Supplementary Information (SI) for Chemical Science.

Supporting Information for

The ubiquitous P(o-tol)$_3$ ligand promotes formation of catalytically active higher order palladacyclic clusters

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1. General Information

1.1 Compound Preparative Techniques

Reagents and solvents were purchased from Merck, Fluorochem, Alfa Aesar, and Fisher and used without further purification. The purity of chemicals was confirmed by NMR spectroscopy prior to use.

1.2 Instrument Details and Methods for Compound Characterization

NMR spectra were obtained in the solvent indicated in the text below, using a Bruker AVIIIHD 600 Widebore instrument (600 MHz [^{1}H], 565 MHz [^{19}F], 243 MHz [^{31}P], 151 MHz [^{13}C]) or a Bruker AVIIIHD 500 instrument (500 MHz [^{1}H], 471 MHz [^{19}F], 203 MHz [^{31}P], 125 MHz [^{13}C]). Chemical shifts (δ) are reported in parts per million (ppm) and were referenced to the residual non-deuterated solvent of the deuterated solvent used; $CDCl_3$: δ ^{1}H = 7.26 ($C\mathit{H}Cl_3$) and ^{13}C = 77.16 ($\mathit{C}DCl_3$); DCM-d_2 : ^{1}H = 5.32 ($CD\mathit{H}Cl_2$) and ^{13}C = 54.0 ($\mathit{C}D_2Cl_2$); THF-d_8 : δ ^{1}H = 3.59 ($OC\mathit{H}_2CH_2$), ^{13}C = 67.57 ($O\mathit{C}H_2CH_2$), ^{1}H = 1.73 ($OCH_2C\mathit{H}_2$) ^{13}C = 25.37 ($OCH_2\mathit{C}H_2$); C_6D_6 : δ ^{1}H = 7.16 ($C_6D_5\mathit{H}$), ^{13}C = 128.06 (C_6D_6). Spectral data were typically collected at 298 K (25 °C), unless stated otherwise. All ^{1}H NMR signals are reported as they appear in the spectrum, which in some cases may lead to there being more protons reported than there are in the compound (according to HRMS). This is often due to residual solvent peaks (either from the NMR solvent or solvent trapped in the compounds during crystallization) overlapping in the aromatic region.

^{31}P NMR spectral data were collected with proton decoupling, unless otherwise stated. Chemical shifts for ^{31}P resonances were calibrated by externally referencing to 85% H_3PO_4 in H_2O (w/w). This was practically carried out by inserting a sealed, vacuum-dried capillary tube containing 85% H_3PO_4 in H_2O (w/w) into an NMR tube containing the sample of interest, collecting a ^{31}P NMR spectrum and setting the $H_3\mathit{P}O_4$ resonance to 0 ppm. ^{19}F spectral data were referenced in the same manner using α,α,α-trifluorotoluene (-63.72 ppm with respect to $CFCl_3$). All ^{13}C NMR spectra were obtained with ^{1}H decoupling. All NMR spectra were processed using MestReNova (MNova) software (v. 14).

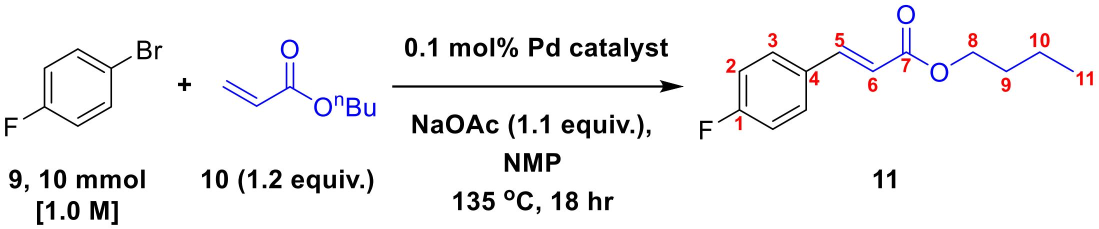
HRMS ESI-MS spectra were measured using a Bruker Daltronics micrOTOF MS, Agilent series 1200LC with electrospray ionization (ESI) or on a Thermo LCQ using electrospray ionization, with <5 ppm error recorded for all HRMS samples. LIFDI (Liquid Injection Field Desorption Ionization) mass spectrometry was carried out using a JEOL AccuTOF GCx-plus instrument (JMS-T200GC), fitted with a probe produced by Linden CMS. The probe was equipped with 13 µm emitters on an AccuTOF. Alternatively, LIFDI-MS was carried out using a Waters GCT Premier MS Agilent 7890A GC instrument. Mass to charge ratios (*m/z*) are reported in Daltons. High resolution mass spectra (HRMS) are reported with <5 ppm error (ESI and LIFDI). For clarity, LIFDI data are reported for ^{106}Pd, the most abundant natural isotope of Pd, which is part of 'exact mass' values. LIFDI ions are reported as the radical cation $M^{+\bullet}$. ESI ions are reported as the $[M+H]^+$ cation, unless a Na or K is present in the molecular formula, in which case the $[M+Na]^+$ or $[M+K]^+$ ion is being measured.

Infrared spectra were obtained using a Bruker ALPHA-Platinum FTIR Spectrometer with a platinum-diamond ATR sampling module. Far IR spectra were obtained using a Bruker Tensor 37 FTIR Spectrometer with a platinum-diamond ATR sampling module. Melting points were determined using a Stuart® SMP3 Melting Point machine. All Heck reaction kinetic experiments were followed using a Mettler Toledo React-IR spectrometer with a diamond probe. IR spectra were collected in real-time every 60 seconds between 4000 and 649 cm^{-1}, with a spectral resolution of 4 cm^{-1}. All reaction temperatures were measured independently from the heating bath using a TENMA 72-7715 electronic thermometer and thermocouple to ensure accurate reaction temperature regulation. All data analysis was carried out on raw, uncorrected data.

For single crystal X-ray crystallographic analysis details, please see Section 4.

2. Experimental Details

2.1 General Procedure: Heck Alkenylation Reaction



9, 10 mmol [1.0 M] **10 (1.2 equiv.)** **11**

An oven-dried three-necked 100 mL round bottom flask was fitted onto a Mettler-Toledo ReactIR probe (flexible silver halide diamond probe), fitted with a condenser. This was evacuated and backfilled with N_2 (three cycles). The flask was charged with NMP (10.0 mL, dried, degassed), then heated to 135 °C, at which point a solvent background IR spectrum was recorded. NaOAc (0.903 g, 11.0 mmol, 1.1 equiv., anhydrous) was added, followed by 1-bromo-4-fluorobenzene **9** (1.1 mL, 1.75 g, 10.0 mmol, 1.0 equiv., stored over molecular sieves), then catalyst (0.005 mmol, 0.1 mol% Pd) was added. The reaction was initiated by the addition of n-butyl acrylate **10** (1.539 g, 1.71 mL, 12.0 mmol, 1.2 equiv., stored over molecular sieves). The reaction progress was monitored by measuring the increase in absorbance at 1509 cm^{-1}, relating to the formation of n-butyl 4-fluorocinnamate **11**, and the decrease in absorbances at 1484 cm^{-1}, relating to the consumption of 1-bromo-4-fluorobenzene **9**, and 1190 cm^{-1}, relating to n-butyl acrylate **10**. To deconvolute the peaks and obtain reasonable quality data, the second derivative of the spectra was used. The reaction was halted when the peaks at these values reached a constant value, indicating completion. At the end of the reaction, a 0.5 mL aliquot of the reaction was analysed by ^{19}F NMR (20 s relaxation delay) to measure the conversion of each reaction. The final conversion was calculated by measuring the ratio of the diagnostic peaks by (^{19}F δ) -115.9 ppm for 1-bromo-4-fluorobenzene **9** and -109.8 ppm for n-butyl 4-fluorocinnamate **11**. The peak absorption data were imported into Excel after subtracting the NMP solvent reference spectrum. All kinetic traces (conversions) were normalised using the final reaction conversion (as calculated *vide supra*) and the value of an appropriate data point just before the aliquot was taken.

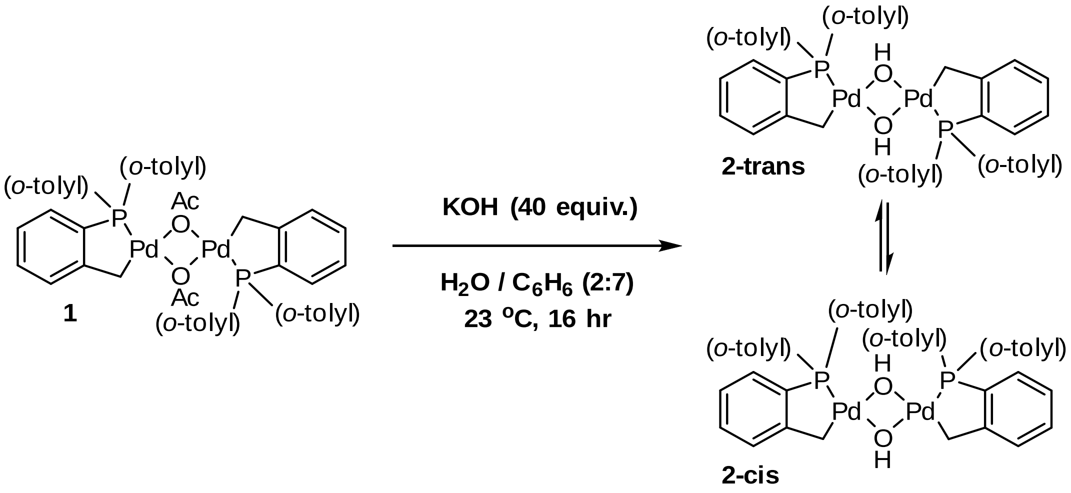
The identity of the product was confirmed by performing a reaction at half-scale in a Schlenk tube following the same procedure. The reaction mixture was extracted into EtOAc (3 x 20 mL), the organic layers were combined and washed with water (5 x 20 mL), dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude was purified by column chromatography (automated Combiflash, 12 g silica cartridge, 5% EtOAc in hexane), $R_f = 0.34$ (5% EtOAc in hexane)) to give the product **11** as a colourless oil (exclusively the *trans* isomer, 812 mg, 73% yield, using Herrmann-Beller palladacycle **1**). (Note: upon isolation, 2% of 4,4'-difluoro-biphenyl by-product co-eluted, which is visible in the ^1H and ^{19}F NMR as a trace impurity) ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.63 (d, *J* = 16.0 Hz, 1H, H-5), 7.54 – 7.47 (m, 2H, H-3), 7.10 – 7.03 (m, 2H, H-2), 6.36 (dd, *J* = 16.0, 0.6 Hz, 1H, H-6), 4.20 (t, *J* = 6.7 Hz, 2H, H-8), 1.73 – 1.63 (m, 2H, H-9), 1.48 – 1.38

(m, 2H, H-10), 0.96 (t, *J* = 7.4 Hz, 3H, H-11); ^{19}F NMR (470 MHz, C*D*Cl$_3$, 298 K) δ -109.85 (tt, *J* = 8.4, 5.4 Hz); ^{13}C NMR (126 MHz, C*D*Cl$_3$, 298 K) δ 167.1 (C-7), 164.0 (d, *J* = 251.3 Hz, C-1), 143.3 (C-5), 130.9 (d, *J* = 3.4 Hz, C-4), 130.0 (d, *J* = 8.5 Hz, C-3), 118.2 (d, *J* = 2.3 Hz, C-6), 116.1 (d, *J* = 22.0 Hz, C-2), 64.6 (C-8), 30.9 (C-9), 19.3 (C-10), 13.9 (C-11); HRMS (ESI$^+$) $(C_{13}H_{15}FO_2Na)^+$ *m/z* (calculated) 245.0948 (found) 245.0949, mass difference 0.3 ppm; FTIR (ATR): ṽ (cm^{-1}) 2960 (C-H aromatic), 2874 (C-H aliphatic), 1708 (s, C=O acrylate), 1639 (C=C alkene), 1600 (C=C aromatic), 1509, 1466, 1415, 1384, 1312, 1279, 1257, 1230, 1196, 1158 (vs, C-O stretch) 1095, 1063, 1025, 980, 868, 829, 790, 738, 509, 414. Data matches the literature for this compound.[1]

Lab book ref. DRH-03-159 (for characterisation data)

2.2 Synthesis of Compounds

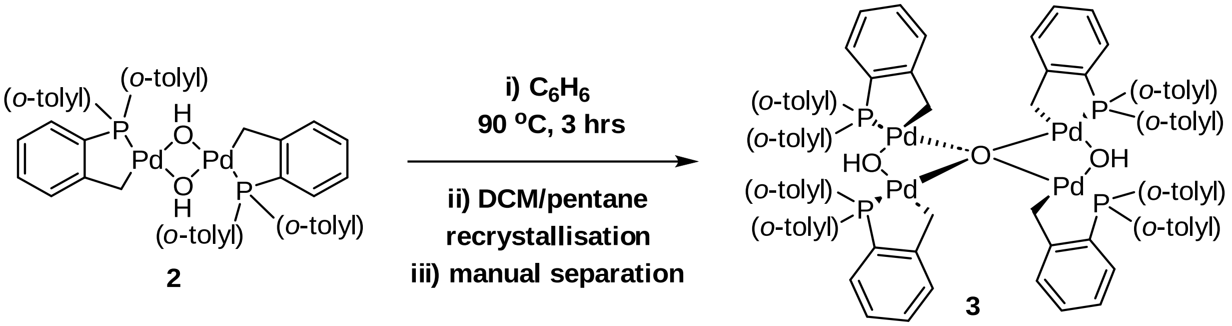
Synthesis of [Pd(P^C)(μ$_2$-OH)]$_2$ Palladacycle 2



All solvents were degassed with N$_2$, and all reactions and manipulations were performed under a nitrogen atmosphere. The Herrmann-Beller palladacycle **1** (750 mg, 0.80 mmol, 1 eq.) was added to benzene (15 mL) and stirred to give a yellow suspension. To this, KOH (2290 mg, 40.8 mmol, 51 eq.) dissolved in deionised water (4 mL) was added, and the biphasic mixture stirred vigorously for 18 h. The cream suspension in the benzene layer was decanted, and the aqueous layer extracted with warm benzene (60 °C, 4 × 6 mL). The organic layers were collected, washed with water (2 × 10 mL) and the solvent removed *in vacuo*, giving a cream coloured product **2** as *cis*/*trans* isomers in a 1:2 ratio in solution (683 mg, 66%); ^{1}H NMR (500 MHz, DCM-*d*$_2$, 203 K) (Note: due to the presence of several isomers in solution at low temperatures, this is a complex NMR spectrum with many peaks. As such, individual environments have only been assigned as aromatic (Ar-H), aliphatic (CH$_3$, CH$_2$), or bridging OH (μ-OH). The reported nucleotides here have been scaled to give an overall count of 42H, which is the theoretical number of protons on the structure, and have been reported to the nearest 0.5 (0.1 for the μ-OH environments) δ; 7.46

– 7.33 (m, 3.5H, Ar-*H*), 7.33 – 7.22 (m, 9H, Ar-*H*), 7.10 (dd, *J* = 13.2, 7.8 Hz, 3H, Ar-*H*), 7.08 – 6.98 (m, 1.5H, Ar-*H*), 6.95 (d, *J* = 11.0 Hz, 1H, Ar-*H*), 6.81 – 6.70 (m, 2.5H, Ar-*H*), 6.71 – 6.61 (m, 1H, Ar-*H*), 3.07 (d, *J* = 14.2 Hz, 0.5H, CH_2), 2.99 (s, ~3H (overlapping with impurity), CH_3), 2.99 – 2.90 (m, 2.5H, CH_2), 2.85 (d, *J* = 6.8 Hz, 1.5H, CH_2), 2.82 (d, *J* = 3.3 Hz, 0.5H, CH_2), 2.79 (s, 1.5H, CH_3), 2.75 (dd, *J* = 14.0, 3.3 Hz, 0.5H, CH_2), 2.64 (d, *J* = 2.9 Hz, 2.5H, CH_3), 2.53 (s, 3.5H, CH_3), 2.36 (s, 1H, CH_3), 2.22 (s, 1.5H, CH_3), -0.65 (s, 0.2H, μ-OH *cis*), -0.93 (s, 0.1H, μ-OH *cis*), -1.26 (d, 1.5H, *J* = 2.7 Hz, μ-OH *trans*), -1.40 (d, 0.5H, *J* = 2.8 Hz, μ-OH *trans*), -2.31 (s, 0.2H, μ-OH *cis*), -2.44 (s, 0.1H, μ-OH *cis*); ^{13}C NMR (135 MHz, DCM-d_2, 298 K) δ; 158.9 (dd, *J* = 31.5, 8.7 Hz, Ar-*C*), 142.8 (Ar-*C*), 135.8 (d, *J* = 56.3 Hz, Ar-*C*), 132.7 (Ar-*C*), 132.6 (Ar-*C*), 132.1 (Ar-*C*), 132.0 (Ar-*C*), 131.2 (d, *J* = 2.2 Hz, Ar-*C*), 131.2 (d, *J* = 2.5 Hz, Ar-*C*), 131.0 (Ar-*C*), 130.7 (Ar-*C*), 128.3 (dd, *J* = 21.5, 8.1 Hz, Ar-*C*), 126.2 (Ar-*C*), 125.8 (Ar-*C*), 125.7 (Ar-*C*), 125.7 (Ar-*C*), 26.6 (CH_2), 24.9 (CH_2), 23.0 (CH_3), 22.9 (CH_3), 22.8 (CH_3); ^{31}P NMR (202.5 MHz, DCM-d_2, 203 K) δ; 34.02 (*trans* isomer), 33.56 (*cis* isomer), 33.37 (*cis* isomer), 33.18 (*trans* isomer); HRMS (ESI$^+$) $(C_{42}H_{43}O_2P_2Pd_2)^+$ *m/z* (calculated) 853.0802 (found) 853.0785, mass difference 1.7 ppm, $(C_{21}H_{22}OPPd)^+$ *m/z* (calculated) 427.0438, (found) 427.0453, mass difference 1.6 ppm. FTIR (ATIR): $\tilde{\nu}$ (cm^{-1}) 3646 (O-H), 3051 (C-H aromatic), 2857 (C-H aliphatic), 1582 (C=C aromatic), 1466, 1440 (C-P), 1283, 1069, 750; Far IR (ATIR) $\tilde{\nu}$ (cm^{-1}) 586, 560, 525, 509, 477, 459, 441, 417, 362, 316, 269, 249; mp. decomposed above 188 °C. Lab book ref. DRH-01-108.

Synthesis of the Palladacyclic $Pd_4(\mu_4\text{-}O)(\mu_2\text{-}OH)_2$ Cluster 3



[Pd(P^C)(μ_2-OH)]$_2$ palladacycle **2** (45 mg, 0.053 mmol) was added to still-dried degassed benzene (3 mL) under Schlenk conditions. The yellow solution was vigorously stirred and refluxed under a static N_2 atmosphere for 2.5 h at 90 °C. The solvent was rapidly removed under vacuum, giving a pale-yellow powder. This powder was transferred to an argon glove box, where it was dissolved in *ca.* 0.8 mL of dry, degassed DCM and placed in a 4 small vials. These vials were placed in larger vials containing *ca.* 1.5 mL pentane, and the system was sealed. After 1 week, a mixture of colourless crystals and vibrant yellow crystals of $Pd_4(\mu_4\text{-}O)(\mu_2\text{-}OH)_2$ cluster **3** suitable for X-ray diffraction were obtained. The yellow crystals from two of the vials were manually separated under a microscope, giving 2.4 mg of **3** (projected total yield = 4.8 mg, 0.0028 mmol, 5%). ^{1}H NMR (500 MHz, DCM-d_2, 203 K) δ; 7.59 – 7.47 (m, 3H, Ar-*H*), 7.44 – 7.33 (m, 2H, Ar-*H*), 7.33 – 7.24 (m, 9H, Ar-*H*), 7.23 – 7.02 (m, 4H, Ar-*H*), 7.01 – 6.93 (m, 4H, Ar-*H*), 6.79 (dt, *J* = 18.8, 8.8 Hz, 4H, Ar-*H*), 6.69 (q, *J* = 9.3 Hz, 1H, Ar-*H*), 6.61 (d, *J* = 7.9 Hz, 1H, Ar-*H*), 6.56 – 6.48 (m, 1H, Ar-*H*), 6.41 (t, *J* = 8.6 Hz, 1H, Ar-*H*), 6.26 (d, *J* = 7.7 Hz, 1H, Ar-*H*), 6.22 (d, *J* = 7.9 Hz, 0.5H, Ar-*H*), 5.56 (d, *J* = 7.5 Hz, 1H), 4.54 (d, *J* = 14.6 Hz, 0.5H, CH_2), 4.48 (d, *J* = 14.0 Hz, 1H, CH_2), 4.42 (d, *J* = 13.6 Hz, 1H, CH_2), 4.36 (d, *J* = 13.8 Hz, 0.5H, CH_2), 4.26 (d, *J* = 13.6 Hz, 1H, CH_2), 3.98 (d, *J* = 14.0 Hz, 1H, CH_2), 3.71 (d, *J* = 14.5 Hz, 1H, CH_2), 3.51 – 3.38 (m, 1H, CH_2), 3.21 (d, *J* = 12.7 Hz, 1H, CH_2), 3.10 – 2.93 (m, 5H, CH_3), 2.88 (s, 6H, CH_3), 2.76 (d, *J* = 7.3 Hz, 4H, CH_3), 2.73 (s, 4H, CH_3), 2.71 – 2.63 (m, 4H, CH_3), 2.60 (s, 1H, CH_3), 2.56 (s, 4H, CH_3), 2.36 (s, 2H, CH_3), 2.25 (s, 1H, CH_3), -3.46 (s, μ-OH, 0.5H), -3.51 (s, μ-OH, 1H), -3.68 (s, μ-OH, 0.5H) (Note: Due to the complexity of the spectra, it is impossible to differentiate between peaks belonging to different isomers of **3** at low temperature. These isomer peaks have been denoted with 0.5H, indicating they are not fully populated proton environments. Additionally, because of the presence of a small amount of **2** forming in solution, only peaks relevant to the Pd_4 cluster **3** have been selected for ^{31}P NMR); ^{31}P NMR (203 MHz, DCM-d_2, 203 K) δ; 32.09, 30.08, 29.99, 29.38, 29.04, 28.85, 28.61; HRMS (LIFDI) $(C_{84}H_{82}O_3P_4Pd_4)^{+\bullet}$ *m/z* (calculated) 1686.13483, (found) 1686.14148, mass difference 3.95 ppm; (ATIR): $\tilde{v}$ (cm^{-1}) 3626 (O-H), 3050 (C-H aromatic), 2858 (C-H aromatic), 1582 (C=C aromatic), 1465, 1448 (C-P), 1282, 1071, 752, 440; Far IR (ATIR) $\tilde{v}$ (cm^{-1}) 583, 559, 523, 494, 468, 451 (Pd-O), 401, 374, 270, 248.

Lab book ref. DRH-01-131 (X-ray diffraction structure ijsf21009), DRH-01-146, DRH-01-152

Special Details for the Characterization and Catalytic use of 3

Due to difficulties in synthesizing and purifying $Pd_4(\mu_4\text{-}O)(\mu_2\text{-}OH)_2$ cluster **3**, the complex was isolated by recrystallizing a mixture of colourless $[Pd(P\text{^}C)(\mu_2\text{-}OH)]_2$ palladacycle **2** and yellow **3** by the method described above. The yellow crystals were manually separated and isolated using needles and scalpels in oil, yielding approximately 2 mg of **3** (2.4 mg by mass, but the presence of oil made accurate weighing impossible). To verify the identity of the yellow crystals, the unit cell parameters of one single crystal was checked against the known unit cell parameters of 3, giving a 100% match (Lab book ref. of crystal structure DRH-01-131). Microscope images of the yellow crystals during crystal picking are shown below. These crystals were characterised by ATIR, dissolved in DCM-d_2 (0.5 mL, dried over CaH_2, freeze-pump-thaw degassed) in an Ar glove box, cooled to -78 °C and characterised by NMR spectroscopy at 203 K. For catalytic use, approximately 1 mg of **3** was dissolved in DCM-d_2 and transferred to the reaction vessel before any other solvents or reagents were charged, and the solvent removed *in vacuo*. The reagents were then charged in accordance with General Procedure 2.1.

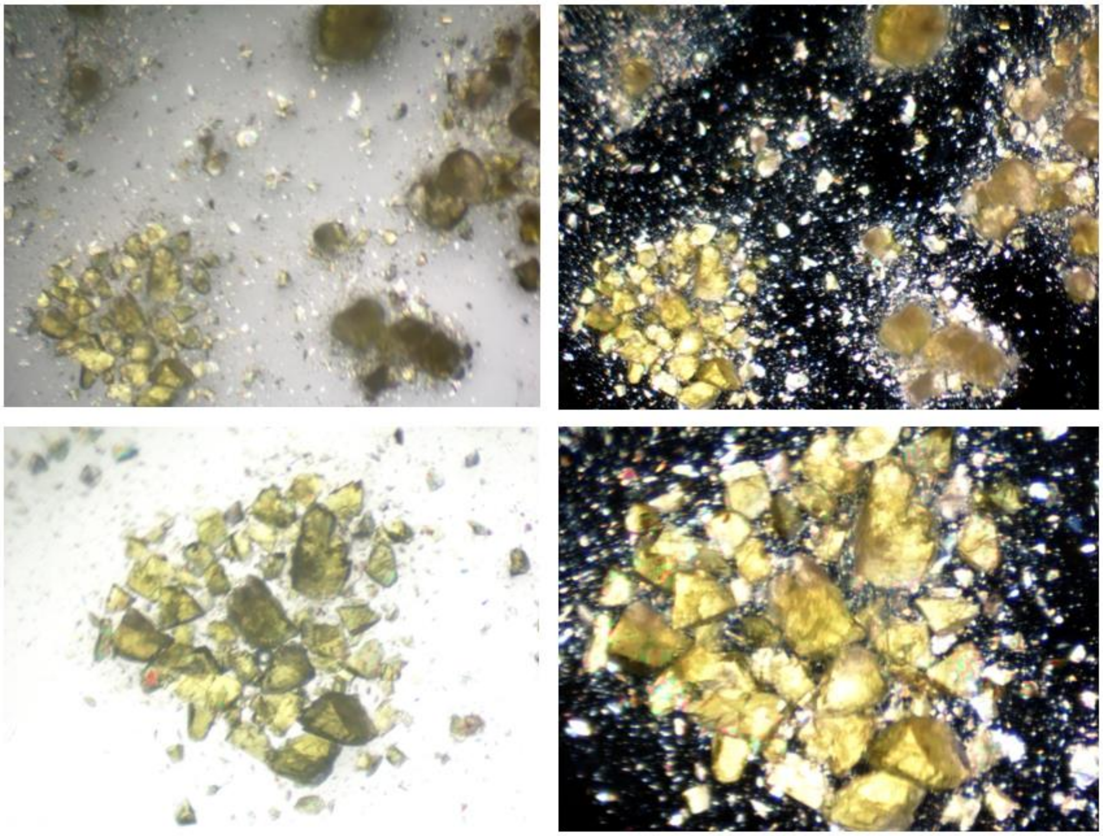
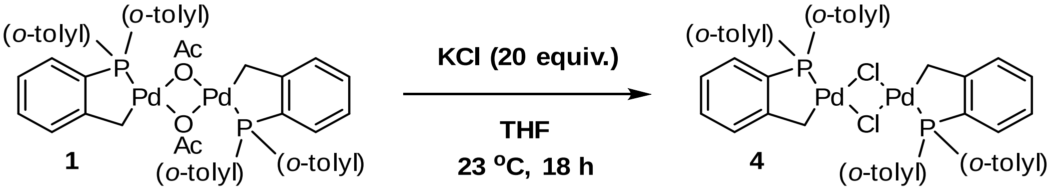


Figure 1: Vivid yellow crystals of the $Pd_4(\mu_4\text{-}O)(\mu_2\text{-}OH)_2$ cluster 41 being manually isolated. Top Left: a mixture of cluster and impure crystals (cloudy/brown). Top Right: same image under plane polarised light. Bottom Left: magnified image of the pure cluster crystals. Bottom Right: same image under plane polarised light.

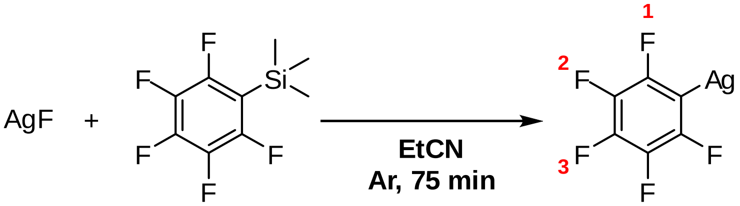
Synthesis of the $[Pd(P\text{^}C)(\mu_2\text{-}Cl)]_2$ Palladacycle 4



The Herrmann-Beller palladacycle **1** (150 mg, 0.16 mmol, 1 eq.) and anhydrous KCl (239 mg, 3.2 mmol, 20 eq.) were added to THF (10 mL, dry, degassed) under N_2. The resulting mixture was rapidly stirred for 18 hours and stirred to give a yellow suspension. Deionised water (10 mL) then DCM (40 mL) were added (Note: This complex is sparingly soluble in DCM, so larger volumes may be needed). The organic layers were collected, washed (water, 2 × 20 mL), and the solvent evaporated (without drying) in vacuo to give the $[Pd(P\text{^}C)(\mu_2\text{-}Cl)]_2$ palladacycle **4** as a bright yellow powder (134 mg, 94%); ^{1}H NMR (500 MHz, DCM-*d*$_2$, 203 K) δ 7.47 – 7.18 (m, 12H, Ar-*H*), 7.18 – 6.94 (m, 8H, Ar-*H*), 6.86 – 6.65 (m, 4H, Ar-*H*), 3.59 – 3.42 (m, 2H, C*H*H), 3.37 (q, *J* = 13.8, 11.3 Hz, 2H, CH*H*), 2.79 (s, 2H, tolyl-*H*), 2.73 (s, 1H, tolyl-*H*), 2.66 (s, 1H, tolyl-*H*), 2.65 (s, 3H, tolyl-*H*), 2.54 (s, 2H, tolyl-*H*), 2.44 (s, 1H, *tolyl-H*), 2.40 (s, 1H, tolyl-*H*), 1.70 (s, 1H, tolyl-*H*); ^{31}P NMR (202 MHz, DCM-d_2, 203 K) δ 39.06 (s), 38.86 (s), 38.76 (s), 38.64 (s). (Note: due to extremely low solubility in tested solvents, it was not possible to get a ^{13}C NMR of this complex. At 203 K, the broad ^{31}P environment observed at room temperature splits into 4 peaks, each representing a structural isomer of this complex); HRMS (LIFDI) $(C_{42}H_{40}P_2Pd_2Cl_2)^{+\bullet}$ m/z (calculated) 888.00465, (found) 888.00508, mass difference 0.49 ppm; (ATIR): ṽ (cm-1) 3053 (C-H aromatic), 2969 (C-H aromatic), 2940 (C-H aliphatic), 2869 (C-H aliphatic), 1586 (C=C aromatic), 1578 (C=C aromatic), 1464, 1440 (C-P), 1283, 1264, 1203, 1162, 1130, 1083, 1052, 805, 757, 714, 579, 559, 518, 479, 469, 461; mp. decomposed above 280 °C.

Lab book ref. DRH-02-130, DRH-03-78

Synthesis of Ag-C_6F_5 Complex



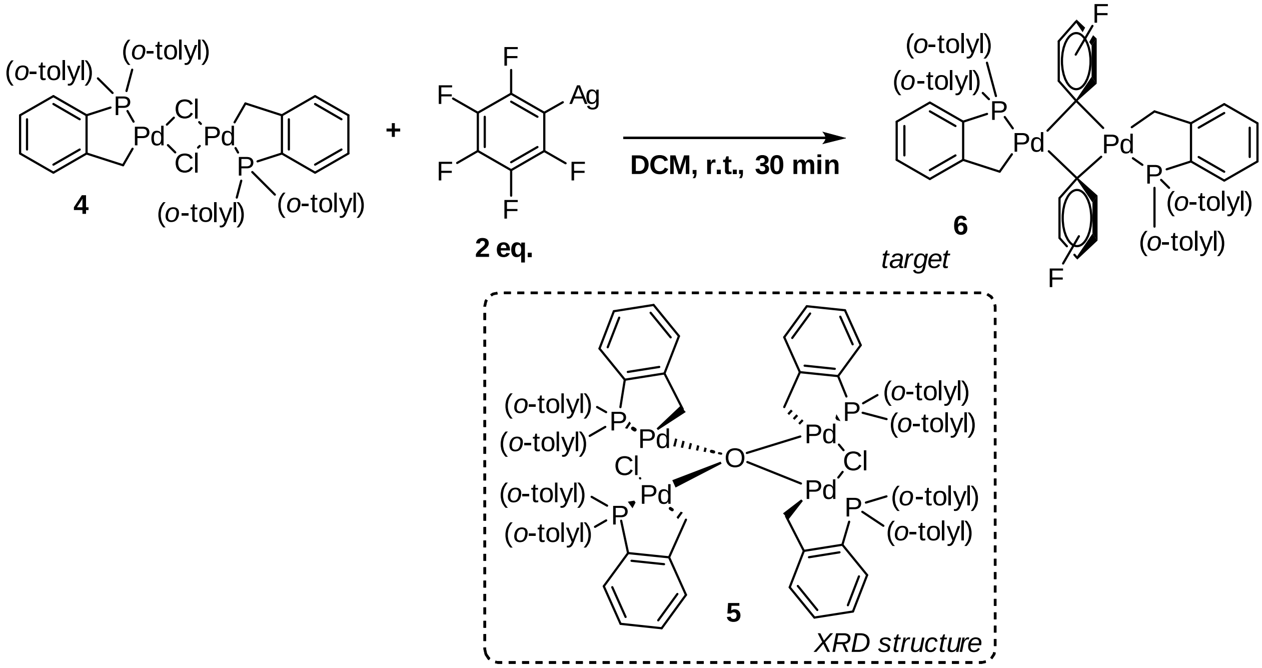
Complex prepared according to a literature procedure by Athavan *et al.*[2]

In an argon glovebox, AgF (302 mg, 2.38 mmol, 1.0 eq.) and dry, degassed EtCN (5 mL) were stirred for 5 min at room temperature under darkness. $Me_3SiC_6F_5$ (450 µL, 2.38 mmol, 1.02 eq.) was added, and the resulting mixture was stirred for a further 75 min. The reaction was removed from the glovebox, and volatiles removed *in vacuo*, giving the product as a pale grey powder (442 mg, 68%). (Note: this complex is unstable in air and sensitive to light and temperature, so was stored in an argon glovebox freezer in a foiled vial) ^{19}F NMR (471 MHz, Acetonitrile-d_3) δ -106.93 (m, 2F, F-1), -159.80 (t, *J* = 19.2 Hz, 1F, F-3), -163.13 (m, 2F, F-2). The ^{19}F NMR data matches the literature.[2]

Lab book ref. DRH-03-73

Isolation of Palladacyclic Pd_4 Cluster 5

Lab book ref. DRH-03-75



In an argon glovebox under darkness, $[Pd(P^\wedge C)(\mu_2\text{-}Cl)]_2$ palladacycle **4** (20 mg, 0.0225 mmol, 1.0 equiv.), AgC_6F_5 (15 mg, 0.0450 mmol, 2.0 equiv.) and dry, degassed DCM (5 mL) were charged in a Schlenk tube and rapidly stirred for 30 min. After this time, 0.5 mL of the dark orange reaction supernatant was removed to a J-young tab NMR tube and analysed by NMR spectroscopy, showing a mixture of species. Of particular interest is the broad peak from ^{31}P δ 40 – 38 ppm, which is symbolic of a bridging cluster complex. This sample was returned to the Ar glovebox and crystallised using slow vapor diffusion in a sealed vial (DCM/pentane, 0.25 mL : 1.5 mL). After several days, a number of bright yellow crystals of **5** suitable for XRD were obtained (~ 2 mg), along with amorphous orange solid that was likely the result of decomposition.

The rest of the sample was removed from the Ar glovebox, the supernatant was decanted, and solvent removed *in* vacuo, giving a red solid with mass 14.4 mg, but LIFDI mass spectrometric analysis showed no presence of **5** or the target product **6**.

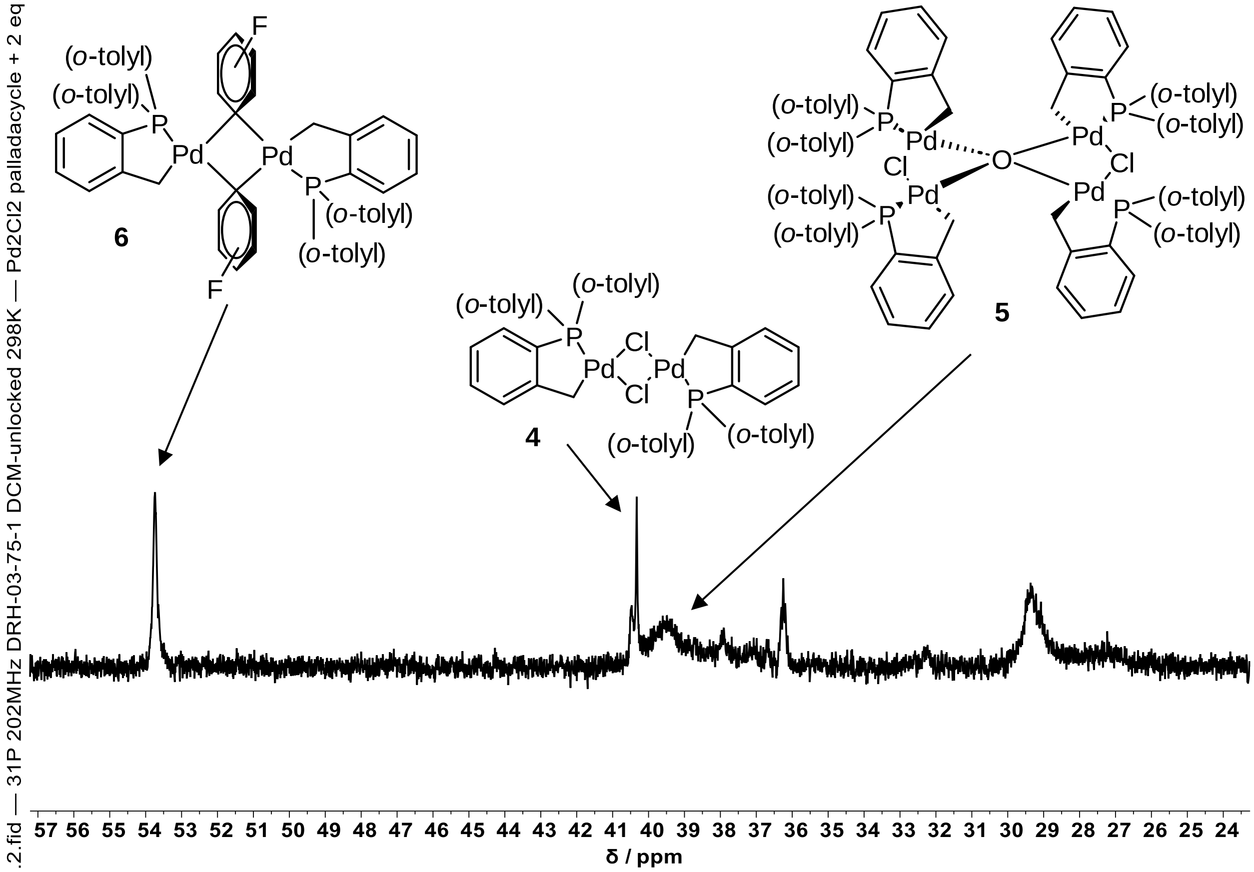
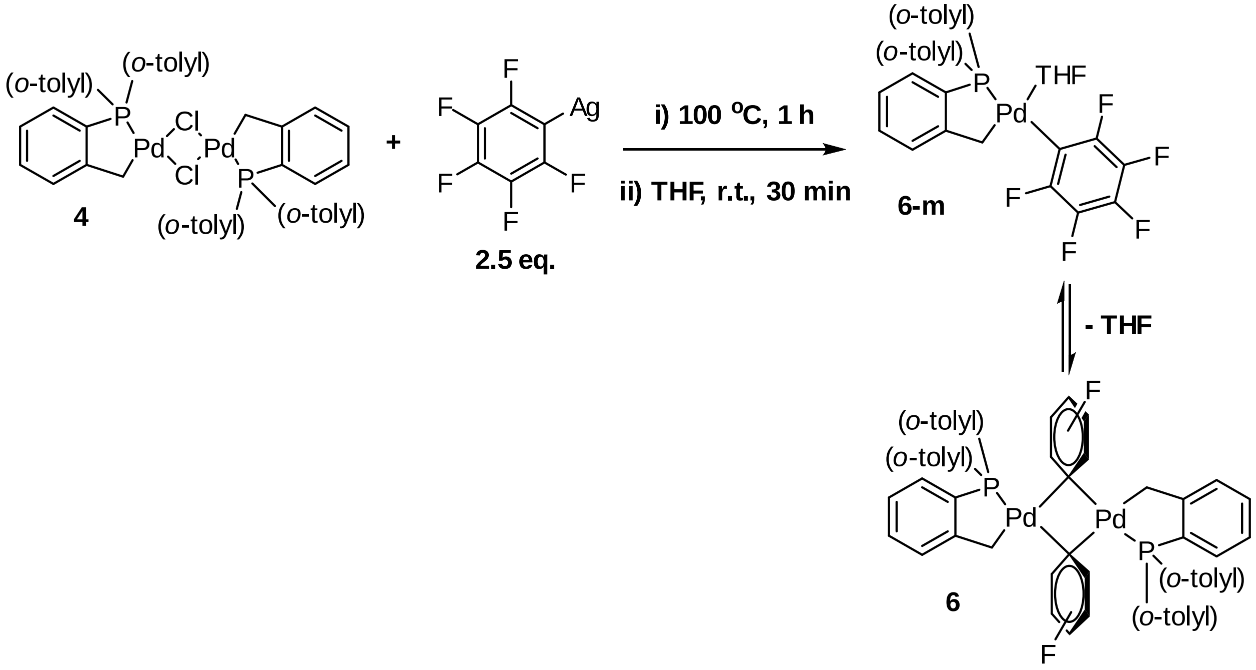


Figure 2: ^{31}P NMR (203 MHz, DCM-unlocked, 128 sc, 298 K) of the reaction mixture showing a potential peak for Pd_4 cluster 5 and the proposed identities of some other relevant peaks. Lab book ref. DRH-03-75-1

Synthesis of [Pd(P^C)(μ_2-Ar^F)]$_2$ Palladacycle 6

Lab book ref. DRH-03-76, DRH-03-79



The synthesis of this complex was based on that from Espinet's work, where bridging Pd-Ar-Pd complexes were synthesised and characterised.[3] The complex is highly water sensitive, rapidly decomposing to Pd black and pentafluorobenzene when exposed to water.

In an argon glovebox, Ag-C_6F_5 complex (47 mg, 0.141 mmol, 2.1 equiv.) was charged into a Schlenk flask under darkness. The complex was heated at 100 °C under vacuum for 1 h to remove any coordinating EtCN ligands, then allowed to cool to room temperature. [Pd(P^C)(μ_2-Cl)]$_2$ palladacycle **4** (60 mg, 0.0674 mmol) was added under N_2, followed by THF (6 mL, dry, degassed). The colourless mixture was stirred for 30 min at room temperature, after which a direct NMR aliquot was taken for analysis. The mixture was allowed to settle, and the liquor isolated by canula filtration. The solvent was removed *in vacuo*, giving a dark red residue. This residue was analysed by NMR (C_6D_6, dry, degassed), and ~10 mg was set up for recrystallization overnight (C_6D_6/pentane) under argon (slow vapor diffusion). A small quantity of orange-yellow crystals of **6** suitable for single crystal XRD were obtained, and these were analysed by FTIR and mass spectrometry.

The bridging Pd-Ar bond is weak and easily cleaved by even a mildly coordinating solvent. As such, in THF, there is exclusively the monomeric complex **6-m**, likely coordinated with THF. As the coordinating solvent is removed, the more stable dimer **6** is formed, and this is what crystallises out. Analysis in dry Benzene-d_6 reveals that even in non-coordinating solvent, the monomer forms. Over longer time periods (ca. 2 days) degradation of the complex is observed, which has made larger scale synthesis and purification impossible. LIFDI mass spectrometry analysis shows only the monomer present, as the dimer **6** likely cleaves under mass spectrometry conditions.

Mixture of monomer and dimer in Benzene-*d*$_6$; ^{31}P NMR (243 MHz, Benzene-*d*$_6$, 298 K) δ 53.17 (dimer), 26.09 (monomer); ^{19}F NMR (565 MHz, Benzene-*d*$_6$, 298 K) δ -95.92 (dimer), -113.77 (d, *J* = 35.5 Hz, monomer), -145.28 (dimer), -160.79 – -161.08 (m, dimer/monomer), -162.34 – -162.55 (m, dimer/monomer).

6-m in THF: ^{31}P NMR (203 MHz, THF-unlocked, 298 K) δ 25.60 (tt, *J* = 12.2, 9.2 Hz); ^{19}F NMR (471 MHz, THF-unlocked, 298 K) δ -114.77 (dt, *J* = 34.2, 9.6 Hz), -163.80 (d, *J* = 21.5 Hz), -164.54.

HRMS (LIFDI) ($C_{27}H_{20}F_5PPd$)$^{+\bullet}$ *m/z* (calculated) 576.02521, (found) 576.02786, mass difference 4.59 ppm. (ATIR): $\tilde{\nu}$ (cm^{-1}) 3060 (C-H aromatic), 2925 (C-H aliphatic), 2857 (C-H aliphatic), 1624 (C=C aromatic), 1590 (C=C aromatic), 1580, 1492 (C-P), 1441 (s, C-F), 1320, 1282, 1263, 1246, 1203, 1132, 1048, 951, 803, 752, 713, 671, 577, 559, 521, 507, 460.

Lab book ref. DRH-03-76, DRH-03-79 (X-ray diffraction structure ijsf22048)

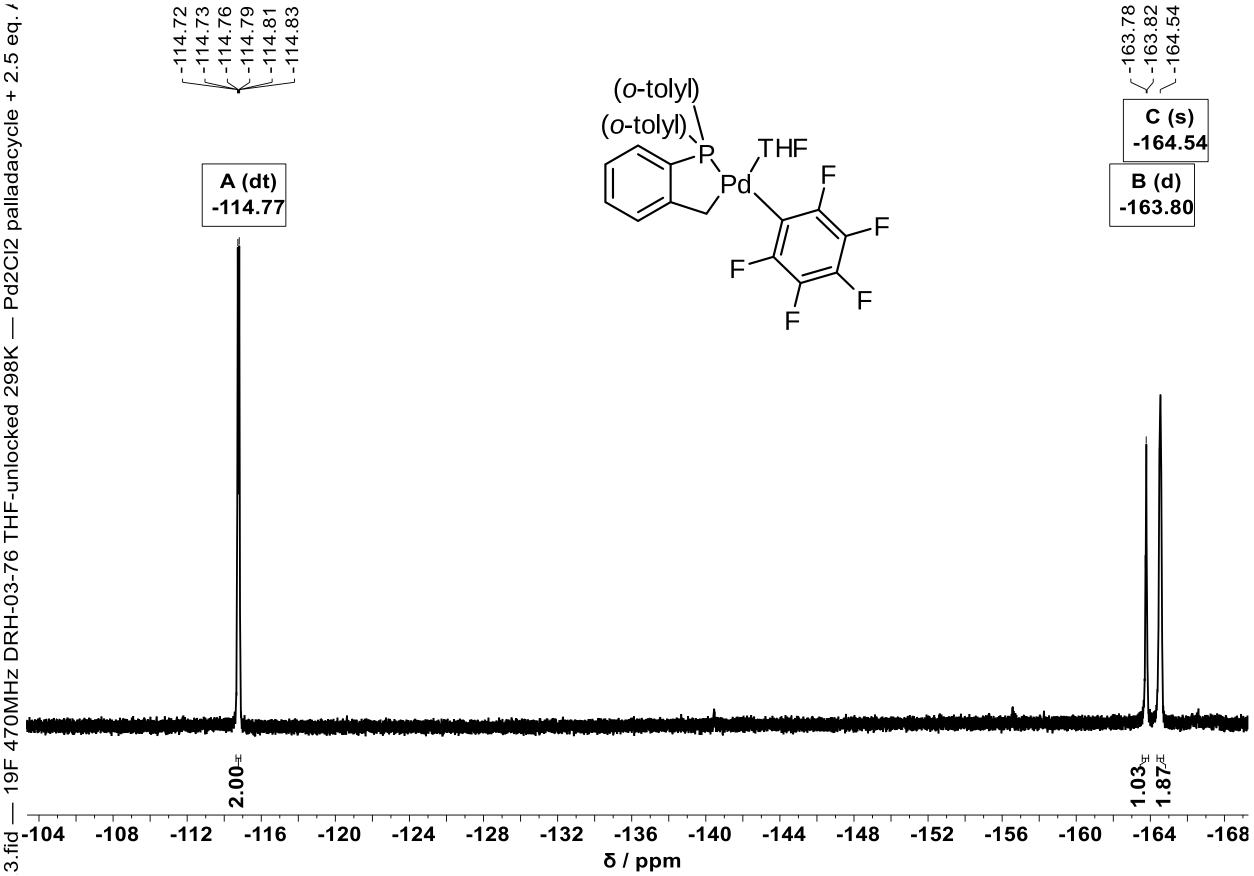


Figure 3: ^{19}F NMR (470 MHz, THF-unlocked, 128 sc, 298 K) of the [Pd(P^C)(Ar^F)] palladacyclic monomer (6-m), with suspected THF coordination. Lab book ref. DRH-03-76

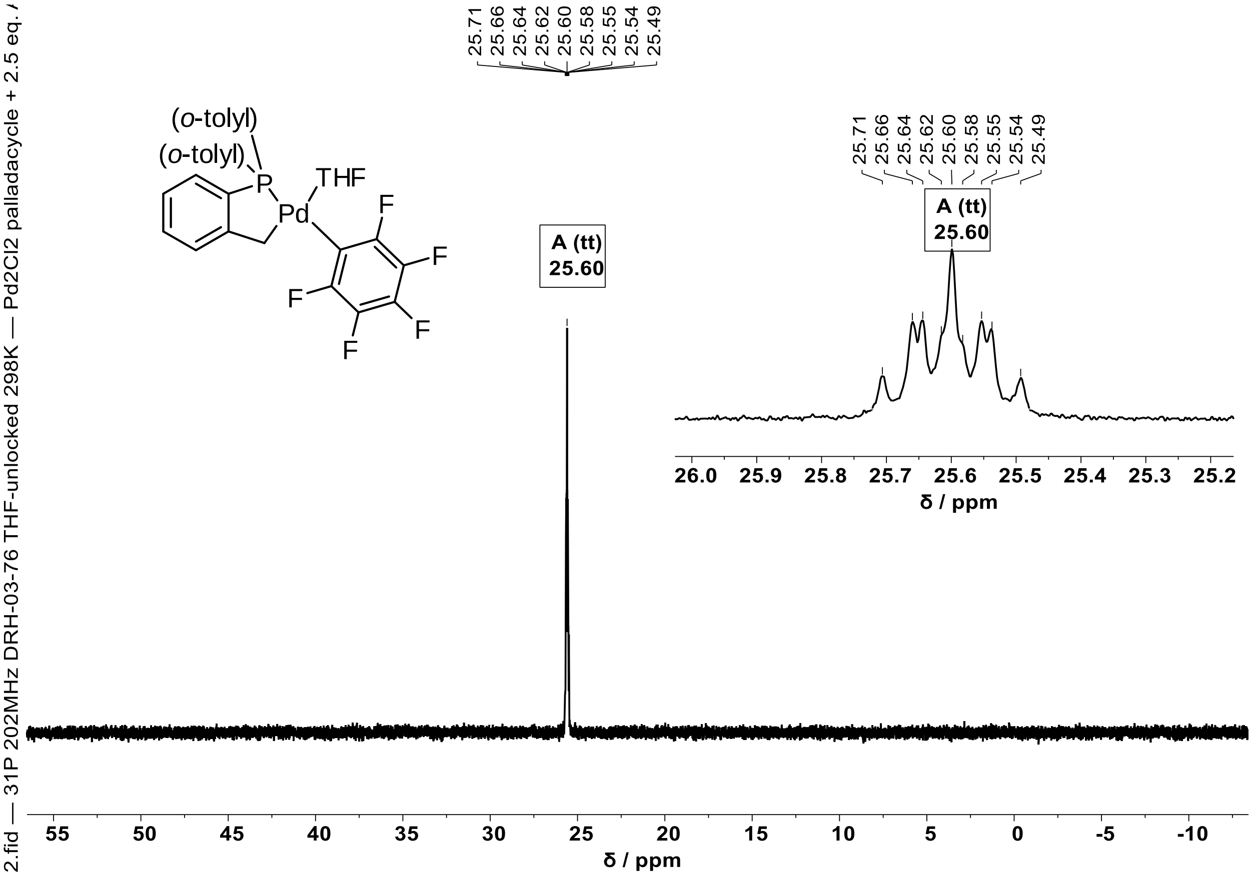


Figure 4: ^{31}P NMR (203 MHz, THF-unlocked, 128 sc, 298 K) of the [Pd(P^C)(Ar^F)] palladacyclic monomer 6-m with suspected THF coordination. Lab book ref. DRH-03-76

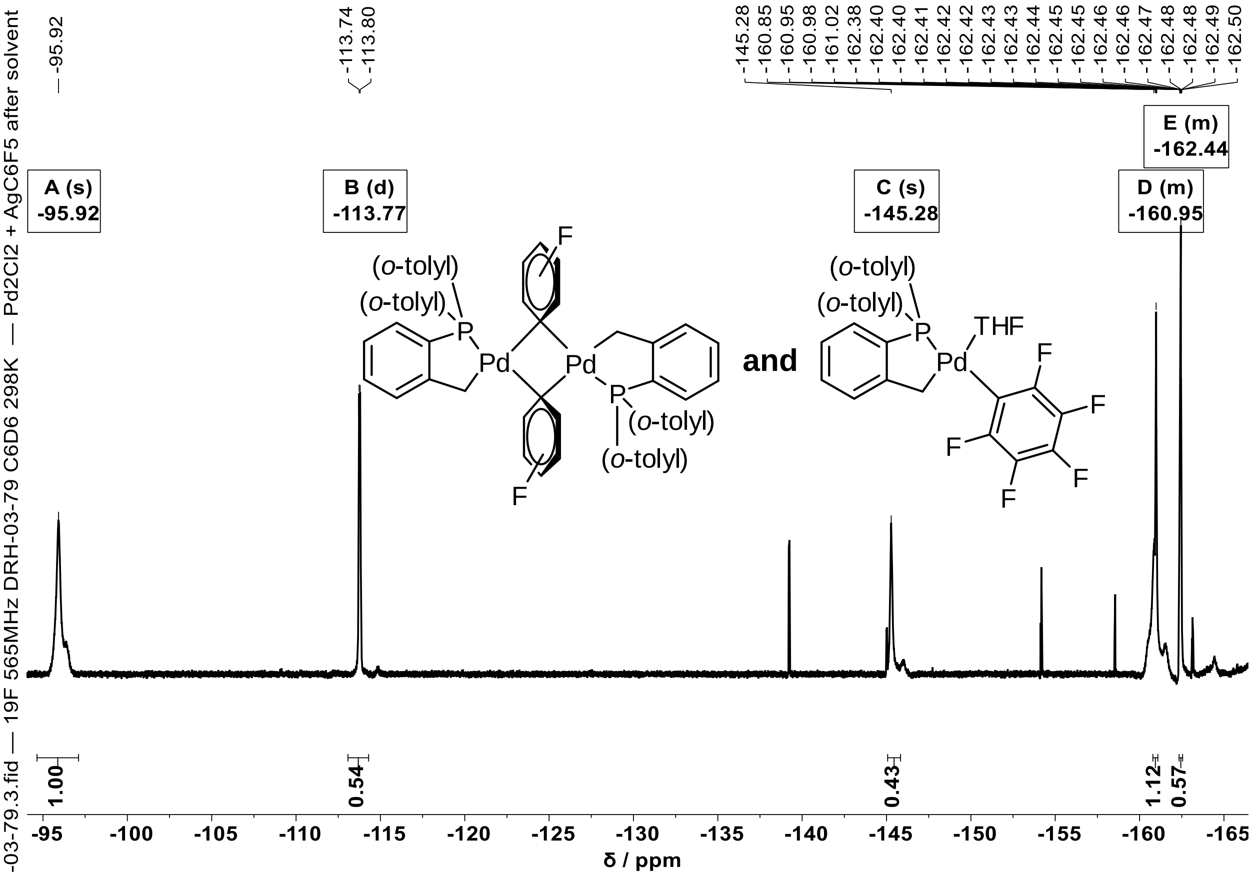


Figure 5: ^{19}F NMR (565 MHz, C_6D_6, 128 sc, 298 K) of the $[Pd(P^\wedge C)(\mu_2\text{-}Ar^F)]_2$ palladacycle 6 and the $[Pd(P^\wedge C)(Ar^F)]$ palladacyclic monomer 6-m in solution. Lab book ref. DRH-03-79

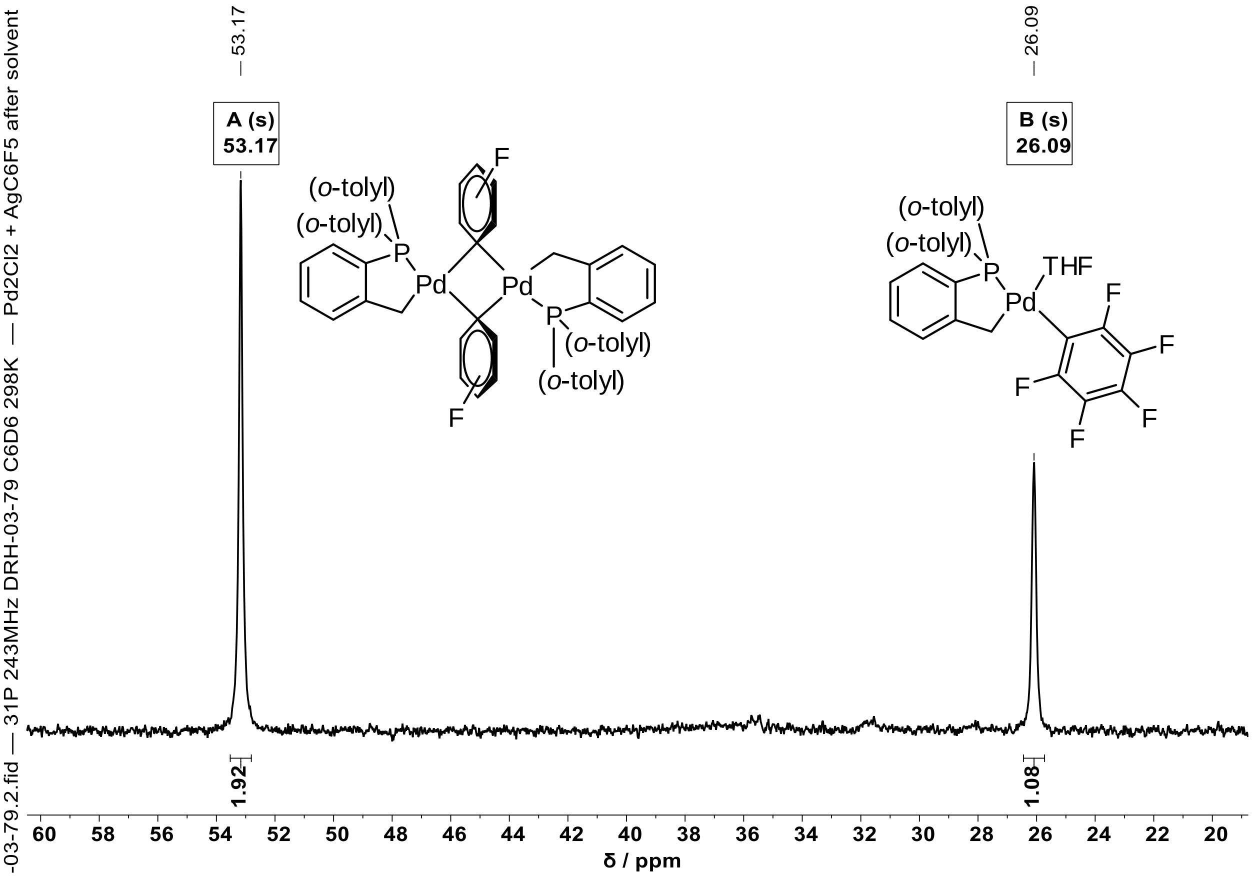
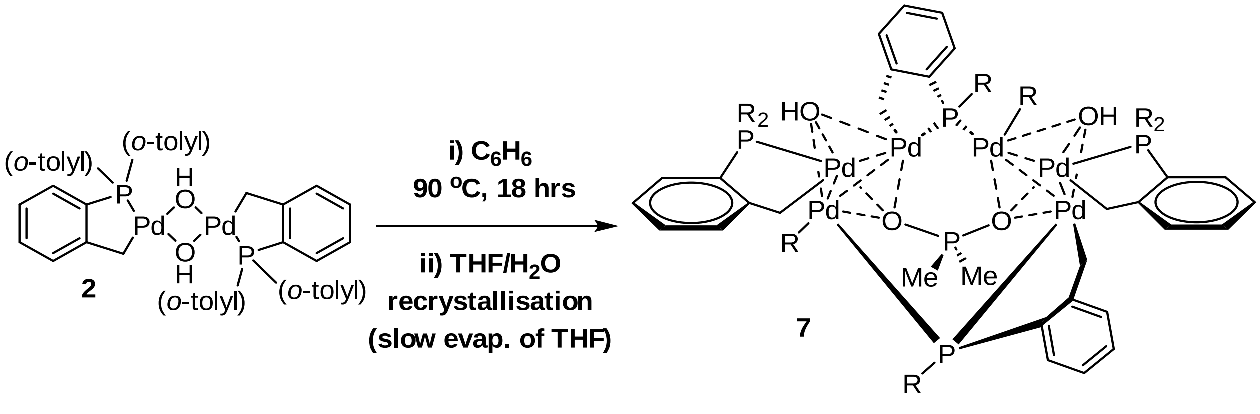


Figure 6: ^{31}P NMR (243 MHz, C_6D_6, 128 sc, 298 K) of the [Pd(P^C)(μ$_2$-Ar^F)]$_2$ palladacycle 6 and the [Pd(P^C)(Ar^F)] palladacyclic monomer 6-m in solution. Lab book ref. DRH-03-79

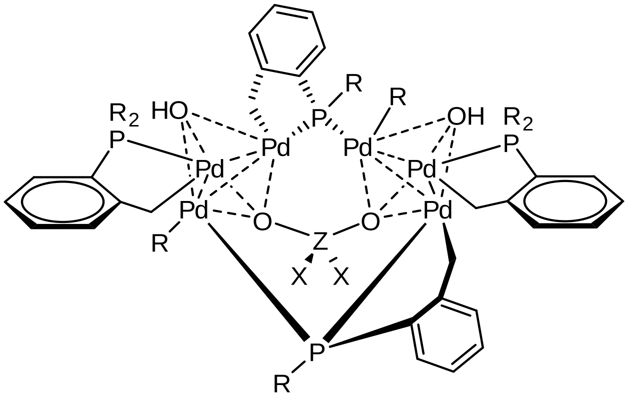
3. Isolation and Confirmation of Structure of Palladacyclic Pd$_6$ cluster 7

Lab book ref. DRH-01-123

[Pd(P^C)(μ$_2$-OH)]$_2$ palladacycle **2** (approx. 30 mg) was added to still-dried (Na) degassed benzene (1mL per 10 mg) under Schlenk conditions. The yellow solution was vigorously stirred and refluxed under a static N$_2$ atmosphere for 21 h at 90 °C. The yellow-brown solution was filtered under N$_2$ to remove Pd black, then the solvent removed *in vacuo*. The solubility of the residue (for the purposes of recrystallisation) was tested by the addition then removal *in vacuo* of 1 mL of the following solvents: dichloromethane, toluene, hexane, pentane, diethyl ether. As the residue was soluble in all these solvents, water was then tested. To the residue, 1.5 mL of degassed water was added, then dry, degassed THF (ca. 1.5 mL) until the solid dissolved. A vent needle was added, and the sample placed in a fridge at 5 °C. After 4 weeks, a small quantity of orange-yellow crystals suitable for X-ray diffraction had formed (< 1 mg). This complex was primarily characterised by single crystal X-ray diffraction and revealed an unexpected complex containing 6 Pd centres arranged in two linked μ$_3$-OR (R = H, P) trigonal bipyramid structures. The two structures are linked via an O-P-O bridge containing two methyl groups. Due to crystal twinning, there is uncertainty as to the identity of these methyl groups, but the P-C bond length of 1.878(9) Å and DFT modelling of alternative groups confirms that this is the most likely identity. This result is the most surprising aspect of the complex, as no obvious source of Me was used – indeed, the only available source is the o-tolyl groups. During crystallization or preparation, there was no DSMO used to supply a linker that would be indistinguishable by XRD. DFT was used to aid identification of this linker (see Section 6 for more details).



R = *o*-tolyl



R = *o*-tolyl

Table 1: Relevant bond lengths and angles for computed structures of the Pd_6 cluster 7. Calculations performed at the b3lyp/def2svp level of theory, with Grimme's 3rd dispersion correction with Becke-Johnson damping. Solvent model (SVD, THF), and a superfine integration grid.

	Bond lengths / Å		**Bond angles / °**	
Complex	**O-Z**	**Z-X**	**O-Z-O**	**X-Z-X**
Crystal structure	***1.631(6)***	***1.878(9)***	***107.9(3)***	***109.7(4)***
Z = P, X = Me (**7a**)	1.58073	1.79819	109.44704	107.53866
Z = S, X = Me (**7b**)	1.86013	1.82205	159.87070	95.60422
Z = P, X = O (**7c**)	1.65532	1.50942	97.62349	121.71443
Z = P, X = OH (**7d**)	1.55819	1.59359	110.95213	99.43078

Due to the highly unusual structure and uncertainty in the fitting, DFT was used to model the Pd_6 cluster **7**. Above are shown selected bond lengths and angles for the atoms of interest. Although there is a significant discrepancy between the crystal structure parameters and those modelled computationally, the proposed identity of the atoms of P and Me seem to give the best agreement with the experimental data.

The other linking bridge is via a phosphido ligand, where one of the o-tolyl groups forms a palladacycle. It is assumed that the other *o*-tolyl group has migrated from the P ligand to the neighboring Pd center. The formal charge on each Pd center is + 5/3, indicating that some reduction compared to the dimer (2) has occurred. There has also been the loss of one phosphine from the structure compared to the dimer. One remarkable thing about this structure is that the palladacycles are retained, even after heating at 90 °C for 21 hours and after 4 weeks of recrystallisation under atmospheric conditions. This is a testament to the robustness of the Pd-C bond and raises questions about the activation of palladacycles under reaction conditions. Unfortunately, not enough material was obtained to fully characterise the complex. ESI mass spectrometry and LIFDI mass spectrometry yielded inconclusive results, but more success was had with NMR and FTIR of the obtained single crystals.

As a brief aside, it has proved challenging to repeat the crystallization of this complex, with several experiments yielding an amorphous glass rather than single crystals.

Calculated IR spectra were also obtained by the same DFT method and used to compare the experimental FTIR data collected.

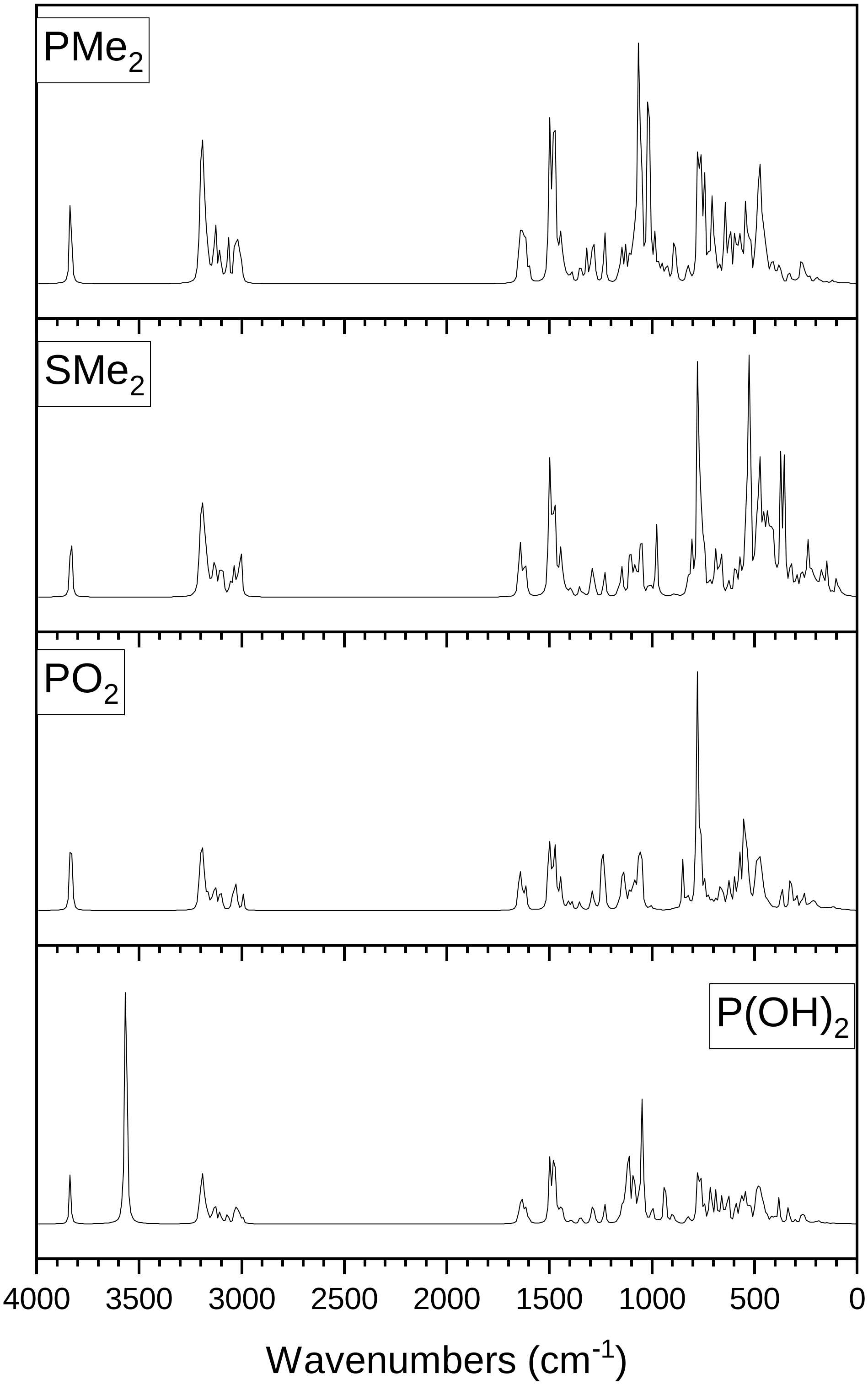


Figure 7: Stacked simulated IR spectra from DFT modelling of the Pd_6 cluster 7, where the linking group = PMe_2, SMe_2, PO_2, $P(OH)_2$.

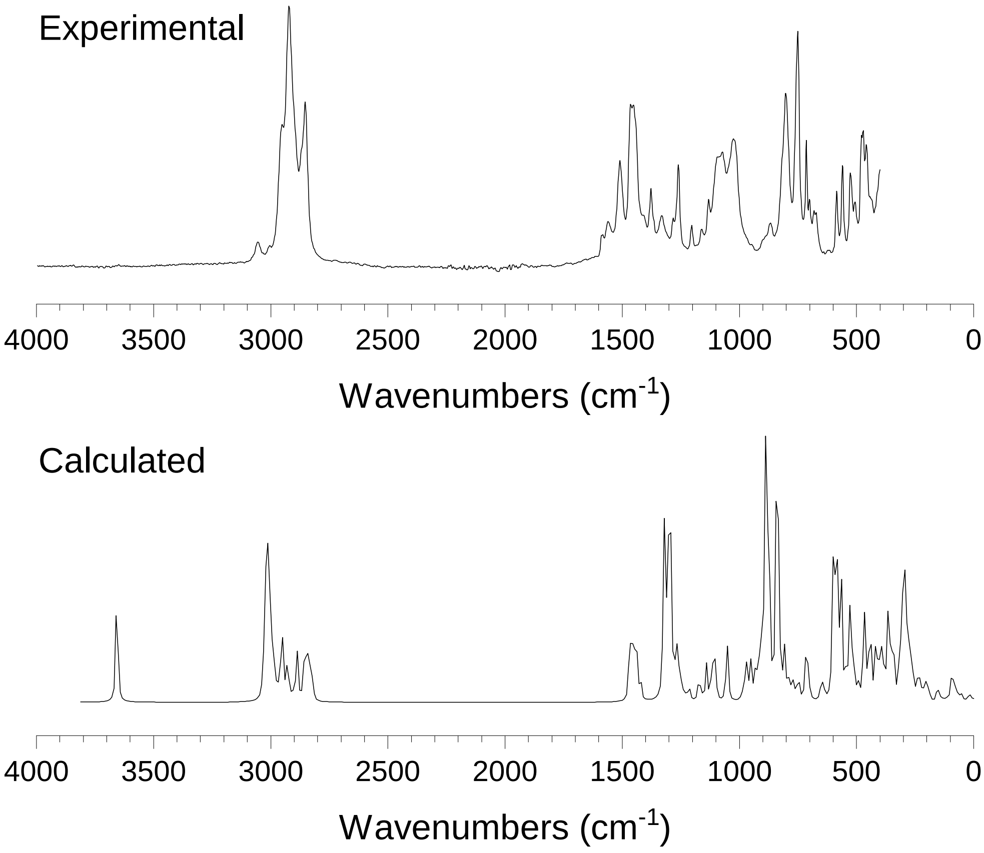


Figure 8: Stacked simulated IR spectra from DFT modelling of the Pd_6 cluster 7; top-experimental, bottom, calculated IR spectrum. The calculated IR spectrum was calibrated by matching the weak O-H stretch at 3660 cm^{-1} in the experimental spectrum.

P-C IR stretches (deformation) are characteristically strong in 1400-1450 cm^{-1} region, which are seen here. P-O stretches are also strong in the 900-1100 region in IR. Difficult to ascribe, but possible matches are highlighted in the spectra above. There are no P-OH bonds (weak at 1740-1600 cm^{-1}) present, indicating that this structure is unfeasible.

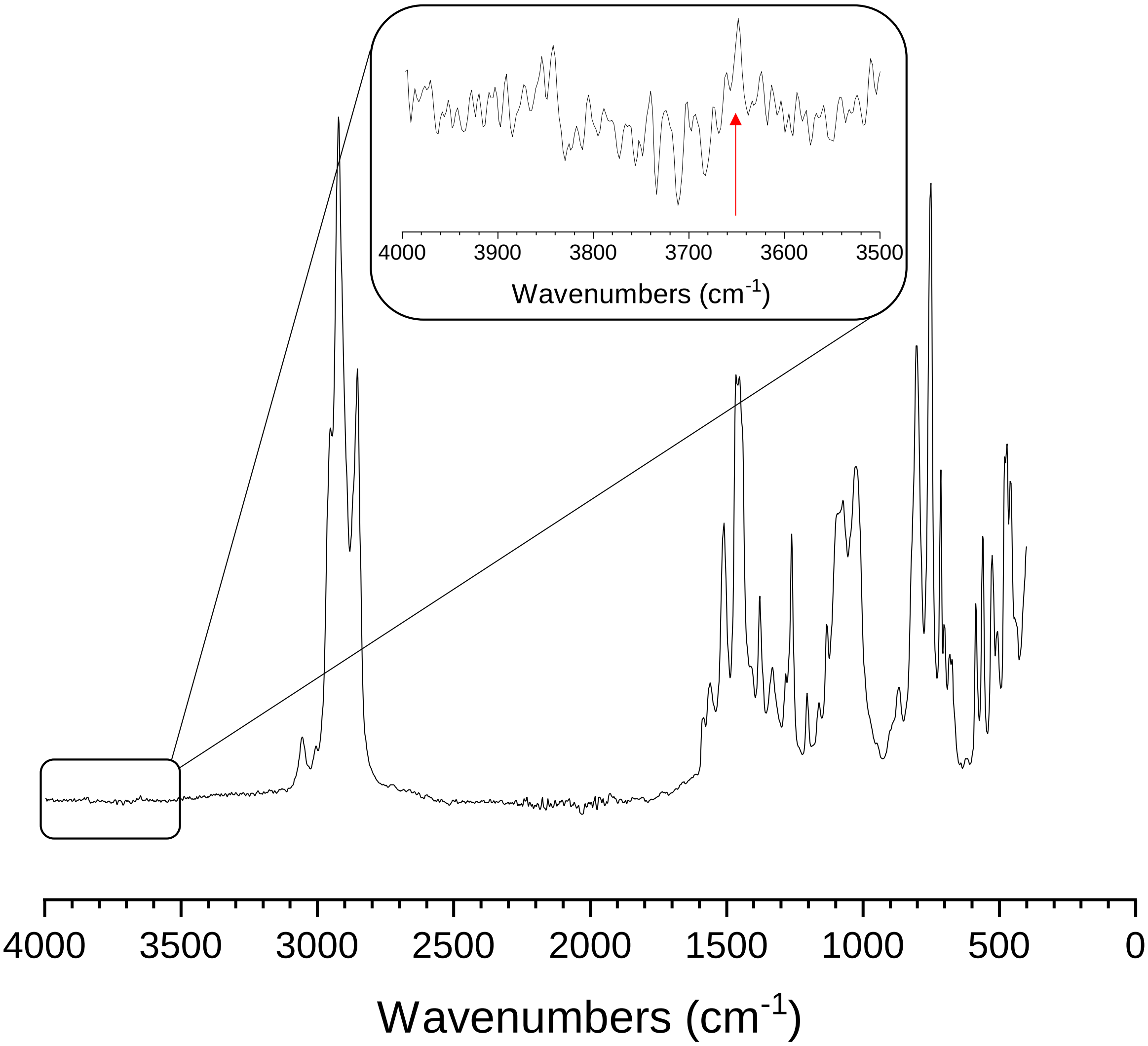


Figure 9: FTIR spectrum of the Pd_6 cluster 7. There remains some grease from the XRD mounting of the single crystals, resulting in an amplified C-H stretch peak at 2900 cm^{-1}. The very weak O-H stretch is magnified here.

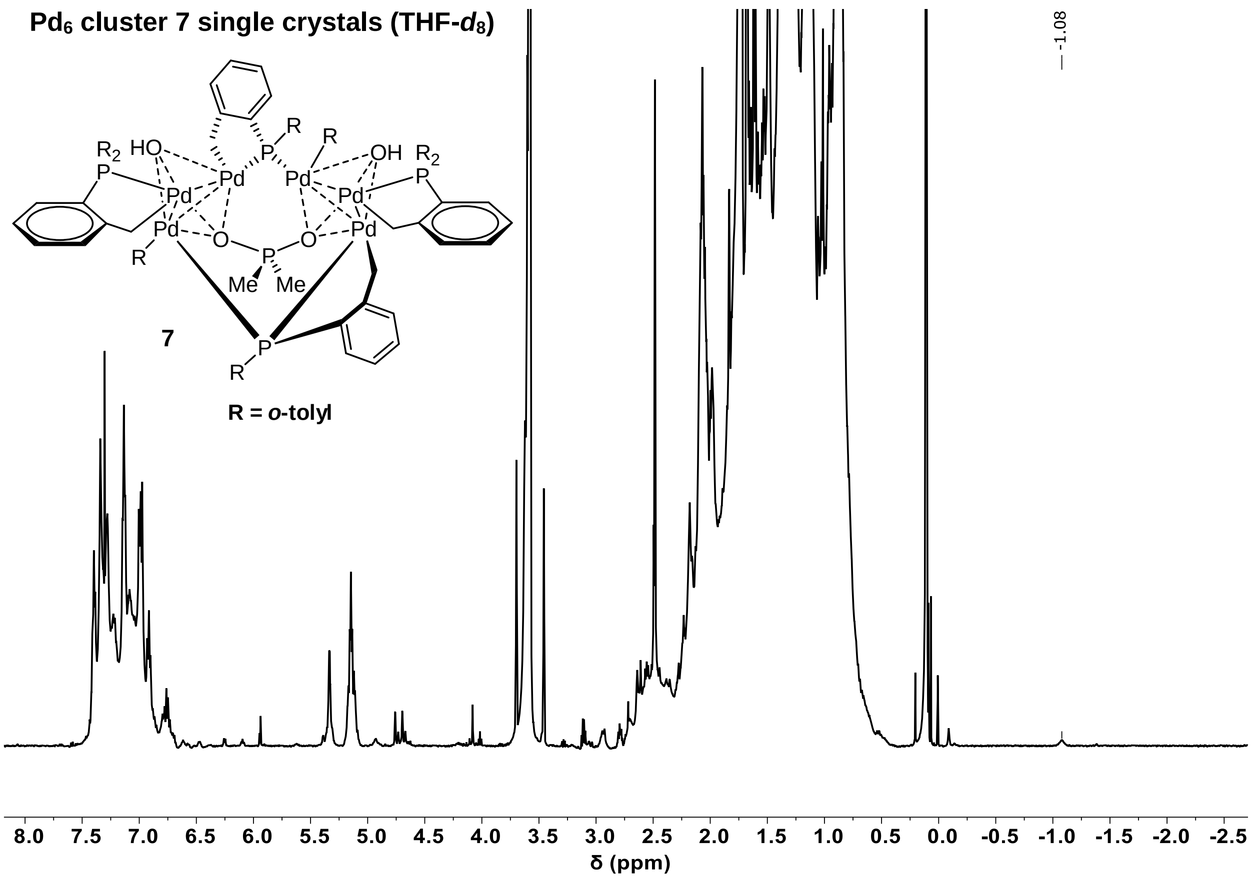


Figure 10: ^{1}H NMR (600 MHz, THF-d_8, 4096 scans, 298 K) spectrum of the Pd_6 cluster 7. Due to the sample being made from individually separated single crystals, there are significant grease peaks from the XRD mounting oil. The relevant $Pd_3(\mu_3\text{-}OH)$ proton signal is shown at -1.08 ppm. Lab book ref. DRH-01-123

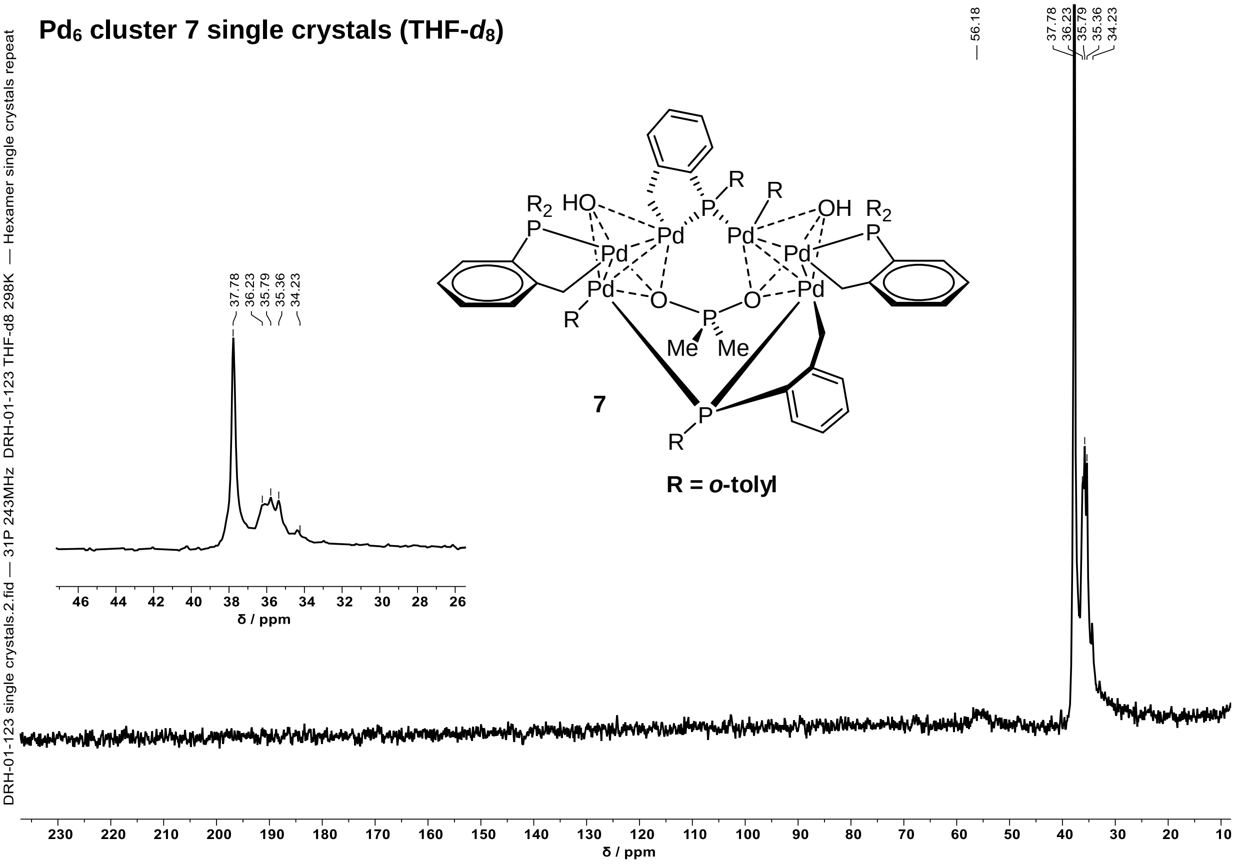
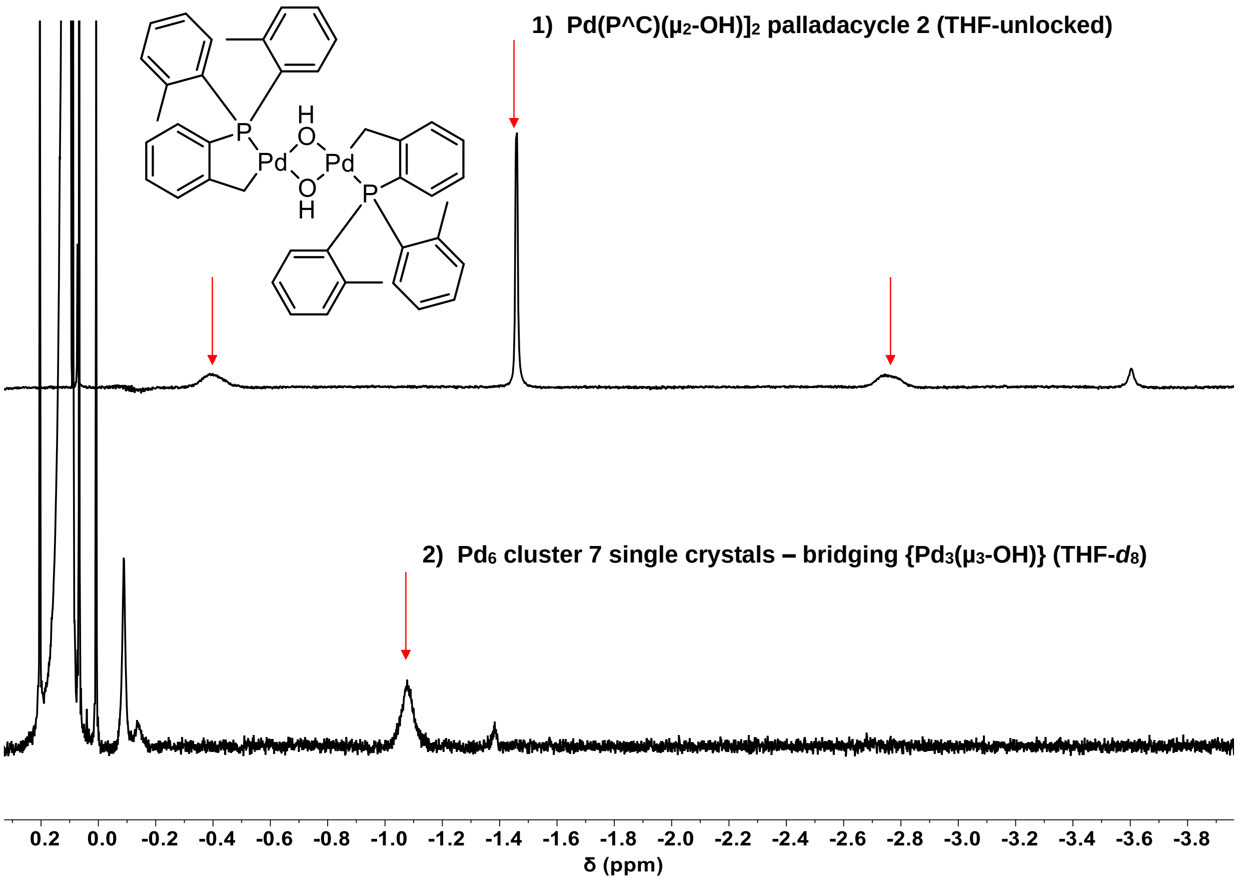


Figure 11: ^{31}P NMR (243 MHz, THF-d_8, 51200 scans, 298 K) spectrum of the Pd$_6$ cluster 7. Lab book ref. DRH-01-123


1) Pd(P^C)(μ_2-OH)]$_2$ palladacycle 2 (THF-unlocked)

2) Pd$_6$ cluster 7 single crystals – bridging {Pd$_3$(μ_3-OH)} (THF-d_8)

Figure 12: ^{1}H NMR (600 MHz, THF-unlocked, 298 K) spectrum of the [Pd(P^C)(μ_2-OH)]$_2$ palladacycle 2 (top) and (600 MHz, THF-d_8, 298 K) Pd$_6$ cluster 7 (bottom). The unlocked spectrum was referenced to the residual solvent peaks of THF-d_8 (3.58 ppm). The relevant OH proton peaks are highlighted for each spectrum.

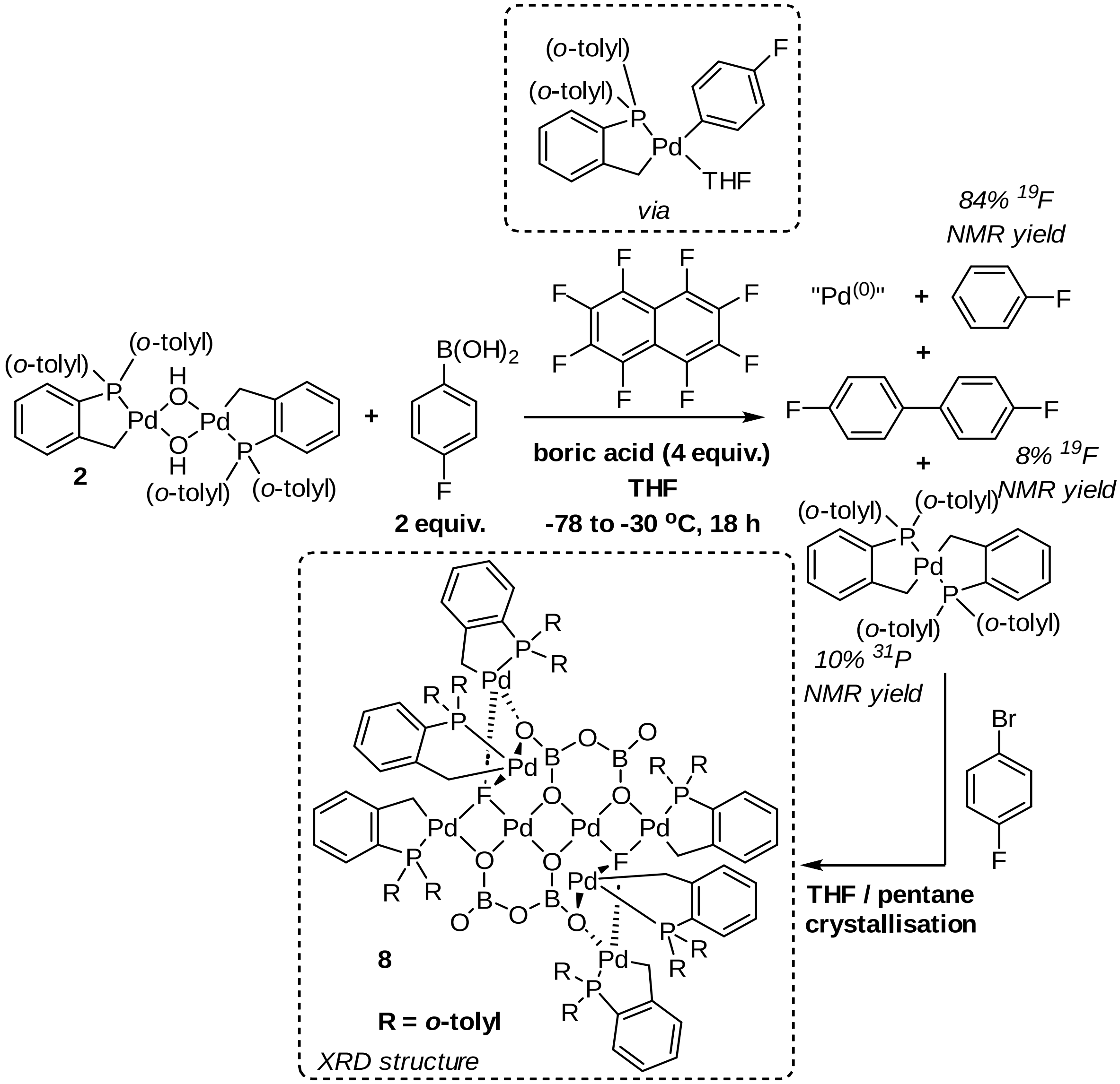
Synthesis of palladacyclic Pd$_8$ 8

Lab book ref. DRH-03-32, DRH-03-32-2

[Pd(P^C)(μ_2-OH)]$_2$ palladacycle **2** (5 mg, 0.00586 mmol, 1 equiv.) and octafluoronapthalene (1.6 mg, 0.00586 mmol, 1 equiv.) were dissolved in THF (0.40 mL, dry, degassed) in a J-Young tap NMR tube under a N_2 atmosphere. The tube was cooled to -78 °C, and 0.10 mL of a stock solution of 4-fluorophenylboronic acid and boroic acid in THF (16.4 mg, 7.2 mg in 1.0 mL dry, degassed THF, 2 equiv., 4 equiv. after addition) was added to the vessel. The tube was sealed under a N_2 atmosphere and vortexed at -78 °C, not shaken, to ensure mixing. The sample was loaded into a pre-cooled NMR spectrometer (500 MHz) at 243 K, and analysed by ^{19}F NMR timecourse (the data is not reported here, as it is not relevant to the cluster formation) over 18 h. After this time, the sample was warmed to room temperature and a ^{31}P NMR spectrum was taken. To see if an active Pd$^{(0)}$ species was present, 4-fluorobromobenzene (1.3 μL, 0.0047 mmol, 0.8

equiv.) was added to the NMR tube under N_2 and the ^{31}P NMR spectrum was recorded over several hours, showing no change. The reaction mixture was set up for crystallisation by slow vapour diffusion (THF / pentane, 0.25 mL : 1.5 mL) in a sealed vial under air, and after 17 months a small number of yellow crystals suitable for XRD (< 1 mg) were obtained, along with a quantity of amorphous solid.

It would appear palladacyclic cluster **8** formed from a proposed $[Pd(P^\wedge C)]_2$ bipalladacycle reacting with a "$Pd^{(0)}$" species and abstracting a fluoride from octafluoronapthalene. The broad peak between ^{31}P δ 40 – 32 ppm after the NMR timecourse at -30 °C is likely representative of **8** and did not change upon the addition of 4-fluorobromobenzene. In the 19F NMR spectrum, a small peak at δ -131.3 ppm can be observed, which could be indicative of a deshielded F in the tetrahedral geometry observed in **8**. The stabilizing $[H_2B_2O_5]^{2-}$ group is from the stabilising boric acid additive.



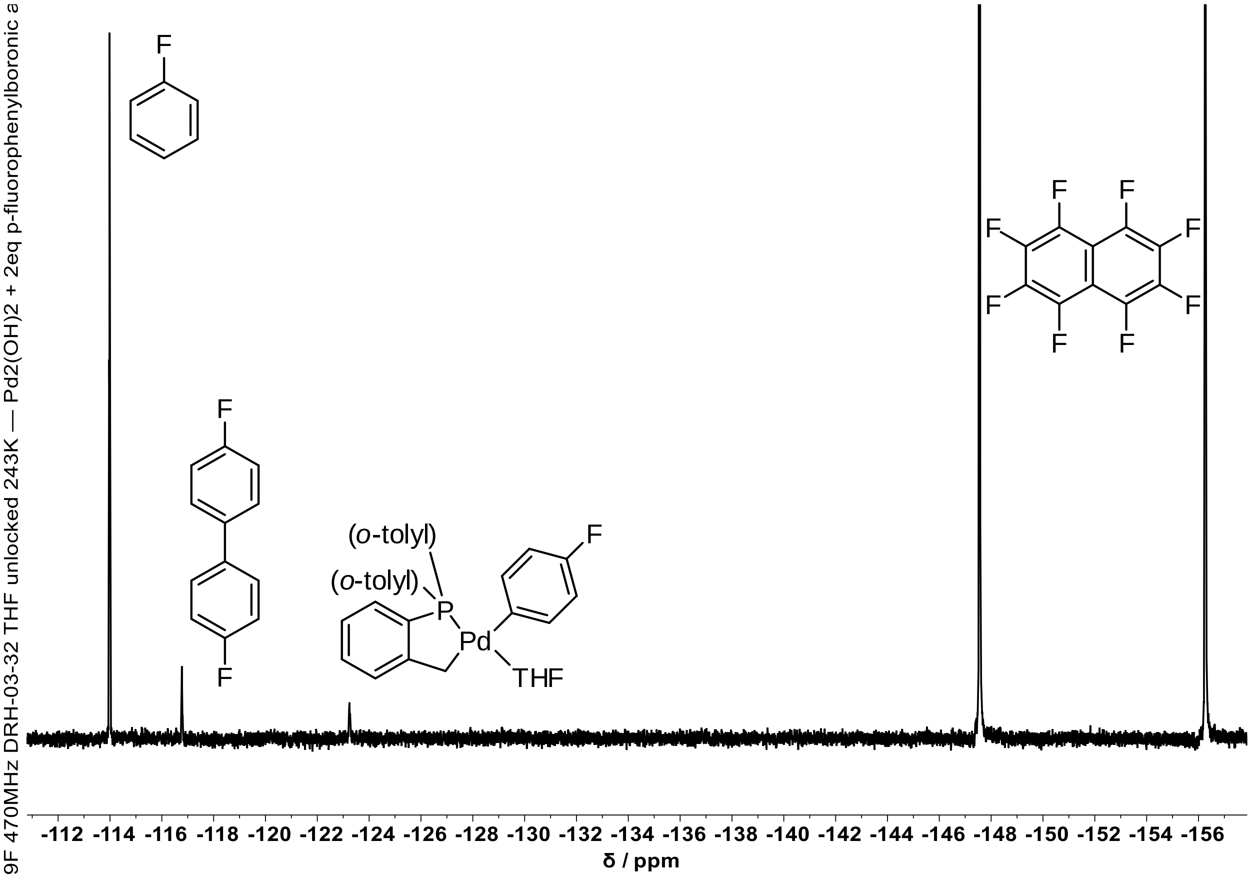


Figure 13: ^{19}F NMR (470 MHz, THF-unlocked, 243 K) spectrum of the reaction mixture potentially containing Pd$_8$ cluster after the kinetic time course (fluorobenzene = 84%, biaryl = 8%, Pd intermediate = 8%). Lab book ref. DRH-03-32 (162)

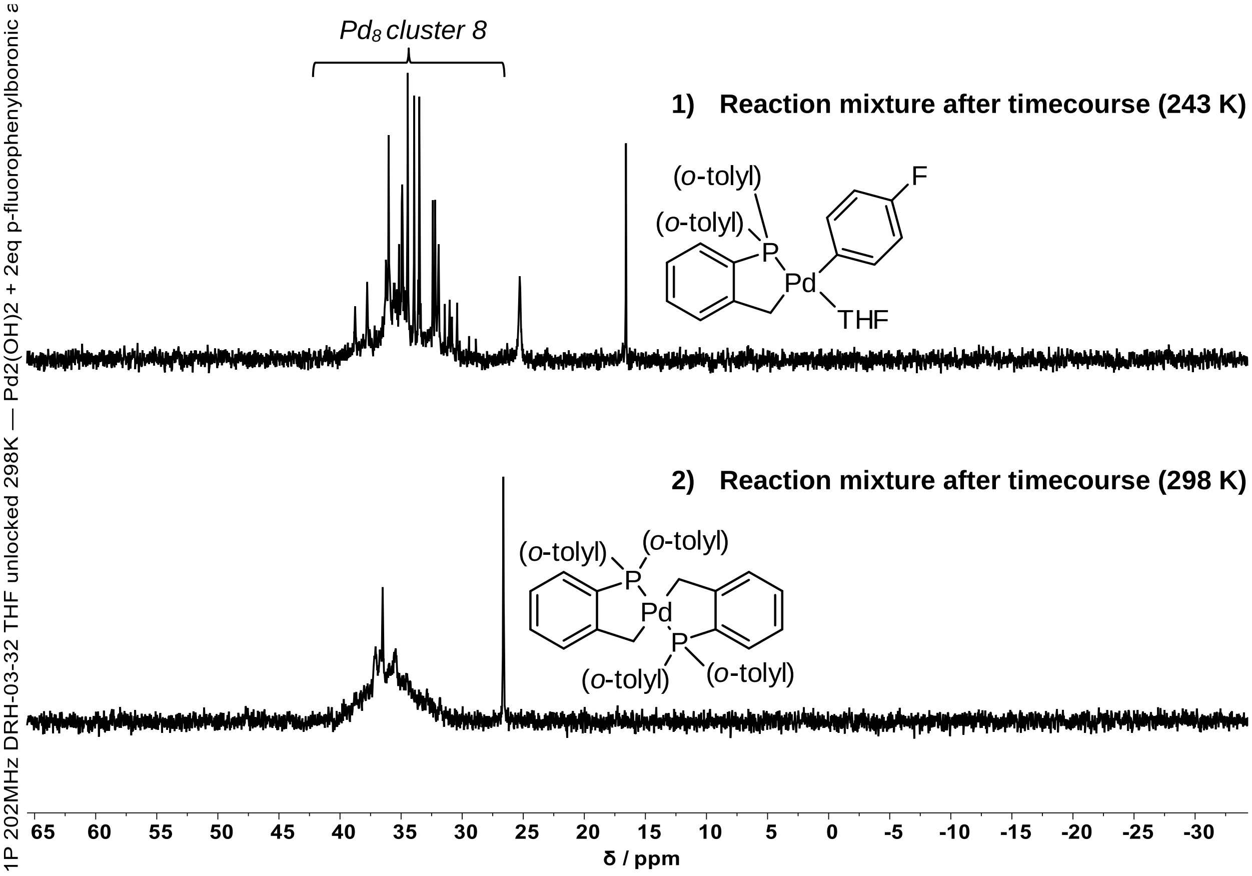


Figure 14: Stacked ^{31}P NMR (202 MHz, THF-unlocked) spectrum of the reaction mixture potentially containing Pd$_8$ cluster 8, 1) after the kinetic time course at 243 K (integral of 40 – 28 ppm region represents 90% of the ^{31}P environments, Pd intermediate = 3%), 2) the same sample at 298 K (integral of 40 – 30 ppm region represents 93% of the ^{31}P environments). Lab book ref. DRH-03-32 (163, 167)

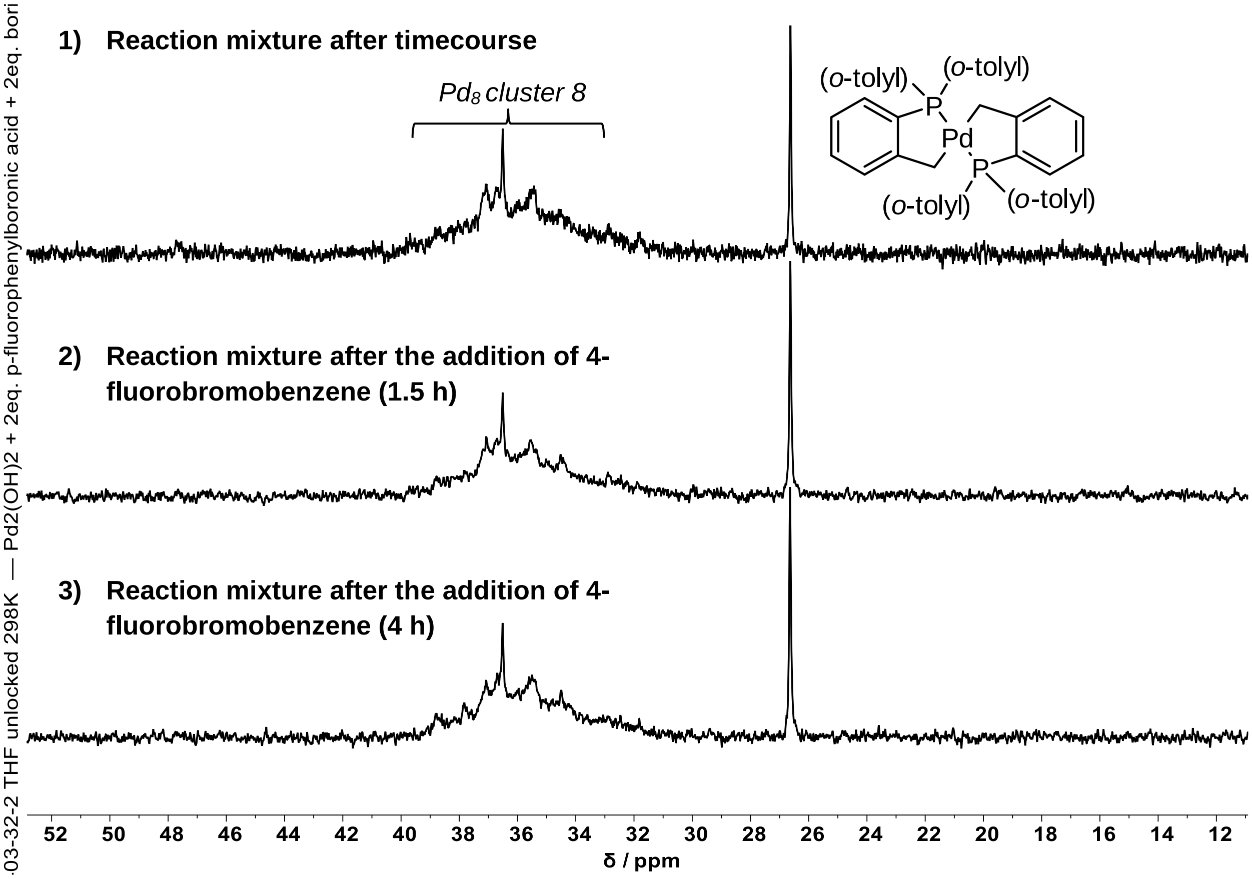


Figure 15: Stacked ^{31}P NMR ((top 202 MHz, others 243 MHz), THF-unlocked, 298 K) spectrum of the reaction mixture potentially containing Pd_8 cluster 8 1) after the kinetic time course at -30 °C, 2) after the addition of 4-fluorobromobenzene (1.5 h), 3) the same sample after 4 h. Lab book ref. DRH-03-32, DRH-03-32-2

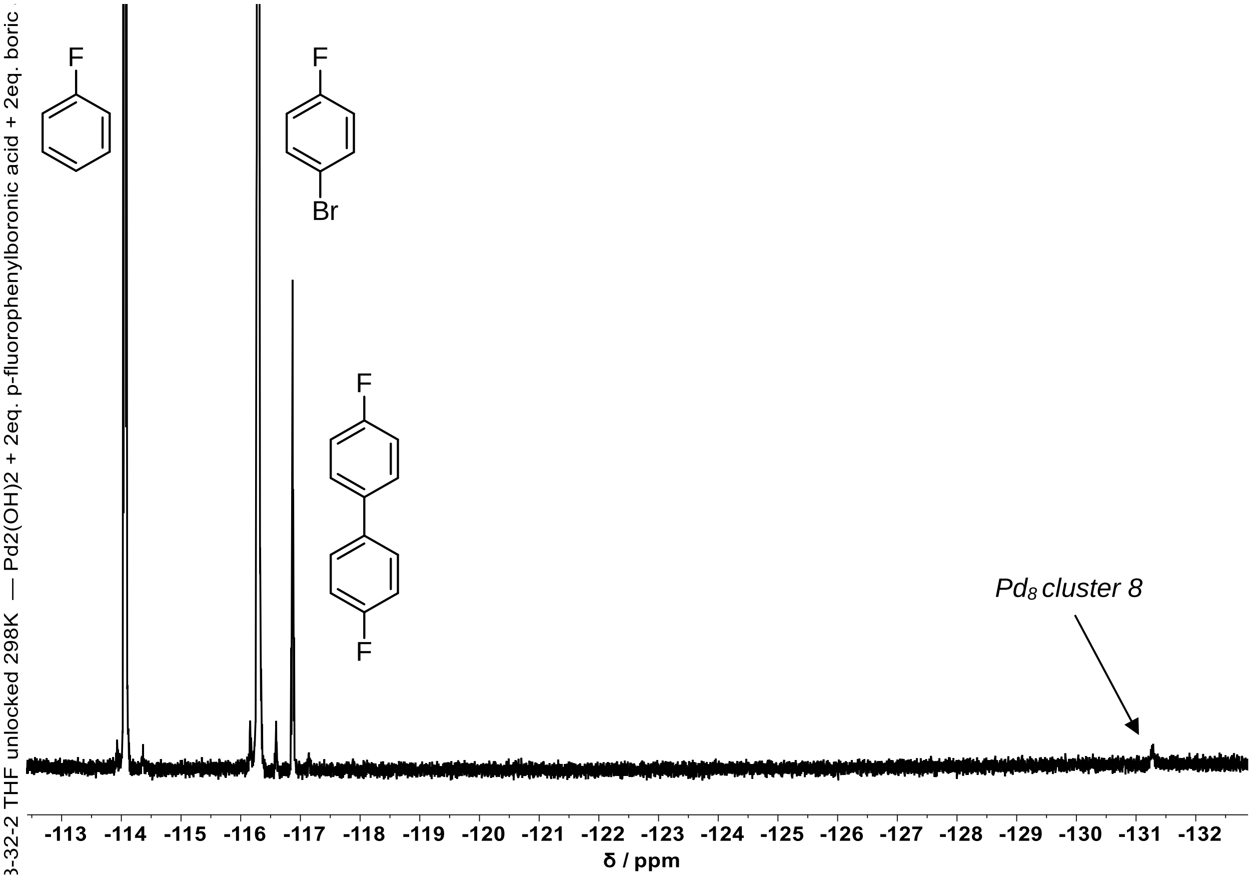
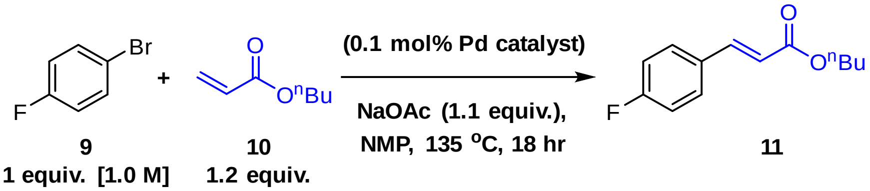


Figure 16: ^{19}F NMR (565 MHz, THF-unlocked, 298 K) spectrum of the reaction mixture containing Pd$_8$ cluster 8 following addition of 4-fluorobromobenzene after 4 days. Lab book ref. DRH-03-32-2

3. *In situ* IR Data – Methodology and Kinetic profiles



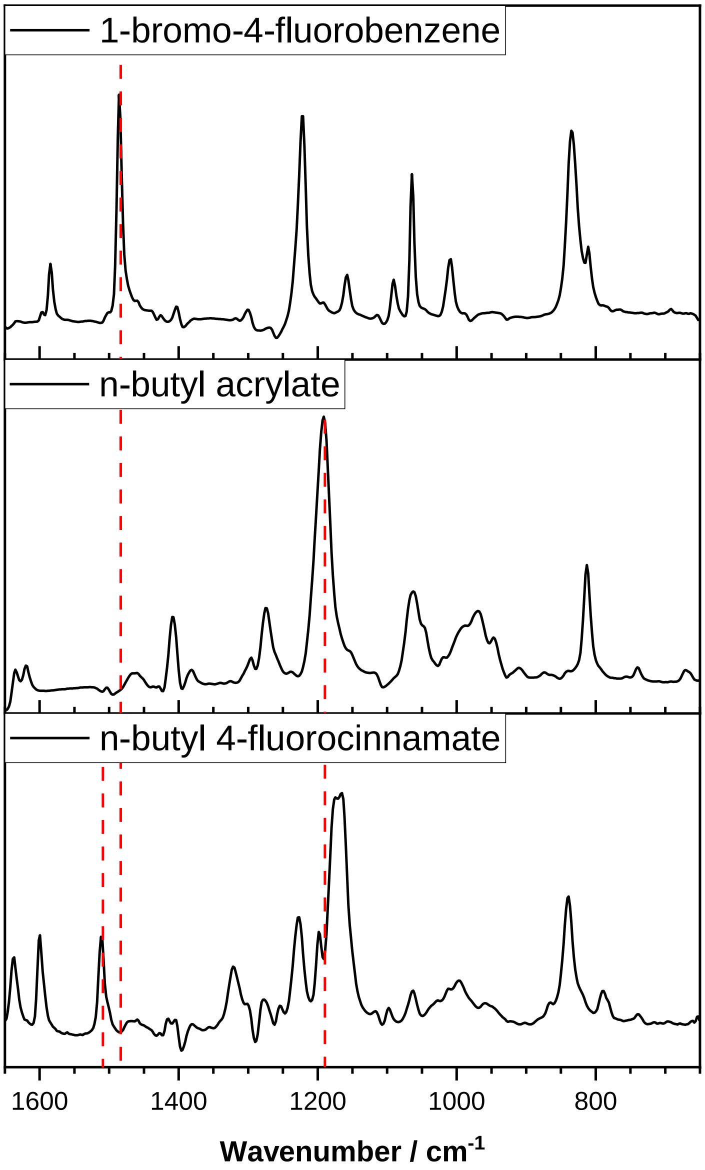


Figure 17: Reference spectra of (top) 1-bromo-4-fluorobenzene (9), (middle) n-butyl acrylate (10) (bottom), n-butyl 4-fluorocinnamate product (11) in NMP solvent. Spectra taken using ReactIR 15 (with Diamond probe) at 23 °C. The key peaks that are followed by IR during the reaction are indicated by the dashed red lines (1484 cm^{-1} for 1-bromo-4-fluorobenzene 9, 1190 cm^{-1} for n-butyl acrylate 10 and 1509 cm^{-1} for n-butyl 4-fluorocinnamate 11.

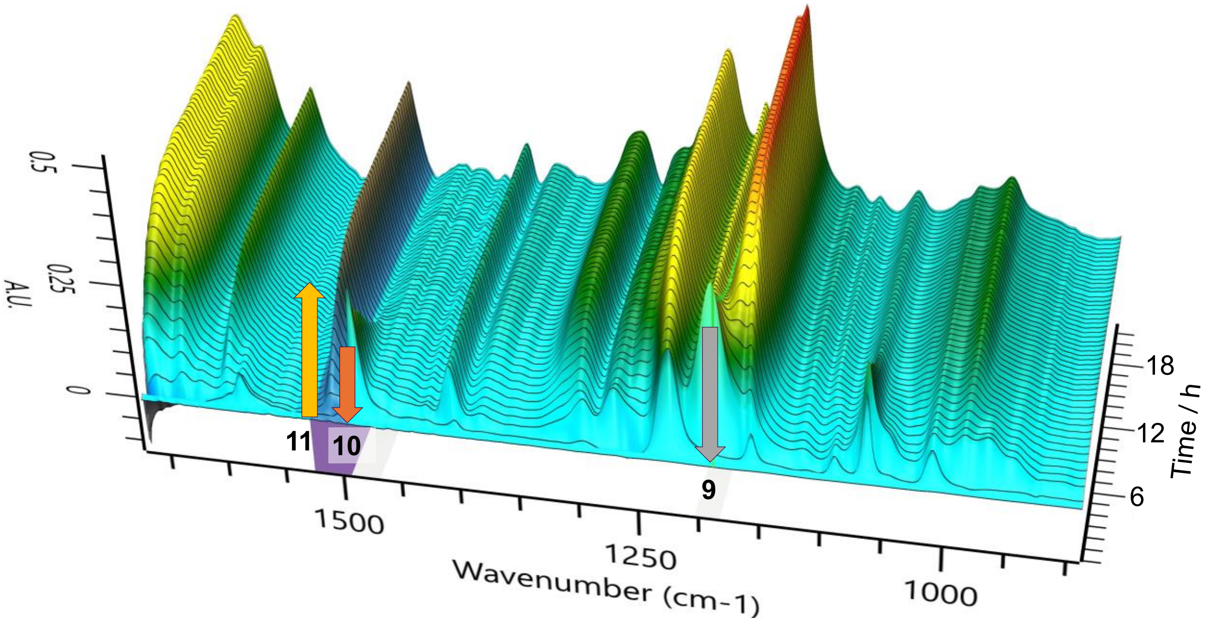


Figure 18: ***in situ*** **IR compilation surface generated by iC IR 7.1 software for the Heck reaction (lab book ref. DRH-01-144)**

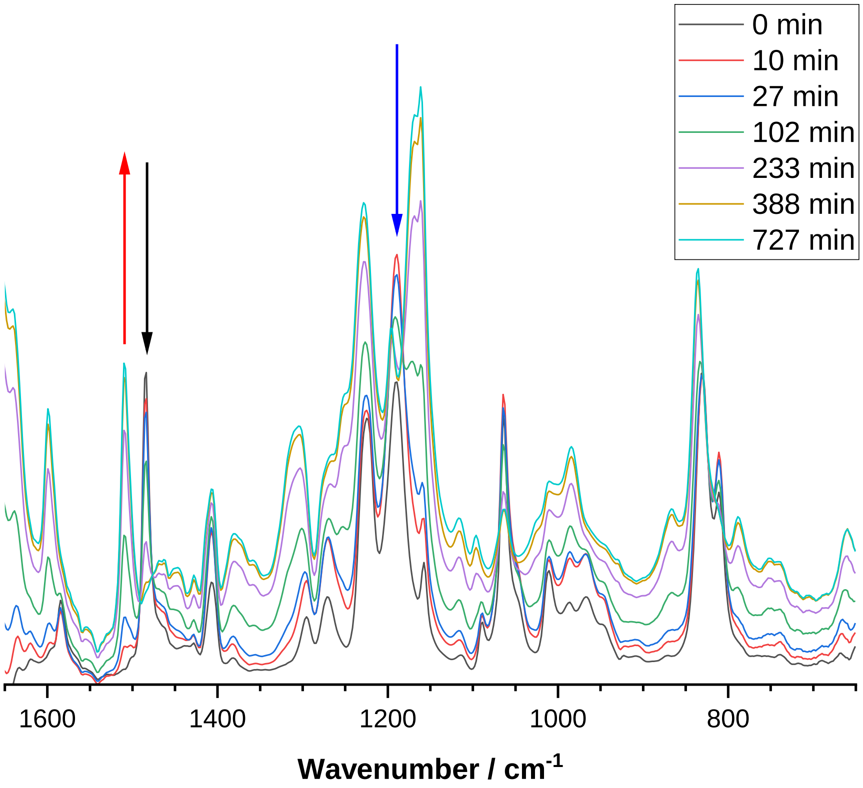


Figure 19: Selected spectra for the Heck reaction (lab book ref. DRH-01-144) over the course of the reaction. The reaction was sampled every 1 min. The direction of key peaks are indicated by arrows (blue for n-butyl acrylate 10 (1190 cm^{-1}), black for 1-bromo-4-fluorobenzene 9 (1484 cm^{-1}) and red for n-butyl 4-fluorocinnamate 11 (1509 cm^{-1})).

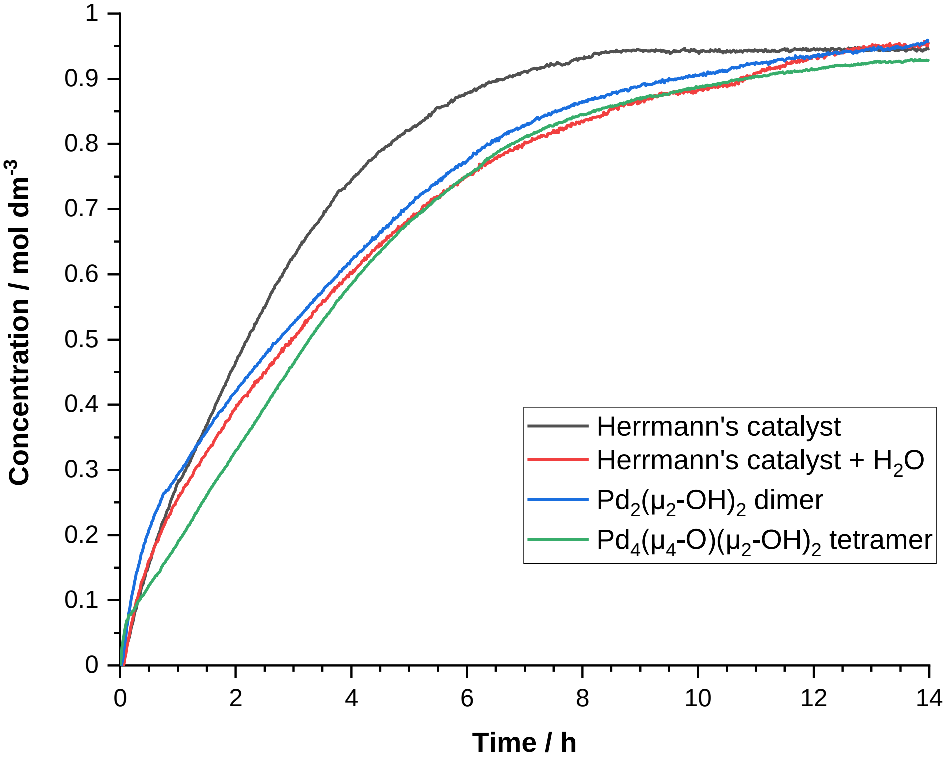


Figure 20: Comparison of Heck reactions (product 11 formation) with different pre-catalysts (General Procedure 2.1)

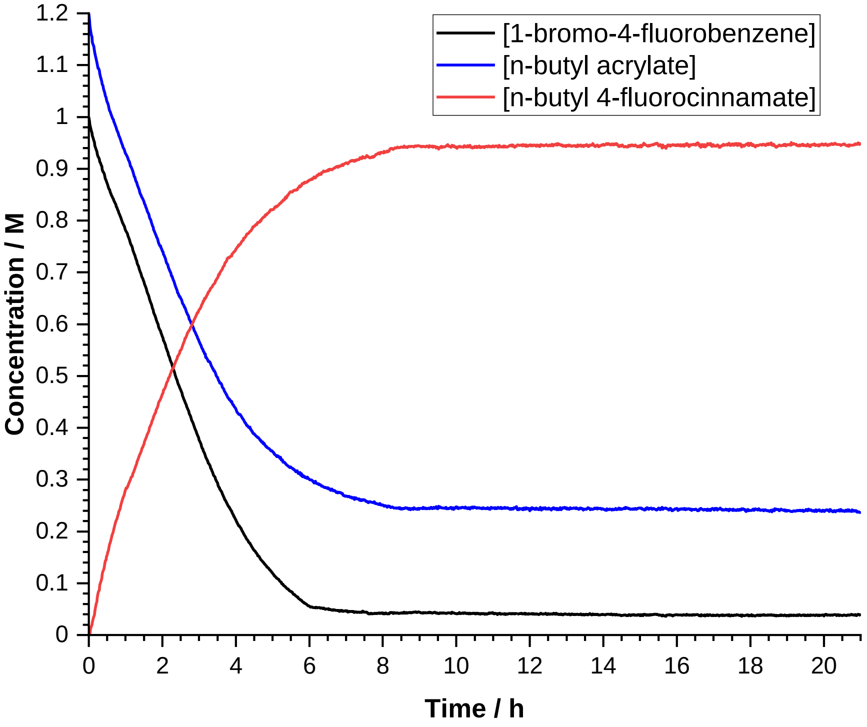


Figure 21: Heck reaction catalysed with commercial Herrmann's catalyst 1 (General Procedure 2.1). Lab book ref. DRH-01-144

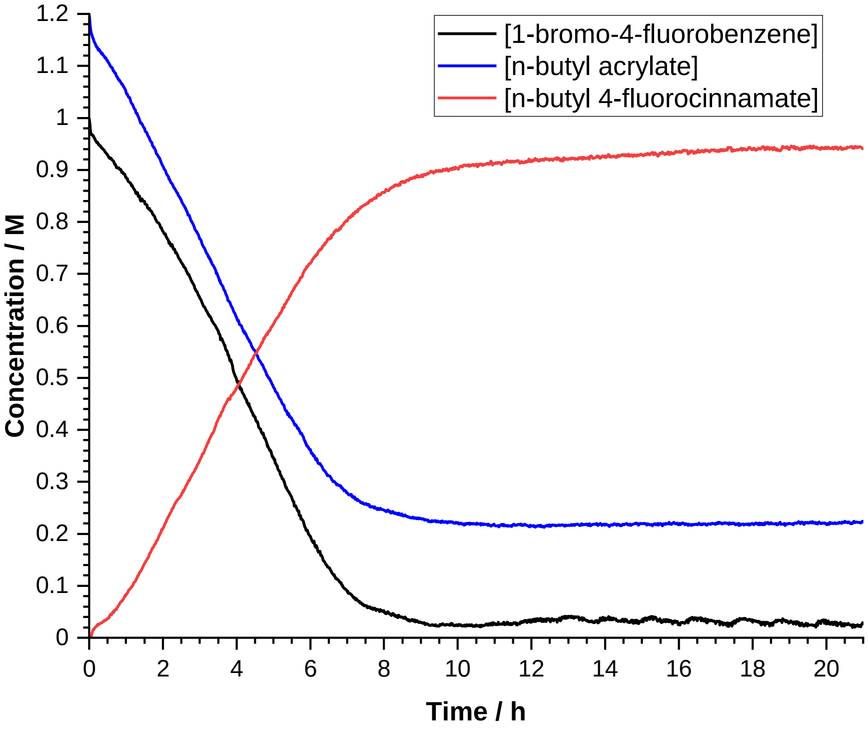


Figure 22: Heck reaction catalysed by commercial Herrmann's catalyst 1 with 50 µL water added (General Procedure 2.1). Lab book ref. DRH-01-145

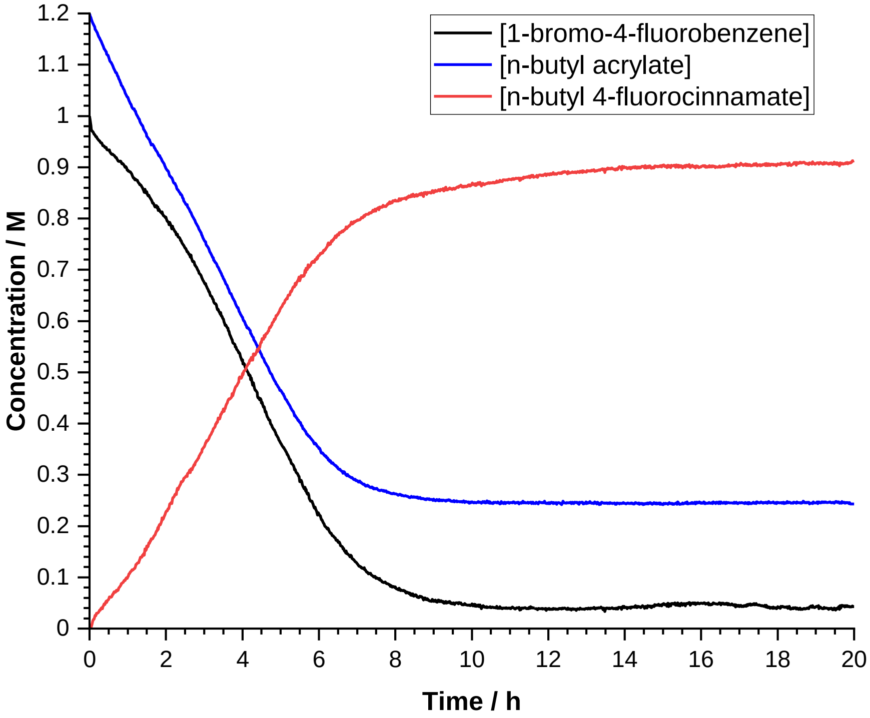


Figure 23: Heck reaction catalysed by $[Pd(P^\wedge C)(\mu_2\text{-}OH)]_2$ palladacycle 2 (General Procedure 2.1). Lab book ref. DRH-01-151

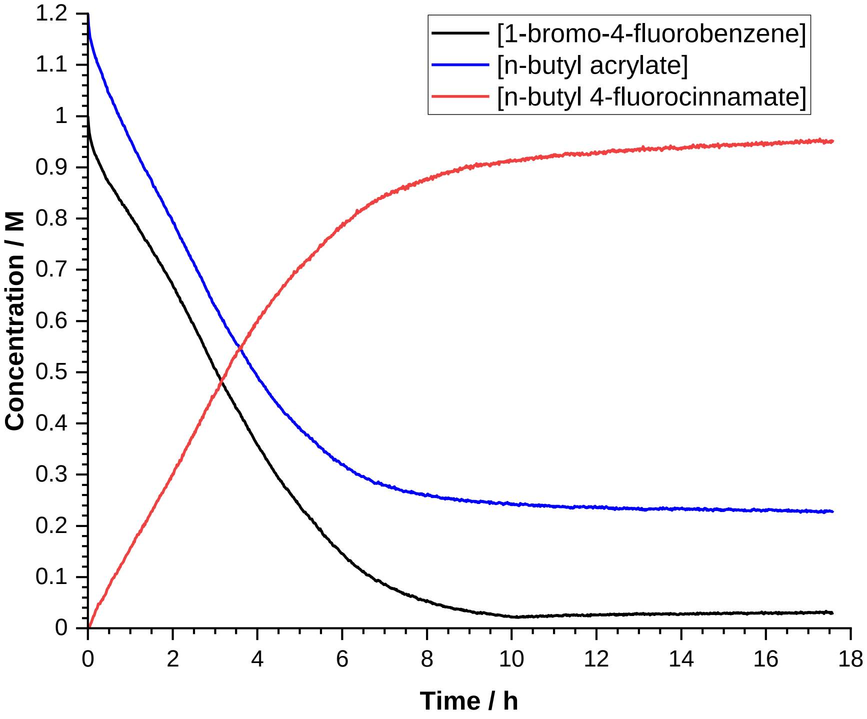


Figure 24: Heck reaction catalysed by palladacyclic Pd_4 cluster 3 (General Procedure 2.1). Lab book ref. DRH-01-146-2

4. X-Ray Crystallography

Diffraction data were collected at 110 K on an Oxford Diffraction SuperNova diffractometer with Cu-K_α radiation (λ = 1.54184 Å) or Mo-K_α radiation (λ = 0.71073), using an EOS CCD camera. The crystal was cooled with an Oxford Instruments Cryojet. Diffractometer control, data collection, initial unit cell determination, frame integration and unit-cell refinement was carried out with "Crysalis".[4] Face-indexed absorption corrections were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.[5] OLEX2[6] was used for overall structure solution and refinement . Within OLEX2, the algorithm used for structure solution was "ShelXT dual-space".[7] Refinement was carried out by full-matrix least-squares used the SHELXL-97[7] algorithm within OLEX2. All non-hydrogen atoms were refined anisotropically. Crystalmaker® software was used to visualise the structures as well as generating the figures presented herein.

ijsf21009: Palladacyclic $Pd_4(\mu_4\text{-}O)(\mu_2\text{-}OH)_2$ Cluster 3 CCDC 2288572 (lab book ref. DRH-01-131)

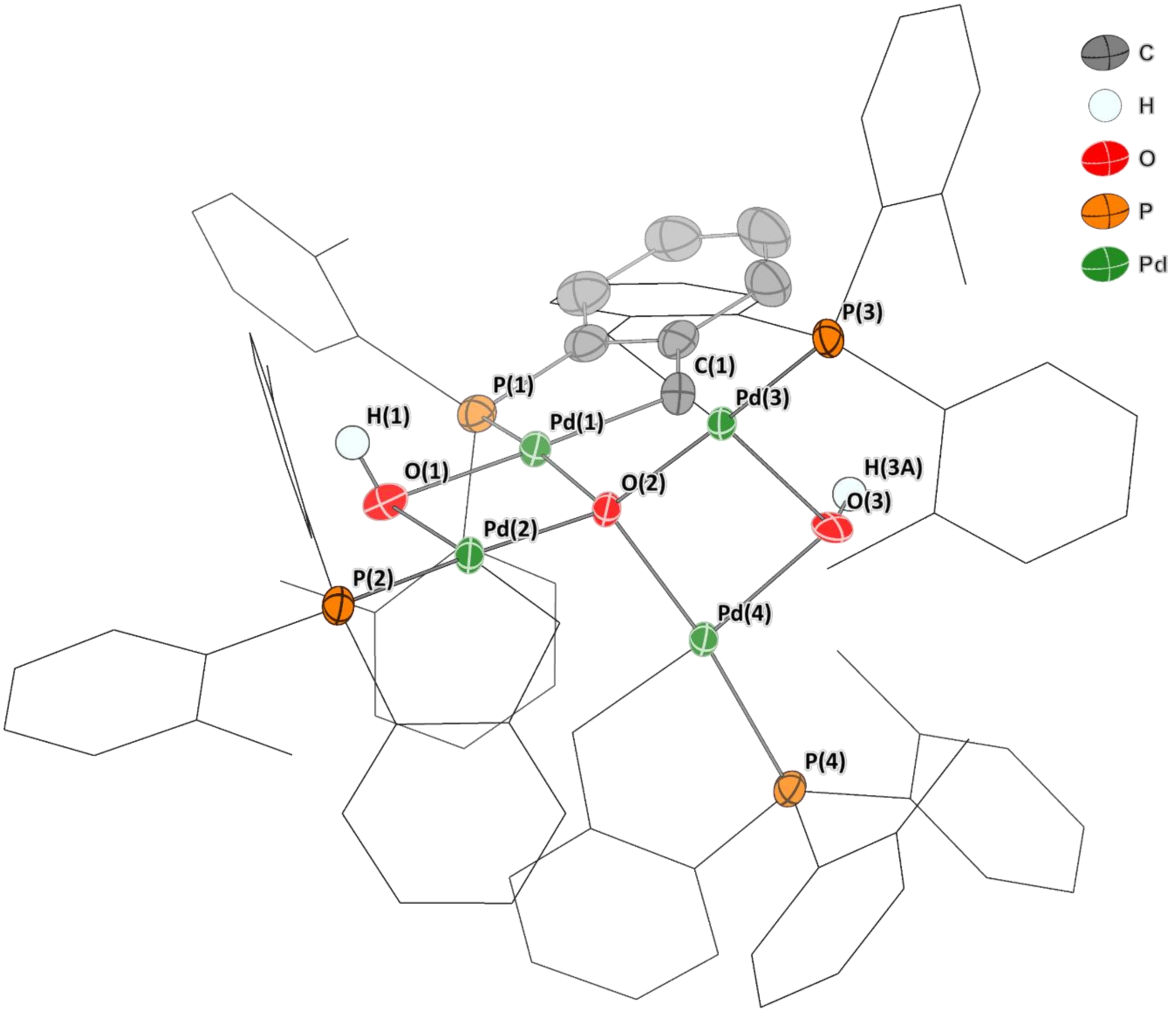


Figure 25: Structure, obtained by X-ray diffraction, of a single crystal of di-*cis*-(μ_2-hydroxido)(μ_4-oxido) di[*o*-(di-*o*-tolylphosphino)benzyl] dipalladium(II) 3 (thermal ellipsoids are set at 50% probability, selected H-atoms are omitted for clarity, for structural clarity most carbon atoms are displayed as a wireframe structure). Selected interatomic lengths /Å: Pd1-C1 = 2.032(4); Pd1-P1 = 2.1841(9); Pd1-O1 = 2.202(2); Pd1-O2 = 2.070(2); Pd1-Pd2 = 3.1785(4). Selected interatomic angles /°: P1-Pd1-C1 = 84.52(12); P1-Pd1-O1 = 102.74(18); Pd1-O1-Pd2 = 92.89(10); Pd1-O2-Pd2 = 99.66(10); Pd3-O2-Pd4 = 97.35(9).

Refinement Special Details

Hydroxyl hydrogens were restrained in position with an O-H bond length of 0.87 angstroms and an H-Pd distance of 2.57 angstroms.

Table 2: X-Ray Diffraction Data for the Pd_4 cluster 3

Identification code	**ijsf21009**
Empirical formula	$C_{84}H_{82}O_3P_4Pd_4$
Formula weight	1688.97
Temperature/K	110.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	13.6277(4)
b/Å	14.8406(4)
c/Å	20.3507(5)
α/°	98.300(2)
β/°	93.130(2)
γ/°	116.152(3)
Volume/Å^3	3623.25(19)
Z	2
ρ_{calc}g/cm^3	1.548
μ/mm^{-1}	9.099
F(000)	1708.0
Crystal size/mm^3	0.13 × 0.07 × 0.04
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.756 to 134.16
Index ranges	$-16 \le h \le 15$, $-14 \le k \le 17$, $-24 \le l \le 24$
Reflections collected	25088
Independent reflections	12912 [R_{int} = 0.0291, R_{sigma} = 0.0404]
Data/restraints/parameters	12912/6/870
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0308, wR_2 = 0.0740
Final R indexes [all data]	R_1 = 0.0378, wR_2 = 0.0777
Largest diff. peak/hole / e Å^{-3}	1.05/-0.68

ijsf22044: Palladaycyclic $Pd_4(\mu_2\text{-}Cl)_2(\mu_4\text{-}O)$ Cluster 5 CCDC 2288580 (lab book ref. DRH-03-75)

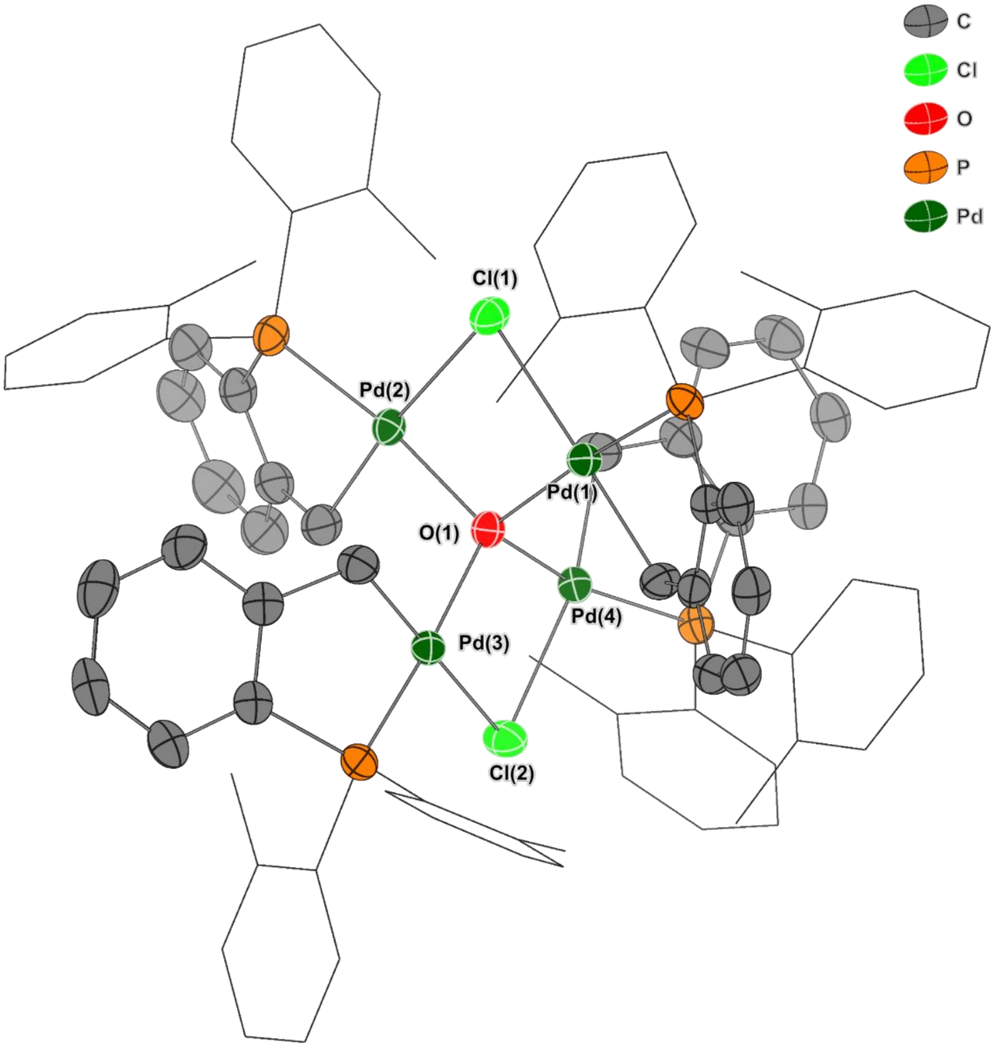


Figure 26: Structure, obtained by X-ray diffraction, of a single crystal of $Pd_4(\mu_2\text{-}Cl)_2(\mu_4\text{-}O)$ cluster 5 (thermal ellipsoids are set at 50% probability, H-atoms are omitted for clarity, for structural clarity most carbon atoms are displayed as a wireframe structure). Selected interatomic lengths /Å: Pd1-Cl1 = 2.4737(8), Pd1-O1 =2.101(2), Pd1-P1 = 2.2093(9), Pd1-C1 = 2.052(3). Selected interatomic angles /°: Pd1-Cl1-Pd2 = 84.35(3), Pd3-Cl2-Pd4 = 84.67(3), Pd1-O1-Pd4 = 103.46(9), Pd2-O1-Pd3 = 113.65(10).

Refinement special details

One of the tolyl groups was disordered and modelled in two positions with refined occupancies of 0.73:0.23(1). The aromatic ring of the minor form was constrained to be a regular hexagon with a C-C bond length of 1.39 angstroms. There was also a site containing a mixture of dichloromethane and pentane in a refined ratio of 0.615:0.385(5). For the pentane, the C-C bond lengths were restrained to be 1.53 angstroms and the C-C-C bond distances to be 2.48 angstroms.

Table 3: X-Ray data for $Pd_4(\mu_2\text{-}Cl)_2(\mu_4\text{-}O)$ cluster 5

Identification code	ijsf22044
Empirical formula	$C_{86.92}H_{86.43}Cl_{4.89}OP_4Pd_4$
Formula weight	1869.86
Temperature/K	110.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	13.9902(2)
b/Å	15.1119(2)
c/Å	19.6630(3)
α/°	82.3168(14)
β/°	83.1543(13)
γ/°	82.3307(13)
Volume/$Å^3$	4061.14(12)
Z	2
$\rho_{calc}g/cm^3$	1.529
μ/mm^{-1}	9.604
F(000)	1886.0
Crystal size/mm^3	0.149 × 0.043 × 0.012
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.046 to 134.16
Index ranges	$-14 \le h \le 16$, $-18 \le k \le 15$, $-23 \le l \le 23$
Reflections collected	50244
Independent reflections	14484 [$R_{int} = 0.0426$, $R_{sigma} = 0.0399$]
Data/restraints/parameters	14484/20/952
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	$R_1 = 0.0333$, $wR_2 = 0.0859$
Final R indexes [all data]	$R_1 = 0.0384$, $wR_2 = 0.0888$
Largest diff. peak/hole / e $Å^{-3}$	1.10/-0.86

ijsf21006a: Palladacyclic Pd_6 Cluster 7 CCDC 2288584 (lab book ref. DRH-01-123)

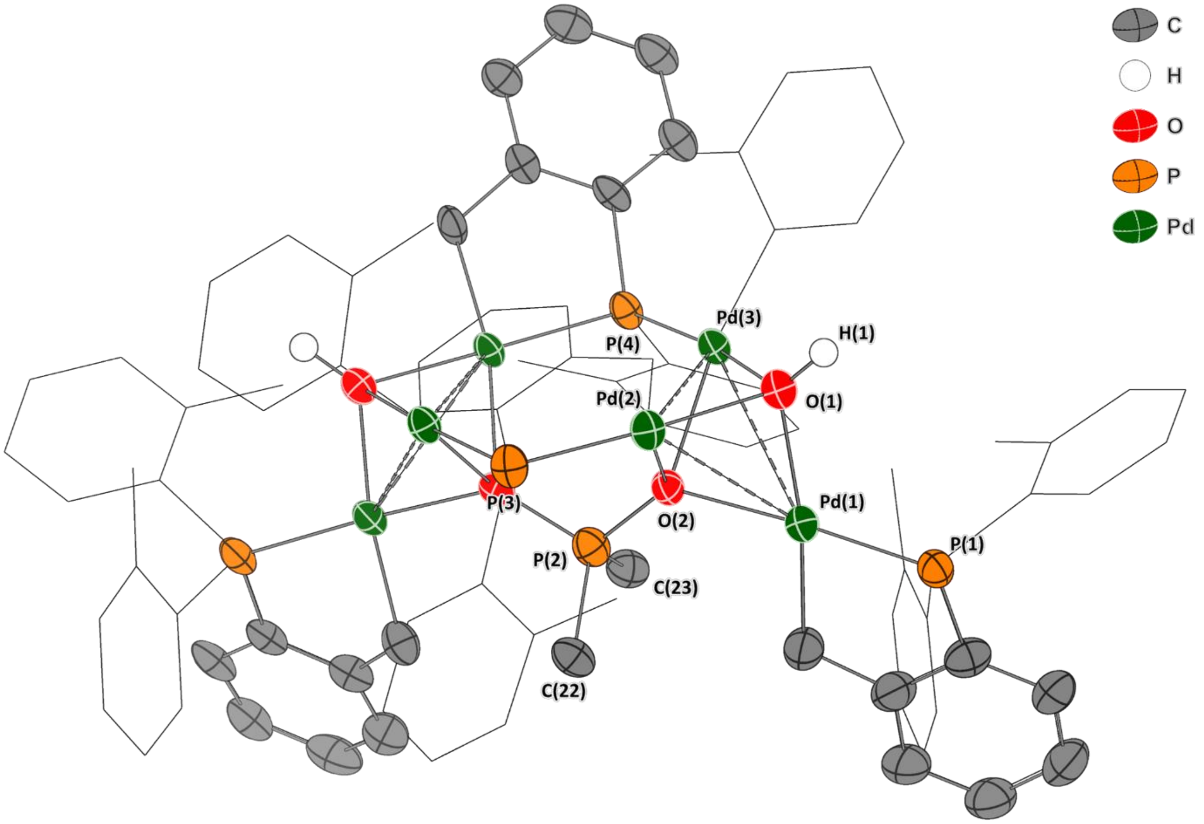


Figure 27: Structure, obtained by X-ray diffraction, of a single crystal of the Palladacyclic Pd_6 Cluster 7 (thermal ellipsoids are set at 50% probability, selected H-atoms are omitted for clarity, for structural clarity most carbon atoms are displayed as a wireframe structure). The unit cell contained two hexameric species and nine tetrahydrofurans of crystallization. Selected bond lengths (Å) and angles (°); Pd1-P1 = 2.201(2); Pd1-O1 = 2.141(6); Pd1-Pd2 = 3.0422(9); Pd2-P3 = 2.218(2); Pd3-P4 = 2.238(2); O2-P2 = 1.631(6); P2-C22 = 1.878(9); Pd1-Pd2-Pd3 = 59.30(2); O1-Pd1-O2 = 70.5(2); Pd1-O2-P2 = 129.7(3); C22-P2-C23 = 109.7(4).

Refinement Special Details

The presence of a large number of relatively high residual density peaks close to the palladium atoms is believed to be due to twinning. Unfortunately, this could be resolved with neither a non-merohedral nor a pseudo-merohedral approach.

The ADP of 4 carbons in one phenyl ring and a number of carbons were restrained to be approximately isotropic. 4 very disordered THFs were modelled using a solvent mask rather than a discrete atom model.

Table 4: X-Ray Diffraction data for the Palladacyclic Pd$_6$ Cluster 7

Identification code	ijsf21006a
Empirical formula	$C_{94}H_{104}O_6P_5Pd_6$
Formula weight	2123.02
Temperature/K	110.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	15.4929(2)
b/Å	20.2644(3)
c/Å	32.5025(5)
α/°	75.5537(14)
β/°	85.6199(13)
γ/°	84.3876(13)
Volume/Å^3	9820.0(3)
Z	4
ρ_{calc}g/cm^3	1.436
μ/mm^{-1}	9.814
F(000)	4268.0
Crystal size/mm^3	0.232 × 0.179 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.01 to 134.156
Index ranges	$-18 \le h \le 18$, $-23 \le k \le 24$, $-38 \le l \le 32$
Reflections collected	95656
Independent reflections	34970 [R_{int} = 0.0570, R_{sigma} = 0.0565]
Data/restraints/parameters	34970/60/2019
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0645, wR_2 = 0.1806
Final R indexes [all data]	R_1 = 0.0750, wR_2 = 0.1890
Largest diff. peak/hole / e Å^{-3}	3.91/-1.58

ijsf23078: Palladacyclic Pd$_8$ Cluster Complex 8 CCDC 2308805 (lab book ref. DRH-03-32-2)

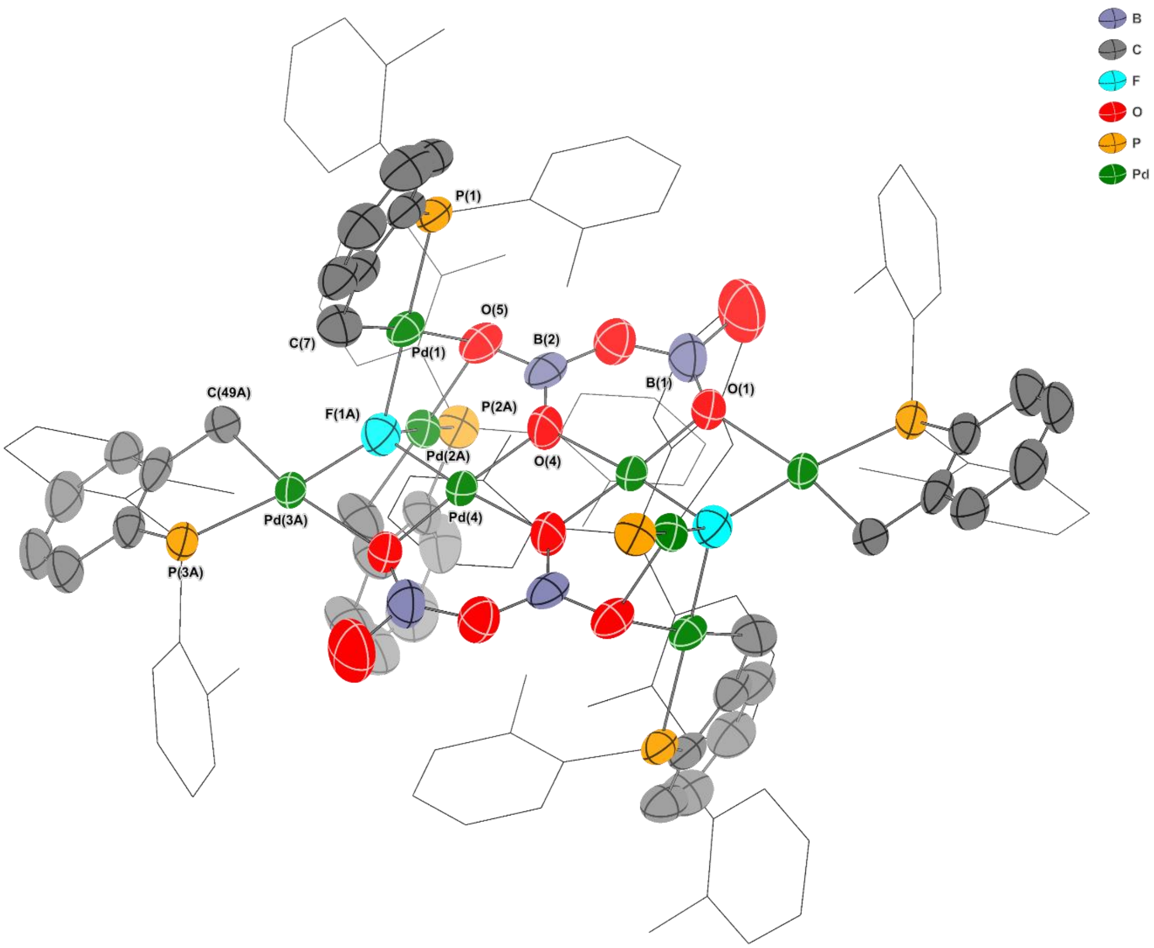


Figure 28: Structure, obtained by X-ray diffraction, of a single crystal of a palladacyclic Pd$_8$ cluster complex 8 (thermal ellipsoids are set at 50% probability, H-atoms are omitted for clarity). Due to high levels of disorder, only one isomer is displayed, and selected carbon atoms are displayed as wireframe structures for clarity. Selected interatomic lengths /Å: P1-Pd1 = 2.1856(10); Pd1-C7 = 2.024(5); Pd1-F1A = 2.02(3); Pd2A-F1A = 2.10(2); Pd3A-F1A = 2.06(3); Pd4-F1A = 2.04(3); Pd4-O1 = 1.991(3); Pd4-O4 = 1.980(3). Selected interatomic angles /°: O4-Pd4-O1 = 95.56(13); Pd1-F1A-Pd2A = 98.7(10); Pd1-F1A-Pd4 = 97.7(13); Pd2A-F1A-Pd3A = 131.2(14); Pd1-F1A-Pd3A = 120.6(13); P1-Pd1-C7 = 83.77(14).

Refinement Special Details

The structure exhibited considerable disorder. All but one benzyl was modelled in two positions with equal occupancy (free refinement of occupancies revealed a 1:1 ratio). In addition, two palladiums, two phosphorus and the fluorine were also modelled in two positions with equal occupancy. The ADPs of each pair of disordered atoms were constrained to be equal (e.g. Pd2a & Pd2b, C8a & C8b). 5 aromatic rings were constrained to be regular hexagons with a C-C bond length of 1.39 angstroms (8a-13a, 8b-13b, 15b-20b, 29a-34a, 29b-24b). The crystal contained highly disordered solvent for which a discrete atom model could not be obtained. Use of a solvent mask gave an estimated void volume of 170 cubic angstroms containing 42 electrons per asymmetric unit. This could be either a tetrahydrofuran, a pentane or a mixture of both.

Table 5: X-Ray Diffraction Data for the palladacyclic Pd_8 cluster complex 8

Identification code	**ijsf23078**
Empirical formula	$C_{63}H_{60}B_2FO_5P_3Pd_4$
Formula weight	1456.24
Temperature/K	110.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	15.0801(3)
b/Å	15.0825(3)
c/Å	16.2726(2)
α/°	79.7260(10)
β/°	74.1320(10)
γ/°	63.091(2)
Volume/Å^3	3168.19(11)
Z	2
ρ_{calc}g/cm^3	1.527
μ/mm^{-1}	10.116
F(000)	1452.0
Crystal size/mm^3	0.104 × 0.067 × 0.044
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.136 to 134.152
Index ranges	$-14 \leq h \leq 18$, $-13 \leq k \leq 18$, $-19 \leq l \leq 19$
Reflections collected	36300
Independent reflections	11292 [R_{int} = 0.0394, R_{sigma} = 0.0407]
Data/restraints/parameters	11292/103/862
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0376, wR_2 = 0.1006
Final R indexes [all data]	R_1 = 0.0469, wR_2 = 0.1056
Largest diff. peak/hole / e Å^{-3}	1.34/-0.54

5. NMR Spectral Data for Organic and Inorganic Compounds

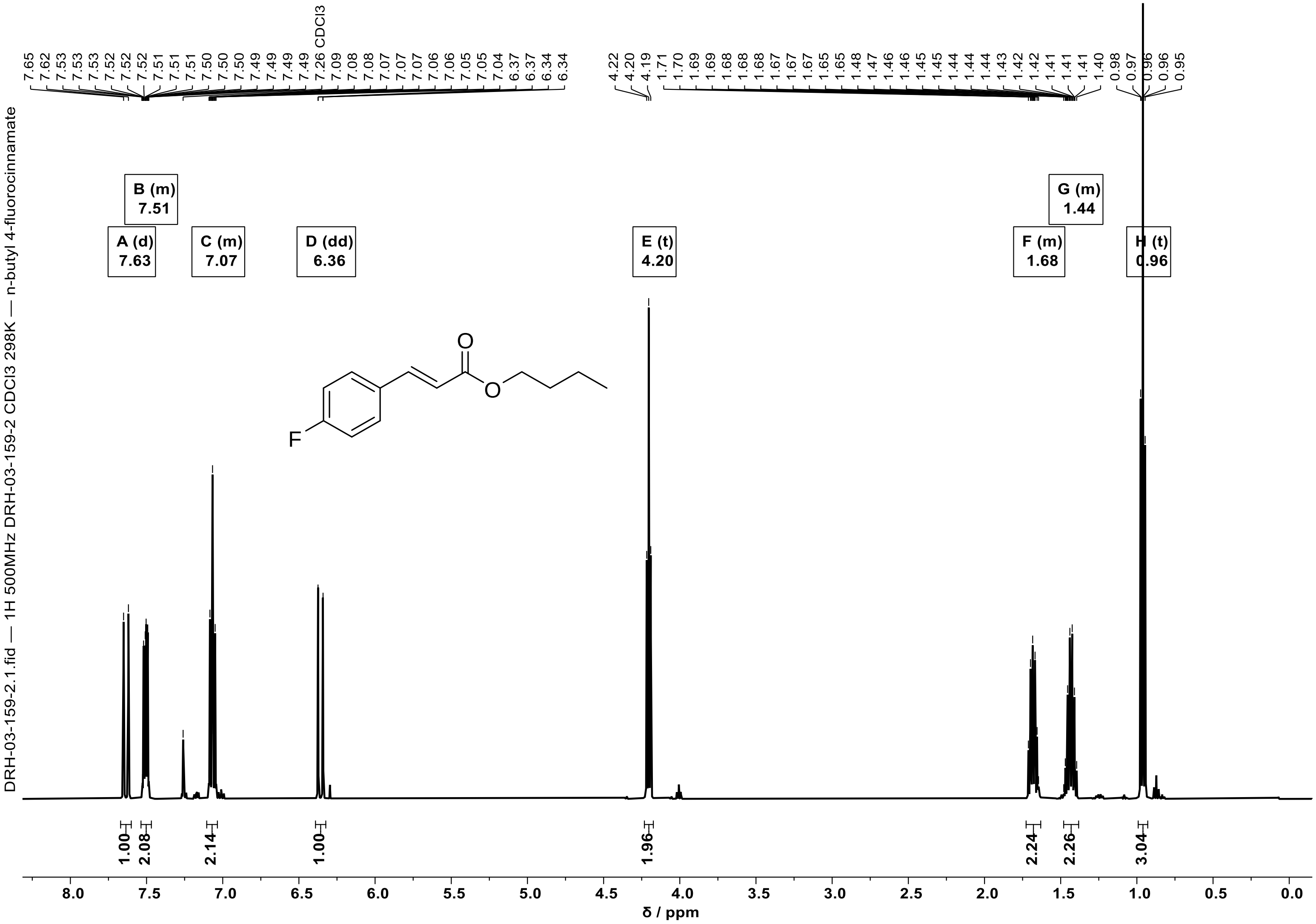


Figure 29: ^{1}H NMR (500 MHz, C*D*Cl$_3$, 32 scans, 298 K) spectrum of n-butyl 4-fluorocinnamate 11. 2% of the biaryl side-product (derived from 9) co-eluted, and is present as a small impurity. Lab book ref. DRH-03-159

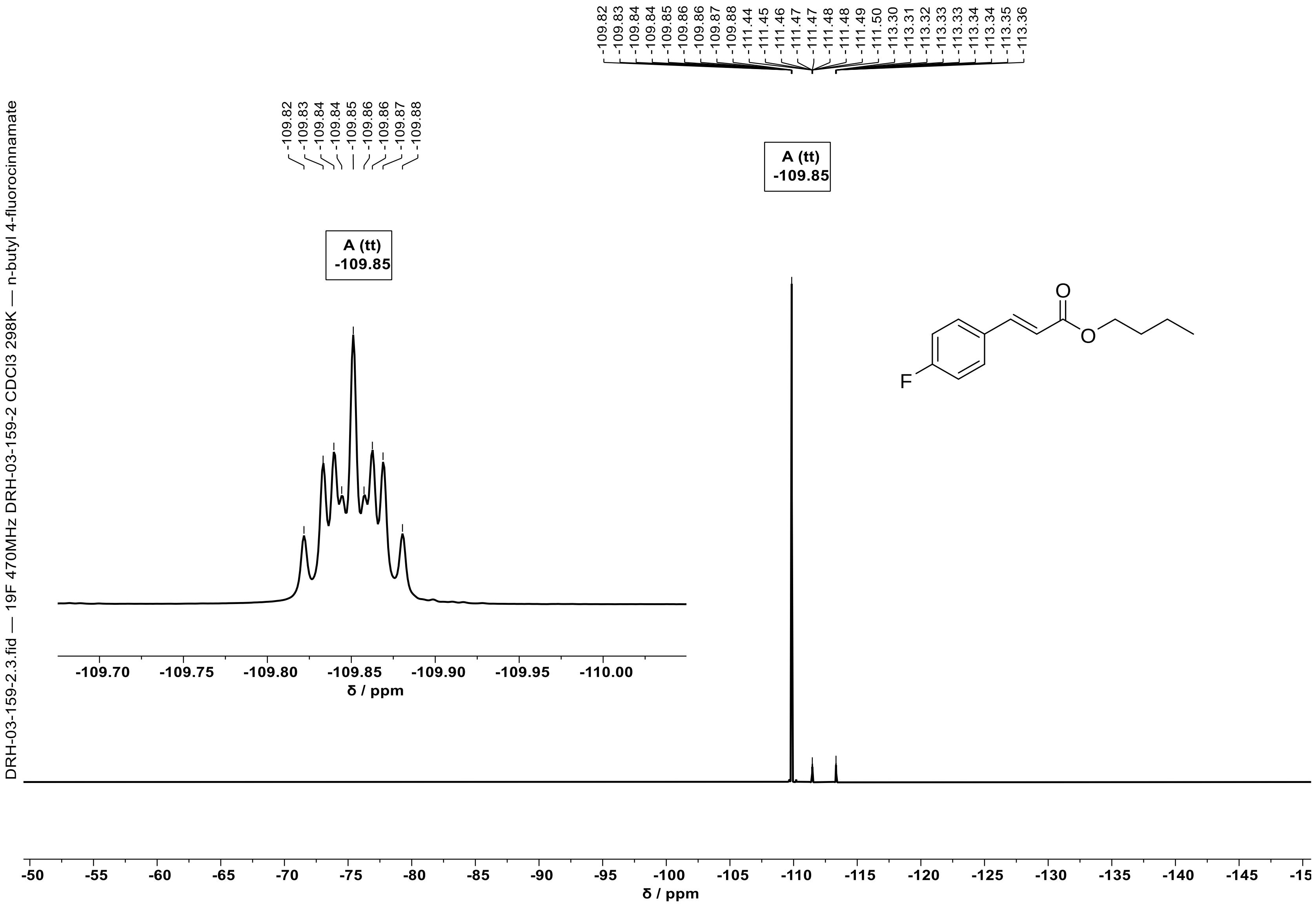


Figure 30: ^{19}F NMR (470 MHz, C*D*Cl$_3$, 64 scans, 298 K) spectrum of n-butyl 4-fluorocinnamate 11. Small impurities are visible at -111.47 and -113.33 ppm (~2%). Lab book ref. DRH-03-159

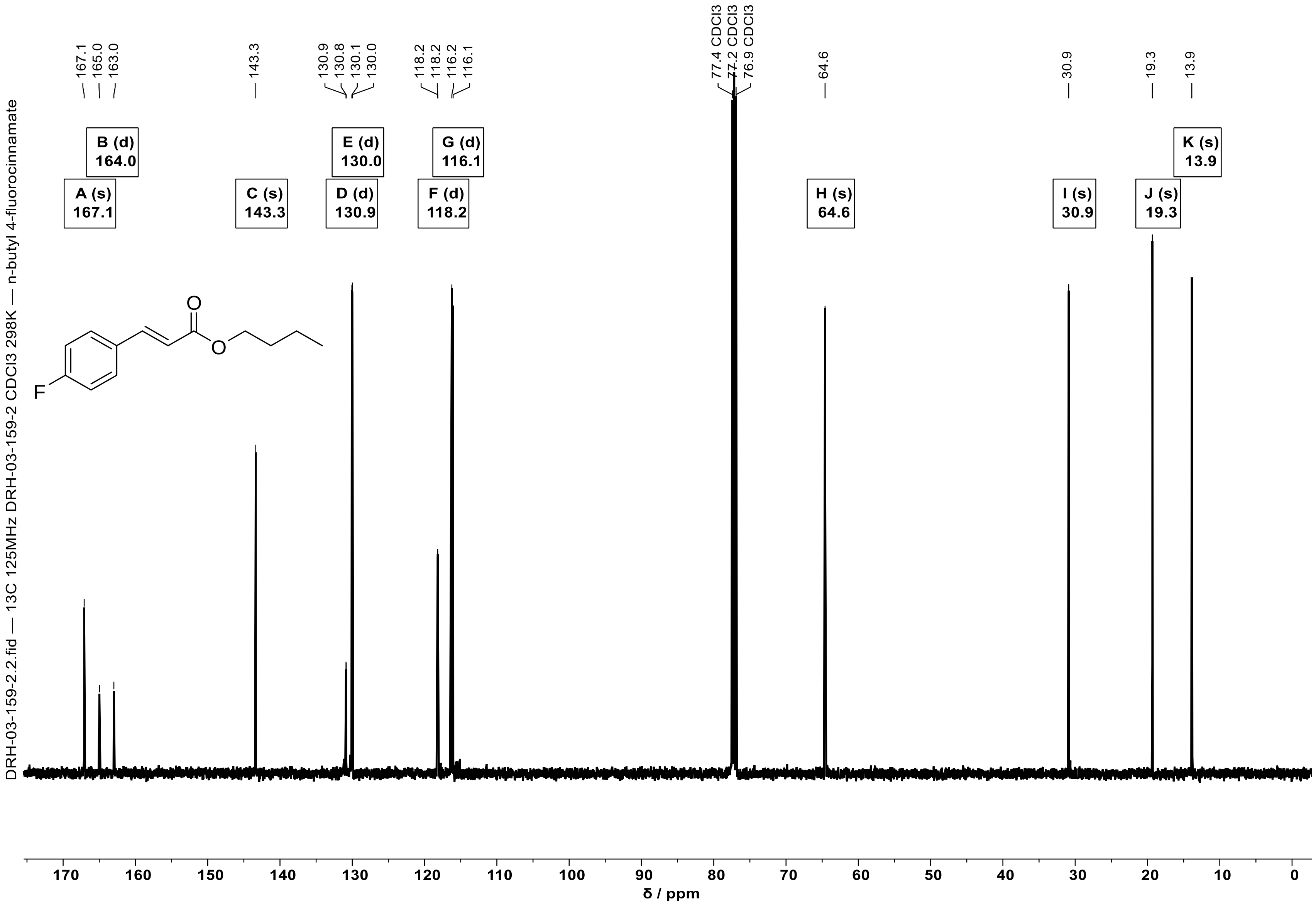


Figure 31: **^{13}C NMR (125 MHz, C*D*Cl$_3$, 128 scans, 298 K) spectrum of n-butyl 4-fluorocinnamate 11. Lab book ref. DRH-03-159**

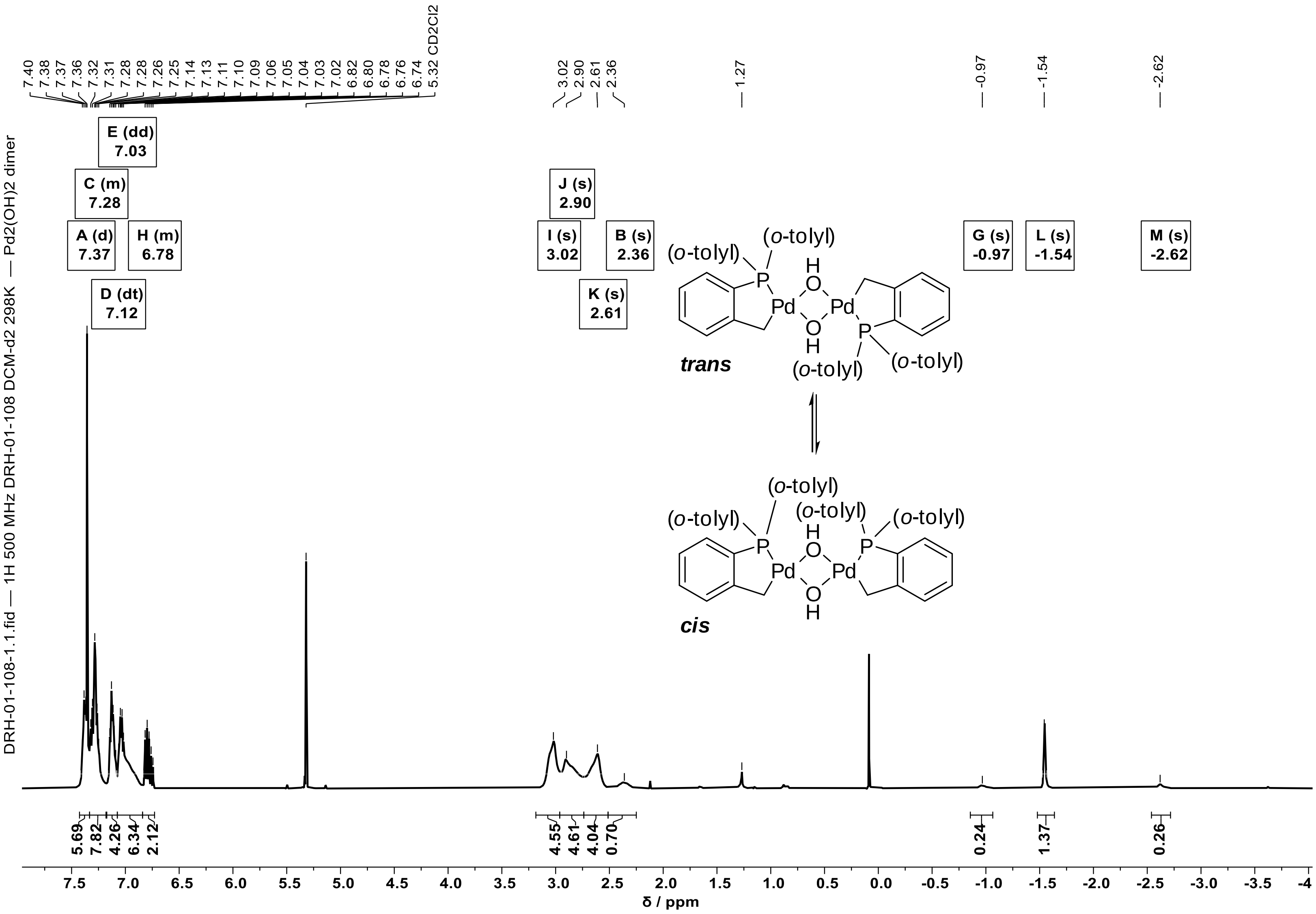


Figure 32: ^{1}H NMR (500 MHz, DCM-d_2, 32 scans, 298 K) spectrum of the [Pd(C^P)(μ_2-OH)]$_2$ palladacycle 2. Due to poor resolution of broad peaks, this sample was re-ran at 203 K to resolve environments. Lab book ref. DRH-01-108

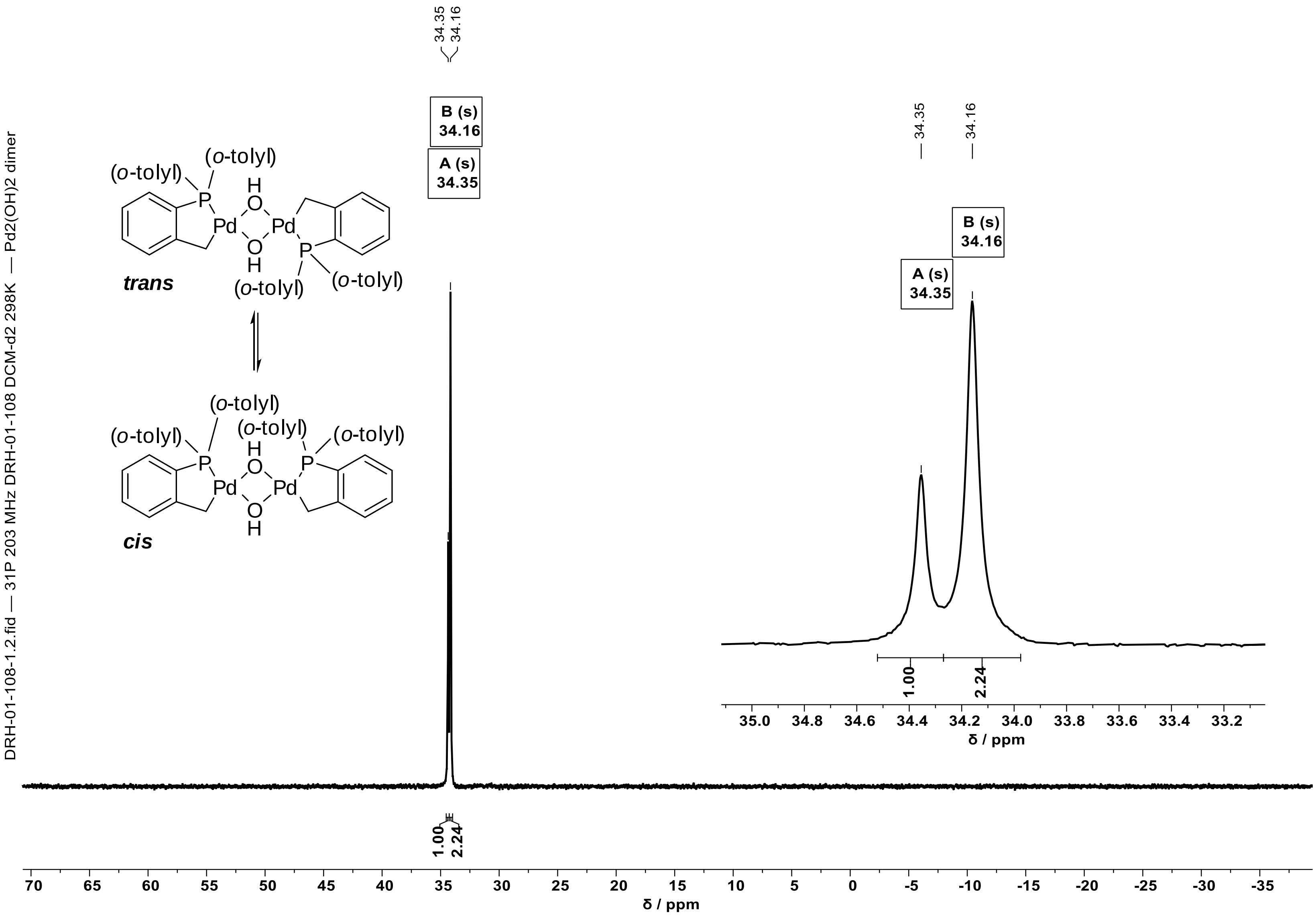


Figure 33: ^{31}P NMR (203 MHz, DCM-d_2, 128 scans, 298 K) spectrum of the $[Pd(C^{\wedge}P)(\mu_2\text{-}OH)]_2$ palladacycle 2. Cis/trans isomers are present, giving two signals. Due to poor resolution of broad peaks, this sample was re-ran at 203 K to resolve environments. Lab book ref. DRH-01-108

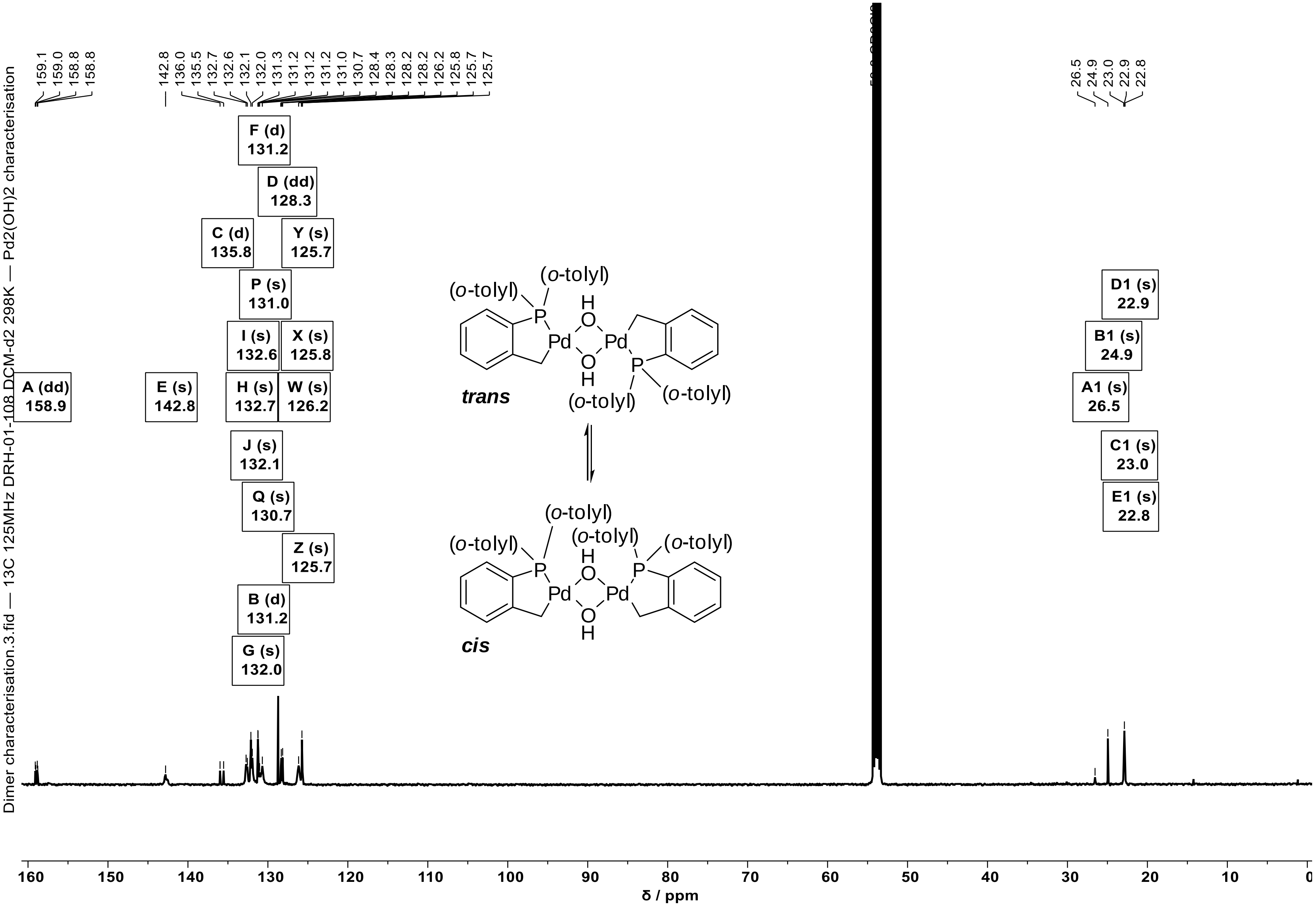


Figure 34: ^{13}C NMR (126 MHz, DCM-d_2, 49732 scans, 298 K) spectrum of the [Pd(C^P)(μ_2-OH)]$_2$ palladacycle 2. Lab book ref. DRH-01-108

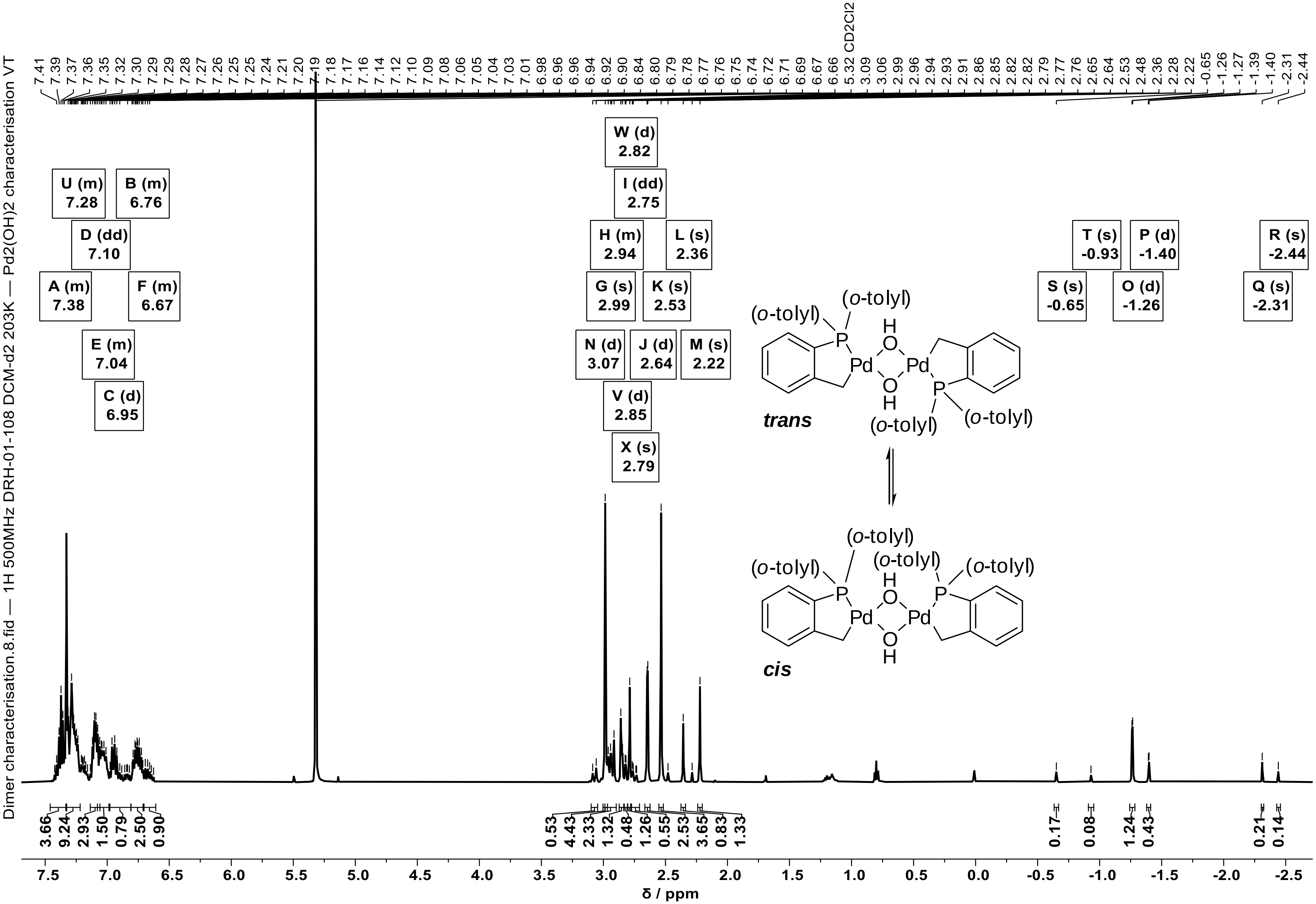


Figure 35: ^1H NMR (500 MHz, DCM-d_2, 64 scans, 203 K) spectrum of the [Pd(C^P)(μ_2-OH)]$_2$ palladacycle 2. Lab book ref. DRH-01-108

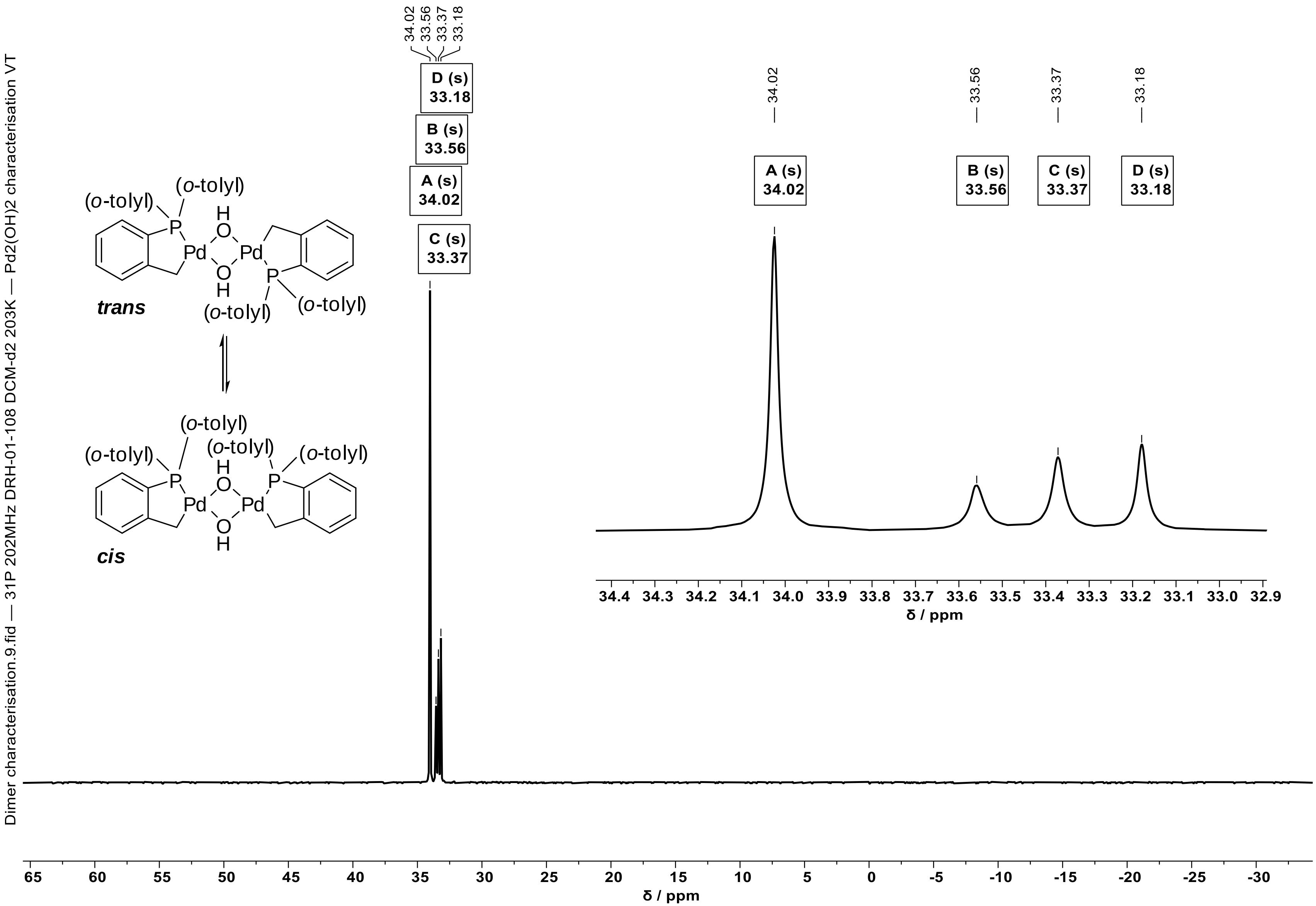


Figure 36: ^{31}P NMR (203 MHz, DCM-d_2, 256 scans, 203 K) spectrum of the $[Pd(C^\wedge P)(\mu_2\text{-}OH)]_2$ palladacycle 2. Lab book ref. DRH-01-108

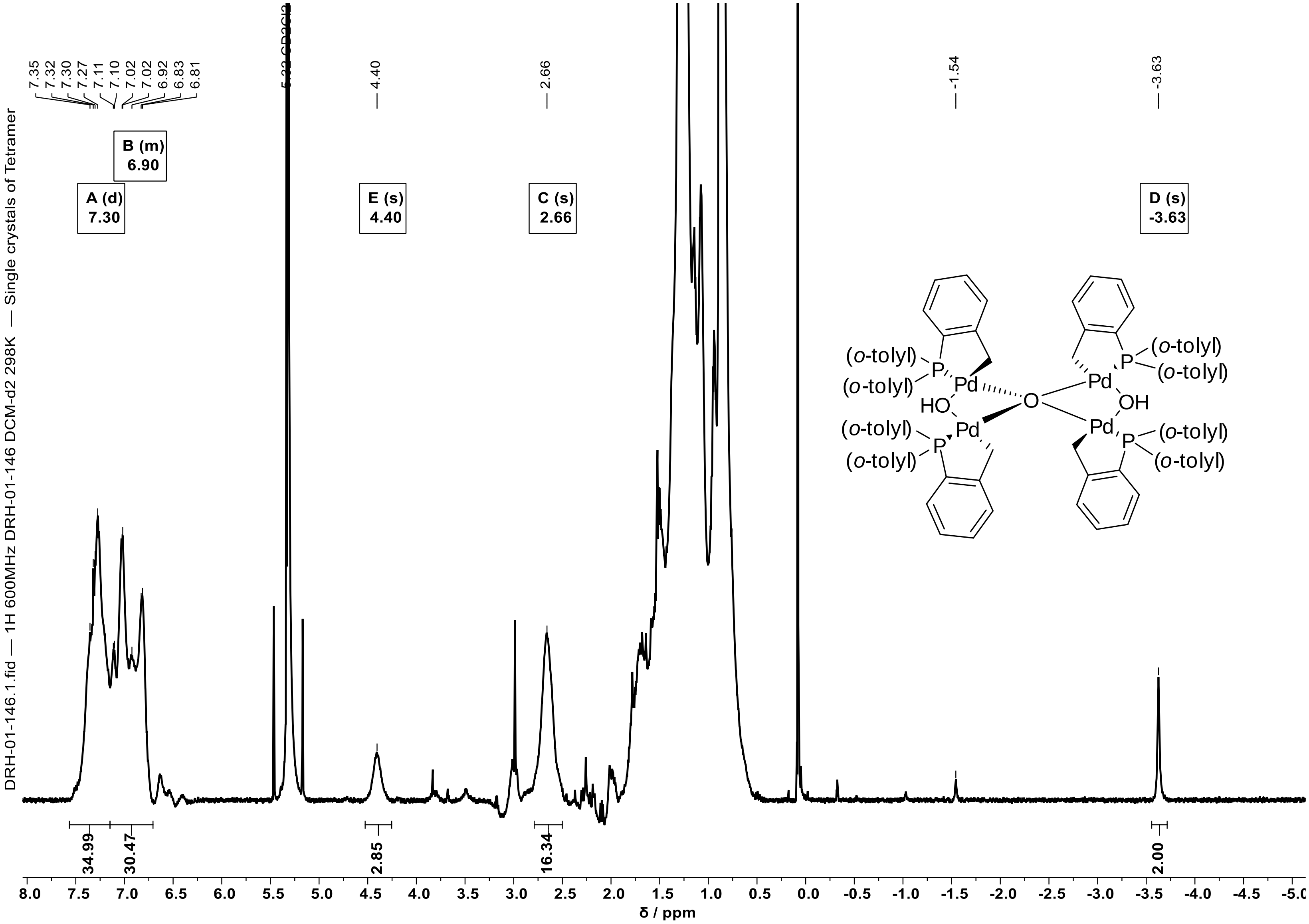


Figure 37: ^{1}H NMR (600 MHz, DCM-d_2, 256 scans, 298 K) spectrum of the palladacyclic Pd$_4$(μ$_4$-O)(μ$_2$-OH)$_2$ cluster 3. The non-integrated region between 2.0 and 0.5 ppm is residual grease from manual separation of single crystals. Lab book ref. DRH-01-146

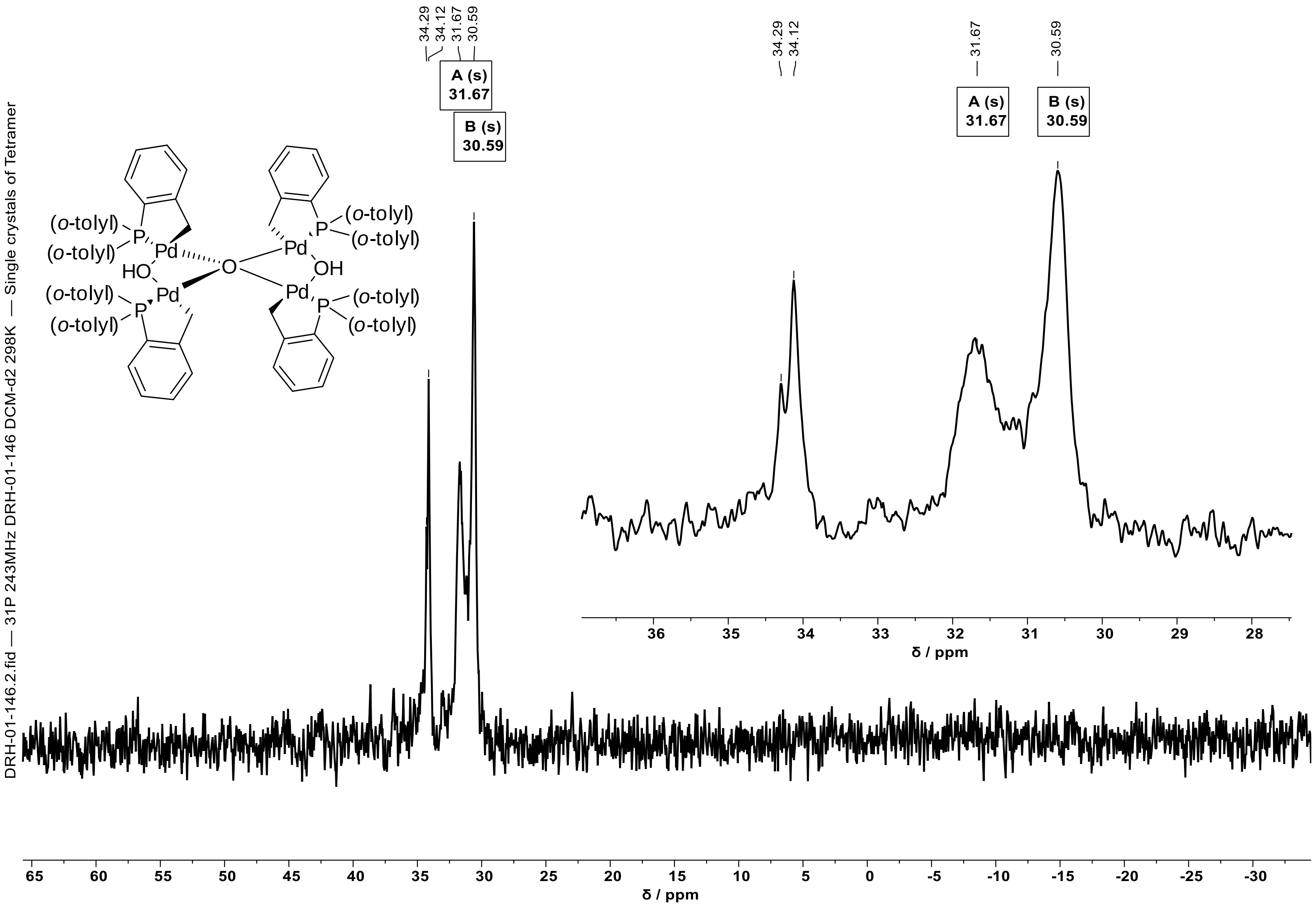


Figure 38: ^{31}P NMR (243 MHz, DCM-d_2, 1024 scans, 298 K) spectrum of the palladacyclic $Pd_4(\mu_4\text{-}O)(\mu_2\text{-}OH)_2$ cluster 3. Lab book ref. DRH-01-146

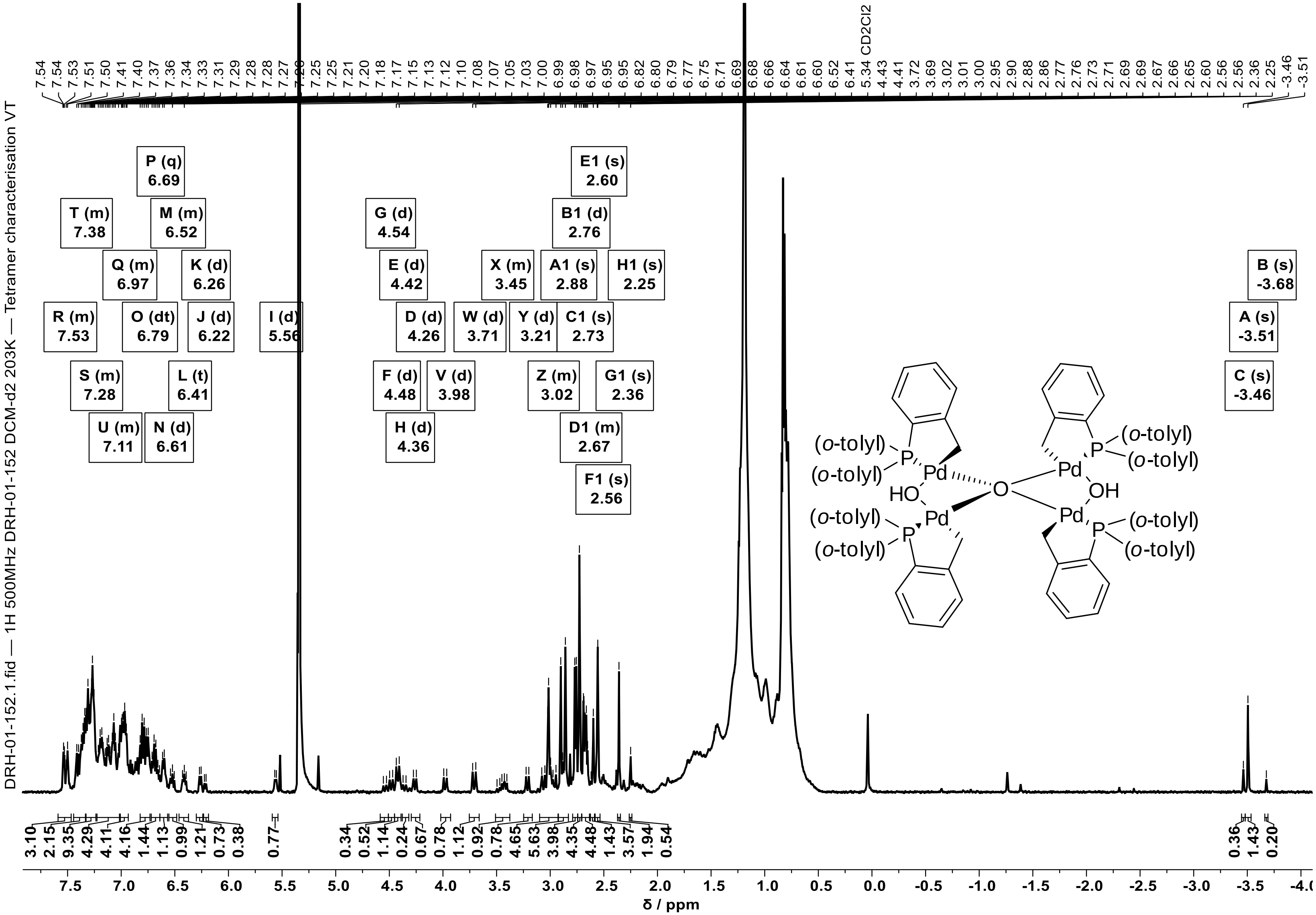


Figure 39: ^{1}H NMR (500 MHz, DCM-d_2, 128 scans, 203 K) spectrum of the palladacyclic Pd$_4$(μ$_4$-O)(μ$_2$-OH)$_2$ cluster 3. The non-integrated region between 2.0 and 0.5 ppm is residual grease from manual separation of single crystals, Lab book ref. DRH-01-152

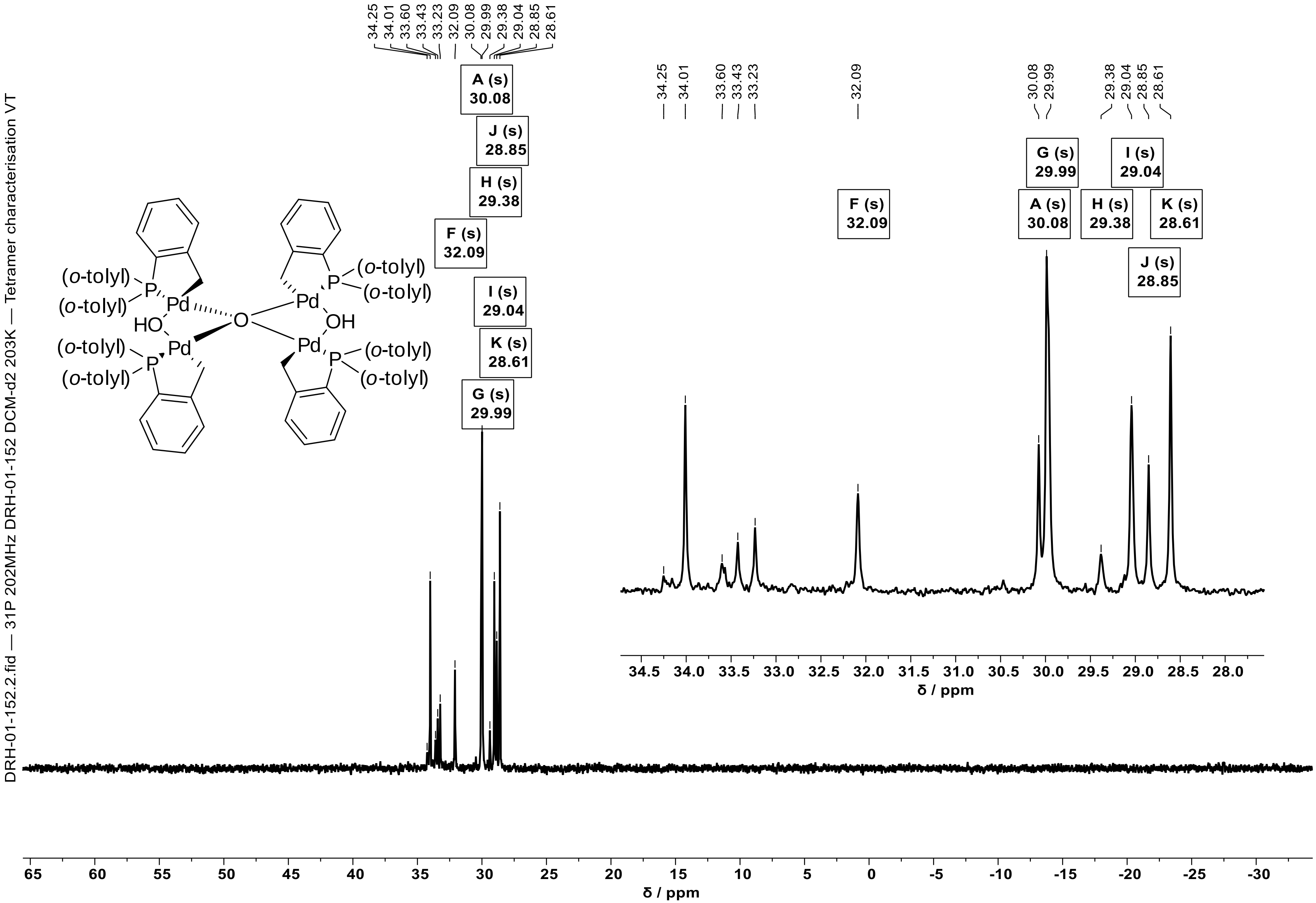


Figure 40: ^{31}P NMR (203 MHz, DCM-d_2, 512 scans, 203 K) spectrum of the palladacyclic Pd$_4$(μ$_4$-O)(μ$_2$-OH)$_2$ cluster 3. Lab book ref. DRH-01-152

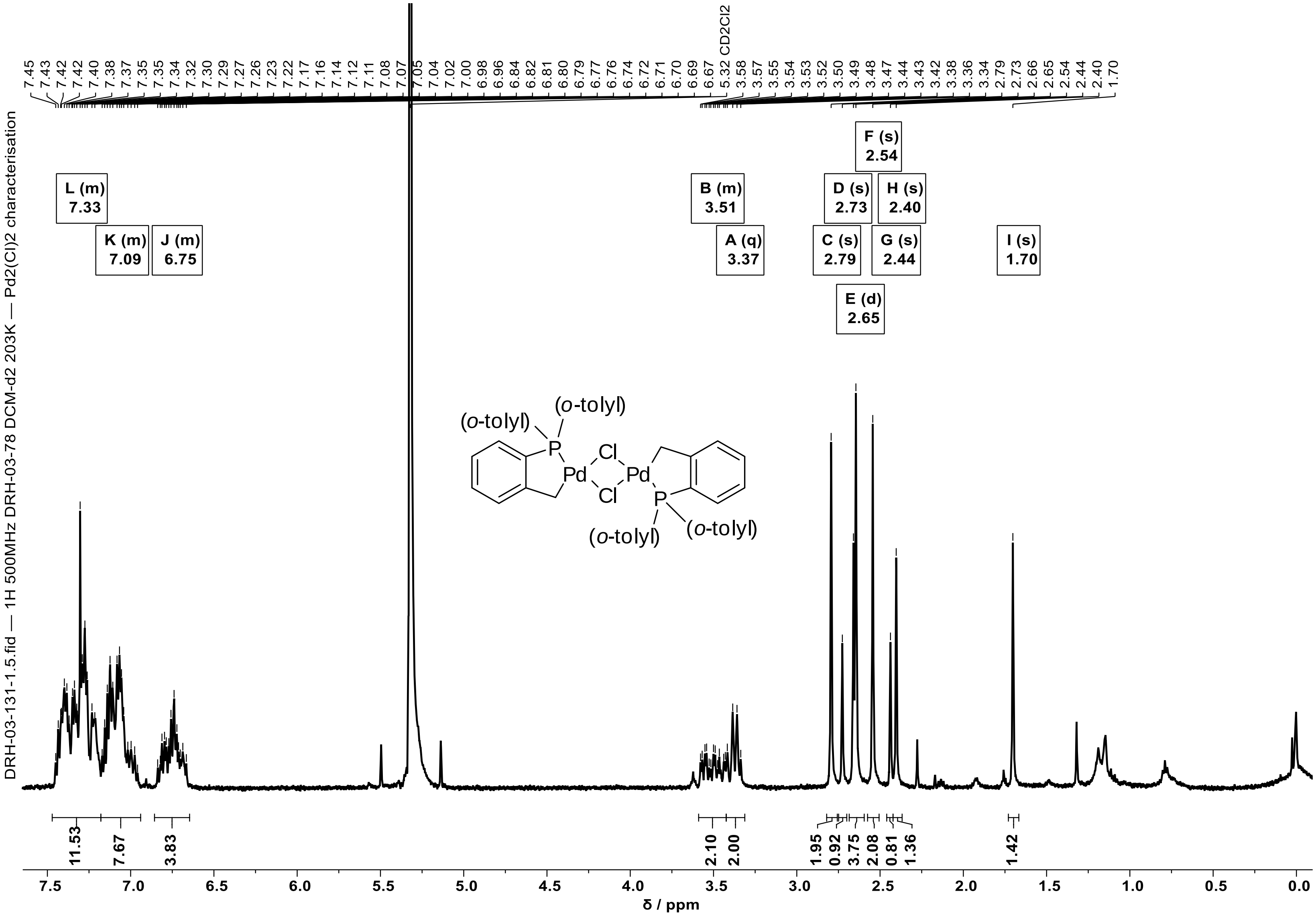


Figure 41: ^{1}H NMR (500 MHz, DCM-d_2, 128 scans, 203 K) spectrum of the [Pd(C^P)(μ_2-Cl)]$_2$ palladacycle 4. Residual solvent signals (most likely water and grease) below 1.5 ppm have not been integrated. Lab book ref. DRH-03-78

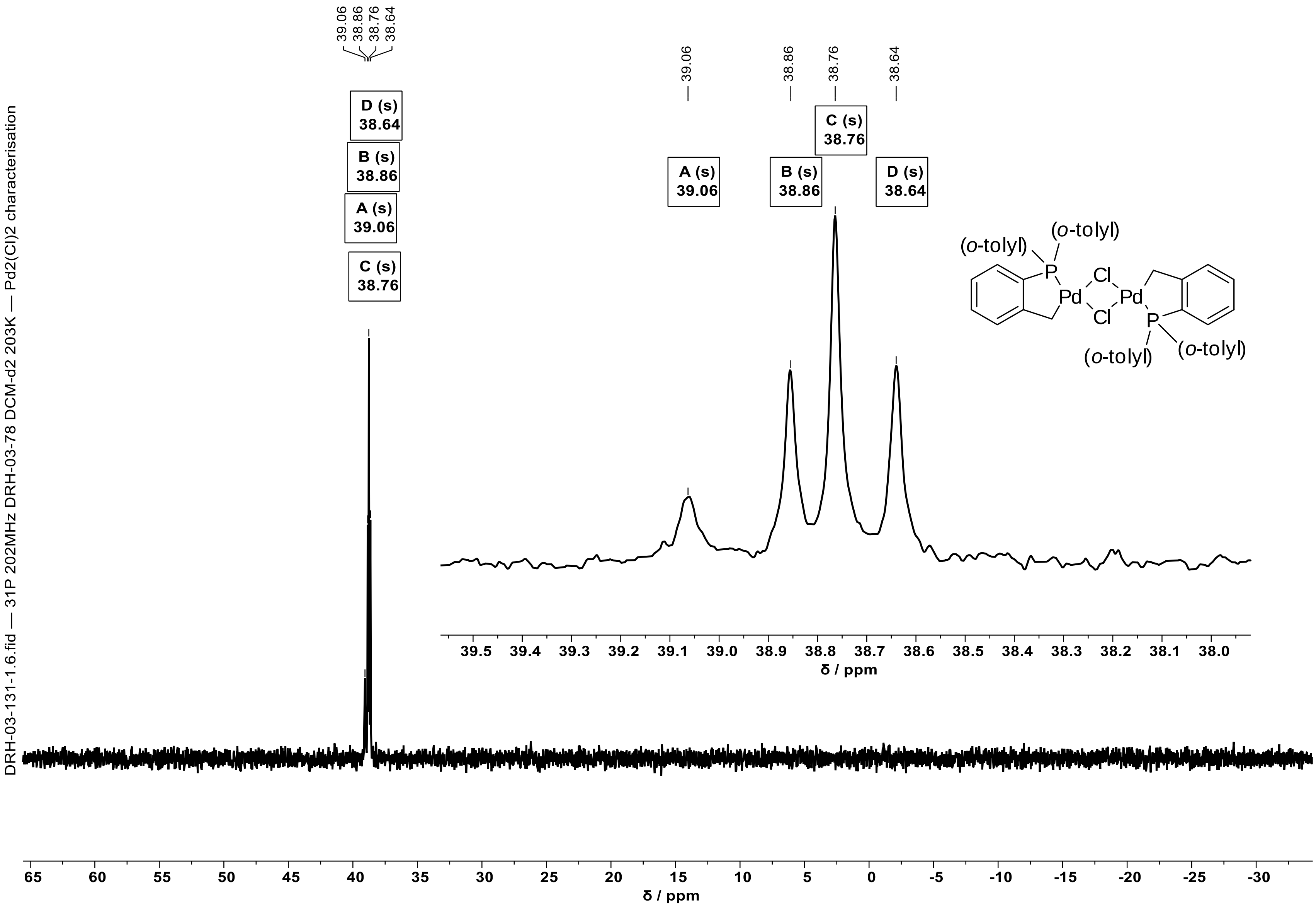


Figure 42: ^{31}P NMR (203 MHz, DCM-d_2, 128 scans, 203 K) spectrum of the [Pd(C^P)(μ_2-Cl)]$_2$ palladacycle 4. Lab book ref. DRH-03-78

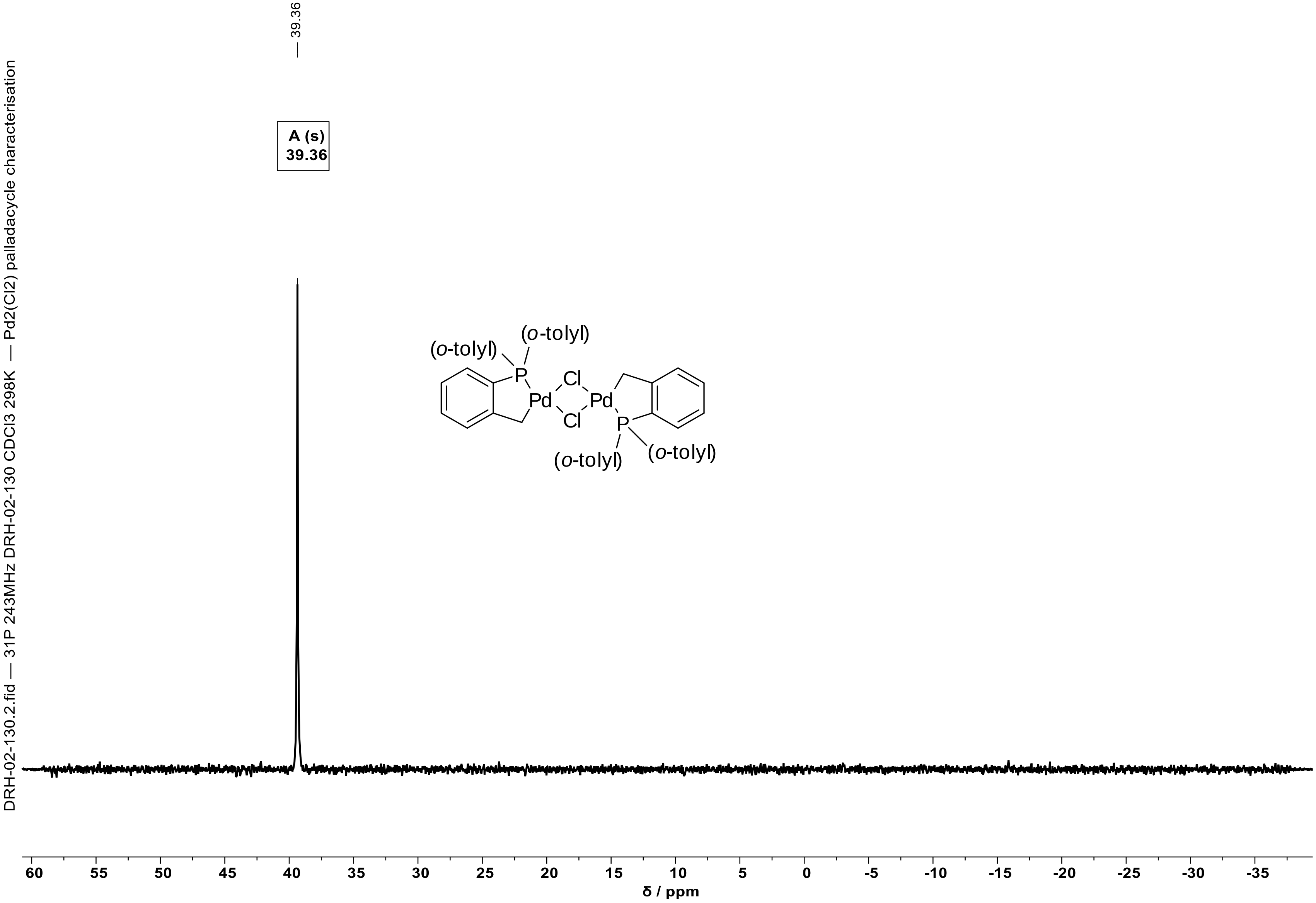


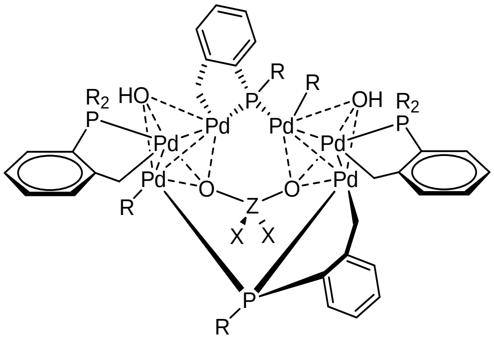
Figure 43: ^{31}P NMR (243 MHz, C*D*Cl$_3$, 128 scans, 298 K) spectrum of the [Pd(C^P)(μ_2-Cl)]$_2$ palladacycle 4. Lab book ref. DRH-02-130

6. Density Functional Theory (DFT) Calculations

Unless stated otherwise, all calculations were performed at the DFT level using the B3LYP functional[8–10] in the Gaussian16(revision A.03) suite of programs.[11] Geometry optimization and frequency calculations were performed using the def2-SVP basis set in the gas phase for all structures with a superfine integration grid for all atoms. The SMD continuum model[12] (solvent = tetrahydrofuran, ε=7.4257) was used for all calculations, alongside the D3 version of Grimme's dispersion corrections with Becke-Johnson damping.[13] Unless stated otherwise, all calculations were carried out at 298.15 K and 1.00 Atm pressure. The nature of stationary points was verified by frequency calculations, with minima having zero imaginary frequencies. All energies are displayed in Hartrees.

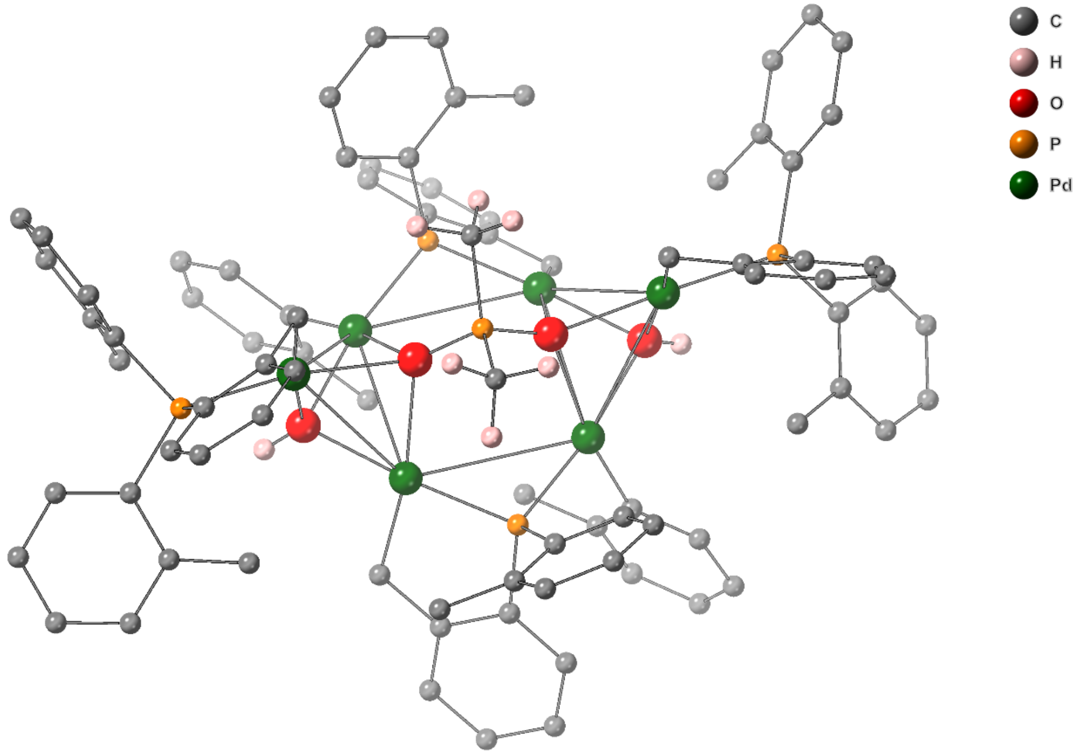
6.1 DFT Calculations – Hexamer Variant Optimised Structure Coordinates

All calculations in this section were done at the def2-SVP level of theory due to the size of the molecule. All optimised structures follow the basic structure shown below, but with varying Z and X groups. The obtained crystal structure for **7** was used as a starting point for all structures. For visual clarity, most H atoms are not shown.



R = *o*-tolyl

Hexamer Z = P, X = Me (7a)



Sum of electronic and zero-point Energies= -6101.973152

Sum of electronic and thermal Energies= -6101.868310

Sum of electronic and thermal Enthalpies= -6101.867366

Sum of electronic and thermal Free Energies= -6102.126534

0 2

C	5.96471132	21.01527388	15.66929326
H	5.68794728	20.31541881	14.85972118
H	7.02749990	20.85712296	15.90510872
C	5.10520857	20.78021662	16.88399143
C	5.42597639	19.86789541	17.89979479
H	6.35283188	19.29149597	17.83571327
C	4.57305979	19.70246153	18.99630365
H	4.84163638	18.99673308	19.78657325
C	3.38611218	20.43895598	19.09815233
H	2.73266683	20.31101156	19.96419953
C	3.05227712	21.35564507	18.09760087
H	2.14479808	21.95936652	18.17627360
C	3.91501556	21.51943194	17.00995403
C	2.47559667	22.06594879	14.50652537
C	1.70219274	20.96494504	14.91046515
H	1.82779938	20.54892611	15.91033408
C	0.77285955	20.38585156	14.04496496
H	0.17929203	19.53138938	14.37795514
C	0.61568427	20.90314799	12.75845453
H	-0.10486226	20.45732500	12.06838422
C	1.38604476	21.99380728	12.34965039
H	1.26324567	22.39490665	11.34039397
C	2.32548297	22.59584022	13.19991488
C	3.13660716	23.75751711	12.69957875
H	2.85591342	24.01379093	11.66906950
H	4.21200557	23.52537065	12.71345975
H	2.99756016	24.65498542	13.32277026
C	3.06779787	24.27439432	16.38315607
C	1.84012388	24.78350781	15.92966852
H	1.26587720	24.22951665	15.18531791
C	1.34344012	25.99226443	16.41915203
H	0.38762849	26.37556487	16.05481270
C	2.07801394	26.70145916	17.37099918
H	1.70550494	27.65328906	17.75736975
C	3.29281711	26.19222914	17.83546207

H	3.85887031	26.74870717	18.58645709
C	3.81430894	24.97829113	17.36471261
C	5.11880147	24.46892861	17.91339385
H	5.55234588	25.18577280	18.62324840
H	5.84889300	24.29287938	17.10583455
H	4.98985942	23.50878115	18.43578895
C	8.54355922	20.77851579	12.99603617
H	7.85303350	21.06846270	12.19534585
H	8.02004766	20.12666944	13.71025554
H	9.40074530	20.24353839	12.56598657
C	9.84488434	21.69402752	15.42172181
H	10.55968205	20.89034836	15.19338696
H	9.07432686	21.32393116	16.11052824
H	10.38660918	22.52228009	15.89052295
C	5.96871539	25.59138922	10.97966516
H	4.91844308	25.25834962	11.04532738
H	6.03765285	26.58124374	11.46467093
C	6.40142331	25.65482996	9.53771981
C	5.85202112	26.57600742	8.62969430
H	5.11972713	27.30873672	8.98158813
C	6.22337533	26.54881803	7.28368784
H	5.78844148	27.26958205	6.58610707
C	7.14345925	25.59703396	6.82098790
H	7.42928355	25.57586221	5.76656508
C	7.71132555	24.69032171	7.71530332
H	8.44819016	23.96300764	7.37067034
C	7.35103004	24.73464057	9.06920834
C	7.89448650	21.97247551	9.82789966
C	9.05679654	21.20845511	9.62160425
H	10.03109404	21.67695086	9.78204740
C	8.98419289	19.86457530	9.25263636
H	9.90174973	19.29037952	9.10300922
C	7.73287725	19.26658839	9.08938481
H	7.65659867	18.21348090	8.80653010
C	6.57164154	20.01678213	9.29431934
H	5.59454739	19.54139734	9.17130119
C	6.62096218	21.37056359	9.66251505
C	5.34081262	22.12307104	9.90397460
H	5.23137142	22.97163825	9.21047253
H	5.32619621	22.54951901	10.92013092
H	4.46715903	21.46651358	9.78661579
C	7.55939485	27.27887001	15.45365427
C	6.91379029	27.54928398	16.66764827
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C	6.57440850	28.86089133	17.02515994
H	6.07086883	29.05273920	17.97699095
C	6.89192067	29.91452054	16.16632209
H	6.64330309	30.94414098	16.43690556
C	7.53276570	29.64591371	14.95217072
H	7.78035238	30.47165650	14.27817475
C	7.87436104	28.33785121	14.57269422
C	8.56340766	28.07979518	13.25834214
H	9.51874711	27.55347067	13.40408268
H	8.76430911	29.01526091	12.71553783
H	7.95604431	27.42796369	12.61155334
C	12.27503455	26.66406188	14.12020936
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H	12.35694992	27.14773449	13.13097425
C	11.76261555	27.63155199	15.15667360
C	12.28796854	28.92773044	15.29959940
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C	10.87114789	29.31915560	17.23311226
H	10.52795512	29.97500645	18.03692906
C	10.32657111	28.04348965	17.09197815
H	9.54980723	27.69626513	17.77553937
C	10.75746935	27.21645826	16.04549727
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C	8.98737897	23.37284790	18.94720923
H	8.04503811	23.05964498	19.40393513
C	10.21187004	22.95991089	19.47756528
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C	11.40354079	23.37052322	18.87414436
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C	12.71941623	24.56634416	17.09405040
H	12.74467290	24.22900991	16.04563264
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H	12.86281008	25.65812599	17.07384393
C	10.60669458	24.93484991	9.25103095
C	11.13532482	24.17521708	8.19720160
H	11.28391943	23.09977566	8.32030686
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H	11.88135419	24.16320015	6.16564622
C	11.27244126	26.14424996	6.79893936
H	11.52273956	26.62260820	5.84824920
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H	10.58746862	27.97902411	7.70982814
C	10.40658165	26.32308276	9.07989370

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H	8.84491043	26.77193689	10.50093221
H	9.69302640	28.21021012	9.87539427
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H	11.50178789	19.73682265	13.49200993
H	12.44318194	19.63688335	11.98265274
C	13.63220703	19.77693482	13.76071042
C	13.64803424	18.91752355	14.87788927
H	12.71013848	18.45672304	15.20312012
C	14.83110539	18.63765949	15.56682661
H	14.80755267	17.96731474	16.43095850
C	16.04638772	19.20088098	15.15405486
H	16.97215453	18.97639770	15.68974903
C	16.05796649	20.07480488	14.06202839
H	16.99253971	20.54997303	13.75289235
C	14.86976888	20.37980815	13.38863738
C	16.17707640	22.76802143	12.38414672
C	17.23062079	22.78594572	11.45383830
H	17.20791575	22.10186570	10.60334118
C	18.30851949	23.66137708	11.59978671
H	19.11822450	23.65593127	10.86553777
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H	19.18020582	25.22903891	12.81358215
C	17.30418452	24.52144775	13.62173598
H	17.33452029	25.20497638	14.47492412
C	16.21077388	23.65154471	13.49592536
C	15.12076961	23.66885510	14.53416726
H	15.26233500	24.50133865	15.23748785
H	15.10048799	22.73248924	15.11542926
H	14.12447485	23.76220705	14.07106578
C	14.94851712	20.92471128	10.49909200
C	15.26632039	19.56160339	10.39972605
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C	15.34979101	18.93098249	9.15542507
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C	15.11426470	19.66733025	7.99298289
H	15.17466213	19.18675841	7.01307882
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H	14.61100533	21.60048353	7.17222739
C	14.70299333	21.67796762	9.32192588
C	14.34081547	23.13744070	9.37974379
H	15.13746166	23.73561996	9.85043245
H	13.43147295	23.29053983	9.98189363
H	14.16040159	23.54283715	8.37504199
O	5.94413876	24.94016275	14.06382320
H	5.22789422	25.58701362	14.09581461
O	7.86838007	23.17823720	14.11338652
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H	12.83930556	24.94092873	11.54434110
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P	9.11784846	22.24089665	13.87064271
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P	14.69877557	21.70212330	12.14337398
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Pd	7.90579353	25.40724639	14.92172202
Pd	10.24066411	24.06517012	10.99223132
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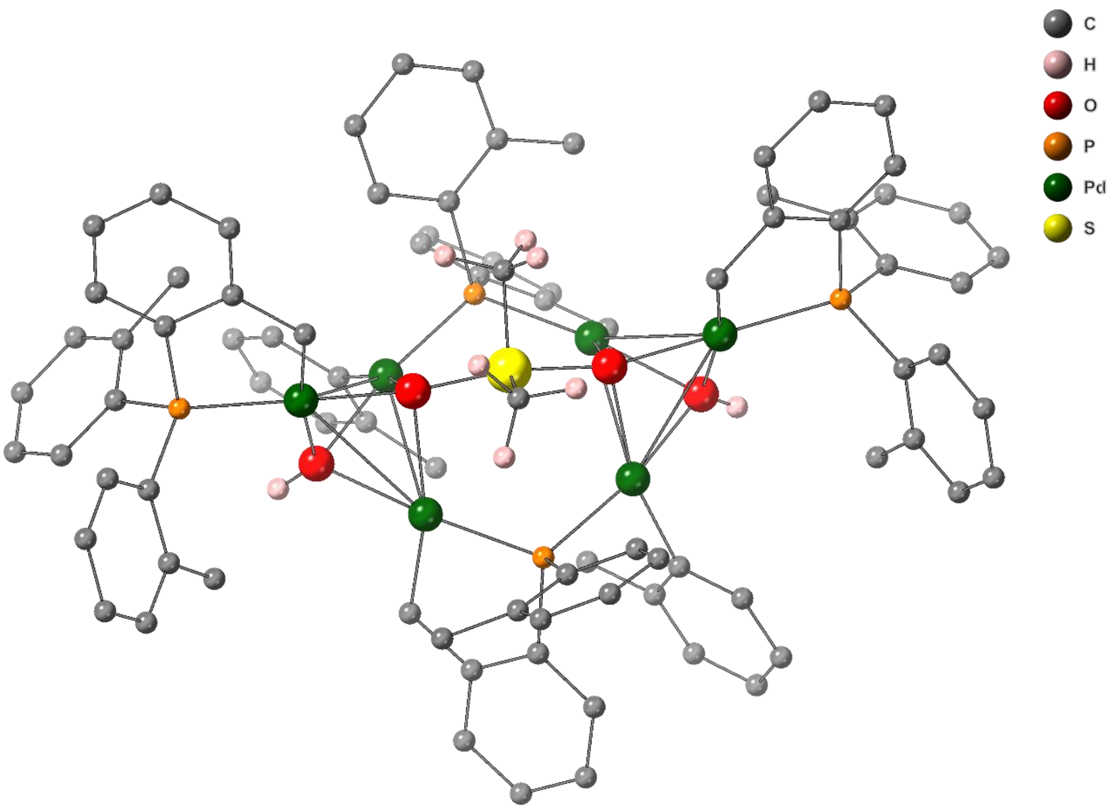
Hexamer Z = S, X = Me (7b)



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C	5.07978000	19.89743000	18.00074200
H	5.99569000	19.30313400	17.93931400
C	4.21980400	19.74294300	19.09209100
H	4.46949000	19.02705100	19.87961700
C	3.04923900	20.50582500	19.19230100
H	2.38865900	20.38961000	20.05474200
C	2.74250300	21.43288600	18.19368400
H	1.84959000	22.05781500	18.27429700
C	3.60898600	21.58333100	17.10491700
C	2.09413500	22.27747400	14.67369600
C	1.24883300	21.23500100	15.08762100
H	1.38117100	20.78698000	16.07265400
C	0.23863600	20.75346900	14.25306300
H	-0.40894100	19.94285700	14.59535500
C	0.06878200	21.31281500	12.98597400
H	-0.71633900	20.94527400	12.32049100
C	0.91028400	22.34483900	12.56523900
H	0.77798100	22.77837200	11.57057000
C	1.93400600	22.84547800	13.38379300
C	2.82113400	23.94450700	12.86660200
H	2.49197100	24.27517200	11.87164900
H	3.86676800	23.60846900	12.79039300
H	2.81804600	24.82117500	13.53283300

C	2.88382400	24.37664700	16.58316700
C	1.67321800	24.96944000	16.19042300
H	1.04526200	24.47517100	15.44731800
C	1.25994000	26.18577200	16.73685200
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C	2.06157400	26.81954300	17.68755000
H	1.75456600	27.77532500	18.11934100
C	3.26128500	26.22866100	18.09075600
H	3.88186100	26.72598200	18.84056700
C	3.70010300	25.00675600	17.55951800
C	4.99323400	24.41094900	18.04712000
H	5.51485600	25.10451700	18.72020300
H	5.66461800	24.16632900	17.20682700
H	4.82148400	23.47108200	18.59437900
C	8.58510800	20.96036100	13.01773100
H	7.88551700	21.14182000	12.19901900
H	8.08080300	20.39837900	13.81402500
H	9.47733400	20.43655200	12.65739700
C	9.70533100	21.90250200	15.28317900
H	10.10583700	20.89632700	15.11366100
H	8.86705900	21.87890100	15.98735800
H	10.50024400	22.55771500	15.64531700
C	6.11139300	25.48086300	10.86948800
H	5.02866000	25.25619400	10.89157900
H	6.25047800	26.47866800	11.32378600
C	6.61650700	25.45214700	9.45114500
C	6.09608000	26.29850600	8.45602500
H	5.33464100	27.03746100	8.72329900
C	6.52818700	26.18746800	7.13332400
H	6.11458100	26.85029400	6.36839400
C	7.47747600	25.21750300	6.78044700
H	7.80659800	25.12089300	5.74290200
C	8.01380900	24.38547000	7.76178000
H	8.76272900	23.63812200	7.49810100
C	7.60087900	24.52013100	9.09482400
C	8.06294900	21.81485100	9.87599700
C	9.22187900	21.05354300	9.64416500
H	10.19531800	21.50789600	9.84607900
C	9.14998000	19.73616700	9.18886700
H	10.06715800	19.16677600	9.01846500
C	7.89917200	19.15842700	8.96182500
H	7.82159900	18.12619200	8.61050400
C	6.74047500	19.90554900	9.18769300
H	5.76276200	19.44865700	9.01074300
C	6.79039400	21.23435500	9.63972200
C	5.50557500	21.98139000	9.87183600
H	5.41481200	22.84581400	9.19526600
H	5.46224400	22.38805600	10.89689900
H	4.63568800	21.32822900	9.71358300
C	7.45421700	27.17862300	15.39845600
C	6.79100300	27.42038200	16.61150700
H	6.52842800	26.58474000	17.26230800
C	6.47055400	28.72296200	17.01406500
H	5.95660600	28.88840700	17.96529900
C	6.82163200	29.80259600	16.20096100
H	6.59065000	30.82625000	16.50774000
C	7.47389200	29.56565400	14.98708100
H	7.74780200	30.41073400	14.34789900
C	7.79419200	28.26563900	14.56322500
C	8.47361400	28.04809200	13.23809400
H	9.26877600	27.29448000	13.31155200
H	8.90710300	28.97969500	12.84506100
H	7.76034700	27.66475700	12.49067900
C	12.13402300	26.66176500	13.94890000
H	13.20025400	26.43714400	14.14168100
H	12.06880900	27.12326300	12.94716400
C	11.60338400	27.58903200	15.00989400
C	12.09828300	28.89382100	15.18305400
H	12.86312800	29.27439400	14.49943900
C	11.63376900	29.69489300	16.22771800
H	12.02675800	30.70757700	16.35219000
C	10.67503100	29.20156400	17.12477400
H	10.31780100	29.82635700	17.94702100
C	10.16319800	27.91664800	16.95209000
H	9.40180700	27.53174100	17.63200600
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C	10.11437900	24.57680800	17.09032600
C	8.93555600	24.19100700	17.75156700
H	7.97490600	24.42570400	17.28818300
C	8.97053200	23.50265200	18.96506700
H	8.03677400	23.21288100	19.45391800
C	10.20547500	23.18666400	19.53560700
H	10.25520100	22.64298900	20.48262500
C	11.38407800	23.56681800	18.88848800
H	12.34945200	23.31567900	19.33674900
C	11.36938600	24.26386400	17.66937300
C	12.66924700	24.63122900	17.00934100
H	12.70605900	24.24885000	15.97655600
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C	10.73926100	24.82161600	9.36862400
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H	11.52983600	23.07582500	8.35883400
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H	12.30929100	19.64171300	12.43432000
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C	14.13072900	18.70572600	14.69240800
H	13.22476600	18.27847300	15.13149100
C	15.38640900	18.23513600	15.08828900
H	15.45448800	17.44303900	15.83879400
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H	17.37023500	20.24412800	13.17083900
C	15.20609100	20.26792000	13.20651600
C	16.25719200	22.84551900	12.34953200
C	17.33554100	22.90304200	11.45171900
H	17.35184500	22.24091700	10.58429900
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H	19.21762000	23.82922000	10.93816800
C	18.36754300	24.64863300	12.75549800
H	19.18117000	25.35935400	12.92067800
C	17.30412100	24.58729900	13.65860900
H	17.29644100	25.24797800	14.52953300
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H	14.84213100	21.88187900	7.08621200
C	14.90867500	21.82324200	9.23592200
C	14.52217700	23.26978900	9.37483700
H	15.29128700	23.84883000	9.90933300
H	13.58722100	23.37205400	9.94448400
H	14.36937500	23.73434300	8.39207600
O	5.74718500	24.90943500	13.97777200
H	5.08082600	25.60790200	13.94984400
O	7.47067700	23.04913200	14.18659200
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P	3.45044500	22.82919900	15.78266200
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Pd	5.52238400	22.88932800	14.93272000
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Pd	7.74875900	25.29365900	14.86320200
Pd	10.49140800	23.81834600	11.05999400
Pd	11.31410800	24.81889200	13.74566500
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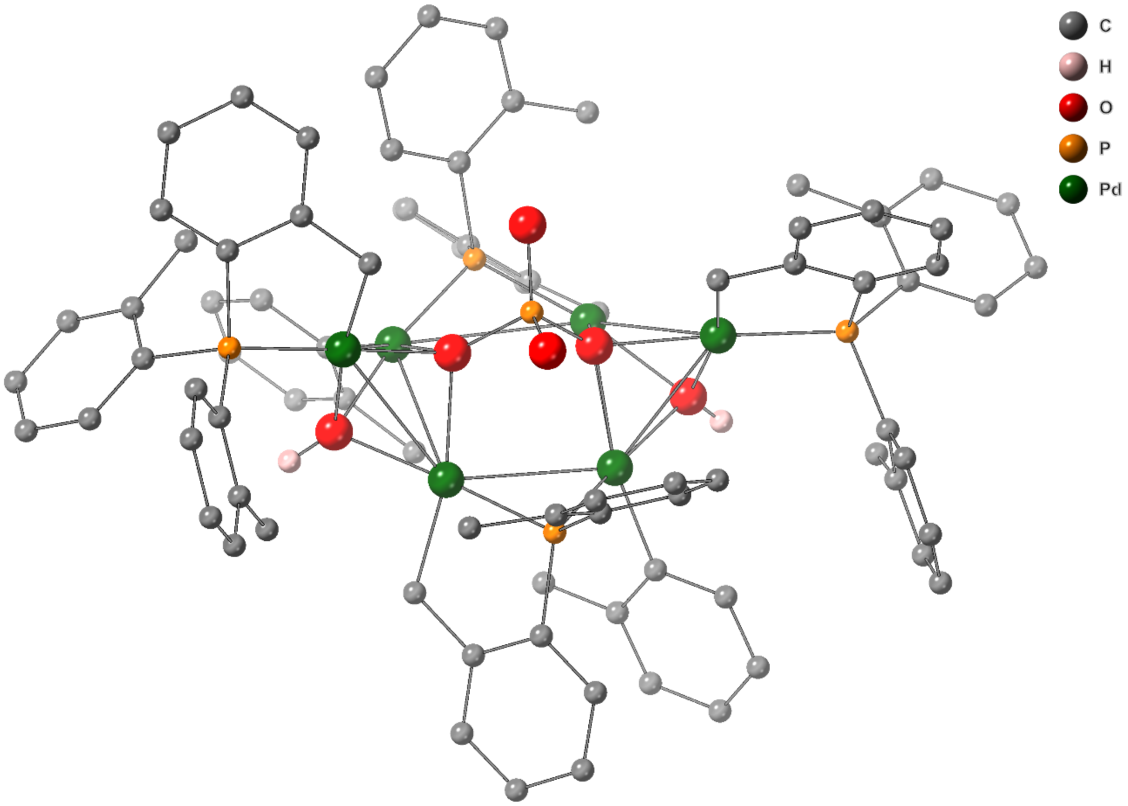
Hexamer Z = P, X = O (7c)



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Sum of electronic and thermal Free Energies= -6172.775303

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H	6.97830351	20.18762346	18.26514633
C	5.05171636	20.35951849	19.23876838
H	5.37076638	19.80426841	20.12477144
C	3.74471727	20.85945552	19.16666237
H	3.04767022	20.69698651	19.99215845
C	3.34476424	21.58973356	18.04470230
H	2.34044317	22.01731857	17.99015530
C	4.25954131	21.80462355	17.00860320
C	2.94990421	21.88997159	14.37390006
C	2.29379117	20.73838950	14.83770206
H	2.37960117	20.44959345	15.88549614
C	1.53693311	19.94567145	13.97314402
H	1.03383107	19.05384835	14.35392304
C	1.43602610	20.29890547	12.62686789
H	0.85095906	19.68524142	11.93737988
C	2.09000715	21.44045054	12.15830985
H	2.01302714	21.71234758	11.10239682
C	2.85555920	22.25380561	13.00716096
C	3.56173426	23.45388070	12.44090590
H	3.29506224	23.60188872	11.38534884
H	4.65316033	23.32778570	12.50502393
H	3.31596824	24.37739777	12.98733491

C	3.04059622	24.31113774	16.05932415
C	1.81260713	24.60451879	15.44533413
H	1.40208310	23.91925870	14.70181607
C	1.10719608	25.76327885	15.77454815
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Pd	10.22734672	24.21504577	11.39145481
Pd	11.26276980	25.28547482	14.04049003
Pd	12.28242991	22.55313461	12.71014594
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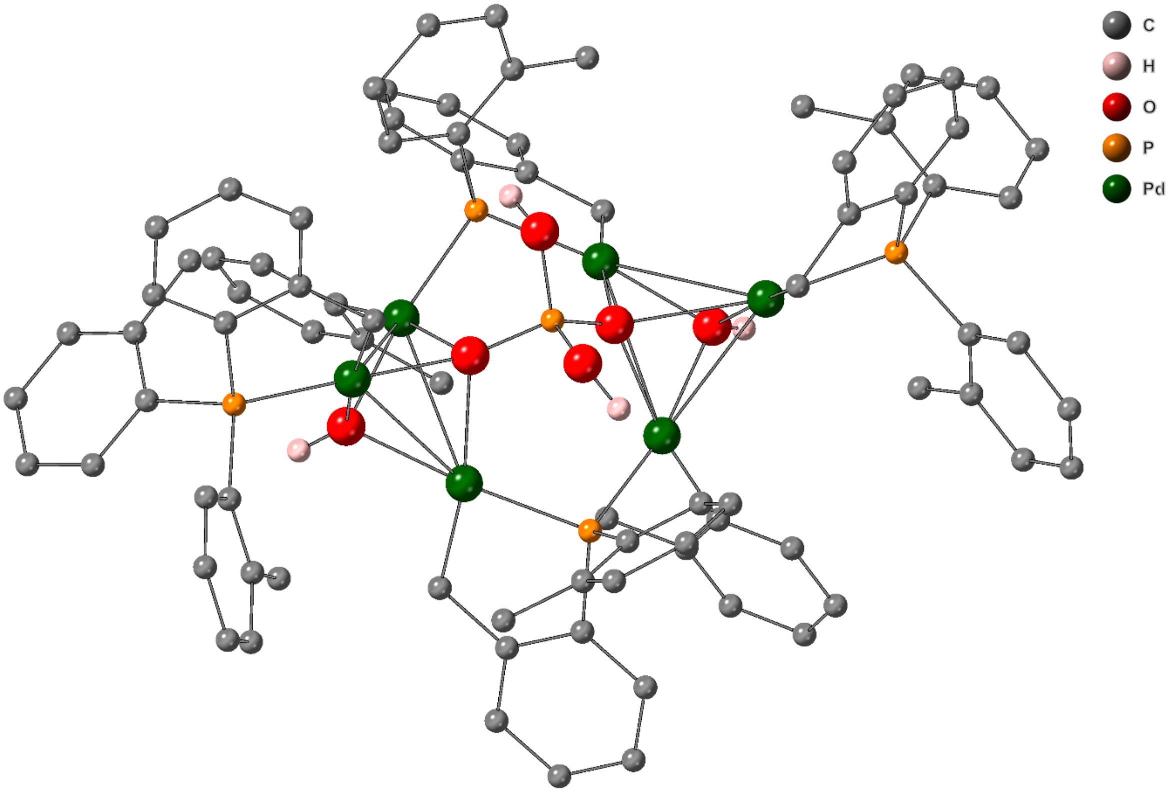
Hexamer Z = P, X = OH (7d)



Sum of electronic and zero-point Energies= -6173.824190

Sum of electronic and thermal Energies= -6173.720329

Sum of electronic and thermal Enthalpies= -6173.719385

Sum of electronic and thermal Free Energies= -6173.976679

0 2

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H	5.79572500	20.55138400	15.04219200
H	7.06510000	21.25736000	16.08038600
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C	5.46021700	20.26708900	18.08898400
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C	4.58803900	20.11687700	19.17251600
H	4.87144900	19.47014400	20.00689600
C	3.36252400	20.79428200	19.20510600
H	2.69352800	20.67887700	20.06099600
C	3.00859900	21.63706500	18.14812100
H	2.06971800	22.19573800	18.17221600
C	3.88997300	21.78681200	17.07304000
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C	0.93429600	20.33828400	14.03466200
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H	0.12195600	20.29009400	12.02984600
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H	1.38334500	22.29112900	11.28181900
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H	2.90027500	24.72205200	13.24436900

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C	7.22813400	24.83377500	6.67114700
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