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

| $\begin{array}{ c c c c c c c c c c c c c c c c c c c$ | | | | | |
|---|---|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| $\begin{array}{cccccc} CDC No. & 2421923 & 2421929 & 2421928 & 2421920 & 2421920 \\ Empirical formula & C_{a}H_{10}O_{2}H_{20}O_{1}H_{20}F_{3}L_{0}O_{2}H_{3} & C_{18}H_{10}F_{3}L_{0}O_{2}H_{3} & C_{18}H_{10}F_{3}L_{0}O_{2}H_{3} & C_{18}H_{10}F_{3}L_{0}O_{2}H_{3} & C_{18}H_{10}F_{3}L_{0}O_{2}H_{3} & M_{2}M_{2} & M_{2}M_{2}M_{2} & M_{2}M_{2}M_{2}M_{2}M_{2}M_{2}M_{2}M_{2}$ | | 1 | 1 ·2(1,3-FIB) | 1 ·2(1,4-FIB) | 1 · FIBiPh |
| $\begin{array}{l c c c c c c c c c c c c c c c c c c c$ | CCDC No. | 2421923 | 2421929 | 2421928 | 2421930 |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | Empirical formula | $C_6H_{10}O_2PtS_4$ | $C_{18}H_{10}F_8I_4O_2PtS_4$ | $C_{18}H_{10}F_8I_4O_2PtS_4$ | $C_{18}H_{10}F_8I_2O_2PtS_4$ |
| T/K 100(2)100(2)100(2)100(2)Radiation $CuK\alpha$ ($\lambda = 1.54184$) $CuK\alpha$ ($\lambda = 1.54184$) $CuK\alpha$ ($\lambda = 1.54184$) $Mo K\alpha$ ($\lambda = 0.71073$)Crystal color, shapeyellow, prismyellow, prismyellow, prismYellow, prismCrystal size/mm³ $0.16 \times 0.05 \times 0.04$ $0.14 \times 0.13 \times 0.1$ $0.142 \times 0.094 \times 0.051$ $0.12 \times 0.09 \times 0.04$ Crystal systemmonoclinictriclinicmonoclinicmonoclinicmonoclinicSpace group P_2 $P1$ P_2 P_2/α a/λ d/λ 7.525(2) $5.9888(2)$ $4.4993(3)$ $22.9538(2)$ b/A 7.6217(2) $8.4835(2)$ $11.1792(7)$ $14.6829(2)$ c/A $0.4277(3)$ $14.2189(2)$ $28.4149(18)$ $7.34950(10)$ a'' 90 $79.259(2)$ $90.952(7)$ $90.3850(10)$ a'' 90 $79.259(2)$ $90.952(7)$ $90.3850(10)$ p'' 90 $88.855(2)$ 90 90 p'' 90 $88.85(2)$ 90 90 T/A^3 $573.27(3)$ $697.88(3)$ $1429.03(16)$ $2476.93(5)$ Z 2.953 2.885 2.648 $\mu'mm^{-1}$ 29.457 47.615 46.507 8.572 $F(000)$ 408.0 560.0 1120.0 1816.0 20 arage/° 8.644 to 139.806 6.434 to 139.798 6.222 to 139.982 5.324 to 60.706 20 arage/° 8.644 to 139.806 6.434 to 139.798 6.221 to 139.983 <td< td=""><td>M_{W}/g</td><td>437.47</td><td>1241.19</td><td>1241.19</td><td>987.39</td></td<> | M_{W}/g | 437.47 | 1241.19 | 1241.19 | 987.39 |
| Radiation $CuKa (\lambda = 1.54184)$ $CuKa (\lambda = 1.54184)$ $CuKa (\lambda = 1.54184)$ $Mo Ka (\lambda = 0.71073)$ Crystal color, shapeyellow, prismyellow, prismyellow, prismyellow, prismyellow, prismCrystal size/mm³ $0.16 \times 0.05 \times 0.04$ $0.14 \times 0.13 \times 0.1$ $0.142 \times 0.09 \times 0.051$ $0.12 \times 0.09 \times 0.04$ Crystal size/mm³ $0.16 \times 0.05 \times 0.04$ triclinicmonoclinicmonoclinicSpace groupP21P-1P21P2, a/A 7.3525(2)5.9888(2)4.4993(3)22.9538(2) b/A 7.6217(2)8.4835(2)11.1792(7)14.6829(2) c/A 10.4277(3)14.2189(2)28.4149(18)7.34950(10) $a/^{0}$ 9079.530(2)9090 $a/^{0}$ 9088.855(2)9090 $p/^{0}$ 101.177(3)79.269(2)90.952(7)90.3850(10) $p/^{0}$ 9088.855(2)9090 p/a^{0} 9088.855(2)9090 p/a^{0} 91142.93311429.031(6)2476.93(5)Z2124 $p_{a}/grcm^{-3}$ 2.5342.9532.8852.648 μ/mm^{-1} 29.45747.61546.5078.572 $F(000)$ 408.0560.01120.01816.0 20 arange/a8.644 to 139.8066.434 to 139.7986.222 to 139.9825.324 to 60.706 20 arange/a8.644 to 139.8066.434 to 139.788, agam0.006910.02921Data/restraints/param | T/K | 100(2) | 100(2) | 100(2) | 100(2) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | Radiation | $CuK\alpha$ ($\lambda = 1.54184$) | $CuK\alpha$ ($\lambda = 1.54184$) | $CuK\alpha$ ($\lambda = 1.54184$) | Mo <i>K</i> α (λ = 0.71073) |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | Crystal color, shape | yellow, prism | yellow, prism | yellow, prism | yellow, prism |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | Crystal size/mm ³ | 0.16 	imes 0.05 	imes 0.04 | $0.14 \times 0.13 \times 0.1$ | $0.142 \times 0.094 \times 0.051$ | $0.12 \times 0.09 \times 0.04$ |
| $\begin{array}{c c c c c c c c c c c c c c c c c c c $ | Crystal system | monoclinic | triclinic | monoclinic | monoclinic |
| $ \begin{array}{c c c c c c c c c c c c c c c c c c c $ | Space group | P21 | P-1 | P21 | P2 ₁ /c |
| $ \begin{array}{c c c c c c c c c c c c c c c c c c c $ | a/Å | 7.3525(2) | 5.9888(2) | 4.4993(3) | 22.9538(2) |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | b/Å | 7.6217(2) | 8.4835(2) | 11.1792(7) | 14.6829(2) |
| $ \begin{array}{c c c c c c c c c c c c c c c c c c c $ | c/Å | 10.4277(3) | 14.2189(2) | 28.4149(18) | 7.34950(10) |
| $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$ | a/° | 90 | 79.530(2) | 90 | 90 |
| $\begin{array}{c c c c c c c c c c c c c c c c c c c $ | β° | 101.177(3) | 79.269(2) | 90.952(7) | 90.3850(10) |
| $ \begin{array}{c c c c c c c c c c c c c c c c c c c $ | y/° | 90 | 88.855(2) | 90 | 90 |
| $ \begin{array}{c c c c c c c c c c c c c c c c c c c $ | V/Å ³ | 573.27(3) | 697.88(3) | 1429.03(16) | 2476.93(5) |
| $ \begin{array}{c c c c c c c c c c c c c c c c c c c $ | Ζ | 2 | 1 | 2 | 4 |
| $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$ | $\rho_{\rm c}/{\rm g}\cdot{\rm cm}^{-3}$ | 2.534 | 2.953 | 2.885 | 2.648 |
| $ \begin{array}{c c c c c c c c c c c c c c c c c c c $ | μ/mm^{-1} | 29.457 | 47.615 | 46.507 | 8.572 |
| $ \begin{array}{c c c c c c c c c c c c c c c c c c c $ | F(000) | 408.0 | 560.0 | 1120.0 | 1816.0 |
| $ \begin{array}{c c c c c c c c c c c c c c c c c c c $ | 2Θ range/° | 8.644 to 139.806 | 6.434 to 139.798 | 6.222 to 139.982 | 5.324 to 60.706 |
| $ \begin{array}{c c} \mbox{Independent reflections} & 2148 [R_{int} = 0.0329, R_{sigma} = & 2604 [R_{int} = 0.0403, R_{sigma} = & 2621 [R_{int} = 0.0593, R_{sigma} = & 7033 [R_{int} = 0.0537, R_{sigma} = & 0.0440] & 0.0694] & 0.0292] \\ \mbox{Data/restraints/parameters} & 2148/7/121 & 2604/0/171 & 2621/0/170 & 7033/0/318 & 0.0292] & 0.0292 & 0.0292 & 0.0292 & 0.0292 & 0.0292 & 0.0292 & 0.0292 & 0.0292 & 0.0292 & 0.02$ | Reflections collected | 4943 | 5787 | 5489 | 58038 |
| Independent reflections 0.0382] 0.0440] 0.0694] 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 $\geq 2\sigma$ (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 / $e \cdot Å^{-3}$ $2.11/-2.02$ $2.29/-1.49$ $2.10/-1.58$ $0.94/-0.59$ | Indexed and and a discus | $2148 [R_{int} = 0.0329, R_{sigma} =$ | $2604 [R_{int} = 0.0403, R_{sigma} =$ | $2621 [R_{int} = 0.0593, R_{sigma} =$ | 7033 $[R_{int} = 0.0537, R_{sigma} =$ |
| $ \begin{array}{c c c c c c c c c c c c c c c c c c c $ | Independent reflections | 0.0382] | 0.0440] | 0.0694] | 0.0292] |
| Goodness-of-fit on F^2 1.0561.0441.0561.083Final R indexes [I $\geq 2\sigma$ (I)]R ₁ = 0.0382, wR ₂ = 0.0990R ₁ = 0.0359, wR ₂ = 0.0961R ₁ = 0.0588, wR ₂ = 0.1519R ₁ = 0.0228, wR ₂ = 0.0443Final R indexes [all data]R ₁ = 0.0386, wR ₂ = 0.0993R ₁ = 0.0368, wR ₂ = 0.0974R ₁ = 0.0692, wR ₂ = 0.1626R ₁ = 0.0284, wR ₂ = 0.0460Largest diff. peak/hole / $e \cdot Å^{-3}$ 2.11/-2.022.29/-1.492.10/-1.580.94/-0.59 | Data/restraints/parameters | 2148/7/121 | 2604/0/171 | 2621/0/170 | 7033/0/318 |
| Final R indexes [$I \ge 2\sigma(I)$] $R_1 = 0.0382$, $wR_2 = 0.0990$ $R_1 = 0.0359$, $wR_2 = 0.0961$ $R_1 = 0.0588$, $wR_2 = 0.1519$ $R_1 = 0.0228$, $wR_2 = 0.0443$ 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 / $e \cdot Å^{-3}$ $2.11/-2.02$ $2.29/-1.49$ $2.10/-1.58$ $0.94/-0.59$ | Goodness-of-fit on F^2 | 1.056 | 1.044 | 1.056 | 1.083 |
| 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 / $e \cdot Å^{-3}$ 2.11/-2.022.29/-1.492.10/-1.580.94/-0.59 | Final <i>R</i> indexes $[I \ge 2\sigma(I)]$ | $R_1 = 0.0382, wR_2 = 0.0990$ | $R_1 = 0.0359, wR_2 = 0.0961$ | $R_1 = 0.0588, wR_2 = 0.1519$ | $R_1 = 0.0228, wR_2 = 0.0443$ |
| Largest diff. peak/hole / e·Å ⁻³ 2.11/-2.02 2.29/-1.49 2.10/-1.58 0.94/-0.59 | Final <i>R</i> 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 / $e \cdot \text{Å}^{-3}$ | 2.11/-2.02 | 2.29/-1.49 | 2.10/-1.58 | 0.94/-0.59 |

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

S1.2 Comparison of bond lengths and angles

| YOS | NAV 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 | 2.325(3) | Pt1–S1 | 2.3269(14) | Pt1–S1 | 2.318(3) | Pt1–S1 | 2.3211(8) |
| | | Pt1–S4 | 2.324(3) | | | | | Pt1–S4 | 2.3191(8) |
| Pt1–S2 | 2.320(6) | Pt1–S2 | 2.331(3) | Pt1–S2 | 2.3217(14) | Pt1–S2 | 2.328(3) | Pt1–S2 | 2.3287(8) |
| | | Pt1–S3 | 2.336(3) | | | | | Pt1–S3 | 2.3322(8) |
| S1C1 | 1.66(3) | S1C1 | 1.70(2) | S1C1 | 1.705(6) | S1C1 | 1.688(16) | S1–C1 | 1.698(3) |
| | | S4–C4 | 1.70(2) | | | | | S4–C4 | 1.692(3) |
| S2C1 | 1.70(3) | S2C1 | 1.70(3) | S2C1 | 1.707(6) | S2C1 | 1.728(16) | S2C1 | 1.698(3) |
| | | S3–C4 | 1.72(2) | | | | | S3–C4 | 1.705(3) |
| C101 | 1.32(3) | C1–O1 | 1.309(16) | C1–O1 | 1.297(7) | C101 | 1.314(19) | C1–O1 | 1.307(4) |
| | | C4–O2 | 1.303(16) | | | | | C4–O2 | 1.305(4) |
| S1–Pt1–S2 | 75.1(3) | S1–Pt1–S2 | 75.09(12) | S1–Pt1–S1 | 75.29(5) | S1–Pt1–S2 | 75.46(12) | S1–Pt1–S2 | 75.14(3) |
| | | S3–Pt1–S4 | 75.16(12) | | | | | S3-Pt1-S4 | 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) |

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

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 cocrystals1.2(1,3-FIB), 1.2(1,4-FIB), and 1.FIBiPh.

| Structure | Contact | <i>d</i> (H···X), Å | $d(\mathbf{C}\cdots\mathbf{X}),\mathbf{\mathring{A}}$ | ∠(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 ($\rho = 0.001 \text{ e/bohr}^3$)² electrostatic potentials³⁻⁵ (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 ($\rho = 0.001$ a.u.) for 1,3-FIB (left), 1,4-FIB (center), and FIBiPh (right) in kcal/mol.

References

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