Electronic Supplementary Information

Engineering Metal Site Behavior: Electrophilic-Nucleophilic Dualism in Square-Planar Platinum(II) through Geometry-Controlled Switching

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S1. X-ray diffraction studies

S1.1 Crystal data and structure refinement

Table S1. Crystal data and structure refinement for **1**, **1**·2(1,3-FIB), **1**·2(1,4-FIB), and **1**·FIBiPh.

	1	**1**·2(1,3-FIB)	**1**·2(1,4-FIB)	**1**·FIBiPh
CCDC No.	2421923	2421929	2421928	2421930
Empirical formula	$C_6H_{10}O_2PtS_4$	$C_{18}H_{10}F_8I_4O_2PtS_4$	$C_{18}H_{10}F_8I_4O_2PtS_4$	$C_{18}H_{10}F_8I_2O_2PtS_4$
M_W/g	437.47	1241.19	1241.19	987.39
T/K	100(2)	100(2)	100(2)	100(2)
Radiation	Cu$K\alpha$ (λ = 1.54184)	Cu$K\alpha$ (λ = 1.54184)	Cu$K\alpha$ (λ = 1.54184)	Mo $K\alpha$ (λ = 0.71073)
Crystal color, shape	yellow, prism	yellow, prism	yellow, prism	yellow, prism
Crystal size/mm^3	0.16 × 0.05 × 0.04	0.14 × 0.13 × 0.1	0.142 × 0.094 × 0.051	0.12 × 0.09 × 0.04
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1$	P-1	$P2_1$	$P2_1/c$
a/Å	7.3525(2)	5.9888(2)	4.4993(3)	22.9538(2)
b/Å	7.6217(2)	8.4835(2)	11.1792(7)	14.6829(2)
c/Å	10.4277(3)	14.2189(2)	28.4149(18)	7.34950(10)
α/°	90	79.530(2)	90	90
β/°	101.177(3)	79.269(2)	90.952(7)	90.3850(10)
γ/°	90	88.855(2)	90	90
V/Å^3	573.27(3)	697.88(3)	1429.03(16)	2476.93(5)
Z	2	1	2	4
ρ_c/g·cm^{-3}	2.534	2.953	2.885	2.648
μ/mm^{-1}	29.457	47.615	46.507	8.572
F(000)	408.0	560.0	1120.0	1816.0
2Θ range/°	8.644 to 139.806	6.434 to 139.798	6.222 to 139.982	5.324 to 60.706
Reflections collected	4943	5787	5489	58038
Independent reflections	2148 [R_{int} = 0.0329, R_{sigma} = 0.0382]	2604 [R_{int} = 0.0403, R_{sigma} = 0.0440]	2621 [R_{int} = 0.0593, R_{sigma} = 0.0694]	7033 [R_{int} = 0.0537, R_{sigma} = 0.0292]
Data/restraints/parameters	2148/7/121	2604/0/171	2621/0/170	7033/0/318
Goodness-of-fit on F^2	1.056	1.044	1.056	1.083
Final R indexes [I≥2σ (I)]	R_1 = 0.0382, wR_2 = 0.0990	R_1 = 0.0359, wR_2 = 0.0961	R_1 = 0.0588, wR_2 = 0.1519	R_1 = 0.0228, wR_2 = 0.0443
Final R indexes [all data]	R_1 = 0.0386, wR_2 = 0.0993	R_1 = 0.0368, wR_2 = 0.0974	R_1 = 0.0692, wR_2 = 0.1626	R_1 = 0.0284, wR_2 = 0.0460
Largest diff. peak/hole / e·Å^{-3}	2.11/-2.02	2.29/-1.49	2.10/-1.58	0.94/-0.59

S1.2 Comparison of bond lengths and angles

Table S2. Selected geometric parameters of **1**, **1**·2(1,3-FIB), **1**·2(1,4-FIB), and **1**·FIBiPh.

YOSNAV[1]		**1**		**1** in **1**·2(1,3-FIB)		**1** in **1**·2(1,4-FIB)		**1** in **1**·2(1,4-FIB)	
Bonds/angles	value in Å/°	Bonds/angles	value in Å/°	Bonds/angles	Value in Å/°	Bonds/angles	Value in Å/°	Bonds/angles	Value in Å/°
Pt1–S1	2.313(7)	Pt1–S1 Pt1–S4	2.325(3) 2.324(3)	Pt1–S1	2.3269(14)	Pt1–S1	2.318(3)	Pt1–S1 Pt1–S4	2.3211(8) 2.3191(8)
Pt1–S2	2.320(6)	Pt1–S2 Pt1–S3	2.331(3) 2.336(3)	Pt1–S2	2.3217(14)	Pt1–S2	2.328(3)	Pt1–S2 Pt1–S3	2.3287(8) 2.3322(8)
S1–C1	1.66(3)	S1–C1 S4–C4	1.70(2) 1.70(2)	S1–C1	1.705(6)	S1–C1	1.688(16)	S1–C1 S4–C4	1.698(3) 1.692(3)
S2–C1	1.70(3)	S2–C1 S3–C4	1.70(3) 1.72(2)	S2–C1	1.707(6)	S2–C1	1.728(16)	S2–C1 S3–C4	1.698(3) 1.705(3)
C1–O1	1.32(3)	C1–O1 C4–O2	1.309(16) 1.303(16)	C1–O1	1.297(7)	C1–O1	1.314(19)	C1–O1 C4–O2	1.307(4) 1.305(4)
S1–Pt1–S2	75.1(3)	S1–Pt1–S2 S3–Pt1–S4	75.09(12) 75.16(12)	S1–Pt1–S1	75.29(5)	S1–Pt1–S2	75.46(12)	S1–Pt1–S2 S3–Pt1–S4	75.14(3) 75.04(3)
S1–Pt1–S1	180	S1–Pt1–S4	179.15(14)	S1–Pt1–S1	180	S1–Pt1–S1	180	S1–Pt1–S4	178.39(3)
S2–Pt1–S2	180	S2–Pt1–S3	179.78(14)	S2–Pt1–S2	180	S2–Pt1–S2	180	S2–Pt1–S3	179.85(3)

S1.3 Hydrogen bonding in the cocrystals

Table S3. Parameters of the C–H···X (X = I, F, S, Pt) HBs in the XRD structures of cocrystals **1**·2(1,3-FIB), **1**·2(1,4-FIB), and **1**·FIBiPh.

Structure	Contact	*d*(H···X), Å	*d*(C···X), Å	∠(C–H···X),°
1·2(1,3-FIB)	C2–H2B···I1S	3.0648(4)	3.944(7)	137.7(4)
	C3–H3C···F4S	2.433(4)	3.447(9)	153.5(4)
	C3–H3A···F2S	2.581(4)	3.469(8)	137.5(4)
	C3–H3B···S1	2.8838(13)	3.787(7)	139.9(4)
1·2(1,4-FIB)	C2–H2B···I1S	3.1770(8)	4.106(16)	143.3(9)
	C3–H3A···F2S	2.417(8)	3.46(2)	159.7(9)
	C2–H2B···F4S	2.564(6)	3.390(15)	131.6(9)
	C2–H2A···C1	2.802(17)	3.74(3)	143.6(9)
1·FIBiPh	C5–H5B···Pt1	2.8511(4)	3.677(3)	132.13(16)
	C6–H6C···I2S	3.1358(4)	4.055(3)	141.90(16)
	C6–H6A···S4	2.8898(7)	3.980(3)	173.95(16)
	C6–H6B···S2	2.9940(7)	3.950(3)	146.08(15)

S2. Theoretical calculations

S2.1 Molecular electrostatic potential surfaces for FIBs

To obtain a preliminary assessment of potential electrostatic interactions between complex **1** and the XB donors, we calculated the surface (ρ = 0.001 e/bohr^3)^2 electrostatic potentials[3-5] (ESP) for isolated FIB molecules, as shown in **Figure S1**. The FIBs demonstrate pronounced positive σ-holes along the C–I bond axes. The ESP maxima, localized at the I-atoms, are nearly identical (28.0–28.1, 28.6–28.8, and 29.4–29.5 kcal/mol for 1,3-FIB, 1,4-FIB, and FIBiPh, respectively), thus confirming that the XB donor's geometry plays a determinative role in the metal-involving interactions.

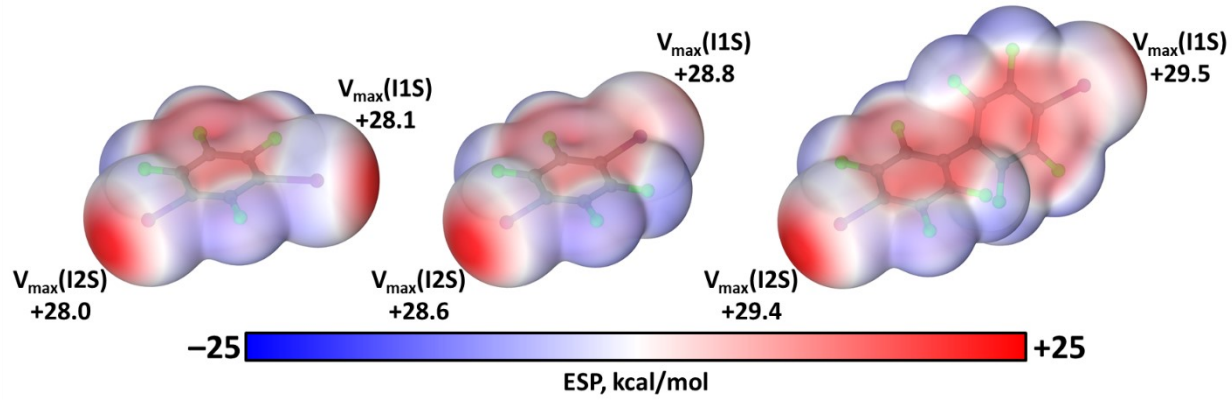

Figure S1. ESP on surface (ρ = 0.001 a.u.) for 1,3-FIB (left), 1,4-FIB (center), and FIBiPh (right) in kcal/mol.

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