catalysts

Supplementary Materials: Synthesis, Structure, and Catalytic Reactivity of Pd(II) Complexes of Proline and Proline Homologs

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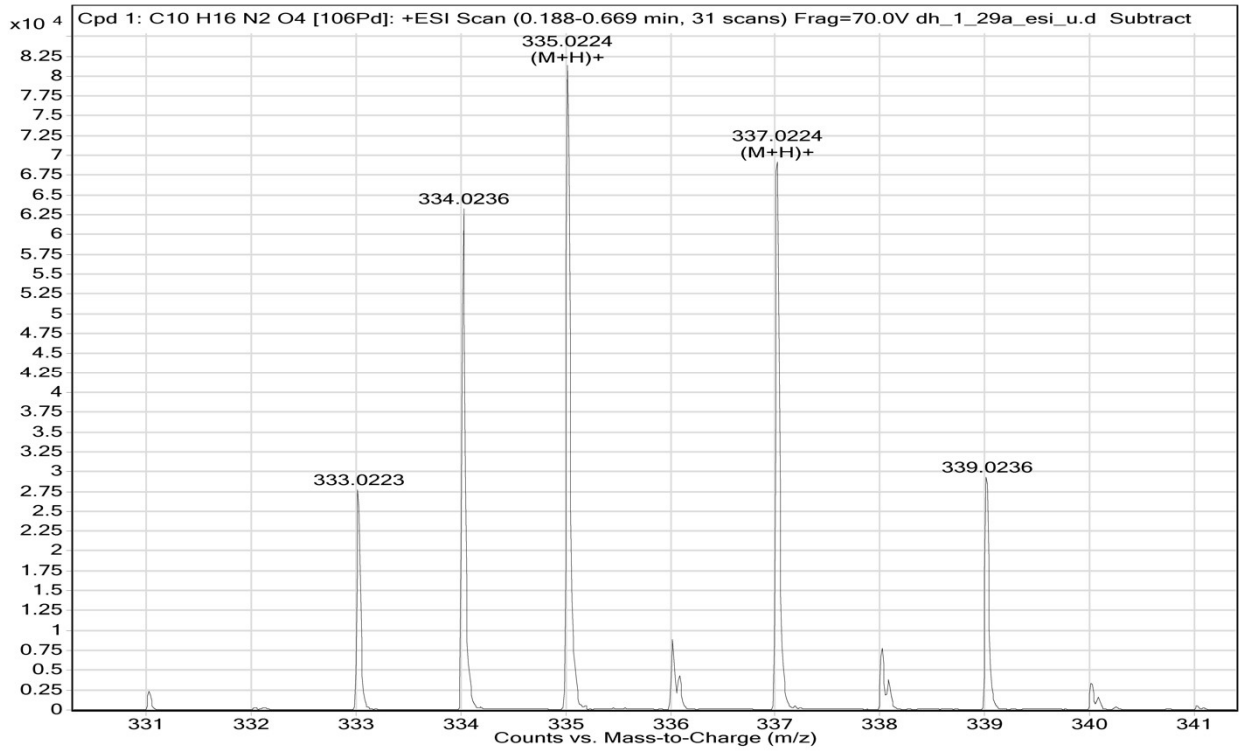

Figure S1. High-resolution time-of-flight mass spectrum of (1) as an example of the typical isotopic splitting pattern seen for palladium complexes with one Pd atom.

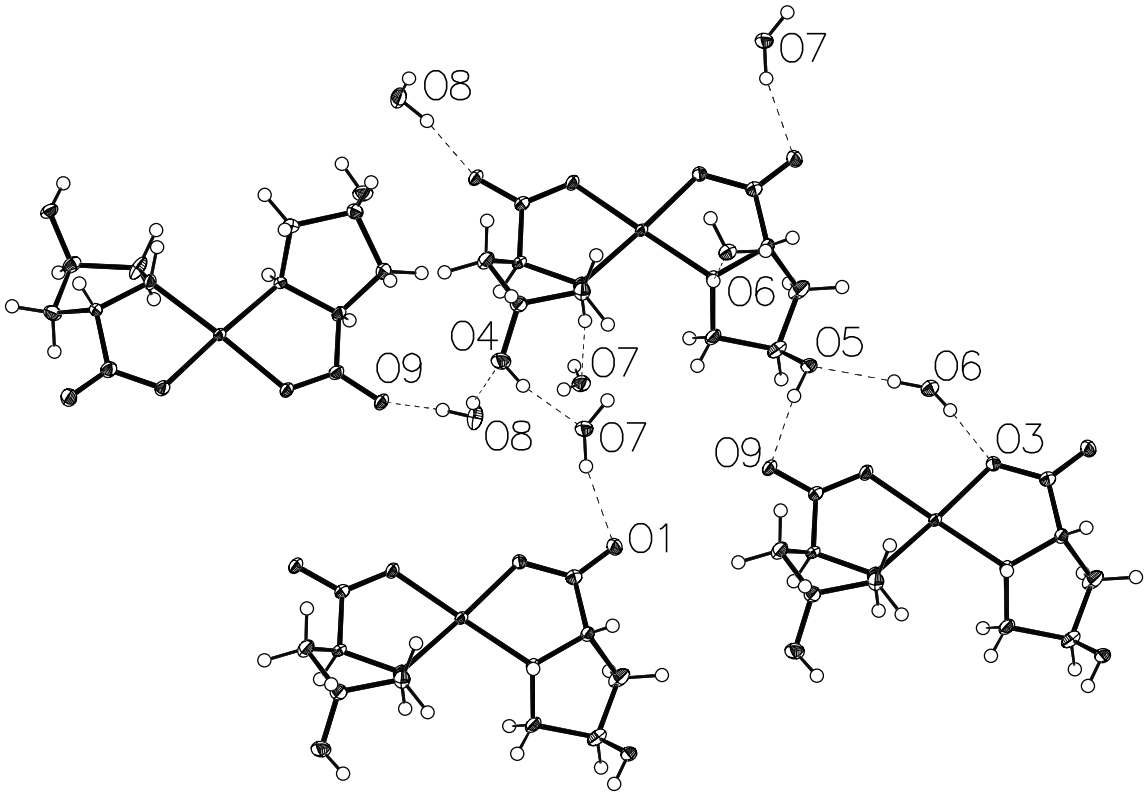

Figure S2. Extended hydrogen-bonding network of *cis*-bis-(trans-4-hydroxyprolinato)palladium(II) (**3**).

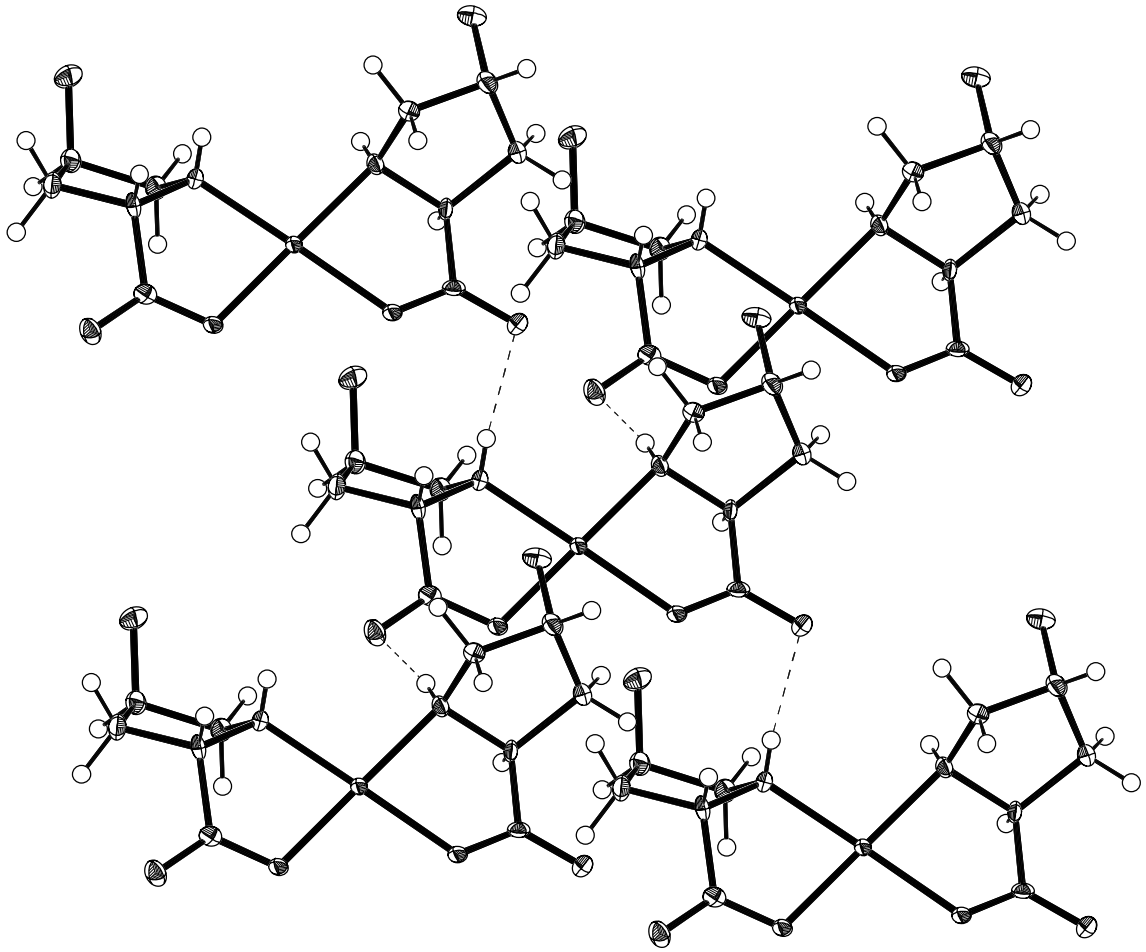

Figure S3. Crystal packing diagram of *cis*-bis-(*trans*-4-fluoroprolinato)palladium(II) (4) showing hydrogen bonding network.

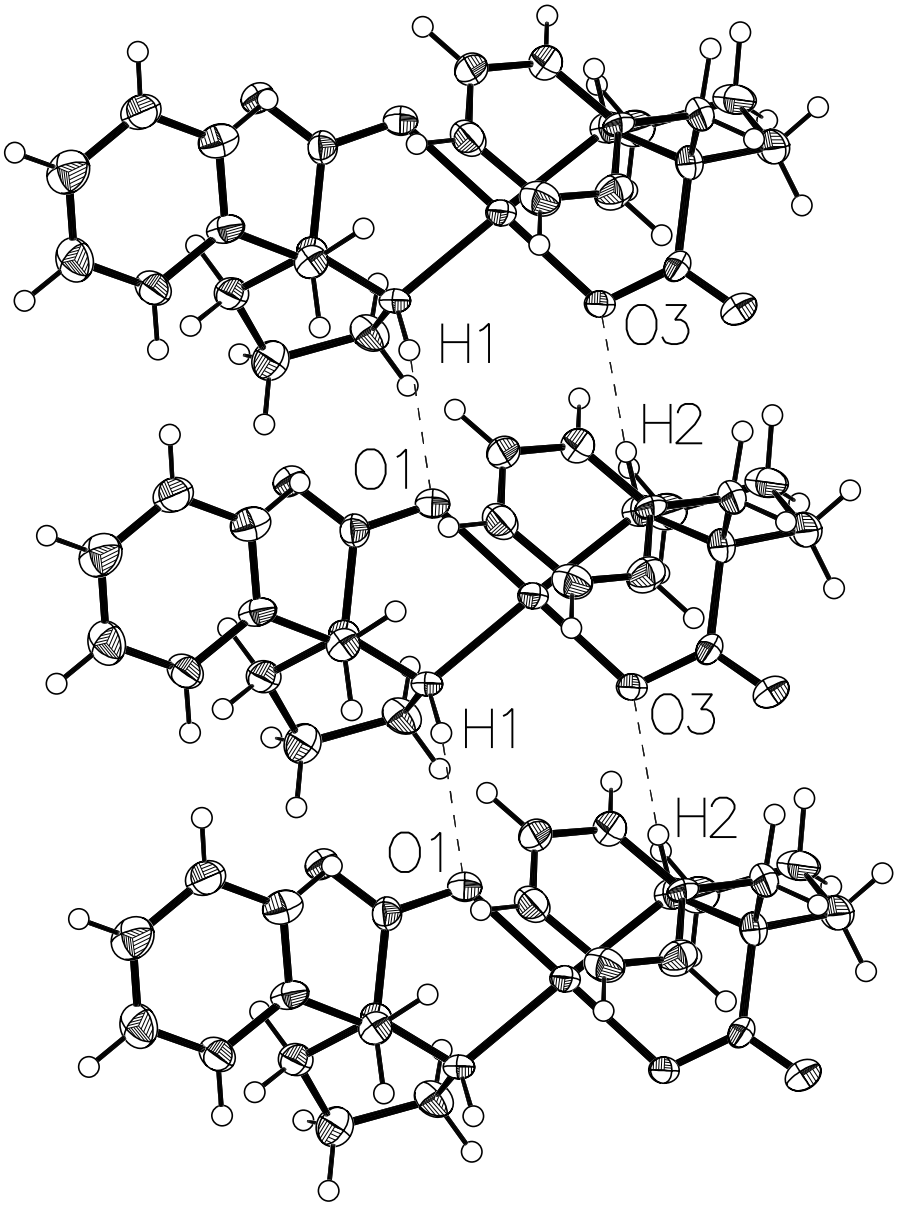

Figure S4. Crystal packing diagram of *trans*-bis-(2-benzylprolinato)palladium(II), (5) showing the hydrogen bonding network.

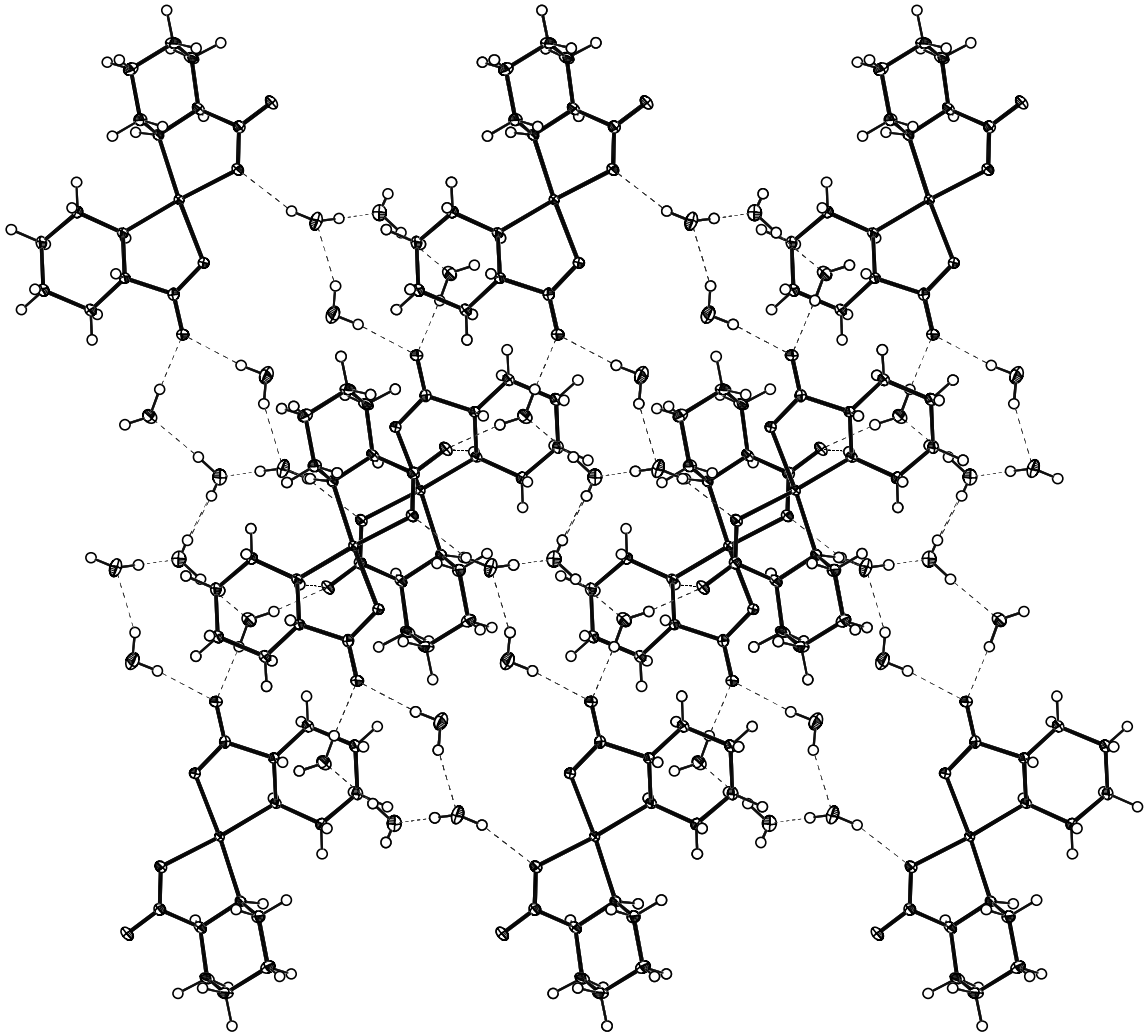

Figure S5. Packing diagram of *cis*-bis-(L-pipecolinato)palladium(II) ($\underline{7}$) as viewed along [010] showing the hydrogen bonding network.

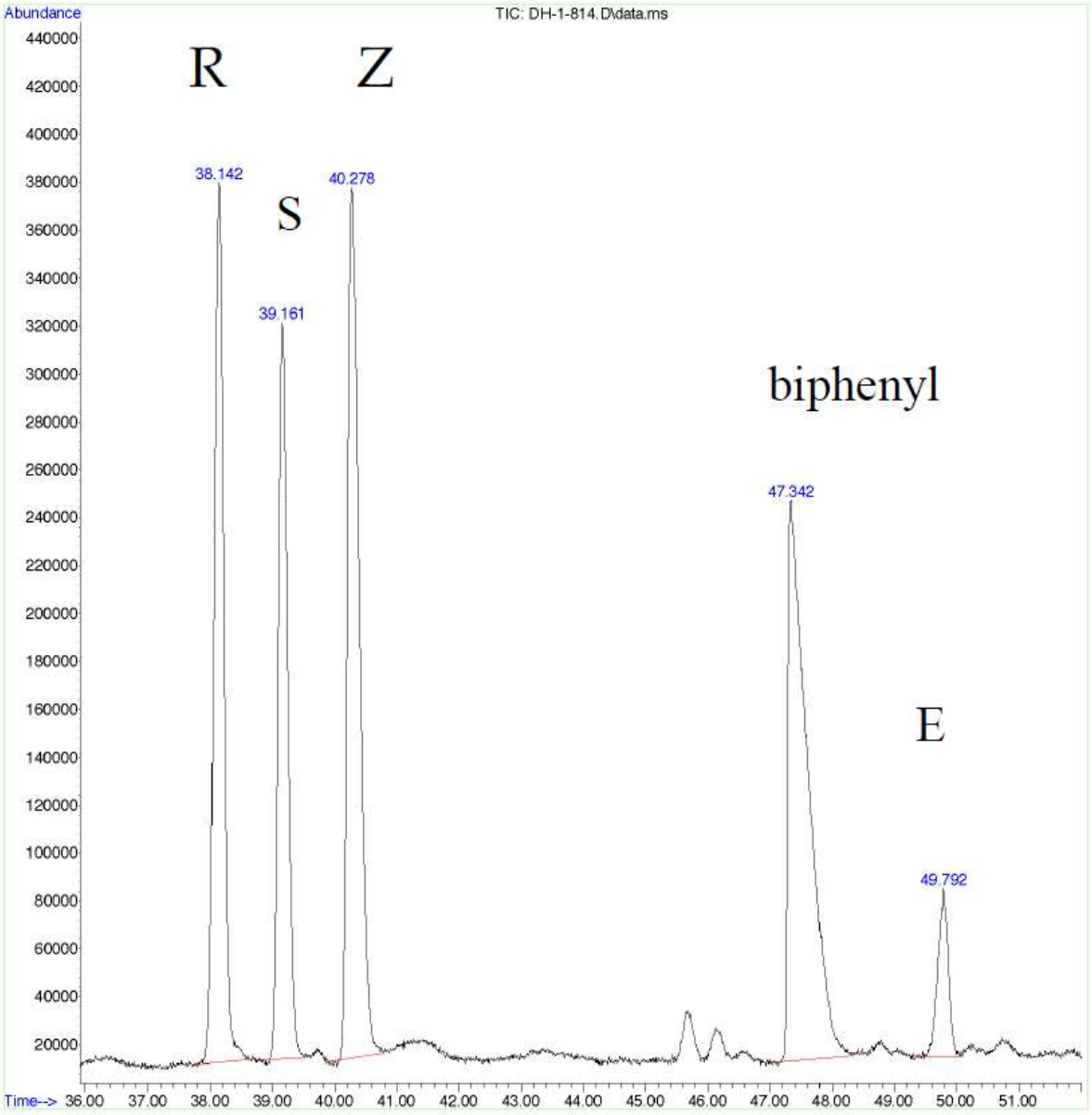

Figure 6. Typical GC-MS trace of the oxidative coupling of phenylboronic acid with methyl tiglate. Peaks R, S, Z, E have masses of 190.2 amu.

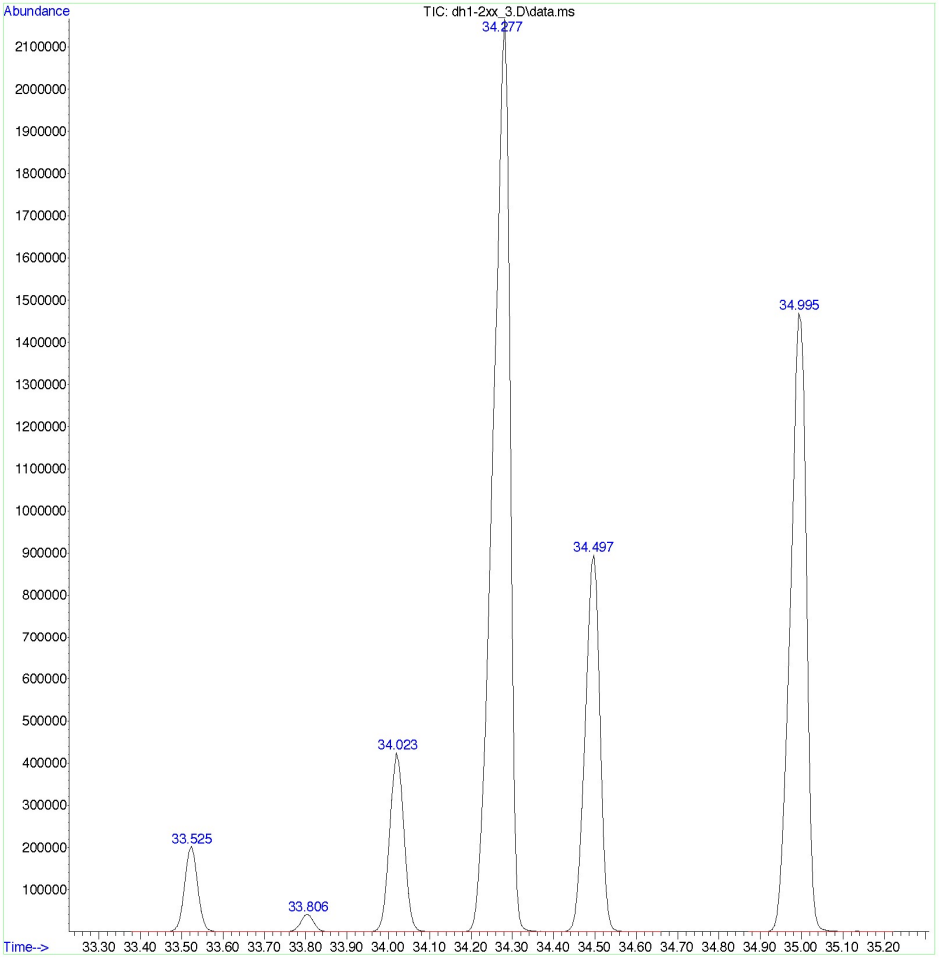

Figure S7. Typical GC-MS trace of the second oxidative coupling products of phenylboronic acid with methyl tiglate. Peaks shown have masses of 266.3 amu.

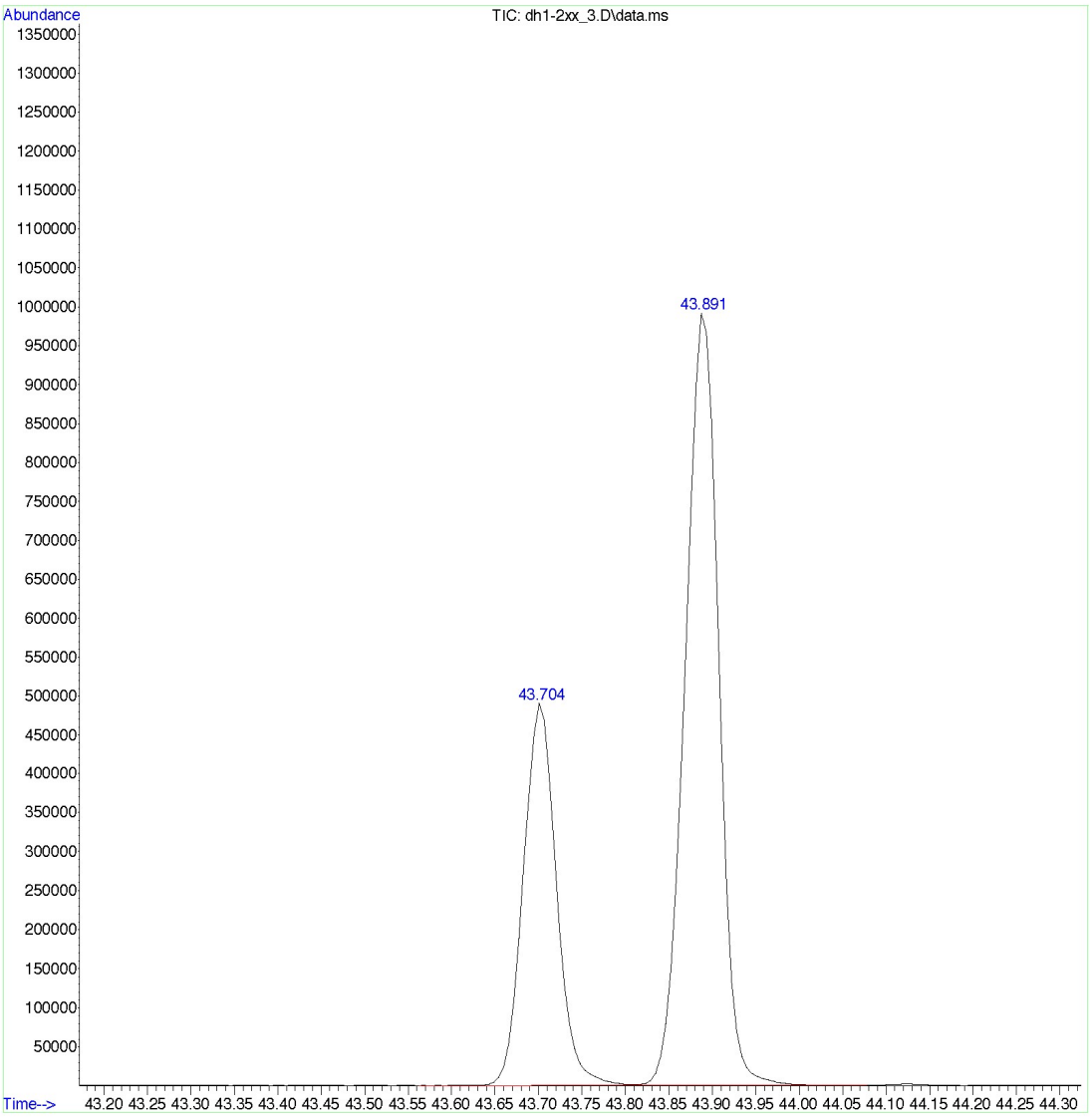

Figure 8. Typical GC-MS trace of the third oxidative coupling products of phenylboronic acid with methyl tiglate. Peaks shown have masses of 342.4 amu.

Report I. Experimental Details and Bond Lengths and Angles for Complex 1.

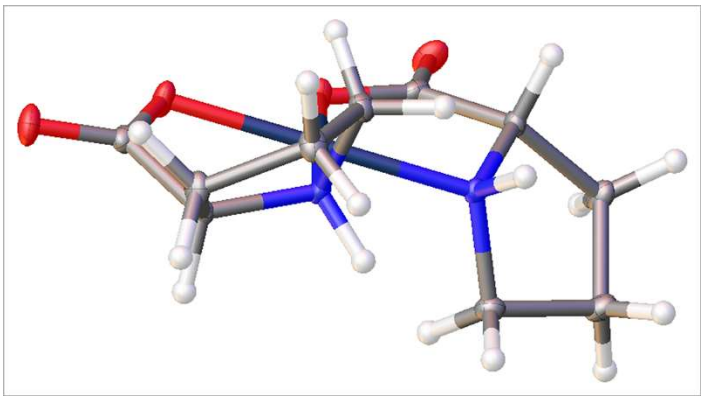

Table 1. data and structure refinement for Complex 1.

Identification code	dh1-29a_ABS
Empirical formula	$C_{10}H_{16}N_2O_4Pd$
Formula weight	334.65
Temperature/K	100.15
Crystal system	orthorhombic
Space group	$C222_1$
a/Å	9.66974(11)
b/Å	10.31486(12)
c/Å	11.94805(14)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1191.72(2)
Z	4
ϱ_{calc}g/cm^3	1.865
μ/mm^{-1}	1.562
F(000)	672.0
Crystal size/mm^3	0.4713 × 0.2226 × 0.1011
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.708 to 64.746
Index ranges	$-14 \le h \le 14$, $-15 \le k \le 15$, $-17 \le l \le 17$
Reflections collected	16692
Independent reflections	2100 [R_{int} = 0.0322, R_{sigma} = 0.0196]
Data/restraints/parameters	2100/0/78
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0167, wR_2 = 0.0361
Final R indexes [all data]	R_1 = 0.0182, wR_2 = 0.0365
Largest diff. peak/hole / e Å^{-3}	0.54/-0.33
Flack parameter	-0.004(14)

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for dh1-29a_ABS, Complex 1. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pd1	5000	4385.9(2)	2500	9.26(5)
O1	3567.7(16)	5692.2(15)	2990.1(14)	14.7(3)
O2	1331.1(17)	5877.0(15)	3381.6(14)	17.2(3)
N1	3556.5(17)	3112.3(17)	3008.2(14)	9.6(3)
C1	2346(2)	5211(2)	3144.5(18)	12.3(4)
C2	2167(2)	3752.6(19)	2960.9(18)	10.0(3)
C3	1263(2)	3086(2)	3854.6(17)	13.5(4)
C4	2235(2)	2138(2)	4460.3(19)	14.6(4)
C5	3683(2)	2646(2)	4190.9(17)	13.3(4)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for dh1-29a_ABS, Complex 1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd1	7.72(8)	6.55(7)	13.50(8)	0	1.26(12)	0
O1	12.2(6)	8.8(6)	23.2(7)	-1.0(6)	3.8(6)	1.7(6)
O2	15.3(7)	13.1(7)	23.2(8)	3.5(6)	5.8(7)	5.9(6)
N1	9.1(7)	8.2(7)	11.3(7)	-0.9(6)	1.1(6)	0.5(6)
C1	15.4(9)	10.5(8)	10.9(9)	1.6(7)	0.0(7)	1.6(7)
C2	7.2(8)	10.1(9)	12.7(8)	0.2(7)	0.6(7)	0.1(7)
C3	10.3(8)	13.5(9)	16.9(9)	2.9(8)	4.2(7)	0.9(8)
C4	14.0(9)	15.8(10)	14.1(9)	4.7(8)	3.5(8)	1.4(8)
C5	12.5(9)	14.9(9)	12.6(9)	2.1(7)	-0.1(8)	2.3(8)

Table 4 Bond Lengths for dh1-29a_ABS, Complex 1

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	O1 [1]	2.0191(15)	N1	C2	1.498(3)
Pd1	O1	2.0191(15)	N1	C5	1.498(3)
Pd1	N1 [1]	2.0107(17)	C1	C2	1.530(3)
Pd1	N1	2.0107(17)	C2	C3	1.542(3)
O1	C1	1.295(3)	C3	C4	1.537(3)
O2	C1	1.231(3)	C4	C5	1.530(3)

[1] 1-X,+Y,1/2-Z.

Table 5 Bond Angles for dh1-29a_ABS, Complex 1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1[1]	Pd1	O1	96.28(9)	O1	C1	C2	117.37(18)
N1[1]	Pd1	O1	178.84(7)	O2	C1	O1	123.1(2)
N1[1]	Pd1	O1 [1]	82.66(6)	O2	C1	C2	119.5(2)
N1	Pd1	O1 [1]	178.84(7)	N1	C2	C1	109.08(17)
N1	Pd1	O1	82.66(6)	N1	C2	C3	106.60(16)
N1[1]	Pd1	N1	98.41(10)	C1	C2	C3	113.77(18)
C1	O1	Pd1	114.28(13)	C4	C3	C2	105.27(16)
C2	N1	Pd1	108.85(12)	C5	C4	C3	104.06(17)
C5	N1	Pd1	115.98(13)	N1	C5	C4	103.51(17)
C5	N1	C2	104.52(15)				

[1] 1-X,+Y,1/2-Z

Table 6 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for dh1-29a_ABS, Complex 1.

Atom	*x*	*y*	*z*	U(eq)
H1	3560	2348	2493	11
H2	1751	3602	2206	12
H3A	884	3732	4385	16
H3B	486	2615	3500	16
H4A	2064	2146	5277	18
H4B	2111	1244	4176	18
H5A	3943	3363	4699	16
H5B	4381	1947	4252	16

Experimental

Single crystals of Complex 1, $C_{10}H_{16}N_2O_4Pd$ [dh1-29a_ABS] were [crystallized from acetone/water]. A suitable crystal was selected and [mounted on a fiber loop.] on a Oxford Diffraction Gemini Ultra diffractometer. The crystal was kept at 100.15 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS-1997 [2] structure solution program using Direct Methods and refined with the ShelXL-1997 [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal Data for $C_{10}H_{16}N_2O_4Pd$ (M =334.65 g/mol): orthorhombic, space group $C222_1$ (no. 20), a = 9.66974(11) Å, b = 10.31486(12) Å, c = 11.94805(14) Å, V = 1191.72(2) Å^3, Z = 4, T = 100.15 K, μ(MoKα) = 1.562 mm^{-1}, $Dcalc$ = 1.865 g/cm^3, 16692 reflections measured (6.708° ≤ 2Θ ≤ 64.746°), 2100 unique (R_{int} = 0.0322, R_{sigma} = 0.0196) which were used in all calculations. The final $R_1$was 0.0167 (I > 2σ(I)) and wR_2 was 0.0365 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

   At 1.2 times of:

   All C(H) groups, All C(H,H) groups, All N(H) groups

   2.a Ternary CH refined with riding coordinates:

   N1(H1), C2(H2)

   2.b Secondary CH2 refined with riding coordinates:

   C3(H3A,H3B), C4(H4A,H4B), C5(H5A,H5B)

Report II. Experimental Details and Bond Lengths and Angles for Complex 2.

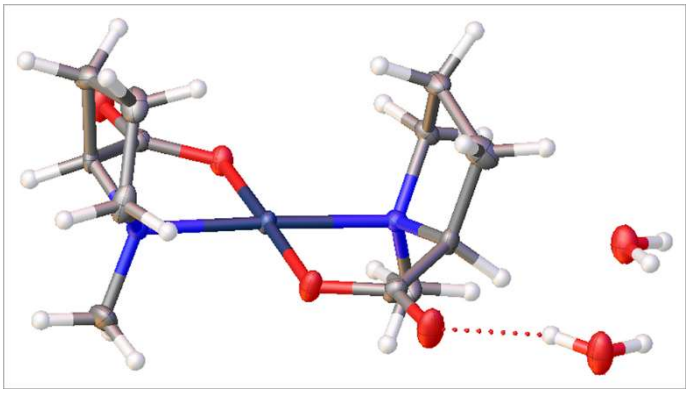

Table 1 Crystal data and structure refinement for Complex 2.

Identification code	dh1-43a_ABS
Empirical formula	$C_{12}H_{24}N_2O_6Pd$
Formula weight	398.73

Temperature/K	100.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.69102(15)
b/Å	9.8633(3)
c/Å	18.4039(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1577.61(6)
Z	4
ρ_{calc}g/cm^3	1.679
μ/mm^{-1}	1.204
F(000)	816.0
Crystal size/mm^3	0.3314 × 0.2354 × 0.1667
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.66 to 55.398
Index ranges	-10 ≤ h ≤ 11, -12 ≤ k ≤ 12, -22 ≤ l ≤ 24
Reflections collected	8854
Independent reflections	3219 [R_{int} = 0.0293, R_{sigma} = 0.0361]
Data/restraints/parameters	3219/0/198
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0228, wR_2 = 0.0448
Final R indexes [all data]	R_1 = 0.0258, wR_2 = 0.0462
Largest diff. peak/hole / e Å^{-3}	0.33/-0.31
Flack parameter	-0.016(19)

Table 2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for dh1-43a_ABS, Complex 2. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Pd1	102.3(3)	5549.1(3)	6272.4(2)	12.49(8)
O1	1046(2)	5564(3)	7263.7(12)	17.1(6)
O2	475(3)	5611(3)	8439.1(12)	23.6(6)
O3	-854(3)	5574(3)	5290.1(12)	20.5(6)
O4	-390(3)	5254(3)	4120.7(12)	30.0(7)
O5	801(3)	4556(4)	2764.1(13)	31.1(7)

O6	5907(3)	5312(3)	4724.7(14)	26.9(7)
N1	-1906(3)	5895(3)	6827.0(15)	13.8(7)
N2	2120(3)	5277(3)	5708.2(15)	13.4(7)
C1	66(4)	5581(3)	7800.2(15)	14.8(7)
C2	-1632(4)	5462(4)	7600.7(17)	13.3(7)
C3	-2202(4)	3981(4)	7647(2)	19.8(9)
C4	-2766(5)	3635(4)	6880(2)	24.4(10)
C5	-3174(4)	5001(4)	6564.5(19)	22.5(10)
C6	-2330(5)	7348(4)	6769(2)	27.0(10)
C7	48(5)	5267(3)	4755.9(16)	17.2(8)
C8	1681(4)	4834(4)	4946.1(18)	16.0(8)
C9	1866(5)	3278(4)	4939(2)	26.6(10)
C10	2249(4)	2889(4)	5725(2)	19.9(9)
C11	3077(4)	4146(4)	6000.2(19)	16.3(8)
C12	2965(4)	6585(4)	5715(2)	23.7(9)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for dh1-43a_ABS, Complex 2. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd1	9.95(12)	16.22(15)	11.30(11)	0.84(10)	1.02(12)	0.45(13)
O1	11.9(12)	24.6(16)	14.9(12)	-2.2(13)	-0.6(10)	-0.2(13)
O2	18.1(13)	38.5(18)	14.0(11)	-2.3(12)	-2.1(9)	0.8(14)
O3	12.7(12)	35.3(18)	13.6(11)	4.0(13)	0.1(10)	4.8(14)
O4	21.9(14)	53(2)	15.1(12)	1.5(12)	-1.4(11)	9.2(14)
O5	16.9(13)	57(2)	19.9(13)	-2.5(15)	-1.1(11)	7.7(16)
O6	17.0(14)	39(2)	24.8(13)	-5.2(14)	-0.4(11)	2.2(15)
N1	11.9(15)	16(2)	13.7(13)	2.0(12)	0.6(12)	2.5(13)
N2	13.3(15)	12.5(19)	14.4(13)	-0.4(12)	0.1(12)	0.3(13)
C1	15.4(17)	13.6(18)	15.3(13)	-0.5(13)	-0.1(15)	-1(3)
C2	11.6(16)	19(2)	9.8(15)	-3.8(16)	2.7(13)	0.2(18)
C3	15.6(19)	18(2)	25.3(19)	4.9(16)	1.1(16)	0.6(16)
C4	20(2)	24(3)	29(2)	-7.8(18)	4.2(18)	-8.7(18)
C5	11.8(18)	42(3)	14.1(17)	-4.1(16)	-1.9(15)	-5.8(17)
C6	22(2)	25(3)	34(2)	7.3(19)	5.6(18)	12(2)
C7	13.6(17)	22(2)	16.1(15)	5.1(13)	-0.5(16)	1(2)
C8	14.2(18)	23(2)	11.0(16)	0.6(15)	2.1(14)	2.3(17)

C9	28(2)	24(3)	27(2)	-9.8(19)	-9.9(18)	3(2)
C10	18(2)	14(2)	28(2)	2.1(16)	4.3(17)	-1.4(17)
C11	15.5(18)	15(2)	18.1(17)	-2.1(15)	-2.0(14)	4.0(16)
C12	20(2)	16(2)	35(2)	-3.1(19)	8.8(18)	-3.1(19)

Table 4 Bond Lengths for dh1-43a_ABS, Complex 2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	O1	2.000(2)	N2	C8	1.518(4)
Pd1	O3	1.990(2)	N2	C11	1.491(4)
Pd1	N1	2.051(3)	N2	C12	1.485(5)
Pd1	N2	2.055(3)	C1	C2	1.525(5)
O1	C1	1.304(4)	C2	C3	1.544(5)
O2	C1	1.229(4)	C3	C4	1.533(5)
O3	C7	1.293(4)	C4	C5	1.509(6)
O4	C7	1.230(4)	C7	C8	1.523(5)
N1	C2	1.506(4)	C8	C9	1.542(6)
N1	C5	1.491(5)	C9	C10	1.533(5)
N1	C6	1.484(5)	C10	C11	1.521(5)

Table 5 Bond Angles for dh1-43a_ABS, Complex 2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Pd1	N1	83.90(10)	C12	N2	C11	111.8(3)
O1	Pd1	N2	96.44(10)	O1	C1	C2	116.6(3)
O3	Pd1	O1	178.76(13)	O2	C1	O1	122.4(3)
O3	Pd1	N1	95.42(10)	O2	C1	C2	120.8(3)
O3	Pd1	N2	84.20(10)	N1	C2	C1	111.0(3)
N1	Pd1	N2	177.91(12)	N1	C2	C3	105.6(3)
C1	O1	Pd1	115.0(2)	C1	C2	C3	111.7(3)
C7	O3	Pd1	115.7(2)	C4	C3	C2	105.2(3)
C2	N1	Pd1	106.8(2)	C5	C4	C3	103.3(3)
C5	N1	Pd1	111.7(2)	N1	C5	C4	103.3(3)
C5	N1	C2	104.8(3)	O3	C7	C8	117.1(3)
C6	N1	Pd1	109.6(2)	O4	C7	O3	122.5(4)
C6	N1	C2	112.4(3)	O4	C7	C8	120.3(3)

C6	N1	C5	111.4(3)	N2	C8	C7	111.4(3)
C8	N2	Pd1	106.9(2)	N2	C8	C9	105.6(3)
C11	N2	Pd1	113.0(2)	C7	C8	C9	112.0(3)
C11	N2	C8	104.9(3)	C10	C9	C8	105.3(3)
C12	N2	Pd1	107.7(2)	C11	C10	C9	102.3(3)
C12	N2	C8	112.5(3)	N2	C11	C10	103.0(3)

Table 6 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for dh1-43a_ABS, Complex 2.

Atom	*x*	*y*	*z*	U(eq)
H5C	1796.48	4498.08	2726.81	47
H5D	548.24	4642.05	3219.14	47
H6D	6902.19	5401.88	4712.21	40
H6E	5563.81	5167.78	4287.2	40
H2	-2256.62	6041.83	7934.69	16
H3A	-1354.78	3368.68	7793.48	24
H3B	-3049.91	3898.09	8003.11	24
H4A	-1946.31	3190.08	6592.67	29
H4B	-3677.09	3033.47	6896.99	29
H5A	-3200.21	4968.12	6027.05	27
H5B	-4184.69	5317.53	6745.78	27
H6A	-1495.8	7906.88	6966.38	40
H6B	-3275.01	7515.65	7045.24	40
H6C	-2497.57	7582.38	6257.8	40
H8	2414.64	5243.16	4589.57	19
H9A	901.55	2835.42	4779.28	32
H9B	2707.47	3004.9	4607.27	32
H10A	1303.73	2707.95	6009.06	24
H10B	2924.73	2081.5	5743.78	24
H11A	3107.07	4165.2	6537.88	20
H11B	4141.53	4190.93	5810.39	20
H12A	2300.69	7302.91	5522.31	36
H12B	3889.64	6508.39	5413.78	36
H12C	3261.09	6807.96	6215.19	36

Experimental

Single crystals of Complex 2, $C_{12}H_{24}N_2O_6Pd$ [dh1-43a_ABS] were [crystallized from water/acetone]. A suitable crystal was selected and[mounted on a fiber loop] on a Oxford Diffraction Gemini Ultra diffractometer. The crystal was kept at 100.15 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS-1997 [2] structure solution program using Direct Methods and refined with the ShelXL-1997 [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal structure determination of Complex 2, [dh1-43a_ABS]

Crystal Data for $C_{12}H_{24}N_2O_6Pd$ (M =398.73 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 8.69102(15) Å, b = 9.8633(3) Å, c = 18.4039(3) Å, V = 1577.61(6) Å^3, Z = 4, T = 100.15 K, μ(MoKα) = 1.204 mm^{-1}, *Dcalc* = 1.679 g/cm^3, 8854 reflections measured (7.66° ≤ 2Θ ≤ 55.398°), 3219 unique (R_{int} = 0.0293, R_{sigma} = 0.0361) which were used in all calculations. The final R_1 was 0.0228 (I > 2σ(I)) and wR_2 was 0.0462 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups, All C(H,H) groups

At 1.5 times of:

All C(H,H,H) groups, All O(H,H) groups

2.a Free rotating group:

O5(H5C,H5D), O6(H6D,H6E)

2.b Ternary CH refined with riding coordinates:

C2(H2), C8(H8)

2.c Secondary CH2 refined with riding coordinates:

C3(H3A,H3B), C4(H4A,H4B), C5(H5A,H5B), C9(H9A,H9B), C10(H10A,H10B), C11(H11A, H11B)

2.d Idealised Me refined as rotating group:

C6(H6A,H6B,H6C), C12(H12A,H12B,H12C)

Report III. Experimental Details and Bond Lengths and Angles for Complex 3.

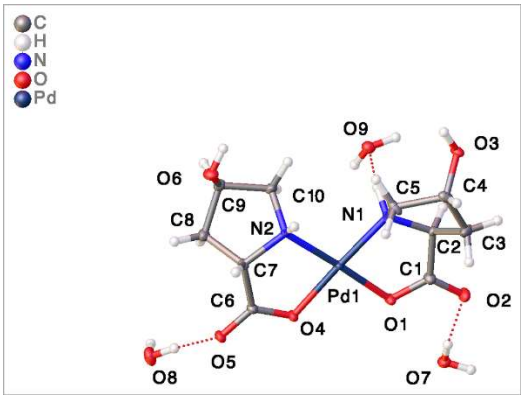

Table 1 Crystal data and structure refinement for dh1-105, Complex 3.

Identification code	dh1-105
Empirical formula	$C_{10}H_{22}N_2O_9Pd$
Formula weight	420.69
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.7784(2)
b/Å	7.58624(13)
c/Å	11.0500(2)
α/°	90
β/°	114.330(3)
γ/°	90
Volume/Å^3	746.90(3)
Z	2
ρ_{calc}g/cm^3	1.871
μ/mm^{-1}	1.291
F(000)	428.0
Crystal size/mm^3	0.334 × 0.2068 × 0.1657
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.054 to 60.124
Index ranges	-13 ≤ h ≤ 13, -10 ≤ k ≤ 10, -15 ≤ l ≤ 15
Reflections collected	15035
Independent reflections	4385 [R_{int} = 0.0427, R_{sigma} = 0.0393]
Data/restraints/parameters	4385/3/216
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0240, wR_2 = 0.0582
Final R indexes [all data]	R_1 = 0.0250, wR_2 = 0.0590

Largest diff. peak/hole / e Å^{-3}	0.85/-0.76
Flack parameter	-0.031(19)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for dh1-105, Complex 3. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pd1	-4547.8(2)	-2822.9(5)	-3765.8(2)	10.06(7)
O1	-5302(2)	-2903(8)	-5744.1(19)	15.5(5)
O2	-7371(3)	-3101(5)	-7606(2)	20.4(7)
O3	-9897(2)	-2421(3)	-4427(2)	15.3(6)
O4	-2402(2)	-2563(5)	-3484(2)	15.0(8)
O5	-78(2)	-2333(3)	-1964(2)	15.2(5)
O6	-2712(3)	-3160(4)	1116(2)	19.1(7)
N1	-6731(3)	-3001(7)	-4110(2)	11.7(7)
N2	-3697(2)	-2748(9)	-1766(2)	10.1(5)
C1	-6745(3)	-3021(7)	-6387(3)	15.6(8)
C2	-7690(3)	-3116(5)	-5587(3)	11.4(8)
C3	-8784(4)	-1559(6)	-5881(4)	22.5(8)
C4	-8884(4)	-1192(5)	-4568(4)	16.0(6)
C5	-7278(4)	-1502(5)	-3573(4)	19.4(7)
C6	-1445(3)	-2449(4)	-2277(3)	12.7(7)
C7	-2020(3)	-2444(4)	-1191(3)	12.0(7)
C8	-1325(4)	-3905(5)	-151(3)	17.4(7)
C9	-2603(4)	-4440(5)	224(3)	14.9(6)
C10	-3940(4)	-4384(5)	-1120(3)	15.3(7)
O7	-5465(3)	-4214(4)	-8786(3)	16.8(5)
O8	2435(3)	-4438(4)	-1319(3)	21.9(6)
O9	-7094(3)	-6644(4)	-3602(2)	15.6(5)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for dh1-105, Complex 3. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd1	7.31(10)	14.45(11)	9.28(10)	0.16(13)	4.28(7)	0.22(13)
O1	10.7(8)	26.6(14)	10.4(8)	-2(2)	5.5(7)	-2.1(19)
O2	14.6(10)	36(2)	10.7(9)	-2.1(12)	5.0(8)	-1.1(12)

O3	12.5(10)	21.6(16)	14.9(10)	-3.7(9)	8.6(8)	-4.2(9)
O4	8.2(9)	26(2)	11.6(9)	0.4(11)	4.7(7)	-0.1(11)
O5	8.4(10)	22.9(14)	14.9(10)	-0.2(9)	5.3(8)	0.2(8)
O6	20.2(11)	25(2)	16.5(10)	-1.8(10)	11.7(9)	-3.0(11)
N1	7.2(9)	17(2)	9.9(9)	-1.4(14)	3.0(8)	2.0(13)
N2	7.9(9)	12.7(13)	10.5(9)	2.9(19)	4.6(7)	0.2(19)
C1	12.9(12)	22(2)	13.9(12)	-1.6(16)	7.2(10)	-0.7(16)
C2	9.3(11)	16(2)	9.3(11)	2.7(12)	3.9(9)	0.9(12)
C3	18.5(17)	33(2)	20.2(17)	13.9(16)	12.1(14)	10.8(16)
C4	13.2(15)	12.8(15)	25.1(17)	1.7(13)	11.1(14)	1.9(12)
C5	10.0(15)	21.1(19)	27.8(18)	-10.7(15)	8.6(14)	-2.9(13)
C6	10.5(13)	16(2)	13.4(13)	-0.7(11)	6.6(11)	-0.6(11)
C7	8.3(12)	17(2)	12.5(12)	-1.0(11)	5.8(10)	1.2(11)
C8	11.8(15)	25.3(18)	16.1(15)	4.9(14)	6.8(13)	4.1(13)
C9	15.0(15)	17.7(16)	12.8(14)	2.3(13)	6.5(12)	1.9(13)
C10	13.9(15)	19.2(17)	12.6(14)	3.6(13)	5.3(12)	-1.6(13)
O7	15.5(12)	21.9(14)	14.8(12)	0.1(10)	8.1(10)	-0.7(10)
O8	12.9(12)	23.5(14)	24.2(13)	-3.1(11)	2.5(11)	2.9(11)
O9	14.7(12)	16.1(12)	17.7(11)	-0.1(10)	8.5(10)	0.4(10)

Table 4 Bond Lengths for dh1-105, Complex 3.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Pd1	O1	1.9995(19)	N1	C5	1.482(6)
Pd1	O4	2.001(2)	N2	C7	1.513(4)
Pd1	N1	2.013(2)	N2	C10	1.499(6)
Pd1	N2	2.016(2)	C1	C2	1.521(4)
O1	C1	1.295(4)	C2	C3	1.535(5)
O2	C1	1.231(4)	C3	C4	1.519(5)
O3	C4	1.415(4)	C4	C5	1.518(5)
O4	C6	1.278(4)	C6	C7	1.520(4)
O5	C6	1.239(4)	C7	C8	1.539(5)
O6	C9	1.419(4)	C8	C9	1.525(5)
N1	C2	1.513(4)	C9	C10	1.522(4)

Table 5 Bond Angles for dh1-105, Complex 3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Pd1	O4	93.64(8)	N1	C2	C3	104.6(3)
O1	Pd1	N1	84.65(9)	C1	C2	C3	112.2(3)
O1	Pd1	N2	177.54(8)	C4	C3	C2	104.6(3)
O4	Pd1	N1	177.49(18)	O3	C4	C3	108.0(3)
O4	Pd1	N2	83.92(9)	O3	C4	C5	112.3(3)
N1	Pd1	N2	97.79(9)	C5	C4	C3	102.1(3)
C1	O1	Pd1	115.41(18)	N1	C5	C4	105.4(3)
C6	O4	Pd1	115.99(19)	O4	C6	C7	118.3(3)
C2	N1	Pd1	110.21(17)	O5	C6	O4	122.5(3)
C5	N1	Pd1	113.8(3)	O5	C6	C7	119.1(3)
C5	N1	C2	108.1(3)	N2	C7	C6	110.9(2)
C7	N2	Pd1	110.57(17)	N2	C7	C8	105.8(3)
C10	N2	Pd1	115.1(3)	C6	C7	C8	113.3(3)
C10	N2	C7	106.4(3)	C9	C8	C7	103.6(3)
O1	C1	C2	118.0(2)	O6	C9	C8	108.1(3)
O2	C1	O1	122.8(3)	O6	C9	C10	112.2(3)
O2	C1	C2	119.2(3)	C10	C9	C8	101.5(3)
N1	C2	C1	111.7(2)	N2	C10	C9	104.3(3)

Table 6 Hydrogen Bonds for dh1-105, Complex 3.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O3	H3	O5[1]	0.84	1.97	2.800(3)	172.3
O6	H6	O7[2]	0.84	2.03	2.853(3)	166.9
N1	H1	O9	1.00	1.94	2.871(6)	153.3
O7	H7A	O2	0.85(3)	1.98(4)	2.808(4)	166(6)
O7	H7B	O8[3]	0.82(4)	1.92(4)	2.710(4)	161(7)
O8	H8C	O5	0.87	1.91	2.766(4)	166.5
O8	H8D	O6[4]	0.87	2.02	2.836(4)	156.3
O9	H9A	O1[5]	0.87	2.02	2.884(4)	173.3

[1]-1+X,+Y,+Z; [2]+X,+Y,1+Z; [3]-1+X,+Y,-1+Z; [4]-X,-1/2+Y,-Z; [5]-1-X,-1/2+Y,-1-Z

Table 7 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for dh1-105, Complex 3.

Atom	*x*	*y*	*z*	U(eq)
H3	-9902.72	-2307.92	-3672.68	23
H6	-3497.37	-3334.36	1232.18	29
H1	-6876.31	-4108.44	-3685.69	14
H2	-4169.47	-1736.9	-1500.01	12
H2A	-8267.31	-4246.18	-5789.69	14
H3A	-8395.33	-516.88	-6179.13	27
H3B	-9779.87	-1873.41	-6577.15	27
H4	-9207.79	47.43	-4525.17	19
H5A	-6657.54	-439.76	-3490.1	23
H5B	-7245.84	-1794.38	-2688.55	23
H7	-1792.6	-1274.19	-733.5	14
H8A	-993.6	-4912.66	-532.9	21
H8B	-456.62	-3453.77	631.32	21
H9	-2445.6	-5649.15	618.73	18
H10A	-3961.14	-5441.96	-1652.07	18
H10B	-4893.73	-4316.1	-1010.66	18
H7A	-5930(60)	-3730(80)	-8370(50)	43(17)
H7B	-6070(60)	-4040(100)	-9550(40)	60(20)
H8C	1563.12	-3924.72	-1590.37	33
H8D	2310.4	-5561.53	-1485.36	33
H9A	-6347.51	-7077.63	-3741.41	23
H9B	-7979.9	-6918.84	-4197.86	23

Experimental

Single crystals of Complex 3, $C_{10}H_{22}N_2O_9Pd$ [dh1-105] were [crystallized from water/acetone]. A suitable crystal was selected and [mounted on a fiber loop] on a Oxford Diffraction Gemini Ultra diffractometer. The crystal was kept at 100.0 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS-1997 [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [dh1-105]

Crystal Data for Complex 3, $C_{10}H_{22}N_2O_9Pd$ (M =420.69 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 9.7784(2) Å, b = 7.58624(13) Å, c = 11.0500(2) Å, β = 114.330(3)°, V = 746.90(3) Å³, Z = 2, T =

100.0 K, μ(MoKα) = 1.291 mm^{-1}, *Dcalc* = 1.871 g/cm^3, 15035 reflections measured (7.054° ≤ 2Θ ≤ 60.124°), 4385 unique (R_{int} = 0.0427, R_{sigma} = 0.0393) which were used in all calculations. The final R_1 was 0.0240 (I > 2σ(I)) and wR_2 was 0.0590 (all data).

Refinement model description

Number of restraints - 3, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups, All C(H,H) groups, All N(H) groups

At 1.5 times of:

All O(H) groups, All O(H,H) groups

2. Restrained distances

O7-H7A = O7-H7B

0.9 with sigma of 0.03

3.a Free rotating group:

O8(H8C,H8D), O9(H9A,H9B)

3.b Ternary CH refined with riding coordinates:

N1(H1), N2(H2), C2(H2A), C4(H4), C7(H7), C9(H9)

3.c Secondary CH2 refined with riding coordinates:

C3(H3A,H3B), C5(H5A,H5B), C8(H8A,H8B), C10(H10A,H10B)

3.d Idealised tetrahedral OH refined as rotating group:

O3(H3), O6(H6)

Report IV. Experimental Details and Bond Lengths and Angles for Complex 4.

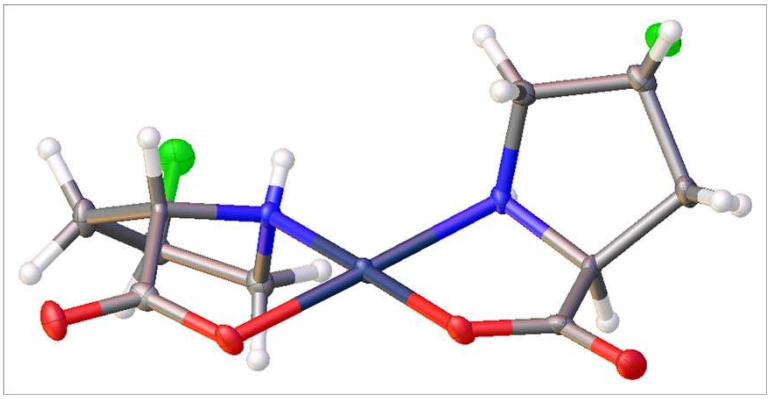

Table 1 Crystal data and structure refinement for dh1-127, Complex 4.

Identification code	dh1-127
Empirical formula	$C_{10}H_{14}N_2O_4F_2Pd$
Formula weight	370.63
Temperature/K	100.15
Crystal system	monoclinic
Space group	C2

a/Å	10.0581(4)
b/Å	9.7330(3)
c/Å	6.3547(3)
α/°	90
β/°	96.618(4)
γ/°	90
Volume/Å^3	617.95(4)
Z	2
ϱ_{calc}g/cm^3	1.992
μ/mm^{-1}	1.539
F(000)	368.0
Crystal size/mm^3	0.2919 × 0.1896 × 0.1105
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	8.158 to 64.822
Index ranges	-14 ≤ h ≤ 15, -14 ≤ k ≤ 14, -9 ≤ l ≤ 9
Reflections collected	6274
Independent reflections	2072 [R_{int} = 0.0381, R_{sigma} = 0.0441]
Data/restraints/parameters	2072/1/91
Goodness-of-fit on F^2	1.117
Final R indexes [I>=2σ (I)]	R_1 = 0.0318, wR_2 = 0.0698
Final R indexes [all data]	R_1 = 0.0329, wR_2 = 0.0701
Largest diff. peak/hole / e Å^{-3}	0.47/-0.69
Flack parameter	0.00(5)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for dh1-127, Complex 4. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pd1	5000	4078.4(9)	5000	10.09(11)
F1	7873(3)	7736(3)	8454(5)	21.0(6)
O1	6423(8)	2709(7)	6081(11)	13.3(13)
O2	8626(4)	2544(4)	6864(7)	18.1(8)
N1	6412(8)	5423(9)	6148(13)	11.7(15)
C1	7607(10)	3222(8)	6381(13)	12.6(15)
C2	7743(9)	4765(9)	6083(14)	11.9(15)
C3	8691(5)	5476(6)	7819(10)	16.8(10)
C4	7799(5)	6345(5)	9072(8)	16.0(9)
C5	6396(5)	5834(5)	8404(7)	14.1(8)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for dh1-127, Complex 4. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd1	10.88(18)	7.49(16)	11.11(18)	0	-2.20(12)	0
F1	24.5(16)	12.5(13)	25.7(16)	-3.5(11)	1.4(13)	-2.4(11)
O1	16(3)	7(3)	15(3)	0(3)	-4(2)	1(3)
O2	16.1(19)	16.2(18)	21(2)	-3.9(17)	-3.7(17)	6.0(13)
N1	9(4)	12(4)	13(3)	0(3)	-1(3)	-2(3)
C1	18(3)	9(3)	10(3)	-3(2)	1(2)	2(2)
C2	7(3)	17(3)	11(3)	-2(2)	-2(2)	3(2)
C3	11(2)	16(2)	22(3)	-4(2)	-4(2)	0.3(17)
C4	18(2)	15(2)	13(2)	-1.6(16)	-4.1(17)	-0.7(16)
C5	15(2)	14(2)	14(2)	-2.8(15)	-0.2(16)	1.0(15)

Table 4 Bond Lengths for dh1-127, Complex 4.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	O1	2.017(7)	N1	C2	1.489(12)
Pd1	$O1^1$	2.017(7)	N1	C5	1.490(9)
Pd1	N1	2.006(9)	C1	C2	1.522(7)
Pd1	$N1^1$	2.006(9)	C2	C3	1.537(11)
F1	C4	1.415(5)	C3	C4	1.522(7)
O1	C1	1.285(12)	C4	C5	1.510(7)
O2	C1	1.228(11)			

^{1}1-X,+Y,1-Z

Table 5 Bond Angles for dh1-127, Complex 4.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Pd1	$O1^1$	97.3(4)	O2	C1	O1	124.1(8)
N1	Pd1	O1	82.11(13)	O2	C1	C2	118.5(10)
$N1^1$	Pd1	O1	178.6(4)	N1	C2	C1	109.1(10)
$N1^1$	Pd1	$O1^1$	82.11(13)	N1	C2	C3	105.7(6)
N1	Pd1	$O1^1$	178.6(4)	C1	C2	C3	114.4(9)
N1	Pd1	$N1^1$	98.5(5)	C4	C3	C2	105.7(5)

C1	O1	Pd1	113.7(6)	F1	C4	C3	109.5(4)
C2	N1	Pd1	108.1(6)	F1	C4	C5	108.3(4)
C2	N1	C5	104.6(6)	C5	C4	C3	105.0(4)
C5	N1	Pd1	116.1(5)	N1	C5	C4	104.2(5)
O1	C1	C2	117.4(10)				

[1]1-X,+Y,1-Z

Table 6 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for dh1-127, Complex 4.

Atom	***x***	***y***	***z***	**U(eq)**
H2	8059	4947	4673	14
H3A	9188	4787	8748	20
H3B	9343	6062	7183	20
H4	8049	6234	10632	19
H5A	6181	5040	9278	17
H5B	5731	6570	8535	17
H1	6420(60)	6020(70)	5470(100)	13(15)

Experimental

Single crystals of Complex 4, $C_{10}H_{14}N_2O_4F_2Pd$ **[dh1-127]** were **[crystallized from water/acetone]**. A suitable crystal was selected and **[mounted on fiber loop]** on a **Oxford Diffraction Gemini Ultra** diffractometer. The crystal was kept at 100.15 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS-1997 [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [dh1-127]

Crystal Data for Complex 4, $C_{10}H_{14}N_2O_4F_2Pd$ (M =370.63 g/mol): monoclinic, space group C2 (no. 5), a = 10.0581(4) Å, b = 9.7330(3) Å, c = 6.3547(3) Å, β = 96.618(4)°, V = 617.95(4) Å^3, Z = 2, T = 100.15 K, μ(MoKα) = 1.539 mm^{-1}, *Dcalc* = 1.992 g/cm^3, 6274 reflections measured (8.158° ≤ 2Θ ≤ 64.822°), 2072 unique (R_{int} = 0.0381, R_{sigma} = 0.0441) which were used in all calculations. The final R_1 was 0.0318 (I > 2σ(I)) and wR_2 was 0.0701 (all data).

Refinement model description

Number of restraints - 1, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups, All C(H,H) groups

2.a Ternary CH refined with riding coordinates:

C2(H2), C4(H4)

2.b Secondary CH2 refined with riding coordinates:

C3(H3A,H3B), C5(H5A,H5B)

Report V. Experimental Details and Bond Lengths and Angles for Complex 5.

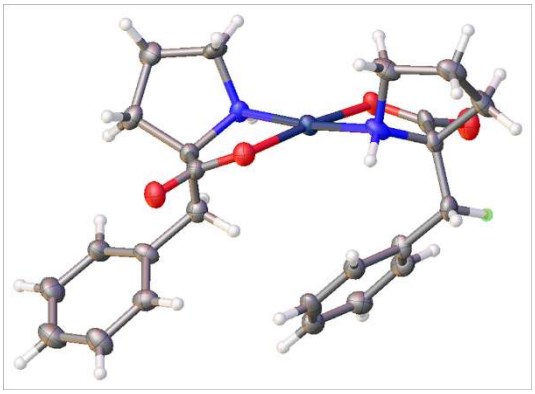

Table 1 Crystal data and structure refinement for dh1-171b, Complex 5.

Identification code	dh1-171b
Empirical formula	$C_{24}H_{28}N_2O_4Pd$
Formula weight	514.88
Temperature/K	100.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.72249(19)
b/Å	18.6628(7)
c/Å	20.0836(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2144.89(13)
Z	4
ϱ_{calc}g/cm^3	1.594
μ/mm^{-1}	7.262
F(000)	1056.0
Crystal size/mm^3	0.0706 × 0.035 × 0.0138
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.466 to 149.698
Index ranges	-6 ≤ h ≤ 7, -22 ≤ k ≤ 16, -25 ≤ l ≤ 23

Reflections collected	10868
Independent reflections	4221 [R_{int} = 0.0862, R_{sigma} = 0.0704]
Data/restraints/parameters	4221/0/280
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0477, wR_2 = 0.1217
Final R indexes [all data]	R_1 = 0.0578, wR_2 = 0.1310
Largest diff. peak/hole / e $Å^{-3}$	0.56/-0.92
Flack parameter	-0.008(15)

Table 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for dh1-171b Complex 5. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pd1	4348.5(10)	5722.8(3)	8055.4(3)	21.04(18)
O1	6925(12)	5492(3)	7413(3)	25.6(13)
O2	7615(12)	5389(4)	6338(4)	28.8(14)
O3	1742(12)	6041(4)	8653(3)	26.0(13)
O4	1063(12)	6850(4)	9434(4)	37.3(16)
N1	2330(13)	5327(4)	7314(4)	21.3(14)
N2	6362(14)	6008(5)	8849(4)	27.1(16)
C22	4939(16)	7884(5)	7004(5)	31(2)
C21	3230(20)	8054(5)	7468(5)	32(2)
C20	3518(17)	7854(5)	8132(6)	32(2)
C19	5491(16)	7511(5)	8349(4)	22.8(15)
C18	5854(18)	7323(5)	9070(4)	27.2(18)
C5	6280(16)	5438(5)	6801(4)	23.3(19)
C4	3591(16)	5417(5)	6657(5)	21.9(17)
C1	1994(19)	4538(5)	7400(5)	29.4(19)
C2	1481(17)	4256(6)	6707(5)	31.7(18)
C3	2931(17)	4746(5)	6253(5)	27.2(18)
C6	2846(17)	6148(5)	6358(5)	27.8(18)
C8	2252(19)	6086(5)	5116(5)	30(2)
C7	3649(15)	6279(5)	5653(5)	25.7(18)
C12	5720(20)	6641(4)	5514(5)	30.6(18)
C11	6407(19)	6789(6)	4864(5)	37(2)
C17	2425(16)	6486(5)	9116(4)	24.6(17)
C16	5075(15)	6559(5)	9254(4)	25.4(19)
C15	5590(20)	6374(6)	9993(4)	35(2)

C14	7242(16)	5720(7)	9978(5)	35(2)
C13	6732(19)	5368(6)	9303(5)	33(2)
C24	7227(18)	7349(5)	7875(5)	28.1(19)
C23	6958(19)	7536(6)	7211(5)	32(2)
C10	5000(20)	6561(6)	4338(6)	41(3)
C9	2930(20)	6206(6)	4466(5)	38(2)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for dh1-171b, Complex 5. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd1	15.5(3)	27.8(3)	19.8(3)	0.2(3)	-0.9(2)	-1.6(2)
O1	18(3)	31(3)	27(3)	-2(2)	-2(3)	2(3)
O2	20(3)	39(3)	28(3)	-5(3)	2(3)	3(3)
O3	17(3)	42(3)	19(3)	-1(3)	0(2)	-6(3)
O4	20(4)	54(4)	37(4)	-13(3)	6(3)	2(3)
N1	13(3)	27(4)	23(4)	-3(3)	0(3)	-2(3)
N2	21(4)	38(4)	22(4)	10(3)	-1(3)	-1(3)
C22	31(5)	36(4)	26(4)	-1(4)	-5(4)	-5(3)
C21	28(5)	34(4)	33(5)	5(4)	-5(4)	-2(4)
C20	28(4)	29(4)	38(5)	-2(4)	5(4)	4(3)
C19	11(4)	33(4)	24(4)	-3(3)	1(3)	4(4)
C18	25(4)	36(4)	20(4)	-7(3)	-3(4)	0(4)
C5	26(5)	23(3)	21(5)	-3(3)	1(3)	-1(3)
C4	19(4)	25(4)	22(4)	-2(3)	0(3)	-3(3)
C1	35(5)	20(3)	33(5)	3(3)	-3(4)	-10(4)
C2	34(5)	26(4)	35(4)	-2(4)	2(4)	5(4)
C3	22(4)	25(4)	35(5)	-8(3)	-1(4)	3(3)
C6	24(4)	32(5)	28(5)	-4(4)	1(4)	1(4)
C8	30(5)	34(4)	26(4)	2(4)	-4(4)	-9(4)
C7	16(4)	33(4)	28(5)	10(4)	1(3)	1(3)
C12	26(4)	28(4)	37(5)	3(3)	4(4)	-1(4)
C11	26(5)	53(6)	31(5)	6(4)	2(4)	0(4)
C17	20(4)	37(4)	17(4)	-3(3)	4(3)	1(3)
C16	26(5)	34(4)	16(4)	-2(3)	-2(3)	-1(3)
C15	28(5)	59(6)	19(4)	5(4)	-3(4)	-6(5)
C14	22(4)	49(5)	32(4)	13(5)	-5(3)	-9(5)

C13	28(5)	44(5)	29(5)	15(4)	-3(4)	3(4)
C24	27(5)	30(4)	27(5)	-2(3)	2(3)	-1(4)
C23	29(5)	43(5)	24(4)	-2(4)	6(4)	-13(4)
C10	42(7)	49(6)	33(5)	12(5)	4(4)	1(4)
C9	46(6)	44(5)	26(5)	5(4)	-6(5)	0(5)

Table 4 Bond Lengths for dh1-171b, Complex 5.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	O1	2.006(7)	C18	C16	1.539(13)
Pd1	O3	2.004(7)	C5	C4	1.567(13)
Pd1	N1	2.024(7)	C4	C3	1.540(12)
Pd1	N2	2.037(8)	C4	C6	1.550(13)
O1	C5	1.287(12)	C1	C2	1.517(13)
O2	C5	1.207(12)	C2	C3	1.534(14)
O3	C17	1.306(12)	C6	C7	1.508(13)
O4	C17	1.215(12)	C8	C7	1.390(14)
N1	C4	1.513(11)	C8	C9	1.380(15)
N1	C1	1.494(11)	C7	C12	1.393(14)
N2	C16	1.503(12)	C12	C11	1.391(14)
N2	C13	1.518(12)	C11	C10	1.394(17)
C22	C21	1.385(15)	C17	C16	1.548(13)
C22	C23	1.389(15)	C16	C15	1.552(12)
C21	C20	1.395(15)	C15	C14	1.544(17)
C20	C19	1.369(13)	C14	C13	1.535(15)
C19	C18	1.504(12)	C24	C23	1.387(14)
C19	C24	1.409(13)	C10	C9	1.380(17)

Table 5 Bond Angles for dh1-171b, Complex 5.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Pd1	N1	82.4(3)	C3	C4	C6	116.4(8)
O1	Pd1	N2	98.3(3)	C6	C4	C5	108.7(7)
O3	Pd1	O1	174.7(3)	N1	C1	C2	105.1(8)
O3	Pd1	N1	97.1(3)	C1	C2	C3	103.5(8)
O3	Pd1	N2	82.8(3)	C2	C3	C4	107.7(8)

N1	Pd1	N2	173.5(3)	C7	C6	C4	115.0(8)
C5	O1	Pd1	114.8(6)	C9	C8	C7	122.0(10)
C17	O3	Pd1	113.1(6)	C8	C7	C6	120.7(8)
C4	N1	Pd1	109.2(5)	C8	C7	C12	117.4(9)
C1	N1	Pd1	110.4(6)	C12	C7	C6	121.8(9)
C1	N1	C4	105.7(7)	C11	C12	C7	121.7(10)
C16	N2	Pd1	108.9(5)	C12	C11	C10	119.2(10)
C16	N2	C13	106.3(7)	O3	C17	C16	118.5(8)
C13	N2	Pd1	110.1(6)	O4	C17	O3	122.5(9)
C21	C22	C23	119.4(10)	O4	C17	C16	119.0(8)
C22	C21	C20	120.0(10)	N2	C16	C18	111.2(7)
C19	C20	C21	121.7(10)	N2	C16	C17	108.8(7)
C20	C19	C18	122.0(9)	N2	C16	C15	105.8(8)
C20	C19	C24	117.8(9)	C18	C16	C17	108.8(8)
C24	C19	C18	120.2(8)	C18	C16	C15	112.4(7)
C19	C18	C16	114.1(7)	C17	C16	C15	109.8(8)
O1	C5	C4	117.4(8)	C14	C15	C16	105.9(8)
O2	C5	O1	124.0(9)	C13	C14	C15	103.8(8)
O2	C5	C4	118.5(8)	N2	C13	C14	102.8(9)
N1	C4	C5	108.0(7)	C23	C24	C19	121.2(10)
N1	C4	C3	104.6(7)	C24	C23	C22	119.8(10)
N1	C4	C6	107.7(7)	C9	C10	C11	120.0(10)
C3	C4	C5	111.0(7)	C8	C9	C10	119.7(11)

Table 6 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for dh1-171b, Complex 5.

Atom	***x***	***y***	***z***	**U(eq)**
H1	786	5578	7303	26
H2	7897	6202	8695	33
H22	4728	8005	6548	37
H21	1873	8307	7333	38
H20	2310	7958	8442	38
H18A	4978	7668	9348	33
H18B	7534	7375	9177	33
H1A	672	4439	7704	35
H1B	3423	4314	7583	35

H2A	-205	4293	6602	38
H2B	1976	3750	6662	38
H3A	2009	4883	5855	33
H3B	4359	4494	6102	33
H6A	1120	6179	6370	33
H6B	3469	6535	6644	33
H8	785	5865	5199	36
H12	6691	6790	5872	37
H11	7817	7041	4779	44
H15A	6349	6784	10219	42
H15B	4126	6256	10231	42
H14A	8897	5872	10008	42
H14B	6894	5388	10349	42
H13A	8067	5073	9152	40
H13B	5314	5065	9325	40
H24	8607	7108	8013	34
H23	8151	7425	6898	38
H10	5462	6651	3892	50
H9	1981	6045	4108	46

Experimental

Single crystals of Complex 5, $C_{24}H_{28}N_2O_4Pd$ [dh1-171b] were [crystallized from water/acetone]. A suitable crystal was selected and [mounted on fiber loop] on a Oxford Diffraction Nova diffractometer. The crystal was kept at 100.15 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS-1997 [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [dh1-171b]

Crystal Data for **Complex** 5, $C_{24}H_{28}N_2O_4Pd$ (M =514.88 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 5.72249(19) Å, b = 18.6628(7) Å, c = 20.0836(7) Å, V = 2144.89(13) Å^3, Z = 4, T = 100.15 K, μ(CuKα) = 7.262 mm^{-1}, *Dcalc* = 1.594 g/cm^3, 10868 reflections measured (6.466° ≤ 2Θ ≤ 149.698°), 4221 unique (R_{int} = 0.0862, R_{sigma} = 0.0704) which were used in all calculations. The final R_1 was 0.0477 (I > 2σ(I)) and wR_2 was 0.1310 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups, All C(H,H) groups, All N(H) groups

2.a Ternary CH refined with riding coordinates:

N1(H1), N2(H2)

2.b Secondary CH2 refined with riding coordinates:

C18(H18A,H18B), C1(H1A,H1B), C2(H2A,H2B), C3(H3A,H3B), C6(H6A,H6B), C15(H15A, H15B), C14(H14A,H14B), C13(H13A,H13B)

2.c Aromatic/amide H refined with riding coordinates:

C22(H22), C21(H21), C20(H20), C8(H8), C12(H12), C11(H11), C24(H24), C23(H23), C10(H10), C9(H9)

This report has been created with Olex2,

Report VI. Experimental Details and Bond Lengths and Angles for Complex 7.

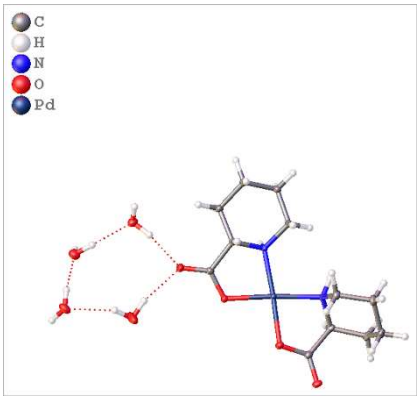

Table 1 Crystal data and structure refinement for DH1-143, Complex 7.

Identification code	DH1-143
Empirical formula	$C_{12}H_{28}N_2O_8Pd$
Formula weight	434.76
Temperature/K	100.1
Crystal system	monoclinic
Space group	C2
a/Å	22.3125(15)
b/Å	7.5996(3)
c/Å	11.8862(8)
α/°	90
β/°	120.134(9)
γ/°	90
Volume/Å^3	1743.1(2)
Z	4
ρ_{calc}g/cm^3	1.657

μ/mm^{-1}	1.105
F(000)	896.0
Crystal size/mm^3	0.7273 × 0.3616 × 0.1707
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.31 to 64.902
Index ranges	-31 ≤ h ≤ 33, -11 ≤ k ≤ 11, -17 ≤ l ≤ 17
Reflections collected	18752
Independent reflections	5852 [R_{int} = 0.0316, R_{sigma} = 0.0346]
Data/restraints/parameters	5852/1/221
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0211, wR_2 = 0.0503
Final R indexes [all data]	R_1 = 0.0233, wR_2 = 0.0526
Largest diff. peak/hole / e Å^{-3}	0.54/-0.52
Flack parameter	-0.044(13)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for DH1-143 Complex 7. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pd1	7728.5(2)	9391.6(4)	9191.5(2)	10.14(5)
O1	6912.7(9)	9555(5)	7371.0(16)	13.8(5)
O2	6637.6(9)	9584(4)	5297.6(16)	20.5(5)
O3	7178.9(10)	10067(3)	10064.1(18)	14.7(4)
O4	7245.9(10)	10068(3)	11995.4(18)	16.8(4)
N1	8222.1(11)	8672(3)	8234(2)	12.0(4)
N2	8507.6(10)	9272(6)	11060.2(18)	12.6(4)
C1	8984.1(13)	8931(4)	8829(2)	17.0(6)
C2	9232.5(14)	8152(4)	7949(3)	18.3(6)
C3	8837.6(14)	8915(4)	6577(2)	17.0(6)
C4	8055.3(14)	8711(4)	6005(3)	17.7(5)
C5	7844.7(12)	9527(6)	6925(2)	12.1(5)
C6	7071.3(12)	9530(6)	6463(2)	13.9(5)
C7	8862.8(14)	11003(4)	11505(2)	16.1(5)
C8	9381.1(15)	10997(4)	12962(3)	19.5(6)
C9	9015.3(16)	10571(4)	13717(3)	20.1(6)
C10	8655.6(16)	8801(4)	13282(3)	17.5(5)
C11	8171.1(14)	8702(4)	11815(2)	13.1(5)
C12	7491.0(14)	9694(4)	11295(2)	14.4(7)

O5	6446.9(11)	8454(3)	2936(2)	20.0(4)
O6	5043.6(12)	8262(3)	1178(2)	24.9(5)
O7	4266.1(11)	10949(3)	1434(2)	22.3(4)
O8	5208.4(12)	10646(5)	4120(2)	44.6(8)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for DH1-143, Complex 7. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd1	9.47(8)	13.65(8)	8.16(8)	0.67(9)	5.07(6)	0.73(9)
O1	11.0(7)	20.4(15)	10.0(7)	0.5(9)	5.3(6)	0.8(10)
O2	13.2(8)	37.2(16)	10.1(7)	1.1(10)	5.3(6)	4.2(11)
O3	14.3(9)	19.5(9)	12.2(8)	0.2(7)	8.1(7)	1.5(7)
O4	19.1(10)	21.1(9)	15.6(9)	0.1(8)	12.8(8)	-0.4(8)
N1	11.2(10)	16.4(10)	9.0(9)	2.3(8)	5.4(8)	2.3(8)
N2	11.9(8)	17.3(13)	9.6(8)	1.9(13)	6.2(6)	3.9(13)
C1	9.3(11)	29.7(17)	11.1(11)	1.0(9)	4.5(9)	3.1(9)
C2	11.8(12)	30.3(15)	14.3(12)	2.2(11)	7.6(10)	4.6(11)
C3	13.5(12)	26.3(16)	13.0(11)	1.5(9)	7.9(10)	2.5(9)
C4	13.2(12)	28.9(14)	12.2(12)	-0.7(10)	7.2(10)	2.3(10)
C5	10.2(9)	16.4(15)	9.6(8)	1.7(12)	4.8(7)	1.2(13)
C6	11.5(9)	17.8(14)	12.9(9)	-0.6(12)	6.6(8)	1.1(13)
C7	15.1(12)	20.4(13)	12.2(12)	-0.4(10)	6.4(10)	-2.7(10)
C8	15.3(13)	25.3(15)	14.1(12)	-1.0(11)	4.4(10)	-3.1(11)
C9	20.0(14)	27.9(15)	10.1(12)	-2.1(11)	5.7(11)	1.8(12)
C10	20.0(13)	22.9(13)	10.7(11)	5.2(10)	8.5(11)	4.5(10)
C11	16.8(12)	13.5(11)	12.0(11)	1.2(9)	9.5(10)	0.6(10)
C12	13.7(10)	18(2)	12.7(10)	-1.2(9)	7.4(9)	-2.3(9)
O5	21.0(10)	24.4(11)	17.5(10)	-1.4(8)	11.8(8)	-1.8(8)
O6	19.5(10)	30.4(12)	26.4(11)	-2.4(9)	12.7(9)	-2.0(9)
O7	13.1(10)	23.9(11)	29.2(12)	1.7(9)	10.0(9)	2.4(8)
O8	15.4(11)	88(2)	28.6(13)	19.5(14)	10.0(10)	9.7(14)

Table 4 Bond Lengths for DH1-143, Complex 7.

Atom	Atom	Length/Å	Atom	Atom	Length/Å

Pd1	O1	2.0141(17)	N2	C11	1.494(3)
Pd1	O3	2.0299(19)	C1	C2	1.528(4)
Pd1	N1	2.016(2)	C2	C3	1.526(4)
Pd1	N2	2.0216(19)	C3	C4	1.530(4)
O1	C6	1.293(3)	C4	C5	1.522(4)
O2	C6	1.230(3)	C5	C6	1.526(3)
O3	C12	1.297(3)	C7	C8	1.525(4)
O4	C12	1.237(3)	C8	C9	1.521(4)
N1	C1	1.491(3)	C9	C10	1.518(4)
N1	C5	1.496(3)	C10	C11	1.524(4)
N2	C7	1.489(5)	C11	C12	1.520(4)

Table 5 Bond Angles for DH1-143, Complex 7.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Pd1	O3	94.67(8)	C5	C4	C3	109.5(2)
O1	Pd1	N1	82.27(8)	N1	C5	C4	110.8(3)
O1	Pd1	N2	176.44(9)	N1	C5	C6	108.6(2)
N1	Pd1	O3	176.65(8)	C4	C5	C6	116.3(2)
N1	Pd1	N2	101.29(9)	O1	C6	C5	115.71(19)
N2	Pd1	O3	81.77(8)	O2	C6	O1	123.3(2)
C6	O1	Pd1	114.65(15)	O2	C6	C5	120.9(2)
C12	O3	Pd1	113.63(17)	N2	C7	C8	111.4(2)
C1	N1	Pd1	120.83(16)	C9	C8	C7	110.2(2)
C1	N1	C5	110.4(2)	C10	C9	C8	109.7(2)
C5	N1	Pd1	106.73(16)	C9	C10	C11	112.5(2)
C7	N2	Pd1	111.2(2)	N2	C11	C10	113.0(2)
C7	N2	C11	112.4(3)	N2	C11	C12	108.2(2)
C11	N2	Pd1	104.98(15)	C12	C11	C10	115.5(2)
N1	C1	C2	110.1(2)	O3	C12	C11	115.3(2)
C3	C2	C1	111.8(2)	O4	C12	O3	122.7(2)
C2	C3	C4	110.7(2)	O4	C12	C11	121.9(2)

Table 6 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for DH1-143, Complex 7.

Atom	***x***	***y***	***z***	**U(eq)**
H1	8140.66	7379.35	8074.25	14
H2	8850.73	8361.53	11141.99	15
H1A	9228.21	8351.85	9691.33	20
H1B	9093.31	10203.64	8955.87	20
H2A	9733.19	8396.04	8328.13	22
H2B	9169.32	6859.62	7904.58	22
H3A	8980.17	8300.64	6014.17	20
H3B	8953.27	10177.34	6602.12	20
H4A	7805.65	9300.11	5147.12	21
H4B	7929.95	7447.42	5878.78	21
H5	7996.68	10784.6	7047.8	15
H7A	8513.09	11934.46	11305.32	19
H7B	9107.91	11277.72	11025.12	19
H8A	9745.75	10109.72	13158.95	23
H8B	9605.84	12164.98	13229.88	23
H9A	9356.7	10538.23	14659.7	24
H9B	8670.08	11496.99	13562.46	24
H10A	8386.2	8580.75	13723.1	21
H10B	9009.93	7864.02	13551.21	21
H11	8048.08	7433.35	11601.7	16
H5A	6728.51	9056.14	2778.73	30
H5B	6556.79	8752.32	3723.5	30
H6A	5472.7	8560.22	1700.72	37
H6B	5049.99	7117.99	1165.7	37
H7C	4512.32	10208.01	1277.02	33
H7D	3864.31	10440.69	1125.32	33
H8C	5615.39	10221.96	4345.09	67
H8D	5054.96	11053.92	3338.74	67

Experimental

Single crystals of Complex 7, $C_{12}H_{28}N_2O_8Pd$ [DH1-143] were [crystallized from water/acetone]. A suitable crystal was selected and [mounted on a fiber loop] on a Xcalibur, Eos, Gemini ultra diffractometer. The crystal was kept at 100.1 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS-1997 [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [DH1-143]

Crystal Data for Complex 7, $C_{12}H_{28}N_2O_8Pd$ (M =434.76 g/mol): monoclinic, space group C2 (no. 5), a = 22.3125(15) Å, b = 7.5996(3) Å, c = 11.8862(8) Å, β = 120.134(9)°, V = 1743.1(2) Å^3, Z = 4, T = 100.1 K, μ(MoKα) = 1.105 mm^{-1}, $Dcalc$ = 1.657 g/cm^3, 18752 reflections measured (7.31° ≤ 2Θ ≤ 64.902°), 5852 unique (R_{int} = 0.0316, R_{sigma} = 0.0346) which were used in all calculations. The final R_1 was 0.0211 (I > 2σ(I)) and wR_2 was 0.0526 (all data).

Refinement model description

Number of restraints - 1, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups, All C(H,H) groups, All N(H) groups

At 1.5 times of:

All O(H,H) groups

2.a Free rotating group:

O5(H5A,H5B), O6(H6A,H6B), O7(H7C,H7D), O8(H8C,H8D)

2.b Ternary CH refined with riding coordinates:

N1(H1), N2(H2), C5(H5), C11(H11)

2.c Secondary CH2 refined with riding coordinates:

C1(H1A,H1B), C2(H2A,H2B), C3(H3A,H3B), C4(H4A,H4B), C7(H7A,H7B), C8(H8A,H8B), C9(H9A,H9B), C10(H10A,H10B)

This report has been created with Olex2, compiled on 2018.05.29 svn.r3508 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

Report VII. Experimental Details and Bond Lengths and Angles for Complex 8.

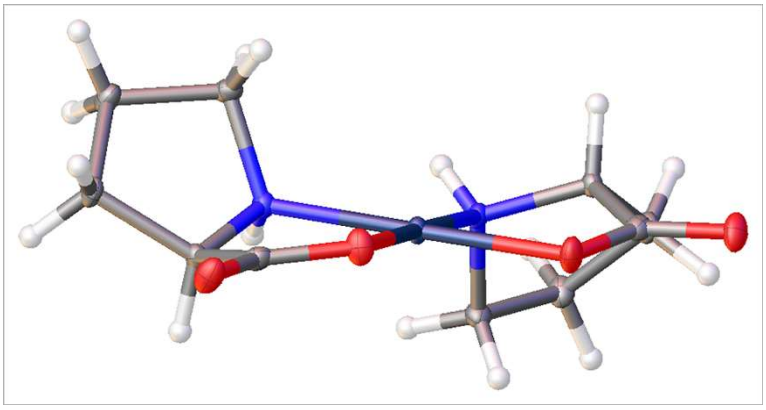

Table 1 Crystal data and structure refinement for dh1-191_abs, Complex 8.

Identification code	dh1-191_abs
Empirical formula	$C_{10}H_{16}N_2O_4Pd$
Formula weight	334.65

Temperature/K	100.15
Crystal system	orthorhombic
Space group	$C222_1$
a/Å	9.6749(2)
b/Å	10.3124(2)
c/Å	11.9527(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1192.53(5)
Z	4
ρ_{calc}g/cm^3	1.864
μ/mm^{-1}	1.561
F(000)	672.0
Crystal size/mm^3	0.265 × 0.1648 × 0.0759
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.904 to 64.796
Index ranges	-14 ≤ h ≤ 14, -14 ≤ k ≤ 15, -17 ≤ l ≤ 17
Reflections collected	12233
Independent reflections	2045 [R_{int} = 0.0516, R_{sigma} = 0.0360]
Data/restraints/parameters	2045/0/82
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0219, wR_2 = 0.0424
Final R indexes [all data]	R_1 = 0.0257, wR_2 = 0.0441
Largest diff. peak/hole / e Å^{-3}	0.70/-0.57
Flack parameter	-0.02(3)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for dh1-191_abs, Complex 8. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pd1	0	4386.4(2)	2500	9.69(7)
O1	1433(2)	5692.7(19)	2987.5(17)	15.5(4)
O2	3671(2)	5878.3(19)	3383.4(18)	17.0(4)
N1	1443(2)	3117(2)	3009.1(19)	10.4(4)
C1	2658(3)	5213(3)	3145(2)	12.6(5)
C2	2830(3)	3756(2)	2961(2)	10.5(5)
C3	3737(3)	3087(3)	3856(2)	13.5(5)

C4	2764(3)	2141(3)	4458(2)	14.8(5)
C5	1319(3)	2645(3)	4190(2)	13.5(5)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for dh1-191_abs, Complex 8. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd1	8.33(10)	7.60(10)	13.15(12)	0	-1.28(16)	0
O1	13.1(9)	10.5(9)	23.0(10)	-2.8(8)	-3.2(7)	-2.2(8)
O2	16.3(9)	12.7(10)	22.0(11)	4.6(8)	-5.4(8)	-5.2(8)
N1	9.5(10)	9.8(10)	11.7(10)	-1.1(9)	-1.3(8)	-0.4(9)
C1	15.8(13)	11.4(12)	10.6(12)	1.2(10)	0.0(10)	-2.5(10)
C2	8.1(11)	11.5(12)	11.9(12)	-0.1(10)	-0.6(10)	-0.4(9)
C3	11.1(11)	14.4(12)	15.0(13)	2.0(11)	-4.2(10)	-0.2(11)
C4	14.3(12)	15.3(13)	14.7(14)	4.5(11)	-3.3(11)	-1.4(10)
C5	13.4(12)	16.0(13)	11.2(12)	2.0(10)	0.3(10)	-2.7(10)

Table 4 Bond Lengths for dh1-191_abs, Complex 8.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	O1[1]	2.0187(19)	N1	C2	1.497(3)
Pd1	O1	2.0187(19)	N1	C5	1.497(3)
Pd1	N1[1]	2.008(2)	C1	C2	1.527(4)
Pd1	N1	2.008(2)	C2	C3	1.546(4)
O1	C1	1.298(3)	C3	C4	1.535(4)
O2	C1	1.230(3)	C4	C5	1.526(4)

[1]-X,+Y,1/2-Z

Table 5 Bond Angles for dh1-191_abs, Complex 8.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1[1]	Pd1	O1	96.28(12)	O1	C1	C2	117.0(2)
N1[1]	Pd1	O1[1]	82.56(8)	O2	C1	O1	123.3(3)
N1	Pd1	O1[1]	178.71(9)	O2	C1	C2	119.6(3)
N1	Pd1	O1	82.56(8)	N1	C2	C1	109.3(2)
N1[1]	Pd1	O1	178.71(9)	N1	C2	C3	106.6(2)

N1[1]	Pd1	N1	98.61(13)	C1	C2	C3	113.7(2)
C1	O1	Pd1	114.48(17)	C4	C3	C2	105.1(2)
C2	N1	Pd1	108.93(16)	C5	C4	C3	104.3(2)
C2	N1	C5	104.5(2)	N1	C5	C4	103.6(2)
C5	N1	Pd1	116.22(17)				

[1]-X,+Y,1/2-Z

Table 6 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for dh1-191_abs, Complex 8.

Atom	*x*	*y*	*z*	U(eq)
H1	1410(30)	2480(30)	2550(40)	14(7)
H2	3246	3605	2206	13
H3A	4514	2615	3502	16
H3B	4117	3732	4387	16
H4A	2888	1247	4174	18
H4B	2933	2147	5275	18
H5A	623	1944	4249	16
H5B	1057	3360	4700	16

Experimental

Single crystals of Complex 8, $C_{10}H_{16}N_2O_4Pd$ [dh1-191_abs] were [crystallized from water/accetone]. A suitable crystal was selected and[mounted on fiber loop] on a Oxford Diffraction Gemini Ultra diffractometer. The crystal was kept at 100.15 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [dh1-191_abs]

Crystal Data for Complex 8, $C_{10}H_{16}N_2O_4Pd$ (M =334.65 g/mol): orthorhombic, space group $C222_1$ (no. 20), a = 9.6749(2) Å, b = 10.3124(2) Å, c = 11.9527(3) Å, V = 1192.53(5) Å^3, Z = 4, T = 100.15 K, μ(MoKα) = 1.561 mm^{-1}, *Dcalc* = 1.864 g/cm^3, 12233 reflections measured (7.904° ≤ 2Θ ≤ 64.796°), 2045 unique (R_{int} = 0.0516, R_{sigma} = 0.0360) which were used in all calculations. The final R_1 was 0.0219 (I > 2σ(I)) and wR_2 was 0.0441 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups, All C(H,H) groups

2.a Ternary CH refined with riding coordinates:

C2(H2)

2.b Secondary CH2 refined with riding coordinates:

C3(H3A,H3B), C4(H4A,H4B), C5(H5A,H5B)

This report has been created with Olex2, compiled on 2018.05.29 svn.r3508 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

VIII. Experimental Details and Bond Lengths and Angles for Complex 9.

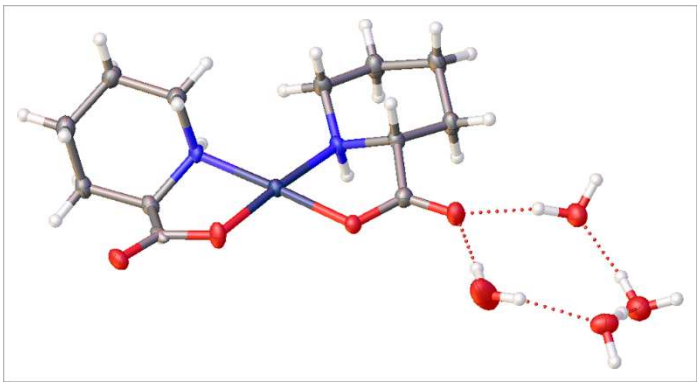

Table 1 Crystal data and structure refinement for dh1-189_ABS.

Identification code	dh1-189_ABS
Empirical formula	$C_{12}H_{28}N_2O_8Pd$
Formula weight	434.76
Temperature/K	100.15
Crystal system	monoclinic
Space group	C2
a/Å	23.0490(7)
b/Å	7.60778(14)
c/Å	11.8928(2)
α/°	90
β/°	123.0605(13)
γ/°	90
Volume/Å^3	1747.78(7)
Z	4
ρ_{calc}g/cm^3	1.652
μ/mm^{-1}	1.102
F(000)	896.0
Crystal size/mm^3	0.1936 × 0.1643 × 0.1225

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.09 to 64.8
Index ranges	$-33 \le h \le 33$, $-11 \le k \le 11$, $-17 \le l \le 17$
Reflections collected	18977
Independent reflections	5827 [R_{int} = 0.0320, R_{sigma} = 0.0331]
Data/restraints/parameters	5827/6/229
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0341, wR_2 = 0.0855
Final R indexes [all data]	R_1 = 0.0373, wR_2 = 0.0888
Largest diff. peak/hole / e Å^{-3}	2.47/-0.94
Flack parameter	-0.009(13)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for dh1-189_ABS, Complex 9. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pd1	2727.6(2)	2385.5(5)	6267.4(2)	15.62(8)
O1	1914.5(13)	2542(8)	6453(3)	16.1(7)
O2	1635.4(15)	2578(7)	7983(3)	25.6(8)
O3	2173.8(16)	3044(5)	4284(3)	22.7(6)
O4	2248.2(17)	3060(5)	2500(3)	23.6(6)
O5	1443.6(19)	1445(5)	9956(4)	28.1(7)
O7	730.9(18)	3936(5)	2884(4)	29.6(7)
N1	3221.7(18)	1670(5)	8215(3)	17.4(6)
N2	3504.5(15)	2305(10)	5964(3)	16.1(6)
C1	2068.1(19)	2522(9)	7674(4)	19.4(7)
C2	2841.7(19)	2533(9)	8762(4)	17.6(8)
C3	3053(2)	1703(7)	10114(4)	24.1(8)
C4	3839(2)	1911(6)	11109(4)	24.8(9)
C5	4232(2)	1155(7)	10520(5)	26.2(9)
C6	3984(2)	1927(6)	9145(4)	22.6(9)
C7	2509(2)	2659(5)	3694(4)	16.4(9)
C8	3176(2)	1693(6)	4539(4)	20.3(7)
C9	3655(3)	1797(6)	4027(5)	22.8(8)
C10	4016(3)	3559(7)	4324(5)	27.4(9)
C11	4380(2)	4000(7)	5805(5)	25.8(9)
C12	3861(2)	4011(6)	6224(4)	20.9(8)
O6	-46(2)	1247(6)	1085(4)	34.3(8)

O8	-207(2)	3625(9)	3700(4)	53.4(14)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for dh1-189_ABS, Complex 9. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd1	17.52(12)	16.40(12)	13.47(12)	0.01(14)	8.78(9)	0.79(15)
O1	16.8(10)	17(2)	16.1(10)	0.6(14)	9.9(9)	2.0(14)
O2	22.1(12)	37(2)	20.4(12)	2.3(16)	13.3(10)	3.0(16)
O3	23.5(14)	30.3(15)	17.1(13)	9.6(12)	12.9(12)	9.8(12)
O4	28.6(15)	25.9(14)	14.5(13)	-0.7(11)	10.7(12)	-0.4(12)
O5	31.8(17)	30.7(18)	23.0(16)	0.7(13)	15.7(14)	-1.9(14)
O7	21.5(15)	26.4(16)	32.1(19)	1.4(14)	8.9(14)	-0.8(13)
N1	19.6(15)	19.9(15)	12.2(14)	0.0(12)	8.3(13)	1.7(12)
N2	18.1(11)	18.3(15)	13.3(11)	2(2)	9.5(10)	-1(2)
C1	19.9(14)	20(2)	19.7(15)	1.5(19)	11.7(12)	2(2)
C2	20.4(14)	19(2)	15.3(13)	-0.3(18)	10.7(12)	2.5(19)
C3	22.5(19)	34(2)	16.9(18)	3.8(16)	11.9(16)	3.6(16)
C4	23.1(18)	36(3)	15.7(17)	0.8(14)	10.5(15)	4.6(15)
C5	22.2(19)	37(2)	20(2)	3.3(18)	11.7(17)	5.7(18)
C6	17.5(16)	33(3)	16.0(17)	2.4(14)	8.4(14)	4.4(14)
C7	29.5(17)	6(3)	10.9(14)	-0.9(11)	9.4(13)	-4.9(13)
C8	25.8(19)	19.6(17)	17.5(18)	-0.4(15)	13.2(16)	2.0(15)
C9	27(2)	26.5(19)	20.2(19)	0.1(15)	16.4(17)	3.6(16)
C10	29(2)	34(2)	25(2)	2.9(18)	17.8(19)	1(2)
C11	23.1(19)	31(2)	27(2)	1.0(18)	16.1(18)	-2.1(17)
C12	21.2(18)	21.7(19)	21.4(19)	-2.8(15)	12.8(16)	-2.5(15)
O6	30.8(18)	40(2)	28.8(19)	-0.3(15)	14.0(16)	2.5(16)
O8	26.3(19)	95(4)	32(2)	12(2)	11.3(17)	-10(2)

Table 4 Bond Lengths for dh1-189_ABS, Complex 9.

Atom	Atom	Length/Å	Atom	Atom	Length/Å

Pd1	O1	2.007(3)	N2	C12	1.476(8)
Pd1	O3	2.039(3)	C1	C2	1.529(5)
Pd1	N1	2.020(3)	C2	C3	1.539(6)
Pd1	N2	2.012(3)	C3	C4	1.539(6)
O1	C1	1.293(4)	C4	C5	1.529(6)
O2	C1	1.237(5)	C5	C6	1.525(6)
O3	C7	1.330(5)	C7	C8	1.492(6)
O4	C7	1.241(5)	C8	C9	1.527(6)
N1	C2	1.498(5)	C9	C10	1.515(7)
N1	C6	1.492(5)	C10	C11	1.518(7)
N2	C8	1.504(6)	C11	C12	1.527(6)

Table 5 Bond Angles for dh1-189_ABS, Complex 9.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
O1	Pd1	O3	94.58(12)	N1	C2	C1	108.6(4)
O1	Pd1	N1	82.29(13)	N1	C2	C3	110.3(4)
O1	Pd1	N2	176.27(19)	C1	C2	C3	116.1(4)
N1	Pd1	O3	176.44(13)	C2	C3	C4	109.2(4)
N2	Pd1	O3	81.76(13)	C5	C4	C3	110.7(4)
N2	Pd1	N1	101.39(14)	C6	C5	C4	112.1(4)
C1	O1	Pd1	115.0(2)	N1	C6	C5	110.2(3)
C7	O3	Pd1	112.3(2)	O3	C7	C8	115.8(3)
C2	N1	Pd1	106.4(3)	O4	C7	O3	119.4(4)
C6	N1	Pd1	120.9(3)	O4	C7	C8	124.7(4)
C6	N1	C2	110.6(3)	N2	C8	C9	113.8(4)
C8	N2	Pd1	105.1(2)	C7	C8	N2	107.9(4)
C12	N2	Pd1	112.6(4)	C7	C8	C9	114.2(4)
C12	N2	C8	112.9(4)	C10	C9	C8	112.2(4)
O1	C1	C2	115.4(3)	C9	C10	C11	110.5(4)
O2	C1	O1	124.1(3)	C10	C11	C12	110.2(4)
O2	C1	C2	120.4(3)	N2	C12	C11	111.8(4)

Table 6 Hydrogen Bonds for dh1-189_ABS, Complex 9.

D	**H**	**A**	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/°**

O5 H5C O4[1]	0.87	1.96	2.825(5)	178.6
O5 H5D O2	0.87	1.91	2.753(5)	161.7
O7 H7B O3	0.87	2.04	2.873(5)	161.4
O8 H8A O2[2]	1.12(8)	1.77(8)	2.879(5)	170(7)
O8 H8B O7	0.87	2.00	2.821(6)	157.1

[1]+X,+Y,1+Z; [2]-X,+Y,1-Z

Table 7 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for dh1-189_ABS, Complex 9.

Atom	*x*	*y*	*z*	U(eq)
H5C	1695.41	1951.29	10734.7	42
H5D	1590.95	1884.02	9480.96	42
H7A	494.75	3234.63	2202.73	44
H7B	1137.95	3453.24	3360.12	44
H1	3139.39	379.35	8214.28	21
H2	3848.76	1403.02	6576.06	19
H2A	2992.23	3790.4	8941.69	21
H3A	2927.95	440.39	9987.8	29
H3B	2803.13	2288.4	10473.72	29
H4A	3953.3	3172.64	11315.46	30
H4B	3982.74	1295.03	11955.69	30
H5A	4732.22	1401.76	11139.43	31
H5B	4170.81	-136.94	10439.81	31
H6A	4093.17	3197.41	9234.53	27
H6B	4227.25	1345.17	8771.34	27
H8	3056.1	424.67	4517.4	24
H9A	4007.79	855.51	4453.4	27
H9B	3382.37	1593.38	3046.11	27
H10A	3672.48	4484.55	3785.1	33
H10B	4359.02	3525.99	4067.35	33
H11A	4602.91	5167.59	5978.78	31
H11B	4745.67	3118.12	6341.41	31
H12A	4106.76	4286.06	7193.25	25
H12B	3513.94	4945.18	5725.36	25
H8A	-740(40)	3090(110)	3030(80)	60(20)
H6C	-510(20)	1320(110)	710(70)	50(20)
H6D	310(30)	1350(160)	920(60)	150(60)
H8B	88.18	4020.06	3522.51	80

Experimental

Single crystals of Complex 9, $C_{12}H_{28}N_2O_8Pd$ [dh1-189_ABS] were [crystallized from water/acetone]. A suitable crystal was selected and[mounted on fiber loop] on a Oxford Diffraction Gemini Ultra diffractometer. The crystal was kept at 100.15 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS-1997 [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [dh1-189_ABS]

Crystal Data for **Complex** 9, $C_{12}H_{28}N_2O_8Pd$ (M =434.76 g/mol): monoclinic, space group C2 (no. 5), a = 23.0490(7) Å, b = 7.60778(14) Å, c = 11.8928(2) Å, β = 123.0605(13)°, V = 1747.78(7) Å^3, Z = 4, T = 100.15 K, μ(MoKα) = 1.102 mm^{-1}, *Dcalc* = 1.652 g/cm^3, 18977 reflections measured (7.09° ≤ 2Θ ≤ 64.8°), 5827 unique (R_{int} = 0.0320, R_{sigma} = 0.0331) which were used in all calculations. The final R_1 was 0.0341 (I > 2σ(I)) and wR_2 was 0.0888 (all data).

Refinement model description

Number of restraints - 6, number of constraints - unknown.

Details:

1. Fixed Uiso

 At 1.2 times of:

  All C(H) groups, All C(H,H) groups, All N(H) groups

 At 1.5 times of:

  All O(H) groups, All O(H,H) groups

2. Restrained distances

 O6-H6C = O6-H6D

 0.9 with sigma of 0.03

3.a Free rotating group:

 O5(H5C,H5D), O7(H7A,H7B), O8(H8B)

3.b Ternary CH refined with riding coordinates:

 N1(H1), N2(H2), C2(H2A), C8(H8)

3.c Secondary CH2 refined with riding coordinates:

 C3(H3A,H3B), C4(H4A,H4B), C5(H5A,H5B), C6(H6A,H6B), C9(H9A,H9B), C10(H10A,

 H10B), C11(H11A,H11B), C12(H12A,H12B)