ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Spin crossover in 2D Iron(II) Phthalazine Cyanometallic Complexes

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Contents of the Supporting Information:

Experimental details

Syntesis of iron (II) *p*-toluenesulphonate hexahydrate ($Fe(OTs)_2 \cdot 6H_2O$)[1]

To iron powder (4.07 g, 72.9 mmol) in a 250-mL, round-bottomed flask equipped with a reflux condenser is added *p*-toluenesulfonic acid monohydrate (13.45 g, 70.7 mmol) and water (20 mL). The mixture is heated to reflux for 5 h. The pale green solution is filtered while hot, and the filter cake is washed with water (3×10 mL). The filtrate is allowed to cool to room temperature, and pale green needles form within 2 h. The crystals are collected by filtration and dried overnight under vacuum at room temperature. Yield: 13.92 g (77.8 %).

1. D. Coucouvanis, in *Inorganic Syntheses*, Wiley, New York, USA, 2002, **33**, 75– 121.

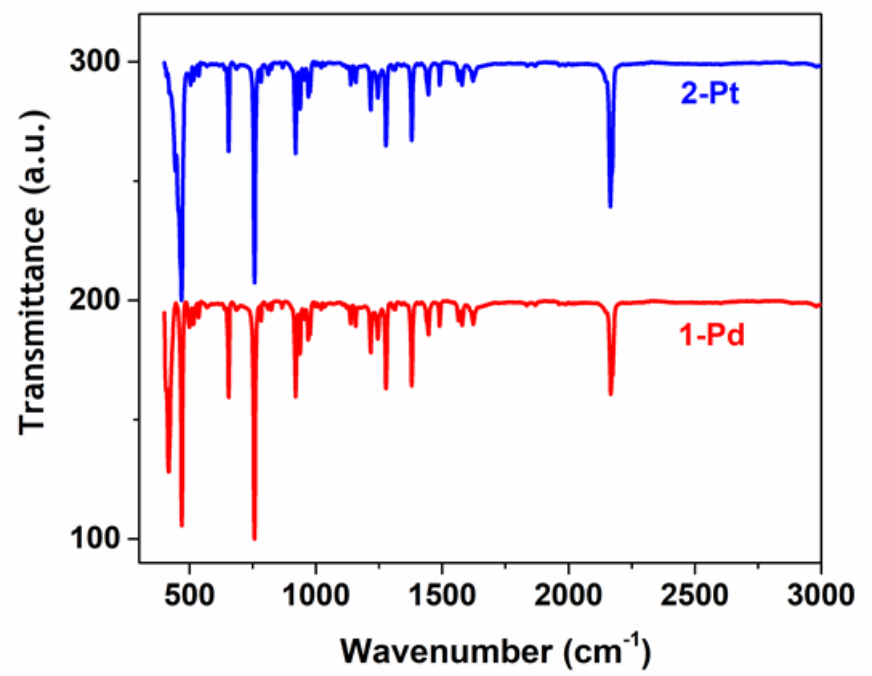

Fig. S1 FT-IR spectrum of **1** and **2** for HS samples at 293 K.

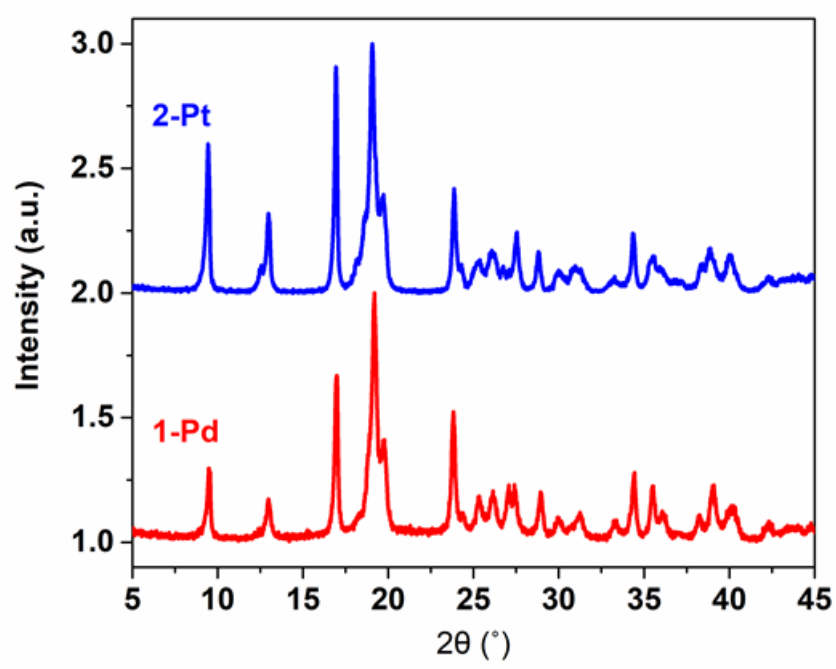

Fig. S2 Experimental PXRD patterns of **1** and **2** for HS samples at 293 K.

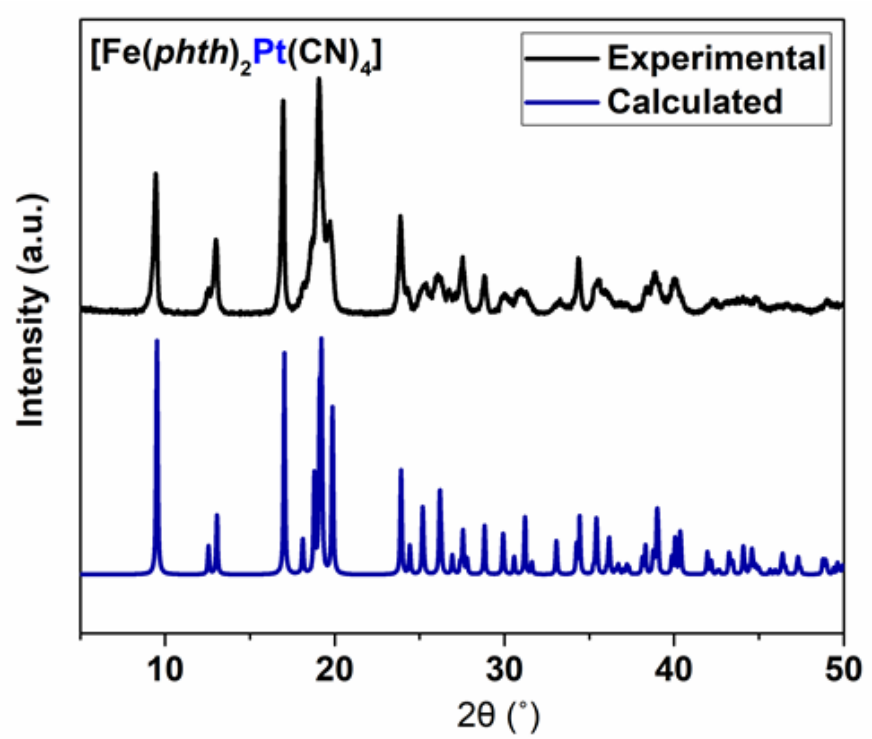

Fig. S3 Experimental and calculated PXRD patterns for **2** in HS state.

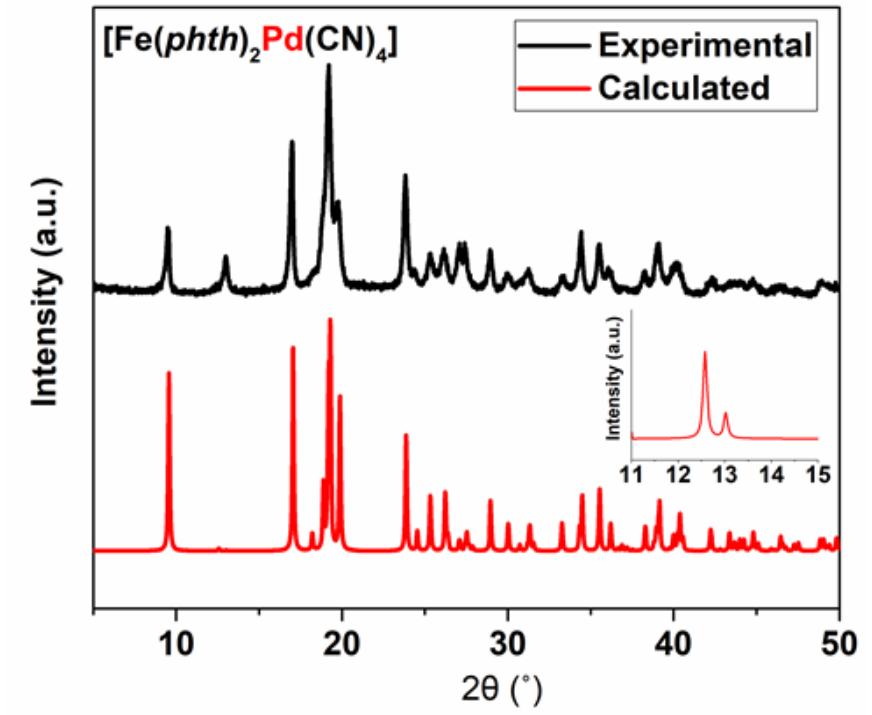

Fig. S4 Experimental and calculated PXRD patterns for **1** in HS state.

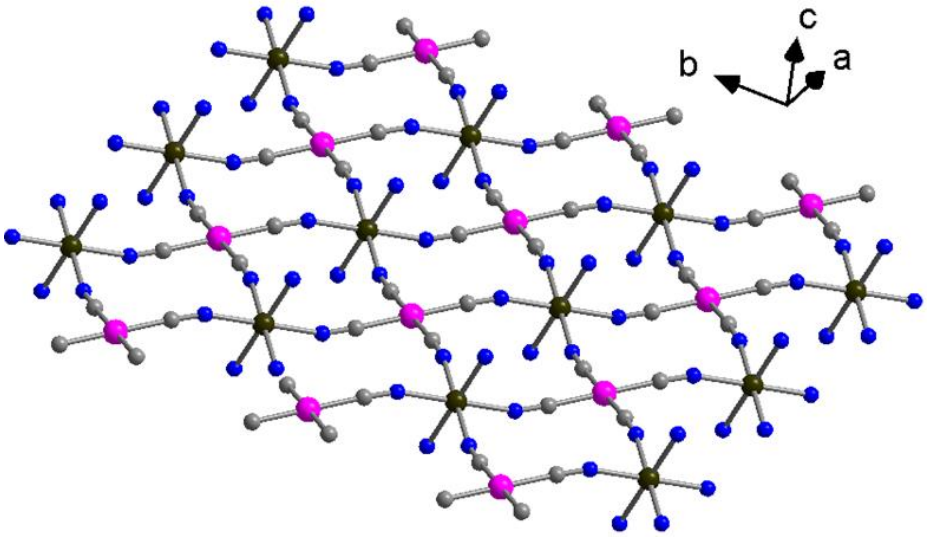

Fig. S5 2D nets of {Fe(Pd(CN)$_4$} in **1** (Fe: olive green, Pd: pink, N: blue, C: gray).

Table S1. Summary of spin transition temperatures for 2D Hofmann-type SCO coordination polymers based on phthalazine (phth), pyridine (py), pyridazine (pdz) and pyrazine (pz).

Composition complex	Pd			Pt		
	SCO*	T_C (K)	ΔT_C (K)	SCO*	T_C (K)	ΔT_C (K)
$[Fe(phth)_2M(CN)_4]$	c	202 / 207	5	c	211 / 218	7
$[Fe(py)_2M(CN)_4]$[2]	nc	208 / 213	5	nc	208 / 216	8
$[Fe(pdz)_2M(CN)_4]$[3]	c	247 / 260	13	c	269 / 283	14
$[Fe(pdz)_2M(CN)_4]\cdot H_2O$[3]	nc	242 / 265	23	nc	235 / 255	20
$[Fe(pz)_2M(CN)_4]\cdot nH_2O$[2] **$Pd^{II}$ (n = 2.5); Pt^{II} (n = 2)**	c	233 / 266	33	c	220 / 240	20

*c = complete SCO; nc = not compete SCO.

2. V. Niel, J. M. Martinez-Agudo, M. C. Muñoz, A. B. Gaspar and J. A. Real, *Inorg. Chem.*, 2001, **40**, 3838–3839.
3. I. A. Gural'skiy, S. I. Shylin, V. Ksenofontov and W. Tremel, *Eur. J. Inorg. Chem.*, 2019, **2019**, 4532–4537.

Table S2. The values of spin transition temperatures for 2D Hofmann-type SCO coordination polymers based on phthalazine (phth) obtained by different techniques.

Complex	Magnetic measurements	Calorimetric measurements	Optical measurements	Spectroscopic measurements (Raman)
$[Fe(phth)_2Pd(CN)_4]$ (1)	$T_{1/2}\downarrow$ = 202 K $T_{1/2}\uparrow$ = 207 K	$T_{1/2}\downarrow$ = 195 K $T_{1/2}\uparrow$ = 204 K	$T_{1/2}\downarrow$ = 193 K $T_{1/2}\uparrow$ = 203 K	$T_{1/2}\downarrow$ = 201 K $T_{1/2}\uparrow$ = 206 K
$[Fe(phth)_2Pt(CN)_4]$ (2)	$T_{1/2}\downarrow$ = 211 K $T_{1/2}\uparrow$ = 218 K	$T_{1/2}\downarrow$ = 202 K $T_{1/2}\uparrow$ = 214 K	$T_{1/2}\downarrow$ = 201 K $T_{1/2}\uparrow$ = 214 K	$T_{1/2}\downarrow$ = 211 K $T_{1/2}\uparrow$ = 220 K

Crystallographic Tables

Table S3. Crystal data and structure refinement for **1** at 260 K.

Identification code	Pd_HS
Empirical formula	$C_{20}H_{12}FeN_8Pd$
Formula weight	526.63
Temperature/K	260
Crystal system	triclinic
Space group	P-1
a/Å	7.2433(4)
b/Å	7.4455(4)
c/Å	10.4263(9)
α/°	71.858(6)
β/°	69.586(6)
γ/°	89.943(5)
Volume/Å^3	497.11(6)
Z	1
ρ_{calc}g/cm^3	1.759
μ/mm^{-1}	1.658
F(000)	260.0
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.418 to 58.876
Index ranges	-9 ≤ h ≤ 9, -10 ≤ k ≤ 10, -13 ≤ l ≤ 13
Reflections collected	7465
Independent reflections	2416 [R_{int} = 0.0284, R_{sigma} = 0.0330]
Data/restraints/parameters	2416/0/139
Goodness-of-fit on F^2	1.141
Final R indexes [I>=2σ (I)]	R_1 = 0.0417, wR_2 = 0.1113
Final R indexes [all data]	R_1 = 0.0444, wR_2 = 0.1134
Largest diff. peak/hole / e Å^{-3}	3.22/-0.58

Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 1 (HS). 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	5000	0	16.64(14)
Fe1	-5000	0	0	18.00(18)
N1	-2621(5)	2169(5)	-515(4)	30.0(8)
N2	2888(5)	1952(5)	436(4)	28.2(7)
N3	-4893(5)	973(5)	-2257(4)	28.6(7)
N4	-3065(6)	1080(6)	-3305(4)	37.1(9)
C1	-1619(6)	3208(5)	-379(4)	22.5(7)
C2	1798(6)	3031(6)	345(4)	23.8(8)
C9	-6321(7)	2228(7)	-4067(5)	31.4(9)
C3	-2901(7)	1720(8)	-4652(5)	40.5(11)
C10	-6417(7)	1467(7)	-2615(5)	31.8(9)
C4	-4454(7)	2368(7)	-5148(5)	34.6(10)
C8	-7932(8)	2847(8)	-4463(6)	43.1(12)
C7	-7632(9)	3646(8)	-5911(7)	50.6(14)
C6	-5782(10)	3768(9)	-6975(6)	53.9(15)
C5	-4204(8)	3135(8)	-6625(6)	48.1(13)

Anisotropic Displacement Parameters (Å^2×10^3) for 1 (HS). 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	14.7(2)	13.2(2)	25.9(2)	-8.31(15)	-10.38(15)	4.15(13)
Fe1	18.2(3)	13.7(4)	28.6(4)	-9.1(3)	-14.4(3)	5.4(3)
N1	31.3(18)	25.2(18)	39(2)	-12.0(16)	-18.4(16)	2.1(14)
N2	32.8(18)	25.2(17)	35.1(19)	-13.6(15)	-19.3(16)	12.1(14)
N3	29.8(17)	28.0(18)	30.1(18)	-8.8(15)	-14.4(15)	3.1(14)
N4	28.7(19)	44(2)	35(2)	-7.6(18)	-12.7(16)	3.6(16)
C1	22.9(18)	17.1(17)	30(2)	-8.5(15)	-12.3(15)	3.3(14)
C2	25.1(18)	20.7(18)	29(2)	-10.4(16)	-12.4(16)	4.6(15)
C9	33(2)	34(2)	31(2)	-10.8(18)	-17.0(18)	3.9(17)
C3	28(2)	50(3)	36(2)	-9(2)	-7.0(19)	-2(2)
C10	29(2)	40(2)	28(2)	-10.8(18)	-11.7(17)	6.6(18)
C4	39(2)	33(2)	30(2)	-6.8(18)	-14.3(19)	-3.2(18)
C8	45(3)	51(3)	40(3)	-14(2)	-24(2)	11(2)
C7	59(3)	52(3)	54(3)	-9(3)	-43(3)	7(3)
C6	71(4)	55(3)	34(3)	2(2)	-32(3)	-13(3)
C5	46(3)	58(3)	29(2)	-4(2)	-10(2)	-12(2)

Bond Lengths for 1 (HS).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	C1	1.991(4)	N3	N4	1.375(5)
Pd1	C1[1]	1.991(4)	N3	C10	1.302(5)
Pd1	C2[1]	1.992(4)	N4	C3	1.296(6)
Pd1	C2	1.992(4)	C9	C10	1.418(6)
Fe1	N1[2]	2.164(3)	C9	C4	1.405(7)
Fe1	N1	2.164(3)	C9	C8	1.400(6)
Fe1	N2[3]	2.140(3)	C3	C4	1.420(7)
Fe1	N2[4]	2.140(3)	C4	C5	1.410(7)
Fe1	N3	2.209(4)	C8	C7	1.376(7)
Fe1	N3[2]	2.209(4)	C7	C6	1.391(9)
N1	C1	1.135(5)	C6	C5	1.358(8)
N2	C2	1.132(5)			

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

Bond Angles for 1 (HS).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1	Pd1	C1[1]	180.0	C1	N1	Fe1	160.7(3)
C1	Pd1	C2	90.15(15)	C2	N2	Fe1[5]	163.8(3)
C1[1]	Pd1	C2[1]	90.15(15)	N4	N3	Fe1	115.6(3)
C1[1]	Pd1	C2	89.85(15)	C10	N3	Fe1	123.8(3)
C1	Pd1	C2[1]	89.85(15)	C10	N3	N4	120.6(4)
C2	Pd1	C2[1]	180.0	C3	N4	N3	118.1(4)
N1	Fe1	N1[2]	180.0	N1	C1	Pd1	176.0(4)
N1	Fe1	N3	91.97(14)	N2	C2	Pd1	175.0(4)
N1[2]	Fe1	N3[2]	91.97(14)	C4	C9	C10	115.9(4)
N1[2]	Fe1	N3	88.03(14)	C8	C9	C10	124.4(4)
N1	Fe1	N3[2]	88.03(14)	C8	C9	C4	119.7(4)
N2[3]	Fe1	N1[2]	90.15(14)	N4	C3	C4	125.3(5)
N2[4]	Fe1	N1[2]	89.85(14)	N3	C10	C9	124.0(4)
N2[4]	Fe1	N1	90.15(14)	C9	C4	C3	116.1(4)
N2[3]	Fe1	N1	89.85(14)	C9	C4	C5	120.1(5)
N2[4]	Fe1	N2[3]	180.00(19)	C5	C4	C3	123.9(5)
N2[4]	Fe1	N3	92.04(14)	C7	C8	C9	119.0(5)
N2[3]	Fe1	N3[2]	92.04(14)	C8	C7	C6	120.9(5)
N2[4]	Fe1	N3[2]	87.96(14)	C5	C6	C7	121.4(5)
N2[3]	Fe1	N3	87.96(14)	C6	C5	C4	118.8(5)
N3	Fe1	N3[2]	180.0				

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

Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1 (HS).

Atom	*x*	*y*	*z*	U(eq)
H3	-1664.82	1758.25	-5350.54	49
H10	-7642.8	1311.83	-1874.11	38
H8	-9185.31	2720.4	-3758.35	52
H7	-8680.66	4111.38	-6182.74	61
H6	-5621.54	4294.07	-7947.48	65
H5	-2979.75	3206.5	-7346.48	58

Aromatic H refined with riding coordinates

Table S4. Crystal data and structure refinement for **1** at 200 K.

Identification code	Pd_LS
Empirical formula	$C_{20}H_{12}FeN_8Pd$
Formula weight	526.63
Temperature/K	200.05(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.0962(7)
b/Å	7.1676(7)
c/Å	10.1546(16)
α/°	71.083(11)
β/°	74.381(11)
γ/°	89.881(8)
Volume/Å^3	468.49(10)
Z	1
ρ_{calc}g/cm^3	1.867
μ/mm^{-1}	1.760
F(000)	260.0
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.422 to 58.964
Index ranges	-6 ≤ h ≤ 9, -7 ≤ k ≤ 9, -8 ≤ l ≤ 13
Reflections collected	3684
Independent reflections	2138 [R_{int} = 0.0360, R_{sigma} = 0.0775]
Data/restraints/parameters	2138/0/139
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0558, wR_2 = 0.1287
Final R indexes [all data]	R_1 = 0.0699, wR_2 = 0.1362
Largest diff. peak/hole / e Å^{-3}	3.70/-1.12

Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 1 (LS). 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	10000	10000	13.1(2)
Fe1	0	5000	10000	11.3(2)
N2	1940(6)	3132(6)	9749(5)	15.1(9)
C1	3191(7)	8097(7)	9757(6)	15.0(11)
N3	206(6)	5957(6)	7894(5)	18.7(10)
N1	2047(6)	6982(6)	9736(5)	15.3(9)
C3	2202(8)	6743(9)	5572(7)	27.0(13)
N4	2043(6)	6131(7)	6946(6)	23.4(11)
C9	-1180(8)	7211(8)	5898(6)	20.5(12)
C8	-2804(9)	7813(9)	5367(7)	28.1(14)
C10	-1317(8)	6444(8)	7386(7)	21.6(12)
C6	-647(10)	8716(9)	2919(7)	33.0(15)
C4	662(8)	7361(9)	4926(7)	24.9(13)
C5	920(9)	8114(9)	3429(7)	30.4(14)
C7	-2508(10)	8582(10)	3896(8)	35.5(16)
C2	3103(8)	2021(8)	9772(6)	15.6(11)

Anisotropic Displacement Parameters (Å^2×10^3) for 1 (LS). 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	8.4(3)	11.4(3)	21.8(4)	-7.6(2)	-5.6(2)	1.43(19)
Fe1	8.9(5)	9.4(5)	17.8(6)	-6.0(4)	-5.3(4)	1.9(4)
N2	17(2)	11(2)	16(2)	-3.7(18)	-2.7(18)	1.2(16)
C1	11(2)	11(2)	27(3)	-9(2)	-10(2)	3.9(19)
N3	15(2)	19(2)	21(3)	-8(2)	-2.2(19)	0.1(17)
N1	16(2)	13(2)	17(2)	-3.7(18)	-7.8(18)	1.8(16)
C3	19(3)	32(3)	24(3)	-7(3)	-1(2)	-3(2)
N4	13(2)	30(3)	24(3)	-7(2)	-3.1(19)	-0.7(18)
C9	21(3)	22(3)	21(3)	-9(2)	-7(2)	1(2)
C8	24(3)	37(4)	27(4)	-12(3)	-10(3)	1(2)
C10	18(3)	25(3)	24(3)	-10(2)	-7(2)	2(2)
C6	42(4)	28(3)	23(4)	-1(3)	-9(3)	-6(3)
C4	23(3)	26(3)	28(3)	-10(3)	-9(3)	-3(2)
C5	28(3)	36(4)	23(3)	-6(3)	-5(3)	-2(3)
C7	31(4)	45(4)	35(4)	-11(3)	-19(3)	-2(3)
C2	16(3)	14(3)	19(3)	-10(2)	-5(2)	1.9(19

Bond Lengths for 1 (LS).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	C1[1]	1.991(5)	N3	N4	1.374(6)
Pd1	C1	1.991(5)	N3	C10	1.318(7)
Pd1	C2[2]	1.977(5)	C3	N4	1.292(8)
Pd1	C2[3]	1.977(5)	C3	C4	1.420(8)
Fe1	N2[4]	1.944(5)	C9	C8	1.410(8)
Fe1	N2	1.944(5)	C9	C10	1.406(8)
Fe1	N3[4]	1.987(5)	C9	C4	1.390(8)
Fe1	N3	1.987(5)	C8	C7	1.370(9)
Fe1	N1	1.937(4)	C6	C5	1.362(9)
Fe1	N1[4]	1.937(4)	C6	C7	1.404(9)
N2	C2	1.145(7)	C4	C5	1.398(9)
C1	N1	1.150(7)			

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

Bond Angles for 1 (LS).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1[1]	Pd1	C1	180.0	C2	N2	Fe1	171.1(5)
C2[2]	Pd1	C1	89.5(2)	N1	C1	Pd1	174.1(5)
C2[2]	Pd1	C1[1]	90.5(2)	N4	N3	Fe1	117.2(3)
C2[3]	Pd1	C1[1]	89.5(2)	C10	N3	Fe1	123.0(4)
C2[3]	Pd1	C1	90.5(2)	C10	N3	N4	119.8(5)
C2[2]	Pd1	C2[3]	180.0	C1	N1	Fe1	171.8(5)
N2[4]	Fe1	N2	180.0	N4	C3	C4	126.2(6)
N2	Fe1	N3	91.49(19)	C3	N4	N3	118.0(5)
N2[4]	Fe1	N3	88.50(19)	C10	C9	C8	123.3(6)
N2	Fe1	N3[4]	88.51(19)	C4	C9	C8	119.5(6)
N2[4]	Fe1	N3[4]	91.50(19)	C4	C9	C10	117.2(5)
N3[4]	Fe1	N3	180.0	C7	C8	C9	118.8(6)
N1	Fe1	N2[4]	89.47(18)	N3	C10	C9	123.7(5)
N1[4]	Fe1	N2	89.47(18)	C5	C6	C7	120.0(6)
N1	Fe1	N2	90.53(18)	C9	C4	C3	115.1(6)
N1[4]	Fe1	N2[4]	90.53(18)	C9	C4	C5	120.7(5)
N1[4]	Fe1	N3	88.08(18)	C5	C4	C3	124.3(6)
N1	Fe1	N3	91.92(18)	C6	C5	C4	119.6(6)
N1[4]	Fe1	N3[4]	91.92(18)	C8	C7	C6	121.4(6)
N1	Fe1	N3[4]	88.08(18)	N2	C2	Pd1[5]	174.9(5)
N1	Fe1	N1[4]	180.0				

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

Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1 (LS).

Atom	*x*	*y*	*z*	U(eq)
H3	3441.44	6782.22	4948.19	32
H8	-4052.07	7691.3	6002.22	34
H10	-2551.69	6269.97	8049.8	26
H6	-484.64	9214.9	1924.05	40
H5	2155.78	8203.79	2784.59	36
H7	-3562.75	9025.45	3536.89	43

Aromatic H refined with riding coordinates

Table S5. Crystal data and structure refinement for **2** at 260 K.

Identification code	Pt_HS
Empirical formula	$C_{20}H_{12}FeN_8Pt$
Formula weight	615.32
Temperature/K	260(1)
Crystal system	triclinic
Space group	P-1
a/Å	7.2754(8)
b/Å	7.4315(9)
c/Å	10.3903(14)
α/°	72.230(11)
β/°	70.501(11)
γ/°	89.988(10)
Volume/Å^3	501.04(11)
Z	1
ρ_{calc}g/cm^3	2.039
μ/mm^{-1}	7.721
F(000)	292.0
Crystal size/mm^3	0.1 × 0.1 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.396 to 58.412
Index ranges	-9 ≤ h ≤ 9, -10 ≤ k ≤ 10, -13 ≤ l ≤ 13
Reflections collected	3951
Independent reflections	2300 [R_{int} = 0.0484, R_{sigma} = 0.0973]
Data/restraints/parameters	2300/0/139
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0546, wR_2 = 0.1052
Final R indexes [all data]	R_1 = 0.0557, wR_2 = 0.1071
Largest diff. peak/hole / e Å^{-3}	4.92/-1.80

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

Atom	*x*	*y*	*z*	U(eq)
Pt1	5000	0	10000	20.67(15)
Fe1	10000	5000	10000	20.7(4)
C9	8657(13)	7213(12)	5934(10)	33(2)
N2	2098(10)	3032(10)	9586(9)	32.0(18)
C1	6658(12)	1810(11)	10334(10)	24.8(18)
C10	8573(13)	6428(12)	7372(10)	32(2)
C4	10481(13)	7390(13)	4873(10)	34(2)
C8	7050(15)	7825(14)	5493(13)	44(3)
N4	11894(11)	6100(11)	6714(9)	38.3(19)
N1	7668(10)	2867(9)	10477(8)	28.5(16)
N3	10080(11)	5960(10)	7745(8)	31.1(17)
C5	10729(17)	8183(15)	3415(12)	52(3)
C7	7329(18)	8648(16)	4054(14)	56(3)
C3	12022(15)	6763(15)	5377(12)	43(2)
C2	3176(12)	1967(11)	9675(10)	25.5(18)
C6	9166(17)	8795(14)	3021(12)	50(3)

Anisotropic Displacement Parameters (Å^2×10^3) for 2 (HS). 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}
Pt1	18.2(2)	16.6(2)	32.7(3)	-12.21(18)	-11.93(19)	5.60(16)
Fe1	18.0(8)	16.3(7)	35.2(10)	-11.8(7)	-15.3(7)	6.5(6)
C9	36(5)	30(5)	31(5)	-9(4)	-12(4)	2(4)
N2	31(4)	29(4)	52(5)	-23(4)	-25(4)	19(3)
C1	19(4)	25(4)	31(5)	-11(4)	-8(4)	5(3)
C10	25(4)	42(5)	28(5)	-7(4)	-14(4)	10(4)
C4	33(5)	34(5)	32(5)	-9(4)	-10(4)	-8(4)
C8	36(5)	53(6)	56(8)	-18(5)	-30(5)	18(5)
N4	25(4)	47(5)	39(5)	-11(4)	-10(4)	6(3)
N1	27(4)	26(4)	38(5)	-13(3)	-15(3)	3(3)
N3	33(4)	31(4)	35(5)	-15(3)	-15(4)	5(3)
C5	56(7)	56(7)	35(6)	-9(5)	-11(6)	-5(6)
C7	63(8)	60(7)	64(9)	-20(6)	-46(7)	16(6)
C3	34(5)	54(6)	35(6)	-13(5)	-3(5)	1(5)
C2	25(4)	19(4)	42(6)	-19(4)	-15(4)	8(3)
C6	69(8)	49(6)	30(6)	2(5)	-30(6)	-6(6)

Bond Lengths for 2 (HS).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pt1	C1	1.988(8)	C9	C8	1.419(12)
Pt1	C1[1]	1.988(8)	N2	C2	1.120(10)
Pt1	C2	2.002(8)	C1	N1	1.151(10)
Pt1	C2[1]	2.002(8)	C10	N3	1.294(11)
Fe1	N2[2]	2.144(7)	C4	C5	1.395(14)
Fe1	N2[3]	2.144(7)	C4	C3	1.411(14)
Fe1	N1	2.144(6)	C8	C7	1.375(15)
Fe1	N1[4]	2.144(6)	N4	N3	1.374(10)
Fe1	N3[4]	2.212(8)	N4	C3	1.295(13)
Fe1	N3	2.212(8)	C5	C6	1.366(15)
C9	C10	1.408(12)	C7	C6	1.386(16)
C9	C4	1.389(13)			

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

Bond Angles for 2 (HS).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1	Pt1	C1[1]	180.0	C10	C9	C8	125.6(9)
C1	Pt1	C2	90.4(3)	C4	C9	C10	116.3(8)
C1[1]	Pt1	C2	89.6(3)	C4	C9	C8	118.1(9)
C1	Pt1	C2[1]	89.6(3)	C2	N2	Fe1[5]	164.3(8)
C1[1]	Pt1	C2[1]	90.4(3)	N1	C1	Pt1	177.5(8)
C2	Pt1	C2[1]	180.0	N3	C10	C9	124.2(9)
N2[2]	Fe1	N2[3]	180.0	C9	C4	C5	120.8(9)
N2[3]	Fe1	N3	92.4(3)	C9	C4	C3	115.5(9)
N2[3]	Fe1	N3[4]	87.6(3)	C5	C4	C3	123.7(10)
N2[2]	Fe1	N3	87.6(3)	C7	C8	C9	120.3(11)
N2[2]	Fe1	N3[4]	92.4(3)	C3	N4	N3	117.1(8)
N1	Fe1	N2[3]	90.0(3)	C1	N1	Fe1	161.1(7)
N1[4]	Fe1	N2[3]	90.0(3)	C10	N3	Fe1	124.2(7)
N1	Fe1	N2[2]	90.0(3)	C10	N3	N4	120.4(8)
N1[4]	Fe1	N2[2]	90.0(3)	N4	N3	Fe1	115.3(5)
N1[4]	Fe1	N1	180.0	C6	C5	C4	119.9(11)
N1[4]	Fe1	N3[4]	87.8(3)	C8	C7	C6	120.0(10)
N1	Fe1	N3	87.8(3)	N4	C3	C4	126.2(10)
N1	Fe1	N3[4]	92.2(3)	N2	C2	Pt1	175.6(9)
N1[4]	Fe1	N3	92.2(3)	C5	C6	C7	120.7(10)
N3[4]	Fe1	N3	180.0				

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

Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2 (HS).

Atom	*x*	*y*	*z*	U(eq)
H10	7354.67	6233.56	8100.75	38
H8	5802.36	7668.27	6181.19	53
H5	11956.65	8293.73	2713.43	62
H7	6284.94	9105.56	3774.04	67
H3	13246.29	6833.1	4682.7	52
H6	9336.56	9317.6	2047.73	60

Aromatic H refined with riding coordinates

Table S6. Crystal data and structure refinement for **2** at 200 K.

Identification code	Pt_LS
Empirical formula	$C_{20}H_{12}FeN_8Pt$
Formula weight	615.32
Temperature/K	200.00(14)
Crystal system	triclinic
Space group	P-1
a/Å	7.1262(5)
b/Å	7.1724(5)
c/Å	10.1727(8)
α/°	71.020(7)
β/°	75.175(6)
γ/°	89.950(6)
Volume/Å^3	473.38(6)
Z	1
ρ_{calc}g/cm^3	2.158
μ/mm^{-1}	8.172
F(000)	292.0
Crystal size/mm^3	0.1 × 0.1 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.398 to 50.046
Index ranges	-7 ≤ h ≤ 8, -8 ≤ k ≤ 7, -12 ≤ l ≤ 11
Reflections collected	3227
Independent reflections	1662 [R_{int} = 0.0427, R_{sigma} = 0.0656]
Data/restraints/parameters	1662/0/139
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0366, wR_2 = 0.0765
Final R indexes [all data]	R_1 = 0.0371, wR_2 = 0.0771
Largest diff. peak/hole / e Å^{-3}	2.54/-1.72

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

Atom	*x*	*y*	*z*	U(eq)
Pt1	0	5000	0	15.50(14)
Fe1	5000	10000	0	14.3(3)
N1	2954(8)	8017(9)	251(6)	18.1(13)
N2	6920(8)	8123(8)	-237(6)	16.3(13)
C1	1831(10)	6924(10)	214(7)	14.7(15)
C2	8043(10)	7020(10)	-224(7)	15.1(15)
N3	4802(8)	9030(8)	2101(6)	18.8(13)
C3	2838(11)	8268(12)	4403(9)	28.0(18)
N4	2972(9)	8881(9)	3035(7)	23.6(14)
C7	7554(12)	6415(13)	6130(9)	36(2)
C9	6207(11)	7780(11)	4113(8)	21.5(16)
C6	5687(12)	6271(12)	7083(9)	34(2)
C10	6314(10)	8557(11)	2630(8)	19.5(16)
C4	4374(10)	7629(11)	5066(8)	20.7(16)
C5	4134(12)	6878(12)	6569(9)	31.2(19)
C8	7818(11)	7174(12)	4664(9)	28.1(18)

Anisotropic Displacement Parameters (Å^2×10^3) for 2 (LS). 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}
Pt1	13.2(2)	12.8(2)	23.2(2)	-7.41(17)	-7.77(16)	2.70(15)
Fe1	13.7(7)	12.0(7)	20.4(8)	-7.0(6)	-8.1(6)	3.1(6)
N1	15(3)	15(3)	26(3)	-7(3)	-8(3)	5(3)
N2	14(3)	12(3)	19(3)	-1(3)	-3(2)	-2(3)
C1	16(4)	9(4)	22(4)	-3(3)	-11(3)	6(3)
C2	13(3)	14(4)	16(4)	-3(3)	-2(3)	2(3)
N3	21(3)	13(3)	23(3)	-7(3)	-6(3)	2(3)
C3	25(4)	28(5)	29(5)	-11(4)	-3(3)	0(4)
N4	22(3)	20(4)	27(4)	-6(3)	-7(3)	4(3)
C7	33(5)	46(6)	36(5)	-15(5)	-21(4)	6(4)
C9	26(4)	14(4)	27(4)	-8(3)	-12(3)	2(3)
C6	42(5)	32(5)	26(4)	-7(4)	-11(4)	-4(4)
C10	11(3)	22(4)	29(4)	-13(4)	-7(3)	2(3)
C4	26(4)	14(4)	25(4)	-7(3)	-10(3)	3(3)
C5	35(5)	24(5)	29(5)	-5(4)	-5(4)	-6(4)
C8	28(4)	30(5)	28(4)	-8(4)	-14(3)	8(4)

Bond Lengths for 2 (LS).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pt1	C1	1.999(7)	N3	N4	1.384(8)
Pt1	C1[1]	1.999(7)	N3	C10	1.321(9)
Pt1	C2[2]	2.010(7)	C3	N4	1.293(10)
Pt1	C2[3]	2.010(7)	C3	C4	1.428(10)
Fe1	N1[4]	1.947(6)	C7	C6	1.413(11)
Fe1	N1	1.947(6)	C7	C8	1.373(11)
Fe1	N2	1.944(6)	C9	C10	1.409(10)
Fe1	N2[4]	1.944(6)	C9	C4	1.394(10)
Fe1	N3[4]	1.987(6)	C9	C8	1.411(10)
Fe1	N3	1.987(6)	C6	C5	1.355(11)
N1	C1	1.137(9)	C4	C5	1.410(11)
N2	C2	1.124(9)			

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

Bond Angles for 2 (LS).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1	Pt1	C1[1]	180.0	C1	N1	Fe1	171.4(6)
C1	Pt1	C2[2]	90.3(3)	C2	N2	Fe1	172.3(6)
C1	Pt1	C2[3]	89.7(3)	N1	C1	Pt1	175.5(6)
C1[1]	Pt1	C2[3]	90.3(3)	N2	C2	Pt1[5]	174.6(6)
C1[1]	Pt1	C2[2]	89.7(3)	N4	N3	Fe1	117.1(4)
C2[3]	Pt1	C2[2]	180.0	C10	N3	Fe1	123.4(5)
N1	Fe1	N1[4]	180.0(3)	C10	N3	N4	119.4(6)
N1	Fe1	N3[4]	88.4(2)	N4	C3	C4	126.7(7)
N1[4]	Fe1	N3	88.4(2)	C3	N4	N3	117.4(6)
N1	Fe1	N3	91.6(2)	C8	C7	C6	120.3(8)
N1[4]	Fe1	N3[4]	91.6(2)	C10	C9	C8	124.2(7)
N2[4]	Fe1	N1[4]	89.4(2)	C4	C9	C10	116.3(7)
N2	Fe1	N1	89.4(2)	C4	C9	C8	119.5(7)
N2	Fe1	N1[4]	90.6(2)	C5	C6	C7	120.7(8)
N2[4]	Fe1	N1	90.6(2)	N3	C10	C9	124.7(6)
N2	Fe1	N2[4]	180.0	C9	C4	C3	115.2(7)
N2	Fe1	N3	88.5(2)	C9	C4	C5	120.2(7)
N2	Fe1	N3[4]	91.5(2)	C5	C4	C3	124.6(7)
N2[4]	Fe1	N3[4]	88.5(2)	C6	C5	C4	119.7(8)
N2[4]	Fe1	N3	91.5(2)	C7	C8	C9	119.6(8)
N3	Fe1	N3[4]	180.0				

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

Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2 (LS).

Atom	*x*	*y*	*z*	U(eq)
H3	1614.92	8241.19	5018.44	34
H7	8608.19	5993.13	6496.88	43
H6	5522.84	5754.09	8075.05	40
H10	7538.33	8749.65	1977.31	23
H5	2914.7	6798.25	7204.17	37
H8	9051.51	7289.07	4037.31	34

Aromatic H refined with riding coordinates