Supporting Information

Backbone-Bridging Promotes Diversity in Heteroleptic Cages
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Supporting Information

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1. Experimental section

1.1. Materials and measurements

Unless otherwise stated, all chemicals were obtained from commercial sources and used as received. Compounds 2I-CBZ, 4I-CBZ (Scheme S1), DCB, 4I-DCB (Scheme S2) and ligand LA\(^{[5]}\), LB\(^{[6]}\) were prepared according to literature procedures. Gel permeation chromatography (GPC) purification of ligands was performed on a JAI 9210-II NEXT GPC System with a JAIGEL HH-2/HH-1 column combination running with CHCl\(_3\) (HPLC grade). High resolution Electrospray Ionization (ESI) mass spectra and trapped ion mobility data were recorded on Bruker ESI timsTOF and (electrospray ionization-trapped ion mobility-time of flight) Compact mass spectrometers. All samples were diluted with spectrum grade CH\(_3\)CN (1:10) prior to measurement. NMR experiments were measured on Bruker AVANCE III (500 or 600 MHz) spectrometers. Chemical shifts for \(^1H\) and \(^{13}C\) are reported in ppm with residual solvent as reference: acetonitrile (1.94 ppm for \(^1H\), 1.32 ppm for \(^{13}C\), DMSO (2.50 ppm for \(^1H\), 39.52 ppm for \(^{13}C\), DMF (2.75 ppm for \(^1H\), 29.76 ppm for \(^{13}C\). Abbreviations for signal multiplicity of \(^1H\) NMR spectra are shown as following: s: singlet, d: doublet, t: triplet, dd: doublet of doublets; dt: doublet of triplets; m: multiplet, br: broad.

1.2. Synthesis of ligands

1.2.1. Synthesis of 1,6-bis(3,6-bis(pyridin-3-ylethynyl)-9H-carbazol-9-yl)hexane (LA\(^{1}\))

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Scheme S1

Compound 4I-CBZ (276 mg, 0.3 mmol, 1 eq.), 3-ethynylpyridine (247 mg, 2.4 mmol, 8 eq.), CuI (17 mg, 0.09 mmol, 0.03 eq.), triethylamine (11 mL), and anhydrous THF (22 mL) were added in a Schlenk tube. After the suspension was degassed (via freeze-thaw cycles) for three times, Pd(PPh\(_3\))\(_2\)Cl\(_2\) (32 mg, 0.045 mmol, 0.015 eq.) was added. The mixture was heated to r.t. and then to 55 \(^\circ\)C for 20 h under the protection of a N\(_2\) atmosphere. After the solvent was evaporated under reduced pressure, the crude product was purified by column chromatography (DCM:MeOH = 100:1 to 30:1) and then by GPC to yield the title compound as a pale yellowish brown solid (106 mg, 43%).

\(^1H\) NMR (500 MHz, 298K, DMSO-d\(_6\)) \(\delta 8.76 (d, \text{ } J = 2.2 \text{ } Hz, 4H), 8.56 (dd, \text{ } J = 4.9, 1.7 \text{ } Hz, 4H), 8.53 (d, \text{ } J = 1.5 \text{ } Hz, 4H), 7.96 (dt, \text{ } J = 7.8, 1.9 \text{ } Hz, 4H), 7.71 – 7.61 (m, 8H), 7.48 – 7.41 (m, 4H), 4.38 (t, \text{ } J = 7.1 \text{ } Hz, 4H), 1.72 (t, \text{ } J = 6.1 \text{ } Hz, 4H), 1.32 (t, \text{ } J = 6.7 \text{ } Hz, 4H).
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**Figure S1.** \(^1H\) NMR spectrum (500 MHz, 298K, DMSO-d\(_6\)) of LA\(^{1}\).

\(^{12}C\) NMR (126 MHz, 298K, DMSO-d\(_6\)) \(\delta 151.42, 148.56, 140.40, 138.24, 129.75, 124.50, 123.62, 121.80, 119.96, 112.29, 110.20, 93.83, 84.62, 42.37, 28.22, 25.89.

S2
1.2.2. Synthesis of 1,4-bis(3,6-bis(pyridin-3-ylethynyl)-9H-carbazol-9-yl)benzene (L^A2)

Scheme S2

Compound 4I-DCB (183 mg, 0.2 mmol, 1 eq.), 3-ethynlypyridine (165 mg, 1.6 mmol, 8 eq.), CuI (12 mg, 0.06 mmol, 0.03 eq.), triethylamine (7 mL), and anhydrous THF (14 mL) were added in a Schlenk tube. After the suspension was degassed (via freeze-thaw cycles) for three times, Pd(PPh3)Cl2 (21 mg, 0.03 mmol, 0.015 eq.) was added. The mixture was heated to r.t. and then to 55 °C for 20 h under the protection of a N2 atmosphere. After the solvent was evaporated under reduced pressure, the crude product was purified by column chromatography (DCM:MeOH = 100:1 to 30:1) and recrystallized from hot DMF to yield the title compound as a pale yellowish brown crystalline solid (80 mg, 49%).

^1H NMR (500 MHz, 298K, DMSO-d6) δ 8.82 (d, J = 2.2 Hz, 4H), 8.70 (d, J = 1.6 Hz, 4H), 8.61 (dd, J = 4.8, 1.7 Hz, 4H), 8.07 – 7.98 (m, 8H), 7.78 (dd, J = 8.5, 1.6 Hz, 4H), 7.70 (d, J = 8.5 Hz, 4H), 7.50 (dd, J = 7.9, 4.8 Hz, 4H).

Figure S3. ^1H NMR spectrum (500 MHz, 298K, DMSO-d6) of L^A2.

^13C NMR (151 MHz, 298K, DMSO-d6) δ 151.51, 148.76, 140.60, 138.40, 130.45, 128.78, 124.78, 123.71, 123.22, 122.63, 119.84, 113.90, 110.82, 93.45, 85.11.
1.3. Self-assembly and characterization of cages

1.3.1. Self-assembly of heteroleptic cage \([\text{Pd}_2\text{L}^4\text{L}^8]^{4+}\) in CD$_3$CN

To a solution of \(\text{L}^8\) (7 mM, 0.7 μmol) in 100 μL CD$_3$CN and a suspension of \(\text{L}^4\) (0.32 mg, 0.7 μmol) in 353 μL CD$_3$CN was added a stock solution of \([\text{Pd(CH}_3\text{CN})_2][\text{BF}_4]_2\) (47 μL, 15 mM/CD$_3$CN, 0.7 μmol). The mixture was heated at 80 °C for 8 h to give a 0.7 mM cage solution.

$^1$H NMR (500 MHz, CD$_3$CN) \(\delta\) 9.59 (d, \(J = 2.0\) Hz, 4H), 9.43 (d, \(J = 1.8\) Hz, 4H), 9.09 (dd, \(J = 5.8, 1.4\) Hz, 4H), 9.03 (dd, \(J = 5.8, 1.3\) Hz, 4H), 8.29 (d, \(J = 1.6\) Hz, 4H), 8.23 (dt, \(J = 7.9, 1.6\) Hz, 4H), 8.13 (dt, \(J = 8.0, 1.6\) Hz, 4H), 7.95 (d, \(J = 7.7\) Hz, 4H), 7.73 (dd, \(J = 8.6, 1.6\) Hz, 4H), 7.66 (ddd, \(J = 8.0, 5.8, 3.7\) Hz, 8H), 7.61 (d, \(J = 1.7\) Hz, 4H), 7.60 – 7.56 (m, 4H), 7.49 (dd, \(J = 7.7, 1.7\) Hz, 4H), 4.34 (t, \(J = 7.2\) Hz, 4H), 1.80 – 1.74 (m, 4H), 1.67 (s, 6H), 1.31 (s, 6H), 1.26 – 1.13 (m, 12H), 0.76 (t, \(J = 7.1\) Hz, 6H).

Figure S5. \(^1\)H NMR spectrum (500 MHz, CD$_3$CN) of heteroleptic cage C.
$^{13}$C NMR (151 MHz, CD$_3$CN) δ 156.78, 153.31, 150.42, 150.20, 149.97, 143.71, 143.12, 142.34, 140.66, 139.73, 136.02, 132.26, 128.99, 128.38, 128.23, 125.41, 124.41, 123.05, 122.84, 122.69, 112.99, 111.50, 98.10, 83.41, 48.30, 44.02, 32.09, 29.97, 29.40, 27.28, 25.72, 23.15, 14.14.

Figure S6. $^{13}$C NMR spectrum (151 MHz, CD$_3$CN) of heteroleptic cage C.

Figure S7. Partial $^1$H NMR spectrum (500 MHz, CD$_3$CN) comparison of ligand L$^A$ (top), ligand L$^B$ (middle), and heteroleptic cage C (bottom).
Figure S8. Partial $^1$H–$^1$H COSY spectrum (500 MHz, CD$_3$CN) of heteroleptic cage C.

Figure S9. Partial $^1$H–$^1$H NOESY spectrum (500 MHz, CD$_3$CN) of heteroleptic cage C.
Figure S10. $^1$H DOSY spectrum (500 MHz, CD$_3$CN) of heteroleptic cage C. Diffusion coefficient for C: $D = 6.17 \times 10^{-10}$ m$^2$s$^{-1}$, log $D = -9.210$, $r = 10.6$ Å.

![H DOSY spectrum](image)

Figure S11. HR-ESI mass spectrum of heteroleptic cage C.

![HR-ESI mass spectrum](image)
1.3.2. Self-assembly of homoleptic cage \([\text{Pd}_2(L^A)_4]^{2+} (C1)\) in DMSO-\(d_6\)

To a solution of \(L^A\) (0.54 mg, 0.7 \(\mu\)mol) in 465 \(\mu\)L DMSO-\(d_6\) was added a stock solution of \([\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2\) (35 \(\mu\)L, 20 mM/DMSO-\(d_6\), 0.7 \(\mu\)mol). The mixture was kept at r.t. for 3 h to give a 0.7 mM solution of cage C1.

\(^1H\) NMR (500 MHz, 298K, DMSO-\(d_6\)) \(\delta\) 9.70 (s, 4H), 9.62 (s, 4H), 9.22 (dd, \(J = 11.4, 5.7\) Hz, 8H), 8.49 (d, \(J = 1.5\) Hz, 4H), 8.47 (d, \(J = 1.3\) Hz, 4H), 8.30 (d, \(J = 7.7\) Hz, 8H), 8.08 (d, \(J = 8.7\) Hz, 4H), 7.96 (d, \(J = 8.7\) Hz, 8H), 7.86 (d, \(J = 8.5\) Hz, 4H), 7.82 (q, \(J = 4.7, 2.5\) Hz, 8H), 4.69 (s, 4H), 4.60 (s, 4H), 1.70 (s, 8H), 1.62 (d, \(J = 6.7\) Hz, 4H), 1.47 (s, 4H).

The observed twofold splitting of signals can be explained as follows: the lantern-shaped cage adopts an overall helical structure, governed by the \([\text{Pd(pyrindine)}_4]\) propellers. Unlike with untethered homoleptic \([\text{Pd}_2L_4]\) cages, flipping between both helical cage enantiomers seems to be slowed down by the backbone bridges, leading to diastereotopic splitting of all protons coming in pairs (which – owing to the dimeric character of the ligands – is true both for all aromatic and aliphatic positions).

\[\text{Figure S12. }^1H\text{ NMR spectrum (500 MHz, 298K, DMSO-}d_6\text{) of homoleptic cage C1.}\]
Figure S13. Partial $^1$H–$^1$H COSY spectrum (500 MHz, 298K, DMSO-$d_6$) of homoleptic cage C1.

Figure S14. Partial $^1$H–$^1$H NOESY spectrum (500 MHz, 298K, DMSO-$d_6$) of homoleptic cage C1.
Figure S15. $^1$H DOSY NMR spectrum (500 MHz, 298K, DMSO-$d_6$) of homolectic cage C1. Diffusion coefficient $D = 6.353 \times 10^{-11} \text{ m}^2\text{s}^{-1}$, $\log D = -10.197$, $r = 17.2 \text{ Å}$. 

$log D = -10.197$
1.3.3. Self-assembly of homoleptic ring/tetrahedron mixture \([\text{Pd}_3(\text{L}^8)_6]^{6+} (R) / [\text{Pd}_4(\text{L}^8)_8]^{8+} (T)\) in DMSO-\(d_6\).

To a solution of \(\text{L}^8\) (7 mM, 2.1 \(\mu\)mol) in 447 \(\mu\)L DMSO-\(d_6\) was added a stock solution of \([\text{Pd}(\text{CH}_3\text{CN})_4]^2(\text{BF}_4)_2\) (53 \(\mu\)L, 20 mM/DMSO-\(d_6\), 1.05 \(\mu\)mol). The mixture was kept at r.t. for 3 h to give a mixture of homoleptic ring/tetrahedron (R/T).

\(^1\)H NMR (500 MHz, 298K, DMSO-\(d_6\)) \(\delta\) 9.96 (s, 12H), 9.92 (s, 8H), 9.80 (s, 8H), 9.48 (d, \(J = 5.6\) Hz, 8H), 9.34 (d, \(J = 5.7\) Hz, 12H), 9.26 (d, \(J = 5.6\) Hz, 8H), 8.61 (d, \(J = 8.3\) Hz, 8H), 8.45 (d, \(J = 8.1\) Hz, 12H), 8.38 (d, \(J = 6.6\) Hz, 28H), 8.20 (d, \(J = 8.0\) Hz, 8H), 8.09 (d, \(J = 17.2\) Hz, 16H), 7.98 – 7.90 (m, 20H), 7.88 (dd, \(J = 8.0, 5.6\) Hz, 12H), 7.81 (t, \(J = 7.4\) Hz, 16H), 7.52 (s, 20H), 1.49 (s, 20H), 1.31 (s, 20H), 1.25 (s, 12H), 0.95 (s, 20H), 0.89 (s, 12H).
Figure S17. $^1$H NMR spectrum (500 MHz, 298K, DMSO-d$_6$) of homoleptic ring/tetrahedron (R/T) mixture.

Figure S18. Partial $^1$H–$^1$H COSY spectrum (500 MHz, 298K, DMSO-d$_6$) of homoleptic ring/tetrahedron (R/T) mixture.
Figure S19. Partial $^1\text{H}$$^1\text{H}$ NOESY spectrum (500 MHz, 298K, DMSO-$d_6$) of homoleptic ring/tetrahedron (R/T) mixture.

Figure S20. $^1\text{H}$ DOSY spectrum (500 MHz, 298K, DMSO-$d_6$) of homoleptic ring/tetrahedron (R/T) mixture. Diffusion coefficient for ring R, $D = 7.731 \times 10^{-11} \text{ m}^2\text{s}^{-1}$, log $D = -10.112$, $r = 14.2 \text{ Å}$, for tetrahedron T $D = 6.561 \times 10^{-11} \text{ m}^2\text{s}^{-1}$, log $D = -10.183$, $r = 16.7 \text{ Å}$.
1.3.4. Self-assembly with $L^A$ and $L^B$ in CD$_3$CN

$L^A$ (0.64 mg, 0.78 μmol) and $L^B$ (1.08 mg, 3.12 μmol) were combined in a small vial, 545 μL CD$_3$CN and a stock solution of [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ (155 μL, 15 mM/CD$_3$CN, 2.34 μmol) were added. The mixture was heated at 80 °C overnight to give a convoluted mixture of five different self-assembled structures.
**Figure S22.** $^1$H NMR spectrum (500 MHz, 298K, CD$_3$CN) of the Pd-mediated assembly of L$^{A1}$ with L$^B$.

$^1$H NMR (500 MHz, 298K, DMSO-$d_6$) δ 10.23 (s, 2H), 9.93 (s, 2H), 9.80 (s, 2H), 9.71 (s, 2H), 9.60 (s, 2H), 9.51 (s, 2H), 9.50 – 9.43 (m, 6H), 9.26 (d, $J = 5.5$ Hz, 2H), 9.21 (d, $J = 5.6$ Hz, 2H), 9.06 (d, $J = 5.7$ Hz, 2H), 8.78 (d, $J = 7.9$ Hz, 2H), 8.59 (d, $J = 8.0$ Hz, 2H), 8.54 (d, $J = 8.0$ Hz, 2H), 8.51 – 8.45 (dd, $J = 12.1$, 7.9 Hz, 4H), 8.42 (s, 2H), 8.33 (d, $J = 7.8$ Hz, 2H), 8.28 (d, $J = 8.0$ Hz, 2H), 8.27 (s, 2H), 8.26 – 8.19 (m, 6H), 8.09 (s, 2H), 8.03 (s, 2H), 8.01 – 7.99 (m, 2H), 7.99 – 7.92 (m, 8H), 7.86 (td, $J = 8.2$, 5.8 Hz, 4H), 7.83 – 7.74 (m, 2H), 7.75 – 7.66 (m, 6H), 7.61 (d, $J = 8.7$ Hz, 2H), 7.58 – 7.46 (m, 4H), 6.94 (s, 2H), 4.40

**Figure S23.** HR-ESI mass spectrum of the Pd-mediated assembly of L$^{A1}$ with L$^B$.

1.3.5. **Self-assembly of heteroleptic pseudo-tetrahedron [Pd$_3$(L$^{A1}$)(L$^B$)]$^{18+}$ (T1) in DMSO-$d_6$**

A solution of L$^{A1}$ (0.29 mg, 0.35 μmol) in 247 μL DMSO-$d_6$ and a solution of L$^B$ (1.4 μmol, 7 mM) in 200 μL DMSO-$d_6$ was combined. To this solution, a stock solution of [Pd(CH$_3$CN)$_4$][(BF$_4$)$_2$] (53 μL, 20 mM/DMSO-$d_6$, 1.05 μmol) was added. The mixture was heated at 80 °C for 8 h to give a 0.7 mM solution of heteroleptic pseudo-tetrahedron T1.

$^1$H NMR (500 MHz, 298K, DMSO-$d_6$) δ 10.23 (s, 2H), 9.93 (s, 2H), 9.80 (s, 2H), 9.71 (s, 2H), 9.60 (s, 2H), 9.51 (s, 2H), 9.50 – 9.43 (m, 6H), 9.26 (d, $J = 5.5$ Hz, 2H), 9.21 (d, $J = 5.6$ Hz, 2H), 9.06 (d, $J = 5.7$ Hz, 2H), 8.78 (d, $J = 7.9$ Hz, 2H), 8.59 (d, $J = 8.0$ Hz, 2H), 8.54 (d, $J = 8.0$ Hz, 2H), 8.51 – 8.45 (dd, $J = 12.1$, 7.9 Hz, 4H), 8.42 (s, 2H), 8.33 (d, $J = 7.8$ Hz, 2H), 8.28 (d, $J = 8.0$ Hz, 2H), 8.27 (s, 2H), 8.26 – 8.19 (m, 6H), 8.09 (s, 2H), 8.03 (s, 2H), 8.01 – 7.99 (m, 2H), 7.99 – 7.92 (m, 8H), 7.86 (td, $J = 8.2$, 5.8 Hz, 4H), 7.83 – 7.74 (m, 2H), 7.75 – 7.66 (m, 6H), 7.61 (d, $J = 8.7$ Hz, 2H), 7.58 – 7.46 (m, 4H), 6.94 (s, 2H), 4.40
(t, J = 7.1 Hz, 2H), 4.15 (t, J = 7.1 Hz, 2H), 1.80 (b, 2H), 1.72 (s, 6H), 1.63 (s, 6H), 1.53 (b, 2H), 1.47 (s, 3H), 1.43 (s, 3H), 1.21 (b, 4H), 1.13 (s, 3H), 0.17 (s, 3H).

Figure S24. $^1$H NMR spectrum (500 MHz, 298K, DMSO-$d_6$) of heteroleptic pseudo-tetrahedron T1.

$^{13}$C NMR (151 MHz, 298K, DMF-$d_7$) δ 172.02, 156.21, 155.92, 155.80, 155.63, 154.84, 153.24, 152.82, 152.01, 151.44, 151.20, 150.60, 150.23, 150.03, 149.88, 149.81, 148.93, 148.31, 148.09, 143.93, 143.66, 141.79, 141.03, 140.89, 140.85, 140.74, 140.39, 140.24, 140.07, 139.82, 139.70, 139.25, 138.77, 138.55, 135.45, 135.14, 134.77, 134.56, 130.72, 130.55, 128.43, 128.25, 128.09, 127.96, 127.80, 127.45, 127.26, 126.93, 126.54, 124.82, 124.26, 123.97, 123.89, 123.21, 122.88, 122.68, 122.55, 122.41, 122.23, 121.95, 121.38, 120.99, 117.91, 111.98, 111.95, 111.15, 110.82, 96.38, 96.26, 81.44, 81.02, 48.18, 47.82, 47.75, 47.25, 42.13, 27.04, 26.73, 26.53, 26.37, 25.90, 24.60, 24.14, 23.53, 22.17.

Figure S25. $^{13}$C NMR spectrum (151 MHz, 298K, DMF-$d_7$) of heteroleptic pseudo-tetrahedron T1.
Figure S26. Partial $^1$H–$^1$H COSY spectrum (500 MHz, 298K, DMSO-$d_6$) of heteroleptic pseudo-tetrahedron T1.

Figure S27. Partial $^1$H–$^1$H NOESY spectrum (500 MHz, 298K, DMSO-$d_6$) of heteroleptic pseudo-tetrahedron T1.
Figure S28. $^1$H DOSY spectrum (500 MHz, 298K, DMSO-$d_6$) of heteroleptic pseudo-tetrahedron T1. Diffusion coefficient $D = 7.908 \times 10^{-11}$ m$^2$s$^{-1}$, $\log D = -10.102$, $r = 13.9$ Å.

ESI-HRMS: $m/z$:  
- calc. for [$\text{Pd}_3(L^{\text{A1}})(L^{\text{B}})_4]^{3+}$ (C$_{158}$H$_{120}$N$_{14}$Pd$_3$): 422.2828, found: 422.2823;  
- calc. for [$\text{Pd}_3(L^{\text{A1}})(L^{\text{B}})_4+\text{BF}_4]^+$(C$_{158}$H$_{120}$N$_{14}$BF$_4$Pd$_3$): 524.1404, found: 524.1395;  
- calc. for [$\text{Pd}_3(L^{\text{A1}})(L^{\text{B}})_4+2\text{BF}_4]^+$(C$_{158}$H$_{120}$N$_{14}$B$_2$F$_8$Pd$_3$): 676.6761, found: 676.6751;  
- calc. for [$\text{Pd}_3(L^{\text{A1}})(L^{\text{B}})_4+3\text{BF}_4]^+$(C$_{158}$H$_{120}$N$_{14}$B$_3$F$_{12}$Pd$_3$): 931.2364, found: 931.2344;  
- calc. for [$\text{Pd}_3(L^{\text{A1}})(L^{\text{B}})_4+4\text{BF}_4]^+$(C$_{158}$H$_{120}$N$_{14}$B$_4$F$_{16}$Pd$_3$): 1440.3567, found: 1440.3520.
1.3.6. Self-assembly of heteroleptic cage dimer \([\text{Pd}_4(L^{\text{A2}})_2(L^{\text{B}})_4]^\text{+}(\text{D2})\) in DMSO-\text{d}_6

A suspension of \(L^{\text{A2}}\) (0.57 mg, 0.7 \(\mu\)mol) in 230 \(\mu\)L DMSO-\text{d}_6 and a solution of \(L^{\text{B}}\) (1.4 \(\mu\)mol, 7 mM) in 200 \(\mu\)L DMSO-\text{d}_6 was added to an NMR tube and carefully heated to obtain a clear solution. Then, a stock solution of \([\text{Pd}(\text{CH}_3\text{CN})_4]\text{[(BF}_4)_2\) (70 \(\mu\)L, 20 mM/DMSO-\text{d}_6, 1.4 \(\mu\)mol) was added. The mixture was heated at 80 \(^\circ\)C for 8 h to give a 0.7 mM solution of cage dimer D2.

\(^1\text{H NMR}\) (500 MHz, 298K, DMSO-\text{d}_6) \(\delta\) 10.09 (s, 8H), 9.81 (s, 8H), 9.38 (d, \(J = 5.7\) Hz, 8H), 9.26 (d, \(J = 5.9\) Hz, 8H), 8.54 (s, 8H), 8.45 (d, \(J = 7.7\) Hz, 8H), 8.33 (d, \(J = 7.8\) Hz, 8H), 8.25 (d, \(J = 8.0\) Hz, 8H), 8.15 (d, \(J = 7.4\) Hz, 8H), 8.08 (s, 4H), 7.86 (m, 24H), 7.60 (d, \(J = 8.4\) Hz, 8H), 7.53 (b, 12H), 1.40 (s, 12H), 0.82 (s, 12H).

Figure S30. \(^1\text{H NMR}\) spectrum (500 MHz, 298K, DMSO-\text{d}_6) of heteroleptic cage dimer D2.
$^{13}$C NMR (151 MHz, 298K, DMSO-$d_6$) δ 171.47, 162.33, 154.67, 153.53, 149.98, 149.64, 148.54, 141.62, 141.36, 139.45, 138.72, 135.18, 134.21, 131.12, 129.05, 128.31, 127.49, 124.34, 122.72, 122.60, 122.18, 120.99, 118.11, 112.41, 111.09, 95.77, 83.38, 47.30, 35.80, 30.79, 28.30, 24.25, 22.52.

Figure S31. $^{13}$C NMR spectrum (151 MHz, 298K, DMSO-$d_6$) of heteroleptic cage dimer D2.

Figure S32. Partial $^1$H–$^1$H COSY spectrum (500 MHz, 298K, DMSO-$d_6$) of heteroleptic cage dimer D2.
Figure S33. Partial $^1$H–$^1$H NOESY spectrum (500 MHz, 298K, DMSO-$d_6$) of heteroleptic cage dimer D2.
Figure S34. $^1$H DOSY spectrum (500 MHz, 298K, DMSO-$d_6$) of heteroleptic cage dimer D2. Diffusion coefficient $D = 6.361 \times 10^{-11} \text{ m}^2\text{s}^{-1}$, $\log D = -10.196$, $r = 17.2 \text{ Å}$.

ESI-HRMS: $m/z$:
- calc. for [Pd$_4$(L$^A_2$)$_2$(L$^B_5$)$_2$]$^+$($C_{216}H_{144}N_{20}Pd_4$): 430.6010, found: 430.6004;
- calc. for [Pd$_4$(L$^A_2$)$_2$(L$^B_5$)$_4$+BF$_4$]$^+$($C_{216}H_{144}N_{20}BF_4$Pd$_4$): 504.5446, found: 504.5441;
- calc. for [Pd$_4$(L$^A_2$)$_2$(L$^B_5$)$_4$+2BF$_4$]$^+$($C_{216}H_{144}N_{20}B_2F_2Pd_4$): 603.1361, found: 603.1355;
- calc. for [Pd$_4$(L$^A_2$)$_2$(L$^B_5$)$_4$+3BF$_4$]$^+$($C_{216}H_{144}N_{20}B_3F_3Pd_4$): 740.9641, found: 740.9631;
- calc. for [Pd$_4$(L$^A_2$)$_2$(L$^B_5$)$_4$+4BF$_4$]$^+$($C_{216}H_{144}N_{20}B_4F_4Pd_4$): 947.9562, found: 947.9548;
- calc. for [Pd$_4$(L$^A_2$)$_2$(L$^B_5$)$_4$+5BF$_4$]$^+$($C_{216}H_{144}N_{20}B_5F_5Pd_4$): 1292.9403, found: 1292.9430.
Figure S35. HR-ESI mass spectrum of heteroleptic cage dimer D2.

1.3.7. Self-assembly of heteroleptic cage dimer $[\text{Pd}(L^A)_2(L^B)_2]^{8+}$ (D2) in DMF-$d_7$

$$\begin{align*}
2 \quad &+ \\
L^A &+ 4 \quad \text{Pd(CH$_3$CN)$_4$}$[BF$_4$]$_2$ \\
& \rightarrow \text{DMF-$d_7$} \\
\end{align*}$$

A suspension of $L^A$ (0.57 mg, 0.7 μmol) in 230 μL DMF-$d_7$ and a solution of $L^B$ (1.4 μmol, 7 mM) in 200 μL DMF-$d_7$ was added to an NMR tube and carefully heated to obtain a clear solution. Then, a stock solution of $[\text{Pd(CH$_3$CN)$_4$}][\text{BF$_4$}]_2$ (70 μL, 20 mM/DMF-$d_7$, 1.4 μmol) was added. The mixture was heated at 80 °C for 8 h to give a 0.7 mM solution of cage D2.

$^1$H NMR (500 MHz, 298K, DMF-$d_7$) δ 10.40 (s, 8H), 10.07 (d, $J = 2.0$ Hz, 8H), 9.64 (dd, $J = 5.9$, 1.5 Hz, 8H), 9.58 – 9.51 (m, 8H), 8.63 (s, 8H), 8.59 (d, $J = 8.0$ Hz, 8H), 8.50 (d, $J = 7.7$ Hz, 8H), 8.30 (dt, $J = 8.1$, 1.6 Hz, 8H), 8.21 (d, $J = 7.7$ Hz, 8H), 8.08 (s, 4H), 8.03 (s, 4H), 7.96 (m, 16H), 7.89 – 7.80 (m, 16H), 7.68 (s, 8H), 1.55 (s, 12H), 0.93 (s, 12H).

$^{13}$C NMR (151 MHz, 298K, DMF-$d_7$) δ 171.86, 155.53, 154.36, 150.54, 150.30, 149.25, 141.73, 141.63, 140.73, 140.34, 139.13, 135.70, 134.87, 131.84, 129.59, 128.76, 127.75, 122.98, 122.80, 121.69, 117.90, 113.49, 111.55, 96.56, 83.13, 47.89, 28.02, 24.83, 22.22.

Figure S36. $^1$H NMR spectrum (500 MHz, 298K, DMF-$d_7$) of heteroleptic cage dimer D2.
2. Cage-to-cage transformation

Figure S38. $^1$H NMR spectra (500 MHz, 298K, DMSO-$d_6$) of the mixture of homoleptic bridged cage C1 and a 1:1 mixture of homoleptic ring R and tetrahedron T at room temperature over the course of 12h. As can be seen, homoleptic species co-exist and no conversion to heteroleptic pseudo-tetrahedron T1 is achieved at this temperature.
Figure S39. $^1$H NMR spectra (500 MHz, 298 K, DMSO-$_d_6$) of pseudo-tetrahedron T1 formation from free ligands and Pd(II) cations (top) compared to cage-to-cage transformation from homoleptic bridged cage C1 and a 1:1 mixture of homoleptic ring R and tetrahedron T to the same heteroleptic pseudo-tetrahedron T1 after heating at 80 °C for 2 h.
Figure S40. $^1$H NMR spectra (500 MHz, DMSO-$d_6$) to compare the behaviour of heteroleptic pseudo-tetrahedron T1 at different temperatures. (* = homoleptic ring R)

This experiment shows that the heteroleptic pseudo-tetrahedron T1 is stable in solution up to 378 K. Moreover, the split proton signals do not coalesce even at elevated temperatures, indicating that the signals splitting is caused by an inherently low symmetry of the topology (not by conformational locking effects), further supporting the assignment to species T1 instead of R1.
3. **Host-Guest study**

**Figure S41.** $^1$H NMR titration (500 MHz, 298K, DMF-$d_7$) of heteroleptic cage dimer D2 with G1 in DMF-$d_7$ (The red double circle represents signal from empty cage dimer D2, while the one with one blue and two blue dots inside represent G1@D2 and 2G1@D2, respectively).  

As the host-guest interactions between cage dimer D1 and G1 were observed to follow slow exchange kinetics, the concentrations of G1@D2, 2G1@D2 and D2 could all be estimated from the $^1$H NMR spectroscopic results. The integrals of protons a and b of ligand L9 were used to approximate $K_1$ and $K_2$ by using the following equations:

$$H + G \rightleftharpoons HG \quad \text{and} \quad HG + G \rightleftharpoons HG_2$$

$$K_1 = \frac{[HG]}{[H][G]} \quad \text{and} \quad K_2 = \frac{[HG_2]}{[HG][G]}$$

where H and G represent host cage dimer D2 and guest G1, respectively. Concentrations obtained from three distinct $^1$H NMR spectra (0.6, 0.8 - 1.0 eq) are tabulated in **Table S1**. Further, from this data, the cooperativity parameter $\alpha = 4K_2/K_1$ was calculated.$^{[7]}$

**Table S1.** Data extracted from the $^1$H NMR spectra of G1 added to D2 to quantify the cooperativity of guest binding.

| Spectrum | 0.6 eq. / mM | 0.8 eq. / mM | 1.0 eq. / mM | Average       |
|----------|--------------|--------------|--------------|---------------|
| [G]      | 0.210        | 0.202        | 0.270        |               |
| [H]      | 0.490        | 0.430        | 0.378        |               |
| [HG]     | 0.210        | 0.182        | 0.216        |               |
| [HG2]    | 0            | 0.088        | 0.107        |               |
| $K_1$    | $2.04 \times 10^3$ M$^{-1}$ | $2.09 \times 10^3$ M$^{-1}$ | $2.12 \times 10^3$ M$^{-1}$ | $(2.08 \pm 0.04) \times 10^3$ M$^{-1}$ |
| $K_2$    | -            | $2.39 \times 10^3$ M$^{-1}$ | $1.83 \times 10^3$ M$^{-1}$ | $(2.11 \pm 0.28) \times 10^3$ M$^{-1}$ |
| $\alpha$ | -            | 4.57         | 3.45         | 4.01          |
4. Ion Mobility Mass Spectrometry

Ion mobility measurements were performed on a Bruker timsTOF instrument combining a trapped ion mobility (TIMS) with a time-of-flight (TOF) mass spectrometer in one instrument. In contrast to the conventional drift tube method to determine mobility data, where ions are carried by an electric field through a stationary drift gas, the TIMS method is based on an electric field ramp to hold ions in place against a carrier gas pushing them in the direction of the analyzer. Consequently, larger sized ions that experience more carrier gas impacts leave the TIMS units first and smaller ions elute later. This method offers a much higher mobility resolution despite a smaller device size.

![Mobilograms obtained by trapped ion mobility ESI-TOF mass spectrometry for heteroleptic pseudo-tetrahedron T1: [Pd₃Lᴬ¹Lᴮ⁴BF₄]⁺⁺ (CCS: 695.2 Å² at m/z 523.94), [Pd₃(Lᴬ¹)(Lᴮ²)⁺⁺⁺BF₄]⁺ (CCS: 652.6 Å² at m/z 676.68), [Pd₃(Lᴬ¹)(Lᴮ²)⁺⁺⁺⁺BF₄]⁺⁺⁺⁺ (CCS: 617.8 Å² at m/z 931.23), [Pd₃(Lᴬ¹)(Lᴮ²)⁺⁺⁺⁺⁺BF₄]⁺⁺⁺⁺⁺ (CCS: 599.8 Å² at m/z 1440.85).]

**Figure S42.** Mobilograms obtained by trapped ion mobility ESI-TOF mass spectrometry for heteroleptic pseudo-tetrahedron T1: [Pd₃(Lᴬ¹)(Lᴮ²)⁺⁺⁺BF₄]⁺⁺⁺⁺ (CCS: 617.8 Å² at m/z 931.23), [Pd₃(Lᴬ¹)(Lᴮ²)⁺⁺⁺⁺⁺BF₄]⁺⁺⁺⁺⁺ (CCS: 599.8 Å² at m/z 1440.85).

| Species | eCCS [Å²] | tCCS (T1) [Å²] | Δ% (T1) | tCCS (R1) [Å²] | Δ% (R1) |
|---------|-----------|----------------|--------|----------------|--------|
| [Pd₃Lᴬ¹Lᴮ⁴BF₄]⁺⁺⁺⁺ | 695.2 | 713.8 | 2.7% | 732.5 | 5.4% |
| [Pd₃Lᴬ¹Lᴮ³⁺⁺⁺⁺BF₄]⁺⁺⁺⁺ | 652.6 | 671.9 | 3.0% | 691.7 | 6.0% |
| [Pd₃Lᴬ¹Lᴹ⁺⁺⁺⁺⁺⁺BF₄]⁺⁺⁺⁺⁺⁺ | 617.8 | 644.9 | 4.4% | 658.6 | 6.6% |
| [Pd₃Lᴬ¹Lᴮ⁴⁺⁺⁺⁺⁺⁺BF₄]⁺⁺⁺⁺⁺⁺⁺⁺ | 599.8 | 643.3 | 7.3% | 652.5 | 8.8% |

**Table S2.** Comparison of experimental collisional cross section (eCCS) values of heteroleptic pseudo-tetrahedron with results derived from Collidoscope software⁸ (tCCS) based on the CREST⁹ (GFN2-xTB) generated models with corresponding number of encapsulated BF₄⁻ counter anions.

Experimental and theoretical data show in accordance that the CCS decreases with increasing number of encapsulated BF₄⁻ counter anions, leading to a stepwise decrease of overall charge. This common phenomenon can be explained by weaker ion–induced dipole and ion–quadrupole interactions with the carrier gas molecules (N₂).¹⁰ and this trend is reproducible by the theoretical calculations. The same observation was also made for the heteroleptic dimer (Table S3).
Figure S43. Mobilograms obtained by trapped ion mobility ESI-TOF mass spectrometry for heteroleptic cage dimer $D_2$: $[\text{Pd}_4(L^A)_2(L^B)_4]^{6+}$ (CCS: 876.1 Å$^2$ and 895.3 Å$^2$ at m/z 603.14), $[\text{Pd}_4(L^A)_2(L^B)_4]^3+$ (CCS: 838.6 Å$^2$ at m/z 740.96), $[\text{Pd}_4(L^A)_2(L^B)_4]^2+$ (CCS: 803.9 Å$^2$ at m/z 947.96), $[\text{Pd}_4(L^A)_2(L^B)_4]^{3+}$ (CCS: 790.6 Å$^2$ at m/z 1292.94).

Figure S44. Mobilograms obtained by trapped ion mobility ESI-TOF mass spectrometry for heteroleptic cage dimer $D_2$ with G$^1$: $[G^1@\text{Pd}_4(L^A)_2(L^B)_4]^4+$ (CCS: 803.3 Å$^2$ at m/z 976.19), $[2G^1@\text{Pd}_4(L^A)_2(L^B)_4]^4+$ (CCS: 814.5 Å$^2$ at m/z 1004.43), $[2G^1@\text{Pd}_4(L^A)_2(L^B)_4+BF_4^-]^3+$ (CCS: 800.7 Å$^2$ at m/z 1367.91).

Table S3. Comparison of experimental collisional cross section (eCCS) values of heteroleptic dimer $D_2$ and $2G^1@D_2$ with results derived from Collidoscope software$^{[8]}$ (tCCS) based models, which were optimized using B97-3c (ORCA, ver. 4.2.1)$^{[11]}$, with corresponding encapsulated BF$_4^-$ counter anions.

| Species | eCCS [Å$^2$] | tCCS [Å$^2$] | tCCS $\Delta_{\%}$ |
|---------|-------------|-------------|-------------------|
| $[\text{Pd}_4(L^A)_2(L^B)_4+2BF_4^-]^{6+}$ | 876.1 | 872.5 | -0.4% |
| $[\text{Pd}_4(L^A)_2(L^B)_4+3BF_4^-]^{5+}$ | 838.6 | 844.7 | 0.7% |
| $[\text{Pd}_4(L^A)_2(L^B)_4+4BF_4^-]^{4+}$ | 803.9 | 821.7 | 2.2% |
| $[\text{Pd}_4(L^A)_2(L^B)_4+5BF_4^-]^{3+}$ | 790.6 | 825.1 | 4.4% |
| $[G^1@\text{Pd}_4(L^A)_2(L^B)_4+2BF_4^-]^{4+}$ | 803.3 | 850.7 | 6.3% |
| $[2G^1@\text{Pd}_4(L^A)_2(L^B)_4]^{4+}$ | 814.5 | 830.0 | 1.9% |
| $[2G^1@\text{Pd}_4(L^A)_2(L^B)_4+BF_4^-]^{3+}$ | 800.7 | 834.2 | 4.2% |

The data reveals that host-guest complex $[2G^1@\text{Pd}_4(L^A)_2(L^B)_4]^{4+}$ features a slightly higher CCS value than “empty” host $[\text{Pd}_4(L^A)_2(L^B)_4+4BF_4^-]^{4+}$ (peak with four counter anions chosen to allow direct comparison), which in turn has a similar CCS value compared to the species with only one guest bound.

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5. Computational studies

**Figure S45.** Model of heteroleptic cage C optimized with B3LYP/def2-SVP (ORCA 4.2.1)\(^{[11]}\) in different views, a) side view, b) top view (a methyl group was used for ligand L\(^a\) instead of its hexyl group to reduce calculation time. Two BF\(_4^–\) counter anions inside the cavity are omitted for clarity).

**Figure S46.** Model of bridged homoletic cage C1, optimized with B3LYP/def2-SVP (ORCA 4.2.1)\(^{[11]}\) in different views, a) side view, b) top view (two BF\(_4^–\) counter anions inside the cavity are omitted for clarity).
Figure S47. Models of two isomeric assemblies of sum formula [Pd₃(L⁴₁)(L⁵)]₄. Left: heteroleptic pseudo-tetrahedron T1 and right: heteroleptic three-ring R1, both showing different topologies (optimized with B97-3c (ORCA 4.2.1)[11]). A subsequent single point energy calculation shows that T1 is energetically more favourable than R1 with a difference of 24 kJ/mol. Colours indicate different chemical environments for substructures of ligands L⁴₁ and L⁵.
### 6. X-ray Crystallography

**Table S4.** Crystallographic data of \([\text{Pd}_4(\text{L}^1)_{2}(\text{L}^2)_{3}]_2(\text{BF}_4)_8\) (D1), \([\text{Pd}_4(\text{L}^2)_{2}(\text{L}^3)_{3}]_2(\text{BF}_4)_8\) (D2), and \([2\text{G}^1+\text{Pd}_6(\text{L}^2)_{3}(\text{L}^3)_{6}]_2(\text{BF}_4)_8\) (P2).

| Compound | D1 | D2 | P2 |
|----------|----|----|----|
| Identification code | kw8i_sq | kw7j_sq | kw25i_sq |
| CCDC number | 2015325 | 2015326 | 2015327 |
| Empirical formula | \(\text{C}_{252}\text{H}_{230}\text{B}_{8}\text{F}_{32}\text{N}_{30}\text{O}_{4}\text{Pd}_{4}\) | \(\text{C}_{260}\text{H}_{220}\text{B}_{26}\text{F}_{36}\text{N}_{28}\text{O}_{8}\text{Pd}_{4}\) | \(\text{C}_{352}\text{H}_{264}\text{B}_{4}\text{F}_{16}\text{N}_{36}\text{O}_{12}\text{Pd}_{6}\) |
| Formula weight | 4862.73 | 4550.73 | 6239.74 |
| Temperature (K) | 100(2) | 100(2) | 100(2) |
| Crystal system | monoclinic | monoclinic | triclinic |
| Space group | \(\text{C}2/c\) | \(\text{C}2/m\) | \(\text{P}\bar{1}\) |
| \(a\) (Å) | 37.7368(13) | 33.2915(16) | 24.9670(9) |
| \(b\) (Å) | 21.2625(7) | 47.548(2) | 33.9028(9) |
| \(c\) (Å) | 33.7991(11) | 11.0729(4) | 34.7518(11) |
| \(\alpha\) (º) | 90 | 90 | 107.529(2) |
| \(\beta\) (º) | 112.9490(10) | 95.136(2) | 102.468(2) |
| \(\gamma\) (º) | 90 | 90 | 105.612(2) |
| Volume (Å\(^3\)) | 24973.2(15) | 17457.2(13) | 25563.7(15) |
| \(Z\) | 4 | 2 | 2 |
| Density (calc.) (Mg/m\(^3\)) | 1.293 | 0.866 | 0.811 |
| Absorption coefficient (mm\(^{-1}\)) | 2.984 | 2.085 | 2.120 |
| \(F(000)\) | 9984 | 4660 | 6392 |
| Crystal size (mm\(^3\)) | 0.400×0.100×0.100 | 0.150×0.050×0.050 | 0.100×0.050×0.050 |
| Crystal colour | yellow | colourless | colourless |
| Crystal shape | block | needle | needle |
| Radiation | CuK\(_\alpha\) (\(\lambda = 1.54178\) Å) | CuK\(_\alpha\) (\(\lambda = 1.54178\) Å) | CuK\(_\alpha\) (\(\lambda = 1.54178\) Å) |
| 2θ range for data collection (º) | 4.87 to 149.59 (0.80 Å) | 3.25 to 108.46 (0.95 Å) | 2.82 to 76.15 (1.25 Å) |
| Reflections collected | 213510 | 77240 | 82967 |
| Independent reflections [R(int)] | 25527 [0.0609] | 10798 [0.1163] | 27072 [0.0994] |
| Data / restraints / parameters | 25527/552/1624 | 10798/1449/776 | 27072/7592/3724 |
| Goodness-of-fit on F\(^2\) | 1.052 | 1.334 | 1.177 |
| \(R_1\) [I>2σ(I)] | 0.0504 | 0.1360 | 0.0992 |
| \(wR_2\) (all data) | 0.1443 | 0.3858 | 0.3434 |
| Largest diff. peak/hole (eÅ\(^3\)) | 1.65/-1.03 | 1.25/-0.51 | 1.03/-0.53 |
6.1. Crystal structure of D1

Yellow block-shaped crystals of $[\text{Pd}_4(\text{L}^4)_2(\text{L}^5)_4](\text{BF}_4)_8$ (D1) were grown by slow vapor diffusion of Et$_2$O into a solution of the assembly product of $\text{L}^4$ and $\text{L}^5$ in CD$_3$CN. Data was collected in-house on a Bruker D8 venture diffractometer equipped with an INCOATEC microfocus sealed tube (Iμs 3.0) using CuKα radiation at 100 K. The data was integrated with APEX3 and the structure was solved by intrinsic phasing/direct methods using SHELXT$^{[12]}$ and refined with SHELXL$^{[13]}$ for full-matrix least-squares routines on $F^2$ and ShelXle$^{[14]}$ as a graphical user interface and the DSR$^{[15]}$ program plugin was employed for modeling.

6.1.1. Specific refinement details of D1.

Stereochemical restraints for the ligands ($\text{L}^4$ and $\text{L}^5$) were generated by the GRADE program using the GRADE Web Server (http://grade.globalphasing.org) and applied in the refinement. A GRADE dictionary for SHELXL contains target values and standard deviations for 1,2-distances (DFIX) and 1,3-distances (DANG), as well as restraints for planar groups (FLAT). All displacements for non-hydrogen atoms were refined anisotropically. The refinement of ADP’s for carbon, nitrogen and oxygen atoms was enabled by a combination of similarity restraints (SIMU) and rigid bond restraints (RIGU). The contribution of the electron density from disordered counterions and solvent molecules, which could not be modeled with discrete atomic positions were handled using the SQUEEZE routine in PLATON. The solvent mask file (.fab) computed by PLATON was included in the SHELXL refinement via the ABIN instruction leaving the measured intensities untouched.

Figure S48. Atomic numbering scheme of residue CHC (ligand $\text{L}^4$).

Figure S49. Atomic numbering scheme of residue ETO (diethyl ether solvent molecule).

Figure S50. Atomic numbering scheme of residue ACN (CH$_3$CN solvent molecule).
Figure S51. View of cage dimer D1 crystal structures: a) showing encapsulated two CH₃CN molecules and one BF₄⁻ anion in each of the outer two cavities, b) showing the distance of coplanar aromatic ligand panels of the carbazole ligand of the wedge-shaped central cavity (distance is given in Ångström; hydrogens, BF₄⁻ anions and other solvent molecules are omitted for clarity).

Table S5. Structural details of cage dimer D1.

| Atoms            | Distance [Å] | Esd [Å] |
|------------------|--------------|---------|
| Pd2_1 Pd1_1      | 13.5967      | 0.0005  |
| Pd2_1 Pd2_1$1$   | 9.8691       | 0.0005  |
| Pd1_1 Pd1_1$1$   | 20.6544      | 0.0007  |
| Pd1_1 Pd2_1$1$   | 19.3550      | 0.0005  |

Symmetry code: $1$=1-x, +y, 3/2-z
6.2. Crystal structure of D2

Colorless needle-shaped crystals of [Pd₄(L²)₂(L⁶)₄(BF₄)₈(D2)] were grown by slow vapor diffusion of isopropyl ether into a solution of D2 in DMF. Data was collected in-house on a Bruker D8 venture diffractometer equipped with an INCOATEC microfocus sealed tube (Iμs 3.0) using CuKα radiation at 100 K. The data was integrated with APEX3 and the structure was solved by intrinsic phasing/direct methods using SHELXT \[12\] and refined with SHELXL \[13\] for full-matrix least-squares routines on F² and ShelXle \[14\] as a graphical user interface and the DSR \[15\] program plugin was employed for modeling.

6.2.1. Specific refinement details of D2.

Stereochemical restraints for the ligands (L² and L⁶) were generated by the GRADE program using the GRADE Web Server (http://grade.globalphasing.org) and applied in the refinement. A GRADE dictionary for SHELXL contains target values and standard deviations for 1,2-distances (DFIX) and 1,3-distances (DANG), as well as restraints for planar groups (FLAT). All displacements for non-hydrogen atoms were refined anisotropically. The refinement of ADP’s for carbon, nitrogen and oxygen atoms was enabled by a combination of similarity restraints (SIMU) and rigid bond restraints (RIGU). The contribution of the electron density from disordered counterions and solvent molecules, which could not be modeled with discrete atomic positions were handled using the SQUEEZE routine in PLATON. The solvent mask file (.fab) computed by PLATON was included in the SHELXL refinement via the ABIN instruction leaving the measured intensities untouched.

Figure S52. Atomic numbering scheme of residue CPC (ligand L²).

Figure S53. Atomic numbering scheme of residue LFP (ligand L⁶).
**Figure S54.** Atomic numbering scheme of residue DMF (DMF solvent molecule).

**Figure S55.** View of cage dimer D2 crystal structure showing one encapsulated DMF molecule and the hydrogen-bonding environment around its carbonyl group (O⋯H separations are given in Ångström). Hydrogens, BF₄⁻ anions and other solvent molecules are omitted for clarity.

**Table S6.** Structural details of cage dimer D2.

| Atoms         | Distance [Å] | Esd [Å] |
|---------------|--------------|---------|
| Pd1_1 Pd1_1$2$ | 15.4528      | 0.0017  |
| Pd1_1 Pd1_1$3$ | 18.3921      | 0.0021  |
| Pd1_1 Pd1_1$4$ | 24.0220      | 0.0018  |

Symmetry code: $2=x$, 1-y, $z$ $3=1-x$, +y, -z $4=1-x$, 1-y, -z
6.3. Crystal structure of P2

Colorless needle-shaped crystals of \([2G^1+Pd_6(L^{A2})_3(L^B)_3](BF_4)_8\) (P2) were grown by slow vapor diffusion of Et_2O into a solution of 2G^1@D2 in DMF. Data was collected in-house on a Bruker D8 venture diffractometer equipped with an INCOATEC microfocus sealed tube (λμs 3.0) using CuKα radiation at 100 K. The data was integrated with APEX3 and the structure was solved by intrinsic phasing/direct methods using SHELTX\(^\text{[12]}\) and refined with SHELXL\(^\text{[13]}\) for full-matrix least-squares routines on \(F^2\) and ShelXle\(^\text{[14]}\) as a graphical user interface and the DSR\(^\text{[15]}\) program plugin was employed for modeling.

6.3.1. Specific refinement details of P2.

Stereoschemical restraints for the ligands (L^{A2} and L^B) were generated by the GRADE program using the GRADE Web Server (http://grade.globalphasing.org) and applied in the refinement. A GRADE dictionary for SHELXL contains target values and standard deviations for 1,2-distances (DFIX) and 1,3-distances (DANG), as well as restraints for planar groups (FLAT). All displacements for non-hydrogen atoms were refined anisotropically. The refinement of ADP’s for carbon, nitrogen and oxygen atoms was enabled by a combination of similarity restraints (SIMU) and rigid bond restraints (RIGU). The contribution of the electron density from disordered counterions and solvent molecules, which could not be modeled with discrete atomic positions were handled using the SQUEEZE routine in PLATON. The solvent mask file (.fab) computed by PLATON was included in the SHELXL refinement via the ABIN instruction leaving the measured intensities untouched.

**Figure S56.** Atomic numbering scheme of residue N7S (guest molecule G^1).

**Figure S57.** Crystal structure of cage trimer P2 showing one G^1 positioned outside the cage boundaries and its hydrogen-bonding environment (O⋯H separations are given in Ångström). Hydrogens, BF_4^- anions and other solvent molecules are omitted for clarity.
Table S7. Structural details of cage trimer P2.

| Atoms                  | Distance [Å] | Esd (Å) | Average |
|------------------------|--------------|---------|---------|
| Pd – Pd Axis           | 15.26        |         |         |
| Pd1_1 Pd2_1            | 15.2910      | 0.0046  |         |
| Pd3_1 Pd4_1            | 15.2392      | 0.0047  |         |
| Pd5_1 Pd6_1            | 15.2628      | 0.0052  |         |
| Pd – Pd surfaces       | 20.36        |         |         |
| Pd1_1 Pd3_1            | 20.3740      | 0.0048  |         |
| Pd1_1 Pd5_1            | 20.2480      | 0.0051  |         |
| Pd3_1 Pd5_1            | 20.4911      | 0.0048  |         |
| Pd2_1 Pd4_1            | 20.2469      | 0.0041  |         |
| Pd2_1 Pd6_1            | 20.4490      | 0.0051  |         |
| Pd4_1 Pd6_1            | 20.3588      | 0.0051  |         |
| Pd-Pd Diagonal         | 25.45        |         |         |
| Pd1_1 Pd4_1            | 25.4188      | 0.0026  |         |
| Pd1_1 Pd6_1            | 25.4350      | 0.0031  |         |
| Pd3_1 Pd2_1            | 25.3922      | 0.0024  |         |
| Pd3_1 Pd6_1            | 25.5741      | 0.0030  |         |
| Pd5_1 Pd2_1            | 25.4487      | 0.0022  |         |
| Pd5_1 Pd4_1            | 25.4129      | 0.0023  |         |
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7. References

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