

Bimetallic complexes with porphyrins containing a cyclometalated phenylpyridine group

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Abstract

Treatment of Ni(HP¹) (H₃P¹ = *meso*-5-[4'-(2''-pyridyl)phenyl]-10,15,20-triphenylporphyrin) with K₂[PdCl₄] in EtOH afforded [Pd{Ni(P¹)}₂(μ-Cl)₂] that reacted with NaS₂CNEt₂ to give Pd(S₂CNEt₂)[Ni(P¹)]. Reaction of Ni(HP¹) with [Ir(H)₂(PPh₃)₂(Me₂-CO)₂][BF₄] afforded Ir(H)Cl(PPh₃)₂[Ni(P¹)]. The crystal structures of Pd(S₂CNEt₂)[Ni(P¹)] and Ir(H)(Cl)(PPh₃)₂[Ni(P¹)] have been determined.

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Keywords: Bimetallic; Cyclometalated; Porphyrin; Nickel; Palladium; Iridium

1. Introduction

Polynuclear metalloporphyrins are of interest due to their potential applications in photoinduced electron transfer [1] and biomimetic redox catalysis [2]. Among various synthetic routes to multiporphyrin arrays [3], one convenient approach is to assemble ligand-appended porphyrins by coordination with appropriate external metal ions. In the past decade, metal-assisted self-assembly of pyridylporphyrins to give dimers and oligomers with interesting architecture and spectral properties has been studied extensively [3–5]. However, analogous multiporphyrins based on cyclometalated C^N ligands have not been well explored [6]. Recently, Pd(II) [7] and Pt(II) [8] complexes with cyclometalated *N*-confused porphyrins have been synthesized. Transition metal complexes containing cyclometalated N^C ligands, particularly 2-phenylpyridine (ppy), have attracted much attention due to their interesting photo-

luminescent properties [9]. For example, Ir(III)–ppy complexes have been used as phosphorescent dopants for organic light-emitting diodes [10] and luminescent labels for biomolecules [11]. In addition, owing to the anionic nature of cyclometalated ligands, polynuclear metal complexes with ppy–porphyrins are electrically neutral and thus have high solubility in organic solvents. In this connection, we seek to synthesize metal complexes with porphyrin-ppy dyads that may have applications in photoinduced electron transfer and bimetallic catalysis. Herein, we report on the synthesis and structural characterization of the first bimetallic complexes with porphyrins containing a cyclometalated ppy group.

2. Experimental

2.1. General information

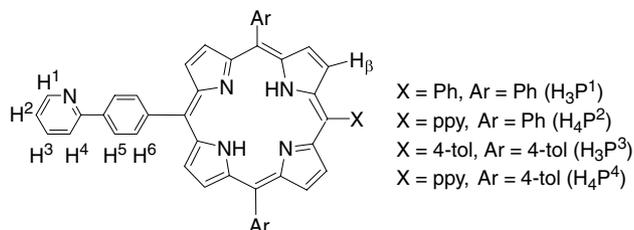
Solvents were purified, distilled, and degassed prior to use. NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300 and 121.5 MHz for

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^1H and ^{31}P , respectively. Chemical shifts (δ , ppm) were reported with reference to SiMe_4 (^1H) and H_3PO_4 (^{31}P). Infrared spectra were recorded on a Perkin–Elmer 16 PC FT-IR spectrophotometer and mass spectra on a Finnigan TSQ 7000 spectrometer. Elemental analyses were performed by Medac Ltd., UK. Benzenedipyrromethane, 4-methylbenzenedipyrromethane [12], and $[\text{Ir}(\text{H})_2(\text{PPh}_3)_2(\text{Me}_2\text{CO})_2][\text{BF}_4]$ [13] were prepared according to literature methods. 4-(2'-Pyridyl)benzaldehyde was purchased from Aldrich Ltd.

2.2. Preparations of ppy-substituted porphyrins (Scheme 1)

A mixture of 4-(2'-pyridyl)benzaldehyde (330 mg, 1.8 mmol) and benzenedipyrromethane (400 mg, 1.8 mmol) in propionic acid (200 ml) was heated at reflux for 1 h. The solvent was removed under reduced pressure and the residue was extracted with dichloromethane and purified by column chromatography (silica gel). H_3P^1 and H_4P^2 were eluted with Et_2O /hexane (1:1) and CH_2Cl_2 /acetone (4:1), respectively. H_3P^3 and H_4P^4 were prepared similarly using 4-methylbenzenedipyrromethane in place of benzenedipyrromethane. The hydrogen atom labeling scheme for the porphyrin ligands is shown below.



H_3P^1 . Yield: 58 mg (9%). ^1H NMR (300 MHz, CDCl_3): δ -2.83 (s, 2H, NH), 7.77 (m, 10H, Ph), 7.92 (m, 1H, H^2), 8.05–8.13 (m, 2H, H^3 and H^4), 8.23 (m, 5H, Ph), 8.36 (dd, $J = J' = 9.0$ Hz, 4H, H^5 and H^6), 8.85–8.94 (m, 9H, H_β and H^1). MS (FAB): m/z 692 ($\text{M}^+ + 1$). UV/Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$) 422 (18), 450 (3.5), 515 (2.6), 551 (2.0), 649 (1.3).

H_4P^2 . Yield: 118 mg (17%). ^1H NMR (300 MHz, CDCl_3): δ -2.71 (s, 2H, NH), 7.38 (t, $J = 7.0$ Hz, 2H, H^2), 7.79–7.81 (m, 5H, Ph), 7.92 (t, $J = 7.0$ Hz, 2H, H^3 or H^4), 8.06 (d, $J = 7.8$ Hz, 2H, H^3 or H^4), 8.23–8.31 (m, 5H, Ph), 8.40 (dd, $J = 8.0$ Hz, 8H, H^5 and H^6), 8.80–8.86 (m, 8H, H_β), 8.87 (d, $J = 2.0$ Hz, 2H, H^1). MS (FAB): m/z 768 ($\text{M}^+ + 1$). UV/Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$) 420 (25), 451 (6.4), 516 (4.0), 554 (1.5), 650 (1.6).

H_3P^3 . Yield: 44 mg (7%). ^1H NMR (300 MHz, CDCl_3): δ -2.48 (s, 2H, NH), 2.72 (s, 9H, *p*-Me) 7.37 (m, 1H, H^2), 7.56 (m, 8H, 4-tol), 7.90 (td, $J = 7.5$ Hz,

$J' = 2$ Hz, 1H, H^3 or H^4), 7.94 (m, 1H, H^4 or H^3), 8.10 (d, $J = 8.0$ Hz, 4H, 4-tol), 8.36 (d, $J = 8.0$ Hz, 4H, H^5 and H^6), 8.86–8.92 (m, 9H, H^1 and H_β). MS (FAB): m/z 734 ($\text{M}^+ + 1$). UV/Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$).

H_4P^4 . Yield: 122 mg (17%). ^1H NMR (300 MHz, CDCl_3): δ -2.32 (s, 2H, NH), 2.72 (s, 6H, *p*-Me), 7.28 (t, $J = 6.8$ Hz, 2H, H^2), 7.80 (m, 8H, 4-tol), 7.94 (d, $J = 7.8$ Hz, 2H, H^3 or H^4), 8.09 (td, $J = 8.0$ Hz, 2H, H^3 or H^4), 8.40 (m, 8H, H^5 and H^6), 8.72–8.79 (m, 10H, H^1 and H_β). MS (FAB): m/z 798 ($\text{M}^+ + 1$). UV/Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$) 420 (26), 452 (7.1), 516 (5.1), 554 (3.2), 592 (2.1), 650 (2.1).

2.3. Preparations of nickel(II) porphyrins

Typically, a solution of $\text{Ni}(\text{acac})_2$ (Hacac = 2,4-pentanedione) (112 mg, 0.44 mmol) in chloroform (20 ml) was added ppy-substituted porphyrin (60 mg, 0.089 mmol) and the mixture was heated at reflux for 4 h. The solvent was pumped off and the residue was extracted with dichloromethane. Recrystallization from methanol at room temperature in air afforded a purple crystalline solid.

$\text{Ni}(\text{HP}^1)$. Yield: 50 mg (75%). ^1H NMR (300 MHz, CDCl_3): δ 7.34 (t, $J = 6.0$ Hz, 1H, ppy), 7.69 (m, 10H, Ph), 7.88 (t, $J = 7.0$ Hz, 1H, ppy), 8.02 (m, 6H, Ph and ppy), 8.14 (d, $J = 8.0$ Hz, 2H, H^5), 8.30 (d, $J = 8.0$ Hz, 2H, H^6), 8.75–8.83 (m, 9H, H^1 and H_β). MS (FAB): m/z 748 ($\text{M}^+ + 1$). UV/Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$) 416 (17), 529 (1.9).

$\text{Ni}(\text{H}_2\text{P}^2)$. Yield: 26 mg (41%). ^1H NMR (300 MHz, CDCl_3): δ 7.35 (t, $J = 6.0$ Hz, 2H, ppy), 7.70 (m, 5H, Ph), 7.89 (t, $J = 5.0$ Hz, 2H, ppy), 7.97–8.02 (m, 7H, Ph and ppy), 8.14 (d, $J = 8.0$ Hz, 4H, H^5), 8.31 (d, $J = 8.0$ Hz, 4H, H^6), 8.76 (d, $J = 5.0$ Hz, 4H, H_β), 8.82 (d, $J = 5.0$ Hz, 4H, H_β), 8.84 (d, $J = 2.0$ Hz, 2H, H^1). MS (FAB): m/z 826 ($\text{M}^+ + 1$). UV/Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$) 418 (16), 529 (1.9).

$\text{Ni}(\text{HP}^3)$. Yield: 51 mg (79%). ^1H NMR (300 MHz, CDCl_3): δ 2.66 (s, 9H, *p*-Me), 7.48 (d, $J = 8.0$ Hz, 6H, 4-tol), 7.74 (t, $J = 7$ Hz, 1H, ppy), 7.89 (d, $J = 8$ Hz, 6H, 4-tol), 8.16 (m, 2H, ppy), 8.19 (d, $J = 6\text{Hz}$, 2H, H^6), 8.39 (d, $J = 8.0$ Hz, 2H, H^5), 8.71–8.79 (m, 8H, H_β), 9.04 (d, $J = 2$ Hz, 1H, H^1). MS (FAB): m/z 790 ($\text{M}^+ + 1$). UV/Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$) 417 (19), 529 (2.4).

2.4. Preparation of $\text{Pd}(\text{S}_2\text{CNET}_2)[\text{Ni}(\text{P}^3)]$ (1)

A mixture of $\text{K}_2[\text{PdCl}_4]$ (14 mg, 0.08 mmol) in methanol (15 ml) and $\text{Ni}(\text{HP}^3)$ (60 mg, 0.08 mmol) in MeOH/THF (3:1, 20 ml) was refluxed overnight. The red precipitate, presumably $[\text{Pd}\{\text{Ni}(\text{P}^3)\}]_2(\mu\text{-Cl})_2$, was collected, washed with Et_2O , and stirred with $\text{NaS}_2\text{CNET}_2$ (36 mg, 0.16 mmol) in $\text{CHCl}_3/\text{acetone}$ at

room temperature for 4 h. The solvent was pumped off and the residue was recrystallized from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give a purple solid. Yield: 23 mg (29%). Anal. Calc. for $\text{C}_{57}\text{H}_{46}\text{N}_6\text{NiPdS}_2 \cdot \text{MeOH} \cdot 1.5\text{H}_2\text{O}$: C, 63.14; H, 4.84; N, 7.62. Found: C, 63.58; H, 4.75; N, 7.40%. ^1H NMR (300 MHz, CDCl_3): δ 1.29 (overlapping t, 6H, Me), 2.65 (s, 9H, *p*-Me), 3.64–3.84 (m, 4H, CH_2), 7.22 (t, $J = 6.0$ Hz, 1H, ppy), 7.47 (d, $J = 7.5$ Hz, 6H, 4-tol), 7.70–7.94 (m, 11H, 4-tol and ppy), 8.53 (d, $J = 6.0$ Hz, 1H, H^1), 8.75 (m, 6H, H_β), 8.87 (d, $J = 5.4$ Hz, 2H, H_β). MS (FAB): m/z 1044 (M^+). UV/Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$) 419 (23), 529 (2.7).

2.5. Preparation of $\text{Pd}(\text{S}_2\text{CNEt}_2)[\text{Ni}(\text{P}^1)]$ (2)

This compound was prepared similarly as for **1** using $\text{Ni}(\text{HP}^1)$ in place of $\text{Ni}(\text{HP}^2)$. Recrystallization from $\text{CH}_2\text{Cl}_2/\text{hexane}$ afforded purple crystals that were suitable for X-ray diffraction. Yield: 15 mg (27%). ^1H NMR (300 MHz, CDCl_3): δ 1.16 (t, $J = 7.0$ Hz, 3H, Me), 1.28 (t, $J = 6.6$ Hz, 3H, Me), 3.62–3.69 (m, 2H, CH_2), 3.79–3.84 (m, 2H, CH_2), 7.23 (t, $J = 6.0$ Hz, 1H, ppy), 7.66–7.75 (m, 10H, Ph), 7.84 (m, 2H, ppy), 7.93–8.01 (m, 7H, Ph and ppy), 8.53 (d, $J = 4.8$ Hz, 1H, ppy), 8.72 (m, 7H, H^1 and H_β), 8.89 (d, $J = 4.8$ Hz, 2H, H_β). MS (FAB): m/z 1003 ($\text{M}^+ + 1$). UV/Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$) 417 (23), 529 (2.2).

2.6. Preparation of $\text{Pd}(\text{S}_2\text{CNEt}_2)[\text{Ni}(\text{HP}^2)]$ (3)

This compound was prepared similarly as for **1** using $\text{Ni}(\text{H}_2\text{P}^2)$ (60 mg, 0.08 mmol) in place of $\text{Ni}(\text{HP}^3)$. Recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ gave a purple solid. Yield: 24 mg (29%). Anal. Calc. for $\text{C}_{59}\text{H}_{43}\text{N}_7\text{NiPdS}_2 \cdot 2.5\text{H}_2\text{O}$: C, 63.09; H, 4.22; N, 8.73. Found: C, 62.63; H, 4.22; N, 8.87%. ^1H NMR (300 MHz, CDCl_3): δ 1.14–1.31 (overlapping t, 6H, Me), 3.65–3.84 (m, 4H, CH_2), 7.34 (t, $J = 6.0$ Hz, 1H, ppy), 7.62–7.74 (m, 11H, Ph and ppy), 7.88–8.01 (m, 6H, ppy), 8.13 (d, $J = 7.8$ Hz, 2H, H^5), 8.30 (d, $J = 8.2$ Hz, 2H, H^6), 8.54 (d, $J = 5.4$ Hz, 1H, ppy), 8.73–8.81 (m, 10H, H_β and H^1). MS (FAB): m/z 1079 (M^+). UV/Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$) 422 (29), 529 (3.9).

2.7. Preparation of $\text{Ir}(\text{H})(\text{Cl})(\text{PPh}_3)_2[\text{Ni}(\text{P}^3)]$ (4)

To a solution of $[\text{Ir}(\text{H})_2(\text{PPh}_3)_2(\text{Me}_2\text{CO})_2][\text{BF}_4]$ (55 mg, 0.061 mmol) in CH_2Cl_2 (20 ml) was added one equivalent of $\text{Ni}(\text{HP}^3)$ (48 mg, 0.061 mmol), and the mixture was stirred at room temperature for 4 h. The solvent was pumped off and the residue was washed with hexane/ Et_2O and then extracted with CH_2Cl_2 . Recrystallization from $\text{CH}_2\text{Cl}_2/\text{hexane}$ afforded a deep red solid. Yield: 32 mg (40%). Anal. Calc. for $\text{C}_{88}\text{H}_{67}\text{ClIrN}_5\text{NiP}_2 \cdot \text{C}_6\text{H}_{14} \cdot 2\text{CH}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$: C, 63.46; H, 4.83; N, 3.85. Found: C, 63.96; H, 4.82; N, 3.58%. ^1H NMR (300 MHz, acetone- d_6): δ -15.45 (t, $J = 7.6$

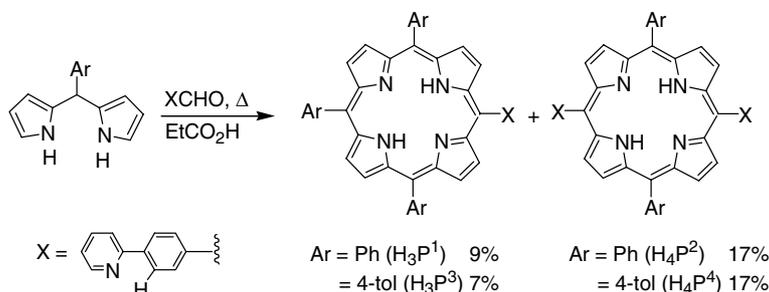
Table 1
Crystallographic data and experimental details for **2** · C_6H_{14} · $0.5\text{CH}_2\text{Cl}_2$ and **5** · C_6H_{14}

	2 · C_6H_{14} · $0.5\text{CH}_2\text{Cl}_2$	5 · C_6H_{14}
Empirical formula	$\text{C}_{60.5}\text{H}_{55}\text{ClN}_6\text{NiPdS}_2$	$\text{C}_{91}\text{H}_{75}\text{ClIrN}_5\text{NiP}_2$
Formula weight	1130.79	1572.75
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
<i>a</i> (Å)	14.615(3)	65.13(1)
<i>b</i> (Å)	17.205(4)	9.585(2)
<i>c</i> (Å)	22.069(5)	24.185(5)
α (°)	77.385(4)	90
β (°)	75.225(4)	90.72(3)
γ (°)	66.922(4)	90
<i>V</i> (Å ³)	4892(2)	15097(5)
<i>Z</i>	4	8
<i>D</i> _{calcd} (g cm ⁻³)	1.535	1.396
<i>T</i> (K)	100(2)	100(2)
μ (Mo K α) (mm ⁻¹)	0.942	2.139
<i>F</i> (000)	2332	6464
Reflections collected	19080	13142
Independent reflections	12653	8189
<i>R</i> ^a , <i>wR</i> ^b (<i>I</i> > 2 σ (<i>I</i>))	0.0590, 0.1563	0.0462, 0.0901
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0997, 0.1727	0.1012, 0.1009
Goodness-of-fit (GoF) ^c	0.996	0.906
Maximum residual density (e/Å ³)	1.391	1.254

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2]^{1/2}$.

^c $\text{GoF} = [\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}$.



Scheme 1. Syntheses of ppy-substituted porphyrins.

Hz, 1H, IrH), 2.81 (s, 9H, *p*-Me), 7.39–7.76 (m, 42H, Ph and 4-tol), 8.08 (m, 6H, ppy), 8.15 (d, $J = 5.0$ Hz, 2H, H_β), 8.73 (d, $J = 5.0$ Hz, 2H, H_β), 8.93 (br. s, 4H, H_β), 9.74 (d, $J = 5.8$ Hz, 1H, H^1). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3): δ 17.26 (s). MS (FAB): m/z 1506 ($\text{M}^+ - \text{Cl}$). IR (KBr, cm^{-1}): 2154 [$\nu(\text{Ir}-\text{H})$]. UV/Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$) 421 (35), 529 (4.2).

2.8. Preparation of $\text{Ir}(\text{H})(\text{Cl})(\text{PPh}_3)_2[\text{Ni}(\text{P}^1)]$ (**5**)

This compound was prepared similarly as for **4** using $\text{Ni}(\text{HP}^1)$ in place of $\text{Ni}(\text{HP}^3)$. Recrystallization from CH_2Cl_2 /hexane afforded deep red crystals that were suitable for X-ray crystallography. Yield: 29 mg (27%). ^1H NMR (300 MHz, CDCl_3): δ -16.3 (t, $J = 7.6$ Hz, 1H, IrH), 6.57 (t, $J = 7.0$ Hz, 1H, ppy), 7.04–7.10 (m, 5H, Ph), 7.18 (m, 15H, Ph), 7.38–7.48 (m, 15H, Ph), 7.71–7.89 (m, 11H, Ph and ppy), 7.98 (m, 6H, H_β and ppy), 8.34 (d, $J = 4.8$ Hz, 1H, H^5), 8.38 (d, $J = 4.8$ Hz, 1H, H^6), 8.74–8.90 (m, 5H, H_β and H^1). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3): δ 13.40 (s). FAB (MS): m/z 1465 ($\text{M}^+ - \text{Cl}$). IR (KBr, cm^{-1}): 2170 [$\nu(\text{Ir}-\text{H})$]. UV/Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$): 422 (37), 529 (4.8).

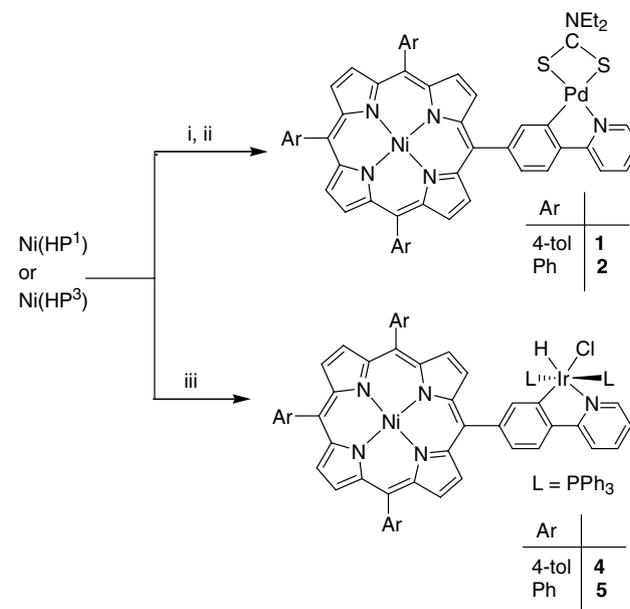
2.9. X-ray diffraction studies

A summary of crystallographic data and experimental details for complexes **2** · C_6H_{14} · $0.5\text{CH}_2\text{Cl}_2$ and **5** · C_6H_{14} are compiled in Table 1. Intensity data were collected on a Bruker SMART APEX 1000 CCD diffractometer using graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 100(2) K. The collected frames were processed with the software SAINT [14]. Structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL [15] software package. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms of C–H bonds were added in idealized positions. For **5**, the carbon atoms in the hexane solvent molecules were disordered and their site occupancies were set to be 0.5. The disordered carbon atoms were refined with fixed C–C bond distances and described without hydrogen atoms.

3. Results and discussion

3.1. Synthesis

In an attempt to prepare ppy-substituted porphyrins, 4-(2'-pyridyl)benzaldehyde was reacted with an equimolar amount of arenediopyromethane (arene = benzene or 4-methylbenzene) in refluxing propionic acid. However, in addition to the expected bis-ppy porphyrins 5,15-bis[4'-(2''-pyridyl)phenyl]-10,20-diarylporphyrin (H_4P^2 and H_4P^4), the mono-ppy porphyrins 5-[4'-(2''-pyridyl)phenyl]-10,15,20-triarylporphyrin (H_3P^1 and H_3P^3) were isolated as minor products (Scheme 1). It seems likely that the formation H_3P^1 and H_3P^3 involves the rearrangement of arenediopyromethane to arenetripyrrolemethane. Metal insertion of these porphyrins with $\text{Ni}(\text{acac})_2$ (Hacac = 2,4-pentanedione) afforded the corresponding $\text{Ni}(\text{II})$ porphyrins (see Section 2). Analogous

Scheme 2. Syntheses of bimetallic complexes with cyclometalated porphyrins: (i) $\text{K}_2[\text{PdCl}_4]$, EtOH, RT; (ii) $\text{Na}(\text{Et}_2\text{NCS}_2)$, acetone/ CH_2Cl_2 , RT; (iii) $[\text{Ir}(\text{H})_2(\text{PPh}_3)_2(\text{Me}_2\text{CO})_2][\text{BF}_4]$, CH_2Cl_2 , RT.

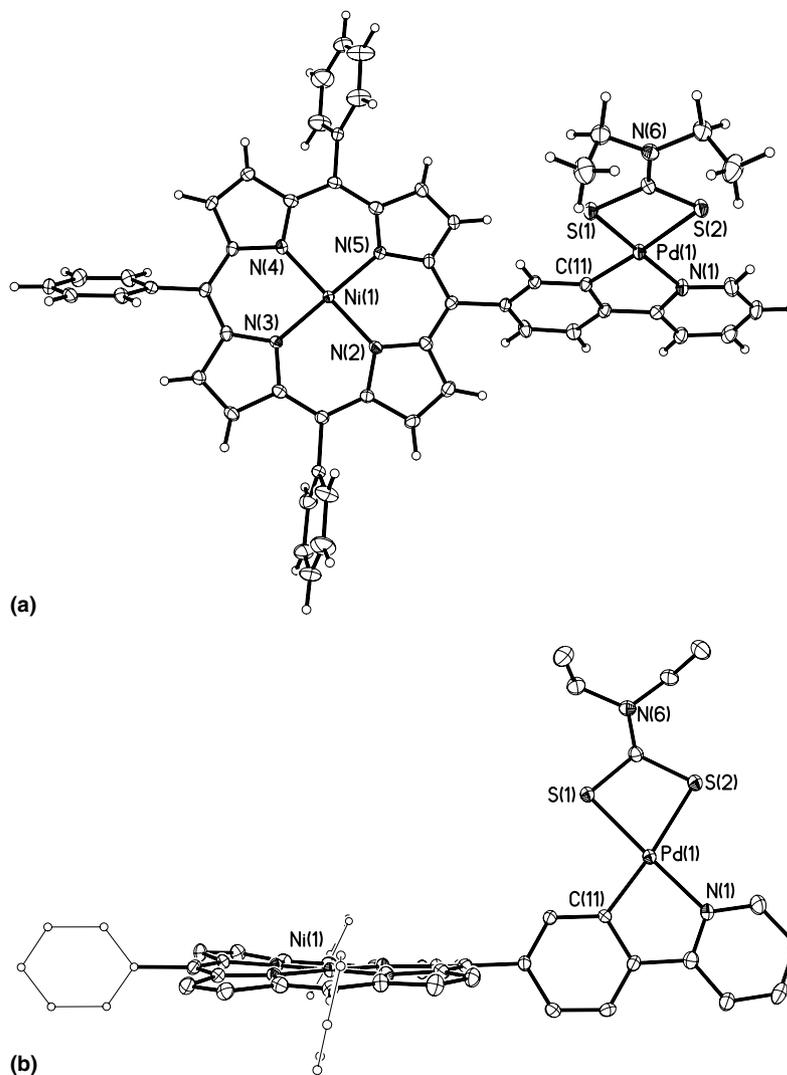


Fig. 1. ORTEP diagram of **2**: (a) top view and (b) side view. The ellipsoids are drawn at 30% probability level. Selected bond distances (Å) and angles (°): Ni(1)–N(2) 1.954(4), Ni(1)–N(3) 1.947(4), Ni(1)–N(4) 1.952(4), Ni(1)–N(5) 1.947(4), Pd(1)–S(1) 2.291(1), Pd(1)–S(2) 2.401(2), Pd(1)–N(1) 2.054(4), Pd(1)–C(11) 2.002(5); C(11)–Pd(1)–N(1) 81.2(2), S(1)–Pd(1)–S(2) 75.13(5), N(2)–Ni(1)–N(3) 90.0(2), N(3)–Ni(1)–N(4) 90.0(2), N(4)–Ni(1)–N(5) 90.0(2), N(5)–Ni(1)–N(2) 90.0(2).

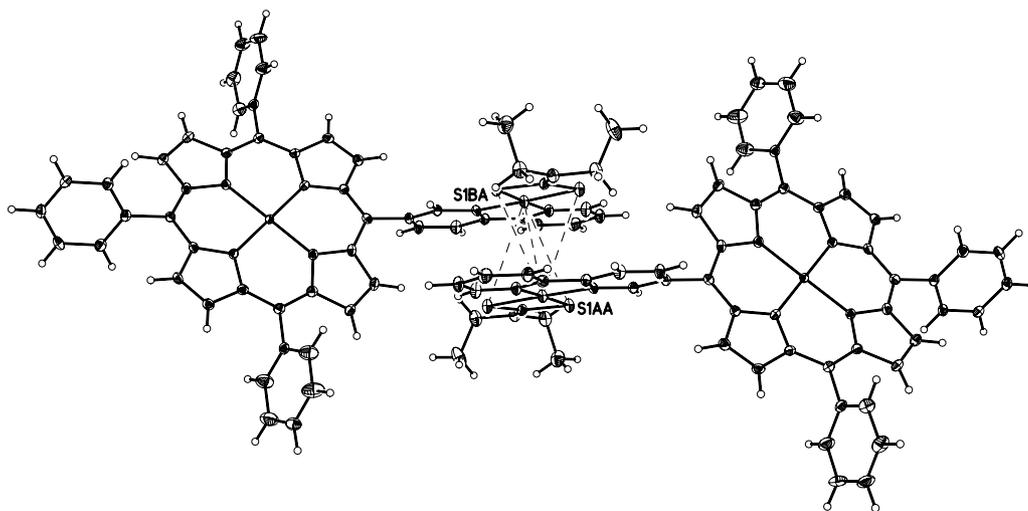


Fig. 2. Part of the crystal packing diagram for **2** · C₆H₁₄ · 0.5CH₂Cl₂ showing intermolecular Pd...Pd¹ [3.827(2) Å] and Pd...Sⁱ [3.833(2) and 3.890(2) Å] contacts.

Fe(III) and Co(II) porphyrins could be prepared similarly using FeCl₂ and Co(CH₃CO₂), respectively.

Cyclometalation of the *meso*-ppy groups in the Ni(II) porphyrins afforded bimetallic complexes. However, metalation of the bis-ppy compounds Ni(H₂P²) and Ni(H₂P⁴) usually yielded mixtures of products that could not be separated easily. Thus, this work focussed on cyclometalation of Ni(II) mono-ppy porphyrins (Scheme 2). Treatment of Ni(HP³) with K₂[PdCl₄] in methanol led to formation of a brown precipitate, presumably the chloro-bridged diporphyrin complex [Pd{Ni(P³)}₂(μ-Cl)₂], which is sparingly soluble in most organic solvents except DMF. Treatment of [Pd{Ni(P³)}₂(μ-Cl)₂] with NaS₂CNEt₂ in CH₂Cl₂/acetone afforded the Pd(II)/Ni(II) complex Pd(S₂CNEt₂)[Ni(P³)] (**1**). Pd(Et₂NCS₂)[Ni(P¹)] (**2**) was prepared similarly from Ni(HP¹) and has been characterized by X-ray crystallography. Attempts to prepare a trinuclear porphyrin complex by reacting Ni(H₂P²) with excess K₂[PdCl₄]/NaS₂CNEt₂ and longer reaction time were unsuccessful. Only the mono-cyclometalated complex Pd(Et₂NCS₂)[Ni(HP²)] (**3**) was isolated. The bis-palladated compound was not formed possibly due to the low solubility of the [Pd{Ni(HP²)}₂(μ-Cl)₂] intermediate that prevented further cyclometalation of the porphyrin.

Similar to 7,8-benzoquinoline and its derivatives [16], the ppy-substituted porphyrins could be cyclometalated readily by Ir(III) hydride compounds. For example, treatment of [Ir(H)₂(PPh₃)₂(Me₂CO)₂][BF₄] [13] with Ni(HP³) and Ni(HP¹) afforded Ir(H)(Cl)(PPh₃)₂[Ni(P³)] (**4**) and Ir(H)(Cl)(PPh₃)₂[Ni(P¹)] (**5**), respectively (Scheme 2). The chloride in **4** and **5** was apparently derived from the CH₂Cl₂ solvent. The presence of the hydride ligand was confirmed by IR [ν (Ir–H) at 2154 and 2170 cm⁻¹] and ¹H NMR (δ –15.45 and –16.20 ppm, respectively) spectroscopy. Consistent with the solid-state structure (vide infra), the hydride for each compound appears as a triplet in the ¹H NMR spectrum due to coupling with the two equivalent PPh₃ ligands. The observation of the hydride resonance at ca. δ –16 ppm suggests that the hydride is *trans* to the pyridyl instead of the phenyl group [13]. An attempt to prepare a trimetallic porphyrin complex by reaction of Ni(H₂P²) with two equivalent of [Ir(H)₂(PPh₃)₂(Me₂CO)₂][BF₄] was not successful.

The optical spectrum of **2** in CH₂Cl₂ displays the Soret band at 417 nm, which is similar to that of Ni(HP¹) (416 nm). On the other hand, the Soret band for **5** is red-shifted by ca. 6 nm and has a higher intensity (ca. 2 times) compared with that for Ni(HP¹). The red shift for **5** probably arises from the deformation of the porphyrin macrocycle (vide infra) [17]. The cyclic voltammogram of **4** in CH₂Cl₂ exhibits couples at 0.58 and 0.86 V vs. Cp₂Fe⁺⁰ that are assigned as the porphyrin-centered oxidations because similar oxidation potentials were also found for the free porphyrin ligand. Com-

plexes **2** and **5** are non-emissive in CH₂Cl₂ solution at room temperature.

3.2. Crystal structures

The solid-state structures of complexes **2** and **5** have been established by X-ray crystallography. Fig. 1 shows the molecular structure of **2**. The porphyrin macrocycle in **2** is essentially planar with a deviation of 0.01 Å from the mean N₄ plane and the geometry around Pd is close to square planar. The plane containing Pd and its coordinating atoms is approximately perpendicular to the porphyrin plane (dihedral angle of ca. 88.4(2)°). The Ni–N distances (av. 1.950(4) Å) are comparable to those in Ni(TPP) (H₂TPP = *meso*-5,10,15,20-tetra-

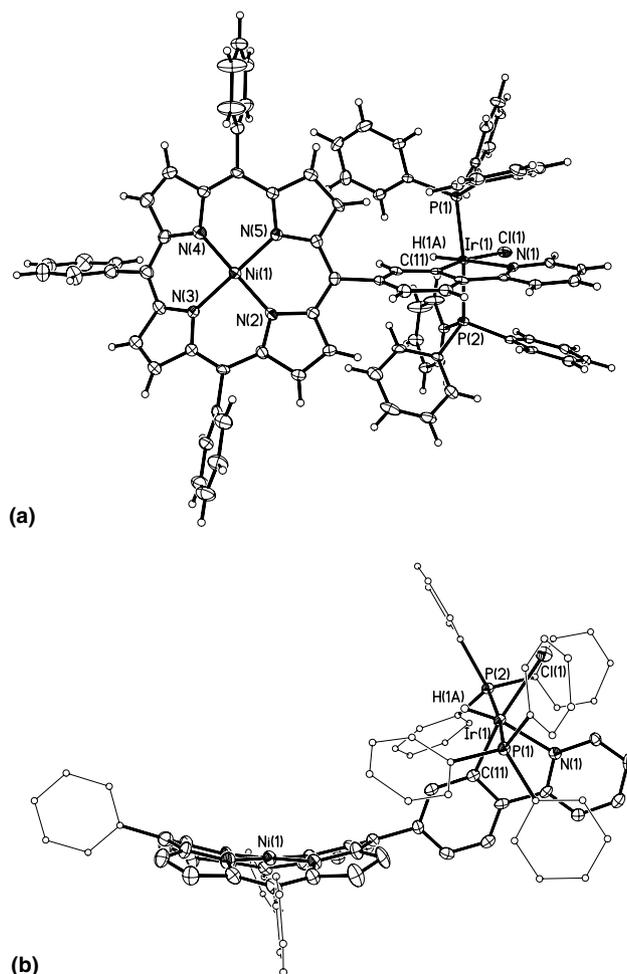


Fig. 3. ORTEP diagram of **5**: (a) top view and (b) side view. The ellipsoids are drawn at 30% probability level. Selected bond distances (Å) and angles (°): Ni(1)–N(2) 1.910(5), Ni(1)–N(3) 1.926(5), Ni(1)–N(4) 1.915(6), Ni(1)–N(5) 1.904(5), Ir(1)–P(1) 2.302(2), Ir(1)–P(2) 2.316(2), Ir(1)–N(1) 2.146(5), Ir(1)–C(11) 2.023(6); C(11)–Ir(1)–N(1) 79.7(2), C(11)–Ir(1)–P(1) 87.0(2), C(11)–Ir(1)–P(2) 94.9(2), N(1)–Ir(1)–P(1) 93.8(1), N(1)–Ir(1)–P(2) 94.4(1), P(1)–Ir(1)–P(2) 171.8(1), N(2)–Ni(1)–N(3) 90.2(2), N(3)–Ni(1)–N(4) 90.1(2), N(4)–Ni(1)–N(5) 89.8(2), N(5)–Ni(1)–N(2) 89.8(2).

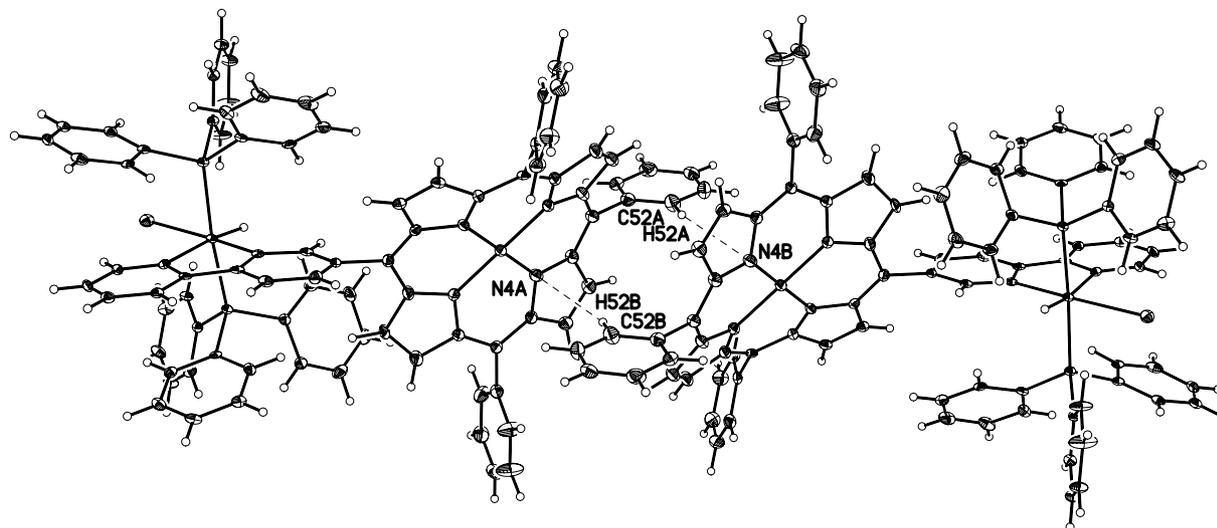


Fig. 4. Part of the crystal packing diagram for $5 \cdot C_6H_{14}$ showing N(pyrrole)···HC(meso-phenyl) hydrogen bonds between two molecules [C(52B)–H(52B) 0.95, H(52B)···N(4A) 2.593(2), C(52B)···N(4A) 3.356(3) Å; C–H···N 164.0(2)°].

phenylporphyrin, 1.931(2) Å [18]. The two Pd–S bonds are not symmetric (2.401(2) and 2.291(2) Å) due to *trans* influence of the phenyl group. The crystal packing diagram of $2 \cdot C_6H_{14} \cdot 0.5CH_2Cl_2$ shows that the lattice consists of pairs of molecules with the Pd···Pd* and Pd···S* separations of 3.827(2) and 3.833(2) and 3.890(2) Å, respectively (Fig. 2).

The molecular structure of **5** is shown in Fig. 3. To our knowledge, this is the first structurally characterized metalloporphyrin that contains a transition metal hydride at its periphery. Unlike **2**, the porphyrin macrocycle in **5** displays a saddle deformation [17] with the mean displacement of the pyrrolic carbons of 0.34 Å, which is comparable to that for other Ni(II) non-planar porphyrin complexes, e.g., Ni(DTPP) (H₂DTPP = 2,3-diethynyl-5,10,15,20-tetraphenyl-porphyrin; 0.32 Å) [19]. Given the planarity of the porphyrin in **2**, the saddle geometry for **5** is probably due to crystal packing effects and/or steric bulk of the PPh₃ ligands. The crystal packing diagram of $5 \cdot C_6H_{14}$ reveals intermolecular hydrogen bonding between a pyrrolic nitrogen and a *meso*-phenyl group of another porphyrin molecule (C···N 3.356(3) Å) (Fig. 4). The average Ni–N distance of 1.914 Å is slightly shorter than that in **2**. The separation between the Ir(III) and Ni(II) centers is ca. 8.6 Å. Similar to [Ir(bq)(PPh₃)₂(H)(H₂O)][SbF₆] (Hbq = 7,8-benzoquinoline) [16a], the geometry around Ir is pseudo-octahedral with two mutually *trans*-PPh₃ ligands. The hydride is *trans* to the pyridyl instead of the phenyl group due to the *trans* influence of the latter that results in a rather long Ir–Cl bond (2.4858(2) Å). The Ir–P, Ir–N, and Ir–C distances (av. 2.309(2), 2.146(5), and 2.023(6) Å, respectively) are similar to those in [Ir(bq)(PPh₃)₂(H)(H₂O)][SbF₆] [16a].

4. Conclusions

In summary, we have synthesized and characterized a new type of bimetallic complex with porphyrins containing a cyclometalated 2-phenylpyridine group. Given the rich coordination chemistry of cyclometalated N[^]C ligands, the ppy–porphyrin dyad may serve as a useful building block for porphyrin dimers and oligomers with interesting structures and properties. With judicious choice of metal ions in the porphyrin and ppy coordination sites, such bimetallic complexes could find applications in redox catalysis and photoinduced electron transfer.

5. Supporting information

Crystallographic data for $2 \cdot C_6H_{14} \cdot 0.5CH_2Cl_2$ and $5 \cdot C_6H_{14}$ have been deposited with the Cambridge Crystallographic Data Centre, CCDC 213142 and 213143, respectively, in CIF format. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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