

Electronic Supporting Information
for
Clathrochelates meet phosphorus: Thiophosphorylation of iron(II)
dichlorochlathrochelate precursor, synthesis of N,S-donor macrobicyclic
ligands and their palladium(II) complexes as potent catalysts of Suzuki cross-
coupling reaction

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Table S1 Crystallographic data and refinement parameters for the phosphorylated iron(II) clathrochelates

	FeBd ₂ ((C ₆ H ₅) ₂ P(S))ClGm (BF) ₂ · CH ₂ Cl ₂	FeBd ₂ ((C ₆ H ₅) ₂ P(S)) (<i>n</i> -C ₄ H ₉ NH)Gm)(BF) ₂ · 2CH ₂ Cl ₂	FeBd ₂ ((C ₆ H ₅) ₂ P(S)) (2-NHCH ₂ Py)Gm)(BF) ₂ · C ₄ H ₁₀ O · CH ₂ Cl ₂	FeBd ₂ ((C ₆ H ₅) ₂ P(S)) (CH ₃ SCH ₂ CH ₂ NCH ₃)Gm)(BF) ₂ · 2CHCl ₃	[FeBd ₂ ((C ₆ H ₅) ₂ P(S))Gm)(BF) ₂] ₂ (NH(CH ₂) ₅ NH) · 3.5CH ₂ Cl ₂
Empirical formula	C ₄₃ H ₃₂ B ₂ Cl ₃ F ₂ FeN ₆ O ₆ PS	C ₄₈ H ₄₄ B ₂ Cl ₄ F ₂ FeN ₇ O ₆ PS	C ₅₃ H ₄₉ B ₂ Cl ₂ F ₂ FeN ₈ O ₇ PS	C ₄₈ H ₄₂ B ₂ Cl ₆ F ₂ FeN ₇ O ₆ PS ₂	C _{92.5} H ₇₉ B ₄ Cl _{3.5} F ₄ Fe ₂ N ₁₄ O ₁₂ P ₂ S ₂
Fw	1013.60	1135.20	1159.40	1236.15	2059.77
Color, habit	red, prism	red, needle	red, needle	purple, prism	red, needle
Crystal size (mm ³)	0.28 × 0.13 × 0.10	0.31 × 0.06 × 0.05	0.31 × 0.06 × 0.05	0.34 × 0.28 × 0.12	0.42 × 0.07 × 0.05
<i>a</i> (Å)	12.863(3)	16.630(2)	11.1261(5)	13.219(14)	11.892(6)
<i>b</i> (Å)	12.141(3)	12.369(1)	12.3086(6)	13.73(2)	19.945(10)
<i>c</i> (Å)	14.571(4)	32.241(3)	22.0017(11)	16.225(18)	24.004(13)
α (°)	90	90	77.363(4)	90.88(4)	113.552(10)
β (°)	101.508(7)	130.445(2)	78.582(4)	100.76(3)	102.415(12)
γ (°)	90	90	64.675(3)	112.68(5)	90.045(12)
<i>V</i> (Å ³)	2230(1)	5046.8(8)	2638.8(2)	2656(6)	5073(5)
<i>Z</i>	2	4	2	2	2
Crystal system	monoclinic	monoclinic	triclinic	triclinic	triclinic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>d</i> _{calc} (g·cm ⁻³)	1.510	1.494	1.459	1.546	1.348
μ (mm ⁻¹)	0.665	0.648	4.450	0.757	0.522
2θ max (°)	56	52	130	52	52
Independent reflections (<i>R</i> _{int})	10516 (0.057)	10994 (0.174)	8568 (0.138)	16319 (0.035)	19903 (0.157)
Obs.refl./restraints/ parameters	7754 / 1 / 586	5753 / 18 / 651	3839 / 0 / 579	10825 / 18 / 653	7994 / 0 / 1018
<i>R</i> _s ^a % [<i>I</i> > 2σ(<i>I</i>)]	0.055	0.087	0.098	0.064	0.078
<i>R</i> _w ^b %	0.094	0.178	0.246	0.146	0.170
<i>F</i> (000)	1032	2328	1196	1260	2115
GOF ^c	1.00	1.01	1.01	1.01	0.834

$$^a R = \sum | |F_o| - |F_c| | / \sum |F_o|, \quad ^b R_w = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2))]^{1/2}, \quad ^c \text{GOF} = [\sum w(F_o^2 - F_c^2)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}$$

Table S2 Crystallographic data and refinement parameters for the palladium(II) complexes of *N,S*-donor macrobicyclic ligands

	[Pd(FeBd ₂ ((C ₆ H ₅) ₂ P(S)) (2-NCH ₂ Py)Gm)(BF ₂) ₂ Cl] · CH ₂ Cl ₂ · 0.5H ₂ O	[Pd(FeBd ₂ ((C ₆ H ₅) ₂ P(S)) (2-NCH ₂ CH ₂ Py)Gm)(BF ₂) ₂ Cl] · 2CH ₂ Cl ₂
Empirical formula	C ₄₉ H ₃₉ B ₂ Cl ₃ F ₂ FeN ₈ O _{6.5} PPdS	C ₅₁ H ₄₂ B ₂ Cl ₅ F ₂ FeN ₈ O ₆ PPdS
Fw	1235.13	1325.07
Color, habit	dark-red, needle	dark-red, prism
Crystal size (mm ³)	0.28 × 0.06 × 0.05	0.27 × 0.25 × 0.16
<i>a</i> (Å)	17.304(8)	16.746(1)
<i>b</i> (Å)	12.319(7)	12.451(1)
<i>c</i> (Å)	25.949(16)	27.367(2)
α (°)	90	90
β (°)	94.57(1)	94.394(1)
γ (°)	90	90
<i>V</i> (Å ³)	5514(5)	5689.4(6)
<i>Z</i>	4	4
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>d</i> _{calc} (g·cm ⁻³)	1.488	1.547
μ (mm ⁻¹)	0.863	0.932
2 θ max (°)	52	52
Independent reflections (<i>R</i> _{int})	10808 (0.161)	11132 (0.081)
Obs.refl./restraints/ parameters	5776 / 34 / 594	7276 / 12 / 683
<i>R</i> _s ^a % [<i>I</i> > 2 σ (<i>I</i>)]	0.082	0.071
<i>R</i> _w ^b %	0.221	0.190
<i>F</i> (000)	2492	2672
GOF ^c	1.00	1.01

$$^a R = \sum | |F_o| - |F_c| | / \sum |F_o|, \quad ^b R_w = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2))]^{1/2}, \quad ^c \text{GOF} = [\sum w(F_o^2 - F_c^2)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}$$

Table S3 Maxima (λ_{max} , nm ($\varepsilon \cdot 10^{-3}$, mol⁻¹ l cm⁻¹)) of the UV–vis spectra for the phosphorylated iron(II) clathrochelates and their palladium(II) complexes

Complex	λ_1 (ε_1)	λ_2 (ε_2)	λ_3 (ε_3)	λ_4 (ε_4)	λ_5 (ε_5)	λ_6 (ε_6)	λ_7 (ε_7)	λ_8 (ε_8)	λ_9 (ε_9)
FeBd ₂ (Cl ₂ Gm)(BF) ₂ [10b]	264 (14)	285 (7.7)		311 (3.6)	399 (3.2)	448 (3.5)	470 (19)		
FeBd ₂ ((C ₆ H ₅) ₂ P(S))ClGm)(BF) ₂	262(33)	299(11)		355(4.0)	412(4.4)	441(7.7)	467(19)	499(15)	514(2.9)
FeBd ₂ ((C ₆ H ₅) ₂ P(S))(n-C ₄ H ₉ NH)Gm)(BF) ₂	256(23)	283(15)	300(11)	356(3.4)	414(3.9)		465(8.2)	496(20)	542(6.6)
FeBd ₂ ((C ₆ H ₅) ₂ P(S))(H ₂ N(CH ₂) ₅ NH)Gm)(BF) ₂	256(24)	289(17)		320(5.1)	378(3.4)	429(3.6)	468(6.3)	496(16)	533(6.9)
FeBd ₂ ((C ₆ H ₅) ₂ P(S))(2-NHCH ₂ Py)Gm)(BF) ₂	256(18)	284(16)		320(3.3)	407(3.1)		469(5.0)	496(12)	533(4.3)
[Pd(FeBd ₂ ((C ₆ H ₅) ₂ P(S))(2-NCH ₂ Py)Gm)(BF) ₂)Cl]	257(34)	287(17)		331(6.4)	428(5.8)	488(12)	525(7.5)	575(4.4)	605(3.2)
FeBd ₂ ((C ₆ H ₅) ₂ P(S))(2-NHCH ₂ CH ₂ Py)Gm)(BF) ₂	250(14)	267(3.6)	277(20)	299(4.8)	406(2.7)			490(20)	543(4.6)
[Pd(FeBd ₂ ((C ₆ H ₅) ₂ P(S))(2-NCH ₂ CH ₂ Py)Gm)(BF) ₂)Cl]	237(51)	271(2.4)	298(3.9)	326(6.6)	386(3.0)	415(2.2)	438(0.7)	488(13)	577(6.4)
FeBd ₂ ((C ₆ H ₅) ₂ P(S))(CH ₃ SCH ₂ CH ₂ NCH ₃)Gm)(BF) ₂	255(28)	267(0.9)	289(17)	290(2.4)	341(4.2)	394(1.0)	482(10)	489(13)	522(2.2)
[FeBd ₂ ((C ₆ H ₅) ₂ P(S))Gm)(BF) ₂] ₂ (NH(CH ₂) ₅ NH)	260(56)	288(30)	307(16)	356(5.9)	415(8.1)		468(15)	497(39)	548(10)