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Bimetallic complexes of porphyrinphenanthroline: Preparation and catalytic activities

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ABSTRACT

Condensation of tetraphenylporphyrin-2,3-dione with 1,10-phenanthroline-5,6-diamine provided porphyrinphenanthroline (**2**) as the desired ligand. Metallation of the porphyrinic site of **2** with CoCl₂, NiCl₂, ZnCl₂ and CuCl₂ afforded the corresponding metal complexes [Co(**2**)] (**8a**), [Ni(**2**)] (**8b**), [Zn(**2**)] (**8c**) and [Cu(**2**)] (**8d**), respectively. Subsequent reactions of these metalloporphyrins with [(COD)PdCl₂] yielded the corresponding bimetallic complexes [Co/Pd (**9a**), Ni/Pd (**9b**), Zn/Pd (**9c**) and Cu/Pd (**9d**)] in high yields. The bimetallic complexes were characterized by both spectroscopic and elemental analyses. In addition, crystal structure of **9c** was determined to confirm its formulation. The use of these bimetallic complexes as pre-catalysts for Mizoroki–Heck coupling reaction has been examined.

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1. Introduction

The highly π -conjugated chromophores are an important class of compounds in material science due to the small HOMO-LUMO gaps of these molecules [1,2]. In this context, the use of porphyrin as a core unit for construction of the extended-conjugation has received much attention and several compounds of this type have been synthesized, using accessible synthetic approaches [3–18]. Compound **1** is a typical example, which is a porphyrin system containing a 1,10-phenanthroline moiety fused at the β -pyrrole positions, prepared by a Schiff base condensation [18,19]. This phenanthroline-appended porphyrin is capable to build various bimetallic complexes, providing the study of the interaction between metal ions through the conjugation [19]. Other related systems have been reported [18-25], but none of these studies concerns the use of the metal complexes for catalysis. Here we would like to report the preparation of a series of bimetallic complexes with meso-tetraphenylporphyrin-phenanthroline 2 and their catalytic activities on the Mizoroki-Heck coupling reaction.



2. Results and discussion

2.1. Synthesis of meso-tetraphenylporphyrinphenanthroline

The synthetic approach leading to the desired compound **2** (Scheme 1) is similar to that employed for **1** by Crossley [18,19]. Porphyrin- α -dione **5** is prepared according to the reaction steps shown in Scheme 1. Starting from copper(II) *meso*-tetraphenylporphyrin **3**, nitration at β -position was achieved by the reaction of **3** with Cu(NO)₂ in acetic anhydride at room temperature for 20 h. Subsequent de-metallation in dichloromethane under acidic conditions afforded the expected β -nitro-tetraphenylporphyrin **4** in 76% yield [26]. In the reduction of nitro functionality to give β -amino-tetraphenylporphyrin (step iii, Scheme 1), we noticed that carrying out the reaction of **4** with SnCl₂ under microwave heating led to a better yield as compared to an oil-bath heating. For the oxidation of β -amino-tetraphenylporphyrin in the presence of air leading to



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i. Cu(NO₃)₂, Ac₂O; ii H₂SO₄, rt; iii SnCl₂, HCl, microwave, 60^oC, 30 min; iv. SiO₂, *hv*, O₂ v. CF₃COOH, CH₂Cl₂, reflux.

Scheme 1.

5 (step iv, Scheme 1), neither oil-bath nor microwave heating promoted the reaction smoothly. In all instances, only trace amount of **5** was obtained. However, when the reaction was performed under irradiation of a 250 W light bulb in an opened-vessel, the oxidation proceeded smoothly within 1 h, providing the dione **5** in 78% isolated yield.

It is well documented that the condensation of *o*-phenylenediamine with 1,2-diones provides the corresponding pyrazine [27]. However, condensation of **5** with 1,10-phenanthroline-5,6-diamine **6** to yield the desired compound **2** appears to be a challenge. When the condensation was performed under refluxing conditions, instead of the expected porphyrin **2**, the reaction provided an unidentified product. Nevertheless, the desired product **2** could be obtained by running the reaction in the presence of trifluoroacetic acid. Typically, a solution of equal molar amount of both reactants in the presence of excess of CF₃COOH was heated to reflux overnight, yielding the porphyrin **2** in 46% isolated yield.

In the ¹H NMR spectrum of **2**, the NH protons of the pyrrole moiety give a singlet at δ – 2.62; three sets of resonances [δ 9.24

(dd, J = 1.7, 4.3 Hz), 8.84 (dd, J = 1.7, 8 Hz) and 7.72 (dd, J = 4.3, 8 Hz) are in the appropriate area ratio and are assigned to the phenanthroline moiety; the *meso*-protons give rise to two set of signals at δ 8.96 and 8.74, respectively. The spectral data of **2** is quite similar to those of the related species [26], which supports the proposed structure. Further confirmation comes from the X-ray crystal structure of its metal complex (See Section 2.2).

2.2. Preparation of bimetallic palladium complexes

Scheme 2 presents the approach for the preparation a series of bimetallic palladium complexes. Reaction of CoCl₂ with an equal molar amount of **2** resulted in the formation of a mixture of **8a**, **10** and the free ligand. However, reaction of **2** with an excess of CoCl₂ provided the bimetallic complex **10** as the exclusive product in 81% yield. De-complexation of the metal ion binding on the phenanthroline moiety leading to **8a** could be achieved by treatment of **10** with ethylenediaminetetraacetic acid (EDTA) [16]. Typically, a dichloromethane solution of **10** mixed with an aqueous buffer



Scheme 2.

solution of EDTA was stirred vigorously for 24 h and the organic layer provided **8a** as the single product upon concentration.

Finally, the same procedures were adopted to produce three other metalloporphyrins **8b–d**. Coordination of **8** with an equal molar of [(COD)PdCl₂] proceeded smoothly to afford the heterobimetallic complexes **9a–d** in high yields.

On the other hand, the preparation of Mg/Pd complex **9e** is quite straight forward. It is known that the coordination strength of phenanthroline moiety toward the palladium is stronger than that toward the magnesium ions. Thus, treatment of **2** with excess of MgBr₂ followed by the addition of [(COD)PdCl₂] promptly afforded the desired **9e** (Mg/Pd) as shown in Eq. (1).



The absorption spectra of **8a–e** are dominated by the features of the metalloporphyrin core, whose molar absorption coefficients are similar to the free ligand. When **8a** was treated with [(COD)PdCl]₂, a fast color change of the reaction mixture occurred, which turned into red-brown, indicating the formation of new complex. Both Soret and Q-band of **9a** had shifted bathochromically by ~20 nm with respect to **8a**, and the molar absorption coefficient had increased (Table 1). For the nickel complex, the Soret band and Q-band of **9b** are quite similar to those of **8b** even the molar absorption coefficient. Other complexes behave similarly. Electronic absorptions of all complexes are listed in Table 1.

In addition to the absorption spectroscopy, characterization of complexes **9b**(Ni/Pd), **9c**(Zn/Pd) and **9e**(Mg/Pd) complexes were performed by NMR spectroscopy, but not **9a** and **9d** due to the paramagnetic nature. Coordination of the palladium ion toward the phenanthroline moiety of **2** is readily confirmed by its ¹H NMR spectrum, which shows the down-field shifts of H(2,9) and H(4,7) on the phenanthroline moiety (Table 2). The coordination-induced shift is larger for protons in the vicinity of the phenanthroline-binding site, which is a typical observation for the related palladium complex of 1,10-phenanthroline (Table 2) [28].

A single crystal X-ray diffraction study of **9c** confirms the formulation as a Zn/Pd bimetallic complex (Fig. 1). The crystal structure of **9c** includes 2.5 molecule of dmso with one being coordinated to metal center and others as disorder solvent packing. As illustrated in Fig. 1, the Zn atom is seated as expected, in a slightly distorted tetragonal pyramidal coordination with dmso (dimethylsulfoxide) bound to the metal center, whereas the palladium atom is in a disordered square planar geometry with the coordination of phenanthroline and two chloride ligands. Selected

Table 1					
Absorption	spectral	data	of	porphyrin	complexes.

Compound	$\lambda_{\max} (\log \varepsilon) (\text{unit: nm})$
2	434 (5.01), 526 (4.08), 597 (3.77), 653 (2.93)
8a	407 (3.52), 434 (3.68), 567 (2.79)
8b	415 (4.67), 458 (4.41), 567 (3.83), 602 (3.52)
8c	414 (4.47), 443(4.57), 566 (3.78)
8d	405 (4.94), 440 (5.00), 559 (4.22), 597 (3.87)
9a	431 (4.69), 459 (4.56), 584 (3.95)
9b	414 (4.76), 443 (4.65), 560 (3.86), 597 (3.62)
9c	433 (5.11), 459 (4.88), 584 (4.28)
9d	417 (3.97), 454 (3.84), 571 (3.53), 609 (2.51).
9e	440 (4.80), 593 (3.89)

Table 2

Partial ¹H NMR data of phenanthroline moiety in complexes 8 and 9.



Entry	Compound	¹ H NMR data (in CDCl ₃ , ppm)		
		H-(2,9)	H-(3,8)	H-(4,7)
1	2	9.24	7.72	8.84
2	8b	9.22	7.90	8.79
3	8c	9.07	7.69	8.81
4	9b	9.68	7.97	8.89
5	9c	9.41	8.08	8.86
6	9e	9.43	8.07	8.91
7	Phen ^a	9.13	7.62	8.27
8 ^b	(Phen)PdCl ₂	9.28	8.15	9.02

^a Phen: 1,10-phenanthroline.

^b Ref. [28].

bond lengths and bond angles are summarized in Table 3 and all are in the normal range as compared to those of the related species.

Analysis of the crystal packing interactions in the crystal of **9c** 2.5(dmso) reveals another interesting consequence of the extended-conjugation porphyrin ligand. Because of the fixed planarity of the conjugated system, **9**c molecules arrange themselves into two-dimensional layer. In the crystal, each complex interacts with the other molecule via π -stacking interactions (Fig. 2). Two of the intermolecular π -stacking interactions involve the phenanthroline ring of one molecule and the porphyrin core of the adjacent **9c** molecule in the anti parallel fashion. Such intermolecular π -stacking interactions allow the palladium center lining up at the other end. The distance between the palladium centers here is around 3.576 Å, showing a fairly weak metal–metal interaction.

2.3. Catalysis

With a series of bimetallic compounds 9a-e in hand, the use of these complexes as pre-catalysts for the Mizoroki–Heck coupling reaction between iodobenzene and butyl acrylate was investigated (Eq. (2)) [29]. First, complex 9c(Zn/Pd) was employed as a preliminary test for the coupling reaction with which to survey the optimized conditions. Results are summarized in Table 4. For carrying out the reactions in a organic solvent, ionic liquid or water, complex 9c(Zn/Pd) proved to be catalytically inactive yielding negligible amounts of the desired product except in DMF. Both organic and inorganic bases do promote the catalytic reaction, but triethylamine provides the best result.





Fig. 1. ORTEP plot of 9c2.5(dmso) (drawn with 30% probability ellipsoids).

Table 3	
Selected bond distances (Å) and bond angles (°) of 9c ·2.5(dmso).	

Zn(1)-N(1) Zn(1)-N(2) Zn(1)-N(3) Zn(1)-N(4) Zn(1)-O(1) Pd(1)-N(7) Pd(1)-N(8) Pd(1)-N(1) Pd(1)-N(1)-N(1) Pd(1)-N(1)-N(1) Pd(1)-N(1)-N(1) Pd(1)-N(1)-N(1)-N(1) Pd(1)-N(1)-N(1)-N(1)-N(1)-N(1)-N(1)-N(1)-N	2.059(4) 2.061(4) 2.049(4) 2.116(4) 2.090(4) 2.028(4) 2.081(4) 2.088(1)	$\begin{array}{c} N(1)-Zn(1)-N(2) \\ N(2)-Zn(1)-N(3) \\ N(3)-Zn(1)-N(4) \\ N(4)-Zn(1)-N(1) \\ N(1)-Zn(1)-O(1) \\ N(7)-Pd(1)-N(8) \\ N(7)-Pd(1)-Cl(1) \\ N(7)-Pd(1)-Cl(2) \end{array}$	89.3(2) 89.1(2) 88.7(2) 87.5(2) 104.1(2) 81.7(2) 93.8(1) 174.6(1)
Pd(1)–N(8) Pd(1)–Cl(1) Pd(1)–Cl(2)	2.081(4) 2.288(1) 2.288(2)	N(7)-Pd(1)-Cl(1) N(7)-Pd(1)-Cl(2)	93.8(1) 174.6(1)



Fig. 2. Crystal packing of 9c 2.5(dmso).

Table 4	
Results of Heck coupling reaction	catalyzed by 9c (Zn/Pd) ^a .

Entry	Solvent	Base (mmol)	Temperature (°C)	Yield ^b
1	DMF	NaOAc (6)	120	27%
2	DMSO	NaOAc (6)	120	3%
3	H_2O	NaOAc (6)	reflux	trace
4	CICH ₂ CH ₂ CI	NaOAc (6)	reflux	trace
5	CH ₃ CN	NaOAc (6)	reflux	trace
6	xylene	NaOAc (6)	120	trace
7	BMIM ^c	NaOAc (6)	120	trace
8	DMF	(CH ₃ CH ₂) ₃ N (6)	120	96%
9	DMF	pyridine (6)	120	trace
10	DMF	$K_2CO_3(6)$	120	53%
11	DMF	$K_{3}PO_{4}(6)$	120	96%

 $^{\rm a}$ Reactions conditions: C₆H₅I (5 mmol), butyl acrylate (6 mmol), **9c**(Zn/Pd) (0.05 mmol), tetraethylammonium bromide (2 mmol) in solvent (5 mL) for 24 h. $^{\rm b}$ Based on the GC analysis.

^c BMIM: 1-butyl-3-methylimidazolium bromide.

The optimized procedure is also applied to other bimetallic palladium complexes and the results are shown in Fig. 3. As shown in the diagram, complex 9c(2n/Pd) appears to be the most active and the yield reaches to 100% after 30 min. Interestingly, we found that the reaction did not prove any acceleration under the irradiation of light. It is noteworthy that the catalytic activities of 9b(Ni/Pd), 9d(Cu/Pd) and 9e(Mg/Pd) do not show any substantially difference among them, but less active than that of 9c(2n/Pd). The complex 9a(Co/Pd) is the least active in this series of bimetallic complexes. This trend is somewhat in line with the relative donating nature of metalloporphyrins, which is consistent with the observation by others' investigation [30,31].

Under the similar reaction conditions, the coupling reaction catalyzed by [(1,10-phenanthroline)PdCl₂] appeared to proceed very slowly; less than 10% of yield was observed after 5 h, indicating that all bimetallic species acting as pre-catalysts for the coupling reaction are superior to that of [(1,10-phenanthroline)PdCl₂]. In addition, complex **8c** did not show any catalytic activity at all, indicating the requirement of palladium ions for the catalysis. In this investigation, the variation of metal ions at the porphyrinic site was found to have considerable effects on the catalytic Mizoroki-Heck reaction, suggesting that the metalloporphyrin core significantly influences the active site of the palladium catalyst. However, the detail interaction needs further research.



Fig. 3. Plot of the yields vs. time for coupling reaction catalyzed by 9a-e.

3. Summary

In conclusion, we have achieved the preparation and characterization of heter-bimetallic porphyrin complexes. These complexes exhibit markedly different catalytic activity on the typical Mizoroki–Heck reaction depending on the central metal ions. Such tunable nature of porphyrins by central metal ions should allow further investigation on effective complexes for catalytic reactions. Although the photo-irradiation did not lead to a better activity of the metal complex during the coupling catalysis, it does imply the usefulness of metalloporphyrin acting as a modulating substituent in other reactions. More fine-tune studies as well as the interactions of metal ions are currently under investigated.

4. Experimental

4.1. General

All reactions and manipulations were performed under a dry nitrogen atmosphere unless otherwise noted. Tetrahydrofuran was distilled under nitrogen from sodium/benzophenone. Dichloromethane was dried over CaH₂ and distilled under nitrogen. Other solvents were degassed before use. Chemicals were purchased from commercial source and used without further purification. Copper(II) *meso*-tetraphenylporphyrin **3** and [(1,10-phenanthroline)PdCl₂] were prepared according to the method reported [32,28]. A buffer solution of EDTA was prepared by mixing Na₂(-H₂EDTA)·2H₂O (372 mg), sodium acetate (0.22 g) and acetic acid (0.21 mL) in water (100 mL).

Nuclear magnetic resonance spectra were recorded in CDCl₃ or dmso- d_6 on a Bruker AVANCE 400 spectrometer. Chemical shifts are given in parts per million relative to Me₄Si for ¹H and ¹³C{¹H} NMR. UV–Vis spectrum was determined on a Hitachi 3310 spectrometer. Microwave irradiation was carried out in a Discovery microwave heating apparatus with temperature controller (CEM Corp., Matthews, NC).

4.2. Synthesis and characterization

4.2.1. Compound (4)

Complex **3** (1.0 g, 1.5 mmol) and acetic anhydride (18 mL) were dissolved in dichloromethane (250 mL). Under nitrogen atmosphere, $Cu(NO_3)_2$ (920 mg, 3.8 mmol) in acetic anhydride (92 mL) was added and the resulting mixture was stirred at room temperature for 20 h. Water (100 mL) was added and the organic layer was separated. Upon concentration of the organic extracts, the residue was re-crystallized from methanol to yield the nitro com-

pound (0.97 g, 90%). This compound was then dissolved in dichloromethane (30 mL). Concentrated sulfuric acid (8 mL) was added to the above solution. This mixture was stirred for 8 min and then poured into ice/water. The CH₂Cl₂ extracts was separated, dried over MgSO₄ and concentrated. The crude product was re-crystallized from methanol to yield **4** as purple solids (0.74 g, 84%): ¹H NMR (CDCl₃): δ 9.03 (s, 1H), 9.00 (d, *J* = 5.2 Hz, 1H), 8.93 (d, *J* = 5.2 Hz, 1H), 8.88 (m, 2H), 8.71 (m, 2H), 8.25–8.16 (m, 8H), 7.79–7.68 (m, 12H), –2.63 (s, 2H, –NH), which is essentially identical to those reported in literature [26].

4.2.2. meso-Tetraphenylporphyrin- α -dione (5)

Concentrated hydrochloric acid (0.14 mL) was added to a mixture of **4** (20 mg, 0.03 mmol) and SnCl₂ (70 mg, 0.36 mmol) in CH₂Cl₂ under nitrogen atmosphere. The mixture was irritated with microwave at 60 °C under the power setting on 60 W for 30 min. After the irritation, the organic layer was separated and dried over Na₂SO₄. Silica gel (100 mg) was added to the above solution and the resulting mixture was shined with light (Bulb light – 100 W) under oxygen atmosphere for 1 h. Upon crystallization, compound **5** was obtained as brown solids (15 mg, 78%). ¹H NMR (CDCl₃): δ 8.75 (d, *J* = 5 Hz, 2H), 8.60 (d, *J* = 5 Hz, 2H), 8.57 (s, 2H), 8.13 (m, 4H), 7.90 (m, 4H), 7.76–7.66 (m, 12H), –1.99 (s, 2H), which is identical to those reported in literature [32].

4.2.3. meso-Tetraphenylporphyrinphenanthroline (2)

Under nitrogen atmosphere, trifluoroacetic acid (25 µL) was added to a mixture of 5 (24 mg, 0.037 mmol) and 1,10-phenanthroline-5,6-diamine (7.8 mg, 0.037 mmol) in CH₂Cl₂ (7 mL). The mixture was heated to reflux with stirring for 24 h. The color of solution turned from brown into dark green. Aqueous NaHCO₃ (4%) was added to neutralize the acid and the organic layer separated. The organic extracts were dried over Na₂SO₄ and concentrated. The residue was chromatographed on silica gel with elution of CH₃OH/CH₂Cl₂(V:V = 1:10) and a purple-red color band was collected to yield 2 as purple-red solids (14 mg, 46%). m.p. > 300 °C; ¹H NMR (CDCl₃, 400 MHz) δ : 9.24 (dd, J = 1.7, 4.3 Hz, 2H), 8.96 (s, 4H), 8.84 (dd, J = 1.7, 8 Hz, 2H), 8.74 (s, 2H), 8.29 (m, 4H), 8.22 (m, 4H), 8.02 (m, 2H), 7.90 (m, 4H), 7.78 (m, 6H), 7.72 (dd, I = 4.3, 8 Hz, 2H), -2.62 (br, s, 2H, NH); ¹³C NMR δ : 155.2, 151.7, 151.5, 142.0, 141.5, 139.4, 138.2, 134.3, 134.1, 133.9, 133.6, 128.3, 128.2, 128.1, 128.0, 127.8, 127.5, 127.4, 127.1, 127.0, 126.8, 126.7, 123.5, 121.6. UV-Vis (CH₂Cl₂): λ_{max} $(\log \varepsilon) = 434 (5.01), 526 (4.08), 597 (3.77), 653 (2.93) \text{ nm. FAB MS}$ $[M+H^+]$ m/z = calcd. for C₅₆H₃₅N₈: 819.30; found: 819.32. Anal. Calc. for C₅₆H₃₄N₈: C, 82.13; H, 4.18; N, 13.68. Found: C, 82.01; H, 3.98; N, 13.35%.

4.2.4. Bicobalt complex (10)

A mixture of **2** (30 mg, 37 µmol) and CoCl₂ (20 mg, 154 µmol) in DMF (10 mL) was heated to reflux for 12 h. After the reaction, the mixture was partitioned in water and dichloromethane. The dichloromethane layer was dried over Na₂SO₄ and concentrated under vacuum to give **10** as purple-red solids (30 mg, 81%): UV–Vis (CH₂Cl₂): λ_{max} (log ε) = 411 (4.68), 561 (3.89). FAB Mass: *m/z* calcd. for C₅₆H₃₂ClCo₂N₈ [M–Cl]⁺ = 969.1; found: 969.0. *Anal.* Calc. for C₅₆H₃₂Cl₂Co₂N₈: C, 66.88; H, 3.21; N, 11.14. Found: C, 66.59; H, 2.92; N, 10.86%.

4.2.5. Complex 8a

Complex **10** (50 mg, 50 µmol) in CH_2Cl_2 (10 mL) was added to the EDTA buffer solution (10 mL) and the resulting mixture was stirred at room temperature for 24 h. The organic layer was then separated, washed with 4% sodium bicarbonate solution, dried and concentrated to yield **8a** as purple solids (35 mg, 80%): UV– Vis (CH_2Cl_2): λ_{max} (log ε) = 364 (3.34), 407 (3.52), 434 (3.68), 567 (2.79); FAB Mass: m/z calcd. for $C_{56}H_{33}CoN_8$ [M+H]⁺: 876.22; found: 876.06. *Anal.* Calc. for $C_{56}H_{32}CoN_8$: C, 76.79; H, 3.68; N, 12.79. Found: C, 76.56; H, 3.38; N, 12.48%.

4.2.6. Complex 8b

A mixture of 2 (58 mg, 70.8 μ mol) and NiCl₂ (18 mg, 141 μ mol) in DMF (10 mL) was heated to reflux for 12 h. After removal of DMF under vacuum, the residue was dissolved in CH₂Cl₂ (50 mL) and then washed with water (100 mL). The organic layer was added to a EDTA buffer solution (100 mL) and the mixture was stirred at ambient temperature for 24 h. The organic layer was then separated, washed with 4% sodium bicarbonate solution, dried and concentrated to yield **8b** as pink solids (84%): ¹H NMR (CDCl₃, 400 MHz) δ : 9.22 (d, J = 4.8 Hz, 2H), 8.79 (d, J = 4.8 Hz, 4H), 8.72 (d, J = 8 Hz, 2H), 8.70 (s, 2H), 8.02 (d, J = 7.2 Hz, 4H), 8.00 (d, J = 7.2 Hz, 4H), 7.90 (m, 2H), 7.78 (m, 4H), 7.66 (m, 8H); ¹³C NMR (CDCl₃, 100 MHz) δ: 151.67, 149.28, 147.45, 147.12, 143.62, 142.08, 141.18, 140.34, 139.88, 137.84, 133.92, 133.31, 133.04, 132.23, 132.03, 131.61, 127.97, 127.88, 127.34, 127.29, 126.92, 123.47, 120.83, 116.31; UV–Vis (CH₂Cl₂): λ_{max} (log ε) = 270 (4.28), 415 (4.67), 458 (4.41), 567 (3.83), 602 (3.52). FAB Mass: *m*/*z* calcd. for C₅₆H₃₃NiN₈ [M+H]⁺: 875.22; found: 875.20. Anal. Calc. for C₅₆H₃₂NiN₈: C, 76.82; H, 3.68; N, 12.80%.

4.2.7. Complex 8c

A saturated solution of zinc acetate in methanol (4 mL) was mixed with a solution of 2 (58 mg, 70.8 μ mol) in CH₂Cl₂ (10 mL). This solution was heated to reflux for 12 h. The color of solution turned into dark green. After removal of organic solvents under vacuum, the residue was dissolved in CH₂Cl₂ (5 mL) and then washed with water (10 mL). The organic layer was added to a EDTA buffer solution (10 mL) and the mixture was stirred at ambient temperature for 24 h. The organic layer was then separated, washed with 4% sodium bicarbonate solution, dried and concentrated to yield 8c as dark green solids (55%): ¹H NMR (CDCl₃, 400 MHz) δ 9.07 (d, J = 3.2 Hz, 2H), 8.93 (d, J = 4.8 Hz, 4H), 8.87 (s, 2H), 8.83 (d, J = 5.4 Hz, 2H), 8.23 (m, 8H), 8.00 (m, 2H), 7.87 $(m, 4H), 7.76 (m, 6H), 7.69 (dd, J = 5.4, 4.8 Hz, 2H); {}^{13}C NMR (CDCl_3, 100)$ 100 MHz) 8: 152.13, 151.33, 150.00, 149.36, 149.30, 147.20, 142.79, 142.31, 139.87, 137.64, 134.13, 133.99, 133.75, 132.36, 131.80, 131.55, 128.11, 127.57, 127.10, 126.88, 126.51, 123.40, 123.28, 118.18; UV–Vis (CH₂Cl₂): λ_{max} (log ε) = 348 (3.83), 414 (4.47), 44 3(4.57), 566 (3.78). FAB Mass m/z calcd. for C₅₆H₃₃ZnN₈ [M+H]⁺: 881.21; found: 881.01. Anal. Calc. for C₅₆H₃₂ZnN₈: C, 76.23; H, 3.66; N, 12.70. Found: C, 75.95; H, 3.28; N, 12.56%.

4.2.8. Complex 9a(Co/Pd)

A mixture of **8a** (10 mg, 11 µmol) and [(COD)PdCl₂] (5.2 mg, 11 µmol) was placed in a flask capped with septum and the reaction vessel was flashed with nitrogen gas. Degassed CH₂Cl₂ (3 mL) was syringed into the flask. The solution was stirred at ambient temperature for 8 h. After the reaction, ether (15 mL) was added to give the red-brown precipitates, which was collected and washed with ether and dichloromethane. The obtained solid was dried under vacuum to provide the desired complex **9a** as deep red solids (73%): UV–Vis (CH₂Cl₂): λ_{max} (log ε) = 284 (4.39), 369 (4.32), 431 (4.69), 459 (4.56), 584 (3.95). ESI HRMS *m/z* calcd. for C₅₆H₃₂Cl₂CoN₈Pd: 1053.0494. Found: 1053.0490. *Anal.* Calc. for C₅₆H₃₂Cl₂CoN₈Pd: C, 63.86; H, 3.06; N, 10.64. Found: C, 63.57; H, 2.87; N, 10.54%.

4.2.9. Complex 9b(Ni/Pd)

The preparation of this complex is similar to that for **9a**. Reaction of **8b** (10 mg, 11 µmol) with [(COD)PdCl₂] (5.2 mg, 11 µmol) provided the desired complex as pink-red solids (83%): ¹H NMR (CDCl₃, 400 MHz) δ : 9.68 (d, *J* = 4.8 Hz, 2H), 8.89 (d, *J* = 8 Hz, 2H), 8.79 (d, *J* = 4.8 Hz, 4H), 8.70 (s, 2H), 7.99 (m, 4H), 7.97 (m, 4H), 7.91 (m, 4H), 7.81 (m, 4H), 7.70 (m, 6H); UV–Vis (CH₂Cl₂): λ_{max} (log ε) = 292 (4.51), 414 (4.76), 443 (4.65), 560 (3.86), 597 (3.62); FAB Mass *m*/*z* calcd. for C₅₆H₃₃Cl₂NiN₈Pd [M+H]⁺: 1051.06; found: 1051.05. *Anal.* Calc. for C₅₆H₃₂Cl₂N₈NiPd: C, 63.88; H, 3.06; N, 10.64. Found: C, 63.39; H, 2.78; N, 10.46%.

4.2.10. Complex 9c(Zn/Pd)

The preparation of this complex is similar to that for **9a**. Reaction of **8c** (10.1 mg, 11 µmol) with [(COD)PdCl₂] (5.2 mg, 11 µmol) yielded the desired complex as dark green solids (67%). Upon crystallization from CH₂Cl₂/dmso, complex [**9c** 2.5(dmso)] was obtained as dark green crystalline solids: ¹H NMR (dmso-*d*₆, 400 MHz) δ 9.41 (d, *J* = 4.8 Hz, 2H), 8.86 (d, *J* = 8 Hz, 2H), 8.79 (d, *J* = 4.8 Hz, 4H), 8.73 (s, 2H), 8.22 (m, 10H), 8.08 (m, 2H), 7.89 (m, 4H), 7.79 (m, 6H); UV–Vis (CH₂Cl₂): λ_{max} (log ε) = 276 (4.72), 351 (4.48), 433 (5.11), 459 (4.88), 584 (4.28). *Anal*. Calc. for C₅₆H₃₂Cl₂N₈ZnPd_{2.5} (CH₃SOCH₃): C, 58.38; H, 3.77; N, 8.93. Found: C, 58.01; H, 3.49; N, 8.78%.

4.2.11. Complex 9d(Cu/Pd)

A solution of 2 (58 mg, 70.8 μ mol) and Cu(CH₃COO)₂ (25 mg, 141 μ mol) in methanol/CH₂Cl₂ (V:V = 1:5) (60 mL) was heated to reflux for 12 h. After removal of solvents, the residue was dissolved in a mixture of dichloromethane (100 mL) and EDTA buffer solution (100 mL). The resulting mixture was stirred for 24 h. The organic layer was then separated, washed with 4% sodium bicarbonate solution and dried over Na2SO4. Upon concentration, 8d was obtained as dark-brown solids. UV-Vis (CH₂Cl₂): λ_{max} (log ε) = 405 (4.94), 440 (5.00), 559 (4.22), 597 (3.87). [(COD)PdCl₂] (30 mg, 64 µmol) was added to a solution of 8d in dichloromethane with stirring for 8 h. Upon concentration of the volume down to 5 mL, ether was added and the brown solids precipitated out from the solution, which was subsequently washed with ether, dichloromethane and methanol. Complex 9d was obtained brown solids (85%): UV–Vis (CH₂Cl₂): λ_{max} (log ε) = 278 (4.26), 417 (3.97), 454 (3.84), 571 (3.53), 609 (sh). Anal. Calc. for C₅₆H₃₂Cl₂CuN₈Pd: C, 63.59; H, 3.05; N, 10.59. Found: C, 63.24; H, 2.75; N, 10.37%.

4.2.12. Complex 9e(Mg/Pd)

A solution of **2** (13.6 mg, 16.6 mol) and MgBr₂· GH_2O (10 mg, 330 mol) in DMF (5 mL) was heated to reflux for 12 h. The color of solution turned from red into dark green. After removal of the solvent, the residue was dissolved in dichloromethane (5 mL) and [(COD)PdCl₂] (5 mg, 16.6 mol) was added. The resulting mixture

was stirred for another 4 h. Ether (20 mL) was added to the reaction mixture to yield green precipitates, which was collected and washed with ether, dichloromethane and methanol (80%): ¹H NMR (dmso-*d*₆, 400 MHz) δ 9.43 (d, *J* = 4.6 Hz, 2H), 8.91 (d, *J* = 8 Hz, 2H), 8.69 (d, *J* = 4.6, 2H), 8.59 (d, *J* = 8 Hz, 2H), 8.66 (s, 2H), 8.25 (m, 6H), 8.19 (m, 4H), 8.07 (m, 2H), 7.90 (m, 4H), 7.80 (m, 6H); UV–Vis (CH₂Cl₂): λ_{max} (log ε) = 279 (4.38), 353 (4.17), 440 (4.8), 593 (3.89). *Anal.* Calc. for C₅₆H₃₂Cl₂MgN₈Pd: C, 66.04; H, 3.17; N, 11.00. Found: C, 65.78; H, 2.87; N, 10.77%.

4.3. Catalysis

To a 10 mL round-bottom flask equipped with a condenser was placed with bimetallic complex (2.5μ mol), phenyl iodide (0.5 mmol), potassium phosphate (1 mmol), butyl acrylate (0.75 mmol) and solvent (0.5 mL). The mixture was heated under refluxing temperature for a certain period. Upon cooling, the reaction mixture was poured into a diluted hydrochloric acid (10%) and extracted with dichloromethane. The extract was dried, concentrated and analyzed by ¹H NMR spectroscopy and GC. Results of the coupling reactions are listed in Table 4.

4.4. X-ray crystallographic analysis

Crystals suitable for X-ray determination were obtained for by recrystallization at room temperature. Cell parameters were determined either by a Nonius Kappa CCD diffractometer. Complex **9c** contains 2.5 molecules of dmso with one coordinating to the metal center and the others being solvents. ORTEP plot of **9c** 2.5(dmso) is drawn with 30% probability ellipsoids and partial labeling for clear view in Fig. 2. Crystal data for **9c** 2.5(dmso): C₆₁H₄₇Cl₂N₈O_{2.5}PdS_{2.5}Zn, Fw = 1254.89, triclinic, $P\bar{1}$ – space group, a = 13.3078(13) Å, b = 14.7930(17) Å, c = 15.2722(19) Å, $\alpha = 103.279(10)^{\circ}$, $\beta = 103.075(9)^{\circ}$, $\gamma = 105.548(10)^{\circ}$, V = 2683.0(5) Å³, Z = 2, $D_{calc} = 1.553$ Mg/m³, $F(0 \ 0 \ 0) = 1278$, crystal size $0.25 \times 0.15 \times 0.10$ mm³. 12 170 reflections collected, 9461 independent reflections ($R_{int} = 0.0586$), $\theta = 3.26-67.99^{\circ}$, fullmatrix least-squares on F^2 for the refinement, $R_1 = 0.0493$, $wR_2 = 0.1066$ ([$I \ge 2\sigma(I)$]), goodness of fit (GOF) on F^2 : 0.913.

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Appendix A. Supplementary material

CCDC 708936 contains the supplementary crystallographic data for **9c**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.ica.2010.07.008.

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