# Resolution of Minor Size Differences in a Family of Heteroleptic Coordination Cages by Trapped Ion Mobility ESI-MS

#### Supporting Information

Kristina E. Ebbert, Laura Schneider, André Platzek, Christoph Drechsler, Bin Chen, Robin Rudolf and Guido H. Clever

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## **1. Experimental Section**

#### 1.1 Materials and measurements

#### **1.1.1 Materials and Machines**

Where necessary, experiments were performed under nitrogen atmosphere using standard Schlenk techniques. Chemicals and standard solvents were purchased from Sigma Aldrich, Acros Organics, Carl Roth, TCI Europe, VWR, ABCR or other suppliers and used as received, if not mentioned otherwise. Dry solvents were purchased or purified and dried over absorbent-filled columns on a GS-Systems solvent purification system (SPS). Reactions were monitored with thin layer chromatography (TLC) using silica coated aluminium plates (Merck, silica 60, fluorescence indicator F254, thickness 0.25 mm). For column chromatography, silica (Merck, silica 60, 0.02 - 0.063 mesh ASTM) was used as the stationary phase, if not mentioned otherwise.

Flash chromatography was performed on a Biotage Isolera One fraction collector with Biotage SNAP Ultra columns.

Recycling gel permeation chromatography (GPC) of ligand L<sup>P</sup> was performed on Japan Analytical Industry NEXT using JAIGEL 1-HH and, 20 mm x 600 mm, flowrate 7 mL/min.

#### 1.1.2 ESI-MS and TIMS-TOF measurements

Mass spectrometry and trapped ion mobility data were measured on Bruker ESI-timsTOF (electrospray ionization-trapped ion mobility-time of flight) and Bruker compact high-resolution LC mass spectrometers (positive/negative mode). For calibration of the TIMS and TOF devices, Agilent ESI-Low Concentration Tuning Mix was used.

Exact conditions for the ion mobility measurements are given in paragraph 3.2.

#### 1.1.3 NMR

The NMR spectroscopic data was measured on the spectrometers Bruker AV 500 Avance NEO and AV 600 Avance III HD. For <sup>1</sup>H NMR spectra, the chemical shifts were calibrated on the signals of the lock solvents (CD<sub>3</sub>CN: 1.94 ppm, (CD<sub>3</sub>)<sub>2</sub>S(O): 2.50). For the <sup>13</sup>C NMR spectra the signals of the lock solvents were used as the internally standard (CD<sub>3</sub>CN: 1.32, 118.26 ppm, (CD<sub>3</sub>)<sub>2</sub>S(O): 39.52 ppm). The chemical shift  $\delta$  is given in ppm, the coupling constants *J* in Hz.

All spectra were recorded in standard 5 mm NMR tubes at 25 °C if not stated otherwise. The <sup>1</sup>H DOSY NMR spectra were recorded with a dstebpgp3s pulse sequence with diffusion delays D20 of 0.06-0.1 s and gradient powers P30 of 1300 to 2600  $\mu$ s.

#### **1.1.4 Computational Studies**

A model of each cage was calculated using Spartan '14 (Version 1.1.8, Wavefunction, Inc., Irvine, CA, **2014**) by a semi-empiric PM6 structure optimization for illustrative purposes. In preparation for the calculations the semi-empiric optimization method GFN-xTB (Version 6.0, Mulliken Center for Theoretical Chemistry, Bonn, Germany, **2019**)<sup>[1]</sup> was used. The programs used for the CCS calculations were: a modified version of MOBCAL (Indiana University Bloomington, Bloomington, IN, **1996**, modified by I. Campuzano et al., Amgen, CA, **2012**)<sup>[2]</sup>, IMoS (Version 1.09, L. Larriba Andaluz, **2013**)<sup>[3][4]</sup> and Collidoscope (Version 1.4, Prell Group, Eugene, OR, **2017**)<sup>[5]</sup>.

#### **1.2 Synthesis**

#### 1.2.1 Ligands L<sup>C</sup>, L<sup>F</sup> and L<sup>P</sup>

Ligands  $L^{C}$ ,  $L^{F}$  and  $L^{P}$  (Scheme SI 1) were prepared according to literature procedures.<sup>[6][7][9]</sup>



Scheme SI 1: Ligands L<sup>C</sup>, L<sup>F</sup>, L<sup>P</sup> and L<sup>P'</sup>.

#### 1.2.2 Characterization of L<sup>F</sup>



Scheme SI 2: Ligand L<sup>F</sup> with proton annotation.

<sup>1</sup>**H NMR (600 MHz, CDCl<sub>3</sub>, 298 K)**:  $\delta = 8.83$  (d,  ${}^{4}J = 1.4$ , 2H, H<sub>g</sub>), 8.62 (dd,  ${}^{3}J = 5.0$ ,  ${}^{4}J = 1.6$ , 2H, H<sub>f</sub>), 7.93 (dt,  ${}^{3}J = 7.9$ ,  ${}^{5}J = 1.8$ , 2H, H<sub>e</sub>), 7.75 (s, 2H, H<sub>c</sub>), 7.72 (d,  ${}^{3}J = 7.6$ , 2H, H<sub>a</sub>), 7.53 (dd,  ${}^{3}J = 7.6$ ,  ${}^{4}J = 1.3$ , 2H, H<sub>b</sub>), 7.42 (dd,  ${}^{3}J = 5.0$ ,  ${}^{4}J = 2.8$ , 2H, H<sub>d</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>, 298 K): δ = 191.7, 151.2, 148.0, 143.7, 139.7, 134.2, 133.1, 128.8, 124.6, 123.6, 120.3, 92.7, 89.0.



Figure SI 1: <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>, 298 K) of L<sup>F</sup> including a zoom into the aromatic region.



Figure SI 2: <sup>13</sup>C NMR spectrum (150 MHz, CDCl<sub>3</sub>, 298 K) of L<sup>F</sup>.



Figure SI 3: Partial <sup>1</sup>H-<sup>1</sup>H COSY spectrum (600 MHz, CDCl<sub>3</sub>, 298 K) of L<sup>F</sup>.

## 1.2.3 Synthesis of L<sup>P'</sup>



Scheme SI:3: Synthesis of  $L^{P'}$  with proton assignments.

500 mg (1.26 mmol, 1 eq) 3,6-dibromo-9,10-dimethoxyphenanthrene (prepared according to literature),<sup>[7]</sup> 455.6 mg (4.42 mmol, 3.5 eq) 4-ethynylpridine, 24.0 mg CuI (126.2  $\mu$ mol, 0.1 eq) and 44.3 mg Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (63.12  $\mu$ mol, 0.05 eq) were combined in a Schlenk tube under nitrogen atmosphere. Dry triethylamine (4 ml) was added and the reaction mixture was subsequently degassed, then heated to 85 °C and stirred under nitrogen atmosphere for 16 h. Afterwards, the mixture was extracted with ethyl acetate and washed with a sat. NH<sub>4</sub>Cl

solution, water and brine. It was dried over MgSO<sub>4</sub> and further purified by automated flash chromatography (pentane/ethyl acetate 10%  $\rightarrow$  40%) followed by GPC purification. The product was isolated as a light brown solid (468,96 µmol, 34%).

<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 298 K):  $\delta = 9.24$  (s, 2H, H<sub>c</sub>), 8.68 (d, <sup>3</sup>*J* = 5.8, 4H, H<sub>e</sub>), 8.23 (d, <sup>3</sup>*J* = 8.4, 2H, H<sub>a</sub>), 7.91 (d, <sup>3</sup>*J* = 8.4, 2H, H<sub>b</sub>), 7.61 (d, <sup>3</sup>*J* = 5.8, 4H, H<sub>d</sub>), 4.06 (s, 6H, OCH<sub>3</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, DMSO-*d*<sub>6</sub>, 298 K):  $\delta$  = 150.5, 144.8, 130.7, 130.5, 129.6, 128.1, 127.9, 125.9, 123.1, 119.7, 94.5, 88.0, 61.6.



Figure SI 4: <sup>1</sup>H NMR spectrum (600 MHz, DMSO-d<sub>6</sub>, 298 K) of L<sup>P</sup> including a zoom into the aromatic region.



Figure SI 5: <sup>13</sup>C NMR spectrum (150 MHz, DMSO-d<sub>6</sub>, 298 K) of L<sup>P</sup>.



Figure SI 6: Partial <sup>1</sup>H-<sup>1</sup>H COSY spectrum (600 MHz, DMSO-d<sub>6</sub>, 298 K) of L<sup>P'</sup>.

## 1.2.4 Formation of homoleptic cages $[Pd_2L^C_4]$ and $[Pd_4L^P_8]$

Formation of homoleptic cages  $[Pd_2L^{C_4}]$  and  $[Pd_4L^{P_8}]$  have been previously reported in CD<sub>3</sub>CN, respectively DMSO.<sup>[6][7]</sup>

## **1.2.5** Formation of homoleptic $[Pd_2L^F_4]$

To a suspension of 3,6-bis(pyridin-3-ylethynyl)-9H-fluoren-9-one  $L^F$  (1.45 mg, 0,0038 mmol) in DMSO (1.35 mL), a solution of  $[Pd(CH_3CN)_4](BF_4)_2$  (15 mM, 0.126 mL) was added. The mixture was stirred at room temperature for 5 minutes to afford  $[Pd_2L^F_4]$  in quantitative yield.

<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 298 K):  $\delta = 9.22$  (dd,  ${}^{3}J = 6.0$ ,  ${}^{4}J = 1.1$ , 8H, H<sub>f</sub>), 9.17 (d,  ${}^{4}J = 1.7$ , 8H, H<sub>g</sub>), 8.43 (dt,  ${}^{3}J = 8.0$ ,  ${}^{5}J = 1.6$ , 8H, H<sub>e</sub>), 7.99 (s (br), 8H, H<sub>c</sub>), 7.86 (dd,  ${}^{3}J = 6.1$ ,  ${}^{4}J = 1.7$ , 8H, H<sub>d</sub>), 7.76 (s (br), 16H, H<sub>a</sub>, H<sub>b</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, DMSO-*d*<sub>6</sub>, 298 K): *δ* = 190.8, 152.0, 151.1, 144.6, 143.3, 135.4, 133.9, 127.4, 127.3, 124.6, 122.6, 122.0, 118.1, 94.8, 87.7.



**Figure SI 7**: <sup>1</sup>H NMR spectrum (600 MHz, DMSO-d<sub>6</sub>, 298 K) of  $[Pd_2L^F_4]$  including a zoom into the aromatic region.



Figure SI 8: <sup>13</sup>C NMR spectrum (150 MHz, DMSO-d<sub>6</sub>, 298 K) of [Pd<sub>2</sub>L<sup>F</sup><sub>4</sub>].



Figure SI 9: Partial <sup>1</sup>H-<sup>1</sup>H COSY spectrum (600 MHz, DMSO-d<sub>6</sub>, 298 K) of [Pd<sub>2</sub>L<sup>F</sup><sub>4</sub>].

## 1.2.6 Synthesis of homoleptic [Pd<sub>3</sub>L<sup>P'</sup><sub>6</sub>]

A solution of  $[Pd(CH_3CN)_4](BF_4)_2$  (60 µL, 15 mM in DMSO-d<sub>6</sub>) was combined with L<sup>P'</sup> (540 µL, 2.8 mM in DMSO-d<sub>6</sub>) and heated at 70 °C for 2 h to afford  $[Pd_3L^{P'}_6]$  in quantitative yield.

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, 298 K):  $\delta = 9.29$  (d, <sup>3</sup>*J* = 6.5, 12H, H<sub>e</sub>), 9.18 (s, 6H, H<sub>c</sub>), 8.25 (d, <sup>3</sup>*J* = 8.6, 6H, H<sub>a</sub>), 7.99 (d, <sup>3</sup>*J* = 6.5, 12H, H<sub>d</sub>), 7.86 (d, <sup>3</sup>*J* = 8.9, 6H, H<sub>b</sub>), 4.04 (s, 36H, OC*H*<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, DMSO-*d*<sub>6</sub>, 298 K):  $\delta = 151.1$ , 144.7, 134.7, 129.9, 129.7, 128.9, 128.7, 127.2, 123.0, 118.3, 118.1, 99.3, 86.3, 61.2.



Figure SI 10: <sup>1</sup>H NMR spectrum (500 MHz, DMSO-d<sub>6</sub>, 298 K) of [Pd<sub>3</sub>L<sup>P'</sup><sub>6</sub>] including a zoom into the aromatic region.



Figure SI 11: <sup>13</sup>C NMR spectrum (150 MHz, DMSO-d<sub>6</sub>, 298 K) of [Pd<sub>3</sub>L<sup>P'</sup><sub>6</sub>]



Figure SI 12: Partial <sup>1</sup>H-<sup>1</sup>H COSY spectrum (500 MHz, DMSO-d<sub>6</sub>, 298 K) of [Pd<sub>3</sub>L<sup>P'</sup><sub>6</sub>].

## 1.2.7 Synthesis of [Pd<sub>2</sub>L<sup>F</sup><sub>2</sub>L<sup>P</sup><sub>2</sub>]

A solution of  $[Pd(CH_3CN)_4](BF_4)_2$  (60 µL, 15 mM in DMSO-d<sub>6</sub>) was combined with a suspension of  $L^P$  (0.33 mg in 270 µL DMSO-d<sub>6</sub>) and a suspension of  $L^F$  (0.32 mg in 270 µL DMSO-d<sub>6</sub>) and left to sit at room temperature for 2 h to afford  $[Pd_2L^F_2L^P_2]$  in quantitative yield.



Figure SI 13: Formation of cage  $[Pd_2L^F_2L^P_2]$ . Proton assignments are shown.

<sup>1</sup>**H NMR (600 MHz, DMSO-***d*<sub>6</sub>, **298 K**):  $\delta = 10.15$  (s, 4H, H<sub>g</sub><sup>·</sup>), 9.55 (d, <sup>3</sup>*J* = 7.7, 4H, H<sub>e</sub>), 9.46 (s, 4H, H<sub>c</sub>), 9.41 (d, <sup>3</sup>*J* = 5.8, 4H, H<sub>f</sub>), 8.63 (d, <sup>3</sup>*J* = 7.8, 4H, H<sub>a</sub>), 8.36 (d, <sup>3</sup>*J* = 9.8, 4H, H<sub>d</sub><sup>·</sup>), 8.21 (m, 16H, H<sub>d</sub>, H<sub>c</sub><sup>·</sup>, H<sub>b</sub>), 7.92 (dd, <sup>3</sup>*J* = 7.1, <sup>4</sup>*J* = 2.5, 4H, H<sub>e</sub><sup>·</sup>), 7.76 (d, <sup>3</sup>*J* = 9.1, 4H, H<sub>a</sub><sup>·</sup>), 7.70 (dd, <sup>3</sup>*J* = 9.1, <sup>4</sup>*J* = 1.2, 4H, H<sub>b</sub><sup>·</sup>), 4.00 (s, 12H, OCH<sub>3</sub>).

<sup>13</sup>C {<sup>1</sup>H} NMR (150 MHz, DMSO-*d*<sub>6</sub>, 298 K): δ = 190.8, 171.4, 163.1, 153.3, 151.0, 150.0, 144.7, 143.4, 142.8, 134.4, 134.0, 131.9, 130.3, 128.1, 127.5, 127.4, 125.2, 124.9, 124.7, 123.7, 123.4, 121.7, 118.1, 94.0, 87.1, 61.2.



**Figure SI 14**: <sup>1</sup>H NMR spectrum (600 MHz, DMSO-d<sub>6</sub>, 298 K) of [Pd<sub>2</sub>L<sup>F</sup><sub>2</sub>L<sup>P</sup><sub>2</sub>] including a zoom into the aromatic region.



Figure SI 15: <sup>13</sup>C NMR spectrum (150 MHz, DMSO-d<sub>6</sub>, 298 K) of [Pd<sub>2</sub>L<sup>F</sup><sub>2</sub>L<sup>P</sup><sub>2</sub>].



Figure SI 16: Partial <sup>1</sup>H-<sup>1</sup>H COSY spectrum (600 MHz, DMSO-d<sub>6</sub>, 298 K) of [Pd<sub>2</sub>L<sup>F</sup><sub>2</sub>L<sup>P</sup><sub>2</sub>].

### 1.2.8 Synthesis of [Pd<sub>2</sub>L<sup>F</sup><sub>2</sub>L<sup>P'</sup><sub>2</sub>]

A solution of  $[Pd(CH_3CN)_4](BF_4)_2$  (60 µL, 15 mM in DMSO-d<sub>6</sub>) was combined with a suspension of  $L^{P'}$  (0.37 mg in 270 µL DMSO-d<sub>6</sub>) and a suspension of  $L^F$  (0.32 mg in 270 µL DMSO-d<sub>6</sub>) and left to sit at room temperature for 2 h to afford  $[Pd_2L^F_2L^{P'}_2]$  in quantitative yield.



Figure SI 17: Formation of cage [Pd<sub>2</sub>L<sup>F</sup><sub>2</sub>L<sup>P'</sup><sub>2</sub>]. Proton assignments are shown.

<sup>1</sup>**H NMR (600 MHz, DMSO-***d*<sub>6</sub>, **298 K**):  $\delta = 9.74$  (d, <sup>4</sup>*J* = 1.3, 4H, H<sub>g</sub>·), 9.41 (d, <sup>3</sup>*J* = 5.3, 4H, H<sub>f</sub>), 9.37 (d, <sup>3</sup>*J* = 6.7, 4H, H), 9.27 (s, 4H, H<sub>c</sub>), 8.37 (d, <sup>3</sup>*J* = 9.7, 4H, H<sub>d</sub>·), 8.22 (d, <sup>3</sup>*J* = 10.2, 4H, H<sub>a</sub>), 8.00 (m, 12H, H<sub>d</sub>, H<sub>c</sub>·), 7.90 (dd, <sup>3</sup>*J* = 6.9, <sup>4</sup>*J* = 2.4, 4H, H<sub>e</sub>·), 7.84 (dd, <sup>3</sup>*J* = 10.4, <sup>4</sup>*J* = 1.3, 4H, H<sub>b</sub>), 7.76 (d, <sup>3</sup>*J* = 9.3, 4H, H<sub>a</sub>·), 7.70 (dd, <sup>3</sup>*J* = 9.1, <sup>4</sup>*J* = 1.3, 4H, H<sub>b</sub>·), 4.02 (s, 12H, OC*H*<sub>3</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, DMSO-*d*<sub>6</sub>, 298 K): δ = 189.1, 151.4, 149.3, 143.2, 141.7, 141.5, 133.1, 132.9, 132.3, 128.2, 128.1, 127.6, 127.2, 125.8, 125.7, 125.6, 123.1, 121.5, 121.3, 120.1, 116.6, 116.4, 98.1, 92.5, 85.8, 85.1, 59.6.



Figure SI 18: <sup>1</sup>H NMR spectrum (600 MHz, DMSO-d<sub>6</sub>, 298 K) of  $[Pd_2L^F_2L^{P'}_2]$  including a zoom into the aromatic region.



Figure SI 19: <sup>13</sup>C NMR spectrum (150 MHz, DMSO-d<sub>6</sub>, 298 K) of [Pd<sub>2</sub>L<sup>F</sup><sub>2</sub>L<sup>P'</sup><sub>2</sub>].



Figure SI 20: Partial <sup>1</sup>H-<sup>1</sup>H COSY spectrum (600 MHz, DMSO-d<sub>6</sub>, 298 K) of [Pd<sub>2</sub>L<sup>F<sub>2</sub>L<sup>P'<sub>2</sub></sup>].</sup>

## 1.2.9 Synthesis of [Pd<sub>2</sub>L<sup>C</sup><sub>2</sub>L<sup>P</sup><sub>2</sub>]

Synthesis and characterization of  $[Pd_2L^C_2L^P_2]$  has been previously described in CD<sub>3</sub>CN.<sup>[8]</sup>

## 1.2.10 Synthesis of [Pd<sub>2</sub>L<sup>C</sup><sub>2</sub>L<sup>P'</sup><sub>2</sub>]

A solution of  $[Pd(CH_3CN)_4](BF_4)_2$  (60 µL, 15 mM in CD<sub>3</sub>CN) was combined with a suspension of L<sup>P</sup> (0.37 mg in 270 µL CD<sub>3</sub>CN) and a suspension of L<sup>C</sup> (0.38 mg in 270 µL CD<sub>3</sub>CN) and heated at 70 °C for 5 h to afford  $[Pd_2L^C_2L^{P'}_2]$  in quantitative yield.



**Figure SI 21**: Formation of cage [Pd<sub>2</sub>L<sup>C</sup><sub>2</sub>L<sup>P'</sup><sub>2</sub>]. Proton assignments are shown.



Figure SI 22: <sup>1</sup>H NMR spectrum (600 MHz, CD<sub>3</sub>CN, 298 K) of [Pd<sub>2</sub>L<sup>C</sup><sub>2</sub>L<sup>P'</sup><sub>2</sub>] including a zoom into the aromatic region.



Figure SI 23: <sup>13</sup>C NMR spectrum (150 MHz, CD<sub>3</sub>CN, 298 K) of [Pd<sub>2</sub>L<sup>C</sup><sub>2</sub>L<sup>P</sup><sub>2</sub>].



Figure SI 24: Partial <sup>1</sup>H-<sup>1</sup>H COSY spectrum (600 MHz, CD<sub>3</sub>CN, 298 K) of [Pd<sub>2</sub>L<sup>C</sup><sub>2</sub>L<sup>P</sup><sub>2</sub>].

#### 1.2.11 Setup of Cage Mixtures

A solution of  $[Pd(CH_3CN)_4](BF_4)_2$  (60 µL, 15 mM in DMSO-d<sub>6</sub>) was combined with L<sup>P</sup> (0.165 mg in 135 µL DMSO-d<sub>6</sub>) L<sup>P</sup> (0.185 mg in 135 µL DMSO-d<sub>6</sub>) and L<sup>F</sup> (0.32 mg in 270 µL DMSO-d<sub>6</sub>) and left to sit at room temperature for 2 h to afford a mixture of  $[Pd_2L^F_2L^P_2]$ ,  $[Pd_2L^F_2L^PL^P]$  and  $[Pd_2L^F_2L^P_2]$ .

A solution of  $[Pd(CH_3CN)_4](BF_4)_2$  (60 µL, 15 mM in CD<sub>3</sub>CN) was combined with L<sup>P</sup> (0.165 mg in 135 µL CD<sub>3</sub>CN) L<sup>P</sup> (0.185 mg in 135 µL CD<sub>3</sub>CN) and L<sup>C</sup> (0.38 mg in 270 µL CD<sub>3</sub>CN) and heated at 70°C for 5 h to afford a mixture of  $[Pd_2L^C_2L^P_2]$ ,  $[Pd_2L^C_2L^PL^P]$  and  $[Pd_2L^C_2L^P_2]$ .

To afford the six cage mixture the samples mentioned above were combined in a 1:1 ratio.

The final ten cages containing mixture was set up using  $L^P$  (0.061 mg in 50 µL CD<sub>3</sub>CN)  $L^{P'}$  (0.068 mg in 50 µL DMSO-d<sub>6</sub>),  $L^C$  (0.070 mg in 50 µL CD<sub>3</sub>CN) and  $L^F$  (0.059 mg in 50 µL DMSO-d<sub>6</sub>), 11 µL of 15 mM [Pd(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> in CD<sub>3</sub>CN and 11 µL of 15 mM [Pd(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> in DMSO-d<sub>6</sub>.

# 2 Further NMR Data

## 2.1 <sup>1</sup>H DOSY NMR Spectrum of the L<sup>F</sup>-based cage mixture



**Figure SI 25**: Partial <sup>1</sup>H NMR spectrum (500 MHz, DMSO-d<sub>6</sub>, 298 K) of a mixture of  $[Pd_2L^F_2L^P_2]$ ,  $[Pd_2L^F_2L^PL^P']$  and  $[Pd_2L^F_2L^{P'}_2]$ . The ratio of the three species (calculated from relative <sup>1</sup>H signal integration values) is approximately 1:1:1.



Figure SI 26: <sup>1</sup>H DOSY NMR spectrum (500 MHz, DMSO-d<sub>6</sub>, 298 K) of a mixture of  $[Pd_2L^F_2L^P_2]$ ,  $[Pd_2L^F_2L^PL^P']$  and  $[Pd_2L^F_2L^P'_2]$ .

# 2.2 <sup>1</sup>H DOSY NMR Spectrum of the L<sup>C</sup> based cage mixture



**Figure SI 27**: Partial <sup>1</sup>H NMR spectrum (500 MHz, CD<sub>3</sub>CN, 298 K) of a mixture of  $[Pd_2L^{C_2}L^{P_2}]$ ,  $[Pd_2L^{C_2}L^{P_L}]^{P'}$  and  $[Pd_2L^{C_2}L^{P'_2}]$ . The ratio of the three species (calculated from relative <sup>1</sup>H signal integration values) equals approximately 1:2:1.



Figure SI 28: <sup>1</sup>H DOSY NMR spectrum (500 MHz, CD<sub>3</sub>CN, 298 K) of a mixture of  $[Pd_2L^{C_2}L^{P_2}]$ ,  $[Pd_2L^{C_2}L^{P_L}]^{P_1}$  and  $[Pd_2L^{C_2}L^{P_2}]^{P_2}$ .

# **3 Mass Spectrometry**

## **3.1 ESI-MS Analysis**

## 3.1.1 [Pd<sub>3</sub>L<sup>P'</sup><sub>6</sub>]



**Figure SI 29**: ESI-MS spectrum of  $[Pd_3L^{P'}_6]$ . The calculated pattern for  $[Pd_3L^{P'}_6 + 2 BF_4]^{4+}$  is shown in the inlet.



Figure SI 30: ESI-MS spectrum of  $[Pd_2L^F_2L^P_2]$ . The calculated pattern for  $[Pd_2L^F_2L^P_2 + BF_4]^{3+}$  is shown in the inlet.

**3.1.3** [Pd<sub>2</sub>L<sup>F</sup><sub>2</sub>L<sup>P'</sup><sub>2</sub>]



**Figure SI 31**: ESI-MS spectrum of  $[Pd_2L^F_2L^{P'}_2]$ . The calculated pattern for  $[Pd_2L^F_2L^{P'}_2 + BF_4]^{3+}$  is shown in the inlet.

## 3.1.4 $[Pd_2L^{C_2}L^{P_2}]$

Synthesis and characterization of this cage can be found in the literature.<sup>[8]</sup>

3.1.5  $[Pd_2L^{C_2}L^{P'_2}]$ 



**Figure SI 32**: ESI-MS spectrum of  $[Pd_2L^{C_2}L^{P'_2}]$ . The calculated pattern for  $[Pd_2L^{C_2}L^{P'_2} + BF_4]^{3+}$  is shown in the inlet.

# 3.1.6 Mixture of $[Pd_2L^F_2L^P_2]$ $[Pd_2L^F_2L^PL^P']$ and $[Pd_2L^F_2L^{P'}_2]$



Figure SI 33: ESI-MS spectrum of a mixture of  $[Pd_2L^F_2L^P_2]$ ,  $[Pd_2L^F_2L^PL^P']$  and  $[Pd_2L^F_2L^P_2]$ . The calculated patterns for  $[Pd_2L^F_2L^P_2 + BF_4]^{3+}$ ,  $[Pd_2L^F_2L^PL^P' + BF_4]^{3+}$  and  $[Pd_2L^F_2L^P'_2 + BF_4]^{3+}$  are shown in the inlets.



**Figure SI 34**: Partial ESI-MS spectrum of a mixture of  $[Pd_2L^F_2L^P_2]$ ,  $[Pd_2L^F_2L^PL^P']$  and  $[Pd_2L^F_2L^P_2]$  zoomed into the region between m/z 450 to 850. The calculated patterns for  $[Pd_2L^F_2L^P_2 + BF_4]^{3+}$ ,  $[Pd_2L^F_2L^PL^P' + BF_4]^{3+}$  and  $[Pd_2L^F_2L^{P'}_2 + BF_4]^{3+}$  are shown in the inlets.



**3.1.7 Mixture**  $[Pd_2L^{C_2}L^{P_2}]$   $[Pd_2L^{C_2}L^{P_2}L^{P'}]$  and  $[Pd_2L^{C_2}L^{P'_2}]$ 

**Figure SI 35**: ESI-MS spectrum of mixture of  $[Pd_2L^C_2L^P_2]$ ,  $[Pd_2L^C_2L^PL^{P'}]$  and  $[Pd_2L^C_2L^{P'}_2]$ . The calculated patterns for  $[Pd_2L^C_2L^P_2 + BF_4]^{3+}$ ,  $[Pd_2L^C_2L^PL^{P'} + BF_4]^{3+}$  and  $[Pd_2L^C_2L^{P'}_2 + BF_4]^{3+}$  are shown in the inlets.

#### 3.1.8 Mixture of all ten heteroleptic cages



**Figure SI 36**: Total ESI-MS spectrum of mixture of  $[Pd_2L^F_2L^P_2]$ ,  $[Pd_2L^F_2L^PL^P']$ ,  $[Pd_2L^F_2L^P_2]$ ,  $[Pd_2L^FL^CL^P_2]$ ,  $[Pd_2L^FL^CL^P_2]$ ,  $[Pd_2L^FL^CL^P_2]$ ,  $[Pd_2L^FL^CL^P_2]$ ,  $[Pd_2L^F_2L^P_2]$ ,  $[Pd_2L^C_2L^P_2]$ ,  $[Pd_2L^C_2L^P_2]$ . The multitude of peaks arises due to the respective cage species with a combination of different counter anions (F<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>). Peak assignment can be taken from Figure SI 37.



**Figure SI 37:** Partial ESI-MS spectrum of mixture of the 3+ species of  $[Pd_2L^F_2L^P_2]$ ,  $[Pd_2L^F_2L^PL^P']$ ,  $[Pd_2L^F_2L^P_2]$ ,  $[Pd_2L^F_2$ 

#### **3.2 Ion Mobility Measurements**

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.

Measurement: After the generation of ions by electrospray ionisation (ESI, conditions see Table SI 1) the desired ions were orthogonally deflected into the TIMS cell consisting of an entrance funnel, the TIMS analyser (carrier gas:  $N_2$ , conditions see Table SI 1). As a result, the ions are stationary trapped. After accumulation (accumulation time see below), a stepwise reduction of the electric field strength leads to a release of ion packages separated by their mobility. After a subsequent focussing, the separated ions are transferred to the TOF-analyser.<sup>[10-12]</sup>

The ion mobility *K* was directly calculated from the trapping electric field strength *E* and the velocity of the carrier gas stream  $v_g$  via

$$K = \frac{v_g}{E} = \frac{A}{U_{release} - U_{out}} \tag{1}$$

where A is a calibration constant (based on calibration standards),  $U_{release}$  is the voltage at which the ions are released from the analyser and  $U_{out}$  is the voltage applied to the exit of the tube. The ion mobility is corrected to standard gas density *via* 

$$K_0 = K \frac{P}{1013 \text{ hPa}} \frac{237 \text{ K}}{T}$$
(2)

to obtain the reduced mobility  $K_0$ , where *P* is the pressure and *T* is the temperature. By using the Mason-Schamp equation, the collisional cross-section  $\Omega$  can be calculated:

$$\Omega = \frac{(18\pi)^{\frac{1}{2}}}{16} \frac{ze}{(k_B T)^{\frac{1}{2}}} \left[\frac{1}{\mu}\right]^{\frac{1}{2}} \frac{1}{K_0} \frac{1}{N_0}$$
(3)

where *ze* is the ion charge,  $k_B$  is the Boltzmann constant,  $\mu$  is the reduced mass of analyte and carrier gas and  $N_0$  is the number density of the neutral gas.<sup>[10-12]</sup>

For calibration of both the TIMS and TOF analysers, commercially available Agilent ESI tune mix was used (https://www.agilent.com/cs/library/certificateofanalysis/G1969-85000cofa872022-U-LB86189.pdf). The instrument was calibrated before each measurement, including each change in the ion mobility resolution mode ("imeX" settings: survey, detect or ultra).

M/z peaks of species that can be compared (3+ peaks of cages containing one BF<sub>4</sub><sup>-</sup> counter anion) were picked in the mass traces and the respective ion mobility was isolated and is shown in the mobilograms depicted in this paper. All mobilograms were smoothened using the Savitzky-Golay method with a factor of 0.005 with exception of the high-resolution measurement of the isomeric cage (smoothened by factor 0.003).

Measurement	Solvent	capillary voltage	end plate offset voltage	nebulizer gas pressure	dry gas flow rate	dry temperature	carrier gas
Standard	DMSO/MeCN (1:20)	3600 V	500 V	0.3 Bar	3.0 L/min	200 °C	$N_2$
High Res. Isomer	DMSO/MeCN (1:20)	3500 V	500 V	0.3 Bar	3.5 L/min	200 °C	$N_2$
	temperature TIMS	entrance pressure	exit pressure	IMS imeX ramp end	IMS imeX ramp start	accumulation time	IMS imeX mode
Standard	305 K	2.59 mbar	0.89 mbar	1.90 1/K0	0.5 1/K0	5.0 ms	Detect
High Res. Isomer	305 K	2.61 mbar	0.91 mbar	1.03 1/K0	0.87 1/K0	5.0 ms	Ultra

Table SI 1: Ion Mobility measurement conditions for each experiment.

Entrance pressure in standard measurements raged from 2.57 - 2.61 mbar while exit pressure ranged from 0.89 - 0.91 mbar.

All samples were prepared in a 1:20 DMSO/MeCN solution and measured with the same IMS conditions to keep the results comparable. The measurements for the calculation of the error have been executed on different days with freshly diluted samples and injection of calibrant before or after the measurement.



Figure SI 38: Ion Mobility spectrum of  $[Pd_2L^F_2L^P_2 + BF_4]^{3+}$ , from a clean solution of  $[Pd_2L^F_2L^P_2]$ .

3.2.2 Ion Mobility of  $[Pd_2L^F_2L^{P'}_2 + BF_4]^{3+}$ 



Figure SI 39: Ion Mobility spectrum of  $[Pd_2L^F_2L^{P'_2} + BF_4]^{3+}$ , from a clean solution of  $[Pd_2L^F_2L^{P'_2}]$ .





Figure SI 40: Ion Mobility spectrum of  $[Pd_2L^C_2L^P_2 + BF_4]^{3+}$ , from a clean solution of  $[Pd_2L^C_2L^P_2]$ .



Figure SI 41: Ion Mobility spectrum of  $[Pd_2L^{C_2}L^{P_2} + BF_4]^{3+}$ , from a clean solution of  $[Pd_2L^{C_2}L^{P_2}]$ .

3.2.5 Ion Mobility of  $[Pd_2L^F_2L^P_2 + BF_4]^{3+}$ ,  $[Pd_2L^F_2L^PL^{P'} + BF_4]^{3+}$  and  $[Pd_2L^F_2L^{P'}_2 + BF_4]^{3+}$  in a mixture



Figure SI 42: Ion Mobility spectrum of  $[Pd_2L^F_2L^P_2 + BF_4]^{3+}$ ,  $[Pd_2L^F_2L^PL^{P'} + BF_4]^{3+}$  and  $[Pd_2L^F_2L^{P'}_2 + BF_4]^{3+}$  measured from one combined sample.

# 3.2.6 Ion Mobility of $[Pd_2L^C_2L^P_2 + BF_4]^{3+}$ , $[Pd_2L^C_2L^PL^{P'} + BF_4]^{3+}$ and $[Pd_2L^C_2L^{P'}_2 + BF_4]^{3+}$ in a mixture



Figure SI 43: Ion Mobility spectrum of  $[Pd_2L^C_2L^P_2 + BF_4]^{3+}$ ,  $[Pd_2L^C_2L^PL^{P'} + BF_4]^{3+}$  and  $[Pd_2L^C_2L^{P'}_2 + BF_4]^{3+}$  measured from one combined sample.

#### 3.2.7 Ion Mobility of a mixture containing six cages



Figure SI 44: Ion Mobility spectrum of  $[Pd_2L^F_2L^P_2 + BF_4]^{3+}$ ,  $[Pd_2L^F_2L^PL^P' + BF_4]^{3+}$ ,  $[Pd_2L^F_2L^P_2 + BF_4]^{3+}$ ,  $[Pd_2L^C_2L^P_2 + B$ 

For the mobilogram of the ten cage mixture, see Figure 5 in the main manuscript.

## **4 CCS Determination**

#### 4.1 Error and molecular radius calculations from eCCS values

The error for the experimental CCS values has been calculated from all measurements for each species as it is given in table SI 2. To validate the values, the ten cage system has been measured five times on different days with a freshly prepared dilution of the sample. Measurements for the single cage systems and three cage systems have been included into the error calculation.

**Table SI 2:** Data achieved from measuring the collisional cross section (CCS) of the different systems. Measurement 1-5 ( $M1_{10}$ - $M5_{10}$ ) includes all ten cages, the system containing three cages (TCM) and the single cage measurements (SCM). Mean value and standard deviation (SD) are given.

Species	M1 <sub>10</sub> CCS [Å <sup>2</sup> ]	M2 <sub>10</sub> CCS [Å <sup>2</sup> ]	M310 CCS [Å <sup>2</sup> ]	M410 CCS [Å <sup>2</sup> ]	M510 CCS [Å <sup>2</sup> ]	TCM CCS [Å <sup>2</sup> ]	SCM CCS [Å <sup>2</sup> ]	Mean CCS [Å <sup>2</sup> ]	SD CCS [Å <sup>2</sup> ]
$[\mathbf{Pd}_{2}\mathbf{L}^{\mathbf{F}}_{2}\mathbf{L}^{\mathbf{P}}_{2}]$	526.5	525.5	526.9	526.3	525.9	527.6	526.0	526.3	0.7
$[\mathbf{Pd}_{2}\mathbf{L}^{\mathrm{F}}_{2} \mathbf{L}^{\mathrm{P}}\mathbf{L}^{\mathrm{P}'}]$	547.9	548.4	548.7	547.8	547.4	547.3		547.9	0.5
$[\mathbf{Pd_2L^F_2L^{P'}2}]$	566.8	565.4	567.0	565.9	565.7	569.1	566.1	566.1	1.3
[Pd <sub>2</sub> L <sup>C</sup> L <sup>F</sup> L <sup>P</sup> <sub>2</sub> + BF <sub>4</sub> ] <sup>3+</sup>	544.1	543.8	544.5	543.7	543.5			543.8	0.4
a) [Pd <sub>2</sub> L <sup>C</sup> L <sup>F</sup> L <sup>P</sup> L <sup>P'</sup> + BF <sub>4</sub> ] <sup>3+</sup>	564.1	561.6	564.0	562.9	562.7			562.9	1.0
b) [Pd <sub>2</sub> L <sup>c</sup> L <sup>F</sup> L <sup>P</sup> L <sup>P'</sup> + BF <sub>4</sub> ] <sup>3+</sup>	568.6	567.2	568.6	567.2	566.9			567.2	0.8
[Pd <sub>2</sub> L <sup>C</sup> L <sup>F</sup> L <sup>P'</sup> <sub>2</sub> + BF <sub>4</sub> ] <sup>3+</sup>	587.2	585.9	587.8	587.2	586.9			587.2	0.7
$[\mathbf{Pd}_{2}\mathbf{L}^{\mathbf{C}}_{2}\mathbf{L}^{\mathbf{P}}_{2}]$	576.3	574.7	576.5	575.6	575.2	574.8	573.4	575.2	1.1
[Pd2L <sup>C</sup> 2L <sup>P</sup> L <sup>P</sup> ']	598.6	596.7	598.8	597.7	597.2	599.2		598.2	1.0
$[\mathbf{Pd_2L^C_2L^{P'_2}}]$	620.2	616.8	619.9	619.1	618.9	619.2	617.9	619.1	1.2

The formula for a system containing two colliding molecules with different radii (here: cage and collision gas  $N_2$ ) is given as (Equation 4):<sup>[13][14]</sup>

$$CCS = \pi (r_1 + r_2)^2$$
(4)

For scattering events in the gas phase, the radius taken into consideration is not the actual atom radius but the kinetic radius determining the size of the sphere of influence of the molecule in question.<sup>[15]</sup> For nitrogen, this radius is given as  $r(N_2) = 1.82$  Å derived from its kinetic diameter.

Table SI 3 gives the averaged radii derived from the eCCS values.

Species	eCCS [BF4@Cage] <sup>3+</sup> [Å <sup>2</sup> ]	Calculated radius according to equation (4) [Å]
$[Pd_2L^F_2L^P_2]$	532.7	11.66
$[\mathbf{Pd_2L^F_2 \ L^PL^P'}]$	552.4	11.93
$[Pd_2L^F_2L^{P'}_2]$	575.2	12.14
[Pd <sub>2</sub> L <sup>C</sup> L <sup>F</sup> L <sup>P</sup> <sub>2</sub> + BF <sub>4</sub> ] <sup>3+</sup>	543.8	11.88
a) [Pd <sub>2</sub> L <sup>C</sup> L <sup>F</sup> L <sup>P</sup> L <sup>P'</sup> + BF <sub>4</sub> ] <sup>3+</sup>	562.9	12.11
b) [Pd <sub>2</sub> L <sup>C</sup> L <sup>F</sup> L <sup>P</sup> L <sup>P'</sup> + BF <sub>4</sub> ] <sup>3+</sup>	567.2	12.16
[Pd <sub>2</sub> L <sup>C</sup> L <sup>F</sup> L <sup>P′</sup> <sub>2</sub> + BF <sub>4</sub> ] <sup>3+</sup>	587.2	12.39
$[\mathbf{Pd}_{2}\mathbf{L}^{\mathbf{C}}_{2}\mathbf{L}^{\mathbf{P}}_{2}]$	575.6	12.25
[Pd <sub>2</sub> L <sup>C</sup> <sub>2</sub> L <sup>P</sup> L <sup>P</sup> ']	600.9	12.52
$[\mathbf{Pd_2L^C_2L^{P'}2}]$	625.1	12.76

Table SI 3: Averaged radii of all ten species [Cage + BF<sub>4</sub>]<sup>3+</sup> calculated using equation (4).

#### 4.2 Calculation of CCS values

In order to obtain refined theoretically determined collisional cross sections three different programs, MOBCAL,<sup>[2]</sup> IMoS<sup>[3][4]</sup> and Collidoscope,<sup>[5]</sup> were used. With MOBCAL and Collidoscope the trajectory method, which consists of a simulation of the interaction of the analyte with the collision gas was chosen. With IMoS a different method, the projectory method averaging the projected 2D area according to Van-der-Waals radii ( $\xi = 1.2$ ), was used. In preparation for the CCS calculations we used GFN-xTB developed by Grimme *et al.*<sup>[1]</sup> as a method for geometry optimization. This way, for each cage, three values (tCCS<sup>PA</sup> tCCS<sup>M</sup> and tCCS<sup>C</sup>) were obtained. Interestingly, MOBCAL and IMoS are able to reproduce the experimentally observed, gradual CCS increase from [Pd<sub>2</sub>L<sup>F</sup><sub>2</sub>L<sup>P</sup><sub>2</sub> + BF<sub>4</sub>]<sup>3+</sup> to [Pd<sub>2</sub>L<sup>C</sup><sub>2</sub>L<sup>P'</sup><sub>2</sub> +

BF<sub>4</sub>]<sup>3+</sup> quite well (with MOBCAL values in average about 6% overestimated, IMoS values about 2% underestimated) while Collidoscope shows a much lower match of the calculated with the observed trend (see Fig. SI 45).

**Table SI 4**: Comparison of experimental (eCCS) values with results derived from softwares MOBCAL (tCCS<sup>M</sup>), IMoS (tCCS<sup>PA</sup>) and Collidoscope (tCCS<sup>C</sup>) based on the GFN-xTB optimized models with one encapsulated  $BF_4^-$  counter anion.

Species	eCCS [Ų]	tCCS <sup>PA</sup> [Å <sup>2</sup> ]	tCCS <sup>M</sup> [Ų]	tCCS <sup>c</sup> [Å <sup>2</sup> ]
$[Pd_2L_2^F L_2^P + BF_4]^{3+}$	$526.3\pm0.7$	491.0	540.8	586.6
$[Pd_{2}L^{F}_{2}L^{P}L^{P'} + BF_{4}]^{3+}$	$547.9\pm0.5$	515.1	566.9	539.2
$[Pd_2L_2^F L_2^{P'} + BF_4]^{3+}$	$566.1 \pm 1.3$	543.7	600.4	648.4
$[\mathbf{P}\mathbf{d}_{2}\mathbf{L}^{\mathrm{C}}\mathbf{L}^{\mathrm{F}}\mathbf{L}^{\mathrm{P}}_{2} + \mathbf{B}\mathbf{F}_{4}]^{3+}$	$543.8\pm0.4$	526.1	572.9	617.7
a) $[Pd_2L^{C}L^{F}L^{P}L^{P'} + BF_4]^{3+}$	$562.9 \pm 1.0$	553.7	601.8	591.6
<b>b</b> ) $[Pd_2L^CL^FL^PL^{P'} + BF_4]^{3+}$	$567.2\pm0.8$	556.6	602.6	643.7
$[Pd_{2}L^{C}L^{F}L^{P'}_{2} + BF_{4}]^{3+}$	$587.2\pm0.7$	581.7	630.6	570.8
$[Pd_2L_2^{C}L_2^{P} + BF_4]^{3+}$	$575.2 \pm 1.1$	565.7	611.9	575.0
$[Pd_2L_2^{C}L_2^{P}L_2^{P'} + BF_4]^{3+}$	$598.2\pm1.0$	591.1	633.8	668.5
$[Pd_2L_2^{C}L_2^{P'} + BF_4]^{3+}$	$619.1\pm1.2$	616.7	664.8	606.3



**Figure SI 45**: Comparison of experimental (eCCS; green) values calculated using the softwares Collidoscope (tCCS<sup>C</sup>; orange:  $[Cage + BF_4]^{3+}$ ), MOBCAL (tCCS<sup>M</sup>; light red:  $[Cage + BF_4]^{3+}$ ) and IMoS (tCCS<sup>PA</sup>; light blue:  $[Cage + BF_4]^{3+}$ ).

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