A Mono-Metallic Pd(II)-Cage Featuring Two Different Polar Binding Sites

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1. General information and instruments

Reagents were obtained from commercial suppliers and used without further purification unless otherwise stated. All solvents were commercially obtained and used without further purification except pyrrole which was distilled and freshly used. Dry solvents were taken from a solvent system MB SPS 800. THF, Et\(_3\)N, DIPEA and iPr\(_2\)NH were dried, distilled and degassed by three freeze-pump-thaw cycles before used in the cross-coupling reactions. CH\(_3\)CN and CHCl\(_3\) were dried before used in the synthesis of the metallo-cage. Routine \(^1\)H NMR and \(^{13}\)C\(^{(1)}\)H\) NMR spectra were recorded on a Bruker Avance 300 (300 MHz for \(^1\)H NMR and 75 MHz for \(^{13}\)C NMR), Bruker Avance 400 (400 MHz for \(^1\)H NMR and 100 MHz for \(^{13}\)C NMR), Bruker Avance 500 (500 MHz for \(^1\)H NMR and 125 MHz for \(^{13}\)C NMR) or Bruker Avance 500 with cryoprobe (500 MHz for \(^1\)H NMR and 125 MHz for \(^{13}\)C NMR). Deuterated solvents used are indicated in the characterization and chemical shifts are given in ppm. Residual solvent peaks were used as reference.\(^1\) All NMR \(J\) values are given in Hz. COSY, NOESY, HMQC and HMBC experiments were recorded to help with the assignation of \(^1\)H and \(^{13}\)C signals. High Resolution Mass Spectra (HRMS) were obtained on a Bruker HPLC-TOF (MicroTOF Focus) with ESI as ionization mode and Bruker HPLC-QqTOF (MaXis Impact) with ESI as ionization mode. IR spectra were recorded on a Bruker Optics FTIR Alpha spectrometer equipped with a DTGS detector, KBr beamsplitter at 4 cm\(^{-1}\) resolution using a one bounce ATR accessory with diamond windows. Melting points were measured on a MP70 Melting Point System Mettler Toledo. Crystal structure determinations were carried out using a Rigaku MicroMax-007HF diffractometer equipped with a PILATUS 200K detector but for [CH\(_3\)CN]₂\(_2\)[\(\text{[1\text{+Pd}]}\)(BF\(_4\))\(_2\)] for which a Bruker Apex II Duo equipped with an APEX II detector was used. Both using MoK\(\alpha\) radiation. Crystal structure solution was achieved using VLD and Patterson methods as implemented in SIR2014 v14.10. Least-squares refinement on F\(^2\) using all measured intensities was carried out using the program SHELX-2018/3. Column chromatography was performed with silica gel technical grade (Sigma-Aldrich), pore size 60 Å, 230-400 mesh particle size, 40-63 μm particle size and Thin Layer Chromatography (TLC) analysis on silica gel 60 F254.
2. Synthesis and characterization data

2.1 Tetra-α isomer of tetra-pyridyl super aryl-extended calix[4]pyrrole 1

![Scheme S1. Synthesis of compound 1.](image)

Tetra-(4-iodophenyl)-calix[4]pyrrole S2 (55 mg, 0.05 mmol, 1 equiv.), Pd(PPh3)2Cl2 (4.09 mg, 0.01 mmol, 0.03 equiv.), Cul (1.78 mg, 0.01 mmol, 0.05 equiv.) and 3-((4'-ethynylphenoxy)methyl)pyridine S1 (58.50 mg, 0.28 mmol, 1.5 equiv.) were kept under Argon atmosphere. Dry THF (5 mL) and dry diisopropylamine (5 mL) were added dropwise. The reaction was stirred at 45ºC for 5 h. After that, the crude was concentrated, redissolved in CH2Cl2 (10 mL) and washed with brine (2x10 mL) and water (10 mL). The organic layer was dried (Na2SO4), filtered and concentrated. The crude was purified by column chromatography on silica gel (3 g, 9:1 CH2Cl2:IPA) and the product was further purified by recrystallization from 1:1 CH2Cl2:CH3CN (4 mL) obtaining a white solid (47 mg, 0.03 mmol, 65% yield). Rf = 0.2 (95:5 CH2Cl2:IPA). 1H NMR (500 MHz, CDCl3, 298 K): δ (ppm): 8.66 (s, 4H); 8.58 (d, J = 5.0 Hz, 4H); 7.75 (d, J = 7.9 Hz, 4H); 7.68 (br s, 4H); 7.48-7.46 (m, 8H); 7.40-7.38 (m, 8H); 7.31 (dd, J = 7.9 Hz, J = 5.0 Hz, 4H); 7.11-7.09 (m, 8H); 6.93-6.91 (m, 8H); 5.77 (s, 8H); 5.08 (s, 8H); 1.98 (s, 12H). 13C{1H} NMR (125 MHz, CDCl3, 298 K): δ (ppm): 158.5; 149.7; 149.1; 136.3; 135.4; 133.3; 132.3; 131.0; 127.6; 123.7; 121.8; 116.3; 115.0; 106.7; 89.2; 88.4; 67.7; 44.8; 28.1 (one carbon signal might be overlapped). HRMS (ESI-TOF) m/z: [M+2H]2+ Calcd for C104H82N8O4 753.3224; Found 753.3254. FTIR vmax (cm⁻¹): 1599; 1512; 1429; 1283; 1241; 1173; 1016; 827; 707. M.p. > 280ºC (decompose).

![Figure S1. 1H NMR (500 MHz, CDCl3, 298 K) spectrum of compound 1. See Scheme S1 for proton assignment. *Solvent residual peaks.](image)
Figure S2. $^{13}$C($^1$H) NMR (500 MHz, CDCl$_3$, 298 K) spectrum of compound 1. See Scheme S1 for proton assignment. *Solvent residual peaks.

Figure S3. a) Experimental and b) theoretical isotopic distributions for [M+2H]$^{2+}$. The exact mass for the monoisotopic peak in a) and b) is indicated.

2.2 3-((4'-Iodophenoxy)methyl)pyridine

![Chemical structure of 3-((4'-Iodophenoxy)methyl)pyridine]

Scheme S2. Synthesis of 3-((4'-iodophenoxy)methyl)pyridine.

4-Iodophenol (400 mg, 1.82 mmol, 1 equiv.) and Cs$_2$CO$_3$ (889 mg, 2.73 mmol, 1.5 equiv.) were suspended in dry DMF (40 mL). The mixture was stirred under Argon atmosphere at 50°C for 30 min. 3-(Bromomethyl)pyridinium hydrobromide (690 mg, 2.73 mmol, 1.5 equiv.) in DMF (20 mL) was added dropwise. The reaction was stirred at 60°C under Argon atmosphere for 5 h. The color changed from yellow to orange-brown. After that, the solvent was removed under vacuum and the solid was redissolved in CH$_2$Cl$_2$ (10 mL) and washed with brine (2x10 mL) and water (10 mL). The organic layer was dried (Na$_2$SO$_4$), filtered and concentrated. The crude was purified by column chromatography on silica gel (20 g, 9:1 CH$_2$Cl$_2$:EtOAc) affording the product as white solid (326 mg, 1.58 mmol, 58% yield). Rf = 0.16 (9:1 CH$_2$Cl$_2$:EtOAc). $^1$H NMR (300 MHz, CDCl$_3$, 298 K): $\delta$(ppm): 8.67 (d, $J$ = 1.9 Hz, 1H); 8.59 (dd, $J$ = 4.8 Hz, $J$ = 1.8 Hz, 1H); 7.76 (ddd, $J$ = 7.8 Hz, $J$ = 1.9 Hz, 1H); 7.59-7.56 (m, 2H); 8.59 (dd, $J$ = 4.8 Hz, $J$ = 1.8 Hz, 1H); 7.76 (ddd, $J$ = 7.8 Hz, $J$ = 1.9 Hz, 1H); 7.59-7.56 (m, 2H);
7.33 (dd, J = 7.8 Hz, J = 4.8 Hz, 1H); 6.77-6.74 (m, 2H); 5.05 (s, 2H). $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K): $\delta$ (ppm): 158.4; 149.8; 149.1; 138.5; 135.3; 132.2; 123.7; 117.4; 83.7; 67.8. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for C$_{12}$H$_{11}$INO 311.9880; Found 311.9872. FTIR $\tilde{\nu}_{\text{max}}$ (cm$^{-1}$) = 1568; 1484; 1427; 1378; 1278; 1226; 1176; 1018; 793; 708. M.p. = 74-76ºC.

Figure S4. $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum of 3-((4'-iodophenoxy)methyl)pyridine. See Scheme S2 for proton assignment. *Solvent residual peaks.

Figure S5. $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) spectrum of 3-((4'-iodophenoxy)methyl)pyridine. See Scheme S2 for proton assignment. *Solvent residual peaks.

Figure S6. a) Experimental and b) theoretical isotopic distributions of [M+H]$^+$. The exact mass for the monoisotopic peak in a) and b) is indicated.
2.3 3-((4'-Ethynylphenoxy)methyl)pyridine S1

Scheme S3. Synthesis of 3-((4'-ethynylphenoxy)methyl)pyridine S1.

Step 1: 3-((4'-Iodophenoxy)methyl)pyridine (300 mg, 0.96 mmol, 1 equiv.), Pd(PPh₃)Cl₂ (43.2 mg, 0.07 mmol, 0.07 equiv.) and CuI (49.6 mg, 0.26 mmol, 0.27 equiv.) were kept under Argon atmosphere for 5 minutes. Dry THF (7 mL) and dry DIPEA (0.50 mL, 2.89 mmol, 3 equiv.) were added. Finally, ethynyltrimethylsilane (0.40 mL, 2.89 mmol, 3 equiv.) was added. The color of the mixture changed from orange to brown. The reaction was stirred at 45°C for 3 h. After that, the solvent was removed under vacuum and the crude was redissolved in CH₂Cl₂ (20 mL) and washed with brine (2x20 mL). The organic layer was dried (Na₂SO₄), filtered and concentrated. The crude was purified by column chromatography on silica gel (12 g, 85:15 CH₂Cl₂:EtOAc, product Rf = 0.4) affording the protected compound as brown oil (191 mg, 0.68 mmol, 70% yield).

Step 2: The protected compound (119 mg, 0.42 mmol, 1 equiv.) was dissolved in dry THF (10 mL) and TBAF (0.47 mL from 1 M solution in THF, 0.47 mmol, 1.1 equiv.) was added dropwise. The reaction was stirred under Argon atmosphere. After 15 min, the reaction was quenched by adding saturated NH₄Cl (10 mL). The organic solvent was removed under vacuum and the crude was extracted with CH₂Cl₂ (2x10 mL). The organic layer was washed with brine (2x20 mL), dried (Na₂SO₄), filtered and concentrated. The crude was purified by column chromatography on silica gel (8 g, 8:2 CH₂Cl₂:EtOAc) affording the product as yellow solid (50 mg, 0.24 mmol, 58% yield). RF = 0.4 (8:2 CH₂Cl₂:EtOAc). ¹H NMR (400 MHz, CDCl₃, 298 K): δ (ppm): 8.69 (s, 1H); 8.61 (d, J = 4.8 Hz, 1H); 7.76 (d, J = 7.8 Hz, 1H); 7.45-7.43 (m, 2H); 7.33 (dd, J = 7.8 Hz, J = 4.8 Hz, 1H); 6.92-6.90 (m, 2H); 5.08 (s, 2H); 3.01 (s, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃, 298 K): δ (ppm): 160.8; 149.8; 149.2; 135.4; 133.9; 132.2; 123.7; 115.1; 114.9; 83.5; 76.2; 67.7. HRMS (ESI-TOF) m/z: [M+H]+ Calcd for C₁₄H₁₂NO 210.0913; Found 210.0912. FTIR $\tilde{\nu}_{\text{max}}$ (cm⁻¹): 3173; 1605; 1577; 1505; 1429; 1379; 1286; 1243; 1170; 1048. M.p. = 76-78°C.

Figure S7. ¹H NMR (400 MHz, CDCl₃, 298 K) spectrum of 3-((4'-ethynylphenoxy)methyl)pyridine S1. See Scheme S3 for proton assignment. *Solvent residual peaks.
**Figure S8.** $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) spectrum of 3-((4'-ethynylphenoxy)methyl)pyridine S1. See Scheme S3 for proton assignment. *Solvent residual peaks.*

**Figure S9.** a) Experimental and b) theoretical isotopic distributions of [M+H]$^+$. The exact mass for the monoisotopic peak in a) and b) is indicated.

2.4 Tetra-α isomer of tetra-pyridyl aryl-extended calix[4]pyrrole 2

![Scheme S4. Synthesis of compound 2.](image)

aaaaa-Tetra-(4-hydroxyphenyl)-calix[4]pyrrole S3$_{3,4}^{3,4}$ (100 mg, 0.14 mmol, 1 equiv.) and Cs$_2$CO$_3$ (1.32 g, 4.05 mmol, 7.5 equiv.) were suspended in dry DMF (2 mL) in a two-neck flask. The mixture was stirred at 50°C under Argon atmosphere for 30 min. 3-(Bromomethyl)pyridinium hydrobromide S4 (273 mg, 1.08 mmol, 2 equiv.) in DMF (1 mL) was added dropwise and the reaction was stirred at 60°C under Argon atmosphere for 4 h. After that, the solvent was removed under vacuum and the crude was redissolved in CH$_2$Cl$_2$ (20 mL). The crude was washed with brine (2x20 mL) and water (20 mL). The organic layer was dried (Na$_2$SO$_4$), filtered and
concentrated. The crude was purified by column chromatography on silica gel (4 g, 9:1 → 8:2 CH₂Cl₂:IPA) and the product was further purified by recrystallization from 1:1 CH₂Cl₂:CH₃CN affording a pale yellow solid (38 mg, 0.04 mmol, 26% yield). Rf = 0.2 (9:1 CH₂Cl₂:IPA). ¹H NMR (500 MHz, CD₂Cl₂, 298 K): δ (ppm): 8.64 (s, 4H); 8.53 (d, J = 4.7 Hz, 4H); 7.77 (d, J = 8.0 Hz, 4H); 7.71 (br s, 4H); 7.31 (dd, J = 8.0 Hz, J = 4.7 Hz, 4H); 7.06-7.04 (m, 8H); 6.86-6.84 (m, 8H); 5.74 (d, J = 2.7 Hz, 8H); 5.05 (s, 8H); 1.95 (s, 12H). ¹³C(¹H) NMR (125 MHz, CD₂Cl₂, 298 K): δ (ppm): 157.5; 149.8; 149.4; 141.4; 137.1; 135.6; 133.1; 128.9; 123.8; 114.2; 106.6; 68.1; 44.5; 28.0. HRMS (ESI-TOF) m/z: [M+H]+ Calcd for C₇₂H₆₅N₈O₄ 1105.5123; Found 1105.5129. FTIR ν max (cm⁻¹): 2976; 1579; 1505; 1427; 1247; 1178; 1012; 832; 768; 708. M.p. > 138ºC (decompose).

Figure S10. ¹H NMR (500 MHz, CD₂Cl₂, 298 K) spectrum of compound 2. See Scheme S4 for proton assignment. *Solvent residual peaks.

Figure S11. ¹³C(¹H) NMR (125 MHz, CD₂Cl₂, 298 K) spectrum of compound 2. See Scheme S4 for proton assignment. *Solvent residual peaks.

Figure S12. a) Experimental and b) theoretical isotopic distributions of [M+H]+. The exact mass for the monoisotopic peak in a) and b) is indicated.
2.5 Cage [1•Pd](BF₄)₂

Procedure A: Tetra-pyridyl 1 (3 mg, 0.003 mmol, 1 equiv.) was dissolved in 2:1 CDCl₃:CD₃CN (1 mL) and added to a NMR tube (0.5 mL). [Pd(CH₃CN)₄](BF₄)₂ (0.13 mL from a 6 mM solution in 2:1 CDCl₃:CD₃CN, 0.002 mmol, ca. 1 equiv.) was added to the calix[4]pyrrole's solution. The NMR tube was hand shake for a few seconds and thermally equilibrated at 40ºC for 24 h. A solution containing [1•Pd]²⁺ was obtained (0.0024 mmol, NMR yield > 70%). ¹H NMR (500 MHz with cryoprobe, 2:1 CDCl₃:CD₃CN, 298 K): δ (ppm): 9.45 (s, 4H); 9.16 (br d, 4H); 7.87 (d, J = 7.8 Hz, 4H); 7.56 (m, 8H); 7.41-7.39 (m, 8H); 7.30-7.28 (m, 8H); 6.99-6.97 (m, 8H); 6.88-6.86 (m, 8H); 6.08 (d, J = 2.4 Hz, 8H); 5.11 (s, 8H); 1.92 (s, 12H). ¹³C{¹H} NMR (125 MHz with cryoprobe, 2:1 CDCl₃:CD₃CN, 298 K): δ (ppm): 158.3; 151.1; 150.1; 149.8; 139.3; 137.9; 137.2; 133.4; 130.8; 128.7; 127.5; 121.0; 116.5; 115.1; 105.3; 88.4; 88.0; 66.6; 44.8; 28.9. HRMS (ESI-TOF) m/z: [M-2(BF₄)]²⁺ Calcd for C₁₀₄H₈₀N₈O₄Pd 803.2674; Found 803.2695.

Figure S13. ¹H NMR (500 MHz with cryoprobe, 2:1 CDCl₃:CD₃CN, 298 K) spectrum of [1•Pd]²⁺ from procedure A. Primed letters correspond to proton signals of [1•Pd]²⁺. See Scheme S1 for proton assignment. 1,3,5-trimethoxybenzene was used as internal standard (I.S.). *Solvent residual peaks.

Figure S14. ¹³C{¹H} NMR (500 MHz with cryoprobe, 2:1 CDCl₃:CD₃CN, 298 K) spectrum of [1•Pd]²⁺ from procedure A. Primed letters correspond to proton signals of [1•Pd]²⁺. See Scheme S1 for proton assignment. 1,3,5-trimethoxybenzene was used as internal standard (I.S.). *Solvent residual peaks.

Figure S15. a) Experimental and b) theoretical isotopic distributions of [M-2(BF₄)]²⁺. The exact mass for the monoisotopic peak in a) and b) is indicated.
Procedure B: Tetra-pyridyl 1 (20.66 mg, 0.014 mmol, 1 equiv.) was dissolved in dry 2:1 CHCl₃:CH₃CN (6.9 mL) in a Schlenk flask. [Pd(CH₃CN)₄](BF₄)₂ (4.2 mL from a 6 mM solution in 2:1 CHCl₃:CH₃CN, 0.025 mmol, ca. 1 equiv.) was added to the calix[4]pyrrole’s solution. The reaction was stirred under Argon atmosphere at 40ºC for 24 h. After that, the crude was filtered using extra 2:1 CHCl₃:CH₃CN (6 mL). The chloroform was removed under reduced pressure. Et₂O (6 mL) was added to the crude solution obtaining a white precipitate. The crude was filtered and the precipitate was washed with extra Et₂O (2 mL). The white solid was dried under high vacuum affording the [1•Pd]²⁺ cage (15 mg, 0.0084 mmol, 60%). The ¹H and ¹³C(¹H) NMR spectra in 2:1 CDCl₃:CD₃CN at 298 K of the isolated cage coincided with those obtained following the procedure A.

![Figure S16. ¹H NMR (500 MHz with cryoprobe, 2:1 CDCl₃:CD₃CN, 298 K) spectrum of [1•Pd]²⁺ from procedure B. Primed letters correspond to proton signals of [1•Pd]²⁺. See Scheme S1 for proton assignment. *Solvent residual peaks.]

![Figure S17. ¹³C(¹H) NMR (500 MHz with cryoprobe, 2:1 CDCl₃:CD₃CN, 298 K) spectrum of [1•Pd]²⁺ from procedure B. Primed letters correspond to proton signals of [1•Pd]²⁺. See Scheme S1 for proton assignment. *Solvent residual peaks.]

The preparation of the [1•Pd]²⁺ cage following the procedure B confirmed that the cage can be isolated as white solid. The yield of the cage with this procedure is in line with that determined by NMR spectroscopic techniques following the procedure A.
3. NMR experiments of tetra-pyridyl super aryl-extended calix[4]pyrrole 1

3.1 Tetra-pyridyl 1 in CDCl₃ and 2:1 CDCl₃:CD₃CN

Figure S18. ¹H NMR (400 MHz, 298 K) spectra of tetra-pyridyl 1 in a) CDCl₃ and b) 2:1 CDCl₃:CD₃CN. See Scheme S1 for proton assignment. *Residual solvent peak, δ(CHCl₃) = 7.26 ppm.

Figure S19. Superposition of the ¹H NMR (400 MHz, 298 K) spectra shown on Figure S18. The spectrum a) was referenced using the residual CHCl₃ signal at δ = 7.26 ppm. The spectrum b) was moved in the chemical shift scale. See Scheme S1 for proton assignment. *Residual solvent peaks.

The ¹H NMR spectrum of tetra-pyridyl 1 in CDCl₃ showed broad proton signals for the pyrrole NHs (Hₐ) and the β-pyrrole protons (H₇). Most likely, 1 was involved in an equilibrium between alternate conformers that is fast on the chemical shift timescale. The superposition of the ¹H NMR spectrum of tetra-pyridyl 1 in 2:1 CDCl₃:CD₃CN, assuming similar chemical shifts for the phenyl and pyridyl proton signals to those observed in CDCl₃ solution, showed that the pyrrole NHs (Hₐ) and the β-pyrrole protons (H₇) sharpened and experienced downfield shifts. These observations supported that the tetra-pyridyl 1 adopted the cone conformation in the 2:1 CDCl₃:CD₃CN solvent mixture.
3.2 Addition of Pd(II) to calix[4]pyrrole 1 in (CD$_3$)$_2$SO

A solution of the tetra-pyridyl 1 (1-2 mM) and 1,3,5-trimethoxybenzene (internal standard, 1-2 mM) was prepared in (CD$_3$)$_2$SO. Subsequently, 0.5 mL of the solution were transferred to a NMR tube. A solution of Pd(II) ([Pd(CH$_3$CN)$_4$](BF$_4$)$_2$, Pd(TFA)$_2$ or Pd(NO$_3$)$_2$ from Sigma-Aldrich or Strem Chemicals) was prepared in (CD$_3$)$_2$SO at 10-15 fold higher concentration (20-30 mM). Immediately, the 0.5 mL of the tetra-pyridyl’s solution was titrated by manually injecting incremental amounts of the Pd(II) solution using a micro syringe. A $^1$H NMR spectrum of the mixture was acquired after each injection and vigorous hand shaking of the NMR tube for few seconds.

Figure S20. $^1$H NMR (400 MHz, (CD$_3$)$_2$SO, 298 K) spectra of a) tetra-pyridyl 1 and b) [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ + 1 (ca. 1:1 molar ratio). Primed letters correspond to proton signals of [1-Pd]$^{2+}$. 1,3,5-trimethoxybenzene was used as internal standard (I.S.). The [1-Pd]$^{2+}$ cage was formed in an extend larger than 70%. See Scheme S1 for proton assignment. *Solvent residual peaks.

Figure S21. $^1$H NMR (400 MHz, (CD$_3$)$_2$SO, 298 K) spectra of a) tetra-pyridyl 1 and b) Pd(TFA)$_2$ + 1 (ca. 1:1 molar ratio). Primed letters correspond to proton signals of [1-Pd]$^{2+}$. 1,3,5-trimethoxybenzene was used as internal standard (I.S.). The [1-Pd]$^{2+}$ cage was formed in an extend of larger than 70%. See Scheme S1 for proton assignment. *Solvent residual peaks.

Figure S22. $^{19}$F($^1$H) NMR (376 MHz, (CD$_3$)$_2$SO, 298 K) spectra of a) [1-Pd]$^{2+}$ and b) Pd(TFA)$_2$. 

S12
The $^1$H NMR spectra of the tetra-pyridyl $\mathbf{1}$ with different Pd(II) salts in (CD$_3$)$_2$SO were very similar and the number of proton signals was in agreement with $C_{4v}$ symmetry. Most likely, the tetra-pyridyl $\mathbf{1}$ and Pd(II) formed the $[1\cdot\text{Pd}]^{2+}$ cage in (CD$_3$)$_2$SO, independently of the salt used, in an extent larger than 70%. The thermal equilibration at 40°C of the $[1\cdot\text{Pd}]^{2+}$ solutions in (CD$_3$)$_2$SO did not produce further changes on the $^1$H NMR spectra. The proton signals of low intensity were indicative of the formation of ill-defined aggregates that are in equilibrium with the cage assembly.

### Table S1. Chemical shifts ($\delta$) and chemical shift changes ($\Delta\delta$) on the proton signals of the 3-pyridyl substituents at the upper rim of $\mathbf{1}$ in (CD$_3$)$_2$SO. Primed letters correspond to proton signals of $[1\cdot\text{Pd}]^{2+}$.

<table>
<thead>
<tr>
<th>Signal</th>
<th>$\delta$ (ppm), $\mathbf{1}$</th>
<th>$\delta$ (ppm), $[1\cdot\text{Pd}]^{2+}$</th>
<th>$\Delta\delta$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h$</td>
<td>8.64</td>
<td>9.32</td>
<td>+0.68</td>
</tr>
<tr>
<td>$i$</td>
<td>8.53</td>
<td>9.23</td>
<td>+0.70</td>
</tr>
<tr>
<td>$j$</td>
<td>7.39</td>
<td>7.77</td>
<td>+0.38</td>
</tr>
<tr>
<td>$k$</td>
<td>7.83</td>
<td>8.15</td>
<td>+0.32</td>
</tr>
</tbody>
</table>

The chemical shift changes on the proton signals of the pyridyl substituents of $\mathbf{1}$ upon addition of Pd(II) were in agreement with the formation of pyridyl-Pd(II) coordination bonds.$^5,6,7,8$

### 3.3 Addition of Pd(II) to calix[4]pyrrole 1 in 2:1 CDCl$_3$:CD$_3$CN

A solution of the tetra-pyridyl $\mathbf{1}$ (1-2 mM) and 1,3,5-trimethoxybenzene (internal standard, 1-2 mM) was prepared in 2:1 CDCl$_3$:CD$_3$CN. Subsequently, 0.5 mL of the solution were transferred to a NMR tube. A solution of Pd(II) ([Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ from Sigma-Aldrich) was prepared in 2:1 CDCl$_3$:CD$_3$CN at higher concentration (5-7 mM). Immediately, the 0.5 mL of the tetra-pyridyl's solution was titrated by manually injecting incremental amounts of the Pd(II) solution using a micro syringe. A $^1$H NMR spectrum of the mixture was acquired after each injection and vigorous hand shaking of the NMR tube for few seconds.

### Table S2. Chemical shifts ($\delta$) and chemical shift changes ($\Delta\delta$) on the proton signals of the 3-pyridyl substituents at the upper rim of $\mathbf{1}$ in 2:1 CDCl$_3$:CD$_3$CN. Primed letters correspond to proton signals of $[1\cdot\text{Pd}]^{2+}$.

<table>
<thead>
<tr>
<th>Signal</th>
<th>$\delta$ (ppm), $\mathbf{1}$</th>
<th>$\delta$ (ppm), $[1\cdot\text{Pd}]^{2+}$</th>
<th>$\Delta\delta$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h$</td>
<td>8.51</td>
<td>9.45</td>
<td>+0.94</td>
</tr>
<tr>
<td>$i$</td>
<td>8.46</td>
<td>9.16</td>
<td>+0.70</td>
</tr>
<tr>
<td>$j$</td>
<td>7.15</td>
<td>7.56</td>
<td>+0.41</td>
</tr>
<tr>
<td>$k$</td>
<td>7.58</td>
<td>7.87</td>
<td>+0.29</td>
</tr>
</tbody>
</table>
The chemical shift changes on the proton signals of the pyridyl substituents of 1 upon addition of Pd(II) were in agreement with the formation of pyridyl-Pd(II) coordination bonds.5,6,7,8

3.4 Thermal equilibration experiment of the [1•Pd]2+ cage

A solution of the tetra-pyridyl 1 (1-2 mM) and 1,3,5-trimethoxybenzene (internal standard, 1-2 mM) was prepared in 2:1 CDCl3:CD3CN. Subsequently, 0.5 mL of the solution were transferred to a NMR tube. A solution of Pd(II) ([Pd(CH3CN)4](BF4)2 from Sigma-Aldrich) was prepared in 2:1 CDCl3:CD3CN at higher concentration (5-7 mM). Immediately, [Pd(CH3CN)4](BF4)2 (ca. 1 molar equiv.) was added to the calix[4]pyrrole’s solution. A 1H NMR spectrum of the mixture was acquired after the injection and vigorous hand shaking of the NMR tube for few seconds. The mixture was thermally equilibrated at 40 ºC in an oil bath for 24, 48 and 120 h and the 1H NMR spectra were acquired.

![NMR spectra](image)

Figure S25. 1H NMR (400 MHz, 2:1 CDCl3:CD3CN, 298 K) spectra of: a) tetra-pyridyl 1; b) [Pd(CH3CN)4](BF4)2 + 1 (ca. 1:1 molar ratio); after equilibration of b) at 40ºC for c) 24 h; d) 48 h and e) 120 h. Primed letters correspond to proton signals of [1•Pd]2+. 1,3,5-trimethoxybenzene was used as internal standard (I.S.). See Scheme S1 for proton assignment. *Solvent residual peaks.

The addition of [Pd(CH3CN)4](BF4)2 to a millimolar solution of tetra-pyridyl 1 produced the formation of the [1•Pd]2+ cage (60%). The same solution was thermally equilibrated at 40ºC for 24 h. The 1H NMR spectrum showed the formation of more than 70% of the [1•Pd]2+ cage. The solution was thermally equilibrated at 40ºC for 48-120 h. However, the 1H NMR spectra did not show further changes on the proton signals of the cage.
3.5 $^1$H DOSY NMR experiments of 1 and [1•Pd]$^{2+}$ cage

$^1$H DOSY NMR experiments in (CD$_3$)$_2$SO

**Figure S26.** (left) $^1$H pseudo 2D-plot of DOSY (500 MHz with cryoprobe, (CD$_3$)$_2$SO, 298 K, D$_{20}$ = 0.15 s; P$_{30}$ = 1.40 ms) of tetra-pyridyl 1 (2 mM); (right) fit of the decay of the signal of proton b to a mono-exponential function using Dynamics Center from Bruker. Errors are indicated as standard deviations. See Scheme S1 for proton assignment. *Solvent residual peaks.

**Figure S27.** (left) $^1$H pseudo 2D-plot DOSY (500 MHz with cryoprobe, (CD$_3$)$_2$SO, 298 K, D$_{20}$ = 0.15 s; P$_{30}$ = 1.40 ms) of [1•Pd](TFA)$_2$ (2 mM); (right) fit of the decay of the signal of proton b’ to a mono-exponential function using Dynamics Center from Bruker. Errors are indicated as standard deviations. Primed letters correspond to proton signals of [1•Pd]$^{2+}$. See Scheme S1 for proton assignment. *Solvent residual peaks.

**Table S3.** Diffusion coefficients ($D$) obtained from the $^1$H DOSY experiments. The dimensions of the putative cylinders, length (a) x radius (b), which showed similar $D$ values to those measured by DOSY NMR spectroscopy are indicated. Errors in $D$ are indicated as standard deviations.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$D$ (m$^2$/s)</th>
<th>-log $D$</th>
<th>a x b (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.18±0.02 x 10$^{-10}$</td>
<td>9.93</td>
<td>21 x 5</td>
</tr>
<tr>
<td>[1•Pd]$^{2+}$</td>
<td>1.16±0.03 x 10$^{-10}$</td>
<td>9.94</td>
<td>21 x 5.1</td>
</tr>
</tbody>
</table>

The tetra-pyridyl 1 and the [1•Pd]$^{2+}$ cage are better represented by a cylindrical shaped object than a sphere. We determined the dimensions of the cylinders using the equations 1-3. First, we estimated the a and b values from the energy minimized structure (MM3) of [1•Pd]$^{2+}$ (*vide infra*). These values were further refined manually in order to minimize the difference between the calculated coefficient values and those measured experimentally ($D_{measured} - D_{calculated} < 1 x 10^{-12}$ m$^2$/s). The cylindrical object corresponding to the optimized values is superimposed with the compounds to verify that the geometrical parameters have a physical significance (see Figure S28).

1) $R = \frac{3}{2} \left( \frac{a}{b} \right)^2$, a = length and b = radius

2) $f = \frac{2^{2/3} a^{2/3}}{ln(2P) = 0.3}$, P = a/b

3) $D = \frac{\kappa a^2}{\eta f}$

The experimentally measured diffusion coefficients for 1 and [1•Pd]$^{2+}$ were very similar indicating the monomolecular nature of the cage.
Figure S28. Energy minimized structure (MM3) of the putative [(CH$_3$)$_2$SO]$_2$⊂[1-Pd]$^{2+}$ cage complex and cylinder indicating its dimensions. The calix[4]pyrrole is depicted in stick representation and the (CH$_3$)$_2$SO molecules are shown as CPK models.

$^1$H DOSY NMR experiments in 2:1 CDCl$_3$:CD$_3$CN

Figure S29. (left) Pseudo 2D plot of $^1$H DOSY (500 MHz with cryoprobe, 2:1 CDCl$_3$:CD$_3$CN, 298 K, D$_2$O = 0.15 s; P$_{30} = 0.80$ ms) of tetra-pyridyl 1 (2 mM); (right) Decay of proton b fitted to a mono-exponential function using Dynamics Center from Bruker. Errors are indicated as standard deviations. See Scheme S1 for proton assignment. *Solvent residual peaks.

Figure S30. (left) Pseudo 2D plot of $^1$H DOSY (500 MHz with cryoprobe, 2:1 CDCl$_3$:CD$_3$CN, 298 K, D$_2$O = 0.15 s; P$_{30} = 0.80$ ms) of [1-Pd]$^{2+}$ (2 mM); (right) Decay of proton b’ fitted to a mono-exponential function using Dynamics Center from Bruker. Errors are indicated as standard deviations. Primed letters correspond to proton signals of [1-Pd]$^{2+}$. See Scheme S1 for proton assignment. *Solvent residual peaks.
Figure S31. (left) Pseudo 2D plot of $^1$H DOSY (500 MHz with cryoprobe, 2:1 CDCl$_3$:CD$_3$CN, 298 K, D$_{20}$ = 0.15 s; P30 = 0.80 ms) of 4c-[1+Pd]$^{2+}$ (2 mM); (right) Decay of proton $b'''$ fitted to a mono-exponential function using Dynamics Center from Bruker. Errors are indicated as standard deviations. Triple primed letters and numbers correspond to proton signals of 4c-[1+Pd]$^{2+}$. See Scheme S1 for proton assignment. *Solvent residual peaks.

Table S4. Diffusion coefficients ($D$) obtained from the $^1$H pseudo 2D DOSY experiments. Errors in $D$ are indicated as standard deviations.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$D$ (m$^2$/s)</th>
<th>$-\log D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.6±0.1 x 10$^{-10}$</td>
<td>9.25</td>
</tr>
<tr>
<td>[1+Pd]$^{2+}$</td>
<td>5.2±0.1 x 10$^{-10}$</td>
<td>9.28</td>
</tr>
<tr>
<td>4c-[1+Pd]$^{2+}$</td>
<td>5.6±0.2 x 10$^{-10}$</td>
<td>9.25</td>
</tr>
</tbody>
</table>

The measured diffusion coefficients of 1 and [1+Pd]$^{2+}$ in 2:1 CDCl$_3$:CD$_3$CN are similar indicating comparable sizes for both species in solution. The cylinders corresponding to the calculated diffusion coefficients were not determined owing to the lack of an accurate value for the viscosity of the 2:1 CDCl$_3$:CD$_3$CN solution.

The diffusion coefficient values determined in (CD$_3$)$_2$SO and 2:1 CDCl$_3$:CD$_3$CN solutions are different. We attribute this finding to the different viscosity of the solvents.
3.6 $^1$H-$^1$H 2D EXSY NMR experiment of the $[1\cdot Pd]^{2+}$ cage

![EXSY NMR spectrum](image)

**Figure S32.** Selected region of the $^1$H-$^1$H 2D EXSY NMR (400 MHz, 2:1 CDCl$_3$:CD$_3$CN, 298 K, $t_{mix} = 0.3$ s) spectrum of 1 + $[1\cdot Pd]^{2+}$ (1:1 molar ratio). Primed letters correspond to proton signals of $[1\cdot Pd]^{2+}$. 1,3,5-trimethoxybenzene was used as internal standard (I.S.). See Scheme S1 for proton assignment. *Solvent residual peak.

The $^1$H-$^1$H 2D EXSY NMR experiment did not show exchange cross-peaks between 1 and $[1\cdot Pd]^{2+}$. This result indicated that the ligand exchange is slow on the EXSY timescale.

3.7 1D GOESY NMR experiments of the $[1\cdot Pd]^{2+}$ cage

![GOESY NMR spectra](image)

**Figure S33.** $^1$H NMR (500 MHz, 2:1 CDCl$_3$:CH$_3$CN, 298 K) spectrum of a) $[1\cdot Pd]^{2+}$; 1D GOESY NMR (500 MHz, 2:1 CDCl$_3$:CH$_3$CN, 298 K) spectra of a) with mixing times ($t_{mix}$) of b) 0.3 s and c) 0.6 s. 1,3,5-trimethoxybenzene was used as internal standard (I.S.). *Solvent residual peaks.

The 1D GOESY NMR spectra of $[1\cdot Pd]^{2+}$ in 2:1 CDCl$_3$:CH$_3$CN at 298 K did not show the proton signals of included CH$_3$CN molecules in the cage. Most likely, the chemical exchange between free and bound CH$_3$CN molecules is fast on the GOESY timescale.
4. NMR experiments of tetra-pyridyl aryl-extended calix[4]pyrrole 2

4.1 Addition of Pd(II) to calix[4]pyrrole 2 in (CD$_3$)$_2$SO

A suspension of the tetra-pyridyl 2 (1-2 mM) and 1,3,5-trimethoxybenzene (internal standard, 1-2 mM) was prepared in (CD$_3$)$_2$SO. Subsequently, 0.5 mL of the suspension were transferred to a NMR tube. A solution of Pd(II) ([Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ from Sigma-Aldrich) was prepared in (CD$_3$)$_2$SO at 10-15 fold higher concentration (20-30 mM). Immediately, the 0.5 mL of the tetra-pyridyl’s suspension was titrated by manually injecting incremental amounts of the Pd(II) solution using a micro syringe. A $^1$H NMR spectrum of the mixture was acquired after each injection and vigorous hand shaking of the NMR tube for few seconds.

![Figure S34. $^1$H NMR (400 MHz, (CD$_3$)$_2$SO, 298 K) spectra of a) tetra-pyridyl 2; b) [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ + 2 (0.5:1 molar ratio); c) [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ + 2 (1:1 molar ratio); d) [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ + 2 (1.5:1 molar ratio) and e) [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ + 2 (2:1 molar ratio). 1,3,5-trimethoxybenzene was used as internal standard (I.S.). See Scheme S4 for proton assignment. *Solvent residual peaks.](image)

The $^1$H NMR spectrum of a millimolar suspension of tetra-pyridyl 2 in (CD$_3$)$_2$SO showed sharp and well-defined proton signals, and its number was in agreement with $C_{4v}$ symmetry. The tetra-pyridyl 2 was not completely soluble in (CD$_3$)$_2$SO. The addition of incremental amounts of [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ to the suspension of 2 produced broad proton signals and the complete dissolution of the calix[4]pyrrole 2. This result indicated that Pd(II) and 2 did not form the [2•Pd]$^{2+}$ cage. Probably, they formed ill-defined aggregates. The thermal equilibration of the mixture containing Pd(II) and 2 (2:1 molar ratio) at 40°C for 24 h did not produce changes on the $^1$H NMR spectra.
4.2 Addition of Pd(II) to calix[4]pyrrole 2 in 2:1 CDCl₃:CD₃CN

A solution of the tetra-pyridyl 2 (1-2 mM) and 1,3,5-trimethoxybenzene (internal standard, 1-2 mM) was prepared in 2:1 CDCl₃:CD₃CN. Subsequently, 0.5 mL of the solution were transferred to a NMR tube. A solution of Pd(II) ([Pd(CH₃CN)₄](BF₄)₂ from Sigma-Aldrich) was prepared in 2:1 CDCl₃:CD₃CN at higher concentration (5-7 mM). Immediately, the 0.5 mL of the tetra-pyridyl’s solution was titrated by manually injecting incremental amounts of the Pd(II) solution using a micro syringe. A ¹H NMR spectrum of the mixture was acquired after each injection and vigorous hand shaking of the NMR tube for few seconds.

![Figure S35. ¹H NMR (400 MHz, 2:1 CDCl₃:CD₃CN, 298 K) spectra of a) tetra-pyridyl 2; b) [Pd(CH₃CN)₄](BF₄)₂ + 2 (0.5:1 molar ratio); c) [Pd(CH₃CN)₄](BF₄)₂ + 2 (1:1 molar ratio); d) [Pd(CH₃CN)₄](BF₄)₂ + 2 (1.5:1 molar ratio) and e) [Pd(CH₃CN)₄](BF₄)₂ + 2 (2:1 molar ratio). 1,3,5-trimethoxybenzene was used as internal standard (I.S.). See Scheme S4 for proton assignment. *Solvent residual peaks.

The ¹H NMR spectrum of a millimolar solution of tetra-pyridyl 2 in 2:1 CDCl₃:CD₃CN showed sharp and well-defined proton signals in agreement with C₄ᵥ symmetry. The addition of incremental amounts of [Pd(CH₃CN)₄](BF₄)₂ to the solution of 2 produced the decrease of the intensity of its proton signals and they were not observed after the addition of more than 1.5 molar equiv. of Pd(II). This result indicated that Pd(II) and 2 did not form the [2•Pd]²⁺ cage in 2:1 CDCl₃:CD₃CN. Probably, they formed ill-defined aggregates. The thermal equilibration of the mixture containing Pd(II) and 2 (2:1 molar ratio) at 40ºC for 24 h did not produce changes on the ¹H NMR spectra.
5. NMR experiments of tetra-pyridyl 1 and [1•Pd]$^{2+}$ with pyridyl N-oxides in 2:1 CDCl$_3$:CD$_3$CN

5.1 Addition of pyridyl N-oxides and Pd(II) to calix[4]pyrrole 1

A solution of the tetra-pyridyl 1 (1-2 mM) and 1,3,5-trimethoxybenzene (internal standard, 1-2 mM) was prepared in 2:1 CDCl$_3$:CD$_3$CN. Subsequently, 0.5 mL of the solution were transferred to a NMR tube. A solution of pyridyl N-oxide 3-5 was prepared in 2:1 CDCl$_3$:CD$_3$CN using the tetra-pyridyl’s solution at higher concentration ([G] = 10-30 mM and [1] = 1-2 mM). A solution of Pd(II) ([Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ from Sigma-Aldrich) was prepared in 2:1 CDCl$_3$:CD$_3$CN at higher concentration (5-7 mM). Immediately, the 0.5 mL of the tetra-pyridyl’s solution was titrated by manually injecting incremental amounts of the pyridyl N-oxide’s solution using a micro syringe. A $^1$H NMR spectrum of the mixture was acquired after each injection and vigorous hand shaking of the NMR tube for few seconds. After the formation of the corresponding 1:1 complex between the pyridyl N-oxide and 1, incremental amounts of Pd(II) were added to the complex’s solution using a micro syringe. A $^1$H NMR spectrum of the mixture was acquired after each injection and vigorous hand shaking of the NMR tube for few seconds. Finally, the solution was thermally equilibrated at 40ºC for 24 h and a $^1$H NMR spectrum was acquired.

![Figure S36. Line-drawing structure of pyridine N-oxide 3.](image)

![Figure S37. $^1$H NMR (300 MHz, 2:1 CDCl$_3$:CD$_3$CN, 298 K) spectrum of compound 3. See Figure S36 for proton assignment. *Solvent residual peaks.](image)

![Figure S38. $^1$H NMR (400 MHz, 2:1 CDCl$_3$:CD$_3$CN, 298 K) spectra of: a) tetra-pyridyl 1; b) 3 + 1 (0.5:1 molar ratio); c) 3 + 1 (1:1 molar ratio) and d) [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ + 3 + 1 (ca. 1:1:1 molar ratio) after thermal equilibration (40ºC for 24 h). Double primed letters and numbers correspond to proton signals of 3⊂1. Triple primed letters and numbers correspond to proton signals of 3⊂[1•Pd]$^{2+}$. 1,3,5-trimethoxybenzene was used as internal standard (I.S.). See Scheme S1 and Figure S36 for proton assignment. *Solvent residual peaks.](image)

The addition of 1 molar equiv. of 3 to a millimolar solution of 1 produced chemical shift changes on the proton signals of 1. Also, the proton signals of 3 appeared upfield shift with respect to those free in solution. The tetra-pyridyl 1 and 3 formed a 1:1 inclusion complex for which we estimated a binding constant larger than 10$^4$ M$^{-1}$. The addition of ca. 1 molar equiv. of [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ to the solution of 3⊂1 provoked chemical shift changes on the proton signals of the precursor complex. The proton signals of 3 remained upfield shift indicating that the
The addition of 1 molar equiv. of 4 to a millimolar solution of 1 produced chemical shift changes on the proton signals of 1. Also, the proton signals of 4 appeared upfield shift with respect to those free in solution. The tetrapyridyl 1 and 4 formed a 1:1 inclusion complex for which we estimated a binding constant larger than 10^4 M⁻¹.

The addition of ca. 1 molar equiv. of [Pd(CH₃CN)₄][BF₄]₂ to the solution of 4·1 provoked chemical shift changes on the proton signals of the complex. The proton signals of 4 remained upfield shift indicating that the guest was included in the aromatic cavity of the cage. The proton signals of the pyridyl substituents of 1 suffered the most noticeable chemical shift changes. This observation indicated that the pyridyl substituents at the upper rim of the SAE-C[4]P were coordinated to a Pd(II) ion. The total amount of [1·Pd]²⁺ formed was larger than 70%. Also, a white precipitate appeared in the NMR tube. The 3·[1·Pd]²⁺ cage complex was quantitatively formed at millimolar concentrations.

Table S5. Chemical shifts (δ) of the proton signals of pyridine N-oxide 3.

<table>
<thead>
<tr>
<th>Signal</th>
<th>δ (ppm), 3</th>
<th>δ (ppm), 3·1</th>
<th>δ (ppm), 3·[1·Pd]²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.15</td>
<td>4.59</td>
<td>4.60</td>
</tr>
<tr>
<td>2</td>
<td>7.30</td>
<td>6.77</td>
<td>6.97</td>
</tr>
<tr>
<td>3</td>
<td>7.30</td>
<td>6.97</td>
<td>6.44</td>
</tr>
</tbody>
</table>

Figure S39. Line-drawing structure of 4,4’-bipyridyl bis-N-oxide 4.

Figure S40. ¹H NMR (400 MHz, 2:1 CDCl₃:CD₃CN, 298 K) spectrum of compound 4. See Figure S39 for proton assignment. *Solvent residual peaks.

Figure S41. ¹H NMR (400 MHz, 2:1 CDCl₃:CD₃CN, 298 K) spectra of: a) tetra-pyridyl 1; b) 4 + 1 (0.5:1 molar ratio); c) 4 + 1 (1:1 molar ratio) and d) [Pd(CH₃CN)₄][BF₄]₂ + 4 + 1 (ca. 1:1:1 molar ratio) after thermal equilibration (40°C for 24 h). Double primed letters and numbers correspond to proton signals of 4·1. Triple primed letters and numbers correspond to proton signals of 4·[1·Pd]²⁺. 1,3,5-trimethoxybenzene was used as internal standard (I.S.). See Scheme S1 and Figure S39 for proton assignment. *Solvent residual peaks.
noticeable chemical shift changes. This observation indicated that the pyridyl substituents at the upper rim of the SAE-C[4]P were coordinated to a Pd(II) ion. The $4c[1+\text{Pd}]^{2+}$ was formed in an extend larger than 70%. Also, the solution was slightly turbid in the NMR tube. We estimated a binding constant value larger than $10^4 \text{ M}^{-1}$ for the $4c[1+\text{Pd}]^{2+}$ complex.

Table S6. Chemical shifts ($\delta$) of the proton signals of 4,4’-bipyridyl bis-N-oxide 4.

<table>
<thead>
<tr>
<th>Signal</th>
<th>$\delta$ (ppm), 4</th>
<th>$\delta$ (ppm), 4-c</th>
<th>$\delta$ (ppm), 4-[1+Pd]$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.19</td>
<td>4.49</td>
<td>4.63</td>
</tr>
<tr>
<td>2</td>
<td>7.57</td>
<td>7.06</td>
<td>7.10</td>
</tr>
<tr>
<td>3</td>
<td>7.57</td>
<td>6.72</td>
<td>6.40</td>
</tr>
<tr>
<td>4</td>
<td>8.19</td>
<td>6.49</td>
<td>6.40</td>
</tr>
</tbody>
</table>

Figure S42. Line-drawing structure of 4-phenylpyridine N-oxide 5.

Figure S43. $^1$H NMR (400 MHz, 2:1 CDCl$_3$:CD$_3$CN, 298 K) spectrum of compound 5. See Figure S42 for proton assignment. *Solvent residual peaks.

Figure S44. $^1$H NMR (400 MHz, 2:1 CDCl$_3$:CD$_3$CN, 298 K) spectra of: a) tetra-pyridyl 1; b) 5 + 1 (0.5:1 molar ratio); c) 5 + 1 (1:1 molar ratio) and d) [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ + 5 + 1 (ca. 1:1:1 molar ratio) after thermal equilibration (40°C for 24 h). Double primed letters and numbers correspond to proton signals of 5 and 1. 1,3,5-trimethoxybenzene was used as internal standard (I.S.). See Scheme S1 and Figure S42 for proton assignment. *Solvent residual peaks.
Figure S45. $^1$H NMR (400 MHz, (CD$_3$)$_2$SO, 298 K) spectrum of the precipitate obtained after thermal equilibration (40°C for 24 h) of a mixture containing [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ + 5 + 1 (ca. 1:1:1 molar ratio). 1,3,5-trimethoxybenzene was used as internal standard (I.S.). *Solvent residual peaks.

Figure S46. $^1$H NMR (400 MHz, 2:1 CDCl$_3$:CD$_3$CN, 298 K) spectra of: a) tetra-pyridyl 1; b) 5 + 1 (0.5:1 molar ratio) and c) [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ + 5 + 1 (ca. 1:0.5:1 molar ratio) after thermal equilibration (40°C for 24 h). Primed letters correspond to proton signals of [1•Pd]$^{2+}$. Double primed letters and numbers correspond to proton signals of 5•1. 1,3,5-trimethoxybenzene was used as internal standard (I.S.). See Scheme S1 and Figure S42 for proton assignment. *Solvent residual peaks.

The addition of 1 molar equiv. of 5 to a millimolar solution of 1 produced chemical shift changes on the proton signals of 1. Also, the proton signals of 5 appeared upfield shift with respect to those free in solution. The tetrapyridyl 1 and 5 formed a 1:1 inclusion complex for which we estimated a binding constant larger than 10$^4$ M$^{-1}$. The addition of ca. 1 molar equiv. of [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ to the solution of 5•1 followed by thermal equilibration provoked the decrease of the intensity of the proton signals of the 5•1 complex and the appearance of proton signals with low intensity. Also, a white precipitate appeared in the NMR tube. These observations suggested the formation of ill-defined aggregates. The mixture was concentrated and redissolved in (CD$_3$)$_2$SO. The acquired $^1$H NMR spectrum of the (CD$_3$)$_2$SO solution showed broad proton signals. We could only assign the signals corresponding to a reduced amount of free 5 in solution.

Interestingly, the addition of ca. 1 molar equiv. of [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ to a solution containing an equimolar mixture of 1 and 5•1 followed by thermal equilibration provoked the disappearance of the proton signals of the 5•1 inclusion complex and the emergence of the proton signals of the [1•Pd]$^{2+}$ cage in a ca. 40% extend.

Table S7. Chemical shifts (δ) of the proton signals of 4-phenylpyridine N-oxide 5.

<table>
<thead>
<tr>
<th>Signal</th>
<th>δ (ppm), 5</th>
<th>δ (ppm), 5•1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.18</td>
<td>4.51</td>
</tr>
<tr>
<td>2</td>
<td>7.55</td>
<td>7.13</td>
</tr>
<tr>
<td>3</td>
<td>7.61</td>
<td>7.20</td>
</tr>
<tr>
<td>4</td>
<td>7.46</td>
<td>6.15</td>
</tr>
<tr>
<td>5</td>
<td>7.40</td>
<td>6.67</td>
</tr>
</tbody>
</table>
5.2 Addition of pyridyl N-oxides to the [1•Pd]^{2+} cage

A solution of the tetra-pyridyl 1 (1-2 mM) and 1,3,5-trimethoxybenzene (internal standard, 1-2 mM) was prepared in 2:1 CDCl₃:CD₃CN. Subsequently, 0.5 mL of the solution were transferred to a NMR tube. A solution of Pd(II) ([Pd(CH₃CN)₄][BF₄]₂ from Sigma-Aldrich) was prepared in 2:1 CDCl₃:CD₃CN at higher concentration (5-7 mM). Immediately, the 0.5 mL of the tetra-pyridyl’s solution was titrated by manually injecting incremental amounts of the Pd(II) solution using a micro syringe. The solution of the [1•Pd]^{2+} cage was thermally equilibrated at 40ºC for 24 h. A solution of pyridyl N-oxide 3-5 was prepared in 2:1 CDCl₃:CD₃CN at higher concentration (10-30 mM). The cage’s solution was titrated by manually injecting incremental amounts of the pyridyl N-oxide’s solution using a micro syringe. A ¹H NMR spectrum of the mixture was acquired after each injection and vigorous hand shaking of the NMR tube for few seconds.

![Figure S47](image)

Figure S47. ¹H NMR (400 MHz, 2:1 CDCl₃:CD₃CN, 298 K) spectra of: a) [1•Pd]^{2+}; b) 3 + [1•Pd]^{2+} (1:1 molar ratio) and c) 3 + [1•Pd]^{2+} (2:1 molar ratio). Primed letters correspond to proton signals of [1•Pd]^{2+}. Triple primed letters and numbers correspond to proton signals of 3⊂[1•Pd]^{2+}. 1,3,5-trimethoxybenzene was used as internal standard (I.S.). See Scheme S1 and Figure S36 for proton assignment.

*Solvent residual peaks.

The addition of N-oxide 3 to a millimolar solution of [1•Pd]^{2+} in 2:1 CDCl₃:CD₃CN produced the immediate formation of the 3⊂[1•Pd]^{2+} cage complex. Thus, the formation of the complex was fast on the human timescale.

![Figure S48](image)

Figure S48. ¹H NMR (400 MHz, 2:1 CDCl₃:CD₃CN, 298 K) spectra of: a) [1•Pd]^{2+}; b) 4 + [1•Pd]^{2+} (1:1 molar ratio) and c) 4 + [1•Pd]^{2+} (2:1 molar ratio). Primed letters correspond to proton signals of [1•Pd]^{2+}. Triple primed letters and numbers correspond to proton signals of 4⊂[1•Pd]^{2+}. 1,3,5-trimethoxybenzene was used as internal standard (I.S.). See Scheme S1 and Figure S39 for proton assignment.

*Solvent residual peaks.

The addition of bis-N-oxide 4 to a millimolar solution of [1•Pd]^{2+} in 2:1 CDCl₃:CD₃CN produced the immediate formation of the 4⊂[1•Pd]^{2+} complex. Thus, the formation of the complex was fast on the human timescale.
Figure S49. $^1$H NMR (400 MHz, 2:1 CDCl$_3$:CD$_3$CN, 298 K) spectra of: a) $[\text{1-Pd}]^{2+}$; b) $5 + [\text{1-Pd}]^{2+}$ (1:1 molar ratio); c) $5 + [\text{1-Pd}]^{2+}$ (2:1 molar ratio) and d) $5 + [\text{1-Pd}]^{2+}$ (5:1 molar ratio). Primed letters correspond to proton signals of $[\text{1-Pd}]^{2+}$. Triple primed letters and numbers correspond to proton signals of $5 \subset [\text{1-Pd}]^{2+}$. 1,3,5-trimethoxybenzene was used as internal standard (I.S.). See Scheme S1 and Figure S42 for proton assignment. *Solvent residual peaks.

Figure S50. $^1$H NMR (400 MHz, 2:1 CDCl$_3$:CD$_3$CN, 298 K) spectra of: a) $[\text{1-Pd}]^{2+}$; b) $5 + [\text{1-Pd}]^{2+}$ (1:1 molar ratio); after thermal equilibration of b) at 40°C for c) 24 h and d) 48 h. Primed letters correspond to proton signals of $[\text{1-Pd}]^{2+}$. 1,3,5-trimethoxybenzene was used as internal standard (I.S.). See Scheme S1 for proton assignment. *Solvent residual peaks.

The addition of incremental amounts of N-oxide 5 to a millimolar solution of $[\text{1-Pd}]^{2+}$ in 2:1 CDCl$_3$:CD$_3$CN produced the immediate formation of the $5c[\text{1-Pd}]^{2+}$ complex. Thus, the formation of the complex was fast on the human timescale. The complex was not quantitatively formed upon the addition of 1 molar equiv. of 5. We estimated a binding constant value ca. 5x10$^2$ M$^{-1}$ for the $5c[\text{1-Pd}]^{2+}$ complex. The solution evolved with time leading to the observation of a white precipitate in the NMR tube and proton signals with low intensity in the $^1$H NMR spectrum. This indicated that the complex was not thermodynamically stable, probably evolving to the formation of ill-defined aggregates.

The time evolution of an equimolar mixture of $[\text{1-Pd}]^{2+}$ and 5 produced the formation of oligomeric aggregates in large extend, that are not visible by $^1$H NMR spectroscopy.
5.3 $^1$H-$^1$H 2D EXSY NMR experiments of 1 and [1•Pd]$^{2+}$ cage with pyridyl N-oxides

The $^1$H-$^1$H 2D EXSY NMR experiments ($\tau_{mix} = 0.3$ s) were performed with pyridine N-oxide 3 (0.5 molar equiv.) and the super aryl-extended calix[4]pyrrole 1 or [1•Pd]$^{2+}$ at 2 mM concentration in 2:1 CDCl$_3$:CD$_3$CN.

Figure S51. $^1$H-$^1$H 2D EXSY NMR (300 MHz, 2:1 CDCl$_3$:CD$_3$CN, 298 K, $\tau_{mix} = 0.3$ s) spectrum of pyridine N-oxide 3 + tetra-pyridyl 1 (0.5:1 molar ratio). Double primed letters correspond to proton signals of 3:c1 complex. See Scheme S1 for proton assignment. *Solvent residual peak.

Figure S52. Selected region of the $^1$H-$^1$H 2D EXSY NMR (300 MHz, 2:1 CDCl$_3$:CD$_3$CN, 298 K, $\tau_{mix} = 0.3$ s) spectrum of pyridine N-oxide 3 + tetra-pyridyl 1 (0.5:1 molar ratio). Double primed letters correspond to proton signals of 3:c1 complex. See Scheme S1 for proton assignment. *Solvent residual peak.
Figure S53. $^1$H-$^1$H 2D EXSY NMR (300 MHz, 2:1 CDCl$_3$:CD$_3$CN, 298 K, $t_{	ext{mix}} = 0.3$ s) spectrum of pyridine N-oxide 3 $+$ [1$\cdot$Pd]$^{2+}$ (0.5:1 molar ratio). Primed letters correspond to proton signals of [1$\cdot$Pd]$^{2+}$. Triple primed letters correspond to proton signals of 3$\subset$[1$\cdot$Pd]$^{2+}$ complex. See Scheme S1 for proton assignment. *Solvent residual peak.

Figure S54. Selected region of the $^1$H-$^1$H 2D EXSY NMR (300 MHz, 2:1 CDCl$_3$:CD$_3$CN, 298 K, $t_{	ext{mix}} = 0.3$ s) spectrum of pyridine N-oxide 3 $+$ [1$\cdot$Pd]$^{2+}$ (0.5:1 molar ratio). Primed letters correspond to proton signals of [1$\cdot$Pd]$^{2+}$. Triple primed letters correspond to proton signals of 3$\subset$[1$\cdot$Pd]$^{2+}$ complex. See Scheme S1 for proton assignment. *Solvent residual peak.

Table S8. Magnetization exchange rate constant ($k$) and energy barrier ($\Delta G^\ddagger$) determined from the above EXSY NMR experiments. Rate constants were determined using EXSY calc. and energy barriers were determined using the Eyring-Polanyi equation.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Exchange on the EXSY timescale</th>
<th>$k$ (s$^{-1}$)</th>
<th>$\Delta G^\ddagger$ (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3$\subset$1</td>
<td>Fast</td>
<td>1.4±0.1</td>
<td>17.2±0.04</td>
</tr>
<tr>
<td>3$\subset$[1$\cdot$Pd]$^{2+}$</td>
<td>Slow</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The two EXSY NMR spectra shown above indicated that the exchange of the N-oxide 3 using the super aryl-extended receptor 1 was fast on the EXSY timescale, while the exchange of the guest was slow in the case of the [1$\cdot$Pd]$^{2+}$ cage. The different dynamics experienced by 1 and [1$\cdot$Pd]$^{2+}$ suggested a modification of the exchange mechanism of the guest.
The $^1$H-$^1$H 2D EXSY NMR experiments ($t_{mix} = 0.3$ s) were performed with pyridine $N$-oxide 3 (3-4 molar equiv.) and the super aryl-extended calix[4]pyrrole 1 or [1•Pd]$^{2+}$ at 2 mM concentration in 2:1 CDCl$_3$:CD$_3$CN.

The two EXSY NMR spectra shown above indicated that the exchange of tetra-pyridyl 1, using an excess of $N$-oxide 3, was fast on the EXSY timescale, while the exchange of the [1•Pd]$^{2+}$ cage was slow. The different dynamics experienced by 1 and [1•Pd]$^{2+}$ suggested a modification of the exchange mechanism of the guest.
The $^1$H-$^1$H 2D NMR EXSY experiment ($t_{mix} = 0.3$ s) was performed with 4,4'-bipyridyl bis-$N$-oxide 4 (2 molar equiv.) and the [1•Pd]$^{2+}$ cage in 2:1 CDCl$_3$:CD$_3$CN.

![Image of 1H-1H 2D EXSY NMR spectrum of bis-$N$-oxide 4 + [1•Pd]$^{2+}$ complex](image1)

**Figure S57.** $^1$H-$^1$H 2D EXSY NMR (400 MHz, 2:1 CDCl$_3$:CD$_3$CN, 298 K, $t_{mix} = 0.3$ s) spectrum of bis-$N$-oxide 4 + [1•Pd]$^{2+}$ (2:1 molar ratio). Triple primed numbers correspond to proton signals of 4⊂[1•Pd]$^{2+}$ complex. Cross-peaks between H$^4$,5 and H$^6$-7 (blue) are residual COSY peaks. *Solvent residual peak.

The $^1$H-$^1$H 2D EXSY NMR spectrum of bis-$N$-oxide 4 (2 molar equiv.) with [1•Pd]$^{2+}$ did not show exchange cross-peaks between the $\alpha$-pyridyl protons respect to the $N$-oxide of free (H$^4$) and bound (H$^4''$) 4. This observation was indicative of a slow chemical exchange between free and bound components on the EXSY NMR timescale.

The $^1$H-$^1$H 2D NMR EXSY experiment ($t_{mix} = 0.3$ s) was performed with 4-phenylpyridine $N$-oxide 5 (0.5 molar equiv.) and the super aryl-extended calix[4]pyrrole 1 in 2:1 CDCl$_3$:CD$_3$CN.

![Image of 1H-1H 2D EXSY NMR spectrum of 4-phenylpyridine $N$-oxide 5 + tetrapyridyl 1](image2)

**Figure S58.** $^1$H-$^1$H 2D EXSY NMR (300 MHz, 2:1 CDCl$_3$:CD$_3$CN, 298 K, $t_{mix} = 0.3$ s) spectrum of 4-phenylpyridine $N$-oxide 5 + tetrapyridyl 1 (0.5:1 molar ratio). Double primed letters correspond to proton signals of 5⊂1 complex. See Scheme S1 for proton assignment. *Solvent residual peak.
Figure S59. Selected region of the $^1$H-$^1$H 2D EXSY NMR (300 MHz, 2:1 CDCl$_3$:CD$_3$CN, 298 K, $t_{mix} = 0.3$ s) spectrum of 4-phenylpyridine $N$-oxide 5 + tetra-pyridyl 1 (0.5:1 molar ratio). Double primed letters correspond to proton signals of 5:1 complex. See Scheme S1 for proton assignment. *Solvent residual peak.

The $^1$H-$^1$H 2D EXSY NMR experiment of 4-phenylpyridine $N$-oxide 5 (0.5 molar equiv.) with 1 did not show exchange cross-peaks between the pyrrole NHs of free (H$^\alpha$) and bound (H$^\alpha''$) 1. This observation was indicative of a slow chemical exchange between free and bound components on the EXSY NMR timescale. Probably, the thermodynamic stability of the 5:1 complex, higher than that of 3:1, was traduced in a higher kinetic stability showing slow dynamics on the EXSY timescale.

Figure S60. “French doors” mechanism involving the four meso-phenyl substituents: a) rotation of the bonds producing a passage; b) guest exchange through the passage and c) rotation of the bonds closing the passage. In b) top view of the passage is highlighted in yellow.
5.4 1D GOESY NMR experiments of [1•Pd]$^{2+}$ cage with pyridine N-oxide 3

Figure 61. $^1$H NMR (400 MHz, 2:1 CDCl$_3$:CH$_3$CN, 298 K) spectrum of a) 3c:[1•Pd]$^{2+}$; 1D GOESY NMR (400 MHz, 2:1 CDCl$_3$:CH$_3$CN, 298 K) spectra of a) with mixing times ($t_{mix}$) of b) 0.3 s and c) 0.6 s. 1,3,5-trimethoxybenzene was used as internal standard (I.S.). *Solvent residual peaks.

The 1D GOESY NMR spectra of 3c:[1•Pd]$^{2+}$ in 2:1 CDCl$_3$:CH$_3$CN at 298 K did not show the proton signals of included CH$_3$CN molecules in the cage. Most likely, the chemical exchange between free and bound CH$_3$CN molecules is fast on the GOESY timescale.
6. Energy minimized structures and calculated packing coefficients

**Figure S62.** Energy minimized structures (MM3) of a) (CH$_3$)$_2$SO ⊂ 1 and b) [(CH$_3$)$_2$SO]$_2$ ⊂ [1•Pd]$.^2$ The calix[4]pyrroles are depicted in stick representation and the (CH$_3$)$_2$SO molecules are shown as CPK models.

**Figure S63.** Energy minimized structures (MM3) of a) CH$_3$CN ⊂ 1 and b) [CH$_3$CN]$_2$ ⊂ [1•Pd]$.^2$. The calix[4]pyrroles are depicted in stick representation and the CH$_3$CN molecules are shown as CPK models.
Figure S64. Energy minimized structures (MM3) of a) [3•CH3CN][1•Pd]2+; b) 4•[1•Pd]2+ and c) 5•[1•Pd]2+. The calix[4]pyrroles are depicted in stick representation. CH3CN and N-oxides are shown as CPK models.

Table S9. Packing coefficients (PC = (V_{guest}/V_{host}) x 100) of the [1•Pd]2+ cage complexes obtained from the energy-minimized structures (MM3). The volumes of the host and the guest/s were determined using SwissPDB.

<table>
<thead>
<tr>
<th>Complex</th>
<th>V_{host} (Å³)</th>
<th>V_{guest} (Å³)</th>
<th>PC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(CH3)2SO]2•[1•Pd]2+</td>
<td>292</td>
<td>153</td>
<td>52</td>
</tr>
<tr>
<td>[CH3CN]2•[1•Pd]2+</td>
<td>172</td>
<td>93</td>
<td>54</td>
</tr>
<tr>
<td>[3•CH3CN]2•[1•Pd]2+</td>
<td>205</td>
<td>134</td>
<td>65</td>
</tr>
<tr>
<td>4•[1•Pd]2+</td>
<td>252</td>
<td>161</td>
<td>64</td>
</tr>
<tr>
<td>5•[1•Pd]2+</td>
<td>251</td>
<td>158</td>
<td>63</td>
</tr>
</tbody>
</table>

* The volume of the cage complexes were determined by replacing the ortho-protons (H₆ and H₇) of adjacent meso-aromatic walls by methyl groups.

The cavity volume of the [1•Pd]2+ cage changed as a function of the bound guest/s. This result suggests that the size adaptability of the volume’s cage to the bound guest/s.

Figure S65. Energy minimized structures (MM3) of a) CH3CN[2•Pd]2+ and b) (CH3)2SO[2•Pd]2+. The calix[4]pyrroles are depicted in stick representation. CH3CN and (CH3)2SO are shown as CPK models.

Table S10. Packing coefficients (PC = (V_{guest}/V_{host}) x 100) of the [2•Pd]2+ cages obtained from the energy minimized structures (MM3). The volumes of the host and the guest/s were determined using SwissPDB.

<table>
<thead>
<tr>
<th>Complex</th>
<th>V_{host} (Å³)</th>
<th>V_{guest} (Å³)</th>
<th>PC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3CN[2•Pd]2+</td>
<td>77</td>
<td>43</td>
<td>56</td>
</tr>
<tr>
<td>(CH3)2SO[2•Pd]2+</td>
<td>125</td>
<td>69</td>
<td>55</td>
</tr>
</tbody>
</table>

The energy minimized structures (MM3) of the [2•Pd]2+ cages showed that the polar heteroatoms of the bound solvent molecules are hydrogen-bonded to the pyrrole NHs of the calix[4]pyrrole unit.
7. X-ray crystal structures

Figure S66. X-ray crystal structures of a) CH$_3$CN⊂1 and b) [CH$_3$CN]$_2$⊂[1•Pd](BF$_4$)$_2$. The cages are shown in ORTEP view with thermal ellipsoids set at 50% probability. Hydrogen atoms are shown as fixed-size spheres of 0.3 Å radius. The CH$_3$CN molecules are shown as CPK models. Tetrafluoroborate anions in b) are omitted for clarity.

The X-ray structure of CH$_3$CN⊂1 shows the receptor in the cone conformation featuring an aromatic cavity with a single polar binding site. The upper section of the cavity collapses owing to edge-to-face CH-π interactions between terminal phenyl substituents.

In the [CH$_3$CN]$_2$⊂[1•Pd](BF$_4$)$_2$ cage complex, the four CH$_2$-O bonds are unidirectionally oriented, giving rise to two cycloenantiomers, P and M, in the crystal packing.

Figure S67. X-ray crystal structure of [3•CH$_3$CN]⊂[1•Pd](BF$_4$)$_2$. The cage is shown in ORTEP view with thermal ellipsoids set at 50% probability. Hydrogen atoms are shown as fixed-size spheres of 0.3 Å radius. The CH$_3$CN molecule and the N-oxide 3 are shown as CPK models. Tetrafluoroborate anions are omitted for clarity.
Figure S68. X-ray crystal structures of a) 4⊂[1•Pd][BF₄]₂ (occupancy = 55%); b) [4•H₂O]⊂[1•Pd][BF₄]₂ (occupancy = 25%), there is a 12% occupancy of this structure lacking the water molecule and c) 4⊂[1•Pd][BF₄]₂ (occupancy = 8%). The cages are shown in ORTEP view with thermal ellipsoids set at 50% probability. Hydrogen atoms are shown as fixed-size spheres of 0.3 Å radius. The H₂O molecule and the bis-N-oxide 4 are shown as CPK models. Tetrafluoroborate anions are omitted for clarity. 

CCDC 1876531 (CH₃CN⊂1); 1876530 ([CH₃CN]₂⊂[1•Pd][BF₄]₂); 1876528 ([3•CH₃CN]⊂[1•Pd][BF₄]₂) and 1876529 (4⊂[1•Pd][BF₄]₂) contain the supplementary crystallographic data for this manuscript. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
8. References