), 8.90 (br s, 8H; d), 8.40 (br s, 16H; e), 8.14 (br s, 8H; c), 6.22 (br s, 16H; -NH₂), 3.18 ppm (br s, 16H; -CH₂-); ¹³C NMR (125 MHz, [D₆]DMSO, TMS): δ = 151.5 (b), 151.0 (a), 138.9 (d), 137.9 (Cq), 136.4 (Cq), 129.0 (e), 127.4 (c), 47.8 ppm (-CH₂-). CSI-MS could not be performed at such a high concentration. However, at lower concentrations, a peak corresponding to **5** was seen (see above) along with the peaks of **3** and **4**.

6: (Concentration of **1** in solution: 20 mm) A suspension of PdCl₂ (8.9 mg, 0.050 mmol) and AgCF₃SO₃ (25.7 mg, 0.100 mmol) in DMSO (or [D₆]DMSO; 5 mL) was stirred at 90 °C for 30 min, whereupon AgCl was precipitated. **1** (23.2 mg, 0.100 mmol) was added to this mixture, and the stirring was continued for another 10 min at 90 °C followed by filtration to obtain a clear solution. Subsequent introduction of chloroform/diethyl ether resulted in precipitation of **6** (37.2 mg, 71%). M.p.: decomp. at 281 °C; ¹H NMR (500 MHz, [D₆]DMSO, TMS) δ = 10.93 (br s, 12H; a), 9.90 (d, *J* = 5.4 Hz, 12H; b), 9.02 (d, *J* = 7.9 Hz, 12H; d), 8.43 (dd, *J* = 7.6, 5.8 Hz, 12H; c), 8.37 ppm (s, 24H; e); ¹³C NMR (125 MHz, [D₆]DMSO, TMS): δ = 151.1 (b), 150.9 (a), 139.5 (d), 138.7 (Cq), 136.1 (Cq), 129.4 (e), 128.5 (c), 121.7 ppm (C_{triflate}); elemental analysis: calcd (%) for C₁₀₂H₂₂N₁₂F₁₈O₁₈Pd₃·6DMSO·4H₂O: C 43.49, H 3.71, N 5.34; found: C 43.16, H 3.39, N 5.02; CSI-MS (33% MeOH added): *m/z* = 409 [(6-(CF₃SO₃)₃+2DMSO+MeOH)³⁺], 425 [(6-(CF₃SO₃)₃+3DMSO+MeOH)³⁺], 441 [(6-(CF₃SO₃)₃+4DMSO+MeOH)³⁺], 510 [(6-(CF₃SO₃)₄+MeOH)⁴⁺], 529 [(6-(CF₃SO₃)₄+DMSO+MeOH)⁴⁺], 549 [(6-(CF₃SO₃)₄+2DMSO+MeOH)⁴⁺], 729 [(6-(CF₃SO₃)₃+MeOH)³⁺], 1169 [(6-(CF₃SO₃)₂+MeOH)²⁺].

7a: (Concentration of **1** in solution: 20 mm) A mixture of **1** (23.2 mg, 0.100 mmol) and Pd(NO₃)₂ (11.5 mg, 0.050 mmol) in DMSO (5 mL) was stirred at 90 °C for 10 min, and the solution was filtered to obtain a clear solution. Subsequent introduction of chloroform/diethyl ether resulted in precipitation of **7a** (28.7 mg, 68%). M.p.: decomp. at 297 °C; ¹H NMR (500 MHz, [D₆]DMSO, TMS): δ = 10.78 (s, 8H; a), 10.22 (s, 8H; a'), 10.14 (d, *J* = 5.5 Hz, 8H; b'), 9.59 (d, *J* = 5.5 Hz, 8H; b), 9.07 (d, *J* = 8.0 Hz, 8H; d'), 8.90 (d, *J* = 8.0 Hz, 8H; d), 8.69 (s, 16H; e'), 8.50 (dd, *J* = 7.7, 5.9 Hz,

8H; c'), 8.40 (s, 16H; e), 8.22 ppm (dd, 8H; c) (a–e: double-walled edges, a'–e': single-walled edges); ^{13}C NMR (125 MHz, $[\text{D}_6]\text{DMSO}$, TMS): δ = 151.1 (b), 150.8 (b'), 150.1 (a'), 149.7 (a), 139.7 (d'), 139.2 (d), 138.4 (Cq), 138.1 (Cq), 136.1 (Cq), 135.9 (Cq), 129.0 (e'), 128.9 (e), 128.7 (e'), 128.1 ppm (c); elemental analysis: calcd (%) for $\text{C}_{128}\text{H}_{96}\text{N}_{24}\text{O}_{24}\text{Pd}_4\cdot 7\text{DMSO}\cdot 3\text{H}_2\text{O}$: C 50.45, H 4.29, N 9.94; found: C 50.05, H 4.12, N 9.92; CSI-MS: m/z = 540 $[(7\text{a}-(\text{NO}_3)_5)+3\text{DMSO}]^{5+}$, 632 $[7\text{a}-(\text{NO}_3)_4]^{4+}$, 864 $[7\text{a}-(\text{NO}_3)_3]^{3+}$, 889 $[7\text{a}-(\text{NO}_3)_3+1\text{DMSO}]^{3+}$.

7b: (Concentration of **1** in solution: 20 mM) A suspension of PdCl_2 (8.9 mg, 0.050 mmol) and AgBF_4 (19.5 mg, 0.100 mmol) in DMSO (5 mL) was stirred at 90 °C for 30 min, whereupon AgCl was precipitated. **1** (23.2 mg, 0.100 mmol) was added to this mixture, and the stirring was continued for another 10 min at 90 °C followed by filtration to obtain a clear solution. Subsequent introduction of chloroform/diethyl ether resulted in precipitation of **7b** (30.4 mg, 66%). M.p.: decomp. at 262 °C; ^1H NMR (500 MHz, $[\text{D}_6]\text{DMSO}$, TMS): δ = 10.50 (s, 8H; a), 10.148 (d, J = 5.6 Hz, 8H; b'), 10.107 (s, 8H; a'), 9.591 (d, J = 5.6 Hz, 8H; b), 9.05 (d, J = 8.0 Hz, 8H; d'), 8.88 (d, J = 8.1 Hz, 8H; d), 8.58 (s, 16H; e'), 8.504 (dd, J = 7.8, 6.0 Hz, 8H; c'), 8.25 (s, 16H; e), 8.25 ppm (merged inside a singlet, 8H; c) (a–e: double-walled edges, a'–e': single-walled edges); ^{13}C NMR (125 MHz, $[\text{D}_6]\text{DMSO}$, TMS): δ = 151.3 (b), 151.0 (b'), 150.2 (a'), 149.6 (a), 140.0 (d'), 139.5 (d), 138.7 (Cq), 138.1 (Cq), 136.4 (Cq), 136.2 (Cq), 129.0 (e and e'), 128.7 (e'), 128.2 ppm (c); elemental analysis: calcd (%) for $\text{C}_{128}\text{H}_{96}\text{N}_{16}\text{B}_8\text{F}_{32}\text{Pd}_4\cdot 8\text{DMSO}\cdot 5\text{H}_2\text{O}$: C 46.83, H 4.20, N 6.07; found: C 46.67, H 4.43, N 5.71; CSI-MS: m/z = 461 $[(7\text{b}-(\text{BF}_4)_6)+4\text{DMSO}]^{6+}$, 474 $[(7\text{b}-(\text{BF}_4)_6)+5\text{DMSO}]^{6+}$, 487 $[(7\text{b}-(\text{BF}_4)_6)+6\text{DMSO}]^{6+}$, 500 $[(7\text{b}-(\text{BF}_4)_6)+7\text{DMSO}]^{6+}$, 539 $[(7\text{b}-(\text{BF}_4)_5)+2\text{DMSO}]^{5+}$, 555 $[(7\text{b}-(\text{BF}_4)_5)+3\text{DMSO}]^{5+}$, 571 $[(7\text{b}-(\text{BF}_4)_5)+4\text{DMSO}]^{5+}$, 586 $[(7\text{b}-(\text{BF}_4)_5)+5\text{DMSO}]^{5+}$, 657 $[(7\text{b}-(\text{BF}_4)_4)]^{4+}$, 677 $[(7\text{b}-(\text{BF}_4)_4)+1\text{DMSO}]^{4+}$, 696 $[(7\text{b}-(\text{BF}_4)_4)+2\text{DMSO}]^{4+}$, 715 $[(7\text{b}-(\text{BF}_4)_4)+3\text{DMSO}]^{4+}$.

Mixture of **8**, **9**, and **10**: (Concentration of **2** in solution: 40 mM) $[\text{Pd}(\text{en})-(\text{NO}_3)_2]$ (58.0 mg, 0.200 mmol) was added to a solution of **2** (61.6 mg, 0.200 mmol) in DMSO (5 mL). The mixture was stirred at 60 °C for 10 min, whereupon a clear solution was obtained. No attempt was made to isolate the mixture of complexes. The experiment was also carried out in $[\text{D}_6]\text{DMSO}$ under the same conditions. ^1H NMR (500 MHz, $[\text{D}_6]\text{DMSO}$, TMS): δ = 10.40 (s, 4H; a of **8**), 9.99 (s, 8H; a of **10**), 9.86 (s, 6H; a of **9**), 9.47 (d, 6H; b of **9**), 9.42 (d, 4H and 8H; b of **9** and **10**, respectively), 8.99–8.94 (m, 4H, 6H, and 8H; d of **8**, **9**, **10**, respectively), 8.54–8.25 (m, 20H, 30H, and 40H; e, f, c of **8**, **9**, **10**, respectively), 6.26 (m; all $-\text{NH}_2$), 3.28 ppm (m; all $-\text{CH}_2$ -).

Mixture of **11a** and **12a**: (Concentration of **2** in solution: 10 mM) A mixture of **2** (15.4 mg, 0.050 mmol) and $\text{Pd}(\text{NO}_3)_2$ (5.8 mg, 0.025 mmol) in DMSO (5 mL) was stirred at 9 °C for 10 min and filtered to obtain a clear solution that is an almost equimolar mixture of **11a** and **12a**. The solution was left to stand at room temperature for two months to obtain a mixture of **12a** with a small proportion of **11a**. The experiment was also carried out in $[\text{D}_6]\text{DMSO}$ under the same conditions. ^1H NMR (500 MHz, $[\text{D}_6]\text{DMSO}$, TMS): δ = 10.76 (s, 8H; a), 10.28 (s, 8H; a'), 10.17 (d, J = 5.05 Hz, 8H; b'), 9.57 (d, J = 5.1 Hz, 8H; b), 9.03 (d, J = 8.1 Hz, 8H; d'), 8.91 (d, J = 7.8 Hz, 8H; d), 8.59 (d, J = 8.1 Hz, 16H; e'), 8.53–8.48 (m, 56H; c' and f', e and f), 8.22 ppm (t, J = 6.7 Hz, 8H; c) (a–f: double-walled edges, a'–f': single-walled edges); ^{13}C NMR (125 MHz, $[\text{D}_6]\text{DMSO}$, TMS) δ = 150.9 (b), 150.5 (b'), 150.5 (a'), 149.5 (a), 140.6 (Cq), 140.3 (Cq), 140.1 (Cq), 139.7 (d'), 138.9 (d), 138.9 (Cq), 135.1 (Cq), 134.7 (Cq), 129.1 (e'), 129.0 (c'), 128.6 (e and f'), 128.3 (f), 128.1 ppm (c); CSI-MS (MeOH added): m/z = 784 $[(12\text{a}-(\text{NO}_3)_4)]^{4+}$, 862 $[(12\text{a}-(\text{NO}_3)_4)+4\text{DMSO}]^{4+}$, 1067 $[(12\text{a}-(\text{NO}_3)_3)+3\text{DMSO}]^{3+}$, and 1142 $[(12\text{a}-(\text{NO}_3)_3)+3\text{DMSO}]^{3+}$; m/z = 1208 $[(11\text{a}-(\text{NO}_3)_2)]^{2+}$.

Mixture of **11b** and **12b**: (Concentration of **2** in solution: 10 mM) A suspension of PdCl_2 (4.4 mg, 0.025 mmol) and AgCF_3SO_3 (12.8 mg, 0.050 mmol) in DMSO (5 mL) was stirred at 90 °C for 30 min, whereupon AgCl was precipitated. **1** (12.9 mg, 0.050 mmol) was added to this mixture, and the stirring was continued for another 10 min at 90 °C followed by filtration to obtain a clear solution of **11b** along with a small proportion of **12b**. The experiment was also carried out in $[\text{D}_6]\text{DMSO}$ under the same conditions. ^1H NMR (500 MHz, $[\text{D}_6]\text{DMSO}$, TMS): δ = 10.46

(br s, 12H; a), 9.88 (d, J = 5.4 Hz, 12H; b), 9.02 (d, J = 7.9 Hz, 12H; d), 8.44 (d, J = 8.1 Hz, 24H and 12H; e and c), 8.31 ppm (d, J = 7.9 Hz, 24H; f) (peaks of **12b** are not described here); ^{13}C NMR (125 MHz, $[\text{D}_6]\text{DMSO}$, TMS): δ = 150.9 (b), 150.1 (a), 139.9 (Cq), 139.5 (d), 139.0 (Cq), 135.4 (Cq), 129.1 and 128.5 (e and c), 127.9 (f), 122.7 ppm ($\text{C}_{\text{triflate}}$); CSI-MS (MeOH added): m/z = 400 $[(11\text{b}-(\text{triflate})_6)+3\text{DMSO}]^{6+}$, 413 $[(11\text{b}-(\text{triflate})_6)+4\text{DMSO}]^{6+}$, 426 $[(11\text{b}-(\text{triflate})_6)+5\text{DMSO}]^{6+}$, 478 $[(11\text{b}-(\text{triflate})_5)+1\text{DMSO}]^{5+}$, 494 $[(11\text{b}-(\text{triflate})_5)+2\text{DMSO}]^{5+}$, 510 $[(11\text{b}-(\text{triflate})_5)+3\text{DMSO}]^{5+}$, 526 $[(11\text{b}-(\text{triflate})_5)+4\text{DMSO}]^{5+}$, 541 $[(11\text{b}-(\text{triflate})_5)+5\text{DMSO}]^{5+}$, 635 $[(11\text{b}-(\text{triflate})_4)+1\text{DMSO}]^{4+}$, 655 $[(11\text{b}-(\text{triflate})_4)+2\text{DMSO}]^{4+}$, 871 $[(11\text{b}-(\text{triflate})_3)]^{3+}$, and 1381 $[(11\text{b}-(\text{triflate})_2)]^{2+}$; m/z = 1212 $[(12\text{b}-(\text{triflate})_3)]^{3+}$.

12c: (Concentration of **2** in solution: 10 mM) A suspension of PdCl_2 (4.4 mg, 0.025 mmol) and AgOTf (13.9 mg, 0.050 mmol) in DMSO (5 mL) was stirred at 90 °C for 30 min, whereupon AgCl was precipitated. **2** (15.4 mg, 0.050 mmol) was added to this mixture, and the stirring was continued for another 10 min at 90 °C followed by filtration to obtain a clear solution. Subsequent introduction of chloroform/diethyl ether resulted in precipitation of **12c** (29.4 mg, 82%). M.p.: decomp. at 270 °C; ^1H NMR (500 MHz, $[\text{D}_6]\text{DMSO}$, TMS): δ = 11.02 (s, 8H; a), 10.69 (s, 8H; a'), 10.24 (d, J = 5.6 Hz, 8H; b'), 9.61 (d, J = 5.6 Hz, 8H; b), 9.06 (d, J = 8.3 Hz, 8H; d'), 8.92 (d, J = 8.1 Hz, 8H; d), 8.67 (d, J = 8.3 Hz, 16H; e'), 8.54 (d, J = 8.1 Hz, 16H; e), 8.54 (merged, 8H; c'), 8.36 (d, J = 8.4 Hz, 16H; f'), 8.31 (bs, 16H; tosylate_{ortho}), 8.27 (d, J = 8.4 Hz, 16H; f), 8.22 (t, J = 6.1 Hz, 8H; c), 7.68 (d, J = 7.9 Hz, 16H; tosylate_{meta}), 2.79 ppm (s, 24H; $-\text{CH}_3$) (a–f: double-walled edges, a'–f': single-walled edges); ^{13}C NMR (125 MHz, $[\text{D}_6]\text{DMSO}$, TMS): δ = 151.0 (b), 150.8 (b'), 150.5 (a'), 149.9 (a), 146.4 (Cq), 140.5 (Cq), 140.2 (Cq), 139.5 (d'), 139.4 (Cq), 138.8 (Cq), 138.7 (d), 138.6 (Cq), 134.8 (Cq), 134.5 (Cq), 129.3 (e' and tosylate_{meta}), 128.7 (e), 128.6 (c'), 128.1 (f'), 127.9 (f and c), 126.6 (tosylate_{ortho}), 21.8 ppm ($-\text{CH}_3$); elemental analysis calcd (%) for $\text{C}_{232}\text{H}_{184}\text{N}_{16}\text{O}_{24}\text{Pd}_4\text{S}_8\cdot 19\text{DMSO}$: C 56.43, H 5.23, N 3.90; found: C 56.16, H 5.01, N 3.87; CSI-MS: m/z = 893 $[(12\text{c}-(\text{tosylate})_4)]^{4+}$, 1248 $[(12\text{c}-(\text{tosylate})_3)]^{3+}$, and 1958 $[(12\text{c}-(\text{tosylate})_2)]^{2+}$.

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