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Controlled translocation of palladium(II) within a 22 ring atom macrocyclic ligand

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Double *aza*-Michael addition of *n*-butylamine to the two acrylamide groups of acyclic N^2,N^6-bis(6-acrylamidopyridin-2-yl)pyridine-2,6-dicarboxamide gives the corresponding macrocycle, **H_4L**. **H_4L** has potential coordination pockets associated with the 2,6-dicarboxamide (head) and the butylamine (tail) regions of the macrocycle. Depending on the conditions employed, macrocyclic complexes with palladium(II) coordinated to either the tail or the head of the macrocycle can be isolated. Thus, treatment of **H_4L** with $[PdCl_2(NCPh)_2]$ and sodium acetate, or $[Pd(OAc)_2]$ gives the closely related "tail-coordinated" complexes $[PdCl(H_3L)]$ (**3a**) or $[Pd(OAc)(H_3L)]$ (**3b**), respectively. However, employment of the bases 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or pyridine during the treatment of **H_4L** with $[Pd(OAc)_2]$ results in the "head-coordinated" complexes $[Pd(NH_2R)(H_2L)]$ (NH_2R = *N*-(3-aminopropyl)caprolactam, which is formed by hydrolysis of DBU) (**5**) or $[Pd(OH_2)(H_2L)]$ (**6**), respectively. Translocation of the palladium ion from the macrocycle tail in **3b** to the head occurs on treatment with either DBU or *N*-(3-aminopropyl)caprolactam. In both cases the product **5** is formed. The aqua ligand in **6** is labile and easily displaced by the *N*-donor ligands *n*-butylamine, *N*-(3-aminopropyl)caprolactam or DBU to give the corresponding complexes $[Pd(NH_2{}^nBu)(H_2L)]$ (**4**), (**5**), or $[Pd(DBU)(H_2L)]$ (**7**). The data suggest that hydrolysis of DBU to produce the *N*-(3-aminopropyl)caprolactam ligand in **5** is catalysed by the acetic acid formed during ligand metallation rather than by coordination to palladium. The X-ray crystal structures of **H_4L**, **3a**, **5** and **6** are reported.

Introduction

The study of large macrocyclic ligands that have two or more potential coordination pockets linked by functional groups that can serve as molecular receptors or activators continues to attract considerable interest.[1, 2] Metal derivatives of macrocycles with these features have been investigated as receptors for anions and small molecules,[3-8] for the binding and activation of molecules during metal catalysed transformations,[9-12] for the formation of rotaxanes, catenanes, and molecular devices,[13-18] and as the basis of molecular switches through the controlled translocation of metal ions between coordination pockets within the macrocyclic ligand.[19-21] In this paper we describe (i) the synthesis of the 22 ring atom macrocyclic ligand **H_4L** (Scheme 1) which has two potential coordination pockets, (ii) the selective coordination of Pd(II) to the "tail" coordination pocket of the macrocycle to give the compounds $[PdX(H_3L)]$ (**3a**, X = Cl**; 3b**, X = OAc) (Scheme 2), (iii) conditions under which the Pd(II) ion in **3b** undergoes translocation to the "head" coordination pocket to give $[Pd(NH_2R)(H_2L)]$ (**4**, R = *n*-Bu; **5**, R = *N*-(3-aminopropyl)caprolactam), (iv) the direct synthesis of the compounds $[Pd(OH_2)(H_2L)]$ (**6**) or **5**, where palladium is coordinated in the "head" pocket, (v) formation of the complexes $[Pd(DBU)(H_2L)]$ (**7**), **4** or **5** through simple displacement of the labile aqua ligand in **6**, (vi) the evidence that hydrolysis of DBU to produce the *N*-(3-aminopropyl)caprolactam ligand in **5** is catalysed by the acetic acid formed during ligand metallation rather than by coordination to palladium, and (vii) the X-ray crystal structure determinations of **H_4L**, **3a**, **5**, and **6**.

Results and discussion

The 22 ring atom macrocyclic ligand **H_4L**, which contains 8 potential nitrogen donors, can be synthesised via the procedure depicted in Scheme 1. Treatment of pyridine-2,6-dicarbonyl dichloride with pyridine-2,6-diamine gives N^2,N^6-bis(6-aminopyridin-2-yl)pyridine-2,6-dicarboxamide[22] (**1**) and treatment of this with acryloyl chloride gives the acyclic compound N^2,N^6-bis(6-acrylamidopyridin-2-yl)pyridine-2,6-dicarboxamide (**2**). In the ^{1}H NMR spectrum of **2** the two amide NH protons associated with the central pyridyl diamide group are observed as a singlet signal at 11.17 ppm and the two acrylamide NH protons are observed as a singlet at 10.51 ppm. The protons associated with the two equivalent vinyl groups appear as the expected doublet of doublet signals at 6.64, 6.35 and 5.83 ppm.

The full details of the spectral and characterizing data for **2** and the other new compounds are recorded in the Experimental section.

The vinyl groups in **2** are disposed towards *aza*-Michael additions[23,24] and on treatment with *n*-butylamine double addition occurs resulting in macrocyclization and formation of $\mathbf{H_4L}$. $\mathbf{H_4L}$ has potential coordination pockets associated with the 2,6-dicarboxamide (head) and the butylamine (tail) regions of the macrocycle (Scheme 1). The amide NH protons of $\mathbf{H_4L}$ appear as two singlets in the ^{1}H NMR spectrum at 10.91 and 10.45 ppm for the head and tail regions, respectively, indicating that the two NH protons in each of these regions are equivalent on the NMR timescale. The presence of a time-averaged or effective C_2 axis through C(4), N(2), and N(8) (see Scheme 1 for numbering of atoms) that relates pairs of carbon atoms in the macrocycle is clearly indicated by the ^{13}C NMR spectrum of $\mathbf{H_4L}$ in which singlet signals are observed for the carbon atoms C(2,6), C(8,13), C(9,14), C(18,21) etc. The observed magnetic equivalence of each of these pairs of carbon atoms is presumably due to conformational rearrangements that are rapid on the NMR timescale and that on average result in equivalent environments for each pair of atoms.

< Insert Scheme 1>

Scheme 1 Synthesis of $\mathbf{H_4L}$.

The single-crystal X-ray structure of $\mathbf{H_4L}$ (**2**) has been determined and the molecular structure is given in Figure 1. The crystal data and refinement details for $\mathbf{H_4L}$ and the other crystal structures reported in this paper are available in the Supporting Information. $\mathbf{H_4L}$ crystallizes in the space group $P2_1/c$, with two independent molecules (A and B) in the asymmetric unit. Since A and B are very nearly identical, molecule A only is depicted in Figure 1. As might be expected, the head group pyridine and two

< Insert Figure 1>

Fig. 1 Molecular structure of $\mathbf{H_4L}$. Thermal ellipsoids are shown at the 50% probability level.

associated *transoid*-carboxamide groups are essentially co-planar.[23, 25] In the tail region of the macrocycle one of the amide groups (N7, C21, O4) also has *transoid*-geometry with the short distance between N7 and the tertiary amine N8 (2.890(4) Å) indicating an intramolecular hydrogen bonding interaction. In contrast, the other amide group in the tail region (N6, C18, O3) exhibits *cisoid*-geometry with two intermolecular short contacts (N6 – N5', 2.980(3) Å; O3 – N1', 2.962(3) Å) that are consistent with hydrogen bonds. Presumably the geometric constraints imposed by the size of the macrocyclic ring, the three rigid pyridine rings, the preferred planar arrangement of the macrocycle's pyridine-2,6-dicarboxamide head group, and the formation of favourable intramolecular hydrogen bonds all contribute to the observed *cisoid*-geometry of this amide in the solid state. Although the two amide groups in the tail region have very different geometric arrangements in the solid-state structure, the NMR data discussed above indicates that in solution rapid conformational rearrangements serves to equilibrate them on the NMR timescale.

Coordination of palladium to the tail of the macrocyclic ligand $\mathbf{H_4L}$ occurs under relatively mild conditions. Thus, if $\mathbf{H_4L}$ is heated under reflux for two hours in 1,2-dichloroethane (DCE) with $[PdCl_2(NCPh)_2]$ and two equivalents of sodium acetate, $[PdCl(H_3L)]$ (**3a**) is formed in good yield (Scheme 2). Similarly, heating $\mathbf{H_4L}$ at 50 °C for 18 hours in DCE with palladium acetate gives the analogue $[Pd(OAc)(H_3L)]$ (**3b**), where acetate is coordinated to palladium instead of chloride. In both cases the palladium occupies a coordination pocket in the tail region where it is bound to the pyridine nitrogen N4, the deprotonated amide nitrogen N6, and the tertiary amine nitrogen N8. The reduction in symmetry of the ligand upon coordination of palladium is evident in the NMR spectra of **3a** and **3b**. Thus, in the ^{1}H NMR spectrum of **3a** a separate signal is observed for each macrocyclic ring proton in the molecule and a separate signal is also observed for each carbon atom in the ^{13}C NMR spectrum. A similar situation is observed in the ^{1}H and ^{13}C NMR spectra of **3b**.

< Insert Scheme 2>

Scheme 2 Syntheses and reactions of complexes **3**-**7**.

The single-crystal X-ray structure of **3a** has been determined and the molecular structure is given in Figure 2. The palladium is coordinated to the tail region of the macrocycle through the three nitrogen donors N4, N6 and N8 and the distances Pd – N(4) 1.972(4), Pd – N(6) 2.045(4), and Pd – N(8) 2.056(4) Å are within the normal ranges for these types of bonds. The fourth coordination site at palladium is occupied by the chloride ion giving an overall distorted square-planar coordination geometry about palladium (N(4)-Pd-N(8), 160.99(17)°; N(6)-Pd-Cl, 164.89(14)°). The mean plane through N(4), N(6), N(8), Cl, Pd is tilted at an angle of 24.6° from the mean plane through N(1-3), C(1, 2, 6, 7) at the head of the macrocycle. As a result, the chloride ligand, which projects towards the head of the macrocycle, does not make a close approach to either of the amide nitrogen atoms N(1) or N(3). The distances Cl···N(1), 3.343(5) Å and Cl···N(3), 3.412(5) Å are well outside the normal range of NH···Cl hydrogen bonding distances (3.00-3.20 Å).[26] The N(7) amide group in the tail region that is not involved in bonding to the palladium has a *cisoid*-geometry with torsion angle N(5)-C(17)-N(7)-C(21) 21.4°.

< Insert Figure 2>

Fig. 2 Molecular structure of **3a**. Thermal ellipsoids are shown at the 50% probability level.

Remarkably, translocation of the palladium from the tail region of **3b** to the head of the macrocycle occurs on heating under reflux a solution of **3b** in THF with *n*-butylamine for 30 minutes (Scheme 2). In the product $[Pd(NH_2n\text{-}Bu)(H_2L)]$ (**4**), which is formed in good (ca. 60%) yield, the palladium is coordinated to the head of the macrocycle through two deprotonated amide nitrogen atoms and a pyridine nitrogen. The coordination sphere around palladium is completed by an *n*-

butylamine ligand. The increased symmetry of **4** compared to **3b** is indicated by the ^{13}C NMR spectrum of **4** where again the presence of an effective C_2 axis through C(4), N(2), Pd, N(8) results in singlet signals for the pairs of carbon atoms (e.g. C(2,6), C(8,13), C(9,14) etc.) in a situation similar to that observed in the ^{13}C NMR spectrum of **2**. The translocation of palladium to the head region of the macrocycle also occurs if **3b** is heated under reflux in THF for 30 minutes with the related primary amine *N*-(3-aminopropyl)caprolactam. The product, $[Pd(NH_2R)(H_2L)]$ (**5**) (NH_2R = *N*-(3-aminopropyl)caprolactam) (Scheme 2), which is formed in high (ca. 80%) yield, is an analogue of **4** and the ^1H and ^{13}C NMR spectra of **5** are closely similar to those of **4**.

The molecular structure of **5**, which was determined by a single-crystal X-ray study, is depicted in Figure 3. The palladium is coordinated to the macrocycle through the pyridine nitrogen N(2), and the two deprotonated amide nitrogen atoms N(1) and (N3). The fourth site of the distorted square-planar geometry about palladium is occupied by the amine nitrogen N(9) of the *N*-(3-aminopropyl)caprolactam ligand. The distances Pd – N(1) (2.048(5) Å), Pd – N(3) (2.053(5) Å), and Pd – N(9) (2.084(5) Å) are unremarkable. However, the Pd – N(2) distance (1.940(5) Å) is at the short end of the range of all Pd – N(pyridine) distances (average Pd – N(py) = 2.050 Å, SD = 0.054 Å, Nr Obs = 6035, CCDC database). The minor mismatch between the constrained geometry of the three nitrogen donor atoms of the macrocycle and the preferred square-planar coordination geometry of Pd(II) that together serve to draw the palladium towards N(2) (the angle N(1) – Pd – N(3) is 161.1(2)°) must contribute to this short distance. The *N*-(3-aminopropyl)caprolactam ligand is oriented so that it projects slightly out of the macrocyclic cavity. Nevertheless, the nitrogen donor of this ligand (N(9)) approaches closely the pyridine nitrogen atoms N(4) and N(5). The distances N(9)···N(4) (2.853(7) Å) and N(9)···N(4) (2.842(7) Å) are shorter than the distances observed for normal NH···N hydrogen bonds (2.94 – 3.15 Å)[26] signifying hydrogen bonding interactions that could be quite strong. N(9) also makes a relatively close approach to O(3) of an amide group in the tail region. The N(9)···O(3) distance of 3.030(7) Å is at the long end of the normal range of NH···O bond lengths (2.81-3.04 Å)[26] suggesting there could be a very weak hydrogen bonding interaction in this case. Unlike the situation in $\mathbf{H_4L}$ and **3b**, both amides in the tail region of **5** have a *transoid*-geometry. However, the N(6), C(18), O(3) amide group is rotated about the N(6) – C(12) bond so that O(3) is directed towards the interior of the macrocycle allowing the close approach to N(9).

< Insert Figure 3>

Fig. 3 Molecular structure of **5**. Thermal ellipsoids are shown at the 50% probability level.

The reversible translocation of a metal ion between the two binding sites of a ditopic ligand that is triggered by an external stimulus (e.g. chemical, electrochemical, photonic, etc.) could form the basis of a bistable molecular switch.[19-21, 27] Therefore, the possibility of reversing the translocation of palladium that occurs in the transformation of **3b** to **5** was explored. A range of different conditions including heating at high temperatures in a range of solvents, and treatment with bases or acids were investigated, but no conditions were found that would return **3b** or **3a** from **5**. The reactions carried out with acids deserve special mention. It was found that regardless of whether **5** was treated with HCl, HO_3SCF_3, or $HO_3S(p\text{-tolyl})$, whether the amount of acid added was 1 equivalent or excess, whether the solvent used was THF or methanol, and the temperature ambient or the boiling point of the solvent, in each case after neutralization **5** was recovered essentially unchanged. Clearly **5** is remarkably stable towards acid-promoted displacement of the *N*-(3-aminopropyl)caprolactam ligand or demetallation.

While investigating the effect of bases on the translocation of palladium from the tail region of the macrocycle in **3b** to the head region, it was found that if **3b** was heated under reflux for 8 hours in THF with 3 equivalents of the base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 20 equivalents of water, **5** is obtained in high (ca. 80%) yield. It was also found that **5** can be produced in similar yield by heating $\mathbf{H_4L}$ under reflux in THF for 18 hours with palladium acetate, 3 equivalents of DBU, and 20 equivalents of water. In both these reactions the *N*-(3-aminopropyl)caprolactam ligand in **5** arises from hydrolysis of DBU, raising the possibility that this reaction may have been catalysed by coordination to palladium. To investigate this possibility, a route was sought to the analogue of **5** which has DBU coordinated to palladium. It was found this compound could be accessed via the complex $[Pd(OH_2)(H_2L)]$ (**6**). Remarkably **6** can be obtained in high yield through the reaction between $\mathbf{H_4L}$ and palladium acetate in pyridine at 50 °C for 2 hours followed by column chromatography on silica gel using a methanol/dichloromethane mixture as eluent (Scheme 2). The putative complex "[Pd(Pyridine)(H_2L)]" that is presumably the initial product formed during the metallation reaction in pyridine could not be isolated in a pure form. The preferred coordination of adventitious water to palladium in place of pyridine during the isolation and purification procedure suggests that the steric repulsions between coordinated pyridine and the macrocyclic ligand in "[Pd(Pyridine)(H_2L)]" are probably significant, especially as the coordinated water in **6** is itself easily displaced by other ligands (see below). In the IR spectrum of **6** a sharp band at 3314 cm^{-1} is assigned to ν(OH) of the coordinated water. In the ^1H NMR spectrum the two protons of the coordinated water are observed as a broad singlet at 3.36 ppm, which very rapidly disappears on addition of D_2O. The remaining signals in the ^1H and ^{13}C NMR spectra are similar to those observed in **4** and **5** suggesting in solution this complex also has an effective C_2 axis passing through N2, Pd, O5, and N8.

The single crystal X-ray structure of **6** has been determined and the molecular structure is given in Figure 4. The palladium is coordinated to the head of the macrocycle through nitrogen atoms N(1-3). The fourth site of the distorted square-planar geometry about palladium is occupied by the oxygen of the water ligand. While the Pd – N(1) and Pd – N(3) distances are unremarkable, the Pd – N(2) distance of 1.908(4) Å is exceptionally short.[28,29] It is considerably shorter than the corresponding distance in the analogous compound **5** (1.940(5) Å) and is within the 20 shortest of the 6035 Pd – N(pyridine) distances reported in the CCDC database. Presumably the weaker *trans*-influence of the aqua ligand is primarily responsible for this shorter distance in **6**

compared to **5**. The Pd – O(5) distance of 2.042(3) Å in **6** is within the normal range found for palladium – neutral oxygen donors. The distances O(5)···N(4) 2.791(5), O(5)···N(5) 2.601(5), and O(5)···O(3) 2.690(4) Å are all relatively short and consistent with the presence of hydrogen bonds between these atoms. As was found in the structure of **5** the two amide groups in the tail region have *transoid*-geometry with one of the groups rotated so that O(3) projects into the macrocyclic cavity, thus enabling hydrogen bond formation with the coordinated water.

< Insert Figure 4>

Fig. 4 Molecular structure of **6**. Thermal ellipsoids are shown at the 50% probability level.

The aqua ligand in **6** is easily displaced by primary amines and on treatment of **6** at ambient temperature with either *N*-(3-aminopropyl)caprolactam or *n*-butylamine **5** or **4,** respectively, are formed quantitatively (Scheme 2). In a similar manner, on treatment of **6** in THF with excess DBU, the complex [Pd(DBU)(H_2L)] (**7**) is obtained (Scheme 2). The signals associated with the DBU ligand are evident in both the ^{1}H and ^{13}C NMR spectra of **7** and the resonances of the macrocycle are similar to those observed for **4, 5** and **6** suggesting that in solution this complex also has an effective C_2 axis passing through N2, Pd, and N8. The crystal structure of **7** has not been obtained, but the DBU presumably coordinates to palladium thought the imine nitrogen atom. Well-characterised examples of transition metal DBU complexes are very rare and only a few X-ray crystal structure determinations of compounds of this type have been reported.[30-35] However, in each case coordination occurs through the imine nitrogen. As might be expected, the DBU ligand in **7** is quite labile and during column chromatography it is replaced by water to return the aqua complex **6**. Furthermore, treatment of **7** with the primary amines *N*-(3-aminopropyl)caprolactam or *n*-butylamine rapidly produces **5** or **4**, respectively (Scheme 2).

With complex **7** in hand, experiments were conducted to determine whether the coordinated DBU in this compound was activated towards hydrolysis and *N*-(3-aminopropyl)caprolactam formation. It was found that if a THF solution of **7** was treated with 200 equivalents of water, either at ambient temperature or on heating under reflux, no formation of free *N*-(3-aminopropyl)caprolactam or the *N*-(3-aminopropyl)caprolactam-containing complex **5** could be detected. However, when a THF solution of **7** containing 20 equivalents of water and 2 equivalents of DBU was heated under reflux for ca. 18 hours (conditions identical to those used in the direct synthesis of **5** in >80% yield from **H_4L**) some of the *N*-(3-aminopropyl)caprolactam-containing complex **5** was formed (ca. 40%), but the majority of the starting DBU complex **7** (ca. 60%) was isolated unchanged. This indicated that the major route to *N*-(3-aminopropyl)caprolactam formation does not involve hydrolysis of the DBU ligand coordinated to palladium in **7**. Attention was therefore directed towards the other species present during the synthesis of **5** from **2** that could promote the hydrolysis of DBU. Three separate blank experiments were conducted and these involved heating DBU, 20 equivalents of water and (i) **H_4L**, or (ii) palladium acetate, or (iii) acetic acid under reflux in THF for 18 hours. The first two blank reactions with the reagents **H_4L** or palladium acetate produced no significant quantities of *N*-(3-aminopropyl)caprolactam. However, in the third blank reaction with acetic acid complete conversion of the DBU to *N*-(3-aminopropyl)caprolactam occurred.[36-39] This strongly suggested that the acetic acid which is formed as a by-product during the metallation of H_4L could be largely responsible for the observed hydrolysis of DBU and formation of *N*-(3-aminopropyl)caprolactam-containing product **5**. Indeed, in support of this proposal it was found that heating the DBU-containing complex **7** under reflux in THF with two equivalents of DBU, two equivalents of acetic acid and 20 equivalents of water resulted in the formation of **5** in high yield within four hours. Furthermore, it was found that heating **3b** under reflux in THF for 6 hours with water (20 eq.) and DBU (5 eq.), also gave **5** in very good yield. In this latter case it appears that the acetic acid formed on metallation of the two head-group amide nitrogen atoms could facilitate hydrolysis of DBU and formation of **5**. Together, these observations suggest that hydrolysis of DBU to produce the *N*-(3-aminopropyl)caprolactam ligand in **5** is primarily catalysed by the acetic acid formed during ligand metallation rather than by coordination to palladium.

Conclusions

In conclusion, it has been demonstrated that depending on the conditions employed, palladium can be directed to coordinate either to the "head" or the "tail" regions of the macrocycle **H_4L**. Thus, treatment of **H_4L** with palladium acetate in THF gives the "tail-coordinated" complex [Pd(OAc)(H_3L)] (**3b**), whereas if the same reaction is carried out in the presence of DBU/H_2O or alternatively if **H_4L** is treated with palladium acetate in the solvent pyridine, the "head-coordinated" complexes [Pd(*N*-(3-aminopropyl)caprolactam)(H_2L)] (**5**) or [Pd(OH_2)(H_2L)] (**6**), respectively, are obtained.

The palladium ion in [Pd(OAc)(H_3L)] (**3b**) undergoes irreversible translocation from the macrocycle tail coordination pocket to the head coordination pocket on heating under reflux in THF with either DBU/H_2O or *N*-(3-aminopropyl)caprolactam. In both cases the remarkably stable product [Pd(*N*-(3-aminopropyl)caprolactam)(H_2L)] (**5**) is formed. It can be speculated that the palladium initially coordinates to the tail region of the macrocycle in a reaction that is under kinetic control, but the observed subsequent coordination to the head region is thermodynamically preferred. The data obtained suggest that the observed DBU hydrolysis reactions that produce the *N*-(3-aminopropyl)caprolactam ligand are most probably catalysed by the acetic acid formed during ligand metallation rather than by coordination of DBU to palladium.

Experimental

Air-sensitive manipulations were carried out under dry nitrogen using standard Schlenk techniques. Acetonitrile was distilled from pulverized calcium hydride. Tetrahydrofuran was distilled from sodium and stored under nitrogen. Dichloromethane was dried using a MBRAUN MB SPS-800 solvent purifier and stored under nitrogen. When used as a solvent or a reagent, water was deionised. Where compounds

were purified by chromatography, basic alumina or silica gel 0.032-0.063 mm was used. Reagents were used as received with the exception of *n*-butylamine, which was distilled from potassium hydroxide. Pyridine and triethylamine were distilled from pulverized calcium hydride. DBU was distilled under reduced pressure. Acryloyl chloride was distilled with 0.5 g of hydroquinone per 200 g of chloride and stored under nitrogen at -10 °C. All other reagents were used as supplied from the manufacturer unless otherwise specified. *N*-(3-Aminopropyl)caprolactam was prepared after the method of Heidelberger *et al*.[36] Bis(benzonitrile)dichloropalladium(II) was prepared after the method of Anderson *et al*.[40] N^2,N^6-bis(6-aminopyridin-2-yl)pyridine-2,6-dicarboxamide **(1)** was prepared by a method that is different to that reported in the literature.[22] IR spectra (4000-400 cm^{-1}) were recorded on a Perkin Elmer Spectrum 400 Spectrometer using an ATR accessory.

^{1}H NMR and ^{13}C NMR spectra spectra were recorded at 300 K on either a Bruker Avance 300 (operating at 300.1, and 75.5 MHz for ^{1}H and ^{13}C) or a Bruker DRX 400 or Avance III 400 (operating at 400.1 and 100.6 MHz for ^{1}H and ^{13}C) spectrometers. Resonances are reported in ppm and ^{1}H NMR spectra referenced to tetramethylsilane (0.00 ppm), or the proteoimpurity in dimethylsulfoxide (2.50 ppm). ^{13}C NMR spectra were referenced to $CDCl_3$ (77.00 ppm) or d_6-DMSO (39.43 ppm). Assignments were made with the aid of 2D NMR experiments. X-ray intensity data for the crystal structures were collected on a Bruker SMART diffractometer with an APEX II CCD area detector using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 87 K for **H_4L, 3a, 5**, and **6**. Structures were solved using Patterson or direct methods (SHELXS-97)[41] and non-hydrogen atoms were refined anisotropically (SHELXL-97).[41] Hydrogen atoms on water molecules were located with CALC-OH[42] and refined with restrained H-O distances. The remaining hydrogen atoms were refined using a riding model. The X-ray data for **H_4L** was squeezed by the method of Sluis and Spek[43] to allow for the presence of disordered solvent of crystallization (either *n*-hexane of octane or both) which could not be satisfactorily modelled. Further information is provided in the cif for **H_4L**. Mass spectra were recorded either on a VG 70-SE mass spectrometer using fast atom bombardment or a Bruker MicrOTOF-QII by direct infusion (electrospray ionisation). Analytical data were obtained from the Microanalytical Laboratory, University of Otago.

Synthesis of N^2,N^6-bis(6-aminopyridin-2-yl)pyridine-2,6-dicarboxamide (1).

2,6-diaminopyridine (8.00 g, 73.3 mmol) and triethylamine (10 mL) were combined in dichloromethane (300 mL) under nitrogen, giving a colourless suspension. 2,6-pyridinedicarbonyl dichloride (3.00 g, 14.7 mmol) in dichloromethane (75 mL) was added dropwise with stirring via a pressure-equalizing dropping funnel over a period of 30 minutes. After this time a cream suspension had formed. Stirring was continued for a total of four hours. The product was filtered and washed thoroughly with dichloromethane, then air-dried to give **1** (5.02 g, 97 %), which was characterized by comparison of the spectral data with those reported.[22]

Synthesis of N^2,N^6-bis(6-acrylamidopyridin-2-yl)pyridine-2,6-dicarboxamide (2).

N^2,N^6-bis(6-aminopyridin-2-yl)pyridine-2,6-dicarboxamide **(1)** (4.000 g, 11.45 mmol) and triethylamine (19.1 mL, 137 mmol, 12.0 eq.) were combined in a flame-dried 1 L three-necked round-bottomed flask fitted with a 150 mL pressure-equalising dropping funnel. The flask was charged with anhydrous tetrahydrofuran (500 mL) and the dropping funnel was also charged with anhydrous tetrahydrofuran (100 mL). Freshly distilled acryloyl chloride (2.79 mL, 34.3 mmol, 3.00 eq.) was added to the dropping funnel, mixed, and the contents were added dropwise to the stirred mixture in the flask over a period of *ca*. 30 minutes. The mixture was then stirred for at ambient temperature for 18 hours, after which time a brown suspension had formed. The solid material was collected by filtration and discarded, and the solvent level of the filtrate lowered to *ca*. 40 mL under reduced pressure. Water (ca. 100 mL) was slowly added to the flask, causing the precipitation of an ochre solid. The remaining tetrahydrofuran was then removed under reduced pressure, the solid collected by filtration and transferred into a 250 mL Erlenmeyer flask. Water (100 mL) was added and the resulting suspension placed in an ultrasonic bath for fifteen minutes. The solid material was collected by filtration using filter paper, washed twice with water (*ca*. 50 mL) and dried *in vacuo* to afford pure **1** as an ochre microcrystalline solid (3.439 g, 73%). Anal. calcd. for $C_{23}H_{19}N_7O_4.1.5H_2O$: C, 57.02; H, 4.58; N, 20.24. Found: C, 57.14; H, 5.37; N, 20.00%. Mass spec. (FAB) calcd. for $C_{23}H_{20}N_7O_4$: *m/z* 458.1577. Found: *m/z* 458.1577. Infrared (cm^{-1}), 3415 (NH), 3289 (NH), 3112 m, 3050 w, 1697 m, 1673 m, 1627 m, 1583 s, 1537 br, 1411 m, 1331 m, 1298 m, 1248 m, 1221 w, 1163 m, 1157 m, 1072 m, 1003 w, 986 w, 799, 749 m, 683 m. ^{1}H NMR (d_6-DMSO): δ (ppm), 11.17 (s, 2H, **N*H*$_{head}$**); 10.51 (s, 2H, **N*H*$_{tail}$**); 8.42 (d, 7.3 Hz, 2H, ***3,5***); 8.34 (t, 7.2 Hz, 1H, ***4***); 8.02 (d, 7.8 Hz, 2H, ***11, 16***); 7.95 (t, 7.9 Hz, 2H, ***10, 15***); 7.89 (d, 7.7 Hz, 2H, ***9, 14***); 6.64 (dd, $^3J_{trans}$=17.0 Hz, $^3J_{cis}$=10.1 Hz, 1H, ***19, 22***); 6.35 (dd, $^3J_{trans}$=17.0 Hz, $^2J_{gem}$=1.4 Hz, 1H, ***20, 23***); 5.83 (dd, $^3J_{cis}$=10.1 Hz, $^2J_{gem}$=1.2 Hz, 1H, ***20', 23***). ^{13}C NMR (d_6-DMSO): δ (ppm), 163.66 (C=O, ***18, 21***); 162.12 (C=O, ***1, 7***); 150.55 (C_q, ***12, 17***); 149.43 (C_q, ***8, 13***); 148.54 (C_q, ***2, 6***); 140.48 (CH, ***10, 15***); 140.14 (CH, ***4***); 131.31 (CH, ***19, 22***); 127.98 (CH_2, ***20, 23***); 125.67 (CH, ***3, 5***); 110.92 (CH, ***9, 14***); 110.35 (CH, ***11, 16***).

Synthesis of H_4L.

2 (750 mg, 1.64 mmol) was dissolved in ethanol (200 mL) under nitrogen in a 500 mL three-necked round-bottomed flask. A solution of *n*-butylamine (138 μL, 1.0 eq.) in ethanol (50 mL) was added dropwise over 30 minutes. After stirring for one hour, the solution was heated under reflux for 72 hours. The resulting slightly cloudy solution was then allowed to cool to room temperature, filtered, and the solvent removed under reduced pressure, leaving a yellow oil. This was dissolved in dichloromethane and on the slow addition of diethyl ether pure **H_4L** was obtained as a cream powder (732 mg, 84 %). A crystal

suitable for single-crystal X-ray diffraction studies was grown by diffusion of *n*-hexane into a saturated solution of **H_4L** in 1,4-dioxane. Anal. calcd. for $C_{27}H_{30}N_8O_4.H_2O$: C, 59.11; H, 5.88; N, 20.43. Found: C, 58.75; H, 6.02; N, 19.84%. Mass spec. (FAB) calcd. for $C_{27}H_{31}N_8O_4$ $[M+H]^+$: *m/z* 531.2468. Found: *m/z* 531.2469. Infrared (cm^{-1}) 3256 br (NH), 3197 br (NH), 3128 br (NH), 1694 m, 1585 s, 1531 m, 1403 s, 1303 m, 1246 m, 1193 w, 1156 m, 1075 m, 1037 w, 1002 w, 891 w, 843 w, 800 m, 747 m, 733 m, 684 w, 653 w, 617 w, 561 w, 545 w, 520 w. ^{1}H NMR (d_6-DMSO): δ (ppm), 10.91 (br s, 2H, **N*H*$_{head}$**); 10.45 (br s, 2H, **N*H*$_{tail}$**); 8.47-8.15 (m, 3H, ***3-5***); 7.94 (d, 4.5 Hz, 4H, ***9, 14* + *11, 16***); 7.74 (m, 2H, ***10, 15***); 2.86 (dd, 9.5 Hz, 5.5 Hz, 4H, ***19, 22***), 2.56 (m, 4H, ***20, 23***); 2.43 (t, 6.8 Hz, 2H, ***24***); 1.32 (m, 4H, ***25*+*26***); 0.83 (t, 6.9 Hz, 3H, ***27***). ^{13}C NMR (d_6-DMSO): δ (ppm), 170.80 (C=O, ***18, 21***); 160.92 (C=O, ***1, 7***); 150.51 (C_q, ***12, 17***); 148.89 (C_q, ***8, 13***); 147.72 (C_q, ***2, 6***); 141.10 (CH, ***10, 15***); 140.83 (CH, ***4***); 125.39 (CH, ***3, 5***); 109.45 (CH, ***9, 14***); 108.17 (CH, ***11, 16***); 62.70 (CH_2, ***19, 22***); 50.22 (CH_2, ***20, 23***); 35.63 (CH_2, ***24***); 29.40 (CH_2, ***25***); 19.79 (CH_2, ***26***); 13.76 (CH_3, ***27***).

Synthesis of [PdCl(H_3L)] (3a)

H_4L (300 mg, 565 μmol), bis(benzonitrile)dichloropalladium(II) (261 mg, 680 μmol, 1.20 eq.) and sodium acetate (231 mg, 2.82 mmol, 5.00 eq.) were combined in a 50 mL two-necked pear-shaped flask and the flask evacuated. An atmosphere of dry nitrogen was re-established and the flask charged with dichloroethane (30 mL). The mixture was heated under reflux for two hours, during which time the ligand dissolved, forming a slightly cloudy orange solution. The solution was cooled to ambient temperature, filtered through celite® and the solvent removed under reduced pressure, affording an orange glass. This was dissolved in dichloromethane (*ca*. 10 mL) and *n*-hexane (*ca*. 10 mL) was slowly added to the flask which was then placed in a laboratory ultrasonic bath for ten minutes. The resulting orange microcrystalline solid was collected by filtration, washed with *n*-hexane (ca. 20 mL), and dried in vacuo to give pure [PdCl(H_3L)] (359 mg, 95%). A crystal suitable for single-crystal X-ray diffraction studies was grown by liquid-liquid diffusion of diethyl ether into a saturated solution of [PdCl(H_3L)] in 1,4-dioxane. Anal. calcd. for $C_{27}H_{29}N_8O_4PdCl.2MeOH$: C, 47.36; H, 5.07; N, 15.23. Found: C, 47.29; H, 4.64; N, 14.62%. Mass spec. (FAB) calcd. for $C_{27}H_{29}N_8O_4{}^{106}Pd$ $[M-Cl]^+$: *m/z* 635.1347. Found: *m/z* 635.1367. Infrared (cm^{-1}) 3428 br, 3306 br (NH), 3227 br (NH), 1691 m, 1682 m, 1632 m, 1598 m, 1581 s, 1535 m, 1531 m, 1455, 1416 m, 1207 m, 1251 m, 1221 w, 1159 m, 1139 m, 1117 m, 1077 m, 1031 w, 999 w, 798 m, 747 w, 723 w, 693 w, 668 w, 532 w. ^{1}H NMR (d_6-DMSO): δ (ppm), 10.85 (s, 1H, **N*H*$_{head}$**); 10.73 (s, 1H, **N*H*$_{head}$**); 8.56 (dd, 7.8 Hz, ^4J=1.0 Hz, 1H, ***5***); 8.42 (d, 8.2 Hz, 1H, ***14***); 8.36 (dd, 7.8 Hz, ^4J=1.1 Hz, 1H, ***3***); 8.11 (t, 7.8 Hz, 1H, ***4***); 8.05 (s, 1H, **N*H*$_{tail}$**); 7.91 (dd, 8.3 Hz, ^4J=0.6 Hz, 1H, ***9***); 7.76 (t, 8.4 Hz, 1H, ***10***); 7.76 (t, 8.0 Hz, 1H, ***15***); 7.19 (dd, 8.2 Hz, ^4J=0.6 Hz, 1H, ***11***); 6.64 (d, 7.7 Hz, 1H, ***16***); 5.14 (ddd, 18.0 Hz, 12.8 Hz, 4.5 Hz, 1H, ***19***); 4.02 (td, 12.7 Hz, 4.6 Hz, 1H, ***20***); 3.73 (m, 1H, ***22***); 3.37 (m, 2H, ***22'*+*23***); 3.12 (ddd, 18.9 Hz, 13.7 Hz, 5.2 Hz, 1H, ***19***); 2.40 (d, 13.8 Hz, 2H, ***25***); 2.29 (td, 12.7 Hz, 4.1 Hz, 1H, ***20***); 1.92-1.76 (m, 1H, ***23'***); 1.44-1.29 (m, 2H, ***26***);1.24 (t, 7.0 Hz, 2H, ***24***); 0.92 (t, 7.4 Hz, 3H, ***27***). ^{13}C NMR (d_6-DMSO): δ (ppm), 172.01 (C=O, ***18***); 167.31 (C_q, ***17***); 165.91 (C=O, ***21***); 162.87 (C=O, ***1***); 162.33 (C=O, ***7***); 150.55 (C_q, ***13***); 149.26 (C_q, ***8***); 149.11 (C_q, ***12***); 149.07 (C_q, ***2***); 148.70 (C_q, ***6***); 142.47 (CH, ***10***); 140.52 (CH, ***15***); 139.05 (CH, ***4***); 126.80 (CH, ***5***); 126.24 (CH, ***3***); 110.44 (CH, ***14***); 109.91 (CH, ***16***); 109.26 (CH, ***11***); 107.01 (CH, ***9***); 60.87 (CH_2, ***23***); 59.55 (CH_2, ***22***); 55.81 (CH_2, ***20***); 35.08 (CH_2, ***19***); 34.34 (CH_2, ***24***); 29.30 (CH_2, ***25***); 20.35 (CH_2, ***26***); 13.90 (CH_3, ***27***).

Synthesis of [Pd(OAc)(H_3L)] (3b)

H_4L (50 mg, 94 μmol) and palladium(II) acetate (21 mg, 95 μmol, 1.0 eq.) were combined in a 25 mL two-necked pear-shaped flask and the flask evacuated. An atmosphere of dry nitrogen was re-established and the flask charged with dichloroethane (5 mL). The reaction mixture was heated in an oil bath set at 50 °C for 18 hours, during which time the ligand dissolved, forming a slightly cloudy orange solution. The solution was cooled to ambient temperature, filtered through celite® and the yellow orange filtrate was poured with rapid stirring into *n*-hexane (150 mL). The precipitate was collected by filtration, recrystallised from dichloromethane and *n*-hexane and dried *in vacuo* to give pure [Pd(H_3L)(OAc)] as an orange microcrystalline solid (57 mg, 87%). Anal. calcd. for $C_{29}H_{32}N_8O_6Pd.1/4CH_2Cl_2$: C, 49.05; H, 4.57; N, 15.64. Found: C, 49.30; H, 4.48; N: 15.38%. Mass spec. (FAB) calcd. for $C_{27}H_{29}N_8O_4{}^{106}Pd$ $[M-OAc]^+$: *m/z* 635.1347. Found: *m/z* 635.1346. Infrared (cm^{-1}): 3358 w, 3339 w, 3239 w, 2959 s, 2932 w, 2872 w 1680 m, 1623 m, 1578 s, 1521m, 1439 s, 1359 s, 1297 w, 1244 s, 1157 w, 1074 w, 1001 w, 793 s, 678 w, 556 w, 404 w. ^{1}H NMR ($CDCl_3$): δ (ppm), 11.01 (s, 1H, **N*H*$_{head}$**); 10.15 (s, 1H, **N*H*$_{head}$**); 8.52-8.49 (m, 1H, ***H5***); 8.37-8.34 (m, 3H, ***NH$_{tail}$, 3, 14***); 8.11 (apparent t, $^3J_{HH}$ = 7.80, 1H, ***4***); 7.85 (apparent d, $^3J_{HH}$ = 8.4, 1H, ***9***); 7.76-7.67 (m, 2H, ***10, 15***); 7.22 (apparent d, $^3J_{HH}$ = 7.8, 1H, ***11***); 6.65 (apparent d, $^3J_{HH}$ = 7.8, 1H, ***16***); 5.08-4.97 (m, 1H, ***19***); 3.77-3.71 (m, 1H, ***20***); 3.47-3.39 (m, 2H, ***22, 23***); 3.16-3.09 (m, $^3J_{HH}$ = 12.0, 1H, ***24***); 2.92-2.83 (m, 1H, ***19***); 2.73-2.69 (m, 1H, ***22***); 2.51-2.4 (m, 2H, ***20, 23***); 2.24-2.15 (m, 2H, ***24***); 2.15 (s, 3H, ***29***), 1.75-1.68 (m, 2H, ***25***); 1.27-1.20 (m, 2H, ***26***); 0.94-0.89 (m, 3H, ***27***). ^{13}C NMR ($CDCl_3$): δ (ppm), 179.17 (*C*=O, ***28***); 172.52 (*C*=O, ***18***); 166.88 (*C*=O, ***21***); 166.25 (C_q, ***12***); 162.68 (*C*=O, ***1***); 162.62 (*C*=O, ***7***), 150.53 (C_q, ***8***); 149.77 (C_q, ***17***); 149.18 (C_q, ***13***); 148.99 (C_q, ***2***); 148.65 (C_q, ***6***); 142.53 (*C*H, ***11***); 140.82 (*C*H, ***10***); 139.43 (*C*H, ***3***); 126.72 (*C*H, ***5***), 126.66 (*C*H, ***4***); 110.09 (*C*H, ***16***), 110.06 (*C*H, ***14***); 109.57 (*C*H, ***15***); 106.99 (*C*H, ***9***); 59.34 (CH_2, ***24***); 58.16 (CH_2, ***22***); 55.02 (CH_2, ***20***); 34.63 (CH_2, ***23***); 34.38 (CH_2, ***19***); 26.97 (CH_2, ***25***); 20.89 (CH_3, ***29***); 23.10 (CH_2, ***26***); 13.96 (CH_3, ***27***).

Synthesis of [Pd(NH_2^nBu)(H_2L)] (4)

[Pd(OH_2)(H_2L)] (27 mg, 41 μmol) was placed in a 20 mL Schlenk tube and the tube evacuated. An atmosphere of dry nitrogen was re-established and the tube charged with dichloromethane (5 mL), forming a yellow suspension. *n*-Butylamine (41 μL, 420 μmol, 10 eq.) was added, resulting in the dissolution of the suspended material and formation of a yellow solution which was stirred at ambient temperature for 90 minutes. The volume of the solution was reduced to *ca*. 1 mL and the product purified by column chromatography (basic alumina, 5% methanol/dichloromethane as eluent), a single yellow band being

collected. The solvent was removed and the residue recrystallized from dichloromethane/*n*-hexane to afford a yellow microcrystalline solid, which was dried *in vacuo* to give pure [Pd($NH_2{}^nBu$)(H_2L)] (17 mg, 59%). Satisfactory elemental analysis was not obtained. Mass spec. (FAB) calcd. for $C_{31}H_{40}N_9O_4{}^{106}Pd$ [M + H]$^+$: *m/z* 708.22380. Found: *m/z* 708.22378. Infrared (cm^{-1}): 3264 w, 3190 w, 3116 w, 1700 m, 1668 m, 1636 s, 1617 s, 1573 s, 1522 s, 1440 s, 1391 m, 1356 s, 1312 m, 1265 w, 1240 m, 1196 w, 1151 m, 1098 w, 1074 w, 797 m, 756 w, 681 w, 657 w, 546 w. ^{1}H NMR (d_6-DMSO): δ (ppm), 10.13 (s, 2 H, N***H*****$_{tail}$**); 8.36 (t, $^3J_{HH}$ = 7.8, 1H, ***4***); 7.97 (d′, $^3J_{HH}$ = 7.8, 2H, ***3***, ***5***); 7.80-7.74 (m, 4H, [***9***, ***14***] and [***10***, ***15***]); 7.35 (d′, $^3J_{HH}$ = 7.2, 2H, ***11***, ***16***); 5.32 (s^{br}, 2H, N***H***$_2$); 2.80-2.77 (m, 4H, ***20***, ***23***); 2.68-2.62 (m, 2H, ***19*** or ***22***); 2.47-2.43 (m, 2H, ***19*** or ***22***); 2.41-2.38 (m, 2H, ***24***); 1.99-1.92 (m, 2H, ***28***); 1.40-1.33 (m, 2H, ***25***); 1.31-1.22 (m, 2H, ***26***); 1.15-1.08 (m, 2H, ***29***); 0.87-0.78 (m, 2H, ***30***); 0.85 (t, $^3J_{HH}$ = 7.3, 3H, ***27***); 0.51 (t, $^3J_{HH}$ = 7.3, 3H, ***31***). ^{13}C NMR (d_6-DMSO): δ (ppm), 170.57 (*C*=O, ***18***, ***21***); 169.04 (*C*=O, ***1***, ***7***); 157.15 (C_q, [***8***, ***13***] or [***12***, ***17***]); 151.40 (C_q, ***2***, ***6***); 149.60 (C_q, [***8***, ***13***] or [***12***, ***17***]); 141.76 (*C*H, ***4***); 139.71 (*C*H, ***10***, ***15***); 126.42 (*C*H, ***3***, ***5***); 115.03 (*C*H, ***9***, ***14***); 108.66 (*C*H, ***11***, ***16***); 53.18 (CH_2, ***24***); 50.70 (CH_2, ***20***, ***23***); 43.00 (CH_2, ***28***); 36.05 (CH_2, ***19***, ***22***); 32.91 (CH_2, ***29***); 28.94 (CH_2, ***25***); 19.87 (CH_2, ***26***); 19.03 (CH_2, ***30***); 13.80 (CH_3, ***27***); 13.09 (CH_3, ***31***).

[Pd(*N*-(3-aminopropyl)caprolactam)(H_2L)] (5)

(i) **H_4L** (500 mg, 942 μmol) and palladium(II) acetate (233 mg, 1.04 mmol, 1.10 eq.) were combined in a 100 mL two-necked round-bottomed flask fitted with a condenser and the flask evacuated. An atmosphere of dry nitrogen was re-established and the flask charged with tetrahydrofuran (50 mL) and water (340 μL, 20 eq), forming an orange solution. DBU (423 μL, 2.83 mmol, 3.00 eq.) was added and the solution was heated under reflux for 18 hours. The solution was cooled to ambient temperature and the solvent removed under reduced pressure. The residue was dissolved in a minimum amount of dichloromethane and purified by column chromatography (basic alumina, 5% methanol/dichloromethane as eluent), the single yellow band being collected. The solvent was removed and the residue recrystallized from dichloromethane/*n*-hexane to afford pure **5** as a yellow microcrystalline solid, which was dried *in vacuo* (614 mg, 81%). A crystal suitable for single-crystal X-ray diffraction was obtained by liquid-liquid diffusion of hexanes into a saturated acetone solution of **5**.

(ii) [Pd(OAc)(H_3L)] (100 mg, 143 μmol) was added to a 25 mL two-necked round-bottomed flask fitted with a condenser and the flask evacuated. An atmosphere of dry nitrogen was re-established and the flask charged with tetrahydrofuran (5 mL) and water (52 μL, 20 eq), forming an orange solution. DBU (107 μL, 715 μmol, 5.00 eq.) was added and the solution was heated under reflux for 8 hours. The solution was cooled to ambient temperature and the solvent removed under reduced pressure. The residue was dissolved in a minimum amount of dichloromethane and purified by column chromatography (basic alumina, 5% methanol/dichloromethane as eluent), the single yellow band being collected. The solvent was removed and the residue recrystallized from dichloromethane/*n*-hexane to afford pure **5** a yellow microcrystalline solid, which was dried *in vacuo* (91 mg, 79%).

(iii) [Pd(OAc)(H_3L)] (100 mg, 143 μmol) was added to a 25 mL two-necked round-bottomed flask fitted with a condenser and the flask evacuated. An atmosphere of dry nitrogen was re-established and the flask charged with tetrahydrofuran (15 mL), *N*-(3-aminopropyl)caprolactam (ACL) (122 μL, 715 μmol, 5.00 eq.) was added and the solution heated under reflux for 30 min. The solvent was removed under reduced pressure. The residue was dissolved in a minimum amount of dichloromethane and purified by column chromatography (basic alumina, 5% methanol/dichloromethane as eluent), the single yellow band being collected. The solvent was removed and the residue recrystallized from dichloromethane/*n*-hexane to afford pure **5** as a yellow microcrystalline solid which was dried *in vacuo* (102 mg, 88%). Anal. calcd. for $C_{36}H_{46}N_{10}O_5Pd{\cdot}½H_2O$: C, 53.10; H, 5.82; N: 17.20. Found: C, 53.37; H, 5.82; N: 16.88%. Mass spec. (FAB) calcd. for $C_{36}H_{47}N_{10}O_5{}^{106}Pd$ [M + H]$^+$: *m/z* 805.27657. Found: *m/z* 805.27499. Infrared (cm^{-1}): 3243 m, 1691 s, 1614 s, 1529 s, 1442 s, 1354 s, 1315 s, 1240 s, 1197 m, 1152 s, 1095 w, 837 w, 800 m, 760 w, 734 w, 681 w, 668 w, 629 w, 548 w. ^{1}H NMR (d_6-DMSO): δ (ppm), 10.14 (s, 2H, **N*H***); 8.36 (t, $^3J_{HH}$ = 7.8, 1H, ***4***); 7.97 (d′, $^3J_{HH}$ = 7.8, 2H, ***3*** and ***5***); 7.81 (d′, $^3J_{HH}$ = 7.8, 2H, ***9*** and ***14***); 7.75 (t′, $^3J_{HH}$ = 7.9, 2H, ***10*** and ***15***); 7.32 (d′, $^3J_{HH}$ = 7.7, 2H, ***11*** and ***16***); 5.46 (s^{br}, 2H, N***H***$_2$); 3.01-3.00 (m, 2H, ***ACL***); 2.92 (t, $^3J_{HH}$ = 6.4, 2H, ***30***); 2.79 (t, $^3J_{HH}$ = 7.2, 4H, ***20*** and ***23***); 2.65-2.61 (m, 2H, ***19*** or ***22***); 2.47-2.43 (m, 2H, ***19*** or ***22***); 2.39 (t, $^3J_{HH}$ = 7.2, 2H, ***24***); 2.22-2.20 (m, 2H, ***ACL***); 1.92-1.87 (m, 2H, ***28***); 1.51-1.47 (m, 2H, ***25***); 1.43-1.31 (m, 6H, ***29*** and ***ACL***); 1.29-1.21 (m, 4H, ***26*** and ***ACL***); 0.86 (t, $^3J_{HH}$ = 7.0, 3H, ***27***). ^{13}C NMR (d_6-DMSO): δ (ppm), 174.29 (*C*=O, ***31***); 170.67 (*C*=O, ***18***, ***21***); 169.14 (*C*=O, ***1***, ***7***); 157.19 (C_q, [***8***, ***13***] or [***12***, ***17***]); 151.38 (C_q, ***2***, ***6***); 149.65 (C_q, [***8***, ***13***] or [***12***, ***17***]); 141.78 (*C*H, ***4***); 139.60 (*C*H, ***10***, ***15***); 126.43 (*C*H, ***3***, ***5***); 114.97 (*C*H, ***9***, ***14***); 108.79 (*C*H, ***11***, ***16***); 53.19 (CH_2, ***24***); 50.65 (CH_2, ***20***, ***23***); 48.21 (CH_2, ***ACL***); 44.21 (CH_2, ***ACL***); 40.97 (CH_2, ***ACL***); 36.18 (CH_2, ***ACL***); 36.04 (CH_2, ***19***, ***22***); 29.86 (CH_2, ***ACL***); 29.05 (CH_2, ***25*** or ***ACL***); 28.99 (CH_2, ***25*** or ***ACL***); 28.39 (CH_2, ***26*** or ***ACL***); 22.83 (CH_2, ***ACL***); 19.93 (CH_2, ***26*** or ***ACL***); 13.85 (CH_3, ***27***).

Synthesis of [Pd(OH_2)(H_2L)] (6)

H_4L (50 mg, 94 μmol) and palladium(II) acetate (42 mg, 190 μmol, 2.0 eq.) were combined in a 20 mL Schlenk tube and the tube evacuated. An atmosphere of dry nitrogen was re-established and the tube charged with pyridine (5 mL). The resulting suspension was heated in an oil bath set at 50 °C for two hours. During this time the reagents dissolved to form a yellow solution. The solution was cooled to ambient temperature and was then added dropwise to *n*-hexane (*ca*. 60 mL), forming a yellow solid. The solvent was removed by filtration and the solid dissolved in a minimum amount of dichloromethane and purified by column chromatography (basic alumina, 5% methanol/dichloromethane as eluent). The single yellow band was collected, the volume of the solvent was reduced, resulting in the crystallization of yellow needles, which were collected and dried *in vacuo* to give pure [Pd(OH_2)(H_2L)] **(6)** (54 mg, 88%). A

crystal suitable for single-crystal X-ray diffraction studies was grown by slow evaporation of a saturated solution of [Pd(OH$_2$)(H$_2$L)] in 5% methanol/dichloromethane. Anal. calcd. for $C_{27}H_{30}N_8O_5Pd$: C, 49.66; H, 4.63; N, 17.16. Found: C, 49.44; H, 4.66; N: 17.13%. Mass spec. (FAB) calcd. for $C_{27}H_{31}N_8O_5{}^{106}Pd$ $[M + H]^+$: *m/z* 653.14522. Found: *m/z* 653.14781. Infrared (cm^{-1}): 3314 w, 3149 w, 1714 w, 1675 m, 1626 s, 1594 s, 1572 s, 1517 m, 1442 s, 1414 m, 1353 s, 1312 w, 1244 w, 1173 w, 1151 m, 1101 w, 1038 w, 1006 w, 894 w, 875 w, 798 m, 756 w, 746 w, 736 w, 677 w, 653 w, 632 w, 570 w, 546 w. ^{1}H NMR (d_6-DMSO): δ (ppm), 10.16 (s, 2 H, N***H*****$_{tail}$**); 8.43 (t, $^3J_{HH}$ = 7.80, 7.8, 1H, ***4***); 8.02 (d, $^3J_{HH}$ = 7.8, 2H, ***3***, ***5***); 7.94 (d′, $^3J_{HH}$ = 6.6, 2H, ***9***, ***14***); 7.75 (t′, $^3J_{HH}$ = 7.9, 7.90, 2H, ***10***, ***15***); 7.69 (s^{br}, 2H, ***11***, ***16***); 3.36 (s^{br}, 2H, O***H***$_2$); 2.85-2.82 (m, 4H, ***20***, ***23***); 2.46 (m, 4H, ***19***, ***22***); 2.41-2.37 (m, 2H, ***24***); 1.45-1.38 (m, 2H, ***25***); 1.29-1.22 (m, 2H, ***26***); 0.86 (t, $^3J_{HH}$ = 7.3, 3H, ***27***). ^{13}C NMR (d_6-DMSO): δ (ppm), 170.61 (***C***=O, ***18***, ***21***); 168.67 (***C***=O, ***1***, ***7***); 156.18 (C_q, [***8***, ***13***] or [***12***, ***17***]); 151.76 (C_q, ***2***, ***6***); 149.84 (C_q, [***8***, ***13***] or [***12***, ***17***]); 142.82 (***C***H, ***4***); 139.98 (***C***H, ***10***, ***15***); 127.01 (***C***H, ***3***, ***5***); 113.15 (***C***H, ***9***, ***14***); 108.16 (***C***H, ***11***, ***16***); 53.19 (***C***H$_2$, ***24***); 49.54 (***C***H$_2$, ***20***, ***23***); 35.36 (***C***H$_2$, ***19***, ***22***); 29.48 (***C***H$_2$, ***25***); 19.84 (***C***H$_2$, ***26***); 13.81 (***C***H$_3$, ***27***).

Synthesis of [Pd(DBU)(H$_2$L)] (7)

[Pd(OH$_2$)(H$_2$L)] (100 mg, 153 μmol) was placed in a 150 mL Schlenk tube and the tube evacuated. An atmosphere of dry nitrogen was re-established and the tube charged with anhydrous tetrahydrofuran (20 mL), forming a yellow suspension. DBU (116 μL, 776 μmol, 5.07 eq.) was added, resulting in the dissolution of the suspended material and formation of a yellow solution which was stirred at ambient temperature for five minutes. At the end of this time, *n*-hexane (*ca*. 80 mL) was added to the solution, forming a yellow microcrystalline solid, which was collected, washed with *n*-hexane (*ca*. 10 mL) and dried *in vacuo* to give pure [Pd(DBU)(H$_2$L)] (92 mg, 76%). Anal. calcd. for $C_{36}H_{44}N_{10}O_4Pd{\cdot}H_2O$: C, 53.70; H, 5.76; N: 17.39. Found: C, 53.77; H, 5.87; N: 17.43%. Mass spec. (FAB) calcd. for $C_{36}H_{45}N_{10}O_4{}^{106}Pd$ $[M + H]^+$: *m/z* 787.26600. Found: *m/z* 787.26607. Infrared (cm^{-1}): 3252 m, 1683 m, 1596 s, 1573 s, 1538 m, 1398 m, 1365 m, 1316 m, 1237 m, 1204 w, 1151 m, 1093 w, 1032 w, 837 w, 799 w, 763 w, 681 w, 626 w, 546 w. ^{1}H NMR (d_6-DMSO): δ (ppm), 10.24 (s^{br}, 2H, N***H*****$_{tail}$**); 8.31 (t, $^3J_{HH}$ = 7.8, 1H, ***4***); 7.88 (d′, $^3J_{HH}$ = 7.8, 2H, ***3***, ***5***); 7.66 (t′, $^3J_{HH}$ = 7.8, 2H, ***10***, ***15***); 7.57 (s^{br}, 2H, ***11***, ***16***); 7.06 (d′^{br}, $^3J_{HH}$ = 6.8, 2H, ***9***, ***14***); 3.65 (s^{br}, 2H, ***DBU***); 3.06-3.01 (m, 4H, ***DBU***); 2.86-2.73 (m, 10H, [***19***, ***22***] and [***20***, ***23***] and ***DBU***); 2.44-2.40 (m, 2H, ***24***); 1.44-1.36 (m, 6H, ***25***, ***DBU***); 1.31-1.22 (m, 4H, ***26***, ***DBU***); 0.84-0.77 (m, 3H, ***27***); 0.71 (s^{br}, 2H, ***DBU***). ^{13}C NMR (d_6-DMSO): δ (ppm), 170.82 (***C***=O or ***C***=N, [***1***, ***7***] or [***18***, ***21***] or ***36***); 168.07 (***C***=O or ***C***=N, [***1***, ***7***] or [***18***, ***21***] or ***36***); 163.91 (***C***=O or ***C***=N, [***1***, ***7***] or [***18***, ***21***] or ***36***); 157.92 (C_q, [***8***, ***13***] or [***12***, ***17***]); 152.45 (C_q, ***2***, ***6***); 150.29 (C_q, [**8**, **13**] or [**12**, **17**]); 141.19 (***C***H, ***4***); 138.60 (***C***H, ***10***, ***15***); 125.81 (***C***H, ***3***, ***5***); 115.77 (***C***H, ***9***, ***14***); 108.66 (***C***H, ***11***, ***16***); 53.15 (***C***H$_2$, ***24***); 51.73 (***C***H$_2$, ***DBU***); 51.09 (***C***H$_2$, ***20***, ***23***); 47.13 (***C***H$_2$, ***DBU***); 46.74 (***C***H$_2$, ***19***, ***22***); 36.83 (***C***H$_2$, ***DBU***); 35.91 (***C***H$_2$, ***DBU***); 28.76 (***C***H$_2$, ***DBU***); 27.67 (***C***H$_2$, ***DBU***); 26.48 (***C***H$_2$, ***DBU***); 23.89 (***C***H$_2$, ***25***); 20.74 (***C***H$_2$, ***DBU***); 19.84 (***C***H$_2$, ***26***); 13.69 (***C***H$_3$, ***27***).

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References

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† Electronic Supplementary Information (ESI) available: Crystal and refinement data for compounds **H$_4$L**, [PdCl(H$_3$L)] (**3a**), [Pd(*N*-(3-aminopropyl)caprolactam)(H$_2$L) (**5**) and [Pd(OH$_2$)(H$_2$L) (**6**) in CIF format. This data is also available from the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 990384-990387.

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Controlled translocation of palladium(II) within a 22 ring atom macrocyclic ligand

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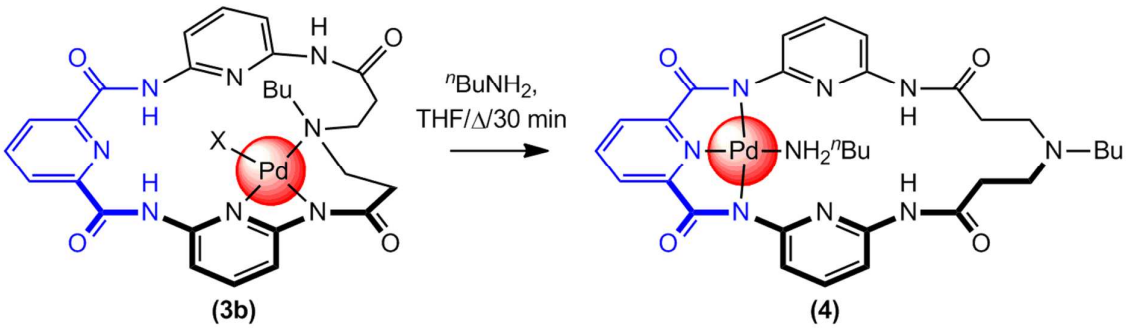
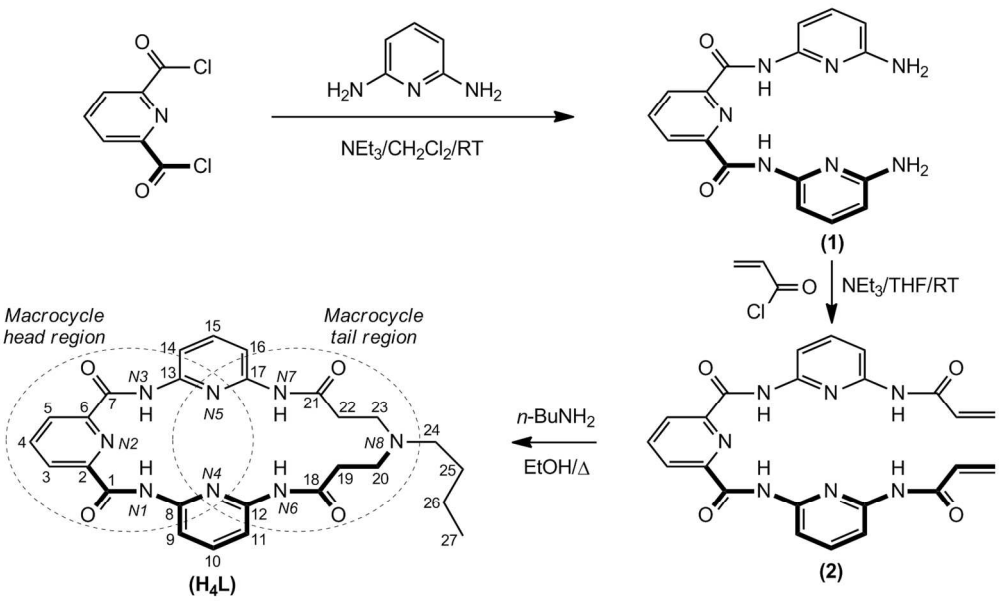
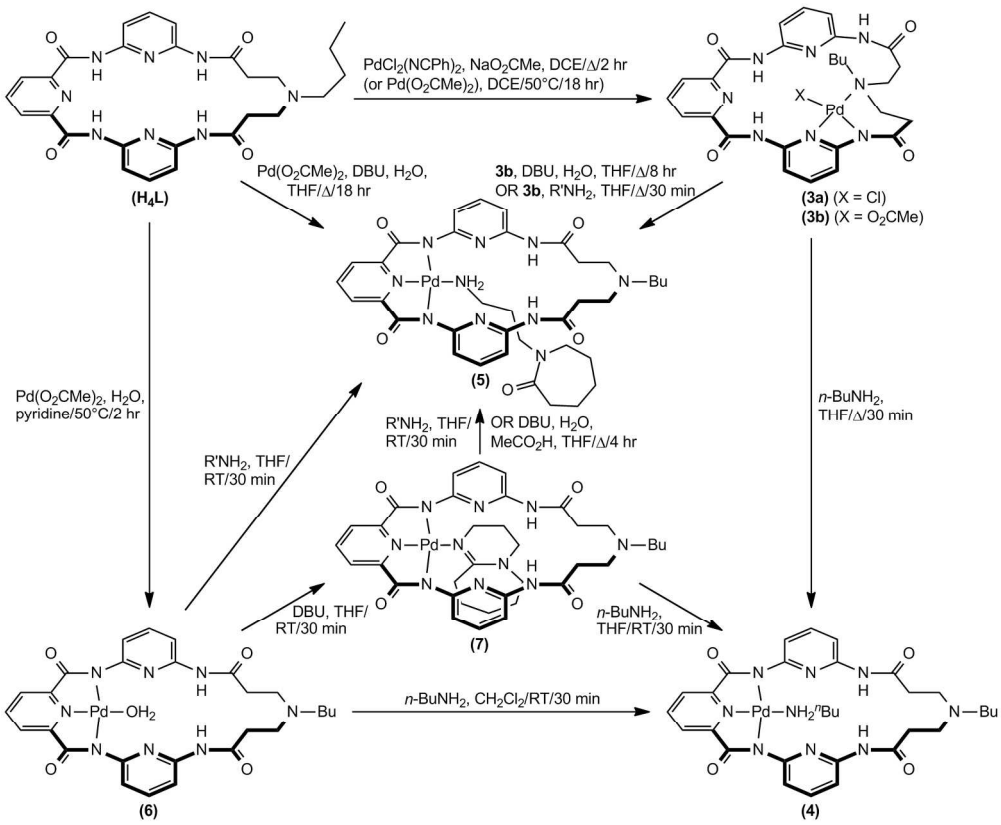
Text and graphic for Table of Contents Entry

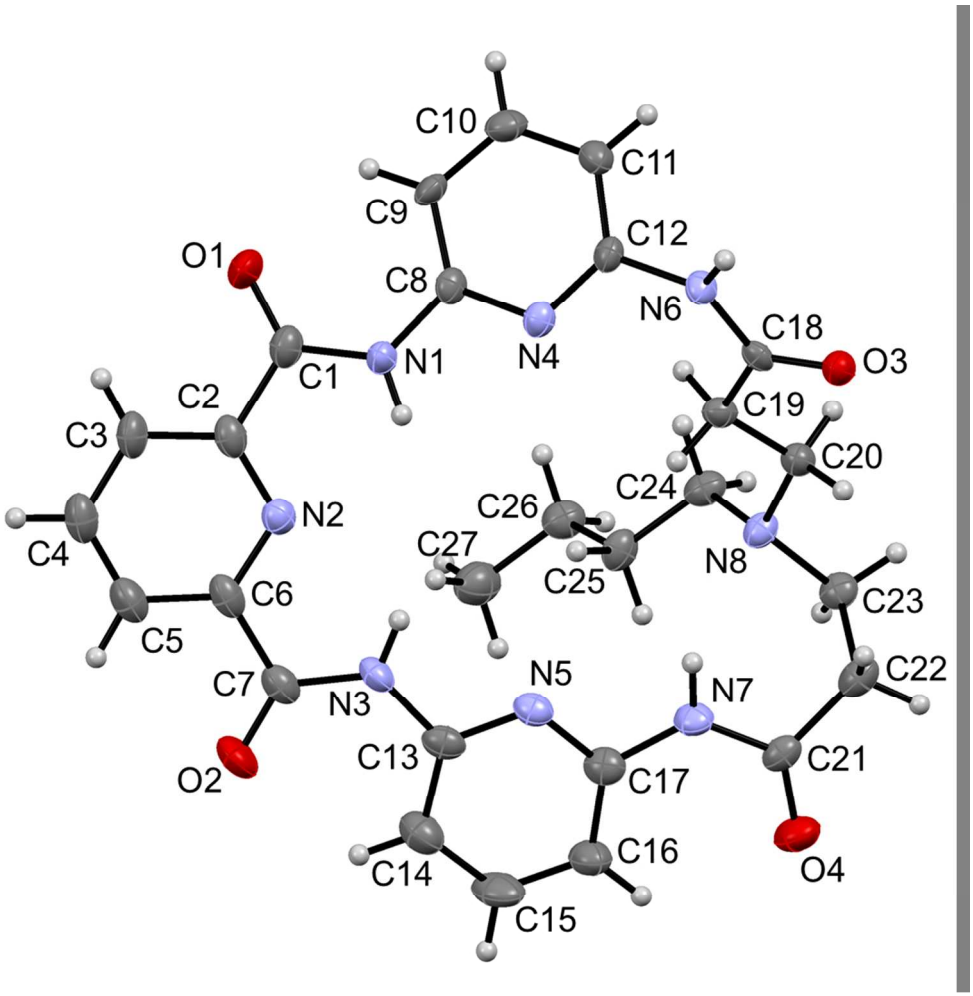
Palladium can be directed to coordinate to the "tail" region of the macrocycle **H_4L** to give **3b**. Translocation of the palladium from the tail coordination pocket to the head coordination pocket occurs on treatment with amines such as *n*-$BuNH_2$ to give **4**.



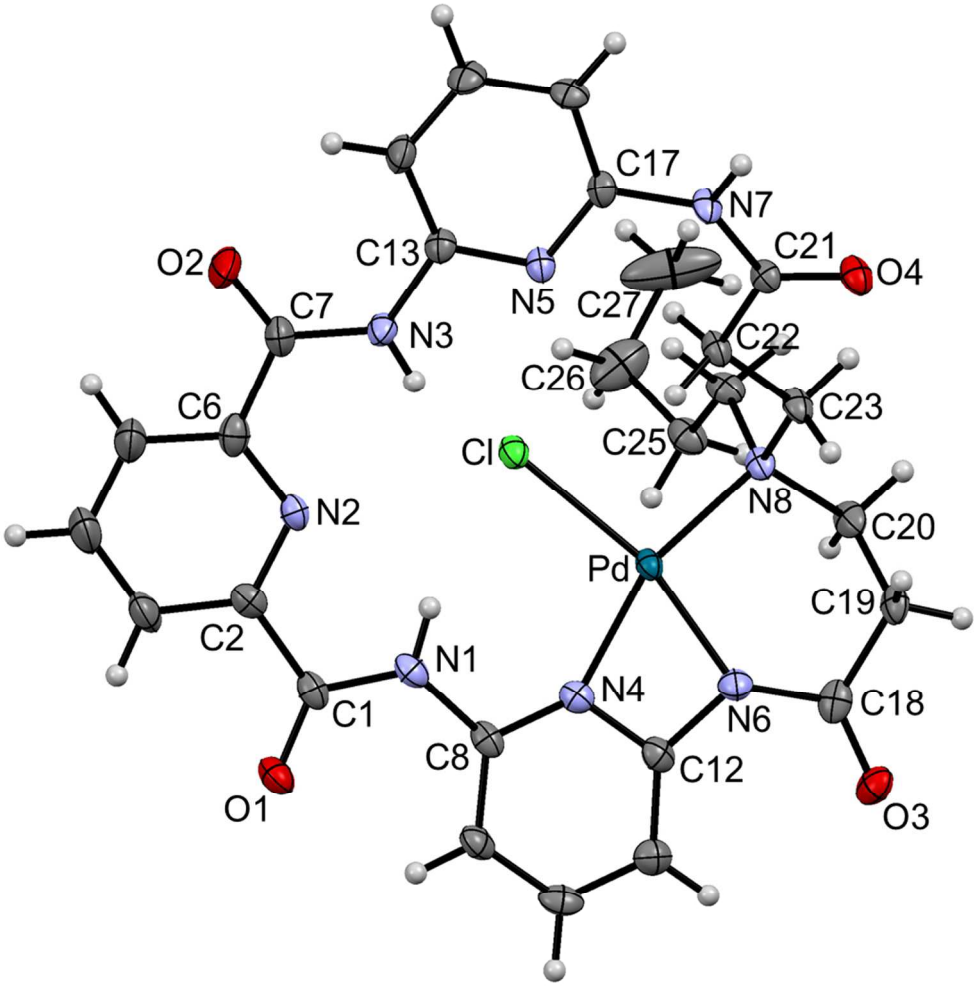
(3b) (4)







Molecular structure of H4L. Thermal ellipsoids are shown at the 50% probability level.



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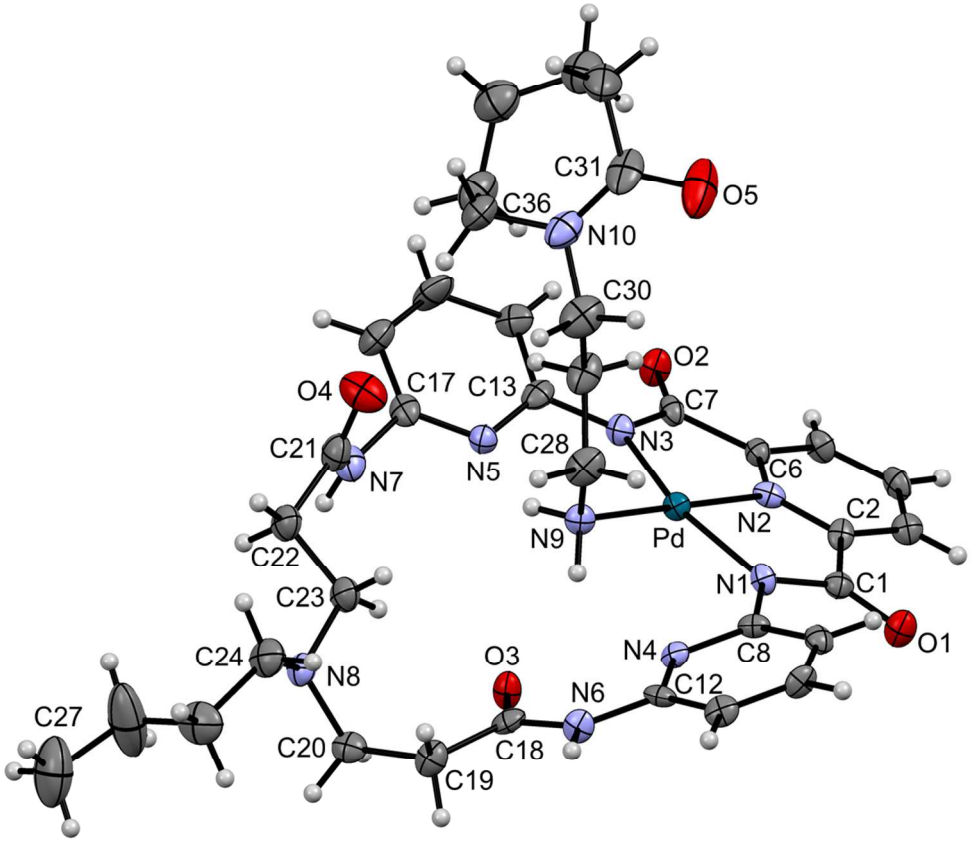

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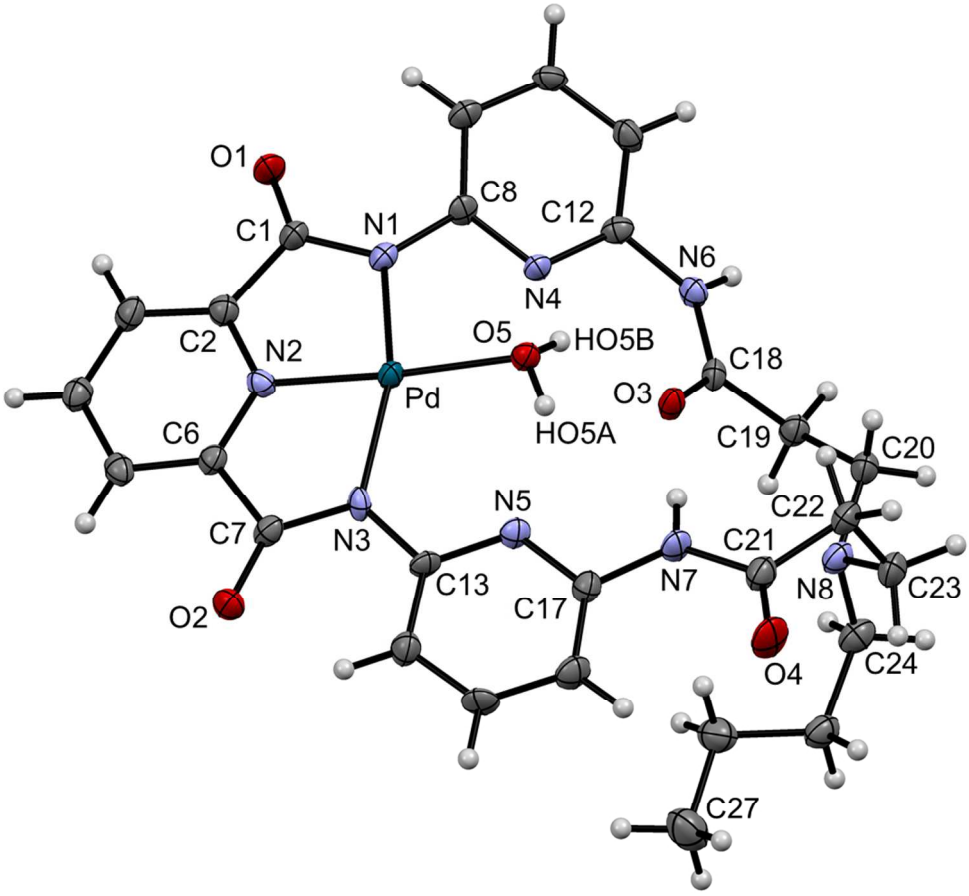

Molecular structure of 6. Thermal ellipsoids are shown at the 50% probability level.