Supporting Information

LiBF₄-Induced Rearrangement and Desymmetrization of a Palladium-Ligand Assembly

S. Sudan, F. Fadaei-Tirani, R. Scopelliti, K. E. Ebbert, G. H. Clever, K. Severin*
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1 General

All reagents were obtained from commercial sources and used without further purification unless stated otherwise. The ligands L1 to L11 were synthesized following literature procedures.[1-11]

NMR spectra were measured on a Bruker Avance Neo spectrometer (1H: 500 MHz, 13C: 125 MHz) equipped with a CPTClxyz 5 mm cryoprobe, a Bruker Avance III spectrometer (1H: 400 MHz) equipped with a BBFO 5 mm probe and a Bruker Avance III spectrometer (1H: 400 MHz) equipped with a Prodigy BBO 5 mm cryoprobe. The chemical shifts are reported in part per million (ppm) using the solvent residual signal as a reference.

High resolution mass spectrometry experiments were carried out using a hybrid ion trap-Orbitrap Fourier transform mass spectrometer, Orbitrap Elite (Thermo Scientific) equipped with a TriVersa Nanomate (Advion) nano-electrospray ionization source. Mass spectra were acquired with a minimum resolution setting of 120,000 at 400 m/z. To reduce the degree of analyte gas phase reactions leading to side products unrelated to solution phase, the transfer capillary temperature was lowered to 50 °C. Experimental parameters were controlled via standard and advanced data acquisition software.
2 Synthesis of the assemblies C1 to C13

Homoleptic assemblies

The literature-known homoleptic assemblies C1 to C11 were obtained as follows: a mixture of the respective ligand (L1–L11, 2 equiv) and [Pd(CH$_3$CN)$_4$]$_4$(BF$_4$)$_2$ (1.0–1.1 equiv) in CD$_3$CN was stirred at 70 °C for 12 h. The formation of the desired product was confirmed by $^1$H NMR spectroscopy (the aromatic parts of the spectra are shown in section 3). In all cases, the spectra matched what has been reported in the literature.$^{[6,8,12–14]}$ The concentrations were adjusted according to the solubility of the ligand and/or the final assembly (Table S1).

Figure S1. Structures of the ligands L1 to L11.

Table S1. Amounts of L1 to L11 and [Pd(CH$_3$CN)$_4$]$_4$(BF$_4$)$_2$ used for the synthesis of the assemblies C1 to C11.

| Assembly | Formula | Ligand | n$_L$ [µmol] | n$_{Pd}$ [µmol] | V$_{tot}$ [mL] | [Pd$_n$L$_{2n}$] [mM] |
|----------|---------|--------|--------------|----------------|----------------|-------------------|
| C1       | [Pd$_4$(L1)$_8$(BF$_4$)$_8$] | L1     | 9.0          | 4.5            | 1.03           | 1.1              |
| C2       | [Pd$_2$(L2)$_4$(BF$_4$)$_4$] | L2     | 4.6          | 2.3            | 1.00           | 1.1              |
| C3       | [Pd$_2$(L3)$_4$(BF$_4$)$_4$] | L3     | 9.7          | 4.9            | 1.07           | 2.3              |
| C4       | [Pd$_2$(L4)$_4$(BF$_4$)$_4$] | L4     | 9.4          | 4.7            | 1.07           | 2.2              |
| C5       | [Pd$_2$(L5)$_4$(BF$_4$)$_4$] | L5     | 6.8          | 3.7            | 0.66           | 2.6              |
| C6       | [Pd$_3$(L6)$_6$(BF$_4$)$_6$] | L6     | 5.6          | 3.1            | 0.61           | 1.6              |
| C7       | [Pd$_2$(L7)$_4$(BF$_4$)$_4$] | L7     | 5.0          | 2.5            | 0.75           | 1.7              |
| C8       | [Pd$_5$(L8)$_{12}$(BF$_4$)$_{12}$] | L8     | 5.2          | 2.6            | 1.00           | 0.8              |
| C9       | [Pd$_5$(L9)$_{12}$(BF$_4$)$_{12}$] | L9     | 14.9         | 7.5            | 1.08           | 1.2              |
| C10      | [Pd$_{12}$(L10)$_{24}$(BF$_4$)$_{24}$] | L10    | 14.1         | 7.7            | 0.72           | 0.8              |
| C11      | [Pd$_2$(L11)$_{4}$(BF$_4$)$_{8}$] | L11    | 3.1          | 1.6            | 0.65           | 0.6              |
Heteroleptic assemblies

The literature-known heteroleptic assemblies C12 and C13 were obtained as follows: an equimolar mixture of the two respective ligands (L4/L5 or L1/L10) and [Pd(CH3CN)4](BF4)_2 in CD3CN was stirred at 70 °C for 12 h. The formation of the desired product was confirmed by 1H NMR spectroscopy (the aromatic parts of the spectra are shown in section 3). In both cases, the spectra matched what has been reported in the literature.[12–14]

![Figure S2. Structures of the ligands L1, L2, L4 and L10.](image)

| Assembly | Formula | L   | nL [µmol] | nPd [µmol] | Vtot [mL] | [Pd_nL_nL’_n] [mM] |
|----------|---------|-----|-----------|------------|-----------|-------------------|
| C12      | [Pd_2(L2)_2(L4)_2](BF4)_4  | L2  | 2.3       | 2.3        | 1.00      | 1.2               |
|          |         | L4  | 2.3       |            |           |                   |
|           |         | L1  | 9.1       | 9.1        | 1.00      | 1.5               |
| C13      | [Pd_6(L1)_6(L10)_6](BF4)_12 | L1  | 9.1       | 9.1        | 1.00      |                   |
|          |         | L10 | 9.1       |            |           |                   |

Table S2. Amounts of L1, L2, L4, L10, and [Pd(CH3CN)4](BF4)_2 used for the synthesis of the heteroleptic assemblies C12 and C13.
3 Screening experiment

An aliquot of a stock solution of LiBF$_4$ in CD$_3$CN was added to an NMR tube containing a solution of the respective Pd assembly (C1 to C13, 1 equiv, [Cx] = 0.4–2.6 mM, Li:[Cx] = 50:1) in CD$_3$CN, and a $^1$H NMR spectrum was recorded immediately after mixing. A second spectrum was recorded for C2 after 20 h equilibration at room temperature (see Figure S4).

The aromatic parts of the $^1$H NMR spectra before and after addition of LiBF$_4$ are shown below. Minor differences between the spectra were observed in several cases. In order to classify as a 'hit', differences of at least 0.05 ppm were observed for signals of protons pointing towards the cage interior. Changes of this magnitude were observed for C1 and C2, and the interaction of these cages with LiBF$_4$ was investigated in more detail.

$[\text{Pd}_4(\text{L1})_8](\text{BF}_4)_8$ (C1)

![Figure S3. $^1$H NMR (400 MHz, CD$_3$CN) spectrum of [Pd$_4$(L1)$_8$](BF$_4$)$_8$ (C1) before (bottom) and after (top) addition of LiBF$_4$.](image-url)
Figure S4. $^1$H NMR (400 MHz, CD$_3$CN) spectrum of [Pd$_2$(L2)$_4$(BF$_4$)$_4$ (C2) before (bottom), directly after addition of LiBF$_4$ (middle), and after equilibration at RT °C for 20 h (top).

Figure S5. $^1$H NMR (400 MHz, CD$_3$CN) spectrum of [Pd$_2$(L3)$_4$(BF$_4$) (C3) before (bottom) and after (top) addition of LiBF$_4$. 
**Figure S6.** $^1$H NMR (400 MHz, CD$_3$CN) spectrum of [Pd$_2$(L4)$_4$(BF$_4$)$_4$ (C4) before (bottom) and after (top) addition of LiBF$_4$.

**Figure S7.** $^1$H NMR (400 MHz, CD$_3$CN) spectrum of [Pd$_2$(L5)$_4$(BF$_4$)$_4$ (C5) before (bottom) and after (top) addition of LiBF$_4$. 
$[\text{Pd}_3(L6)_6](\text{BF}_4)_6$ (C6)

$[\text{Pd}_2(L7)_4](\text{BF}_4)_4$ (C7)

**Figure S8.** $^1$H NMR (400 MHz, CD$_3$CN) spectrum of $[\text{Pd}_3(L6)_6](\text{BF}_4)_6$ (C6) before (bottom) and after (top) addition of LiBF$_4$.

**Figure S9.** $^1$H NMR (400 MHz, CD$_3$CN) spectrum of $[\text{Pd}_2(L7)_4](\text{BF}_4)_4$ (C7) before (bottom) and after (top) addition of LiBF$_4$. 
**Figure S10.** $^1$H NMR (400 MHz, CD$_3$CN) spectrum of [Pd$_6$(L8)$_{12}$](BF$_4$)$_{12}$ (C8) before (bottom) and after (top) addition of LiBF$_4$.

**Figure S11.** $^1$H NMR (400 MHz, CD$_3$CN) spectrum of [Pd$_6$(L9)$_{12}$](BF$_4$)$_{12}$ (C9) before (bottom) and after (top) addition of LiBF$_4$. 
**Figure S12.** $^1$H NMR (400 MHz, CD$_3$CN) spectrum of $[\text{Pd}_{12}(\text{L10})_{24}](\text{BF}_4)_{24}$ (C10) before (bottom) and after (top) addition of LiBF$_4$.

**Figure S13.** $^1$H NMR (400 MHz, CD$_3$CN) spectrum of $[\{\text{Pd}_2(\text{L11})_4\}_2](\text{BF}_4)_8$ (C11) before (bottom) and after (top) addition of LiBF$_4$. 
Figure S14. $^1$H NMR (400 MHz, CD$_3$CN) spectrum of [Pd$_2$(L2)$_2$(L4)$_2$](BF$_4$)$_4$ (C12) before (bottom) and after (top) addition of LiBF$_4$.

Figure S15. $^1$H NMR (400 MHz, CD$_3$CN) spectrum of [Pd$_6$(L1)$_6$(L10)$_6$](BF$_4$)$_{12}$ (C13) before (bottom) and after (top) addition of LiBF$_4$. 
3.1 NMR titration

Aliquots (0.92 µL) of a 2.17 M stock solution of LiBF₄ in CD₃CN were added to a solution of [Pd₄(L1)₈](BF₄)₈ (400 µL, 0.5 mM) in an NMR tube. ¹H NMR spectra were recorded directly after each addition.

Figure S16. ¹H NMR (400 MHz, CD₃CN) spectrum of [Pd₄(L1)₈](BF₄)₈ in the presence of increasing amounts of LiBF₄.
Figure S17. Chemical shifts of protons $H_a$ and $H_a'$ as a function of the [LiBF$_4$]/[Pd$_4$(L1)$_8$] ratio. The data were fitted to a 1:1 binding model using the online tool available at: http://supramolecular.org. Dilution effects were accounted for.

4 Synthesis and characterization of [Pd$_4$(L2)$_8$](BF$_4$)$_8$

[Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ (7.65 µmol, 148.1 µL of a 51.7 mM stock solution in CD$_3$CN, 1 eq.) and LiBF$_4$ (114.8 µmol, 130.1 µL of a 882 mM stock solution in CD$_3$CN, 15 eq.) were added to a suspension of L2 (15.30 µmol, 8.90 mg, 2 eq.) in CD$_3$CN (635 µL) and the mixture was heated at 70 °C for 12 h to give [Pd$_4$(L2)$_8$](BF$_4$)$_8$. $^1$H NMR spectroscopy confirmed the full conversion to the expected assembly.
**Figure S18.** $^1$H NMR (400 MHz, CD$_3$CN) spectrum of [Pd$_4$(L$_2$)$_8$](BF$_4$)$_8$.

**Figure S19.** $^{13}$C NMR (125 MHz, CD$_3$CN) spectrum of [Pd$_4$(L$_2$)$_8$](BF$_4$)$_8$. 
**Figure S20.** Zoom in the region 83.6 to 97.7 ppm of the $^{13}$C NMR (125 MHz, CD$_3$CN) spectrum of $[\text{Pd}_4(\text{L}2)_8](\text{BF}_4)_8$. A total of 16 alkyne carbon signals can be observed.

**Figure S21.** $^1$H-$^1$H COSY NMR (500 MHz, CD$_3$CN) spectrum of $[\text{Pd}_4(\text{L}2)_8](\text{BF}_4)_8$. 
**Figure S22.** $^1$H-$^{13}$C HSQC NMR (500 MHz, CD$_3$CN) spectrum of [Pd$_4$(L2)$_8$](BF$_4$)$_8$.

**Figure S23.** Zoom in the region 8.3 to 10.9 ppm and 146 to 163 ppm of the $^1$H-$^{13}$C HSQC NMR (500 MHz, CD$_3$CN) spectrum of [Pd$_4$(L2)$_8$](BF$_4$)$_8$. 
Figure S24. $^1$H-$^1$H NOESY NMR (500 MHz, CD$_3$CN) spectrum of [Pd$_4$(L2)$_8$](BF$_4$)$_8$.

Figure S25. $^1$H DOSY NMR (400 MHz, CD$_3$CN) spectrum of [Pd$_4$(L2)$_8$](BF$_4$)$_8$. 
Figure S26. Aromatic region of the $^1$H NMR spectra (400 MHz, CD$_3$CN) of [Pd$_4$(L$^2$)$_8$](BF$_4$)$_8$ recorded at 298 K (a) 323 K (b) 333 K (c) and 343 K (d).

Figure S27. HRMS of a mixture of [Pd$_2$(L$^2$)$_4$](BF$_4$)$_4$ (1 eq.) and LiBF$_4$ (50 eq.) in CD$_3$CN after equilibration at RT for 20 h. The main peaks can be attributed to a species with the formula $\{[$Pd$_4$(L$^2$)$_8$(LiBF$_4$)$_2$](BF$_4$)$_x\}^{2+}$. 

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Figure S28. HRMS of a mixture of [Pd₂(L₂)₄](BF₄)₄ (1 eq.) and LiBF₄ (50 eq.) in CD₃CN after equilibration at RT for 20 h, comparing the 1109–1102 m/z region (bottom) and the calculated mass spectrum for {[Pd₄(L₂)₈(LiBF₄)₂](BF₄)₃}⁵⁺ (top).
4.1 Time-dependence of the \([\text{Pd}_2(\text{L}2)_4]\) to \([\text{Pd}_4(\text{L}2)_8]\) transformation

An aliquot (35.9 µL, 50 eq.) of a 741.7 mM stock solution of LiBF\(_4\) was added to 460 µL of a 1.16 mM solution (1 eq.) of \([\text{Pd}_2(\text{L}2)_4](\text{BF}_4)_4\) in an NMR tube, and \(^1\text{H}\) NMR spectra were recorded at different time intervals until complete conversion to \([\text{Pd}_4(\text{L}2)_8](\text{BF}_4)_8\) was observed. The experiment was conducted at room temperature.

![Aromatic region of the \(^1\text{H}\) NMR spectra recorded at different time intervals after the addition of 50 eq. of LiBF\(_4\) to a solution of \([\text{Pd}_2(\text{L}2)_4](\text{BF}_4)_4\) at r.t.](image)

**Figure S29.** a) Aromatic region of the \(^1\text{H}\) NMR spectra recorded at different time intervals after the addition of 50 eq. of LiBF\(_4\) to a solution of \([\text{Pd}_2(\text{L}2)_4](\text{BF}_4)_4\) at r.t.. b) The conversion as a as a function of time as determined by integration of the signal at 10.7 ppm. The data could fitted to a first order kinetic model (\(t_{1/2} = 135\) min).
4.2 Synthesis in the presence of water

\[ \text{[Pd(CH}_3\text{CN)}_4(\text{BF}_4)_2 (1.36 \mu\text{mol, 30.3 \muL of a 44.8 mM stock solution in CD}_3\text{CN, 1 eq.}) was added to a suspension of L2 (2.72 \mu\text{mol, 1.58 mg, 2 eq.) in CD}_3\text{CN (870 \muL). Subsequently, D}_2\text{O (100 \muL, 10 vol%) was added and the mixture was heated at 70 °C for 5 days to ensure equilibration. The resulting solution was analyzed by } ^1\text{H NMR spectroscopy and HRMS.} \]

\[ \text{Figure S30. } ^1\text{H NMR spectrum of a mixture of L2 (2 eq.) and [Pd(CH}_3\text{CN)}_4(\text{BF}_4)_2 (1 eq.) after equilibration in D}_2\text{O/CD}_3\text{CN (1:9) (a), and of [Pd}_2\text{(L2)}_4(\text{BF}_4)_4 in CD}_3\text{CN for comparison (b).} \]

\[ \text{Figure S31. HRMS of a mixture of L2 (2 eq.) and [Pd(CH}_3\text{CN)}_4(\text{BF}_4)_2 (1 eq.) after equilibration in D}_2\text{O/CD}_3\text{CN (1:9). The main peaks can be attributed to a species with the formula } \{[\text{Pd}_2\text{(L2)}_5(\text{BF}_4)_4]^{2+}.} \]
5 Additional salts and anhydrous conditions

5.1 Na\(^+\), K\(^+\) and Cs\(^+\) salts

Aliquots of stock solutions of NaOTf (2.8 µL, 1.6 µmol, 5 eq.), KPF\(_6\) (16.6 µL, 1.6 µmol, 5 eq.) and CsBPh\(_4\) (131.6 µL, 1.6, 5 eq.) in CD\(_3\)CN were added to three separate NMR tubes containing a solution of [Pd\(_2\)(L\(_2\))\(_4\)](BF\(_4\))\(_4\) (450 µL, 0.32 µmol, 1 eq.). \(^1\)H NMR spectra were recorded directly afterwards.

Figure S32. Aromatic region of the \(^1\)H NMR spectra (400 MHz, CD\(_3\)CN) of the equilibrated mixture of [Pd\(_2\)(L\(_2\))\(_4\)](BF\(_4\))\(_4\) with CsBPh\(_4\) (a), KPF\(_6\) (b), NaOTf (c) and of [Pd\(_2\)(L\(_2\))\(_4\)](BF\(_4\))\(_4\) alone (d).
5.2 Mixture of LiOTf and NaOTf

Aliquots of stock solutions of LiOTf (18.3 µL, 18.2 µmol, 50 eq) and NaOTf (33.0 µL, 18.3 µmol, 50 eq.) in CD$_3$CN were added to a solution of [Pd$_2$(L2)$_4$](BF$_4$)$_4$ (450 µL, 0.37 µmol, 1 eq.) in an NMR tube and the mixture was allowed to equilibrate for 72 h at RT.

a) + LiOTf (50 eq)

b) + NaOTf & LiOTf (50 eq each)

c) + NaOTf (50 eq)

d) [Pd$_2$(L2)$_4$]$^{4+}$

**Figure S33.** Aromatic region of the $^1$H NMR spectra (400 MHz, CD$_3$CN) of the equilibrated mixture of [Pd$_2$(L2)$_4$](BF$_4$)$_4$ with LiOTf (a), NaOTf and LiOTf (b), NaOTf (c) and of [Pd$_2$(L2)$_4$](BF$_4$)$_4$ alone (d).
5.3 Addition of LiBF$_4$ under dry conditions

LiBF$_4$ was dried for 48 h at 70 °C under vacuum and stored under an N$_2$ atmosphere. [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ (90.2 µL, 2.74 µmol, 1 eq.) was added to a suspension of ligand L$_2$ (2.9 mg, 4.98 µmol, 2 eq.) in CD$_3$CN (1.4 mL) under an atmosphere of N$_2$ and the mixture was stirred at RT for 48 h in the presence of 4 Å molecular sieves. The formation of [Pd$_2$(L$_2$)$_4$](BF$_4$)$_4$ was confirmed by $^1$H NMR spectroscopy. An aliquot of the [Pd$_4$(L$_2$)$_8$](BF$_4$)$_8$ stock solution (500 µL, 1 eq.) was then transferred to a vial containing dry LiBF$_4$ (3.2 mg, 83 eq.). A $^1$H NMR spectrum was recorded after 72 h at RT. D$_2$O (0.5 µL) was then added to the tube and another $^1$H NMR spectrum was recorded after equilibration for 72 h at RT.

![Figure S34](image_url)

Figure S34. Aromatic region of the $^1$H NMR spectra (400 MHz, CD$_3$CN) of the equilibrated mixture of [Pd$_2$(L$_2$)$_4$]$^{4+}$ with LiBF$_4$ and D$_2$O (a), LiBF$_4$ (b) and of [Pd$_2$(L$_2$)$_4$]$^{4+}$ alone (c). (b) and (c) were measured in absence of water.
6 Crystallographic Data

6.1 [Pd₄(L1)₈LiBF₄](BF₄)₈

Suitable crystals for SCXRD analysis could be obtained by slow diffusion of diisopropylether in a solution of [Pd₄(L1)₈LiBF₄](BF₄)₈ in CD₃CN.

A clear pale colourless plate-shaped crystal with dimensions 0.54 × 0.31 × 0.17 mm³ was mounted. Data were collected using a SuperNova, Dual, Cu at home/near, Atlas diffractometer operating at \( T = 140.00(10) \) K.

Data were measured using \( \omega \) scans with Cu \( K_{\alpha} \) radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro 1.171.41.104a (Rigaku OD, 2021). The maximum resolution that was achieved was \( \theta = 72.782^\circ \) (0.81 Å).

The unit cell was refined using CrysAlisPro 1.171.41.104a (Rigaku OD, 2021) on 89581 reflections, 26% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro 1.171.41.104a (Rigaku OD, 2021). The final completeness is 99.70 % out to 72.782° in \( \theta \). A gaussian absorption correction was performed using CrysAlisPro 1.171.41.104a (Rigaku Oxford Diffraction, 2021). The numerical absorption correction was based on gaussian integration over a multifaceted crystal model. The empirical absorption correction was done using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The absorption coefficient \( \mu \) of this crystal is 3.545 mm⁻¹ at this wavelength (\( \lambda = 1.54184\text{Å} \)) and the minimum and maximum transmissions are 0.296 and 1.000.

The structure was solved and the space group \( P-1 \) (# 2) determined by the ShelXT (Sheldrick, 2015) structure solution program using dual methods and refined by fullcycle matrix least squares minimisation on \( F^2 \) using version 2018/3 of ShelXL 2018/3 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_\text{smtbx_masks_special_details}: A solvent mask was calculated and 3660 electrons were found in a volume of 16656Å³ in 1 void per unit cell. This is consistent with the presence of 9[BF₄], 65[CH₃CN] per Asymmetric Unit which account for 3598 electrons per unit cell. There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: \( Z \) is 2 and \( Z' \) is 1.
Table S3. Crystal data and structure refinement for [Pd₄(L¹)₈LiBF₄](BF₄)₈

| Property                      | Value                     |
|-------------------------------|--------------------------|
| Formula                       | C₅₂₆H₄₀₅B₂₇F₁₀₈Li₄N₇₁Pd₁₆ |
| Dcalc/ g cm⁻³                 | 1.024                    |
| μ/mm⁻¹                        | 3.545                    |
| Formula Weight                | 11794.22                 |
| Colour                        | clear pale colourless    |
| Shape                         | plate-shaped             |
| Size/mm³                      | 0.54×0.31×0.17           |
| T/K                           | 140.00(10)               |
| Crystal System                | triclinic                |
| Space Group                   | P-1                      |
| a/Å                           | 23.38369(19)             |
| b/Å                           | 40.6967(5)               |
| c/Å                           | 43.4302(5)               |
| α/°                           | 68.4751(10)              |
| β/°                           | 84.4522(8)               |
| γ/°                           | 89.4978(8)               |
| V/Å³                          | 38251.4(7)               |
| Z                             | 2                        |
| Z'                            | 1                        |
| Wavelength/Å                  | 1.54184                  |
| Radiation type                | Cu Kα                    |
| θ_min/°                      | 2.757                    |
| θ_max/°                      | 72.782                   |
| Measured Refl's.              | 340353                   |
| Indep't Refl's                | 148054                   |
| Refl's I≥2 σ(I)               | 109799                   |
| Rint                          | 0.0511                   |
| Parameters                    | 6746                     |
| Restraints                    | 6311                     |
| Largest Peak                  | 3.467                    |
| Deepest Hole                  | -1.319                   |
| Goof                          | 1.033                    |
| wR₂ (all data)               | 0.2188                   |
| wR₂                           | 0.2026                   |
| R₁ (all data)                 | 0.0925                   |
| R₁                             | 0.0738                   |
| CCDC Number                   | 2149704                  |
Suitable crystals for SCXRD analysis could be obtained by slow diffusion of diisopropylether in a solution of [Pd₄(L₁)₈NaBF₄](BF₄)₈ in CD₃CN.

A clear pale colourless prism-shaped crystal with dimensions 0.39 × 0.28 × 0.24 mm³ was mounted. Data were collected using a SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer operating at $T = 140.00(10)$ K.

Data were measured using $\omega$ scans using Cu $K_\alpha$ radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro 1.171.40.82a (Rigaku OD, 2020). The maximum resolution that was achieved was $\theta = 66.601^\circ$ (0.84 Å).

The unit cell was refined using CrysAlisPro 1.171.40.82a (Rigaku OD, 2020) on 25267 reflections, 36% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro 1.171.40.82a (Rigaku OD, 2020). The final completeness is 98.70% out to 66.601° in $\theta$. A gaussian absorption correction was performed using CrysAlisPro 1.171.40.82a (Rigaku Oxford Diffraction, 2020). The numerical absorption correction was based on gaussian integration over a multifaceted crystal model. The empirical absorption correction was done using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The absorption coefficient $\mu$ of this crystal is 3.842 mm⁻¹ at this wavelength ($\lambda = 1.54184\text{Å}$) and the minimum and maximum transmissions are 0.297 and 0.995.

The structure was solved and the space group $P-1$ (# 2) determined by the ShelXT (Sheldrick, 2015) structure solution program using dual methods and refined by full matrix least squares minimisation on $F^2$ using version 2018/3 of ShelXL (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

A solvent mask was calculated and 623 electrons were found in a volume of 3641Å³ in 1 void per unit cell. This is consistent with the presence of 14[CH₃CN] per Asymmetric Unit which account for 616 electrons per unit cell.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: $Z$ is 2 and $Z'$ is 1.
**Figure S35.** Molecular structure of [Pd₄(L1)₈(NaBF₄)](BF₄)₈ in the crystal. Color coding: Pd: blue, Na: purple, C: grey, N: light blue, B: pink, F: light green. Hydrogen atoms are not shown for clarity.

**Figure S36.** Zoom-in on the coordination environment of Na⁺ within the cavity of [Pd₄(L1)₈]³⁺.

**Table S4.** Selected Na⋯F distances.

| r(Na⋯F#) [Å] | F1       | F5       | F9       | F10      | F13      |
|--------------|----------|----------|----------|----------|----------|
| 2.097(12)    | 2.196(12) | 2.477(13) | 2.534(13) | 2.382(16) |
**Table S5.** Crystal data and structure refinement for [Pd₄(L₁)₈NaBF₄](BF₄)₈

| Property                        | Value                        |
|---------------------------------|------------------------------|
| **Formula**                     | C₁₂₈H₉₆B₉F₃₆N₁₆NaPd₄        |
| **D<sub>calc</sub> / g cm⁻³**    | 1.129                        |
| **μ/mm⁻¹**                      | 3.842                        |
| **Formula Weight**              | 3088.08                      |
| **Colour**                      | clear pale colourless        |
| **Shape**                       | prism-shaped                 |
| **Size/mm³**                    | 0.39×0.28×0.24               |
| **T/K**                         | 140.00(10)                   |
| **Crystal System**              | triclinic                    |
| **Space Group**                 | P-1                          |
| **a/Å**                         | 19.6957(6)                   |
| **b/Å**                         | 21.0264(5)                   |
| **c/Å**                         | 23.0290(6)                   |
| **α/°**                         | 84.518(2)                    |
| **β/°**                         | 88.705(2)                    |
| **γ/°**                         | 73.184(2)                    |
| **V/Å³**                        | 9087.3(4)                    |
| **Z**                           | 2                            |
| **Z’**                          | 1                            |
| **Wavelength/Å**                | 1.54184                      |
| **Radiation type**              | Cu Kα                       |
| **θ<sub>min</sub> /°**          | 3.217                        |
| **θ<sub>max</sub> /°**          | 66.601                       |
| **Measured Refl's.**            | 70432                        |
| **Indep't Refl's**              | 31706                        |
| **Refl's I≥2 σ(I)**             | 25122                        |
| **R<sub>int</sub>**             | 0.0421                       |
| **Parameters**                  | 1747                         |
| **Restraints**                  | 1803                         |
| **Largest Peak**                | 4.351                        |
| **Deepest Hole**                | -1.878                       |
| **GooF**                        | 1.566                        |
| **wR<sub>2</sub>**              | 0.3771                       |
| **wR<sub>2</sub> (all data)**   | 0.3590                       |
| **R<sub>1</sub> (all data)**    | 0.1382                       |
| **R<sub>1</sub>**               | 0.1234                       |
| **CCDC Number**                 | 2157181                      |
6.3 \([\text{Pd}_4(\text{L}2)_8(\text{LiBF}_4)_2(\text{H}_2\text{O})_2](\text{BF}_4)_8]\)

Suitable crystals for SCXRD analysis could be obtained by slow diffusion of diethylether in a solution of \([\text{Pd}_4(\text{L}2)_8(\text{LiBF}_4)_2(\text{H}_2\text{O})_2](\text{BF}_4)_8]\) in CD$_3$CN.

A clear intense yellow irregular-shaped crystal with dimensions $0.36 \times 0.26 \times 0.24$ mm$^3$ was mounted. Data were collected using a XtaLAB Synergy R, DW system, HyPix-Arc 150 diffractometer operating at $T = 139.99(10)$ K.

Data were measured using $\omega$ scans with CuK$_\alpha$ radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlis$^\text{Pro}$ 1.171.41.110a (Rigaku OD, 2021).\[^{15}\] The maximum resolution achieved was $\theta = 66.600^\circ$ (0.84 Å).

The unit cell was refined using CrysAlis$^\text{Pro}$ 1.171.41.110a (Rigaku OD, 2021)\[^{15}\] on 188926 reflections, 29% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlis$^\text{Pro}$ 1.171.41.110a (Rigaku OD, 2021).\[^{15}\] The final completeness is 99.80 % out to 66.600$^\circ$ in $\theta$. A Gaussian absorption correction was performed using CrysAlis$^\text{Pro}$ 1.171.41.121a (Rigaku Oxford Diffraction, 2021)\[^{15}\] Numerical absorption correction based on Gaussian integration over a multifaceted crystal model. Empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK scaling algorithm. The absorption coefficient $\mu$ of this material is 1.987 mm$^{-1}$ at this wavelength ($\lambda = 1.54184$Å) and the minimum and maximum transmissions are 0.316 and 1.000.

The structure was solved in the space group $P2_1/c$ (# 14) by the ShelXT 2018/2 (Sheldrick, 2015)\[^{16,17}\] structure solution program using dual methods and refined by full matrix least squares minimisation on $F^2$ using version 2018/3 of ShelXL 2018/3 (Sheldrick, 2015).\[^{16,17}\] All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: $Z$ is 4 and $Z'$ is 1.

Additional counter-ions and solvent molecules, too disordered to be located in the electron density map, were taken into account using the Olex2 solvent-mask procedure (3735.2 electrons were found in a volume of 14240.7 Å$^3$ in one void per unit cell).\[^{18}\]
### Table S6. Crystal data and structure refinement for [Pd₄(L₂)₈(LiBF₄)₂(H₂O)₂][BF₄]₈

| Property                        | Value                  |
|---------------------------------|------------------------|
| Formula                         | C₃₂₈H₂₅₂B₂F₈Li₂N₂₄O₁₀Pd₄ |
| D(calc) / g cm⁻³                 | 0.963                  |
| μ/mm⁻¹                          | 1.987                  |
| Formula Weight                  | 5302.62                |
| Colour                          | clear intense yellow   |
| Shape                           | irregular-shaped       |
| Size/mm³                        | 0.36×0.26×0.24         |
| T/K                             | 139.99(10)             |
| Crystal System                  | monoclinic             |
| Space Group                     | P2₁/c                  |
| a/Å                             | 40.1776(3)             |
| b/Å                             | 19.75538(13)           |
| c/Å                             | 48.7857(4)             |
| α/°                             | 90                     |
| β/°                             | 109.1126(8)            |
| γ/°                             | 90                     |
| V/Å³                            | 36587.8(5)             |
| Z                               | 4                      |
| Z'                              | 1                      |
| Wavelength/Å                    | 1.54184                |
| Radiation type                  | CuKα                   |
| θ(min)°                        | 2.328                  |
| θ(max)°                        | 66.600                 |
| Measured Refl's.                | 647648                 |
| Indep't Refl's                  | 64508                  |
| Refl's I≥2σ(I)                  | 48832                  |
| R_{int}                         | 0.0436                 |
| Parameters                      | 3399                   |
| Restraints                      | 5792                   |
| Largest Peak/e Å⁻³              | 2.300                  |
| Deepest Hole/e Å⁻³              | -1.257                 |
| GooF                            | 1.078                  |
| wR² (all data)                  | 0.2832                 |
| wR²                             | 0.2652                 |
| R₁ (all data)                   | 0.0982                 |
| R₁                              | 0.0844                 |
| CCDC Number                     | 2130316                |
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