Light-powered Dissipative Assembly of Diazocine Coordination Cages

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1. General procedures

All chemicals, except otherwise specified, were obtained from commercial sources and used without further purification. (Z)-3,8-Diiodo-11,12-dihydrodibenzo[e,g][1,2]diazocine\[^{[S1]}\] was prepared according to a literature procedure. The tetrabutyl ammonium salt of the guest was prepared according to a previously reported procedure.\[^{[S2]}\] Recycling gel permeation chromatography was performed on a JAI LC-9210 II NEXT GPC system equipped with Jaigel 1H and 2H columns in series using chloroform as the eluent (HPLC grade). NMR measurements were all conducted at 298 K on Avance-500 and Avance-600 instruments from Bruker and an INOVA 500 MHz machine from Varian. Mass measurements were performed using a Bruker TIMS-TOF mass spectrometer equipped with an electrospray ionization (ESI) source and trapped ion mobility spectrometry (TIMS) set up. The irradiations at 385 nm and 530 nm were performed placing the NMR tubes or the cuvettes in front of LED lamps (3x 1.4 W Power LED, 25 nm, FWHM) from Sahlmann photonics, Kiel, or using fiber coupled LEDs (Power output 9.6 mW for 530 nm and 10.7 mW for 385 nm) from Thor Labs. UV-Vis spectra were recorded on Agilent 8453 and Jasco V-750 UV-Visible spectrophotometers.
2. Synthesis of ligands and palladium(II) assemblies

2.1 Preparation of the ligand

2.1.1 (Z)-3,8-Bis(pyridin-3-ylethynyl)-11,12-dihydrodibenzo[c,g]-[1,2]diazocine (cis-L)

![cis-L](image)

To a stirred solution of (Z)-3,8-diiodo-11,12-dihydrodibenzo[c,g][1,2]diazocine (265 mg, 576 μmol) in 50 mL toluene were added CuI (178 mg, 28.8 μmol), Pd(PPh₃)₂Cl₂ (40.0 mg, 57.6 μmol) and triethylamine (25 mL). The reaction mixture was stirred for 20 min before addition of 3-ethynylpyridine (178 mg, 1.73 mmol). After further stirring at 50 °C for 3 h and cooling to room temperature, the mixture was filtrated over Celite and the solvent was evaporated under reduced pressure. The precipitate was purified by flash column chromatography (cyclohexane/ethyl acetate, 5% → 80%) to afford the product as a yellow solid (90.0 mg, 219 μmol, 38%).

¹H NMR (600 MHz, DMF-d₇, 298K) δ 8.76 (d, ⁴J = 1.7 Hz, 2H), 8.61 (dd, ³J = 4.9, ⁴J = 1.7 Hz, 2H), 7.98 (dt, ³J = 7.9, ⁴J = 1.9 Hz, 2H), 7.48 (ddd, ³J = 7.9, 4.8, ⁴J = 0.9 Hz, 2H), 7.34 (dd, ³J = 7.9, ⁴J = 1.7 Hz, 2H), 7.26 (d, ³J = 7.9 Hz, 2H), 7.18 (d, ⁴J = 1.7 Hz, 2H), 2.98 (d, ⁴J = 2.5 Hz, 4H, C₂H₄). Diffusion coefficient 4.35 x 10⁻¹⁰ m²/s, DOSY-derived hydrodynamic radius 5.84 Å in DMF-d₇ at 298K. ¹³C NMR (151 MHz, DMF, 298K) δ 155.71, 151.98, 149.31, 138.61, 130.74, 130.47, 129.83, 123.87, 123.64, 121.23, 121.02, 119.66, 91.18, 86.72, 31.02. MS (EI, 70eV): m/z (%) = 410 (42), 382 (100), 303 (23), 266 (18). MS (EI, HR, 70 eV): C₂₈H₁₈N₄, m/z = calc.: 410.15315, found: 410.15218.
Figure S1. $^1$H NMR spectrum (600 MHz, DMF-$d_7$, 298K) of cis-L.

Figure S2. $^{13}$C NMR spectrum (151 MHz, DMF-$d_7$, 298K) of cis-L.

Figure S3. $^1$H-$^1$H COSY spectrum (600 MHz, DMF-$d_7$, 298K) of cis-L.
2.1.2 (E)-3,8-Bis(pyridin-3-ylenyl)-11,12-dihydrodibenzo[c,g]-[1,2]diazocine (trans-L)

Scheme S1. Interconversion between cis-L and trans-L by light and thermal relaxation

The metastable trans-form of ligand trans-L was obtained directly from cis-L by 385 nm UV irradiation at RT, as a mixture containing 62% trans-L and 38% cis-L upon reaching the photostationary state (as determined by NMR and UV-vis spectroscopy). $^1$H NMR (500 MHz, DMF-$d_7$, 298K) δ = 8.86 (d, $^4J = 1.4$ Hz, 2H), 8.66 (dd, $^4J = 1.6$, $^3J = 4.8$ Hz, 2H), 8.08 (td, $^4J = 1.9$, $^3J = 7.9$ Hz, 2H), 7.92 (d, $^4J = 1.6$ Hz, 2H), 7.58 (dd, $^4J = 1.7$, $^3J = 7.9$ Hz, 2H), 7.55 (ddd, $^4J = 0.9$, $^3J = 4.9$, 7.9 Hz, 2H), 7.37 (d, $^3J = 7.9$ Hz, 2H), 2.89 (br, 4H, $C_2H_4$), Diffusion coefficient $6.22 \times 10^{-10}$ m²/s for trans-L, DOSY-derived hydrodynamic radius 4.08 Å in DMF-$d_7$ at 298K.

Figure S4. $^1$H NMR spectrum (500 MHz, DMF-$d_7$, 298 K) of trans-L and cis-L (integration ratio 62:38), highlighted in red color: trans-L.
Figure S5. DOSY spectrum (500 MHz, DMF-d$_7$, 298 K) of a mixture of trans-L (D = 6.22 x 10^{-10} m$^2$/s) and cis-L (D = 4.35 x 10^{-10} m$^2$/s).
2.2. Synthesis of palladium(II) assemblies

2.2.1 Synthesis of cis-Cage, \([Pd_n(cis-L)_2]_n(BF_4)_2\)

We use the term “cis-Cage” here to describe the equilibrated mixture containing the \([Pd_3(cis-L)_4]\) cage as major component next to higher nuclear assemblies such as \([Pd_5(cis-L)_6]\) and oligomeric species.

A \(N,N'\)-dimethylformamide (DMF, 450 \(\mu\)L) solution of \(cis-L\) (1.4 \(\mu\)mol, 0.57 mg) was added to a DMF (50 \(\mu\)L) solution of \([Pd(CH_3CN)_4](BF_4)_2\) (0.7 \(\mu\)mol, 0.3 mg) and the reaction mixture was heated for 5 h at 70 °C. \(^1\)H NMR (500 MHz, DMF-\(d_7\), 298K) \(\delta\) 9.71, 9.54, 8.28, 7.84, 7.35, 6.66, 3.03. DOSY-derived hydrodynamic radius of the major component 11.8 Å. ESI-TOF-MS \(m/z = 463.1050\) (calcd for \([PdL_2]^{2+}, [PdL_4]^{4+}, [PdL_6]^6^+\), 463.1043), 647.1404 (calcd for \([Pd_2L_4+(BF_4)]^{3+}\), 647.1421), 738.9091 (calcd for \([Pd_3L_6+2(BF_4)]^{4+}\), 738.9106), 1013.2120 (calcd for \([PdL_2+(BF_4)]^+, [Pd_2L_4+2(BF_4)]^{2+}, [Pd_3L_6+3(BF_4)]^{3+}\), 1013.2152).

2.2.2 Synthesis of cis-Ring, \([Pd_2Cl_2(cis-L)_2]\)

A DMF solution (2 mL) of \(PdCl_2(CH_3CN)_2\) (0.01 mmol, 2.6 mg) was slowly added to a dichloromethane solution (3 mL) of \(cis-L\) (0.01 mmol, 4.1 mg). After 2 days, yellow crystals were obtained from the solution. \(^1\)H NMR (500 MHz, DMF-\(d_7\), 298K) \(\delta\) 9.00 (d, 2H, \(^4J = 1.8\) Hz), 8.98 (d, 2H, \(^4J = 1.9\) Hz), 8.85 (dd, 4H, \(^3J = 5.8\) Hz, \(^4J = 1.5\) Hz), 8.2 (m, 4H), 7.67 (dd, 4H, \(^3J = 7.9\) Hz, \(^3J = 6.0\) Hz), 7.37 (m, 4H), 7.27 (m, 4H), 2.98 (m, \(C_2H_4\)). The NMR signals, especially protons \(H_a\) and \(H_b\), shows splitting, ascribed to the possible presence of two isomers, transoid and cisoid rings, as evidenced in section 5.1

2.2.3 Synthesis of trans-Cage, \([Pd_2(trans-L)_4](BF_4)_4\)

A DMF solution (450 \(\mu\)L) of \(cis-L\) (1.4 \(\mu\)mol, 0.57 mg) was irradiated by a 385 nm LED lamp for 10 minutes. In a dark room, \([Pd(CH_3CN)_4](BF_4)_2\) (0.7 \(\mu\)mol, 0.3 mg), dissolved in 50 \(\mu\)L DMF, was added to the solution. \(^1\)H NMR (500 MHz, DMF-\(d_7\), 298K) \(\delta\) 9.80 (s, 2H), 9.63 (br, 2H), 8.40 (d, \(^3J = 7.8\) Hz, 2H), 7.94 (t, \(^3J = 6.7\) Hz, 2H), 7.75 (br, 2H), 7.38 (d, \(^3J = 7.1\) Hz, 2H), 7.37 (d, \(^3J = 7.9\) Hz, 2H), 2.95 (br, 4H, \(C_2H_4\)). Diffusion coefficient \(2.21 \times 10^{-10}\) m\(^2\)/s, DOSY-derived hydrodynamic radius 11.5 Å. ESI-TOF-MS \(m/z = 463.6042\) (calcd for \([Pd_2L_4]^{4+}\), 463.6055), 647.1386 (calcd for \([Pd_2L_4+(BF_4)]^{3+}\), 647.1421), 1013.2093 (calcd for \([Pd_2L_4+2(BF_4)]^{2+}\), 1013.2152).
Figure S6. $^1$H NMR spectrum (500 MHz, DMF-$d_7$, 298 K) for cis-L and cis-Cage.

Figure S7. COSY spectra (500 MHz, DMF-$d_7$, 298 K) for cis-Cage.
Figure S8. DOSY spectrum (500 MHz, DMF-\textit{d}_7, 298 K) for the \textit{cis}-Cage mixture ($D = 2.15 \times 10^{-10}$ m$^2$/s), relaxation fitting for the area between 8.23 and 8.40 ppm shown in the inset.

Figure S9. COSY spectra (500 MHz, DMF-\textit{d}_7, 298 K) for \textit{trans}-Cage.
**Figure S10.** $^1$H NMR spectrum (500 MHz, DMF-$d_7$, 298 K) for *cis*-L and *cis*-Ring, residual L signals highlighted in beige.

**Figure S11.** COSY spectra (500 MHz, DMF-$d_7$, 298 K) for *cis*-Ring.
Figure S12. ESI-MS spectrum of cis-Cage with measured and calculated isotopic patterns of a) overlap of \([\text{Pd}_2\text{cis-L}_4 + 2(\text{BF}_4)]^{2+}\) and \([\text{Pd}_3\text{cis-L}_6 + 3(\text{BF}_4)]^{3+}\); b) \([\text{Pd}_3\text{cis-L}_6 + 2(\text{BF}_4)]^{4+}\); c) \([\text{Pd}_2\text{cis-L}_4 + \text{BF}_4]^{3+}\); d) \([\text{Pd}_3\text{cis-L}_6 + \text{BF}_4]^{5+}\).
Figure S13. ESI-MS spectrum of trans-Cage with measured and calculated isotopic patterns of a) overlap of $[\text{Pd}_2\text{trans-L}_4 + 2(\text{BF}_4)]^{2+}$ and minor presence of $[\text{Pd}_3\text{trans-L}_6 + 3(\text{BF}_4)]^{3+}$; b) $[\text{Pd}_2\text{trans-L}_4 + (\text{BF}_4)]^{3+}$. 
Figure S14. $^1$H NMR (500 MHz, DMF-$d_7$, 298 K) showing **trans-Cage** formation with internal standard ($^{1}$,3,5-tris-tert-butylbenzene (InRef), *solvent residue). All spectra were obtained from the same stock solution, signals for the pyridine protons of *cis* and *trans*-ligands are highlighted in red. (Integral color code: red for *trans*-isomers, gray for *cis*-isomers, blue for InRef)
According to integral ratios, (a) molecular ratio cis-L : InRef = 0.96 : 1; (b) cis-Cage : InRef = 0.96 : 1, → entire cis-L is consumed for cis-Cage formation; (c) 385 nm irradiation causes photoswitching of cis-Cage to trans-Cage, trans-C : InRef = 0.67 : 1, → the yield for trans-Cage is 69%; (d) ratio cis-L : trans-L : InRef = 0.36 : 0.61 : 1, 63% PSS; (e)-(i) stepwise addition of palladium(II) precursor, (e) cis-L : trans-L : trans-Cage : InRef = 0.31 : 0.47 : 0.15 : 1, → the yield for trans-Cage is 16%; (f) cis-L : trans-L : trans-Cage : InRef = 0.3 : 0.28 : 0.37 : 1, → the yield for trans-Cage is 38%; (g) cis-L : trans-L : trans-Cage : InRef = 0.24 : 0.15 : 0.51 : 1, → the yield for trans-Cage is 55%; (h) cis-L : trans-L : trans-Cage : InRef = 0.12 : 0.05 : 0.62 : 1, → the yield for trans-Cage is 65%; (i) trans-Cage : InRef = 0.68 : 1, → the yield for trans-Cage is 70%.
3. Photoswitching properties

3.1. Determination of the photostationary state of L (PSS @ 385 nm)

**Figure S15.** Measurement of the photostationary state (PSS @ 385 nm) by $^1$H-NMR spectroscopy in acetonitrile-$d_3$ at 300 K. The sample was first measured without irradiation, then the compound was irradiated twice at 385 nm for 5 min. At the end, the sample was irradiated at 530 nm for 5 min. The irradiation experiment took place in a NMR tube (1 mg of substance, 500 μL of acetonitrile-$d_3$).
Figure S16. UV-vis spectra of the ligand. black line: unexposed (cis-L), red line: PSS (385 nm) and blue line (530 nm). The UV-vis spectra were measured in acetonitrile at 298 K. Concentration: 1.52 mmol/L.
3.2. Thermal relaxation of meta-stable *trans*-L and *trans*-Cage to stable *cis*-forms

Figure S17. Time-dependent $^1$H NMR monitoring (500 MHz, DMF-$d_7$, 298 K) of the thermal relaxation of *trans*-L.
Figure S18. Time-dependent $^1$H NMR monitoring (500 MHz, DMF-$d_7$, 298 K) of the thermal relaxation of trans-Cage.
Figure S19. Time-dependent UV-Vis spectra at \( T = 298 \text{ K} \) (1.12 mM in DMF), for the thermal relaxation of \textit{trans-L}.

Figure S20. Absorbance decay of \textit{trans-L} monitored at \( \lambda = 487 \text{ nm} \) at \( T = 298 \text{ K} \) (black squares), and fitting following a 1\textsuperscript{st} order kinetics (red line).
**Figure S21.** Time dependent UV-Vis spectra at $T = 303$ K (1.12 mM in DMF), for the thermal relaxation of \textit{trans-L}.

**Figure S22.** Absorbance decay of \textit{trans-L} monitored at $\lambda = 486$ nm at $T = 303$ K (black squares), and fitting following a 1\textsuperscript{st} order kinetics (red line).
**Figure S23.** Time dependent UV-Vis spectra at $T = 308$ K (1.12 mM in DMF), for the thermal relaxation of *trans-L*.

**Figure S24.** Absorbance decay of *trans-L* monitored at $\lambda = 486$ nm at $T = 308$ K (black squares), and fitting following a 1st order kinetics (red line).
**Figure S25.** Time dependent UV-Vis spectra at $T = 288$ K (1.12 mM given as ligand concentration, in DMF), for the thermal relaxation of *trans*-Cage.

**Figure S26.** Absorbance decay of *trans*-Cage monitored at $\lambda = 483$ nm at $T = 288$ K (black squares), and fitting following a 1$^{\text{st}}$ order kinetics (red line).
Figure S27. Time dependent UV-Vis spectra at $T = 298$ K (1.12 mM given as ligand concentration, in DMF), for the thermal relaxation of trans-Cage.

Figure S28. Absorbance decay of trans-Cage monitored at $\lambda = 486$ nm at $T = 298$ K (black squares), and fitting following a 1st order kinetics (red line).
**Figure S29.** Time dependent UV-Vis spectra at $T = 303$ K (1.12 mM given as ligand concentration, in DMF), for the thermal relaxation of trans-Cage.

**Figure S30.** Absorbance decay of trans-Cage monitored at $\lambda = 484$ nm at $T = 303$ K (black squares), and fitting following a 1st order kinetics (red line).
Figure S31. Time dependent UV-Vis spectra at $T = 308$ K (1.12 mM given as ligand concentration, in DMF), for the thermal relaxation of **trans-Cage**.

Figure S32. Absorbance decay of **trans-Cage** monitored at $\lambda = 485$ nm at $T = 308$ K (black squares), and fitting following a 1$^{\text{st}}$ order kinetics (red line).
Table S1. Calculated rate constants and half-life time for trans-L and trans-Cage.

Table S2. Activation energies for the thermal relaxations of trans-L and trans-Cage.
Figure S34. Photoswitching effect by light exposure and thermal relaxation, (a) \textit{trans-Cage}; (b) sample (a) was kept at room temperature in a dark for 16 h; (c) sample (b) was irradiated at 385 nm for 10 min; (d) sample (c) under irradiation at 530 nm for 10 min; (e) sample (d) irradiated at 385 nm for 10 min.

4. X-ray crystallography

4.1. Crystallization

4.1.1 \textit{Cis-Ring}, [Pd$_2$Cl$_4$(cis-L)$_2$]

\textit{Cis-Ring} crystals were obtained from slow diffusion in a mixed solution of DMF and CH$_2$Cl$_2$. After 2 days, block-shaped yellow crystals suitable for X-ray data collection were obtained from the solution.

4.1.2 \textit{Trans-Cage}, [Pd$_2$(trans-L)$_4$(BF$_4$)$_4$]

\textit{Trans-Cage} was crystallized from DMF solution by a slow vapor-phase transfer of diethyl ether in a refrigerator (4 ℃) in the dark. After 2 days, red rod-shaped crystals suitable for X-ray diffraction measurement were formed.
4.2. Data collection details

Single crystals for X-ray structural analyses of cis-Ring and trans-Cage were mounted at room temperature in NVH oil. Data were collected in-house on a Bruker D8 Venture diffractometer equipped with an INCOATEC micro focus sealed tube (I$\mu$s 3.0) using MoK$_\alpha$ (for cis-Ring), CuK$_\alpha$ (trans-Cage) for radiation at 100 K. The resolution was cut off at 0.90 Å for cis-Ring, 1.05 Å for trans-Cage, after which the signal to noise ratio has dropped below I/σ(I) < 2.0. The data was integrated with APEX3. The structures were solved by intrinsic phasing/direct methods using SHELXT\textsuperscript{[S3]} and refined with SHELXL (2018/2)\textsuperscript{[S4]} for full-matrix least-squares routines on $F^2$ and ShelXle\textsuperscript{[S5]} as a graphical user interface.

4.2.1 Refinement details for trans-Cage

Stereochemical restraints for the TDP ligands (trans-L) 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).\textsuperscript{[S6]} 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\textsuperscript{[S7]} routine in PLATON.\textsuperscript{[S8]} The solvent mask file (.fab) computed by PLATON were included in the SHELXL refinement via the ABIN instruction leaving the measured intensities untouched. In the structure, one of ligand backbones is disordered occupying 30% and 70% for each part. One BF$_4$ anion and solvent molecules were disordered in positions.

4.2.2 Refinement details for cis-Ring

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\textsuperscript{[S7]} routine in PLATON.\textsuperscript{[S8]}
Table S3. Crystallographic data of *cis-Ring* and *trans-Cage*

|                      | *cis-Ring*               | *trans-Cage*              |
|----------------------|--------------------------|---------------------------|
| CCDC No.             | 2117885                  | 2117884                   |
| Empirical formula    | C_{28} H_{42} Cl_{10} N_{8} Pd_{2} | C_{112} H_{72} B_{4} F_{16} N_{16} Pd_{2} |
| Formula weight       | 1418.29                  | 2201.89                   |
| Temperature (K)      | 173(2)                   | 100(2)                    |
| Wavelength (Å)       | 0.71073                  | 1.54178                   |
| Crystal system       | Triclinic                | Triclinic                 |
| Space group          | P-1                      | P-1                       |
| Unit cell dimensions, a (Å) | 8.7981(18)             | 11.9511(12)               |
| b (Å)                | 12.744(3)                | 13.8353(14)               |
| c (Å)                | 17.038(3)                | 26.520(2)                 |
| α (°)                | 74.13(3)                 | 75.167(5)                 |
| β (°)                | 76.99(3)                 | 81.070(5)                 |
| γ (°)                | 76.72(3)                 | 89.999(5)                 |
| Volume (Å³)          | 1761.4(7) Å³            | 4183.9(7) Å³             |
| Z                    | 1                        | 1                         |
| Density (calculated) (Mg/m³) | 1.337                  | 0.874                     |
| Absorption coefficient (mm⁻¹) | 0.928                  | 2.185                     |
| F(000)               | 708                      | 1112                      |
| Crystal size (mm³)   | 0.150 x 0.130 x 0.110    | 0.150 x 0.130 x 0.110     |
| Theta range for data collection (°) | 1.262 to 23.252          | 3.307 to 47.437           |
| Index ranges         | -9<=h<=9, -11<=h<=11,    | -13<=k<=13, -25<=l<=25   |
| Reflections collected | 53232                   | 34809                     |
| Independent reflections | 4946                    | 7252                      |
| Completeness to theta | 97.80%                  | 94.50%                    |
| Absorption correction | Semi-empirical from    | Semi-empirical from       |
|                      | equivalents              | equivalents               |
| Max. and min.        | 0.903 and 0.870          | 0.7493 and 0.5304         |
| transmission         |                          |                           |
| Refinement method    | Full-matrix least-squares on F² | Full-matrix least-squares on F² |
| Data / restraints / parameters | 4946 / 0 / 371          | 7252 / 1269 / 813         |
| Goodness-of-fit on F² | 1.11                     | 1.464                     |
| Final R indices [I>2sigma(I)] | R1 = 0.0484, wR2 = 0.1402 | R1 = 0.1211, wR2 = 0.3537 |
| R indices (all data) | R1 = 0.0517, wR2 = 0.1429 | R1 = 0.1624, wR2 = 0.3872 |
| Extinction coefficient | n/a                     | n/a                       |
| Largest diff. peak and hole (e.Å³) | 2.141 and -0.536 | 0.607 and -0.447 |
5. DFT calculations

5.1. Gas-phase electronic energies for ring conformers

Gas-phase electronic energies of the experimentally observed $[(\text{PdCl}_2)_2(\text{cis-L})_2]_0$ ring in its *transoid*-conformation (with both N=N bridges looking into the ring cavity) were compared to other conceivable conformational isomers:

| Table S4. Gas phase electronic energies for possible ring conformations formed by two ligands in *cis*-photoisomeric form and two PdCl$_2$ units. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | $E(\omega\text{B97X-D/def2-SVP})/\text{H}$ | $E(\omega\text{B97X-D/def2-TZVP})/\text{H}$ | $\Delta E(\text{TZVP})/\text{kJ mol}^{-1}$ | front view | side view |
| *transoid* ring | -4686.812447     | -4690.327667    | 0               |              |          |
| *cisoid* ring   | -4686.812778     | -4690.327737    | -0.18           |              |          |
| *transoid* ring, one N=N flipped outwards | -4686.811809 | -4690.327034 | 1.66 | | |
| *transoid* ring, both N=N flipped outwards | -4686.810998 | -4690.326204 | 3.84 | | |

Compared to the experimentally found *transoid*-geometry, the *cisoid* isomer is of almost the same energy in these gas-phase calculations but has a much larger dipole moment (0.02 vs. 0.98 D). The *transoid* isomers with one or both N=N bridges flipped outside are 1.7 and 3.8 kJ/mol higher in energy.

5.2. Comparison of strain in *cis*-Ring, *cis*-Cage and *trans*-Cage

To learn about the enthalpic contributions of the ring-strain that builds up upon assembly of the *cis*-/*trans*-ligand isomers with metal precursors [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ and PdCl$_2$(CH$_3$CN)$_2$, respectively, we performed a series of gas-phase DFT calculations.
To estimate the strain energy that is imposed on the ligands by complex formation, the ligand substructures were cut out from the geometry-optimized ring/cages and single-point energies of these structures were compared to the corresponding energies of the fully relaxed (geometry optimized on same level as ring/cages) ligand isomers.

**Table S5.** Absolute energies [Hartree] of the ligands cis-L and trans-L in their fully optimized geometry and in their geometry in the ring [(PdCl₂)₂(cis-L)₂]₀ as well as in the cages [Pd₂(cis-L)₄]⁴⁺ and [Pd₂(trans-L)₄]⁴⁺. ∆E\text{ligand} is the energy difference between the fully geometry optimized ligand and the energy of the same ligand in the geometry that it adopts in the corresponding complex (ring or cage).

|                  | E(ωB97X-D/def2-TZVP)/H | ∆E\text{ligand} [kJ mol⁻¹] |
|------------------|------------------------|----------------------------|
| cis-L optimized  | -1296.643206           | 0                          |
| cis-L cut from opt. [(PdCl₂)₂(cis-L)₂]₀ ring | -1296.641384 | 4.78                        |
| cis-L cut from opt. [Pd₂(cis-L)₄]⁴⁺ cage | -1296.638185 | 13.18                       |
| trans-L optimized | -1296.625722           | 0                          |
| trans-L from opt. [Pd₂(trans-L)₄]⁴⁺ cage | -1296.622917 | 7.37                        |

The cis ligand (cis-L) experiences significantly more strain when incorporated in the cis cage ([Pd₂(cis-L)₄]⁴⁺) than in the cis ring [(PdCl₂)₂(cis-L)₂]₀. The results are in agreement with the experimental observation that the cis ring is readily formed while the cis cage is only one of many species in a mixture of assembly products. The trans ligand (trans-L) only suffers moderate strain within the trans cage [Pd₂(trans-L)₄]⁴⁺, which supports the fact that the trans cage is the major complex formed by the trans ligand in solution.

Additionally, the strain imposed on the coordination sites by the ligands was calculated, by comparing the energies of the [Pd(Cl₂)(pyridine)₂]₀ substructures of the rings and the [Pd(pyridine)₄]²⁺ substructures of the cages (free valence after formal C\text{pyridine}-C\text{ethinyl} bond cleavage saturated with H) with the fully optimized structures of [Pd(Cl₂)(pyridine)₂]₀ and [Pd(pyridine)₄]²⁺.
Table S6. Absolute energies [Hartree] of the [PdCl₂(pyridine)]⁰ and the [Pd(pyridine)]²⁺ unit in their fully optimized geometry and in their geometry in the ring ([PdCl₂(cis-L)]⁰ as well as in the cages [Pd₂(cis-L)]⁴⁺ and [Pd₂(trans-L)]⁴⁺. ΔE_{coord.} is the energy difference between the fully geometry optimized coordination site and the energy of the same coordination site in the geometry that it adopts in the corresponding complex (ring or cage).

| Coordination Site                  | E(ωB97X-D/def2-TZVP)/H | ΔE_{coord.} [kJ mol⁻¹] |
|-----------------------------------|-------------------------|------------------------|
| [PdCl₂(pyridine)]⁰ optimized      | -1545.089916            | 0                      |
| [PdCl₂(pyridine)]⁰ cut from       | -1545.088934            | 2.58                   |
| ([PdCl₂(cis-L)]⁰ ring             |                         |                        |
| [Pd(pyridine)]²⁺ optimized        | -1120.715382            | 0                      |
| [Pd(pyridine)]²⁺ cut from         | -1120.711613            | 9.90                   |
| [Pd₂(cis-L)]⁴⁺ cage               |                         |                        |
| [Pd(pyridine)]²⁺ cut from         | -1120.710964            | 11.60                  |
| [Pd₂(trans-L)]⁴⁺ cage             |                         |                        |

The strain energy imposed on the Pd coordination sites is very low for cis ring ([PdCl₂(cis-L)]⁰) and almost 4 times higher for the cis cage. The coordination site is slightly more strained in the trans cage ([Pd₂(trans-L)]⁴⁺) as compared to the cis cage ([Pd₂(cis-L)]⁴⁺). In summary, the calculations predict that the cis ring is favored over the cis cage. If we assume that the total strain energy (E_{strain}), in a first approximation, is the sum of the strain energies of the ligands (ΔE_{ligand}) and the coordination sites (ΔE_{coord.}): E_{strain} = n·ΔE_{ligand} + 2·ΔE_{coord.}, we obtain a strain energy (E_{strain}) of the cis cage of 72.5 kJ·mol⁻¹ and 52.7 kJ·mol⁻¹ for the trans cage. Hence, the trans cage is significantly less strained than the cis cage.

Absolute and reliable values for the free enthalpy of formation of the complexes are beyond the predictive power of the simple DFT methods used here since entropies and solvent effects are neglected. The interpretation therefore is restricted to the relative energies of very similar systems, where error canceling can be expected to provide reliable trends.
6. Host-guest chemistry

6.1 General procedure for host-guest titrations

Host-guest titrations were carried out by stepwise addition of 2,6-naphthalenedisulfonate (G, as tetrabutyl ammonium salt in DMF-d$_7$) into a DMF-d$_7$ solution of cis- or trans-Cage (0.7 mM) in an NMR tube. $^1$H NMR spectra were recorded immediately after vigorous mixing the solution. The titration with trans-Cage (Figure 5b in the main text) was conducted in the dark.

![Figure S35](image)

$^1$H NMR spectra (500 MHz, DMF-d$_7$, 298 K) for titration experiment of cis-Cage with G.
7. ESI-MS and Ion Mobility spectrometry

7.1 General procedure.

All measurements were performed using a Bruker TIMS-TOF mass spectrometer equipped with electrospray ionization (ESI) source and trapped ion mobility spectrometry (TIMS) set up. Both mass and IMS calibrations were performed using Agilent Tune-Mix™ as purchased and reported drift tube collision cross section (CCS) by Stow et al.[89] were used for CCS calibration. All samples were diluted with ACN to achieve a final 25 µM concentration which were then electrosprayed at 180 µL/h flow rate. The optimized parameters are as following: Capillary voltage: 2500 V, End plate offset: 200 V, Nebulizer: 0.3 bar, Dry gas flow: 3L/min, Dry gas temperature: 75 °C, Funnel 1 RF: 150 V, Funnel 2 RF: 150 V, Multiple RF: 100 V, Deflection delta: 60 V, Transfer time: 70 µS, Prepulse storage: 15 µS, Quadrupole ion energy: 7V and Collision energy: 5 V. For TIMS, all the ions were accumulated for 5 s and a 450 ms ramp time was used. Tunnel in and out pressure were 2.78 mbar and 0.96 mbar, respectively with a pressure difference of 1.82 mbar. In all the measurements the resolving power (CCS/ΔCCS) was above 180.

![Figure S36](image.png)

**Figure S36.** ESI-MS spectrum of cis-Cage with isotopic patterns of [Pd₃cis-L₅+G]⁴⁺ and [Pd₄cis-L₇+2G]⁴⁺ shown in the inset.
Figure S37. CCS values for *cis*-Cage (red line) *trans*-Cage (black line) measured for the signal corresponding to the $[\text{Pd}_2(\text{L})_4]^{4+}$ species at 463.11 m/z.

Figure S38. CCS values for *cis*-Cage (red line) *trans*-Cage (black line) measured for the signal corresponding to the $[\text{Pd}_2(\text{L})_4](\text{BF}_4)_2^{2+}$ species at 1013.21 m/z.
Figure S39. Comparison of the CCS values for *cis*-Cage signals corresponding to the 4+ species with formula $[\text{Pd}_2(\text{L})_4]^{4+}$ (463.11 m/z, black line), and $[\text{Pd}_3(\text{L})_6](\text{BF}_4)_2^{4+}$ (738.91 m/z, red line).

Figure S40. CCS values for *cis*-Cage and *trans*-Cage with and without the addition of the guest and upon irradiation. Signals corresponding to the 2+ species, with formula $[\text{Pd}_2(\text{L})_4](\text{BF}_4)_2^{2+}$ (1013.21 m/z) and $[\text{Pd}_2(\text{L})_4+\text{G}]^{2+}$ (1070.18 m/z).
8. References

[S1] Moormann, W., Langbehn, D., Herges, R. *Beilstein J. Org. Chem.* **2019**, *15*, 727.

[S2] Clever, G. H., Kawamura, W. Shionoya M. *Inorg. Chem.* **2011**, *50*, 4689.

[S3] Sheldrick, G. M. *Acta Crystallogr. Sect. A*. **2015**, *71*, 3.

[S4] Sheldrick, G. M. *Acta Crystallogr. Sect. C*. **2015**, *71*, 3.

[S5] Hübschle, C. B. Sheldrick, G. M., Dittrich, B. *J. Appl. Cryst.*, **2011**, *44*, 1281.

[S6] Thorn, A., Dittrich, B., Sheldrick, G. M. *Acta Crystallogr. Sect. A* **2012**, *68*, 448-451.

[S7] Spek, A. *Acta Crystallogr. Sect. C*, **2015**, *71*, 9.

[S8] Spek, A. *Acta Crystallogr. Sect. D*, **2009**, *65*, 148.

[S9] Stow, S. M., Causon, T. J., Zheng, X., Kurulugama, R.T., Mairinger, T., May, J. C., Rennie, E. E., Baker, E. S., Smith, R. D., McLean, J. A., Hann, S., Fjeldsted, J. C. *Anal. Chem.*, **2017**, *89*, 9048.