Supplementary Material (ESI) for Dalton Transactions
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Supporting information

Use of di-1,2,3-triazole “click’ ligands to self-assemble dipalladium(II) coordinatively saturated, quadruply stranded helicate cages.

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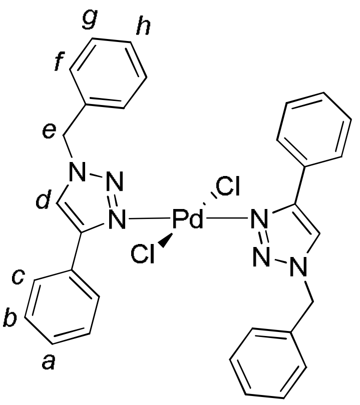
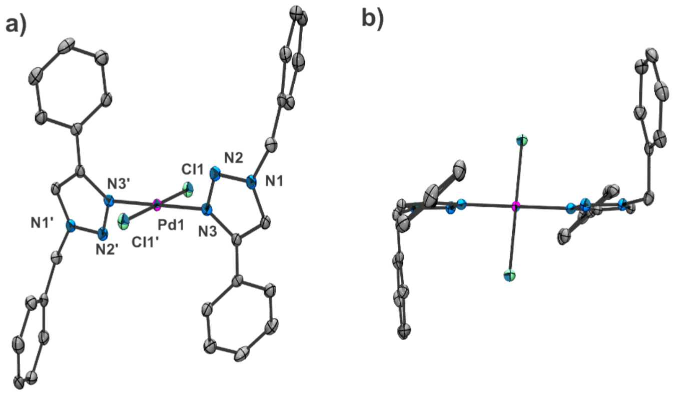
Experimental

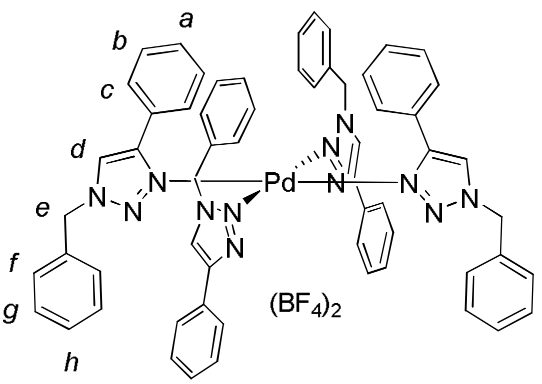
General Experimental Section. Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. The ligands **4a** and **4b** were prepared as previously described. Dry CH_2Cl_2 and CH_3CN were obtained by passing the solvents through an activated alumina column on a PureSolvTM solvent purification system (Innovative Technologies, Inc., MA). Petrol refers to the fraction of petroleum ether boiling in the range 40-60 °C. Flash column chromatography was carried out using Kiesegel C60 (Fisher) as the stationary phase. Analytical TLC was performed on precoated silica gel plates (0.25 mm thick, 60F254, Merck, Germany) and observed under UV light. All melting points were determined using a Sanyo Gallenkamp apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a 500 MHz Varian UNITY INOVA or 400 MHz Varian 400 MR spectrometer at 298 K. Chemical shifts are reported in parts per million and referenced to residual solvent. Coupling constants (J) are reported in Hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, quint. = quintet, q = quartet, t = triplet, d = doublet, s = singlet, br = broad. IR spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR spectrometer using KBr discs. Microanalyses were performed at the Campbell Microanalytical Laboratory at the University of Otago. ESI Mass Spectra were collected on a Bruker micro-TOF-Q spectrometer.

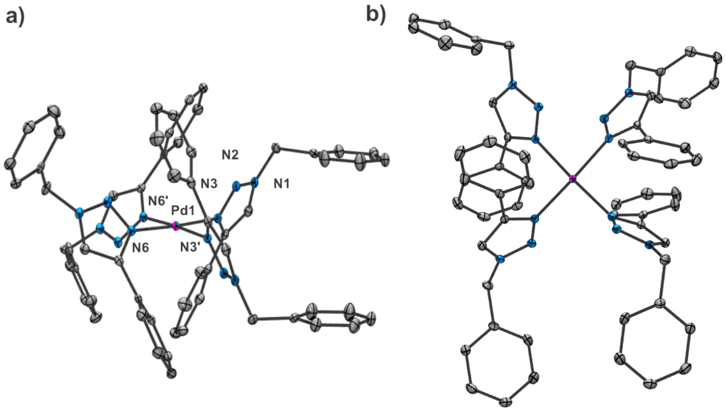
Safety Note: Sodium azide is toxic and appropriate precautions should be taken. As low molecular weight organic azides are potentially explosive, care must be taken during their handling.[27] *Generally, when the total number of carbon (C) plus oxygen (O) atoms is less than the total number of nitrogen atoms (N) by a ratio of three, i.e.,* $(C + O) / N < 3$, *the compound is considered an explosion hazard. A standard PVC blast shield was used when necessary. Additionally, copper azides and acetylides are explosive when dry, and their traces should be removed before the CuAAC reaction products are dried. This is achieved by pouring the crude reaction mixture into 100 mL of aqueous EDTA/*NH_4OH.



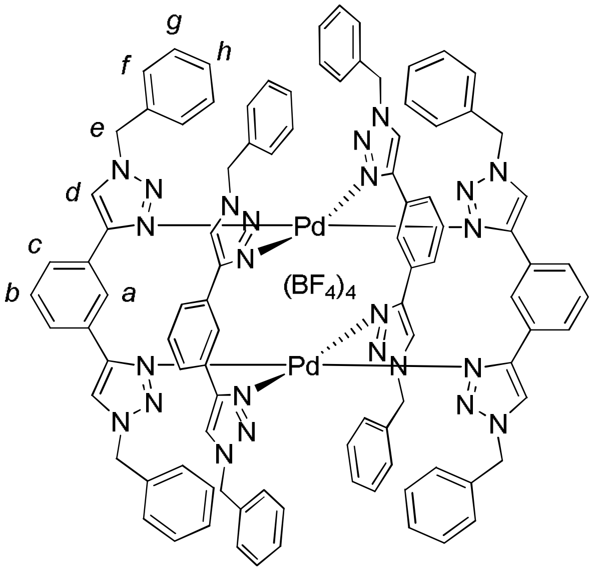


3a. $Pd(CH_3CN)_2Cl_2$ (0.040 g, 0.154 mmol, 1 equiv.) in acetone (2.5 mL) was added to a solution of **1** (0.073 g, 0.308 mmol, 2 equiv.) in acetone (2.5 mL). After stirring at room temperature for 1 h the solution was filtered through a plug of cotton wool and vapour diffused with diethyl ether, producing large, yellow, X-ray quality crystals of **3a**. Yield 0.072 g, 72 %. Mp 170 ˚C (decomp.); ^{1}H NMR (400 MHz, *d*$_6$-DMSO) δ 8.63 (s, 2H, H_d), 7.84 (d, J = 7.3, 4H, H_c), 7.38 (m, 16H, $H_{a,b,e,f,h}$), 5.64 (s, 4H, H_e); ^{13}C NMR (125 MHz, *d*$_6$-DMSO) δ 146.6, 135.9, 130.6, 128.8, 128.8, 128.1, 127.8, 127.5, 125.1, 121.5, 52.9; I. R. (KBr): υ (cm^{-1}) 3137, 3114, 3041, 3035, 1708, 1612, 1581, 1563, 1498, 1488, 1454, 1359, 1242, 1173, 1106, 1030, 1006, 815, 759, 740, 695; HRESI-MS (DMSO/MeOH): m/z = 375.9845 [Pd(**1**)Cl]$^+$ (calc. for $C_{15}H_{13}ClN_3Pd$ 375.9833), 575.1255 [Pd(**1**)$_2$(-H)]$^+$ (calc. for $C_{30}H_{25}N_6Pd$ 575.1176), 848.2111 [Pd(Cl)(**1**)$_3$] (calc. for $C_{45}H_{39}ClN_6Pd$ 848.2056); Anal. calc for $C_{30}H_{26}Cl_2N_6Pd$: C, 55.61; H, 4.04; N, 12.97; Found C, 55.52; H, 4.10; N, 12.98.

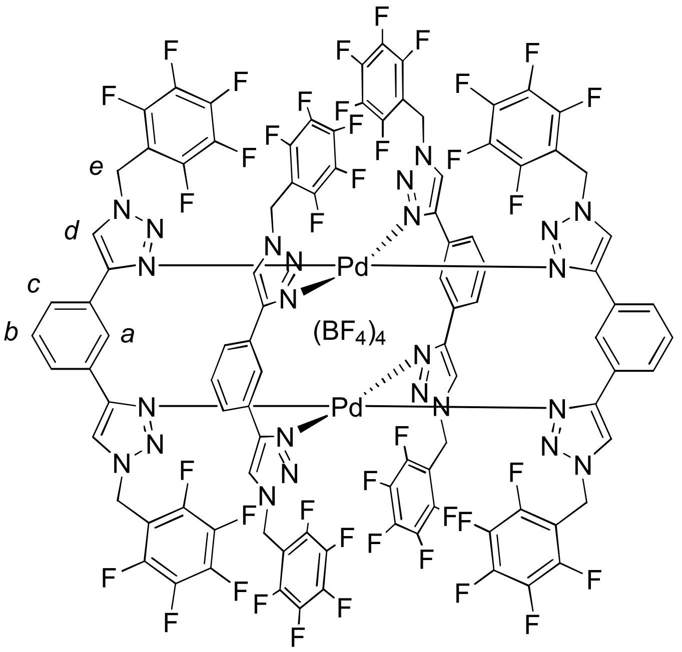




3c. [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ (0.040 g, 0.0.090 mmol, 1 equiv.) in acetone (2.5 mL) was added to a solution of **1** (0.085 g, 0.360 mmol, 4 equiv.) in acetone (2.5 mL). After stirring at room temperature for 1 h the solution was filtered through a plug of cotton wool and vapour diffused with diethyl ether, producing large, yellow, X-ray quality crystals of **3c**. Yield 0.088 g, 80 %. Mp 184 °C (decomp.); ^{1}H NMR (500 MHz, CD$_3$CN) δ 7.85 (s, 4H, H$_d$), 7.66 – 7.56 (m, 24H, H$_{b,f,g}$), 7.36 – 7.25 (m, 8H, H$_{a,h}$), 7.05 (dd, *J* = 5.3, 3.4, 8H, H$_c$), 5.17 (s, 8H, H$_e$); ^{13}C NMR (125 MHz, CD$_3$CN) δ 150.2, 134.3, 131.9, 130.5, 130.4, 130.3, 130.1, 129.7, 127.7, 126.1, 56.9; I. R. (KBr): υ (cm^{-1}) 3142, 3116, 3043, 3035, 1958, 1895, 1817, 1612, 1581, 1563, 1498, 1488, 1458, 1445, 1428, 1376, 1354, 1280, 1250, 1229, 1212, 1162, 1118, 1037, 1009, 920, 839, 764, 728; HRESI-MS (acetone/MeOH): *m/z* = 575.1333 [Pd(**1**)$_2$(-H)]$^+$ (calc. for C$_{30}$H$_{25}$N$_6$Pd 575.1176), 830.2424 [Pd(**1**)$_3$F]$^+$ (calc. for C$_{45}$H$_{39}$FN$_9$Pd 830.2347), 1133.3564 [Pd(**1**)$_4$](BF$_4$)$^+$ (calc. for C$_{60}$H$_{52}$BF$_4$N$_{12}$Pd 1133.3502); Anal. calc for C$_{60}$H$_{52}$B$_2$F$_8$N$_{12}$Pd: C, 59.01; H, 4.29; N, 13.76; Found C, 59.03; H, 4.27; N, 13.92.



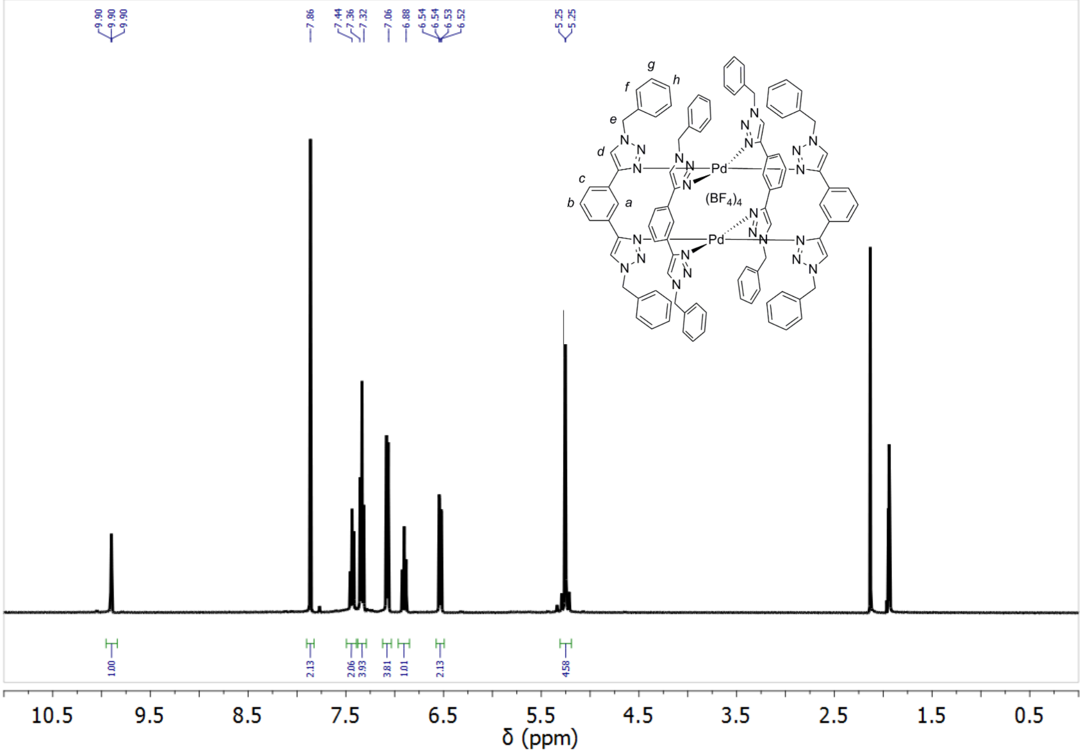
4a. $[Pd(CH_3CN)_4](BF_4)_2$ (0.066 g, 0.149 mmol, 1 equiv.) in acetonitrle (3.5 mL) was added to a solution of **3a** (0.117 g, 0.297 mmol, 2 equiv.) in acetone (3.5 mL). After stirring at room temperature for 1 h the solution was filtered through a plug of cotton wool and vapour diffused with diethyl ether, producing large, yellow, X-ray quality crystals of **4a**. Yield 0.138 g, 87 %. Mp >230 °C; ^{1}H NMR (500 MHz, CD_3CN) δ 9.90 (t, J = 1.6, 4H, H_a), 7.86 (s, 8H, H_d), 7.47 – 7.40 (m, 2H, H_h), 7.33 (m, 16H, H_g), 7.07 (dd, J = 8.0, 0.9, 16H, H_f), 6.90 (t, J = 7.9, 4H, H_b), 6.53 (dd, J = 7.9, 1.7, 8H, H_c); ^{13}C NMR (125 MHz, CD_3CN) δ 147.33, 133.98, 132.01, 131.12, 130.88, 130.5 (x2), 127.11, 126.42, 121.96, 57.26; I. R. (KBr): υ (cm^{-1}) 3137, 3059, 1622, 1586, 1568, 1497, 1485, 1457, 1409, 1350, 1306, 1230, 1207, 1166, 1119, 1001, 874, 801, 759, 713; HRESI-MS (CH_3CN): m/z = 393.1859 [**3a**+H]$^+$ (calc. for $C_{24}H_{21}N_6$ 393.1828), 600.5063 $[Pd_2($**3a**$)_4]F^{3+}$ (calc. for $C_{96}H_{80}FN_{24}Pd_2$ 600.5019), 704.1632 $[Pd_2($**3a**$)_3].H_2O^{2+}$ (calc. for $C_{27}H_{62}N_{18}OPd_2$ 704.1714), 978.2609 $[Pd_2($**3a**$)_4](BF_4)_2^{2+}$ (calc. for $C_{96}H_{80}B_2F_8N_{24}Pd_2$ 978.2565), 2043.5155 $[Pd_2($**3a**$)_4](BF_4)_3^+$ (calc. for $C_{96}H_{80}B_3F_{12}N_{24}Pd_2$ 2043.5159); Anal. calc for $C_{96}H_{80}B_4F_{16}N_{24}Pd_2 \bullet 2(H_2O)$: C, 53.24; H, 3.91; N, 15.52; Found C, 53.06; H, 3.70; N, 15.53.



4b. [Pd(CH_3CN)$_4$](BF_4)$_2$ (0.088 g, 0.198 mmol, 2 equiv.) in acetonitrile (6 mL) was added to a solution of **3b** (0.227 g, 0.396 mmol, 4 equiv.) in hot acetonitrile (9 mL). After stirring at room temperature for 1 h the solution was filtered through a plug of cotton wool and vapour diffused with diethyl ether, producing a cream coloured precipitate of **4b**. Yield 0.220 g, 79 %. Mp >230 ˚C; ^{1}H NMR (400 MHz, CD_3CN) δ 10.03 (s, 4H, H_a), 8.11 (s, 8H, H_d), 7.31 (t, *J* = 7.9, 4H, H_b), 7.13 (dd, *J* = 1.6, 7.9, 8H, H_c), 5.38 (dd, *J* = 15.3, 34.2, 16H, H_e); ^{13}C NMR (125 MHz, CD_3CN) δ 147.6, 146.9, 143.9, 139.0, 132.1, 131.7, 128.1, 126.4, 122.2, 110.1, 44.6; I. R. (KBr): υ (cm^{-1}) 3140, 3096, 1660, 1623, 1559, 1496, 1487, 1456, 1436, 1412, 1354, 1310, 1227, 1179, 1132, 1057, 1028, 971, 920, 805, 763, 696; HRESI-MS (CH_3CN): *m/z* = 625.5457 [Pd_2(**3b**)$_4$]$^{4+}$ (calc. for $C_{96}H_{40}F_{40}N_{24}Pd_2$ 625.5704), 863.0563 [Pd_2(**3b**)$_4$](BF_4)$^{3+}$ (calc. for $C_{96}H_{40}BF_{44}N_{24}Pd_2$ 863.0287), 1338.0760 [Pd_2(**3b**)$_4$](BF_4)$_2^{2+}$ (calc. for $C_{96}H_{40}B_2F_{48}N_{24}Pd_2$ 1338.0701), 2762.6539 [Pd_2(**3b**)$_4$](BF_4)$_3^{+}$ (calc. for $C_{96}H_{40}$ $B_3F_{52}N_{24}Pd_2$ 2762.6956); Anal. calc for $C_{96}H_{40}B_4F_{56}N_{24}Pd_2$•3($H_2O$): C, 39.71; H, 1.60; N, 11.58; Found C, 39.46; H, 1.49; N, 11.59.

1. ^{1}H NMR spectra of synthesized compounds.

^{1}H NMR (d_3-acetonitrile, 298 K) of **4a**.



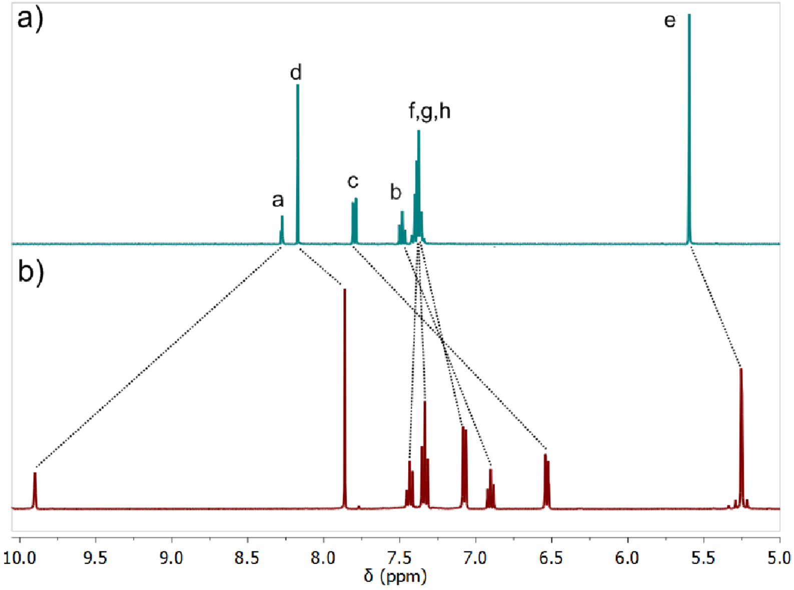
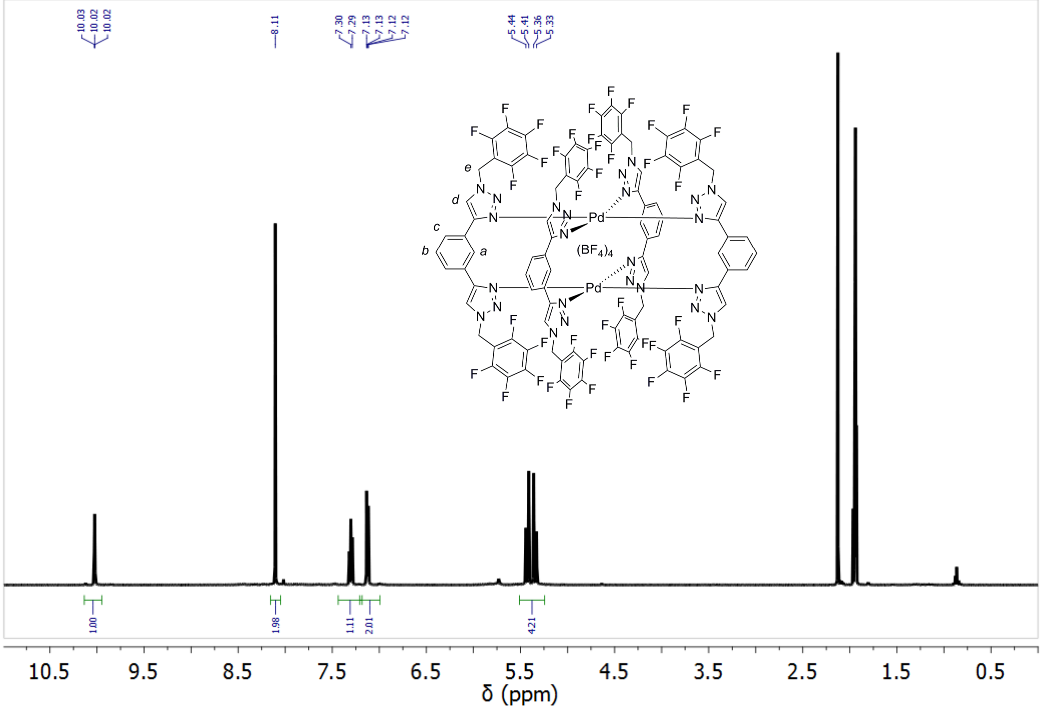


Figure 1. Partial ^{1}H NMR spectra (400 MHz, d_3-acetonitrile, 298 K) of a) Ligand **3a**, b) palladium cage complex **4a**.

^{1}H NMR (d_3-acetonitrile, 298 K) of **4b**.



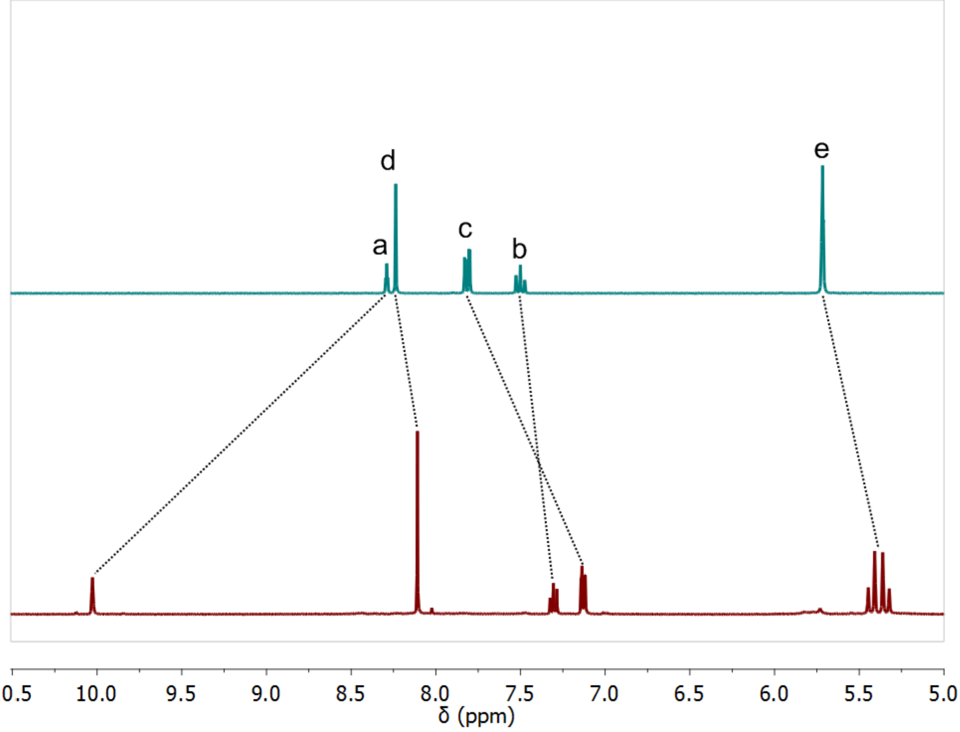


Figure 2. Partial ^{1}H NMR spectra (400 MHz, d_3-acetonitrile, 298 K) of a) Ligand **3b**, b) palladium cage complex **4b**.

2. DOSY NMR spectra of synthesized compounds.

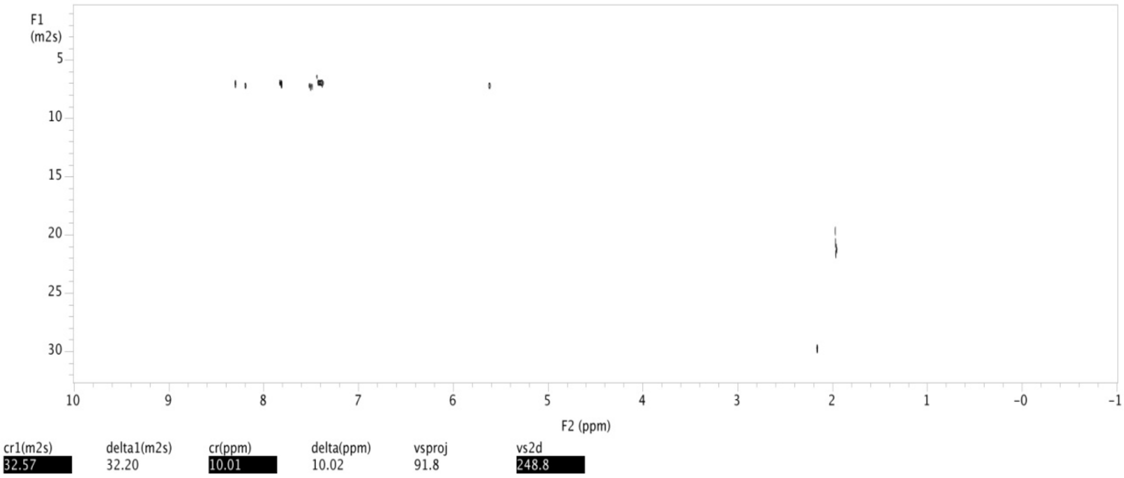


Figure 3a. The full DOSY NMR spectra (d_3-acetonitrile, 298 K) recorded for the ligand **3a.**

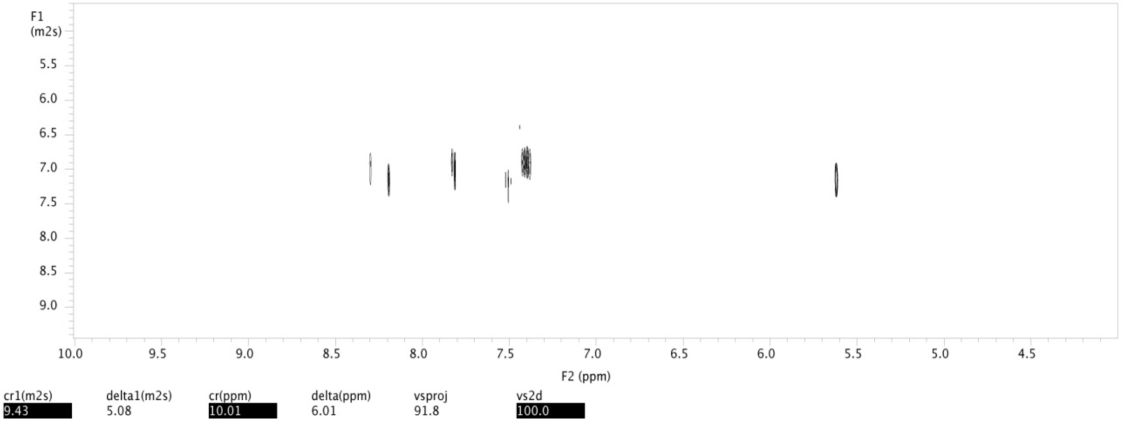


Figure 3b. A partial DOSY NMR spectra (d_3-acetonitrile, 298 K) recorded for the ligand **3a.**

The mean diffusion coefficient was 6.95 x 10^{-10} m^2/s.

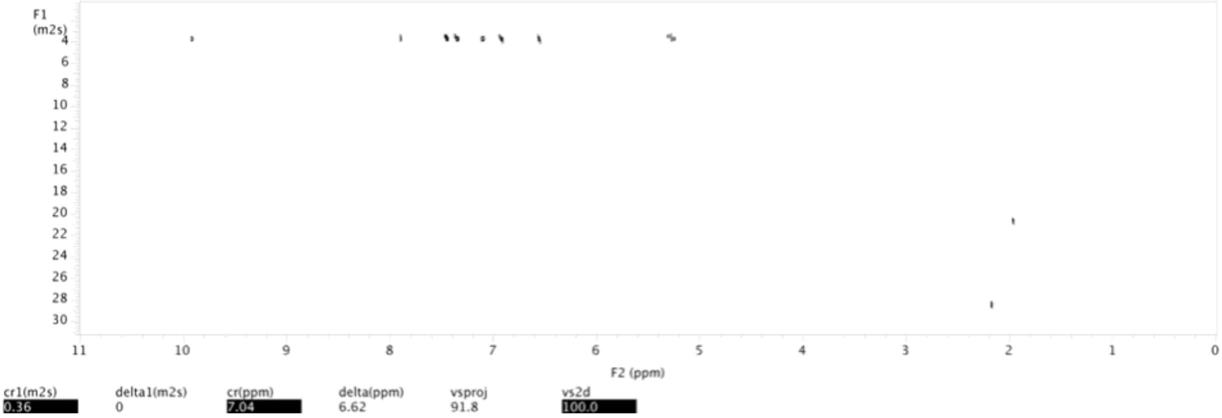


Figure 4a. The full DOSY NMR spectra (d_3-acetonitrile, 298 K) recorded for the cage **4a.**

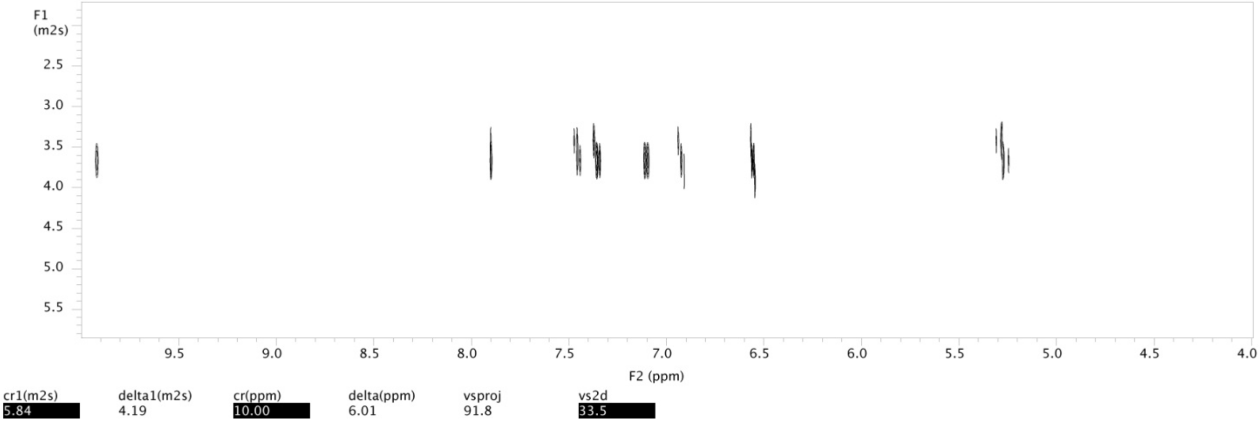


Figure 4b. A partial DOSY NMR spectra (d_3-acetonitrile, 298 K) showing only the signals of the palladium cage complex **4a.** The mean diffusion coefficient was 3.51 x 10^{-10} m^2/s respectively, giving a $D_{complex}/D_{ligand}$ ratio of 0.50:1.

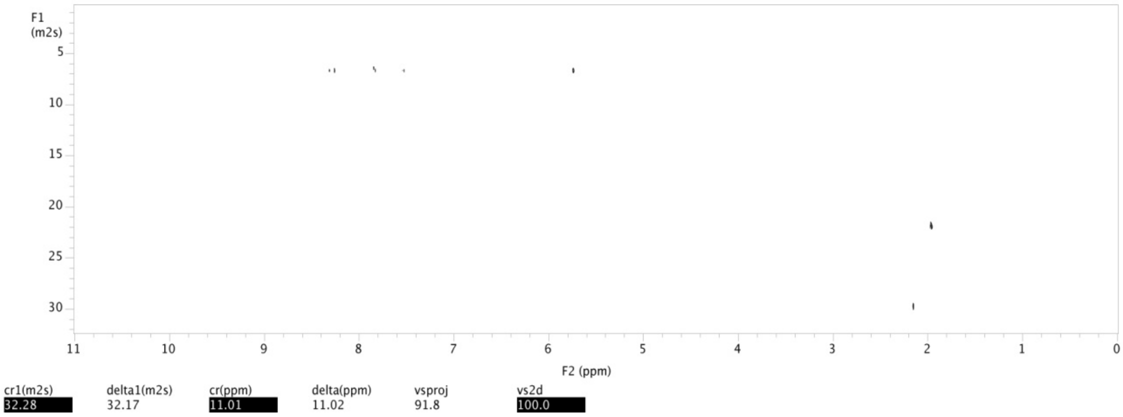


Figure 5a. The full DOSY NMR spectra (*d*$_3$-acetonitrile, 298 K) recorded for the ligand **3b.**

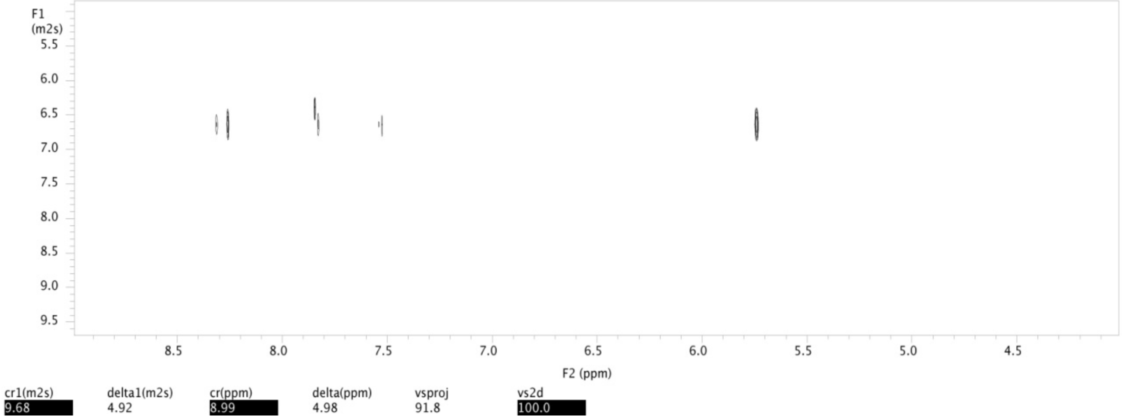


Figure 5b. A partial DOSY NMR spectra (*d*$_3$-acetonitrile, 298 K) recorded for the ligand **3b.**

The mean diffusion coefficient was 6.51×10^{-10} m^2/s.

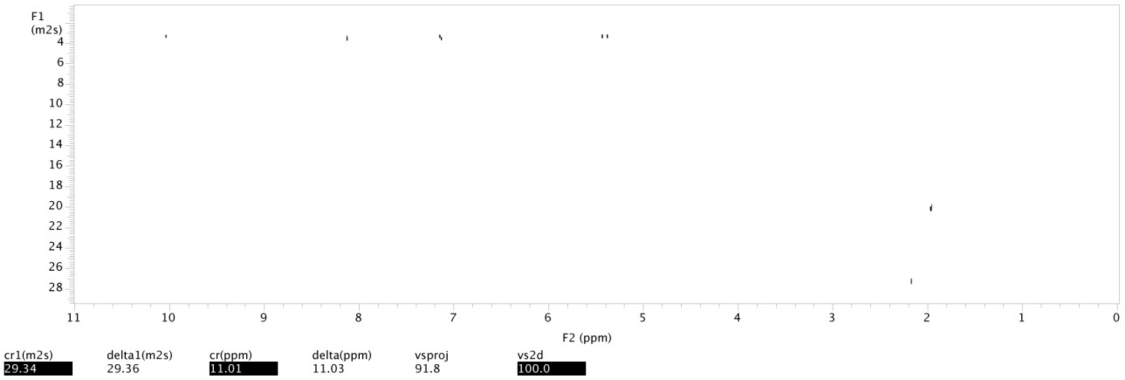


Figure 6a. The full DOSY NMR spectra (d_3-acetonitrile, 298 K) recorded for the cage **4b.**

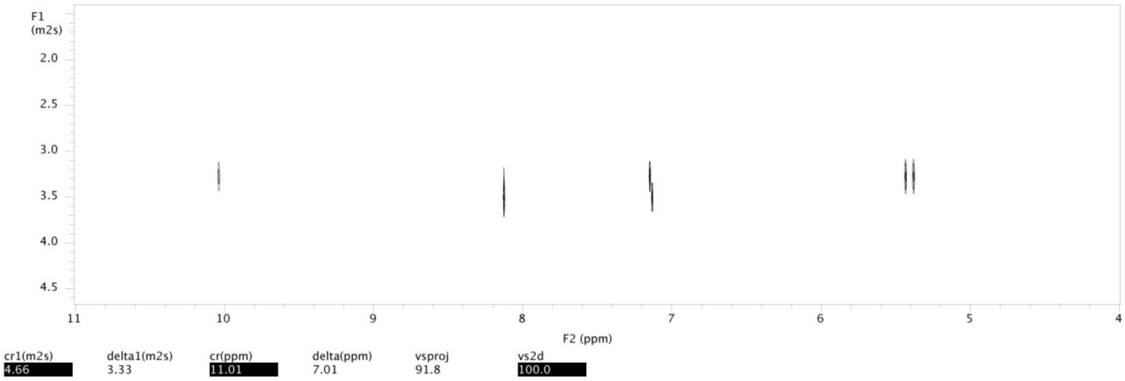


Figure 6b. A partial DOSY NMR spectra (d_3-acetonitrile, 298 K) showing only the signals of the palladium cage complex **4b.** The mean diffusion coefficient was 3.25×10^{-10} m^2/s respectively, giving a $D_{complex}/D_{ligand}$ ratio of 0.50:1.

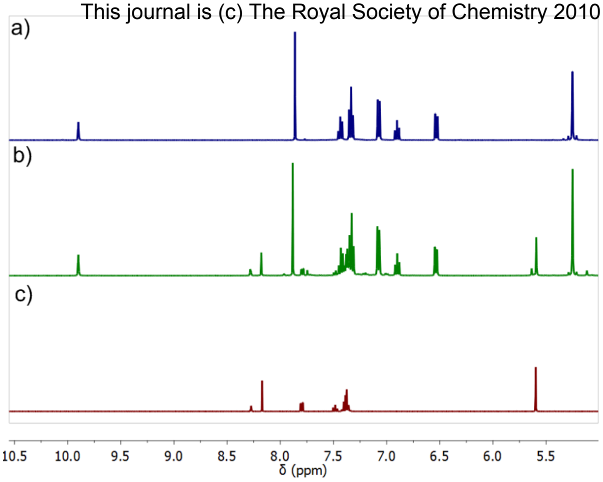


Figure 7a. Partial ^{1}H NMR spectra (400 MHz, d_3-acetonitrile, 298 K) of a) the cage **4a**, b) a 1:1 mixture of the **3a** and **4a**, c) the Ligand **3b.**

b) shows that the palladium cage is stable in the presence of excess ligand.

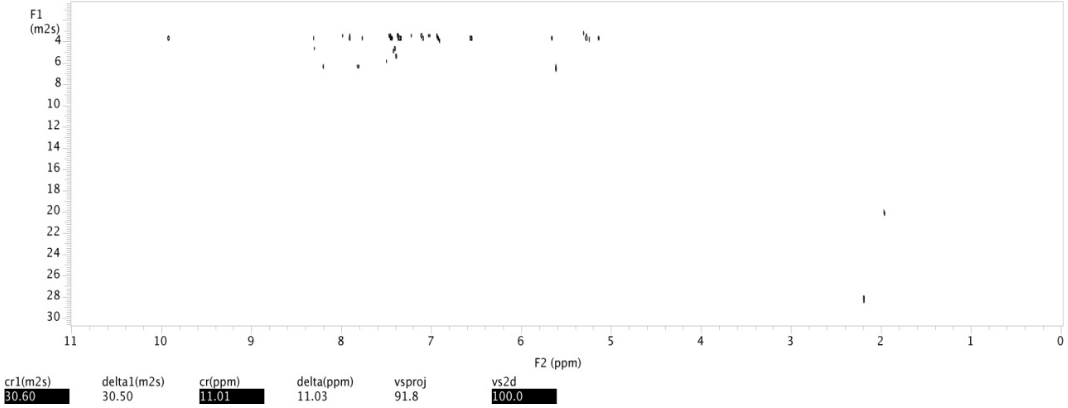


Figure 7b. DOSY spectra (d_3-acetonitrile, 298 K) recorded for a 1:1 mixture of ligand **3a** and palladium cage complex **4a.**

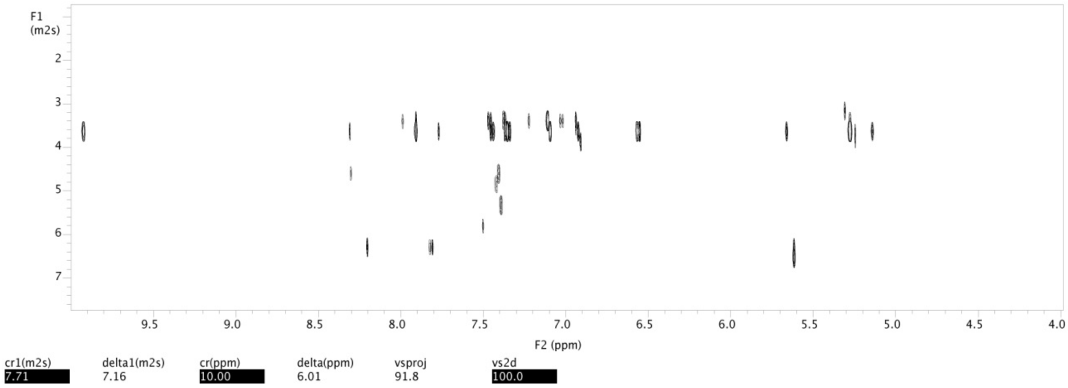


Figure 7c. Partial DOSY spectra (d_3-acetonitrile, 298 K) recorded for a 1:1 mixture of ligand **3a** and palladium cage complex **4a.** Illustrating that the ligand and the palladium cage have different mean diffusion coefficients.

3. SPARTAN molecular models of the cage complex, **4a.**

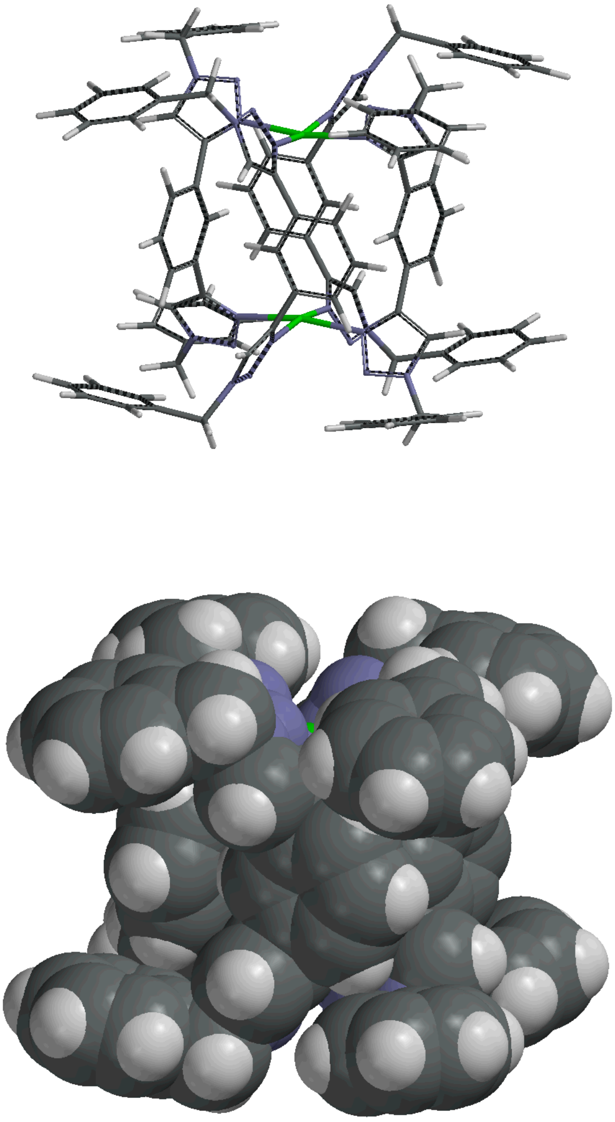


Figure 3. Space Filling (CPK, bottom) and tube (top) molecular models of the palladium (II) cage complex formed between **3a** and [Pd(CH_3CN)$_4$](BF_4). (Spartan '06 Essential Edition for Windows, Wavefunction, Irvine, CA)

4. HR-ESMS Spectra of the palladium cage complexes.

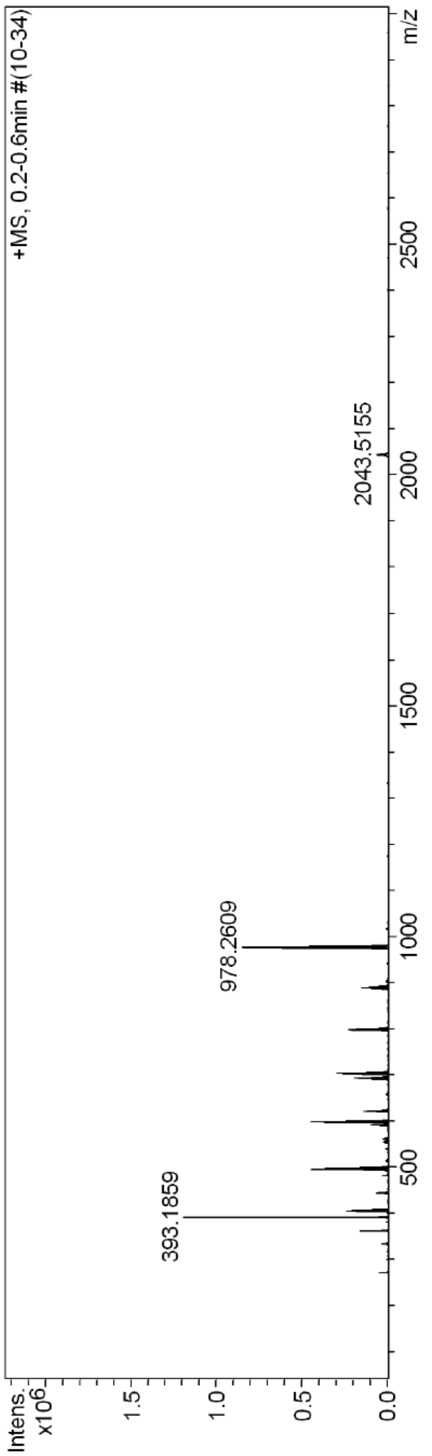


Figure 4. HR-ESMS (CH_3CN) of $[Pd_2(\mathbf{3a})_4](BF_4)_4$, **4a**: *m/z* = 393.1859 $[\mathbf{3a}+H]^+$ (calc. for $C_{24}H_{21}N_6$ 393.1828), 600.5063 $[Pd_2(\mathbf{3a})_4]F^{3+}$ (calc. for $C_{96}H_{80}FN_{24}Pd_2$ 600.5019), 704.1632 $[Pd_2(\mathbf{3a})_3].H_2O^{2+}$ (calc. for $C_{27}H_{62}N_{18}OPd_2$ 704.1714), 978.2609 $[Pd_2(\mathbf{3a})_4](BF_4)_2^{2+}$ (calc. for $C_{96}H_{80}B_2F_8N_{24}Pd_2$ 978.2565), 2043.5155 $[Pd_2(\mathbf{3a})_4](BF_4)_3^+$ (calc. for $C_{96}H_{80}B_3F_{12}N_{24}Pd_2$ 2043.5159).

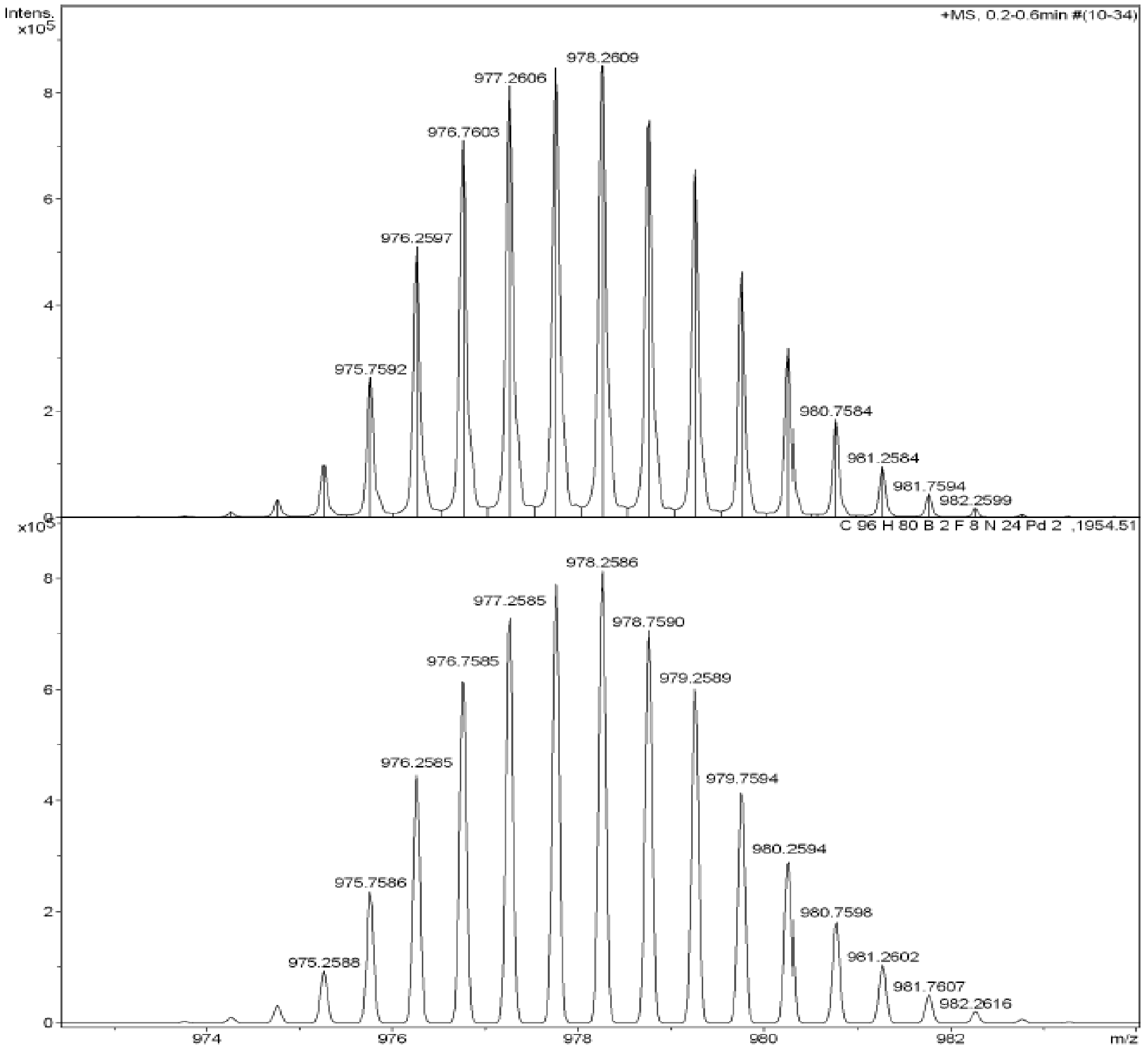


Figure 5. Observed (top) and calculated (bottom) isotopic distribution for the $[Pd_2(\mathbf{3a})_4](BF_4)_2^{2+}$ ion.

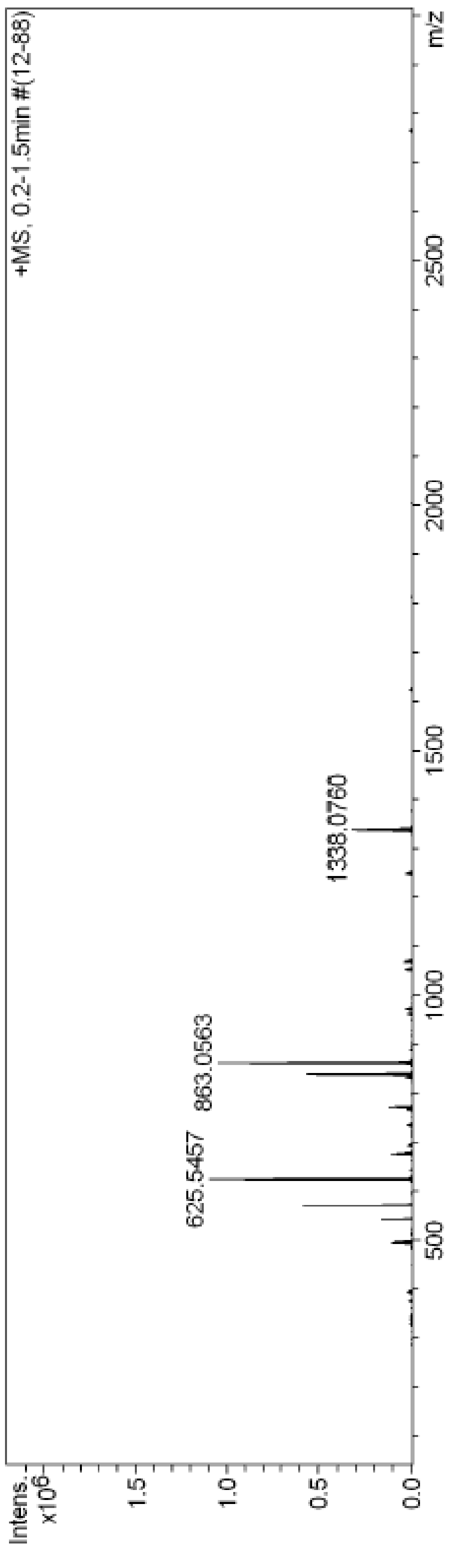


Figure 6. HR-ESMS (CH_3CN) of [Pd_2(**3b**)$_4$](BF_4)$_4$, **4b**: *m/z* = 625.5457 [Pd_2(**3b**)$_4$]$^{4+}$ (calc. for $C_{96}H_{40}F_{40}N_{24}Pd_2$ 625.5704), 863.0563 [Pd_2(**3b**)$_4$](BF_4)$^{3+}$ (calc. for $C_{96}H_{40}BF_{44}N_{24}Pd_2$ 863.0287), 1338.0760 [Pd_2(**3a**)$_4$](BF_4)$_2$$^{2+}$ (calc. for $C_{96}H_{40}B_2F_{48}N_{24}Pd_2$ 1338.0698).

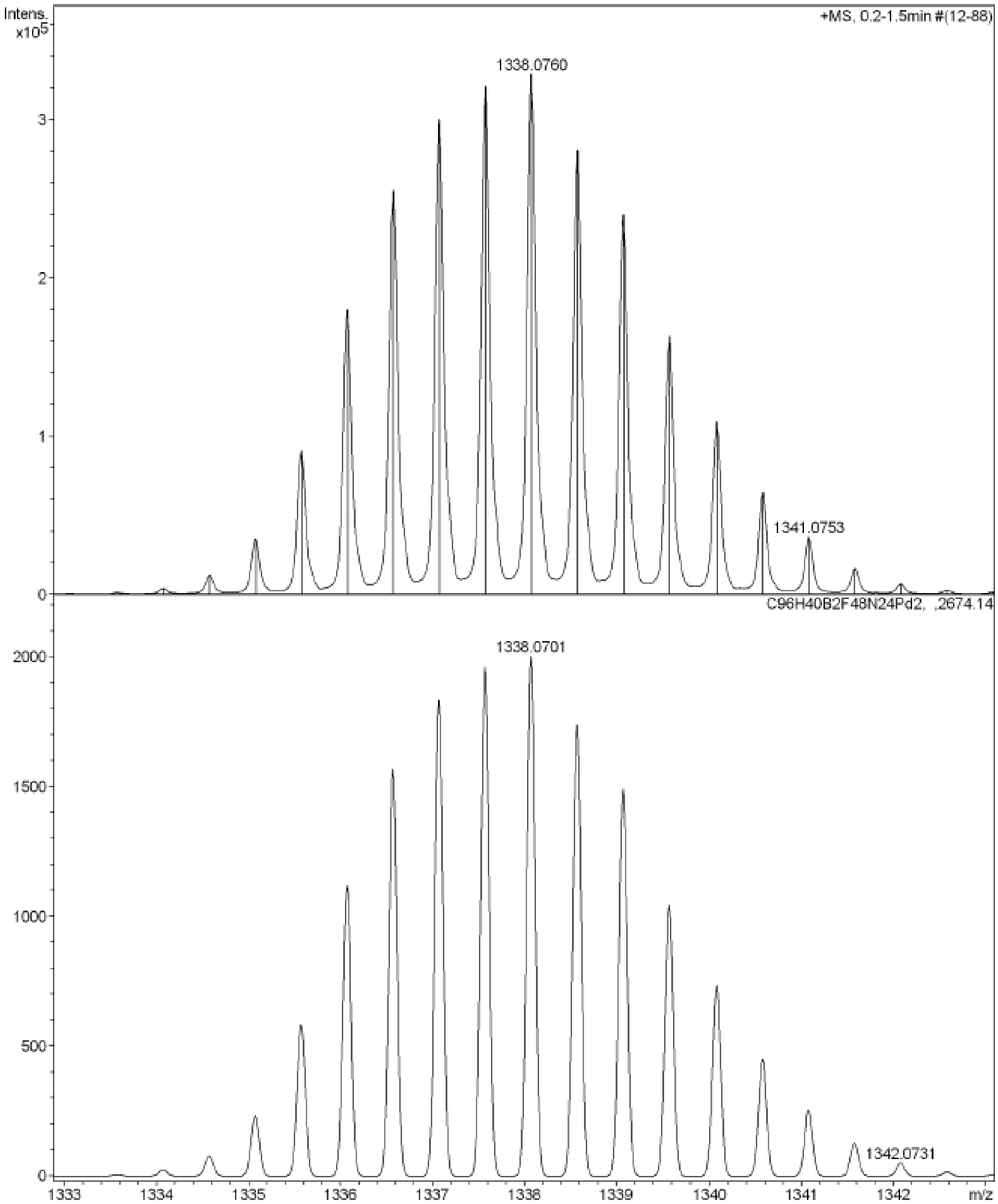


Figure 7. Observed (top) and calculated (bottom) isotopic distribution for the $[Pd_2(\mathbf{3b})_4](BF_4)_2^{2+}$ ion.

5. X-ray Crystallographic Data

5.1 X-ray data collection and refinement. X-ray data for **2a**, **2b**, and **4a** were recorded with a Bruker APEX II CCD diffractometer at 89(2) K using Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods using SIR97,[28] with the resulting Fourier maps revealing the location of all non-hydrogen atoms. Weighted full matrix refinement on F^2 was carried out using SHELXL-97[29] with all non-hydrogen atoms being refined anisotropically. The hydrogen atoms were included in calculated positions and were refined as riding atoms with individual (or group, if appropriate) isotropic displacement parameters. Following the location of the all the cage atoms and BF_4^- counter ions of **4a** in the ΔF map there was still residual electron density present within channels through the structure. This was modelled as disordered CH_3CN and H_2O solvate molecules. The bond lengths in the CH_3CN have been restrained to reasonable values using DFIX commands and the molecule refined isotropically due to the large thermal parameters observed when the atoms were refined anisotropically. The hydrogen atoms were place in calculated positions. After this there was still further residual electron density present within channels through the structure. Despite not appearing to hydrogen bond to a suitable acceptor atom this could only be sensible modelled as an isolated molecule of water. The anisotropically refined oxygen atom has relatively large thermal parameter but is could be caused by disorder due the lack of suitable a suitable hydrogen bond acceptor atom.

All ORTEP[30] diagrams have been drawn with 50% probability ellipsoids. Crystal data and collection parameters are given in Table 1. The CIF files CCDC 762916 (**2a**), CCDC 762918 (**2b**), and CCDC 762916 (**4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033.

Table 5.1: Crystal data and structure refinement for **2a, 2b** and **4a.**

Identification code	**2a** (CCDC 762917)	**2b** (CCDC 762918)	**4a** (CCDC 762916)
Empirical formula	$C_{30}H_{26}N_6Cl_2Pd$	$C_{60}H_{52}B_2F_8N_{12}Pd$	$2(C_{96}H_{80}N_{24}Pd_2)$, $8(BF_4)$, $2(C_2N)$, (H_2O)
Formula weight	647.87	1221.16	4359.89
Temperature	89(2)	89(2)	89(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	C2/c	C2/c
a/Å, b/Å, c/Å	8.359(5), 10.659(6), 15.168(9)	23.049(2), 17.376(1), 16.972(1)	30.5603(16), 30.6231(16), 22.7124(13)
α/°, β/°, γ/°,	90, 103.825(27), 90	90, 125.440(2), 90	90, 111.738(3), 90
Volume/Å^3	1312.3(13)	5537.9(7)	19743.9(18)
Z	2	4	4
ρ_{calc}mg/mm^3	1.64	1.465	1.467
m/mm^{-1}	0.944	0.415	0.456
F(000)	656	2496	8856
Crystal size	0.69 × 0.4 × 0.16	0.58 × 0.4 × 0.12	0.56 × 0.35 × 0.29
Theta range for data collection	3.15 to 25.5°	2.34 to 25.5°	0.98 to 24.31
Index ranges	$-10 \leq h \leq 10$, $-12 \leq k \leq 12$, $-18 \leq l \leq 18$	$-27 \leq h \leq 27$, $-20 \leq k \leq 21$, $-20 \leq l \leq 18$	$-33 \leq h \leq 33$, $-35 \leq k \leq 35$, $-26 \leq l \leq 26$
Reflections collected	18711	48793	136929
Independent reflections	2431[R(int) = 0.0313]	5157[R(int) = 0.0429]	16015[R(int) = 0.052]
Data/restraints/parameters	2431/0/178	5157/0/375	16015/2/1297
Goodness-of-fit on F^2	1.051	0.975	1.1
Final R indexes [I>2σ (I)]	$R_1 = 0.0191$, $wR_2 = 0.0447$	$R_1 = 0.0232$, $wR_2 = 0.053$	$R_1 = 0.0557$, $wR_2 = 0.1458$
Final R indexes [all data]	$R_1 = 0.0218$, $wR_2 = 0.0461$	$R_1 = 0.0257$, $wR_2 = 0.0544$	$R_1 = 0.0653$, $wR_2 = 0.1558$
Largest diff. peak/hole	0.372/-0.311	0.288/-0.484	1.747/-0.866

6. References

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