Supporting Information

Self-assembly of a heterometallic molecular triangle using an ambidentate ligand and self-selection for a single linkage isomer

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Synthesis of complex-1

To a 2-mL methanol solution containing 10.8 mg (0.01 mmol) of *cis*-(dppf)Pd(H_2O)$_2$(OTf)$_2$, a methanol solution of 1.45 mg (1 mL) of sodiumnicotinate (0.01 mmol) was added drop-by-drop with continuous stirring (5 min). A sharp color change from light green to wine red was noticed. ^{1}H NMR (CD_3OD, 300 MHz): δ 8.8 (s, 3H, L-H_2); 7.3 (s, 6H, L-$H_{5,4}$); 8.1; 7.9 ; 7.7 ; 6.7 (20H, m, phenyl protons); 5.5 ; 5.1 ; 4.7 ; 3.85 (8H, ferrocene) ppm. ^{31}P{1H} NMR (CD_3OD, 121.4 MHz): δ 32, 39 ppm. Anal. Calcd for $C_{123}H_{96}N_3O_{15}P_6Pd_3F_9S_3Fe_3$: C, 52.79; H, 3.43; N, 1.50 % Found: C, 52.43; H, 3.79; N, 1.73 %. Yield: 91%.

Experimental details on X-ray data collection and refinements

The crystals of complex-1 displayed rapid loss of solvent when removed from the mother liquor. X-ray data were collected using a Bruker X8 Apex II diffractometer equipped with monochromated Mo-Kα radiation (λ = 0.71073 Å). Collection temperatures were maintained at 123 K using an Oxford Cryosystems open-flow N_2 cryostream. Data integration and scaling were performed using the Bruker Apex II [1] suite of programs and corrected for the effects of absorption with SADABS.[1] Initial solutions were obtained

via direct methods with SHELXS-97 [2] before refinement using conventional alternating cycles of least-squares on F^2 with SHELXL-97 [2] using the graphical interface package X-Seed.[3] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed in idealized positions and allowed to ride on the atoms to which they were attached. Hydrogen atom thermal parameters were tied to the atom to which they were attached. Solvent molecules within the structure show significant signs of disorder with large displacement ellipsoids and were refined without hydrogen atoms. Two of the three unique trifluoromethanesulfonate counter-anions are disorder over two positions with the occupancies freely refined against each other (63:37 and 54:46).

References

[1] *Apex II & SADABS*, 2005, Bruker AXS Ltd., Madison, Wisconsin.

[2] *SHELXS-97 & SHELXL-97*, Sheldrik, G. M. **1997**, University of Göttingen.

[3] Barbour, L. J. *J. Supramol. Chem.,* **2001**, *1*, 189.

Table S1 - Crystal data and details of the structure determination for complex-1

Formula	C_{138} H_{138} F_9 Fe_3 N_3 O_{26} P_6 Pd_3 S_3
Formula Weight	3151.93
Crystal System	Monoclinic
Space group	C2/c(No. 15)
a, b, c [Angstrom]	49.293(9) 23.145(4) 25.561(5)
alpha, beta, gamma [deg]	90 106.793(3) 90
V [Ang^3]	27919(9)
Z	8

D(calc) [g/cm**3]	1.500
Mu(MoKa) [/mm]	0.877
F(000)	12704
Crystal Size [mm]	0.10 x 0.25 x 0.35
Temperature (K)	123
Radiation [Angstrom]	MoK 0.71073
Theta Min-Max [Deg]	4.1, 25.0
Tot., Uniq. Data, R(int)	53829, 22419, 0.073
Observed data [I > 2.0 sigma(I)]	14946
Nref, Npar	22419, 1880
R, wR2, S	0.0854, 0.2413, 1.03
w = 1/[\s^2^(Fo^2^)+(0.2000P)^2^]	where P=(Fo^2^+2Fc^2^)/3
Max. and Av. Shift/Error	0.01, 0.00
Min. and Max. Resd. Dens. [e/Ang^3]	-1.82, 1.56

Table S2 - Final coordinates and equivalent isotropic displacement Parameters of the non-Hydrogen atoms for: complex-1

Atom	x	y	z	U(eq) [Ang^2]
Pd1	0.11137(1)	0.94464(2)	0.03649(3)	0.0305
Pd2	0.13123(1)	0.66321(2)	0.16501(3)	0.0310
Pd3	0.27016(1)	0.77580(2)	0.14452(3)	0.0314
Fe1	0.07189(2)	1.10852(4)	0.03103(5)	0.0360
Fe2	0.09114(3)	0.57901(5)	0.26573(7)	0.0512
Fe3	0.35252(2)	0.79695(5)	0.25567(6)	0.0423
P1	0.13064(4)	1.03093(8)	0.07359(10)	0.0318

P2	0.06527(4)	0.96499(8)	0.02537(10)	0.0322
P3	0.09914(4)	0.70271(8)	0.20402(10)	0.0353
P4	0.15093(5)	0.60061(8)	0.23377(10)	0.0376
P5	0.29895(4)	0.70816(8)	0.19941(10)	0.0334
P6	0.30315(4)	0.84506(8)	0.14734(10)	0.0354
O1	0.11635(11)	0.7252(2)	0.1060(2)	0.0352
O2	0.09566(11)	0.6609(2)	0.0407(3)	0.0400
O3	0.23684(10)	0.7208(2)	0.1444(2)	0.0345
O4	0.23710(11)	0.6933(2)	0.0606(3)	0.0418
O5	0.15239(10)	0.9243(2)	0.0407(2)	0.0347
O6	0.16060(11)	0.8644(2)	0.1127(2)	0.0389
N1	0.09972(13)	0.8619(3)	0.0028(3)	0.0313
N2	0.15974(13)	0.6374(2)	0.1226(3)	0.0336
N3	0.23945(13)	0.8240(3)	0.0884(3)	0.0313
C1	0.09006(16)	0.8537(3)	-0.0501(4)	0.0358
C2	0.08220(19)	0.7997(3)	-0.0726(4)	0.0460
C3	0.08499(17)	0.7527(3)	-0.0378(4)	0.0405
C4	0.09608(14)	0.7618(3)	0.0176(4)	0.0301
C5	0.10312(15)	0.8165(3)	0.0370(4)	0.0321

Table S3 - Bond distances (Angstrom)for:complex-1

Pd1-P1	2.296(2)	Fe2-C83	2.036(10)
Pd1-P2	2.257(2)	Fe2-C84	2.063(10)

Pd1-O5	2.048(5)	Fe2-C85	2.079(11)
Pd1-N1	2.110(7)	Fe2-C86	2.016(11)
Pd2-P3	2.290(2)	Fe3-C111	1.997(7)
Pd2-P4	2.268(2)	Fe3-C112	2.030(8)
Pd2-O1	2.057(5)	Fe3-C113	2.073(9)
Pd2-N2	2.095(7)	Fe3-C114	2.075(8)
Pd3-P5	2.298(2)	Fe3-C115	2.023(8)
Pd3-P6	2.270(2)	Fe3-C116	2.003(8)
Pd3-O3	2.077(5)	Fe3-C117	2.028(9)
Pd3-N3	2.083(7)	Fe3-C118	2.046(9)
Fe1-C43	2.005(9)	Fe3-C119	2.053(8)
Fe1-C44	2.010(10)	Fe3-C120	2.021(8)
Fe1-C45	2.051(9)	S1B-O1B	1.413(16)
Fe1-C46	2.084(8)	S1B-O2B	1.475(17)
Fe1-C47	2.035(8)	S1B-O3B	1.422(13)
Fe1-C48	2.000(8)	S1B-C1B	1.802(19)
Fe1-C49	2.016(8)	S1C-C1C	1.89(4)
Fe1-C50	2.047(9)	S1C-O3C	1.43(3)
Fe1-C51	2.073(10)	S1C-O2C	1.40(3)
Fe1-C52	2.034(9)	S1C-O1C	1.45(3)
Fe2-C77	2.024(7)	S1D-O3D	1.42(2)
Fe2-C78	2.038(10)	S1D-O1D	1.57(2)
Fe2-C79	2.075(11)	S1D-C1D	1.84(3)

Fe2-C80	2.030(11)	S1D-O2D	1.418(19)
Fe2-C81	2.014(10)	S1E-O1E	1.449(12)
Fe2-C82	1.999(10)	S1E-C1E	1.71(3)

Table S4 - Bond Angles (Degrees) for:Complex-1

P1-Pd1-P2	98.74(7)	C44-Fe1-C46	67.7(3)
P1-Pd1-O5	83.91(14)	C44-Fe1-C47	69.4(4)
P1-Pd1-N1	171.67(19)	C44-Fe1-C48	108.0(3)
P2-Pd1-O5	175.79(15)	C44-Fe1-C49	109.0(4)
P2-Pd1-N1	89.58(19)	C44-Fe1-C50	139.4(4)
O5-Pd1-N1	87.8(2)	C44-Fe1-C51	176.8(3)
P3-Pd2-P4	96.46(9)	C44-Fe1-C52	137.0(3)
P3-Pd2-O1	84.03(16)	C45-Fe1-C46	39.2(3)
P3-Pd2-N2	172.06(16)	C45-Fe1-C47	68.2(4)
P4-Pd2-O1	174.69(16)	C45-Fe1-C48	136.0(3)
P4-Pd2-N2	91.02(19)	C45-Fe1-C49	108.0(4)
O1-Pd2-N2	88.3(2)	C45-Fe1-C50	112.4(3)
P5-Pd3-P6	98.70(8)	C45-Fe1-C51	141.6(3)
P5-Pd3-O3	86.10(14)	C45-Fe1-C52	177.3(3)
P5-Pd3-N3	169.4(2)	C46-Fe1-C47	40.9(3)
P6-Pd3-O3	172.65(15)	C46-Fe1-C48	175.2(4)
P6-Pd3-N3	90.9(2)	C46-Fe1-C49	135.1(3)

O3 -Pd3-N3	84.9(2)	C46-Fe1-C50	112.3(3)
C43-Fe1-C44	41.2(4)	C46-Fe1-C51	115.5(3)
C43-Fe1-C45	68.7(3)	C46-Fe1-C52	143.2(3)
C43-Fe1-C46	68.8(3)	C47-Fe1-C48	140.8(3)
C43-Fe1-C47	41.8(3)	C47-Fe1-C49	175.8(3)
C43-Fe1-C48	109.7(3)	C47-Fe1-C50	138.8(3)
C43-Fe1-C49	139.1(3)	C47-Fe1-C51	113.3(4)
C43-Fe1-C50	178.8(3)	C47-Fe1-C52	113.0(4)
C43-Fe1-C51	139.6(4)	C48-Fe1-C49	43.2(3)
C43-Fe1-C52	110.4(3)	C48-Fe1-C50	69.2(3)
C44-Fe1-C45	40.7(3)	C48-Fe1-C51	68.8(3)

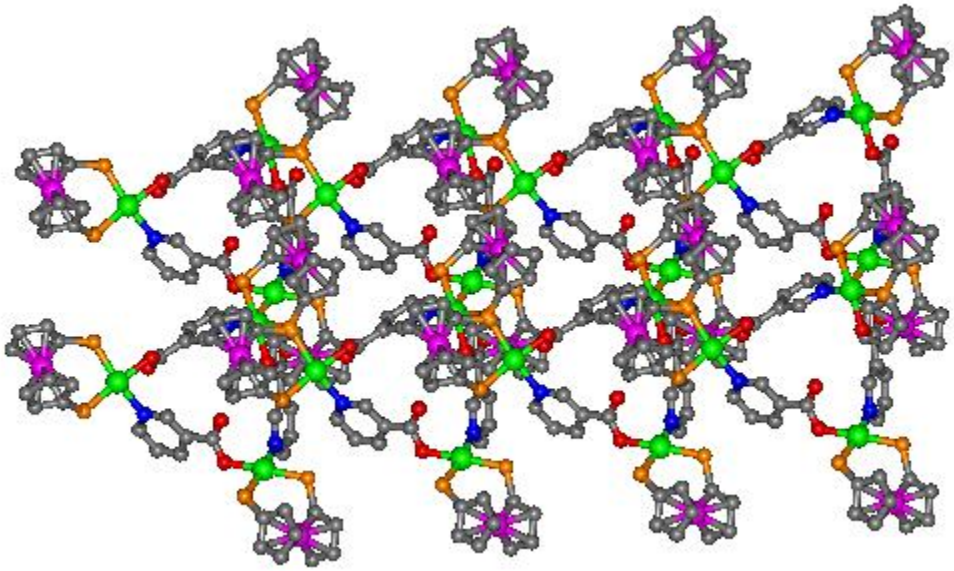

Fig. S1: Packing diagram of complex-1.

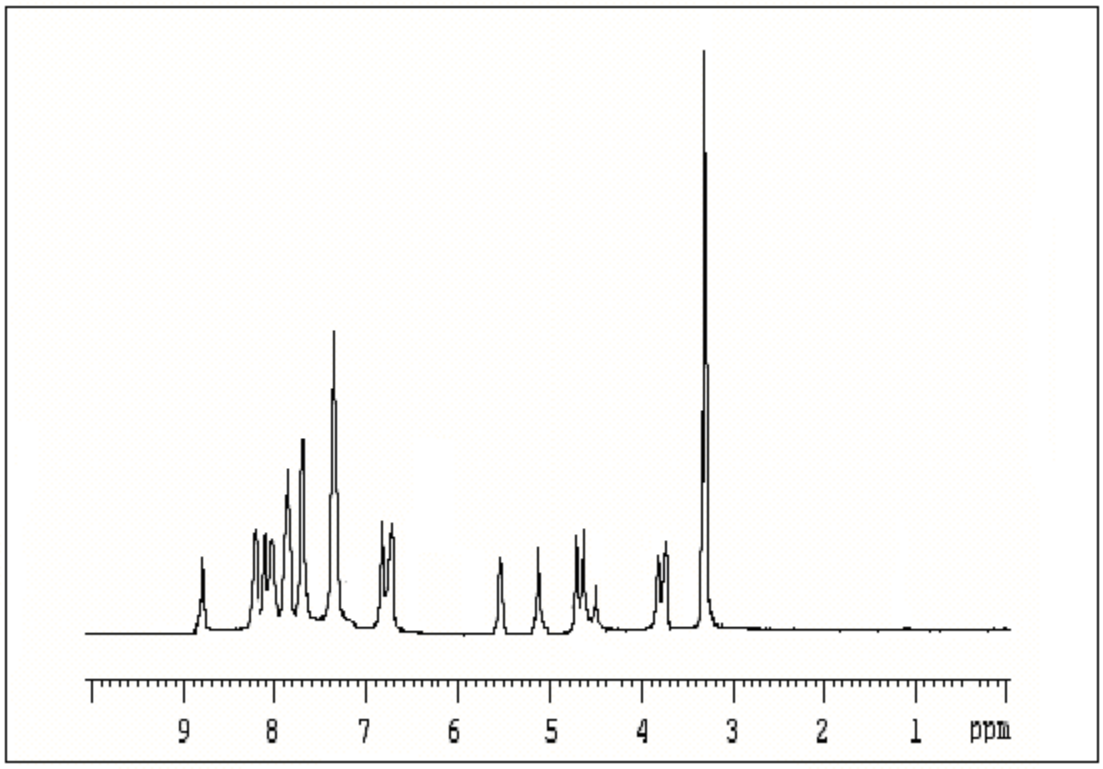

Fig.S2: ^{1}H NMR of complex-**1.**

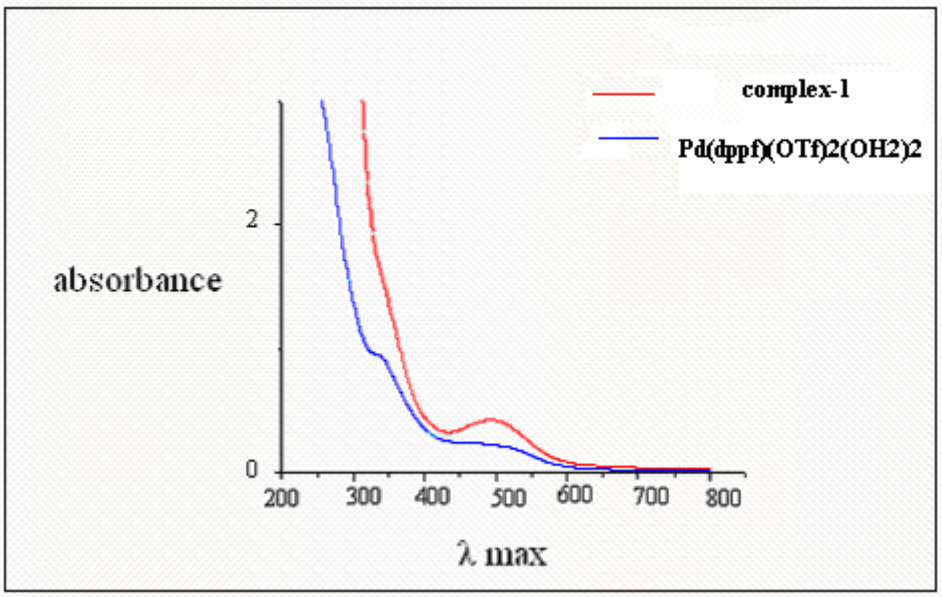

Fig. S3: Absorption spectra of the complex-**1** and $Pd(dppf)(OTf)_2(OH_2)_2$

taking 1.5×10^{-4} M solution in both the cases.