Electronic Supplementary Material (ESI) for Dalton Transactions.

Table SI1.- Crystal and structure refinement data for compounds **2**, **3**, **4**, **7**, **8**.

Compound	2	3	4	7	8
Empirical formula	$C_{48}H_{37}ClN_2O_2P_2Pd_2$	$C_{43.50}H_{36}NO_{1.50}P_2Pd$	$C_{50}H_{42}NOP_3Pd$	$C_{77}H_{64}Cl_6N_2O_2P_4Pd_2$	$C_{36}H_{28}Cl_2O_2P_2Pd_2$
Molecular weight	983.98	765.07	872.15	1598.68	838.22
Temperature	100.0(2) K	100(2) K	100(2) K	100(2) K	293(2) K
Wavelenght	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71069 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P 21/n	C 2/c	C 2/c	I 2/a	P 21/n
Unit cell dimensions	a = 13.6607(5) Å α = 90º b = 16.4857(6) Å β = 108.269º c = 19.0403(8) Å γ = 90º	*a* = 17.7768(7) Å *α* = 90º *b* = 9.4520(4) Å *β* = 98.266(2)º *c* = 42.7751(14) Å *γ* = 90º	*a* = 24.4601(12) Å *α* = 90º *b* = 14.8032(7) Å *β* = 98.606(3)º *c* = 25.3318(12) Å *γ* = 90º	*a* = 23.8548(12) Å *α* = 90º *b* = 9.0603(5) Å *β* = 106.589(3)º *c* = 35.985(2) Å *γ* = 90º	*a* = 16.503(5) Å *α* = 90.000(5)º *b* = 10.164(5) Å *β* = 95.459(5)º *c* = 19.571(5) Å *γ* = 90.000(5)º
Volume	4071.9(3)Å^3	7112.7(5) Å^3	9069.1(8) Å^3	7453.8(7) Å^3	3268(2) Å^3
Z	4	8	8	4	4
Calculated density	1.605 Mg/m^3	1.429 Mg/m^3	1.278 Mg/m^3	1.425 Mg/m^3	1.704 Mg/m^3
Absortion coefficient	1.070 mm^{-1}	0.649 mm^{-1}	0.551 mm^{-1}	0.830 mm^{-1}	1.394 mm^{-1}
F(000)	1976	3136	3584	3240	1664
Crystal size	0.280 x 0.200 x 0.150 mm	0.300 x 0.250 x 0.170 mm	0.180 x 0.170 x 0.070 mm	0.200 x 0.180 x 0.120 mm	0.24 x 0.12 x 0.08 mm
Θ Range for data collection	1.672 to 30.583°	0.962 to 28.357°	1.862 to 26.372°	1.181 to 29.575°	1.543 to 26.371°
Index ranges	-19<=*h*<=19 -23<=*k*<=23 -27<=*l*<=26	-23<=*h*<=23 -12<=*k*<=12 -48<=*l*<=56	-30<=*h*<=30 -18<=*k*<=18 -30<=*l*<=31	-33<=*h*<=33 -10<=*k*<=12 -49<=*l*<=49	-20<=*h*<=15 -12<=*k*<=12 -24<=*l*<=24
Reflections collected/independent	67644 / 12435 [R_{int} = 0.0747]	48007 / 8896 [R_{int} = 0.0446]	63330 / 9259 [R_{int} = 0.0606]	56722 / 10462 [R_{int} = 0.0602]	27307 / 6677 [R_{int} = 0.0716]
Data/restrictions/parameter	12435 / 31 / 560	8896 / 0 / 444	9259 / 0 / 505	10462 / 0 / 428	6677 / 0 / 397
Goodness-of-fit on F^2	1.071	1.131	0.962	1.105	1.017
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0463, wR_2 = 0.0855	R_1 = 0.0466, wR_2 = 0.0806	R_1 = 0.0407, wR_2 = 0.0839	R_1 = 0.0492, wR_2 = 0.1327	R_1 = 0.0438, wR_2 = 0.0875
***R* Indices (all data)**	R_1 = 0.0683, wR_2 = 0.0916	R_1 = 0.0560, wR_2 = 0.0842	R_1 = 0.0672, wR_2 = 0.0910	R_1 = 0.0641, wR_2 = 0.1396	R_1 = 0.0751, wR_2 = 0.0979

Table SI2.- Selected bond distances (Å) and angles (°) for compound **2**.

Bond	Length/Å	Angle	(˚)
Pd(1)-C(25)	1.960(3)	C(25)-Pd(1)-N(1)	88.71(14)
Pd(1)-N(1)	2.010(3)	C(25)-Pd(1)-O(1)	169.85(12)
Pd(1)-O(1)	2.116(2)	N(1)-Pd(1)-O(1)	81.26(11)
Pd(1)-Cl(1)	2.3373(9)	C(25)-Pd(1)-Cl(1)	95.12(11)
Pd(2)-C(26)	1.963(3)	N(1)-Pd(1)-Cl(1)	176.17(9)
Pd(2)-N(2)	1.993(3)	O(1)-Pd(1)-Cl(1)	94.91(7)
Pd(2)-O(2)	2.123(2)	C(26)-Pd(2)-N(2)	88.14(14)
Pd(2)-Cl(1)	2.3421(9)	C(26)-Pd(2)-O(2)	168.60(13)
P(1)-N(1)	1.619(3)	N(2)-Pd(2)-O(2)	81.36(11)
P(1)-C(20)	1.783(4)	C(26)-Pd(2)-Cl(1)	95.81(12)
P(1)-C(14)	1.808(3)	N(2)-Pd(2)-Cl(1)	174.31(9)
P(1)-C(8)	1.814(3)	O(2)-Pd(2)-Cl(1)	94.98(7)
P(2)-N(2)	1.611(3)	N(1)-P(1)-C(20)	101.41(17)
P(2)-C(31)	1.784(4)	N(2)-P(2)-C(31)	101.49(17)
P(2)-C(38)	1.805(3)	Pd(1)-Cl(1)-Pd(2)	93.61(3)
P(2)-C(32)	1.811(3)	C(49)-O(2)-Pd(2)	110.0(2)
O(2)-C(49)	1.376(4)	C(2)-O(1)-Pd(1)	110.4(2)
O(1)-C(2)	1.374(4)	C(7)-N(1)-Pd(1)	112.8(2)
N(1)-C(7)	1.431(4)	P(1)-N(1)-Pd(1)	112.74(16)
N(2)-C(44)	1.436(5)	C(44)-N(2)-Pd(2)	113.5(2)
C(2)-C(7)	1.389(5)	P(2)-N(2)-Pd(2)	116.00(18)
C(44)-C(49)	1.387(5)	O(1)-C(2)-C(7)	118.7(3)
C(20)-C(25)	1.420(5)	O(2)-C(49)-C(44)	119.0(3)
C(26)-C(31)	1.415(5)	C(2)-C(7)-N(1)	116.4(3)
		C(49)-C(44)-N(2)	115.9(3)
		C(20)-C(25)-Pd(1)	115.0(3)
		C(31)-C(26)-Pd(2)	116.1(3)

Table SI3.- Selected bond distances (Å) and angles (°) for compound **3**.

Bond	Length/Å	Angle	(˚)
Pd(1)-C(25)	2.013(3)	C(25)-Pd(1)-N(1)	88.02(10)
Pd(1)-N(1)	2.052(2)	C(25)-Pd(1)-O(1)	169.23(9)
Pd(1)-O(1)	2.0625(18)	N(1)-Pd(1)-O(1)	81.42(8)
Pd(1)-P(2)	2.2334(7)	C(25)-Pd(1)-P(2)	92.02(8)
P(1)-N(1)	1.617(3)	N(1)-Pd(1)-P(2)	178.22(7)
P(1)-C(20)	1.780(3)	O(1)-Pd(1)-P(2)	98.46(6)
P(1)-C(8)	1.798(3)	N(1)-Pd(1)-P(1)	31.17(6)
P(1)-C(14)	1.804(3)	O(1)-Pd(1)-P(1)	107.35(5)
P(2)-C(26)	1.818(3)	P(2)-Pd(1)-P(1)	147.90(2)
P(2)-C(38)	1.821(3)	N(1)-P(1)-C(20)	102.68(12)
P(2)-C(32)	1.825(3)	O(1)-C(2)-C(7)	120.6(2)
C(25)-C(20)	1.412(4)	C(2)-C(7)-N(1)	124.9(3)
C(7)-N(1)	1.419(3)	C(25)-C(20)-P(1)	121.4(2)
C(2)-O(1)	1.327(3)	C(7)-N(1)-P(1)	124.41(18)
C(7)-C(2)	1.413(4)	C(7)-N(1)-Pd(1)	111.37(17)
		P(1)-N(1)-Pd(1)	107.77(11)
		C(2)-O(1)-Pd(1)	111.29(16)

Table SI4.- Selected bond distances (Å) and angles (°) for compound **4**.

Bond	Length/Å	Angle	(˚)
Pd(1)-C(25)	2.063(3)	C(25)-Pd(1)-N(1)	83.74(11)
Pd(1)-N(1)	2.102(2)	C(25)-Pd(1)-P(2)	92.89(8)
Pd(1)-P(2)	2.2348(8)	N(1)-Pd(1)-P(2)	173.02(7)
Pd(1)-P(3)	2.3548(8)	C(25)-Pd(1)-P(3)	176.62(8)
P(1)-N(1)	1.602(2)	N(1)-Pd(1)-P(3)	98.54(7)
P(1)-C(20)	1.789(3)	P(2)-Pd(1)-P(3)	84.58(3)
P(1)-C(14)	1.793(3)	C(7)-N(1)-P(1)	128.6(2)
P(1)-C(8)	1.818(3)	C(7)-N(1)-Pd(1)	123.68(19)
O(1)-C(2)	1.356(4)	P(1)-N(1)-Pd(1)	107.66(13)
N(1)-C(7)	1.419(4)	C(25)-C(20)-P(1)	114.3(2)
P(2)-C(26)	1.812(3)	C(50)-P(2)-Pd(1)	108.64(10)
P(2)-C(32)	1.817(3)	C(51)-P(3)-Pd(1)	106.30(11)
P(2)-C(50)	1.830(3)	C(51)-C(50)-P(2)	108.5(2)
P(3)-C(44)	1.811(3)	C(50)-C(51)-P(3)	108.8(2)
P(3)-C(38)	1.821(3)	C(51)-P(3)-Pd(1)	106.30(11)
P(3)-C(51)	1.840(3)	N(1)-P(1)-C(20)	101.37(13)
C(20)-C(25)	1.398(4)		
C(50)-C(51)	1.508(4)		

Table SI5.- Selected bond distances (Å) and angles (°) for compound **7**.

Bond	Length/Å	Angle	(˚)
N(1)-Pd(1)	2.032(3)	C(25)- Pd(1)-N(1)	87.55(11)
O(1)- Pd(1)	2.066(2)	C(25)- Pd(1)-O(1)	168.60(11)
P(2)- Pd(1)	2.2384(8)	N(1)- Pd(1)-O(1)	81.63(9)
C(25)- Pd(1)	2.006(3)	C(25)- Pd(1)-P(2)	98.88(9)
N(1)-P(1)	1.602(3)	N(1)- Pd(1)-P(2)	173.38(7)
C(2)-O(1)	1.333(4)	O(1)- Pd(1)-P(2)	91.85(7)
C(8)-P(1)	1.809(3)	P(1)-N(1)-PD1	117.15(14)
C(14)-P(1)	1.808(3)	C(7)-N(1)-P(1)	129.9(2)
C(20)-P(1)	1.792(3)	C(7)-N(1)- Pd(1)	112.6(2)
C(26)-P(2)	1.821(3)	C(2)-O(1)- Pd(1)	111.33(18)
C(32)-P(2)	1.832(3)	C(25)-C(20)-P(1)	117.4(2)
C(38)-P(2)	1.832(3)	C(20)-C(25)- Pd(1)	115.2(2)
C(7)-N(1)	1.414(4)	N(1)-C(7)-C(2)	114.2(3)
C(2)-C(7)	1.424(4)	O(1)-C(2)-C(7)	120.2(3)
C(38)-C(39)	1.531(4)	C(38)-P(2)- Pd(1)	110.81(11)

Table SI6.- Selected bond distances (Å) and angles (°) for compound **8**.

Bond	**Length/Å**	**Angle**	**(˚)**
C(1)- Pd(1)	1.960(4)	C(1)- Pd(1)-O(1)	86.79(16)
O(1)- Pd(1)	2.053(3)	C(1)- Pd(1)- Cl(1)	94.58(14)
Pd(1)-Cl(1) (*trans* O)	2.3008(14)	O(1)- Pd(1)- Cl(1)	178.61(9)
Pd(1)- Cl(1) #1 (*trans* C)	2.4383(14)	C(1)-Pd(1)-Cl(1) #1	176.40(14)
O(1)-P(1)	1.519(3)	O(1)-Pd(1)-Cl(1) #1	92.26(9)
C(6)-P(1)	1.781(5)	Cl(1)-Pd(1)-Cl(1) #1	86.40(5)
C(1)-C(6)	1.404(6)	Pd(1)-Cl(1)-Pd(1)#1	93.60(5)
		Pd(2)-Cl(2)-Pd(2)#2	93.80(5)
		P(1)-O(1)- Pd(1)	114.45(17)
		O(1)-P(1)-C(6)	105.31(19)
		C(6)-C(1)- Pd(1)	116.9(3)
		C(1)-C(6)-P(1)	113.8(3)

DFT Calculations

DFT calculations were performed for compound **2**, using as the starting structure the one obtained by X-ray diffraction. To do that the g16[1] package of programs at the B3LYP/LANL2DZ-ECP[2]/6-31-G(d) level of theory was used. Frequency test resulted in all positive frequencies, confirming the stationary point. NBO version 3.1 analysis was also carried out to obtain more information about the electron density in the O(2)–H···O(1) moiety.

The optimization gave as a result a longer O(2)–H distance (from 0.95 Å in the calculated X-ray data, to 1.05 Å) and the NBO analysis showed the presence of a strong intramolecular hydrogen bond ([*E*(2)] *ca.* 100 Kcal/mol) between the H and O(1). This high value of [*E*(2)][3] suggests the presence of an equilibrium where the H could be placed either in both oxygen atoms. In addition, the calculated charges of both oxygens are of similar value, thus confirming the presence of this equilibrium. Finally, the electron density plot does not provide useful information due to that the the O–H···O moiety is encapsulated in an apolar pocket into the molecule, as shown in the picture.

References

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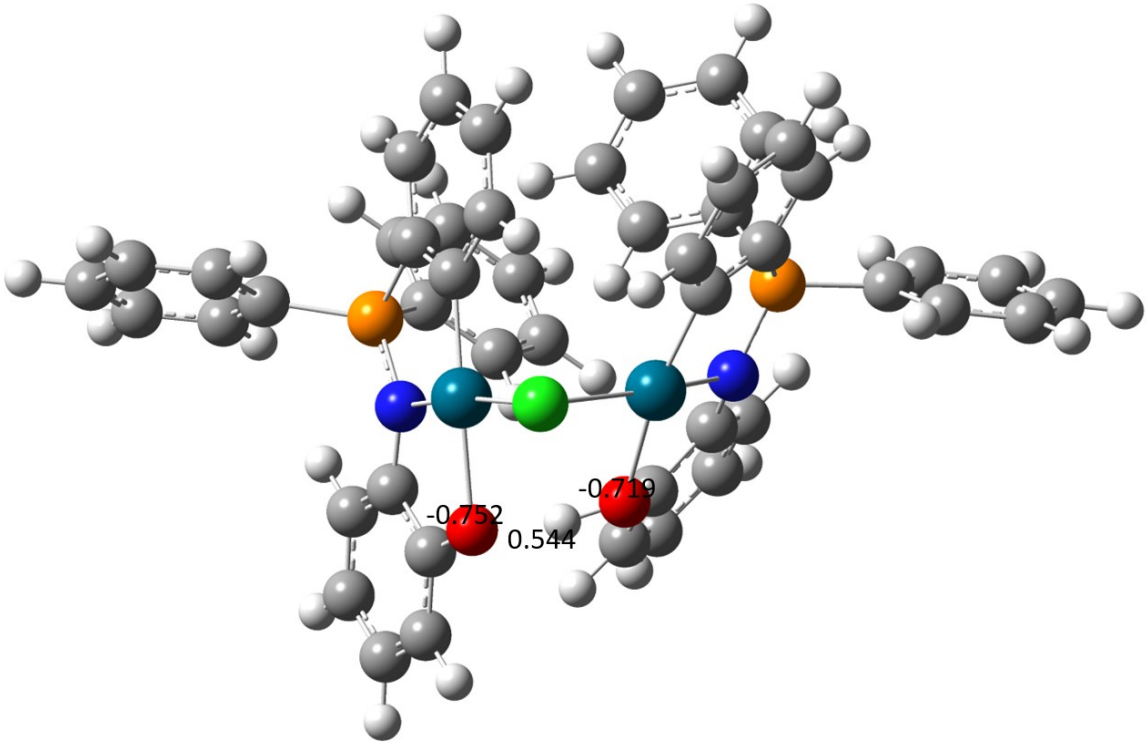
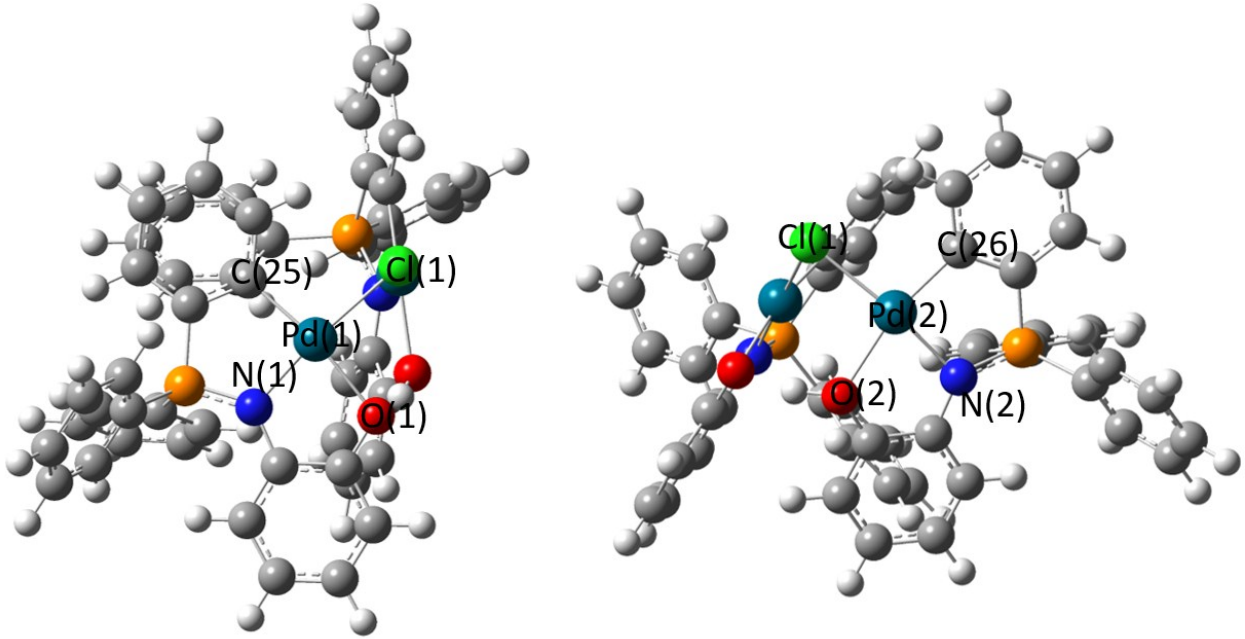


Figure SI 1.- DFT optimized structure showing the charges for the O(1)·····H-O(2) group.

Coordinates for the final optimized structure for compound 2

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 P                 -3.13773400    0.48435000    0.71545700
 P                  3.45012200    0.46017600    0.17638800
 Cl                 0.20313300   -3.76690900   -0.05930500
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 H                 -0.36290600   -1.71306200   -2.56027000
 O                 -1.72154200   -2.21027900   -2.31541600
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 N                  2.53506200   -0.11028300   -1.04938500
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H	0.67108700	4.13133800	3.52597400
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H	4.39090500	2.51388900	2.11357900
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C	0.24048700	2.00879800	-3.90076200
H	-0.38515100	2.53320000	-4.61690900
C	0.00762200	0.65383400	-3.64418300
H	-0.79453300	0.12249600	-4.14634600
C	0.79832000	-0.03107800	-2.72368100