Supporting Information for

Complexes of 2,5-bis(α-pyridyl)pyrrolate with Pd(II) and Pt(II): A mono-anionic iso π-electron ligand analog of terpyridine

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Contents.

Density Functional Theory. Density Functional Theory calculations (B3LYP) were carried out using Gaussian ’03, Gaussian ’09 or the GAMESS suite of quantum programs. In Gaussian, structures were first minimized using the 3-21G basis set, and the resulting coordinates used as the input file for higher level bases. For the calculation of H(PDP), the basis set was 6-31G*, and for the calculation of **1-Cl**, a mixed pseudopotential basis set, 6-31G* (C, H, N) and 3-21G (Pd, Cl) were used. The MIDI basis set was used for the determination of the structure of **1-Cl** using the GAMESS package for comparison to the results from the mixed basis set. Results were qualitatively similar (Fig. S1).

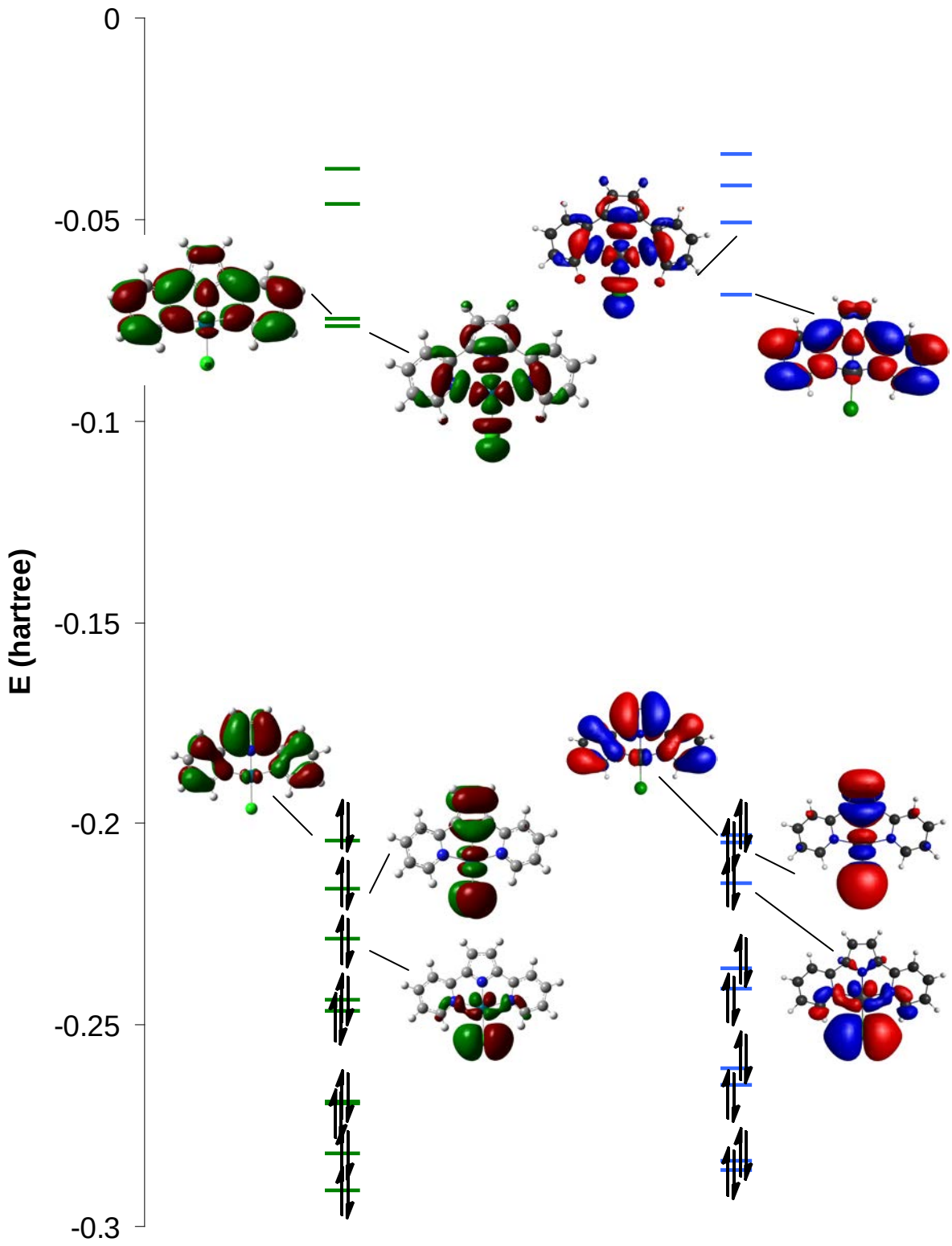

Figure S1. Frontier orbital surfaces and orbital energy diagram from DFT methods (B3LYP). Left (green and red): Mixed basis consisting of 6-31G* (CHN) and 3-21G (Pd, Cl). Right (blue and red): MIDI basis set.

Charge Decomposition Analysis-Output from QMForge[61]

Charge decomposition analysis of C:/Documents and Settings/MZdilla/My Documents/Gaussian/py-pyrole paper/CDA.log using the following fragments:
Frag1 (C:/Documents and Settings/MZdilla/My Documents/Gaussian/py-pyrole paper/fragm1.log)
Frag2 (C:/Documents and Settings/MZdilla/My Documents/Gaussian/py-pyrole paper/fragm2.log)

Created on Wed May 23 13:38:21 2012

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  92:   0.000   0.000   0.000   0.000
.......
 307:   0.000   0.000   0.000   0.000
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NMR Spectra

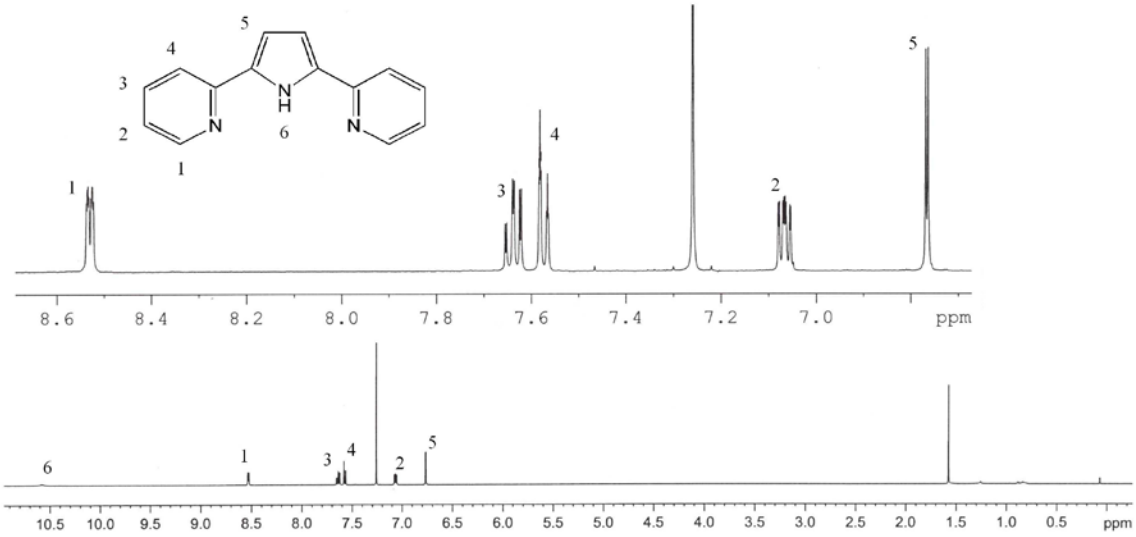

Figure S2. ^{1}H NMR spectrum of H(PDP) in $CDCl_3$

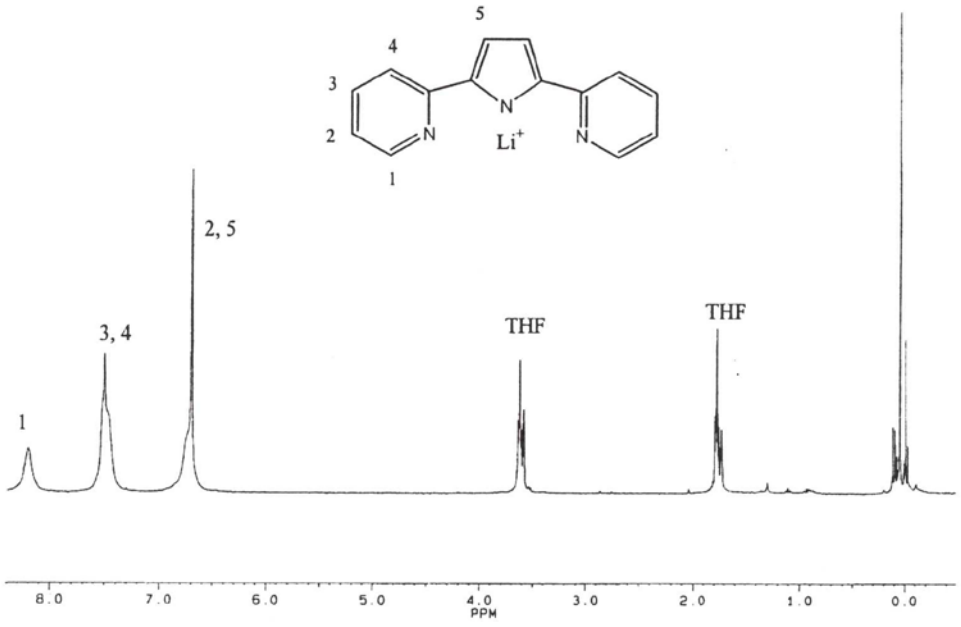

Figure S3. ^{1}H NMR spectrum of Li(PDP) in THF-d_8.

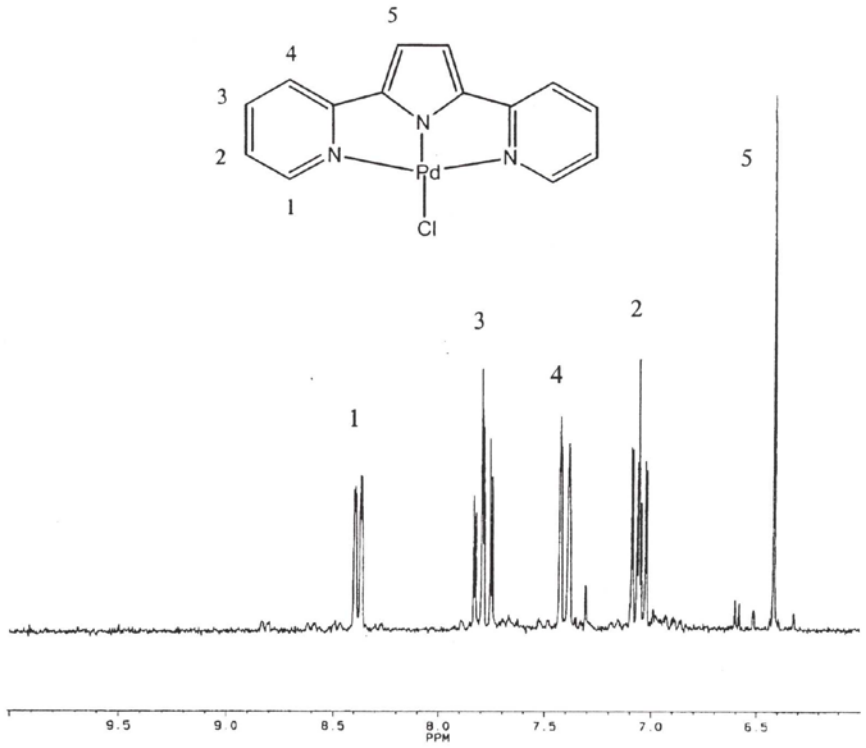

Figure S4. ^{1}H NMR spectrum of (PDP)Pd-Cl (**1**) in THF-d_8.

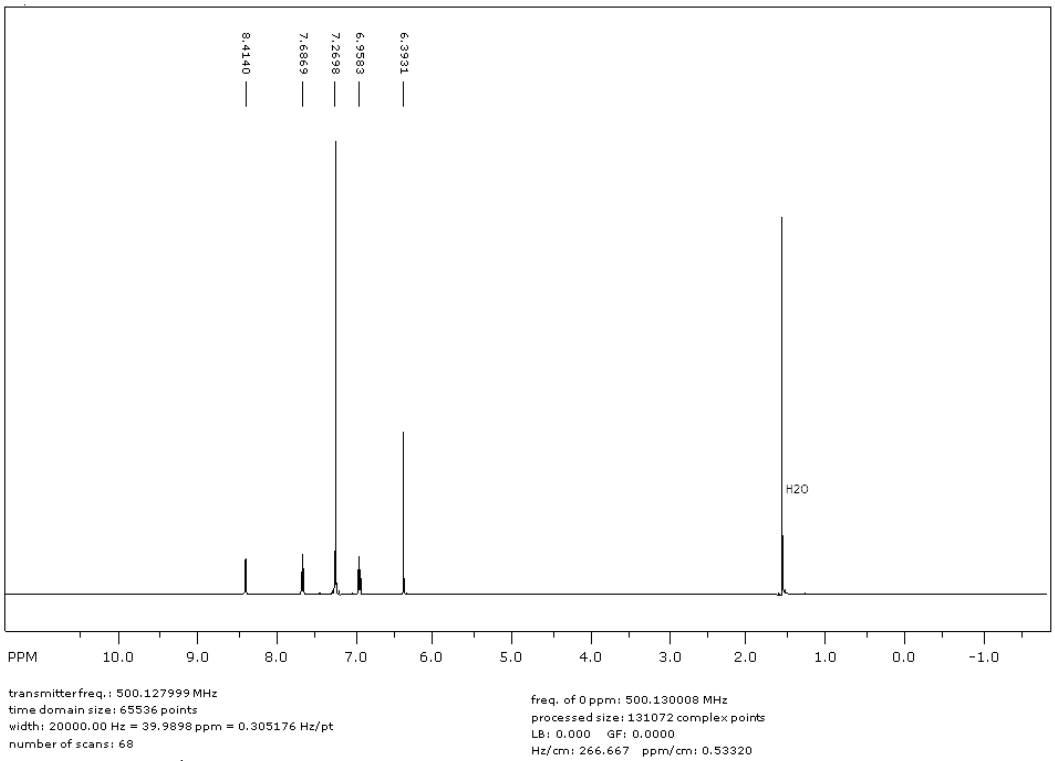

Figure S5. ^{1}H NMR spectrum of (PDP)Pd-Cl (**1**) in chloroform-*d*

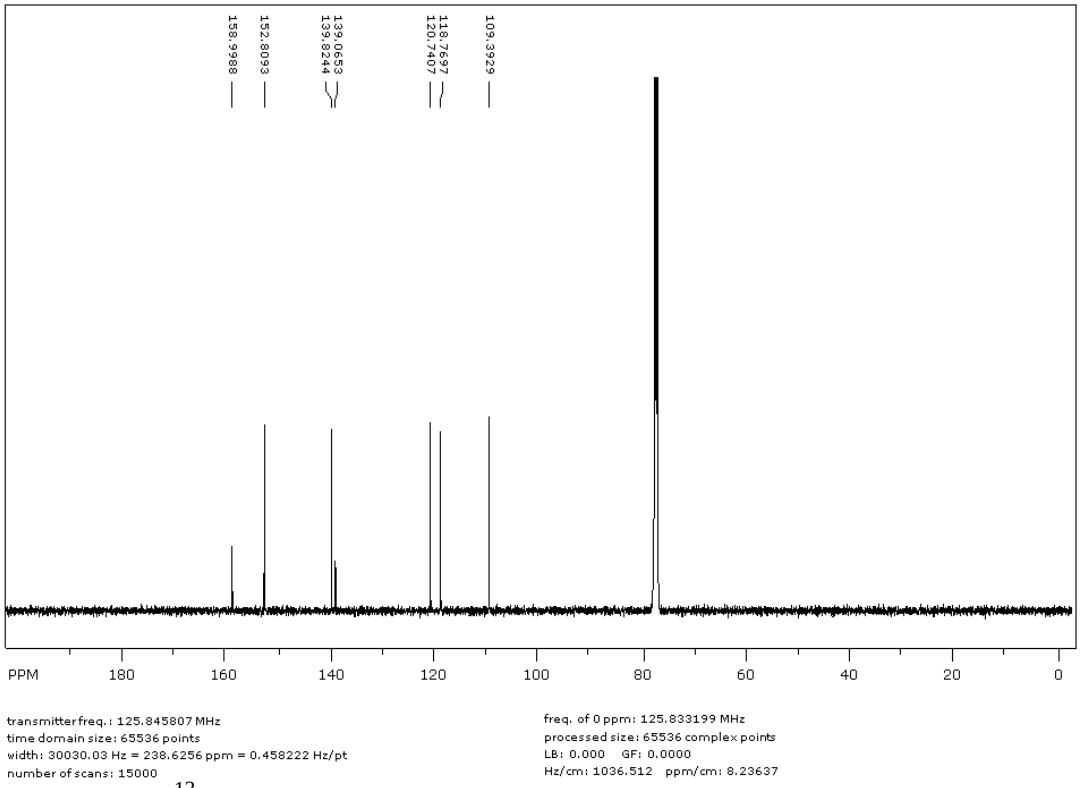

Figure S6. ^{13}C NMR spectrum of (PDP)Pd-Cl (**1**) in chloroform-*d*

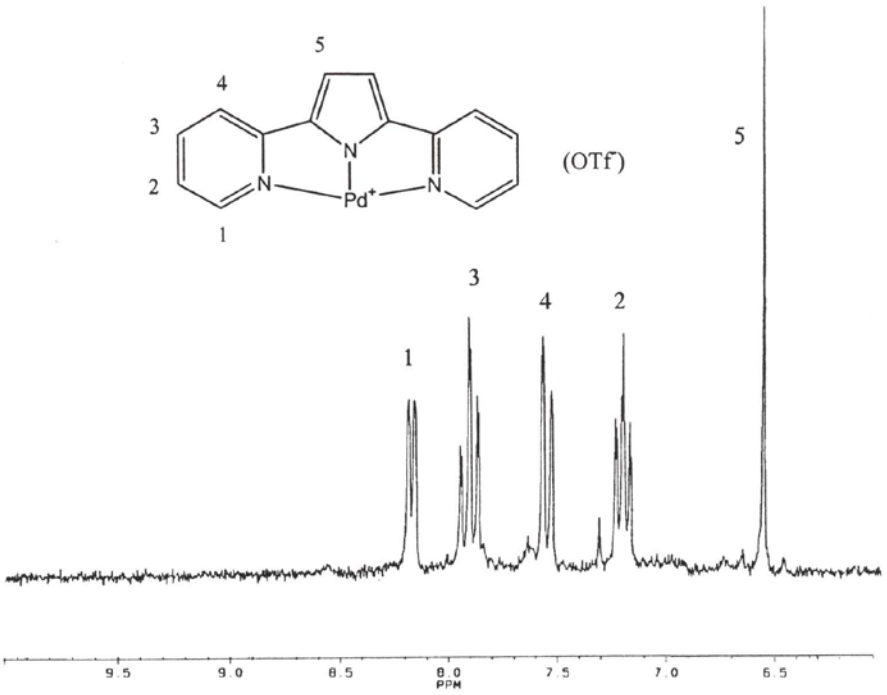

Figure S7. ^{1}H NMR spectrum of (PDP)Pd-OH_2]$^{+}$ [OTf]$^{-}$ (**2**) in THF-d_8.

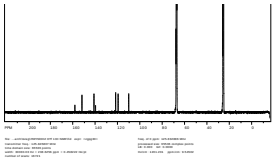

Figure S8. ^{13}C NMR spectrum of (PDP)Pd-OH_2]$^{+}$ [OTf]$^{-}$ (**2**) in THF-d_8.

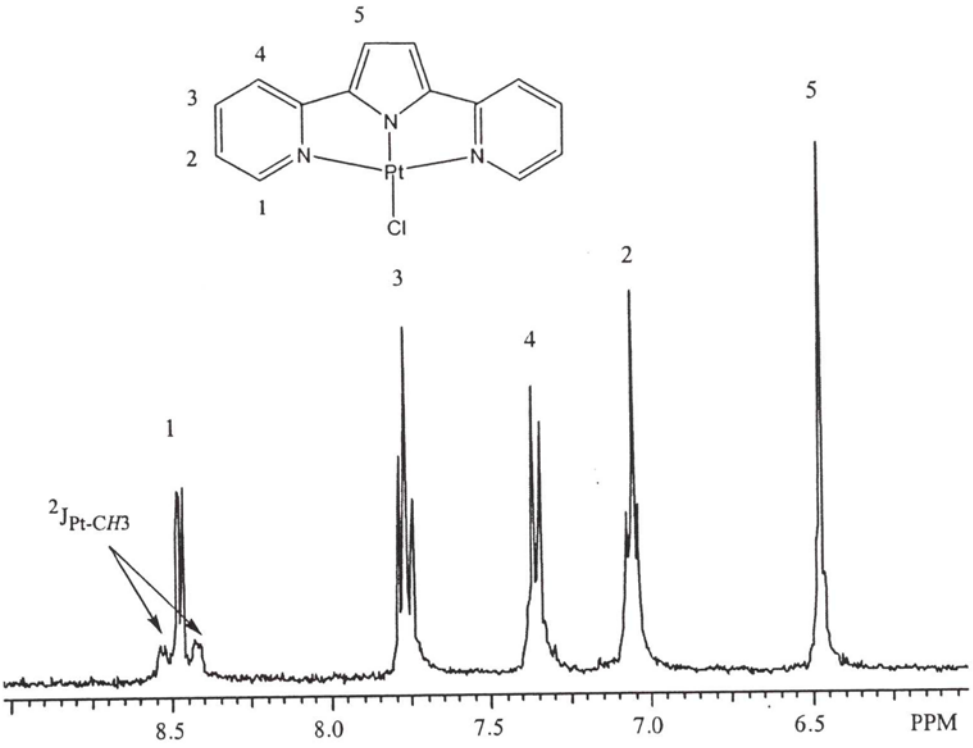

Figure S9. ^{1}H NMR spectrum of (PDP)Pt-Cl (**3**) in THF-d_8.

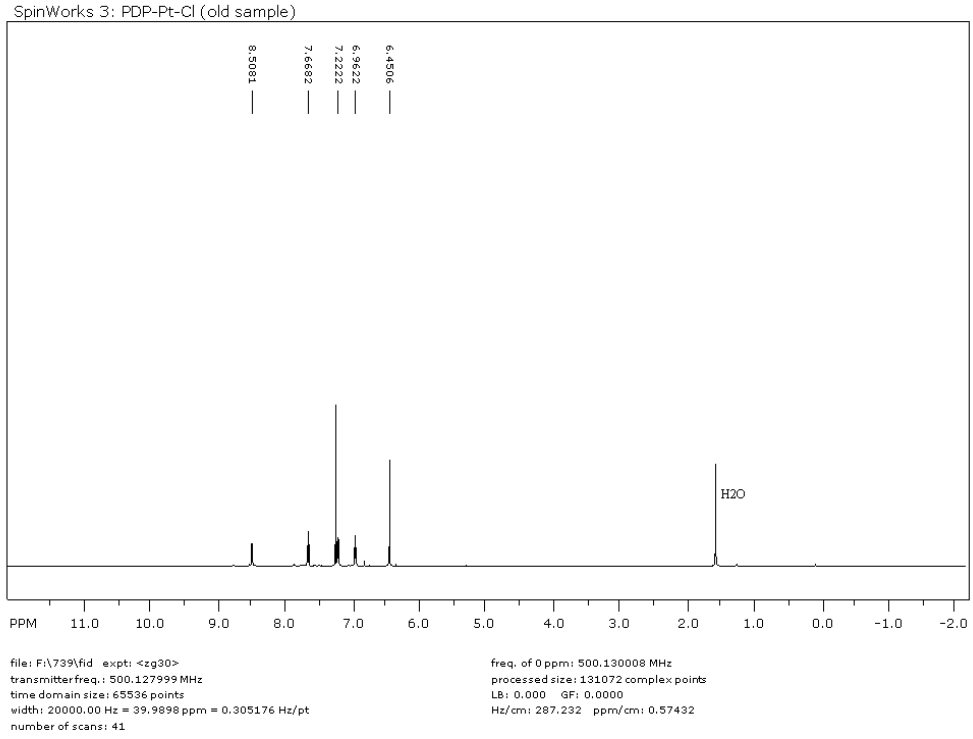

Figure S10. ^{1}H NMR spectrum of (PDP)Pt-Cl (**3**) in chloroform-*d*

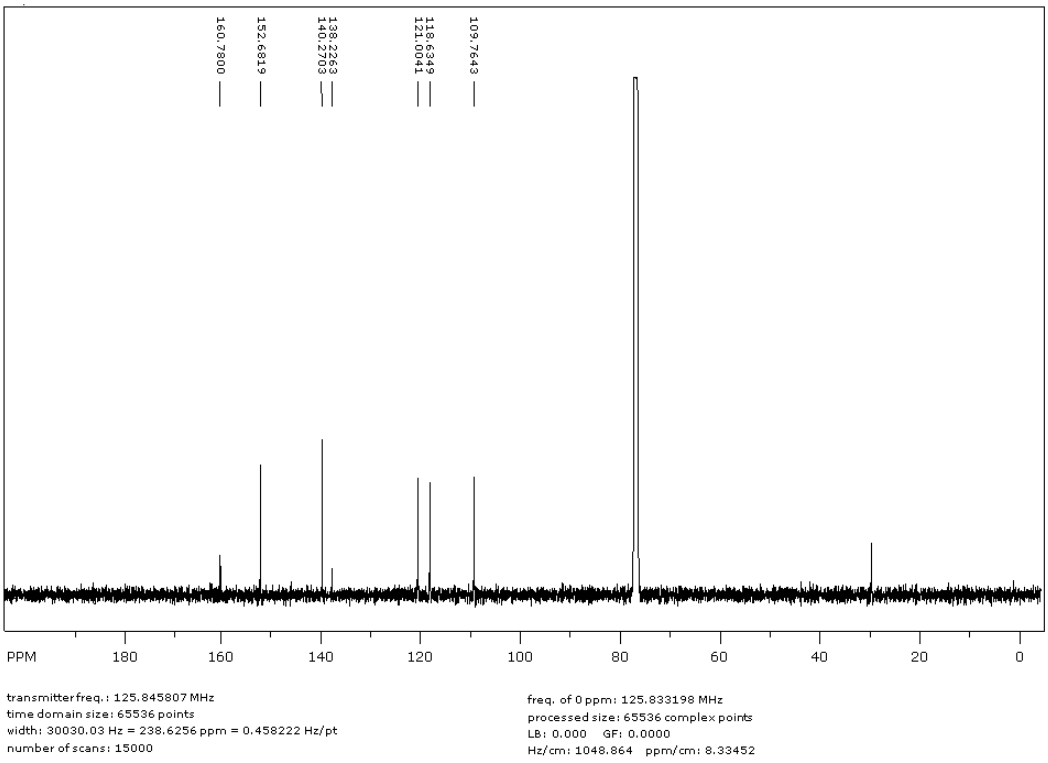

Figure S11. ^{13}C NMR spectrum of (PDP)Pt-Cl (**3**) in chloroform-*d*

UV-Visible Absorption Spectra

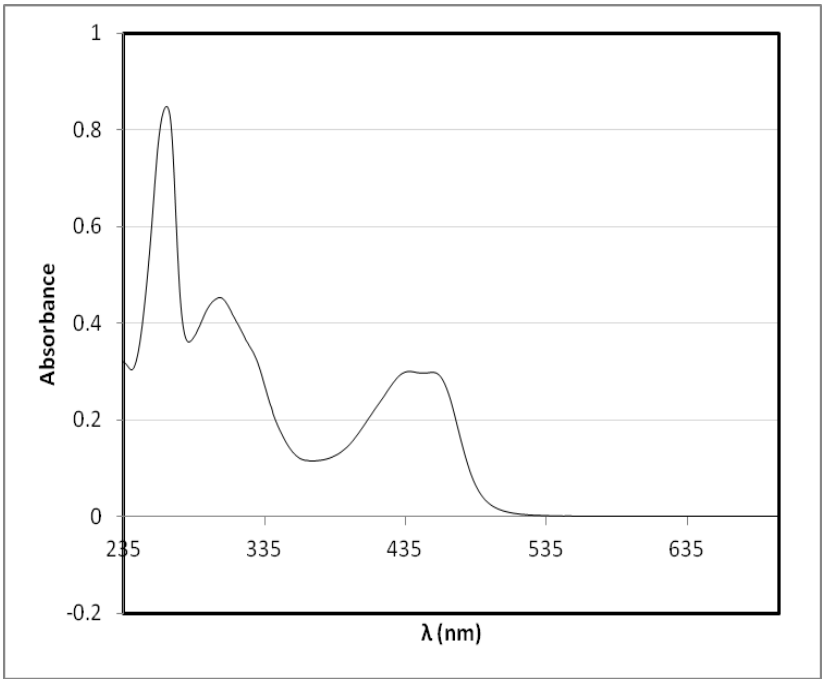

Figure S12. UV-Vis Absorption spectrum of (PDP)Pd-Cl (**1**) in dichloromethane. λ_{max} = 265 (ε 36849), 303 (19662), 437 (13027), 454 (12945)

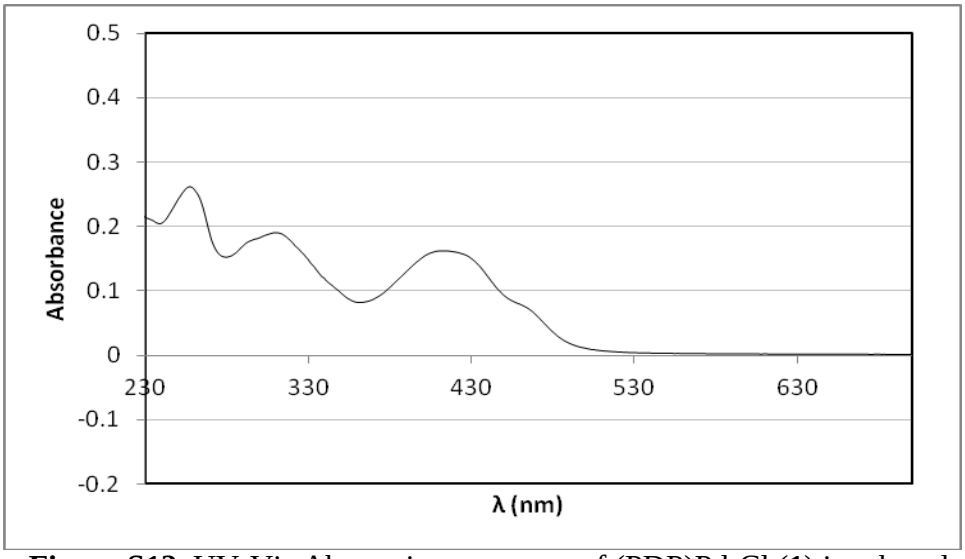

Figure S12. UV-Vis Absorption spectrum of (PDP)Pd-Cl (**1**) in ethanol. λ_{max} = 258 nm (7816), 311 nm (5672), 414 nm (4839).

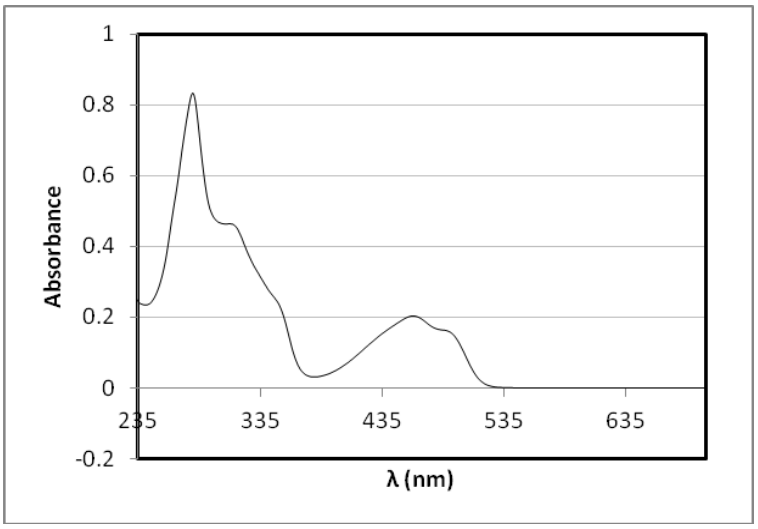

Figure S14. UV-Vis Absorption spectrum of (PDP)Pt-Cl (**3**) in dichloromethane. λ_{max} = 280 (ε 25287), 310 (14093), 459 (6171), 486 (4960)

Cyclic Voltammetry

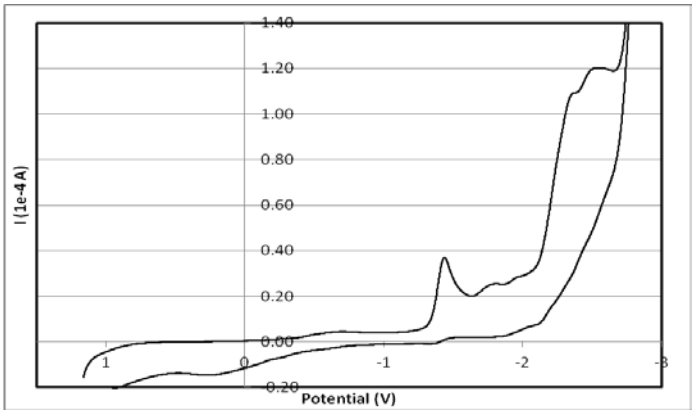

Figure S15. Cyclic voltammagram of (PDP)Pd-Cl (**1**) in acetonitrile. Scan rate = 0.1V/s. Potentials are vs. NHE.

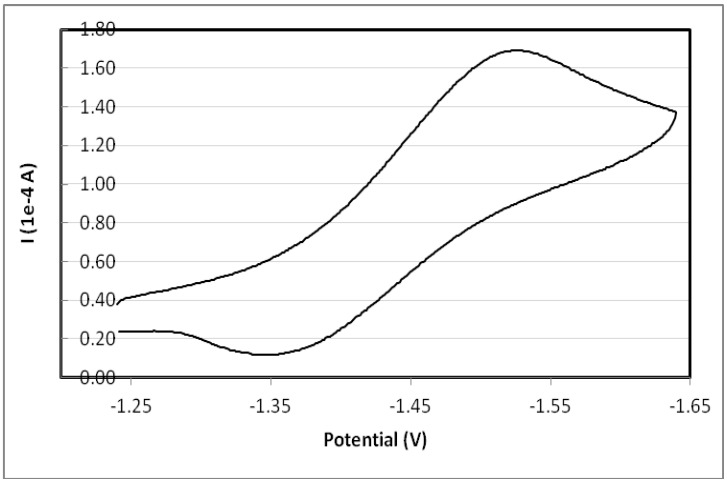

Figure S16. Rapid scan cyclic voltammagram of (PDP)Pd-Cl (**1**) in acetonitrile in the region of -1.45V vs. NHE. Scan rate = 1 V/s

Infrared Spectra

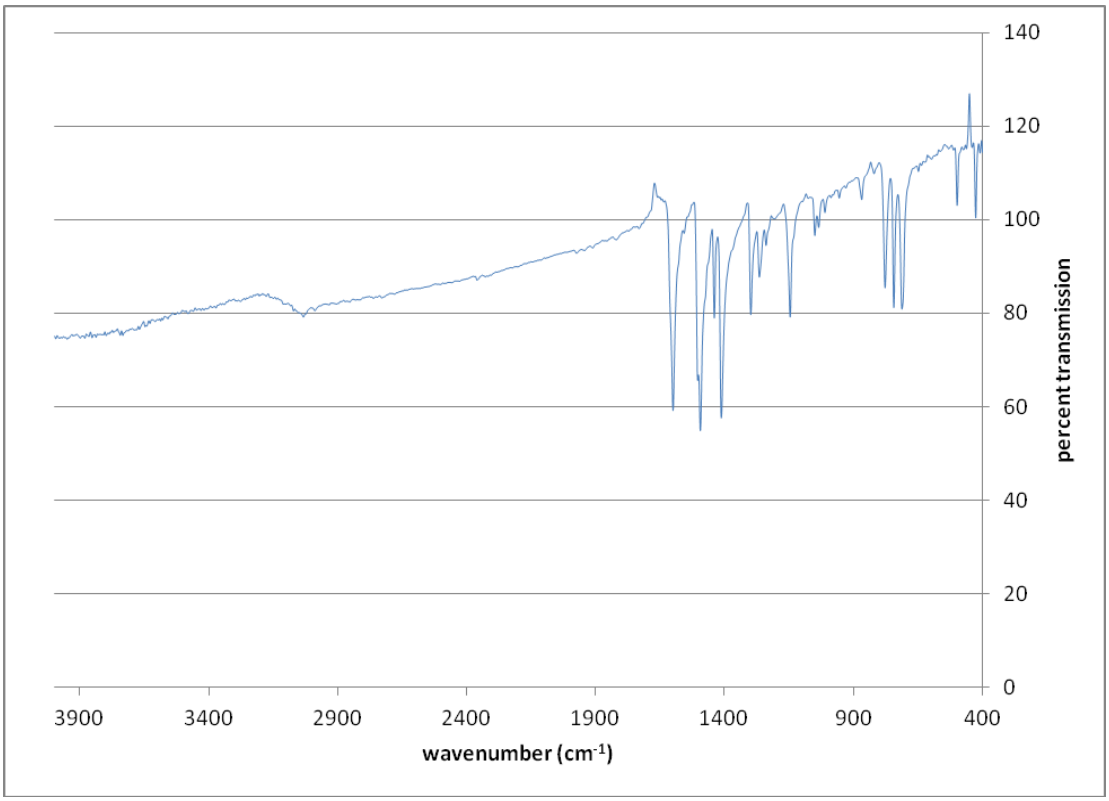

Figure S17. IR Spectrum of PDPPd-Cl (1) (KBr Pellet)

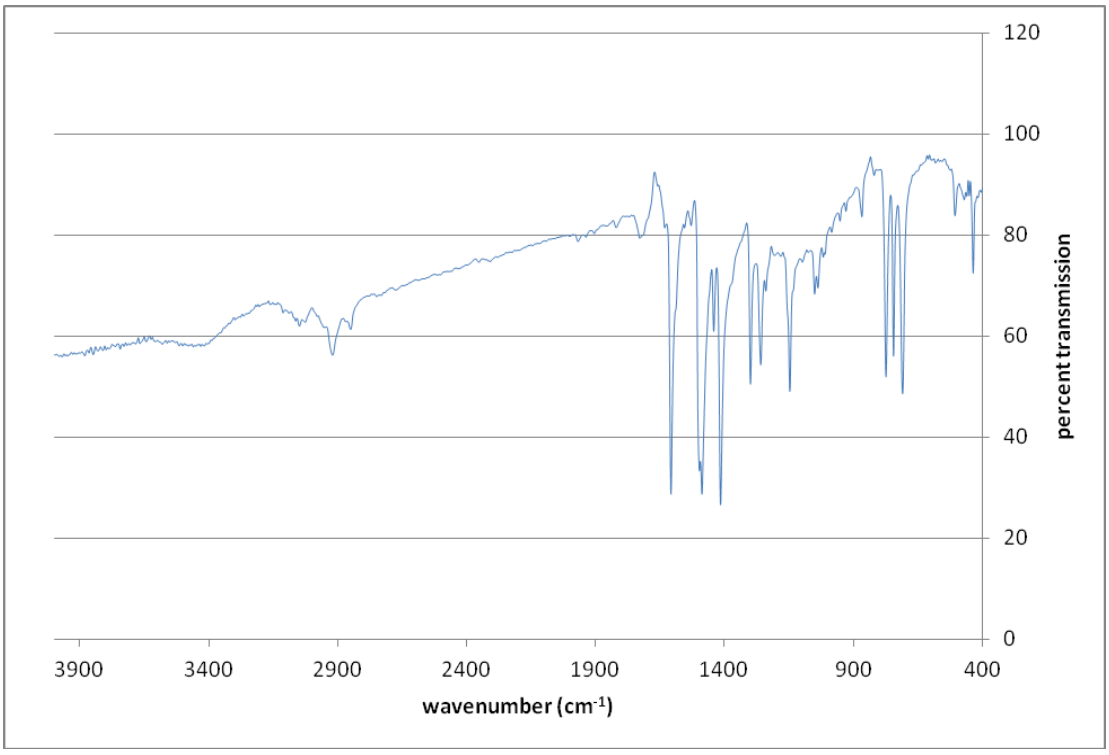

Figure S18. IR Spectrum of PDPPt-Cl (3) (KBr Pellet)

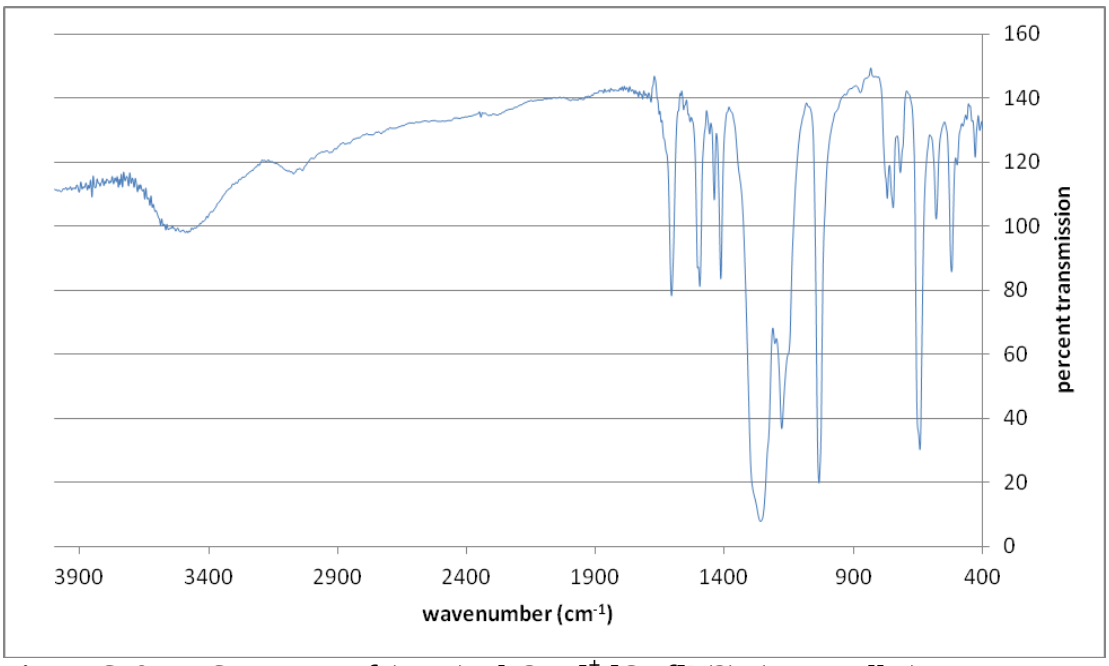

Figure S19. IR Spectrum of (PDP)Pd-OH_2]$^+$ [OTf]$^-$ (2) (KBr Pellet)

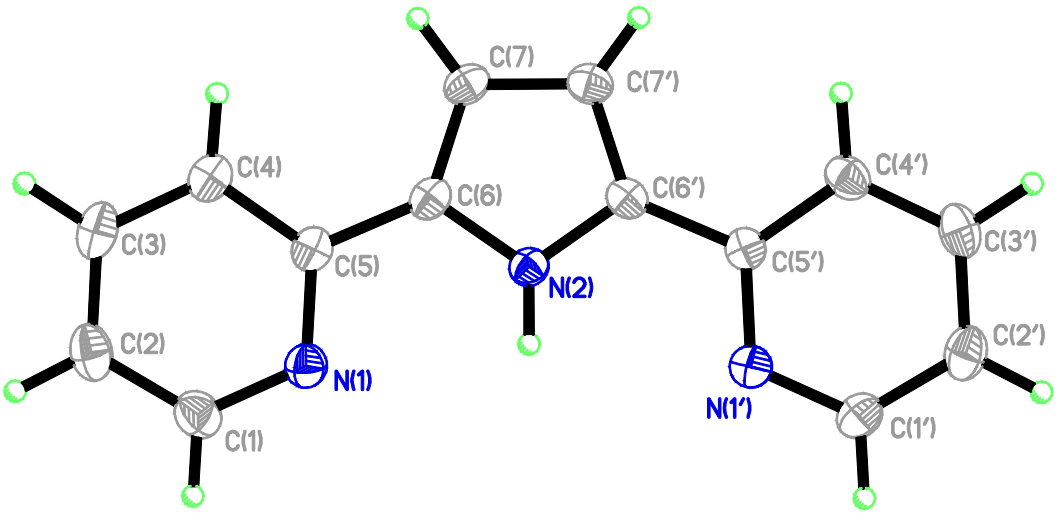

Figure X1. Structure of PDP(H) ligand with thermal ellipsoids (50%), and hydrogens shown as open circles.

Table X1.1. Sample and crystal data for (PDP)H.

Chemical formula	$C_{14}H_{11}N_3$	
Formula weight	221.26	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.200 x 0.200 x 0.330 mm	
Crystal system	orthorhombic	
Space group	P $2_12_12_1$	
Unit cell dimensions	a = 5.9045(7) Å	α = 90°
	b = 12.7669(16) Å	β = 90°
	c = 15.3114(18) Å	γ = 90°
Volume	1154.2(2) $Å^3$	
Z	4	
Density (calculated)	1.273 Mg/cm^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	464	

Table X1.2. Data collection and structure refinement for (PDP)H.

Theta range for data collection	2.08 to 27.91°
Index ranges	-7<=h<=7, -16<=k<=14, -19<=l<=20
Reflections collected	6749
Independent reflections	2769 [R(int) = 0.0193]
Max. and min. transmission	0.9845 and 0.9745
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-97 (Sheldrick, 2008)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	2769 / 0 / 154
Goodness-of-fit on F^2	1.027[a]
Final R indices[b]	2510 data; I>2σ(I) R1 = 0.0344, wR2 = 0.0775
	all data R1 = 0.0405, wR2 = 0.0807
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0382P)^2+0.1960P]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	0.0(20)
Largest diff. peak and hole	0.154 and -0.181 eÅ^{-3}
R.M.S. deviation from mean	0.034 eÅ^{-3}

[a] $S = [\Sigma\, w(F_{obs}^2 - F_{calc}^2)^2 / (m-n)]^{1/2}$ [b] $R_1 = (\Sigma\, ||F_{obs}| - |F_{calc}||)/\Sigma|F_{obs}|$; $wR_2 = [(\Sigma\, w(F_{obs}^2 - F_{calc}^2)^2)/\Sigma\, wF_{obs}^2]^{1/2}$

Table X1.3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for (PDP)H.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.4255(3)	0.88864(11)	0.51074(10)	0.0305(3)
C1'	0.4266(2)	0.37018(10)	0.22845(8)	0.0257(3)
C2	0.3277(3)	0.83685(11)	0.58101(10)	0.0327(3)
C2'	0.3236(3)	0.46404(11)	0.20706(9)	0.0298(3)
C3	0.1219(3)	0.87284(11)	0.61196(9)	0.0322(3)
C3'	0.1134(2)	0.48559(11)	0.24287(9)	0.0301(3)
C4	0.0214(2)	0.95803(11)	0.57164(8)	0.0269(3)
C4'	0.0142(3)	0.41296(10)	0.29780(9)	0.0255(3)
C5	0.1308(2)	0.00520(10)	0.50078(8)	0.0215(3)
C5'	0.1283(2)	0.31905(10)	0.31475(7)	0.0199(3)

	x/a	y/b	z/c	U(eq)
C6	0.0333(2)	0.09630(10)	0.45723(8)	0.0211(3)
C6'	0.0312(2)	0.23905(9)	0.37173(8)	0.0201(3)
C7'	0.8179(2)	0.23005(10)	0.40863(8)	0.0235(3)
C7	0.8205(2)	0.14041(10)	0.46260(8)	0.0232(3)
N1	0.3324(2)	0.97165(8)	0.47077(7)	0.0258(2)
N1'	0.3346(2)	0.29764(8)	0.28130(6)	0.0227(2)
N2	0.15837(19)	0.15673(8)	0.40114(6)	0.0199(2)

Table X1.4. Bond lengths (Å) for (PDP)H.

C1-N1	1.3417(18)	C1-C2	1.389(2)
C1-H1A	0.95	C1'-N1'	1.3447(16)
C1'-C2'	1.3832(19)	C1'-H1'A	0.95
C2-C3	1.383(2)	C2-H2A	0.95
C2'-C3'	1.385(2)	C2'-H2'A	0.95
C3-C4	1.384(2)	C3-H3A	0.95
C3'-C4'	1.3819(19)	C3'-H3'A	0.95
C4-C5	1.3990(18)	C4-H4A	0.95
C4'-C5'	1.3996(18)	C4'-H4'A	0.95
C5-N1	1.3460(17)	C5-C6	1.4590(18)
C5'-N1'	1.3493(17)	C5'-C6'	1.4605(17)
C6-N2	1.3704(16)	C6-C7	1.3792(19)
C6'-N2	1.3677(16)	C6'-C7'	1.3854(18)
C7'-C7	1.4116(18)	C7'-H7'A	0.95
C7-H7A	0.95	N2-H2B	0.88

Table X1.5. Bond angles (°) for (PDP)H.

N1-C1-C2	123.99(14)	N1-C1-H1A	118.0
C2-C1-H1A	118.0	N1'-C1'-C2'	124.15(13)
N1'-C1'-H1'A	117.9	C2'-C1'-H1'A	117.9
C3-C2-C1	118.22(13)	C3-C2-H2A	120.9
C1-C2-H2A	120.9	C1'-C2'-C3'	118.21(13)
C1'-C2'-H2'A	120.9	C3'-C2'-H2'A	120.9
C2-C3-C4	119.02(13)	C2-C3-H3A	120.5
C4-C3-H3A	120.5	C4'-C3'-C2'	119.18(13)
C4'-C3'-H3'A	120.4	C2'-C3'-H3'A	120.4

Table X1.5 (cont)

C3-C4-C5	119.08(13)	C3-C4-H4A	120.5
C5-C4-H4A	120.5	C3'-C4'-C5'	118.92(13)
C3'-C4'-H4'A	120.5	C5'-C4'-H4'A	120.5
N1-C5-C4	122.43(12)	N1-C5-C6	116.52(11)
C4-C5-C6	121.02(12)	N1'-C5'-C4'	122.53(12)
N1'-C5'-C6'	116.06(11)	C4'-C5'-C6'	121.40(12)
N2-C6-C7	107.36(11)	N2-C6-C5	121.51(12)
C7-C6-C5	131.12(12)	N2-C6'-C7'	107.52(11)
N2-C6'-C5'	121.24(11)	C7'-C6'-C5'	131.19(12)
C6'-C7'-C7	107.21(12)	C6'-C7'-H7'A	126.4
C7-C7'-H7'A	126.4	C6-C7-C7'	107.83(12)
C6-C7-H7A	126.1	C7'-C7-H7A	126.1
C1-N1-C5	117.26(12)	C1'-N1'-C5'	116.98(11)
C6'-N2-C6	110.07(11)	C6'-N2-H2B	125.0
C6-N2-H2B	125.0		

Table X1.6. Anisotropic atomic displacement parameters (Å^2) for (PDP)H.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0309(8)	0.0255(7)	0.0350(7)	-0.0001(6)	-0.0011(6)	0.0033(6)
C1'	0.0269(6)	0.0296(7)	0.0207(6)	-0.0008(5)	0.0009(5)	-0.0033(6)
C2	0.0403(9)	0.0230(6)	0.0347(7)	0.0052(6)	-0.0065(7)	-0.0014(7)
C2'	0.0367(8)	0.0309(7)	0.0218(6)	0.0067(5)	-0.0031(6)	-0.0046(7)
C3	0.0410(9)	0.0290(7)	0.0265(6)	0.0065(6)	0.0003(6)	-0.0073(7)
C3'	0.0377(8)	0.0259(7)	0.0266(6)	0.0054(5)	-0.0067(6)	0.0044(6)
C4	0.0294(8)	0.0268(6)	0.0244(6)	0.0008(5)	0.0022(6)	-0.0034(6)
C4'	0.0262(7)	0.0271(6)	0.0231(6)	-0.0003(5)	-0.0025(6)	0.0044(6)
C5	0.0252(7)	0.0195(6)	0.0198(5)	-0.0029(5)	-0.0015(5)	-0.0047(5)
C5'	0.0231(7)	0.0216(6)	0.0150(5)	-0.0022(4)	-0.0034(5)	-0.0003(5)
C6	0.0251(7)	0.0215(6)	0.0167(5)	-0.0034(5)	0.0014(5)	-0.0038(5)
C6'	0.0225(7)	0.0195(6)	0.0184(5)	-0.0045(4)	-0.0024(5)	0.0011(5)
C7'	0.0234(7)	0.0253(6)	0.0219(6)	-0.0042(5)	-0.0006(6)	0.0019(6)
C7	0.0238(7)	0.0260(6)	0.0197(6)	-0.0044(5)	0.0027(6)	-0.0035(6)
N1	0.0266(6)	0.0230(5)	0.0277(5)	0.0011(5)	0.0014(5)	-0.0007(5)
N1'	0.0236(5)	0.0243(5)	0.0201(5)	-0.0014(4)	-0.0012(5)	0.0000(5)
N2	0.0210(5)	0.0202(5)	0.0184(5)	-0.0015(4)	0.0012(5)	-0.0001(5)

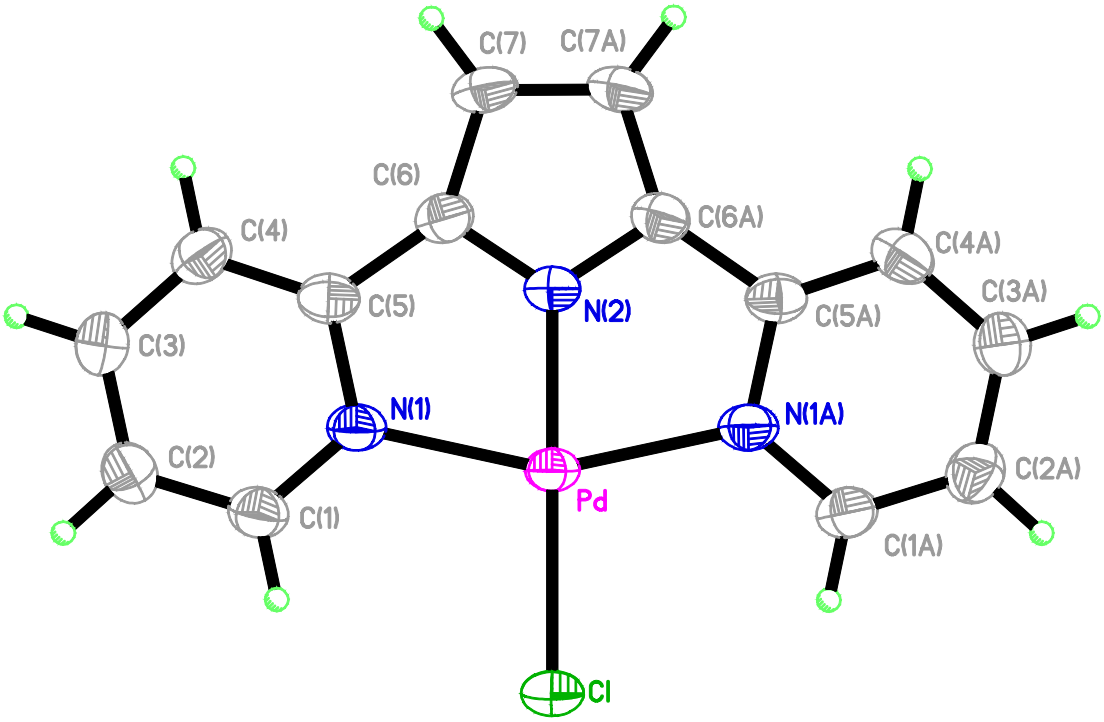

Figure X2. Structure of (PDP)PdCl (**1**)with thermal ellipsoids (50%), and hydrogens shown as open circles.

Table X2.1. Sample and crystal data for PdCl (1).

Chemical formula	$C_{14}H_{10}ClN_3Pd$	
Formula weight	362.10	
Temperature	200(2) K	
Wavelength	0.71069 Å	
Crystal size	0.020 x 0.040 x 0.380 mm	
Crystal system	monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 10.6112(9) Å	α = 90°
	b = 13.4902(15) Å	β = 99.556(6)°
	c = 8.8782(9) Å	γ = 90°
Volume	1253.3(2) $Å^3$	
Z	4	
Density (calculated)	1.919 Mg/cm^3	
Absorption coefficient	1.680 mm^{-1}	
F(000)	712	

Table X2.2. Data collection and structure refinement for (PDP)PdCl (1).

Theta range for data collection	2.46 to 25.34°
Index ranges	-12<=h<=12, -16<=k<=16, -10<=l<=9
Reflections collected	4789
Independent reflections	1143 [R(int) = 0.0467]
Structure solution technique	direct methods
Structure solution program	SIR92 (Altomare, 1993)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-93 (Sheldrick, 1993)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	1143 / 0 / 89
Goodness-of-fit on F^2	1.106[a]
Final R indices[b]	1143 data; I>2σ(I) R1 = 0.0459, wR2 = 0.1036
	all data R1 = 0.0490, wR2 = 0.1060
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0496P)^2+9.3146P]$ where $P=(F_o^2+2F_c^2)/3$
Extinction coefficient	0.0022(5)
Largest diff. peak and hole	0.715 and -1.438 eÅ^{-3}
R.M.S. deviation from mean	0.140 eÅ^{-3}

[a] $S = [\Sigma\, w(F_{obs}^2 - F_{calc}^2)^2 / (m-n)]^{1/2}$ [b] $R_1 = (\Sigma\, ||F_{obs}| - |F_{calc}||)/\Sigma|F_{obs}|$; $wR_2 = [(\Sigma\, w(F_{obs}^2 - F_{calc}^2)^2)/\Sigma\, wF_{obs}^2]^{1/2}$

Table X2.3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for PdCl (1).

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Pd	0.5	0.07807(4)	0.75	0.0304(3)
Cl	0.5	0.25081(13)	0.75	0.0430(5)
N1	0.6445(5)	0.0453(3)	0.6268(6)	0.0346(11)
N2	0.5	0.9383(4)	0.75	0.0329(14)
C1	0.7171(6)	0.1110(4)	0.5645(7)	0.0375(13)
C2	0.8132(6)	0.0804(4)	0.4857(8)	0.0421(14)
C3	0.8343(6)	0.9809(5)	0.4699(8)	0.0426(14)
C4	0.7609(6)	0.9128(4)	0.5329(7)	0.0400(14)
C5	0.6650(6)	0.9455(4)	0.6089(6)	0.0336(12)
C6	0.5794(6)	0.8834(4)	0.6815(7)	0.0347(12)
C7	0.5492(6)	0.7842(4)	0.7064(7)	0.0413(14)

Table X2.4. Bond lengths (Å) for PdCl (1).

Pd-N2	1.885(6)	Pd-N1#1	2.073(5)
Pd-N1	2.073(5)	Pd-Cl	2.330(2)
N1-C1	1.351(7)	N1-C5	1.377(7)
N2-C6#1	1.341(6)	N2-C6	1.341(6)
C1-C2	1.391(9)	C2-C3	1.372(8)
C3-C4	1.382(9)	C4-C5	1.384(8)
C5-C6	1.461(8)	C6-C7	1.402(8)
C7-C7#1	1.400(13)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1, y, -z+3/2

Table X2.5. Bond angles (°) for PdCl (1).

N2-Pd-N1#1	77.71(12)	N2-Pd-N1	77.70(12)
N1#1-Pd-N1	155.4(2)	N2-Pd-Cl	180.0
N1#1-Pd-Cl	102.29(12)	N1-Pd-Cl	102.30(12)
C1-N1-C5	118.8(5)	C1-N1-Pd	126.8(4)
C5-N1-Pd	114.4(4)	C6#1-N2-C6	113.0(6)
C6#1-N2-Pd	123.5(3)	C6-N2-Pd	123.5(3)
N1-C1-C2	121.8(5)	C3-C2-C1	119.2(5)
C2-C3-C4	119.8(5)	C3-C4-C5	119.7(5)
N1-C5-C4	120.8(5)	N1-C5-C6	112.8(5)
C4-C5-C6	126.4(5)	N2-C6-C7	106.2(5)
N2-C6-C5	111.5(5)	C7-C6-C5	142.3(5)
C7#1-C7-C6	107.3(3)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1, y, -z+3/2

Table X2.6. Anisotropic atomic displacement parameters (Å^2) for PdCl (1).

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	0.0331(4)	0.0208(3)	0.0376(4)	0	0.0066(3)	0
Cl	0.0530(13)	0.0220(8)	0.0571(13)	0	0.0181(10)	0
N1	0.037(3)	0.024(2)	0.043(3)	0.002(2)	0.006(2)	0.001(2)
N2	0.038(4)	0.023(3)	0.038(4)	0	0.009(3)	0
C1	0.039(3)	0.029(3)	0.043(3)	0.003(2)	0.006(3)	-0.001(2)
C2	0.037(3)	0.042(3)	0.049(4)	0.003(3)	0.011(3)	-0.004(2)
C3	0.034(3)	0.045(3)	0.051(4)	0.000(3)	0.013(3)	0.002(3)
C4	0.037(3)	0.035(3)	0.047(3)	-0.008(3)	0.006(3)	0.004(2)
C5	0.038(3)	0.028(3)	0.032(3)	-0.002(2)	0.000(2)	-0.002(2)
C6	0.037(3)	0.028(3)	0.039(3)	-0.001(2)	0.006(2)	0.003(2)
C7	0.052(4)	0.023(2)	0.050(4)	-0.003(2)	0.011(3)	0.004(2)

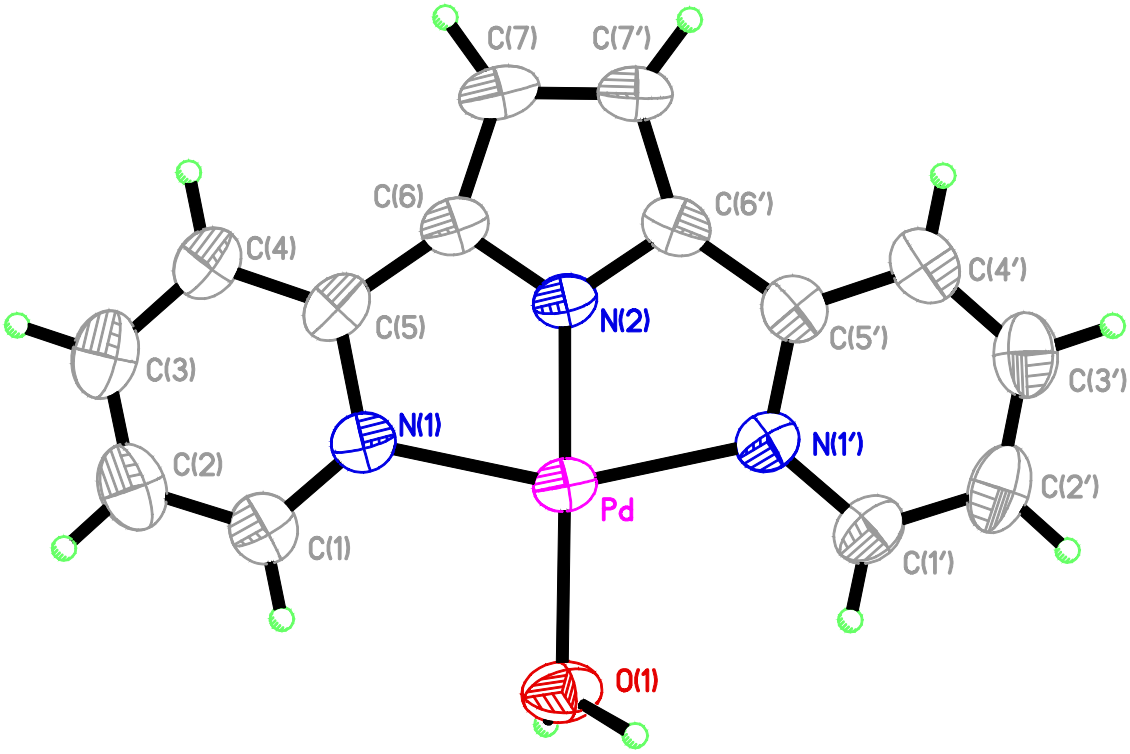

Figure X3. Structure of $(PDP)Pd(OH)_2]^+[OTf]^-\cdot H_2O$ (**2**) with thermal ellipsoids (30%), and hydrogens shown as open circles. Triflate counterion and solvent water not shown.

Table X3.1. Sample and crystal data for $(PDP)Pd(OH)_2]^+[OTf]^-\cdot H_2O$ (2).

Chemical formula	$C_{15}H_{14}F_3N_3O_5PdS$	
Formula weight	511.75	
Temperature	295(1) K	
Wavelength	0.71069 Å	
Crystal size	0.07 x 0.10 x 0.27 mm	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.8162(5) Å	α = 94.8250(10)°
	b = 12.8499(7) Å	β = 106.811(4)°
	c = 6.9992(4) Å	γ = 110.907(3)°
Volume	929.26(8) $Å^3$	
Z	2	
Density (calculated)	1.829 Mg/cm^3	
Absorption coefficient	1.173 mm^{-1}	
F(000)	508	

Table X3.2. Data collection and structure refinement for $(PDP)Pd(OH)_2]^+[OTf]^- \cdot H_2O$ (2).

Theta range for data collection	3.06 to 25.35°	
Reflections collected	7770	
Independent reflections	3128 [R(int) = 0.0264]	
Max. and min. transmission	1.0000 and 0.6832	
Structure solution technique	direct methods	
Structure solution program	SIR92 (Altomare, 1993)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-93 (Sheldrick, 1993)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3128 / 0 / 254	
Goodness-of-fit on F^2	1.111[a]	
Final R indices[b]	2830 data; $I>2\sigma(I)$	R1 = 0.0496, wR2 = 0.1175
	all data	R1 = 0.0560, wR2 = 0.1221
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0548P)^2+1.5735P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.485 and -0.860 eÅ^{-3}	
R.M.S. deviation from mean	0.082 eÅ^{-3}	

[a] $S = [\Sigma\, w(F_{obs}^2 - F_{calc}^2)^2 / (m-n)]^{1/2}$ [b] $R_1 = (\Sigma\, ||F_{obs}| - |F_{calc}||)/\Sigma|F_{obs}|$; $wR_2 = [(\Sigma\, w(F_{obs}^2 - F_{calc}^2)^2)/\Sigma\, wF_{obs}^2]^{1/2}$

Table X3.3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for $(PDP)Pd(OH)_2]^+[OTf]^- \cdot H_2O$ (2).

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Pd1	0.17016(4)	0.56567(4)	0.34130(6)	0.05674(18)
N1	0.0902(5)	0.3921(4)	0.3340(7)	0.0621(11)
N1'	0.1688(5)	0.7242(4)	0.3021(7)	0.0619(11)
N2	0.9952(4)	0.5325(4)	0.2397(7)	0.0592(11)
C1	0.1521(8)	0.3257(5)	0.3915(10)	0.0788(18)
C1'	0.2719(7)	0.8233(5)	0.3440(10)	0.0787(18)
C2	0.0873(10)	0.2102(7)	0.3792(11)	0.096(2)
C2'	0.2580(10)	0.9227(5)	0.3062(11)	0.097(3)
C3	0.9559(10)	0.1645(7)	0.3101(11)	0.093(2)
C3'	0.1368(10)	0.9205(7)	0.2254(11)	0.092(2)

	x/a	y/b	z/c	U(eq)
C4	0.8890(7)	0.2322(5)	0.2507(9)	0.0763(18)
C4'	0.0317(8)	0.8212(5)	0.1841(10)	0.080(2)
C5	0.9564(5)	0.3463(5)	0.2634(8)	0.0655(15)
C5'	0.0474(7)	0.7220(5)	0.2225(8)	0.0669(15)
C6	0.9026(5)	0.4284(5)	0.2086(8)	0.0626(14)
C6'	0.9461(5)	0.6101(5)	0.1873(8)	0.0644(15)
C7	0.7839(5)	0.4405(5)	0.1295(9)	0.0750(18)
C7'	0.8115(5)	0.5520(5)	0.1161(9)	0.0735(17)
O1	0.3666(5)	0.6004(4)	0.4640(7)	0.0863(13)
O2	0.5142(5)	0.5602(4)	0.2721(7)	0.0827(13)
S1	0.61630(17)	0.78765(13)	0.9263(2)	0.0728(4)
F1	0.6290(5)	0.9768(4)	0.1086(11)	0.145(2)
F2	0.6573(14)	0.8604(8)	0.2973(11)	0.254(6)
F3	0.4726(9)	0.8327(5)	0.1009(17)	0.205(4)
C8	0.5884(11)	0.8687(8)	0.1125(18)	0.114(3)
O3	0.5709(5)	0.6752(4)	0.9568(9)	0.1011(17)
O4	0.5330(7)	0.8006(5)	0.7420(9)	0.136(3)
O5	0.7475(5)	0.8439(5)	0.9603(13)	0.142(3)

Table X3.4. Bond lengths (Å) for (PDP)Pd(OH)$_2$]$^+$[OTf]$^-$·H$_2$O (2).

Pd1-N2	1.853(5)	Pd1-N1	2.078(5)
Pd1-N1'	2.084(5)	Pd1-O1	2.090(5)
N1-C1	1.326(9)	N1-C5	1.387(8)
N1'-C1'	1.346(8)	N1'-C5'	1.369(8)
N2-C6	1.342(7)	N2-C6'	1.348(8)
C1-C2	1.389(11)	C1'-C2'	1.381(11)
C2-C3	1.363(12)	C2'-C3'	1.368(12)
C3-C4	1.384(11)	C3'-C4'	1.361(11)
C4-C5	1.377(9)	C4'-C5'	1.389(9)
C5-C6	1.440(9)	C5'-C6'	1.450(9)
C6-C7	1.421(9)	C6'-C7'	1.403(9)
C7-C7'	1.370(10)	S1-O5	1.393(6)
S1-O3	1.409(5)	S1-O4	1.442(6)
S1-C8	1.777(10)	F1-C8	1.303(10)
F2-C8	1.350(13)	F3-C8	1.253(12)

Table X3.5. Bond angles (°) for (PDP)Pd(OH)$_2$]$^+$[OTf]$^-$·H$_2$O (2).

N2-Pd1-N1	78.1(2)	N2-Pd1-N1'	78.0(2)
N1-Pd1-N1'	156.1(2)	N2-Pd1-O1	178.1(2)
N1-Pd1-O1	100.6(2)	N1'-Pd1-O1	103.3(2)
C1-N1-C5	119.6(6)	C1-N1-Pd1	127.5(5)
C5-N1-Pd1	112.9(4)	C1'-N1'-C5'	119.4(6)
C1'-N1'-Pd1	127.1(5)	C5'-N1'-Pd1	113.5(4)
C6-N2-C6'	112.2(5)	C6-N2-Pd1	124.0(4)
C6'-N2-Pd1	123.8(4)	N1-C1-C2	122.1(8)
N1'-C1'-C2'	121.5(8)	C3-C2-C1	118.7(8)
C3'-C2'-C1'	119.2(8)	C2-C3-C4	120.4(8)
C4'-C3'-C2'	120.0(8)	C5-C4-C3	119.4(7)
C3'-C4'-C5'	120.0(8)	C4-C5-N1	119.9(6)
C4-C5-C6	126.6(7)	N1-C5-C6	113.4(5)
N1'-C5'-C4'	119.9(6)	N1'-C5'-C6'	113.3(5)
C4'-C5'-C6'	126.8(7)	N2-C6-C7	105.7(6)
N2-C6-C5	111.5(5)	C7-C6-C5	142.8(6)
N2-C6'-C7'	106.6(6)	N2-C6'-C5'	111.4(5)
C7'-C6'-C5'	142.0(6)	C7'-C7-C6	107.9(6)
C7-C7'-C6'	107.7(6)	O5-S1-O3	118.3(4)
O5-S1-O4	114.4(5)	O3-S1-O4	112.0(4)
O5-S1-C8	104.0(5)	O3-S1-C8	105.2(4)
O4-S1-C8	100.2(5)	F3-C8-F1	109.0(10)
F3-C8-F2	107.4(11)	F1-C8-F2	106.6(9)
F3-C8-S1	113.3(7)	F1-C8-S1	113.0(8)
F2-C8-S1	107.1(8)		

Table X3.6. Anisotropic atomic displacement parameters (Å^2) for (PDP)Pd(OH)$_2$]$^+$[OTf]$^-$·H$_2$O (2).

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd1	0.0496(2)	0.0668(2)	0.0494(2)	0.00502(18)	0.01690(18)	0.0200(2)
N1	0.062(3)	0.070(3)	0.050(2)	0.007(2)	0.018(2)	0.024(2)
N1'	0.061(3)	0.068(3)	0.056(3)	0.009(2)	0.025(2)	0.021(2)
N2	0.050(3)	0.068(3)	0.056(3)	0.009(2)	0.019(2)	0.020(2)
C1	0.092(5)	0.080(5)	0.064(4)	0.008(3)	0.026(3)	0.037(4)
C1'	0.078(5)	0.079(5)	0.071(4)	0.009(3)	0.033(3)	0.018(3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C2	0.135(8)	0.088(5)	0.079(5)	0.015(4)	0.040(5)	0.059(5)
C2'	0.129(8)	0.067(5)	0.090(5)	0.019(4)	0.054(5)	0.020(4)
C3	0.128(7)	0.070(4)	0.075(4)	0.006(4)	0.044(5)	0.027(5)
C3'	0.125(7)	0.076(5)	0.087(5)	0.022(4)	0.050(5)	0.041(5)
C4	0.081(5)	0.072(4)	0.060(4)	0.004(3)	0.025(3)	0.015(3)
C4'	0.104(6)	0.092(5)	0.060(4)	0.023(3)	0.034(4)	0.052(4)
C5	0.072(4)	0.066(4)	0.045(3)	0.000(2)	0.025(3)	0.011(3)
C5'	0.082(5)	0.078(4)	0.050(3)	0.013(3)	0.030(3)	0.037(3)
C6	0.056(4)	0.073(4)	0.050(3)	0.003(3)	0.018(2)	0.020(3)
C6'	0.067(4)	0.085(4)	0.049(3)	0.015(3)	0.021(3)	0.037(3)
C7	0.048(4)	0.101(5)	0.062(3)	0.000(3)	0.019(3)	0.017(3)
C7'	0.056(4)	0.096(5)	0.068(4)	0.010(3)	0.021(3)	0.032(3)
O1	0.070(3)	0.100(3)	0.085(3)	0.003(3)	0.024(2)	0.036(3)
O2	0.088(3)	0.076(3)	0.098(3)	0.026(2)	0.043(3)	0.037(2)
S1	0.0658(10)	0.0602(9)	0.0878(11)	0.0132(8)	0.0269(8)	0.0201(7)
F1	0.144(5)	0.061(3)	0.205(6)	-0.010(3)	0.054(4)	0.027(3)
F2	0.437(18)	0.204(9)	0.106(5)	0.009(5)	0.058(8)	0.142(10)
F3	0.184(8)	0.129(5)	0.330(12)	-0.010(6)	0.185(9)	0.031(5)
C8	0.110(8)	0.078(6)	0.137(8)	0.003(5)	0.040(6)	0.023(5)
O3	0.130(5)	0.063(3)	0.125(4)	0.031(3)	0.061(4)	0.039(3)
O4	0.171(7)	0.096(4)	0.091(4)	0.016(3)	-0.019(4)	0.049(4)
O5	0.078(4)	0.119(5)	0.240(8)	0.055(5)	0.069(5)	0.038(3)

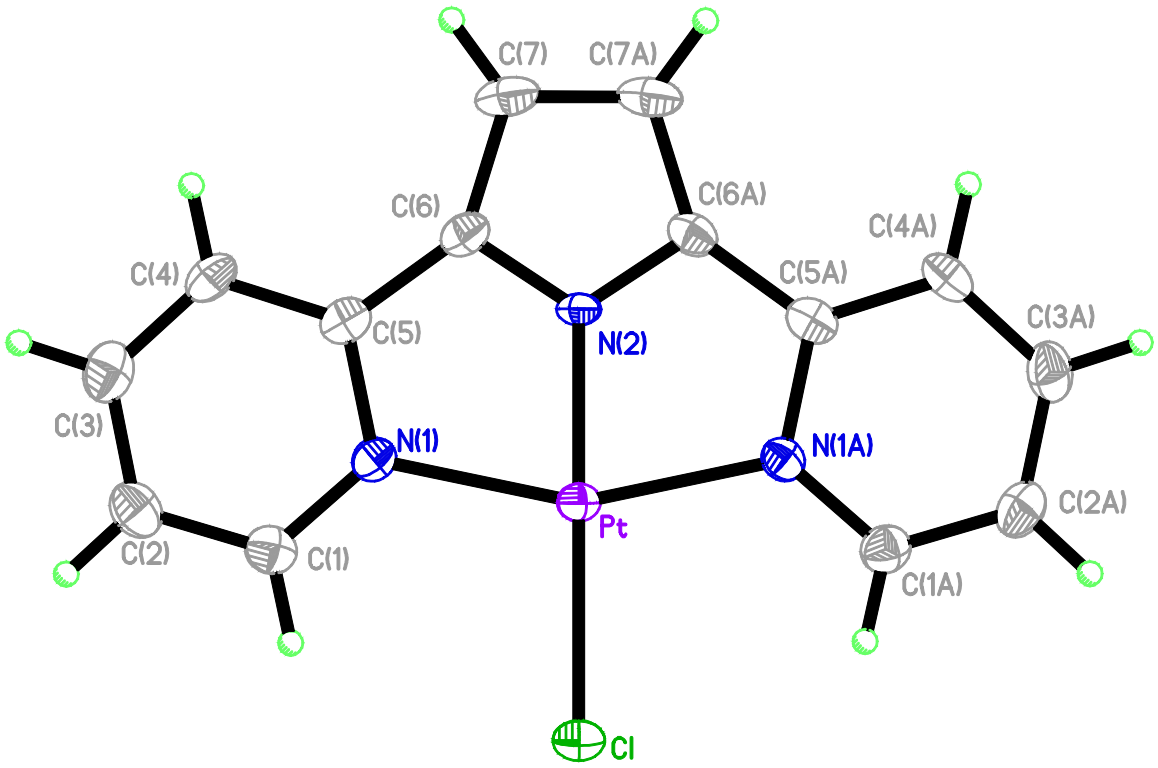

Figure X4. Structure of (PDP)PdCl (**3**) with thermal ellipsoids (50%), and hydrogens shown as open circles.

Table X4.1. Sample and crystal data for (PDP)PtCl.

Chemical formula	$C_{14}H_{10}ClN_3Pt$	
Formula weight	450.79	
Temperature	143(2) K	
Wavelength	0.71069 Å	
Crystal size	0.020 x 0.020 x 0.480 mm	
Crystal system	monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 10.769(3) Å	α = 90°
	b = 13.456(4) Å	β = 98.944(6)°
	c = 8.751(2) Å	γ = 90°
Volume	1252.7(6) $Å^3$	
Z	4	
Density (calculated)	2.390 Mg/cm^3	
Absorption coefficient	11.401 mm^{-1}	
F(000)	840	

Table X4.2. Data collection and structure refinement for (PDP)PtCl.

Theta range for data collection	3.03 to 27.47°
Index ranges	-13<=h<=11, -13<=k<=16, -8<=l<=10
Reflections collected	4100
Independent reflections	1281 [R(int) = 0.0231]
Max. and min. transmission	1.0000 and 0.7353
Structure solution technique	direct methods
Structure solution program	SIR92 (Altomare, 1993)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-93 (Sheldrick, 1993)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	1281 / 0 / 88
Goodness-of-fit on F^2	1.144[a]
Final R indices[b]	1281 data; I>2σ(I) R1 = 0.0209, wR2 = 0.0497
	all data R1 = 0.0224, wR2 = 0.0500
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0205P)^2+8.4294P]$ where $P=(F_o^2+2F_c^2)/3$
Extinction coefficient	0.0022(5)
Largest diff. peak and hole	0.684 and -1.500 eÅ^{-3}
R.M.S. deviation from mean	0.149 eÅ^{-3}

[a] $S = [\Sigma\, w(F_{obs}^2 - F_{calc}^2)^2 / (m-n)]^{1/2}$ [b] $R_1 = (\Sigma\, ||F_{obs}| - |F_{calc}||)/\Sigma|F_{obs}|$; $wR_2 = [(\Sigma\, w(F_{obs}^2 - F_{calc}^2)^2)/\Sigma\, wF_{obs}^2]^{1/2}$

Table X4.3. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for (PDP)PtCl.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Pt	0.5	0.42436(2)	0.75	0.01686(9)
Cl	0.5	0.25091(11)	0.75	0.0281(4)
N1	0.6445(3)	0.4556(3)	0.6290(4)	0.0184(7)
N2	0.5	0.5650(3)	0.75	0.0177(11)
C1	0.7164(4)	0.3900(4)	0.5668(5)	0.0240(10)
C2	0.8138(5)	0.4191(4)	0.4900(6)	0.0275(11)
C3	0.8360(4)	0.5194(4)	0.4769(6)	0.0279(11)
C4	0.7638(4)	0.5881(3)	0.5381(6)	0.0233(10)
C5	0.6659(4)	0.5567(3)	0.6138(5)	0.0196(9)
C6	0.5810(4)	0.6196(3)	0.6836(5)	0.0211(9)
C7	0.5501(5)	0.7198(3)	0.7077(6)	0.0286(11)

Table X4.4. Bond lengths (Å) for (PDP)PtCl.

Pt-N2	1.893(5)	Pt-N1#1	2.057(4)
Pt-N1	2.057(4)	Pt-Cl	2.334(2)
N1-C1	1.344(6)	N1-C5	1.390(6)
N2-C6#1	1.340(5)	N2-C6	1.340(5)
C1-C2	1.387(7)	C2-C3	1.379(7)
C3-C4	1.370(7)	C4-C5	1.395(6)
C5-C6	1.449(6)	C6-C7	1.412(7)
C7-C7#1	1.400(10)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1, y, -z+3/2

Table X4.5. Bond angles (°) for (PDP)PtCl.

N2-Pt-N1#1	78.22(11)	N2-Pt-N1	78.22(11)
N1#1-Pt-N1	156.4(2)	N2-Pt-Cl	180.0
N1#1-Pt-Cl	101.78(11)	N1-Pt-Cl	101.78(11)
C1-N1-C5	119.3(4)	C1-N1-Pt	127.2(3)
C5-N1-Pt	113.5(3)	C6#1-N2-C6	113.5(5)
C6#1-N2-Pt	123.2(3)	C6-N2-Pt	123.2(3)
N1-C1-C2	122.5(5)	C3-C2-C1	118.1(5)
C4-C3-C2	120.7(4)	C3-C4-C5	119.9(4)
N1-C5-C4	119.4(4)	N1-C5-C6	114.0(4)
C4-C5-C6	126.6(4)	N2-C6-C7	105.9(4)
N2-C6-C5	111.0(4)	C7-C6-C5	143.1(4)
C7#1-C7-C6	107.3(3)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1, y, -z+3/2

Table 6. Anisotropic atomic displacement parameters (Å^2) for (PDP)PtCl.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt	0.01706(13)	0.01443(14)	0.0186(2)	0	0.00127(9)	0
Cl	0.0332(9)	0.0158(8)	0.0373(10)	0	0.0117(7)	0
N1	0.017(2)	0.019(2)	0.018(2)	0.0004(14)	0.0008(14)	-0.0020(15)
N2	0.020(3)	0.010(2)	0.023(3)	0	0.004(2)	0
C1	0.022(2)	0.023(2)	0.026(3)	-0.001(2)	0.001(2)	0.001(2)
C2	0.022(2)	0.031(3)	0.029(3)	-0.003(2)	0.002(2)	0.005(2)
C3	0.017(2)	0.037(3)	0.030(3)	0.005(2)	0.002(2)	0.000(2)
C4	0.023(2)	0.023(2)	0.023(3)	0.003(2)	0.001(2)	-0.008(2)
C5	0.021(2)	0.021(2)	0.014(2)	0.001(2)	-0.004(2)	-0.004(2)
C6	0.025(2)	0.019(2)	0.018(2)	0.002(2)	0.002(2)	-0.004(2)
C7	0.044(3)	0.015(2)	0.026(3)	0.001(2)	0.001(2)	-0.004(2)

References