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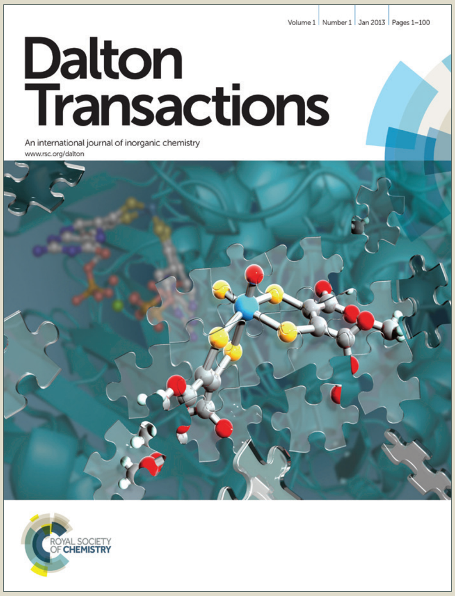

Cyclometalated Pd(II) and Ir(III) 2-(4-bromophenyl)pyridine complexes with *N*-heterocyclic carbenes (NHCs) and acetylacetonate (acac): synthesis, structures, luminescent properties and application in one-pot oxidation/ Suzuki coupling of aryl chlorides containing hydroxymethyl

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Abstract: A series of cyclopalladated 2-(4-bromophenyl)pyridine (bpp) complexes [Pd(bpp)(NHC)Cl] **1–3**, [Pd(bpp)(acac)] **4**, cyclometalated iridium(III) complexes $[Ir(bpp)_2Cl]_2$ **5** and $[Ir(bpp)_2(acac)]$ **6** have been synthesized and characterized. Their detailed structures have been determined by X-ray diffraction and plenty of intermolecular C–H···X (Cl, Br, π) and π···π interactions were found in the their crystals. Cyclometalated complexes **1–4** and **6** exhibit luminescence with emission peaks of 390–543 nm in dichloromethane solution under UV irradiation. Their application to coupling reactions of aryl chlorides containing hydroxymethyl was also investigated. An efficient **3**/Cu cocatalyzed oxidation/Suzuki reaction for the synthesis of biarylaldehydes from chlorophenylmethanol and arylboronic acids in air has been developed. In addition, **6**/**3**-cocatalyzed one-pot reaction of acetylferrocene, (2-amino-5-chlorophenyl)methanol, and arylboronic acids provided 6-aryl-2-ferrocenylquinolines in moderate to good yields.

Introduction

Cyclometalation has become one of the most popular organometallic reactions, providing a straightforward entry to cyclometalated complexes that feature a metal-carbon bond.[1] Among them, cyclometalated palladium(II),[2] iridium(III)[3] complexes have been successfully

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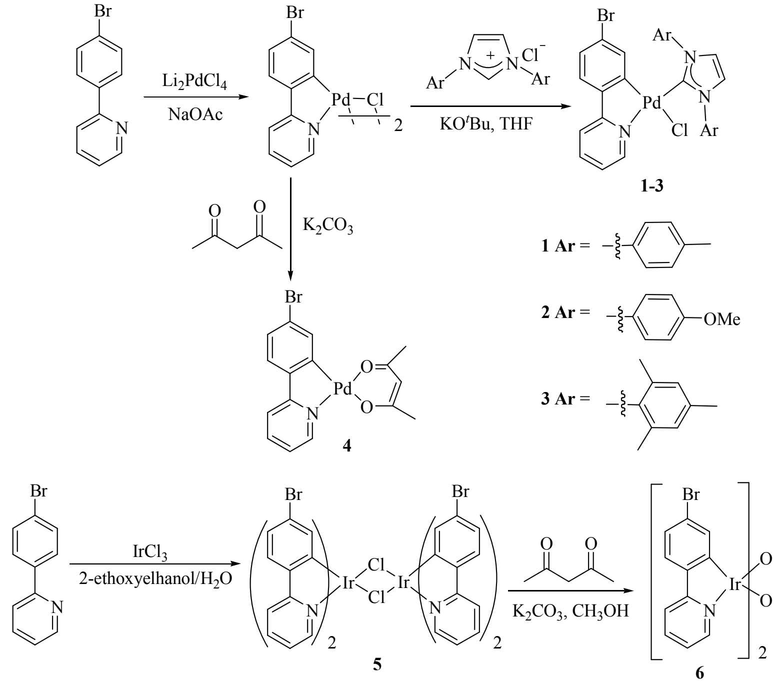
developed as highly active precatalysts for coupling reactions. For example, Buchwald[4] and Ishii[5] groups have reported the use of dialkylbiaryl phosphine-palladacycle complexes and $[Ir(cod)Cl]_2/PPh_3$ as efficient catalysts for Suzuki reaction of unactivated aryl chlorides and the α-alkylation of alcohols. As an alternative, NHCs have been proved to be excellent ligands in transition-metal-catalyzed coupling reactions.[6] Especially the NHC-palladacycles reported by the groups of Nolan,[7] Herrmann[8] have been successfully applied to coupling reactions of aryl chlorides. However, aryl halides containing hydroxymethyl as substrates have been relatively less reported.[9] Alcohols are of great importance as cheap and readily available materials for the preparation of pharmaceutical products and fine chemicals. In addition, palladium-catalyzed aerobic alcohol oxidation to carbonyl compounds is one of the most common classes of oxidation reactions in organic chemistry.[10] Great recent progress has been obtained for the palladium-catalyzed oxidation by using NHC ligands reported by the group of Sigman.[11] We have also developed NHC-palladacycles/Cu[12] and cyclometallated Ir/Pd[13] cocatalyzed α-alkylation/Suzuki reaction for the synthesis of 2,6-diarylquinolines from (2-amino-5-bromophenyl)methanol. To our knowledge, there are no reports concerning the reactions involving oxidation and Suzuki reaction for the synthesis of biarylaldehydes from aryl chlorides containing hydroxymethyl and arylboronic acids.

On the other hand, cyclometalated iridium complexes have attracted a great deal of attention due to their possoble applications as organic light-emitting diodes (OLEDs).[14] In these studies, acetylacetonate (acac) is one of the most widely used ancillary ligands that provided additional possibilities for the tuning of the electro-optical properties. Furthermore, the use of NHCs as ancillary ligands has opened new avanues for the design of phosphorescent materials, because of their high stability and excellent color purity.[15] However, the luminescence of NHC-palladacycles have not been reported up to now. As a continuation of our interest in the application of cyclometalated complexes,[16] we prepared four new palladacycles **1–4** and two cyclometalated Ir complexes **5–6** (Scheme 1) and examined their luminescent properties and catalytic activity. Here, we also reported that **3**/$Cu(OAc)_2$ and **6**/**3**-cocatalyzed one-pot reaction of aryl chlorides containing hydroxymethyl, providing a series of biarylaldehydes and 6-aryl-2-ferrocenylquinolines.

Results and discussion

Synthesis and characterization of the complexes 1–6



Scheme 1 Synthesis of palladacycles **1**–**4** and cyclometalated iridium complexes **5**–**6**.

The preparation of six new cyclometalated palladium, iridium complexes **1–6** is as follows (Scheme 1). The cyclopalladation reaction was carried out with bpp and 1 equivalent of Li_2PdCl_4 and NaOAc in methanol at rt for 12 h. The formed yellow solids were collected by filtration, and can be assigned as a chloride-bridged palladacyclic dimer.[16*a-b*] Because of its poor solubility in all common organic solvents, it was not characterized and directly subjected to bridge-splitting reaction. Three NHC adducts of palladacycles **1–3** have been easily prepared *in situ* from the reaction of the above dimer and 1,3-bis(4-methylphenyl) imidazolium chloride (ITolHCl), 1,3-bis(4-methoxyphenyl) imidazolium chloride (IMeOHCl) or 1,3-bis(2,4,6-trimethylphenyl) imidazolium chloride (IMesHCl) in THF at rt under N_2. The chloride-bridged dimer $[Ir(bpp)_2Cl]_2$ **5** was synthesized according to the reported procedure.[17] Then, the Pd(II), Ir(III) dimers were directly subjected to bridge-splitting reactions with acac to produce the mononuclear cyclometalated Pd(II), Ir(III) acac complexes **4** and **6**.

These complexes were characterized by elemental analysis, IR, ESI-MS, and ^{1}H NMR. The ^{1}H NMR spectra of these complexes were consistent with the proposed structures. The lowest field resonance appear as doublet at δ 8.43–9.24 ppm, and is assigned to the proton ortho to the nitrogen in the pyridyl ring. NHC-palladacycles **1–3** all exhibit singlets for the methyl groups of the NHCs at δ 2.31, 3.57 and 2.43, 2.29, 2.26 ppm, respectively. In the mass spectra of **1–3**, the most intense peak was attributed to $[M–Cl]^+$. The acac *CH* proton is observed as a sharp singlet at δ 5.41 and 5.30 ppm for complexes **4** and **6**, respectively. Furthermore, the X-ray molecular structures of all complexes were determined.

X-ray molecular structures of palladacycles

Single crystal structure analyses reveal that **1–4** are mononuclear and the palladium centers feature square planar coordination geometry. The molecules are shown in Fig. 1–4. The bicyclic system formed by the palladacycle and the pyridyl ring is approximately coplanar (dihedral angles of 5.7°, 0.6°, 3.8° and 1.5°, 0.9° for complexes **1–4**, respectively). The Pd–C_{bpp} and Pd–N_{bpp} bond lengths are elongated to 1.990(2) and 2.071(2) Å in **1**, 1.992(3) and 2.070(2) Å in **2**, 1.984(4) and 2.083(3) Å in **3**, due to the stronger electron-withdrawing ability of chloride anion. The Pd–C_{carb} [1.998(3) Å] bond length of **3** is similar to those of related carbene adducts [1.992–1.998 Å],[18] while it is longer than those of **1–2** [1.976(2) and 1.981(3) Å] possibly due to the steric bulk of the IMes ligand.

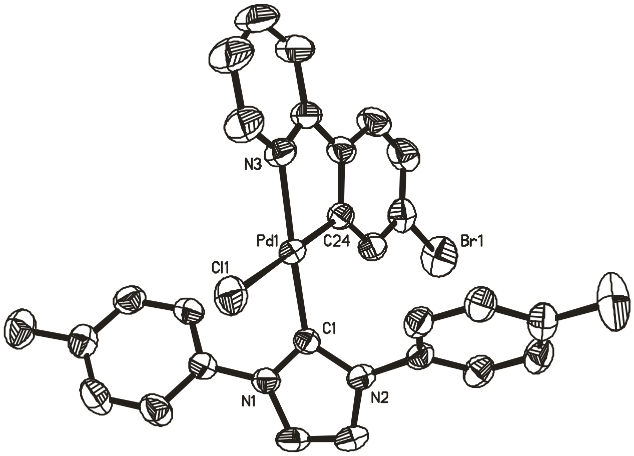


Fig. 1 The molecular structure of **1** with displacement ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity. Selected bonds distances (Å): Pd(1)–C(1) 1.976(2), Pd(1)–C(24) 1.990(2), Pd(1)–N(3), 2.071(2), Pd(1)–Cl(1), 2.4205(7).

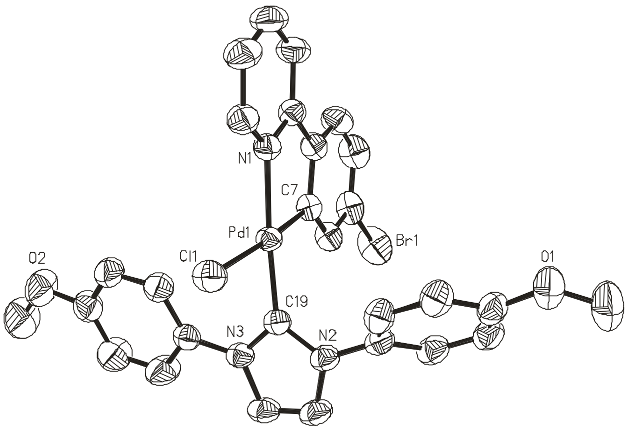


Fig. 2 The molecular structure of **2** with displacement ellipsoids drawn at the 50% probability level. H atoms and CH_2Cl_2 are omitted for clarity. Selected bonds distances (Å): Pd(1)–C(19) 1.981(3), Pd(1)–C(7) 1.992(3), Pd(1)–N(1) 2.070(2), Pd(1)–Cl(1) 2.4255(10).

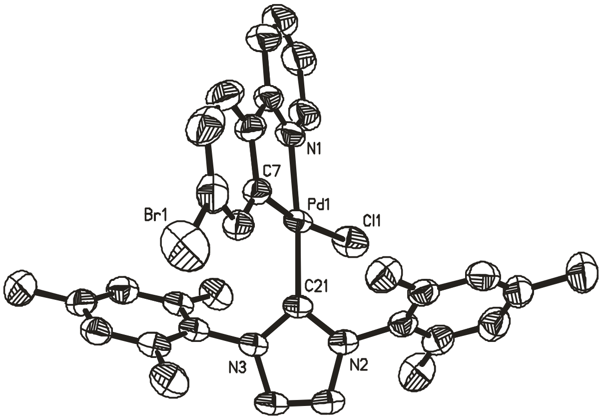


Fig. 3 The molecular structure of **3** with displacement ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity. Selected bonds distances (Å): Pd(1)–C(7) 1.984(4), Pd(1)–C(21) 1.998(3), Pd(1)–N(1) 2.083(3), Pd(1)–Cl(1) 2.4061(11).

For **4**, it crystallizes in triclinic *P*–1 space group with two mononuclear molecules [Pd(bpp)(acac)] in each asymmetric unit. The two crystallographic independent Pd(II) ions have the same coordination mode which is chelated by one acac ligand and one bpp ligand, yielding one five-member ring (NCCCPd) and one six-member ring (OCCCOPd) around the Pd(II) center (Fig. 4). The Pd–C_{bpp} and Pd–N_{bpp} bond lengths are found to be in the range of 1.958(7)–1.955(9) and 2.006(6)–2.031(7) Å, respectively, which are comparable to those of other reported cyclopalladated diketonate complexes.[19] In addition, the bpp and acac ligands are almost coplanar in **4**, whereas for **1–3** the imidazole rings of the NHC ligands are almost perpendicular to the bpp plane [76.64(7)^o for **1**, 87.40(9)^o for **2**, and 73.08(13)^o for **3**) for the sake of steric hindrance.

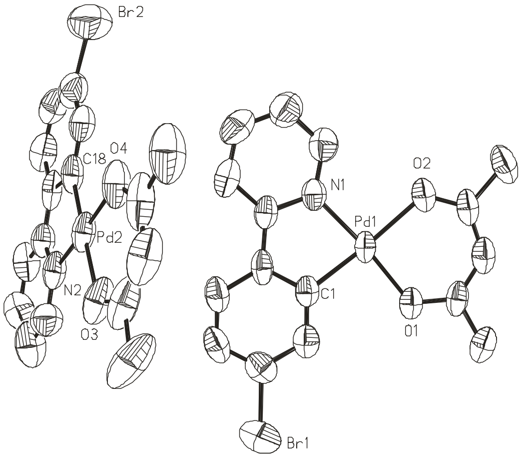


Fig. 4 The molecular structure of **4** with displacement ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity. Selected bonds distances (Å): Pd(1)–C(1) 1.958(7), Pd(1)–N(1) 2.006(6), Pd(1)–O(1) 2.010(5), Pd(1)–O(2) 2.088(5), Pd(2)–C(18) 1.955(9), Pd(2)–O(4) 2.015(7), Pd(2)–N(2) 2.031(7), Pd(2)–O(3) 2.072(7).

Conventional and unconventional hydrogen interactions are very interesting in crystal engineering and supramolecular chemistry.[20] In **1–3**, there are a plenty of C–H···Cl and C–H···Br interactions with the D···A distances and DHA angles varying from 3.273(5) to 3.821(4) Å, and 123.2 to 166.4°, respectively. Besides C–H···Cl and C–H···Br interactions, there are also some π···π interactions between the metal-involved rings and aromatic groups of bpp and NHC ligands (Table 1). A closer look at the structures reveals the presence of C–H···π interactions in **1–2**, and **4** (Table 2).

Table 1 Geometric parameters of the π···π interactions in **1–4**

Complex	π···π	Cg^{a}···Cg (Å)	α^{b}	β^{c}	Cg···plane (Cg^{2}) (Å)	Symm. op. on Cg^{2}
1	C18→N3···C18→N3	3.577(1)	0	76.49(1)	3.478(1)	–x, –y, –z
2	N1→C5···C6→C11	3.747(3)	1.07(2)	73.42(2)	3.591(3)	1–x, 1–y, 1–z
3	C1→N1···C1→N1	3.463(1)	0	82.7(1)	3.435(1)	1.5–x, 0.5–y, 1–z
4	Pd2→O4···Pd2→N2	3.644(3)	5.74(3)	69.69(1)	3.417(3)	1–x, –y, 1–z
	Pd1→N1···Pd1→O1	3.621(4)	3.27(3)	69.74(1)	3.397(4)	1–x, 1–y, –z

[a] Cg = centre of gravity of the interacting ring. [b] α = angle between the planes of the two interacting rings. [c] β = angle between the Cg···Cg line and the plane of the first interacting ring.

Table 2 Geometric parameters of the C–H···π interactions in **1–2** and **4**

Complex	H···centroid (Å)	C···centroid (Å)	C–H···centroid (°)
	2.962(1)	3.775(1)	143.32(1)

1	2.664(1)	3.557(2)	161.09(1)
2	3.069(7)	3.97(1)	165.8(3)
4	2.8944(4)	3.7597(5)	150.49(2)
	3.0012(4)	3.9482(5)	169.15(2)
	2.8593(5)	3.5836(5)	133.01(2)
	3.0388(5)	3.9385(6)	156.63(2)

For **1** and **2**, both bpp and NHC ligands can serve as H–donor or acceptor of C–H···π interactions (Fig. 5). In the case of **4**, the C–H···π interactions are formed between the methyl groups of acac ligands and pyridine or benzene ring of bpp ligands with the H···centroid (aromatic ring) and C···centroid distances fall in the range of 2.8593(5)–3.0388(5) and 3.5836(5)–3.9482(5) Å, respectively. The H···centroid distances of **4** are longer than those of $B(C_6F_5)_3$-stabilized benzene-ammonia and benzene water compounds, but shorter than that of Cu(II)–carboxylate.[21] But in **3**, no obvious C–H···π interactions can be found. These unconventional hydrogen interactions work together and assemble the respective mononuclear molecules into 3D supramolecular structures (Fig. 6).

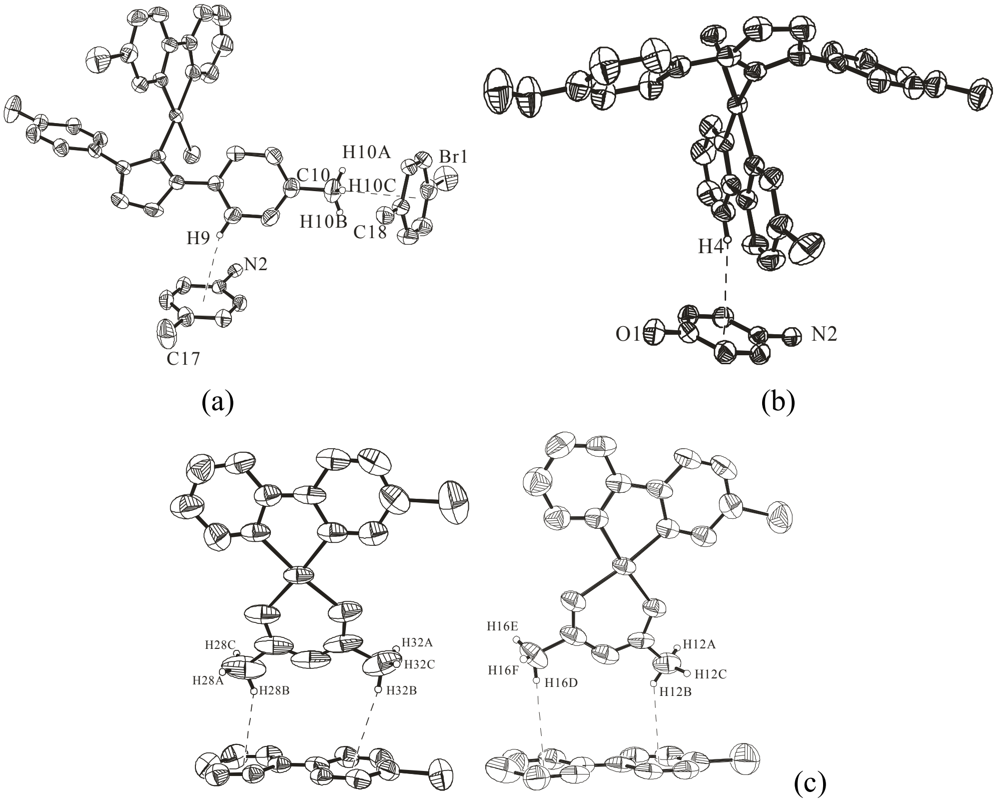
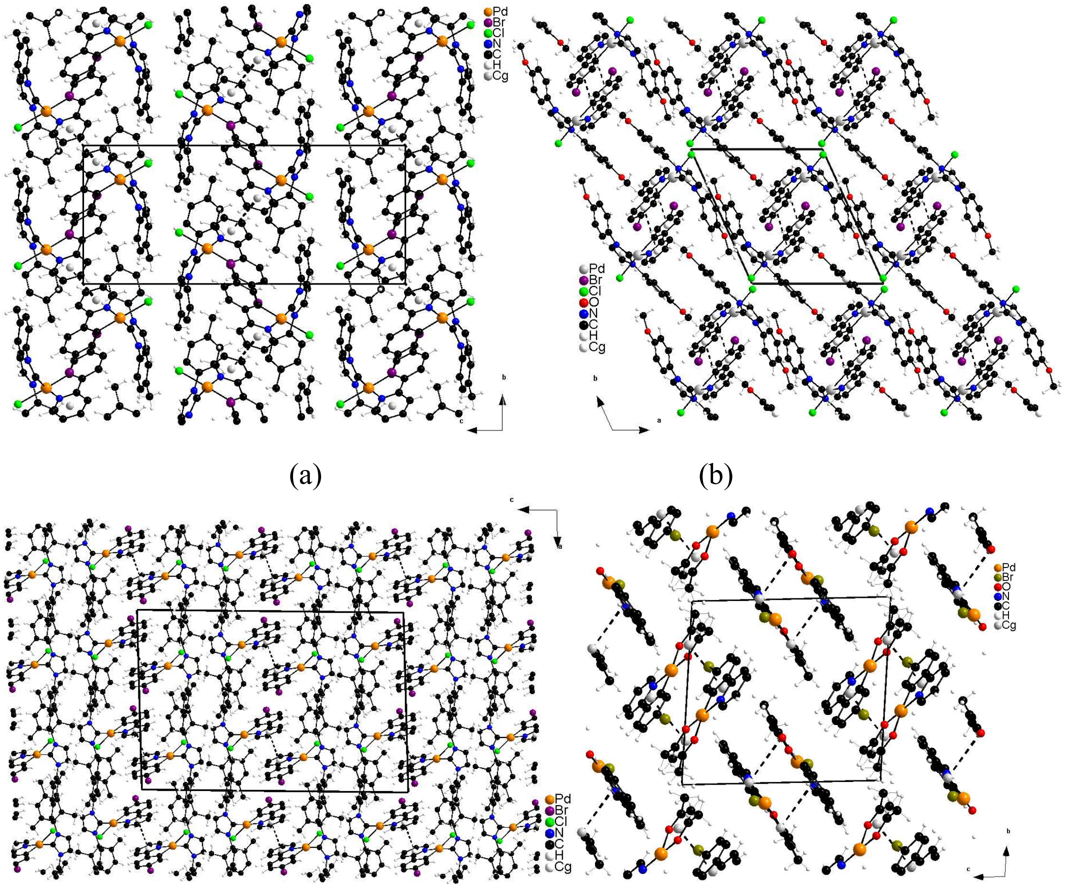


Fig. 5 C–H···π interactions found in complexes **1(a)–2(b)** and **4(c)**.



(a) (b)

(c) (d)

Fig. 6 Three-dimensional packing diagrams of **1(a), 2(b), 3(c)** and **4(d)**. The π···π interactions are shown as dotted lines.

X-ray molecular structures of cyclometalated iridium complexes

Although many structures of mononuclear cyclometalated iridium complexes have been determined,[3] there are very limited reports on the structures of dinuclear Cl-bridged dimers.[11*b*,22] The dimer **5** adopts the *racemate* form, rather than the *meso* form. Each iridium atom locates at a distorted octahedral environment with *cis*–C–C and *trans*–N–N chelate dispositions. A two-fold axis passes through both chlorine atoms, thus, the asymmetric unit consists of half of the molecule (Fig. 7). The central iridium atom in **6** is surrounded by two bbp and one acac with *cis*–C–C, *trans*–N–N and *cis*–O–O chelate dispositions (Fig. 8). The Ir–C, Ir–N and Ir–O bond lengths are similar to reported values of cyclometalated 2-phenylpyridine (ppy) iridium complex $(ppy)_2Ir(acac)$.[23] The crystal structure of **6** is also similar to that of $(ppy)_2Ir(acac)$ by the existence of π···π interaction with a ca. 3.838 Å face-face separation between the adjacent ring planes.

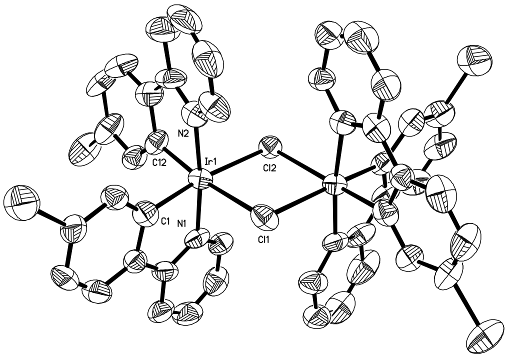


Fig. 7 The molecular structure of **5** with displacement ellipsoids drawn at the 50% probability level. H atoms and CH_2Cl_2 are omitted for clarity. Selected bonds distances (Å): Ir(1)–N(1) 2.070(6), Ir(1)–N(2) 2.077(6), Ir(1)–C(1) 1.998(12), Ir(1)–C(12) 1.989(10), Ir(1)–Cl(1) 2.494(3), Ir(1)–Cl(2) 2.530(3).

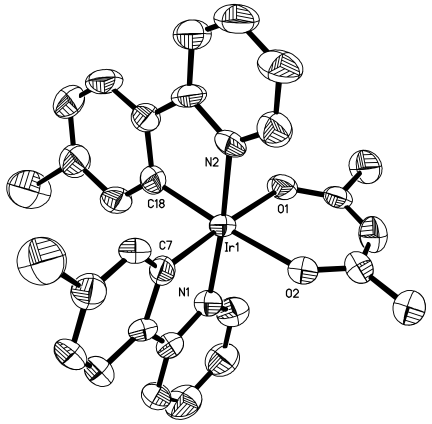


Fig. 8 The molecular structure of **6** with displacement ellipsoids drawn at the 50% probability level. H atoms and CH_2Cl_2 are omitted for clarity. Selected bonds distances (Å): Ir(1)–C(7) 1.994(11), Ir(1)–C(18) 1.996(12), Ir(1)–N(1) 2.049(10), Ir(1)–N(2) 2.014(11), Ir(1)–O(1) 2.158(8), Ir(1)–O(2) 2.140(8).

Luminescent properties

The UV-Vis absorption and photoluminescence (PL) spectra of these complexes in CH_2Cl_2 at rt are shown in Figs. 9–10 and Table 3. The absorption spectra of **1**–**3** have similar features. Two intense absorption peaks appear at 220 nm and 295 nm, and weaker absorptions were also observed between 295 nm and 375 nm, respectively. These absorption bands all can be assigned to the ligand localized π-π* transitions. Three NHC-palladacycles all exhibit luminescence in CH_2Cl_2 at rt. **1** and **3** display emission peaks at 390 nm and 394 nm suggesting that steric factors have less influence on the luminescence. However, the emission peak (414 nm) of **2** containing $–OCH_3$ is obviously higher than those of **1** and **3** containing –CH_3, indicating that the inductive effect of the substituents on the NHC ligand have more effect on the luminescence. The absorption spectra of cyclometalated acac complexes **4** and **6** are very different to each other. Complex **4** shows three intense absorption bands from ligands below 375 nm, in contrast, complex **6** exhibits obvious metal-to-ligand charge transition (MLCT) absorption bands between 407 nm and 510 nm. Thus, the emission (λ_{max} = 543 nm) of complex **6** should be phosphorescence, the emission (λ_{max} = 391 nm) of complex **4** is fluorescence. Similar to the luminescence of $(ppy)_2Ir(acac)$,[23] **6** shows a yellow phosphorescence, which implies that it not only can be used as emitting material in yellow OLEDs, also can be used in the fabrication of white OLEDs combined with blue emitters.

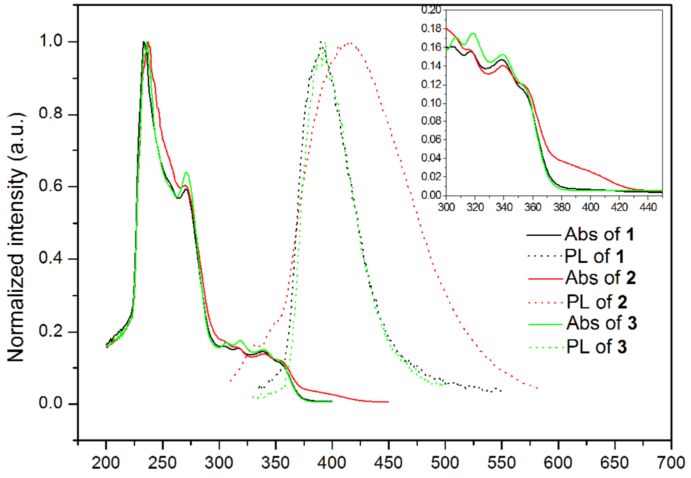


Fig. 9 Normalized absorption and emission of **1–3** in CH_2Cl_2 at rt.

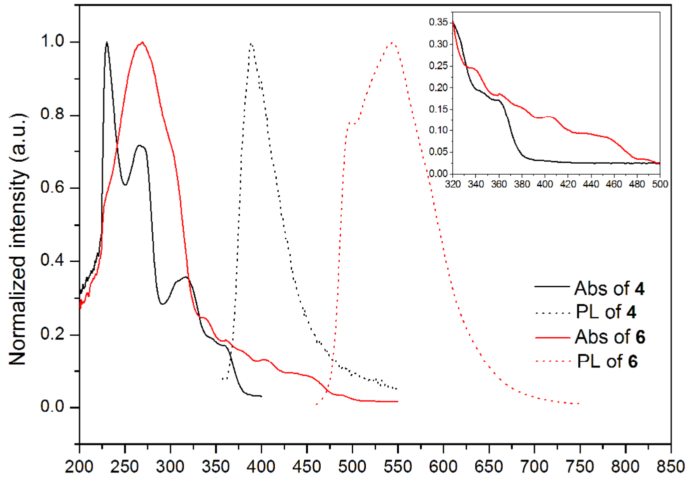


Fig. 10 Normalized absorption and emission of **4** and **6** in CH_2Cl_2 at rt.

Table 3 Photophysical data for **1–4** and **6**

Complex	λ_{abs}/nm (ε × 10^{-3}/M^{-1} cm^{-1})[a]	λ_{em}(λ_{ex})/nm	Stokes shift/nm	Φ^{b}(%)
1	233 (2.08), 270 (1.13), 317 (0.19), 339 (0.22), 353 (0.16)	390 (353)	37	2.4
2	235 (2.57), 268 (1.49), 318 (0.34), 339 (0.41), 353 (0.38)	414 (353)	51	3.6
3	235 (2.25), 270 (1.31), 318 (0.27), 339 (0.29), 353 (0.20)	394 (353)	41	1.7
4	229 (0.45), 265 (0.27), 316 (0.133), 359 (0.08)	391 (359)	32	1.8
6	268 (0.96), 337 (0.21), 361 (0.14), 407 (0.10), 454 (0.06), 488 (0.01)	543 (407)	136	6.3

[a] Measured in CH_2Cl_2 (10 × 10^{-5} M). [b] Measured in CH_2Cl_2 used 9, 10-diphenylanthracene and *fac*-Ir(ppy)$_3$ as the reference standard for **1–4** and **6**, respectively.

Moreover, the electrochemical property of **6** was investigated by cyclic voltammetry in CH_2Cl_2 solution containing 0.1 M tetrabutylammonium hexafluorophosphate with 0.05 V/s scan rate. The cyclic voltammogram shows a reversible oxidation wave due to iridium(III/IV) with $E_{1/2}^{ox}$ of 1.04 V vs. Ag/AgCl (Fig. 11). The highest occupied molecular orbital (HOMO) energy level was calculated to be –5.36 eV relative to the value of –4.8 eV for ferrocene (Fc) with respect to zero vacuum level.[24] The lowest unoccupied molecular orbital (LUMO) energy level was estimated to be –2.88 eV according to the HOMO energy level value in combination with the band gap derived from the absorption band edge.

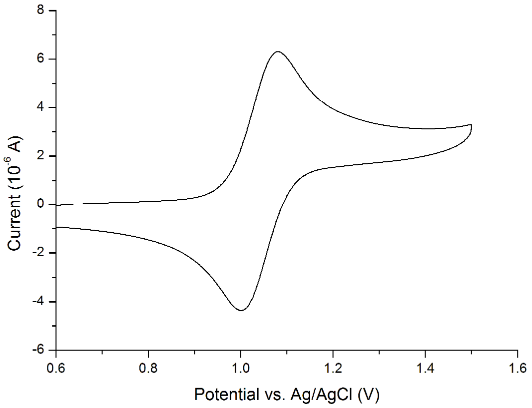
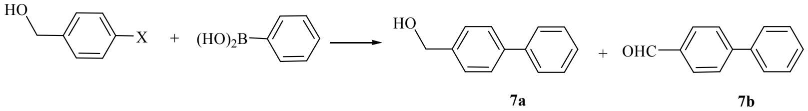


Fig. 11 The cyclic voltammetry spectra of **6**.

Pd/Cu cocatalyzed oxidation/Suzuki reaction

Palladium-catalyzed Suzuki coupling is well-known as being one of the most versatile and utilized reactions for the construction of C–C bond, in particular for the formation of biaryls.[2,4] Generally, Suzuki coupling of aryl halides containing hydroxymethyl produced the corresponding biarylalcohols.[25] Initially, we have examined the catalytic activity of palladacycles **1–4** for the Suzuki reaction of (4-bromophenyl) methanol with phenylboronic acid. Based on our previous experiments in palladacylic precatalysts for Suzuki coupling,[20b,d] the reaction was performed under nitrogen atmosphere in dioxane in the presence of Cs_2CO_3 as base at 110 °C for 18 h. **3** was the most efficient among these palladacycles **1–4** and produced the expected coupled product **7a** in 93% with a catalyst loading of 1 mol% (Table 4, entries 1–4). In the case of (4-chlorophenyl)methanol, **1** and **2** were almost inactive under the same reaction conditions, however, **3** generated **7a** in a good yield (82%, entry 7). Then, the coupling of (4-chlorophenyl)methanol was performed in air. It is interesting that an unexpected coupled product **7b** was obtained besides **7a** (entries 8–10). The results indicated that palladacycles can also catalyze aerobic alcohol oxidation in above reaction.

Table 4 Suzuki coupling of aryl halides containing hydroxymethyl with phenyl boronic acid catalyzed by palladacycles[a]

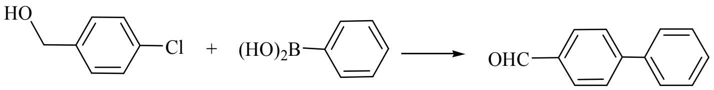


Entry	X	Catalyst (mol%)	**7a** Yield (%)[b]	**7b** Yield (%)[b]
1	Br	**1** (1)	51	0
2	Br	**2** (1)	58	0
3	Br	**3** (1)	93	0
4	Br	**4** (1)	16	0
5	Cl	**1** (1)	trace	0
6	Cl	**2** (1)	trace	0
7	Cl	**3** (1)	82	0
8[c]	Cl	**1** (1)	trace	24
9[c]	Cl	**2** (1)	trace	29
10[c]	Cl	**3** (1)	47	45

[a] Reaction conditions: aryl halides containing hydroxymethyl (0.5 mmol), phenylboronic acid (0.75 mmol), Cs_2CO_3 (1.0 mmol), dioxane (3 mL), 110 °C, 18 h, nitrogen atmosphere. [b] Isolated yield. [c] In air.

On the basis of this finding, we were interested to see whether the palladacycles could efficiently catalyze the reactions involving oxidation and Suzuki reaction for the synthesis of biarylaldehydes. The results from this study are summarized in Table 5. Under the same reaction conditions (Cs_2CO_3, dioxane, air), the yield was improved by the addition of copper salts (entries 1–3) suggesting that copper participated in the catalytic cycles. **3**/$CuCl_2$ system was obviously more active than the other two systems. Different copper salts/palladacycle **3** were then tested (entries 4–6). The results indicated that **3**/$Cu(OAc)_2$ was the best among these tested catalysts (92%, entry 6). Other reaction conditions (entries 7–12) such as K_2CO_3 in dioxane and Cs_2CO_3 in toluene also afforded good yields (85% and 88%, respectively).

Table 5 Optimization of the reaction conditions[a]



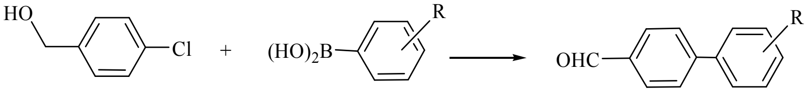
Entry	Catalyst (mol%)	Base	Solvent	Yield (%)[b]
1	**1**/$CuCl_2$ (1/5)	Cs_2CO_3	dioxane	53
2	**2**/$CuCl_2$ (1/5)	Cs_2CO_3	dioxane	60
3	**3**/$CuCl_2$ (1/5)	Cs_2CO_3	dioxane	81
4	**3**/CuCl (1/5)	Cs_2CO_3	dioxane	72
5	**3**/CuI (1/5)	Cs_2CO_3	dioxane	64
6	**3**/$Cu(OAc)_2$ (1/5)	Cs_2CO_3	dioxane	92
7	**3**/$Cu(OAc)_2$ (1/5)	K_2CO_3	dioxane	85
8	**3**/$Cu(OAc)_2$ (1/5)	Na_2CO_3	dioxane	67
9	**3**/$Cu(OAc)_2$ (1/5)	K_3PO_4	dioxane	56
10	**3**/$Cu(OAc)_2$ (1/5)	Cs_2CO_3	toluene	88
11	**3**/$Cu(OAc)_2$ (1/5)	Cs_2CO_3	THF	55
12	**3**/$Cu(OAc)_2$ (1/5)	Cs_2CO_3	DMF	62

[a] Reaction conditions: (4-chlorophenyl)methanol (0.5 mmol), phenylboronic acid (0.75 mmol), base (1.0 mmol), solvent (3 mL), 110 °C, 18 h, air atmosphere. [b] Isolated yield.

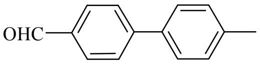
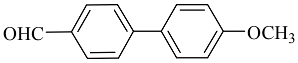
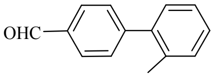
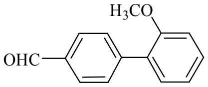
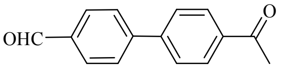
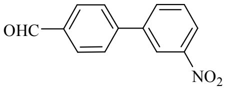
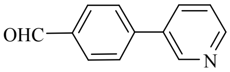
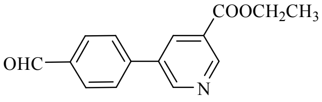
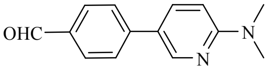
To test this procedure, the coupling reactions of (4-chlorophenyl)methanol with a variety of electronically and structurally diverse arylboronic acids were investigated (Table 6). Electron-donating substrates reacted to give the correponding products **7c** and **7d**, the yields (93% and 95%) are higher than the yields of electron-withdrawing substrates containing –CO– and –NO_2 groups. A slightly decrease in the yields (86% and 82%) of *meta*-substitution products **7e** and **7f** was observed. The method proved to be effective for pyridinylboronic acids bearing functional groups, including esters (**7j**) and amines (**7k**).

Table 6 Reaction of (4-chlorophenyl)methanol with arylboronic acids catalyzed by **3**/

Cu(OAc)$_2$[a]



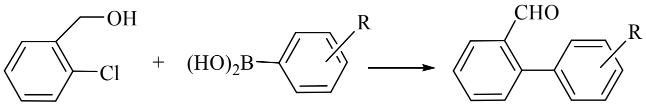
7c-k[b]

 **7c**, 93%	 **7d**, 95%	 **7e**, 86%
 **7f**, 82%	 **7g**, 87%	 **7h**, 88%
 **7i**, 83%	 **7j**, 76%	 **7k**, 85%

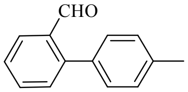
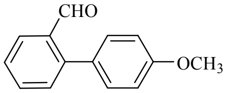
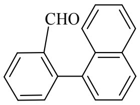
[a] Reaction conditions: (4-chlorophenyl)methanol (0.5 mmol), arylboronic acid (0.75 mmol), **3**/Cu(OAc)$_2$ (0.005/0.025 mmol), Cs$_2$CO$_3$ (1.0 mmol), dioxane (3 mL), 110 ^{o}C, 18 h, air atmosphere. [b] Isolated yield.

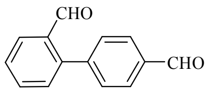
This newly developed coupling protocol was also successfully applied to synthesis of 2-biarylcarboxaldehydes via oxidation and Suzuki reaction of (2-chlorophenyl)methanol (Table 7). Similar to the results of (4-chlorophenyl)methanol, the corresponding 2-biaryl-carboxaldehydes **8a–8c** were also obtained with good yields (86–91%). On the basis of the success of this approach, we were interested to see whether **3**/Cu(OAc)$_2$ could efficiently cocatalyze double oxidation and Suzuki reaction of hydroxymethylphenylboronic. The desired products biphenyldialdehydes **8d–8f** were isolated in moderate yields (53–76%). Compared with the yields of **7i-7k**, the yields of **8g-8i** starting from the same arylboronic acid were slightly decrease possibly due to the steric hindrance.

Table 7 Reaction of (2-chlorophenyl)methanol with arylboronic acids catalyzed by **3**/ Cu(OAc)$_2$[a]

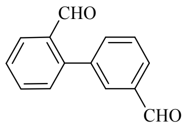


8a-i[b]

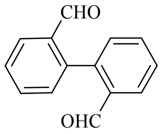
 **8a**, 91%	 **8b**, 90%	 **8c**, 86%



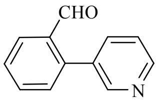
8d, 76%



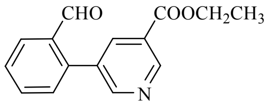
8e, 71%



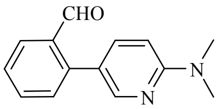
8f, 53%



8g, 75%



8h, 71%

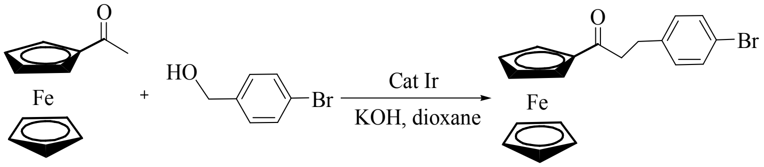


8i, 77%

[a] Reaction conditions: (2-chlorophenyl)methanol (0.5 mmol), arylboronic acid (0.75 mmol), **3**/Cu(OAc)$_2$ (0.005/0.025 mmol), Cs$_2$CO$_3$ (1.0 mmol), dioxane (3 mL), 110 ^{o}C, 18 h, air atmosphere. [b] Isolated yield.

Ir/Pd cocatalyzed α-alkylation and Suzuki reaction

In recent years, there has been significant interest in the metal-catalyzed hydrogen autotransfer process by alcohols as a more benign alternative to potentially genotoxic halides.[26] Although iridium complexes serve as efficient catalysts for the hydrogen transfer process,[3] cyclometalated iridium acac complexes-catalyzed α-alkylation of alcohols have not been explored up to now. Considering that cyclometalated iridium complexes are active catalysts for α-alkylation of alcohols,[13,16*d*] we hypothesized that the cyclometalated iridium acac complex **6** can catalyze the α-alkylation of acetylferrocene with benzyl alcohol. Thus, the reaction of (4-bromophenyl)methanol with acetylferrocene was performed under nitrogen atmosphere in dioxane in the presence of 2 mol [Ir]% of **5** or **6** as catalyst and KOH as base at 110 ^{o}C for 12 h (Scheme 2). To our delight, **6** displayed highly catalytic activity producing the desired product in an excellent yield (91%). However, the dimer **5** generated the product only in 40% yield. Furthermore, we also investigated one-pot synthesis of 6-aryl-2-ferrocenylquinolines via Ir/Pd-cocatalyzed α-alkylation/Suzuki reaction, using the present cyclometalated complexes **1–6** as catalysts.

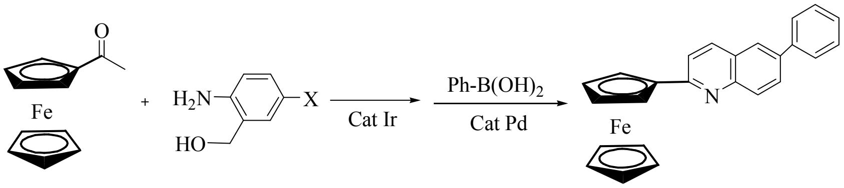


5 (1 mol%) 40%

6 (2 mol%) 91%

Scheme 2 α-Alkylation of acetylferrocene catalyzed by **5** and **6**.

Table 8 Synthesis of 2-ferrocenyl-6-phenylquinoline[a]

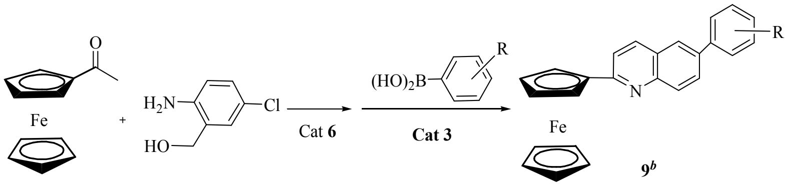


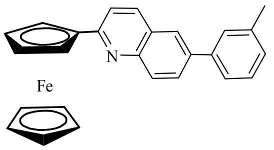
Entry	X	Catalyst (mol%)	Yield (%)[b]
1	Br	**6/1** (2/1)	82
2	Br	**6/2** (2/1)	85
3	Br	**6/3** (2/1)	94
4	Cl	**6**/Pd(OAc)$_2$ (2/3)	0
5	Cl	**6/1** (2/1)	trace
6	Cl	**6/2** (2/1)	trace
7	Cl	**6/3** (2/1)	87

[a] Reaction conditions: acetylferrocene (0.5 mmol), (2-amino-5-halophenyl)methanol (0.6 mmol), phenylboronic acid (0.75 mmol), KOH/Cs_2CO_3 (0.5 mmol/1 mmol), dioxane (3 mL), 110 °C, nitrogen atmosphere. [b] Isolated yield.

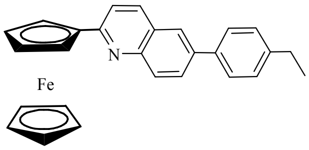
We have previously shown that PPh_3-cyclometallated iridium hydride is an efficient catalyst for the one-pot synthesis of 6-aryl-2-ferrocenylquinolines with 3 mol% Pd(OAc)$_2$.[13] Under the same conditions, acetylferrocene, (2-amino-5-bromophenyl)methanol and phenylboronic acid were efficiently converted to the 6-phenyl-2-ferrocenylquinoline in high yields (82–94%) with a catalytic loading as low as 1 mol% palladacycles **1–3**, respectively (Table 8, entries 1–3). For cheaper and more available (2-amino-5-chlorophenyl)methanol, Pd(OAc)$_2$, **1** and **2** were almost inactive (entries 4–6), but **3** displayed high efficiency (87%, entry 7). The scope of the procedure was further investigated by varying the arylboronic acids (Table 9). The corresponding 6-aryl-2-ferrocenylquinolines **9a**–**9g** were isolated in good yields (81–93%). The hindered arylboronic acids provided the products **9h** and **9i** in moderate yields (72% and 60%, respectively). The detailed structures of **9h** was confirmed by single-crystal X-ray crystallography (Fig 12).

Table 9 One-pot synthesis of 6-aryl-2-ferrocenylquinolines[a]

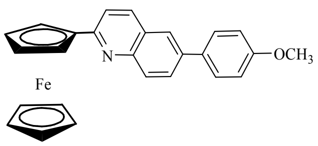




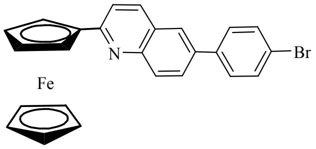
9a, 89%



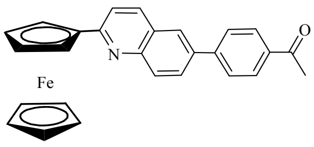
9b, 91%



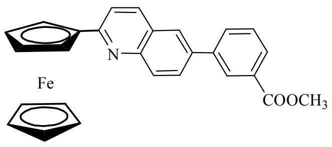
9c, 93%



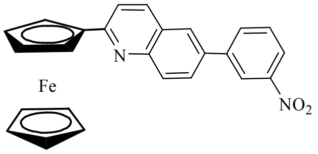
9d, 81%



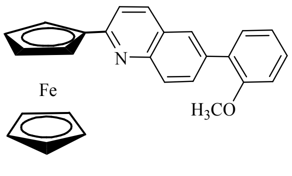
9e, 85%



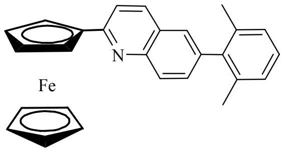
9f, 84%



9g, 87%



9h, 72%



9i, 60%

[a] Reaction conditions: acetylferrocene (0.5 mmol), (2-amino-5-chlorophenyl)methanol (0.6 mmol), arylboronic acids (0.75 mmol), **6/3** (2 mol%/1 mol%), KOH/Cs_2CO_3 (0.5 mmol/1 mmol), dioxane (3 mL), 110 °C, nitrogen atmosphere. [b] Isolated yield.

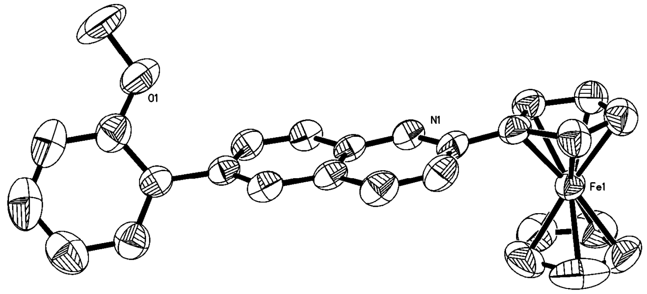


Fig. 12 The molecular structure of **9h** with displacement ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity.

Conclusion

In summary, a series of cyclometallated complexes have been synthesized and characterized. X-ray diffraction analysis confirms that there are variety of intermolecular C–H···X (Cl, Br, π) and π···π interactions in the their crystals. These cyclometallated complexes show emissions ranging from the purple to the yellow region. Their catalytic activity was evaluated in the coupling reactions of aryl chlorides containing hydroxymethyl. We have developed an efficient NHC-palladacycle/Cu(OAc)$_2$ cocatalyzed oxidation and Suzuki reaction for the synthesis of biarylaldehydes in air. Cyclometalated Ir acac complex **6** was an efficient catalyst for the α-alkylation of acetylferrocene. It was also successfully applied to one-pot synthesis of 6-aryl-2-ferrocenylquinolines from (2-amino-5-chlorophenyl)methanol using palladacycle **3** as cocatalyst.

Experimental section

General information

Solvents were dried and freshly distilled prior to use. All reagents and substrates were commercially available. (2-amino-5-chlorophenyl)methanol was synthesized according to the reported procedure.[27] IR spectra were collected on a Bruker VECTOR22 spectrophotometer in KBr pellets. Elemental analyses were determined with a Carlo Erba 1160 Elemental Analyzer. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker DPX–400 spectrometer in $CDCl_3$ with TMS as an internal standard. Mass spectra were measured on a LC–MSD–Trap–XCT instrument. The absorption and photoluminescence spectra were recorded on a Hitachi U–3010 UV–Vis spectrophotometer and a Hitachi F–4500 fluorescence spectrophotometer in CH_2Cl_2 at rt, respectively. Cyclic voltammetry was performed on a CHI620C electrochemical analyzer. The electrolytic cell was a conventional three-electrode cell consisting of a Pt bottom working electrode, a Pt wire counter electrode and Ag/AgCl reference electrode.

Preparation of complexes 1–3

A mixture of 2-(4-bromophenyl)pyridine (bpp) (1 mmol), Li_2PdCl_4 (1 mmol) and NaOAc (1.1 mmol) in 10 mL of dry methanol was stirred for 12 h at rt. The yellow solids (0.694g, 93%) were collected by filtration and washed several times with methanol. A Schlenk tube was charged with the above palladacyclic dimer (0.5 mmol), the corresponding imidazolium salts (1.25 mmol) and KO^{t}Bu (2.5 mmol) under nitrogen. Dry THF was added by a cannula and stirred at rt for 3 hours. The product was separated by passing through a short silica gel column with CH_2Cl_2 as eluent, the second band was collected and afforded the corresponding carbene adducts **1–3**.

[Pd(bpp)(Itol)Cl] (1). Yield: 0.559 g, 90%. IR (KBr, cm^{-1}): 3073, 2987, 2859, 1697, 1605, 1506, 1454, 1401, 1270, 1109, 1046, 1017, 895, 786, 740, 688, 654. ^{1}H NMR (400 MHz,

$CDCl_3$): δ 9.22 (d, J = 5.2 Hz, 1H), 7.89 (d, J = 8.0 Hz, 4H), 7.68 (t, J = 7.6 Hz, 1H), 7.42–7.45 (m, 3H), 7.26 (s, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.11–7.16 (m, 2H), 7.03 (d, J = 8.0 Hz, 1H), 6.22 (s, 1H), 2.31 (s, 6H). MS (EI) m/z = 586.0 $(M–Cl)^+$. Elemental analysis calcd (%) for $C_{28}H_{23}BrClN_3Pd$: C 53.96, H 3.72, N 6.74. Found: C 54.18, H 3.61, N 6.85.

[Pd(bpp)(IMeO)Cl] (2). Yield: 0.601 g, 92%. IR (KBr, cm^{-1}): 3567, 3213, 2949, 1840, 1652, 1521, 1427, 1362, 1284, 1202, 1145, 1025, 948, 920, 855, 801, 737, 703. ^1H NMR (400 MHz, $CDCl_3$): δ 9.13 (d, J = 5.2 Hz, 1H), 7.86 (d, J = 8.0 Hz, 4H), 7.43 (t, J = 7.6 Hz, 1H), 7.35 (s, 2H), 7.04 (d, J = 8.0 Hz, 1H), 6.98 (t, J = 6.4 Hz, 1H), 6.74–6.85 (m, 6H), 6.15 (s, 1H), 3.57 (s, 6H). MS (EI) m/z = 618.0 $(M–Cl)^+$. Elemental analysis calcd (%) for $C_{28}H_{23}BrClN_3O_2Pd$: C 51.32, H 3.54, N 6.41. Found: C 51.45, H 3.43, N 6.47.

[Pd(bpp)(IMes)Cl] (3). Yield: 0.582 g, 86%. IR (KBr, cm^{-1}): 2921, 2852, 1693, 1603, 1567, 1510, 1484, 1418, 1328, 1252, 925, 908, 848, 751, 735, 704, 690, 657. ^1H NMR (400 MHz, $CDCl_3$): δ 9.24 (d, J = 5.2 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.67–7.73 (m, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.25 (s, 1H), 7.02 (d, J = 8.2 Hz, 2H), 6.93 (s, 2H), 6.79 (d, J = 8.0 Hz, 2H), 6.31 (s, 1H), 2.43 (s, 6H), 2.29 (s, 6H), 2.26 (s, 6H). MS (EI) m/z = 642.1 $(M–Cl)^+$. Elemental analysis calcd (%) for $C_{32}H_{31}BrClN_3Pd$: C 56.57, H 4.60, N 6.19. Found: C 56.51, H 4.52, N 6.35.

[Pd(bpp)(acac)] (4). The above palladacyclic dimer (0.5 mmol), acac (0.25 mmol), K_2CO_3 (0.5 mmol), and ethanol (10 mL) were added into a three-neck flask. The mixture was refluxed under nitrogen for 12 h and then cooled to room temperature. A yellow precipitate was filtered and washed with water and ethanol several times. The resulted yellow solid was purified by passing through a short silica gel column with CH_2Cl_2 as eluent to give **4**. Yield: 0.371 g, 85%. IR (KBr, cm^{-1}): 2971, 2440, 1604, 1511, 1388, 1370, 1260, 1017, 1007, 890, 822, 719, 704, 695, 655. ^1H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, J = 5.2 Hz, 1H), 7.81 (t, J = 7.6 Hz, 1H), 7.66 (s, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.25 (s, 2H), 7.18 (t, J = 6.4 Hz, 1H), 5.41 (s, 1H), 2.12 (s, 3H), 2.06 (s, 3H). MS (EI) m/z = 437.9 $(M+H)^+$. Elemental analysis calcd (%) for $C_{16}H_{14}BrNO_2Pd$: C 43.81, H 3.22, N 3.19. Found: C 43.89, H 3.05, N 3.23.

Preparation of complexes 5–6

Iridium trichloride (0.5 mmol), bpp (1.5 mmol), 2-ethoxyethanol (15 mL), and water (5 mL) were added into a three-neck flask. The mixture was refluxed under nitrogen for 24 h and then cooled to rt. A yellow precipitate was filtered and washed with water and ethanol several times. The resulted yellow solid was purified by passing through a short silica gel column with CH_2Cl_2/ethyl acetate (3:1) as eluent to give solids **5**. Then, the complex **5** (0.1 mmol), acac (0.22 mmol), K_2CO_3 (0.4 mmol), and 2-ethoxyethanol (10 mL) were added into a three-neck flask. The mixture was refluxed under nitrogen for 12 h and then cooled to rt. A yellow precipitate was filtered and washed with water and ethanol several times. The resulted yellow solid was purified by passing through a short silica gel column with CH_2Cl_2 as eluent to give solids **6**.

$[Ir(bpp)_2Cl]_2$ (5). Yield: 0.609 g, 88%. IR (KBr, cm^{-1}): 2768, 1605, 1564, 1530, 1471, 1418, 1369, 1298, 1160, 1005, 883, 868, 766, 749, 719, 711, 644. ^1H NMR (400 MHz, $CDCl_3$): δ 9.11 (d, J = 5.2 Hz, 4H), 7.87(d, J = 8.0 Hz, 4H), 7.81(d, J = 8.0 Hz, 4H), 7.58 (d, J = 7.2 Hz, 4H), 7.48 (t, J = 7.2 Hz, 4H), 6.96 (d, J = 8.0 Hz, 4H), 6.83 (s, 4H). MS (EI) m/z = 1383.8 (M^+). Elemental analysis calcd (%) for $C_{44}H_{28}Br_4Cl_2Ir_2N_4$: C 38.08, H 2.03, N 4.04. Found: C 38.15, H 1.98, N 4.01.

$[Ir(bpp)_2(acac)]$ (6). Yield: 0.643 g, 85%. IR (KBr, cm^{-1}): 2993, 1816, 1582, 1510, 1474, 1367, 1252, 1228, 1056, 1004, 879, 868, 788, 766, 748, 722, 714, 693. ^1H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, J = 5.2 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H), 7.77 (t, J = 7.8 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.19 (t, J = 6.4 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 6.29 (s, 2H), 5.30 (s, 1H), 1.79 (s, 6H). MS (EI) m/z = 757.0 $(M+H)^+$. Elemental analysis calcd (%) for $C_{27}H_{21}Br_2IrN_2O_2$: C 42.81, H 2.79, N 3.70. Found: C 42.89, H 2.71, N 3.77.

Single-crystal structure determination

Single crystal X-ray diffraction measurements of **1**, **2**, **4–6** and **9h** were carried out on a Bruker SMART APEX II CCD diffractometer (Mo Kα radiation, λ = 71.073 pm) at rt. Crystallographic data for **3** was measured on a Xcalibur, Eos, Gemini diffractometer. Crystal structures were solved by direct methods using SHELXS, subsequent difference Fourier analyses and least squares refinement with SHELXL–97[28] allowed for the location of the atom positions. All non-hydrogen atoms were refined anisotropically. In the final step of the crystal structure refinement hydrogen atoms of idealized –CH_2 and –CH_3 groups were added and treated with the riding atom mode, their isotropic displacement factor was chosen as 1.2 and 1.5 times the preceding carbon atom, respectively. One CH_2Cl_2 molecule (Cl3, Cl4, C29) in **2** is disordered over two positions with an occupancy of 0.5, it is also refined isotropically. C23 to C27 in **4** were refined isotropically because of their higher thermal parameters.

General procedure for synthesis of biarylaldehydes

A 10 mL round–bottom flask was charged with the prescribed amount of catalyst Pd/Cu, aryl halides containing hydroxymethyl (0.5 mmol), arylboronic acid (0.75 mmol), the selected base (1.0 mmol) and solvent (3 mL) in air. The reaction mixture was then placed in an oil bath and heated at 110 °C for 18 h. After removal of the solvent, the resulting residue was purified by flash chromatography on silica gel using CH_2Cl_2/petroleum ether (1/1) as eluent. The products **7a**,[9b] **7b**,[29a] **7c**,[29b] **7d**,[29c] **7e-g**,[29d] **7h**,[29a] **7i**[29e] and **8a-c**,[30a] **8d**,[30b] **8e-f**,[30c] **8g**[29f] are known compounds except for **7j–k** and **8h–i**.

4-(5-Ethoxycarbonylpyridin-3-yl)benzaldehyde (7j). Yield: 0.194 g, 76%. IR (KBr, cm^{-1}): 2818, 1721, 1701, 1607, 1565, 1452, 1362, 1307, 1251, 1216, 1173, 1110, 1022, 915, 829, 762, 702. ^1H NMR (400 MHz, $CDCl_3$): δ 10.10 (s, 1H), 9.26 (s, 1H), 9.05 (s, 1H), 8.54 (s, 1H), 8.04 (d, J = 6.8 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 4.48 (q, 2H), 1.46 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.6, 165.0, 151.7, 150.3, 142.5, 136.1, 135.4, 135.1, 130.5, 127.8, 126.5, 61.8, 14.3. MS (EI) m/z = 254.1 (M^+). Elemental analysis calcd (%) for $C_{15}H_{13}NO_3$: C 70.58, H 5.13, N 5.49. Found: C 70.65, H 5.02, N 5.56.

4-(4-Dimethylaminopyridin-3-yl)benzaldehyde (7k). Yield: 0.192 g, 85%. IR (KBr, cm^{-1}): 2853, 1690, 1592, 1523, 1503, 1388, 1282, 1213, 1170, 1067, 1030, 958, 832, 807, 778, 690. ^1H NMR (400 MHz, $CDCl_3$): δ 9.99 (s, 1H), 8.50 (s, 1H), 7.90 (d, J = 7.2 Hz, 2H), 7.73 (d, J = 8.8 Hz, 1H), 7.66 (d, J = 8.4 Hz, 2H), 6.59 (d, J = 8.8 Hz, 1H), 3.20 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.8, 159.0, 146.7, 144.4, 135.7, 134.3, 130.5, 128.2, 126.0, 122.5, 105.8, 38.1. MS (EI) m/z = 225.1 (M^+). Elemental analysis calcd (%) for $C_{14}H_{14}N_2O$: C 74.31, H 6.24, N 12.38. Found: C 74.37, H 6.13, N 12.42.

2-(5-Ethoxycarbonylpyridin-3-yl)benzaldehyde (8h). Yield: 0.181 g, 71%. IR (KBr, cm^{-1}): 2874, 1719, 1596, 1445, 1364, 1294, 1267, 1248, 1198, 1109, 1019, 974, 823, 782, 759, 711. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 9.29 (s, 1H), 8.80 (s, 1H), 8.34 (s, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.71–7.75 (m, *1*H), 7.62 (m, 1H), 7.45 (d, J = 8.0 Hz, 1H), 4.46 (q, 2H), 1.43 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 164.9, 153.4, 150.2, 140.5, 137.7, 134.0, 133.7, 131.2, 129.2, 125.9, 61.7, 14.3. MS (EI) m/z = 254.1 (M^+). Elemental analysis calcd (%) for $C_{15}H_{13}NO_3$: C 70.58, H 5.13, N 5.49. Found: C 70.63, H 5.06, N 5.54.

2-(4-Dimethylaminopyridin-3-yl)benzaldehyde (8i). Yield: 0.174 g, 77%. IR (KBr, cm^{-1}): 2850, 1687, 1601, 1547, 1515, 1479, 1439, 1386, 1320, 1192, 1152, 1063, 957, 828, 812, 768, 733. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.05 (s, 1H), 8.19 (s, 1H), 8.00 (d, J = 7.2 Hz, 1H), 7.59–7.62 (m, 1H), 7.39–7.49 (m, 3H), 6.60 (d, J = 8.8 Hz, 1H), 3.15 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3, 158.8, 148.6, 143.2, 138.6, 133.8, 130.7, 128.0, 127.3, 120.7, 105.2, 38.1. MS (EI) m/z = 225.1 (M^+). Elemental analysis calcd (%) for $C_{14}H_{14}N_2O$: C 74.31, H 6.24, N 12.38. Found: C 74.40, H 6.15, N 12.47.

General procedure for synthesis of 6-aryl-2-ferrocenylquinolines

In a Schlenk tube, a mixture of the acetylferrocene (0.5 mmol), (2-amino-5-chlorophenyl) methanol (0.6 mmol), KOH (0.5 mmol), and **6** (0.01 mmol) in dioxane (3 mL) was evacuated and charged with nitrogen. The mixture was heated at 110 °C for 12 h then allowed to cool to rt. The vessel was opened, and arylboronic acids (0.75 mmol), Cs_2CO_3 (1.0 mmol), and **3** (0.005 mmol) were added to it under nitrogen. The mixture was heated at 110 °C for another 12 h. After removal of the solvent, the resulting residue was purified by column chromatography on silica gel using CH_2Cl_2 as eluent. The products 6-aryl-2-ferrocenyl quinolines **9c-i**[13] are known compounds except for **9a-b**.

2-Ferrocenyl-6-(3-methylphenyl)quinoline (9a). Yield: 0.179 g, 89%. IR (KBr, cm^{-1}): 2922, 1593, 1478, 1378, 1337, 1287, 1180, 1135, 1104, 1012, 905, 894, 837. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (m, 2H), 7.97 (s, 2H), 7.56–7.64 (m, 3H), 7.43 (t, 1H), 7.26 (d, J = 7.6 Hz, 2H), 5.13 (s, 2H), 4.53 (s, 2H), 4.12 (s, 5H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 140.6, 138.6, 138.3, 135.7, 129.3, 129.2, 128.9, 128.3, 128.1, 125.3, 124.5, 119.9, 83.9, 70.5, 69.7, 68.0, 21.6. MS (EI, 70 eV) m/z = 404.1 $(M + H)^+$. Elemental analysis calcd (%) for $C_{26}H_{21}FeN$: C 77.43, H 5.25, N 3.47. Found: C 77.57, H 5.10, N 3.59.

2-Ferrocenyl-6-(4-ethylphenyl)quinoline (9b). Yield: 0.190 g, 91%. IR (KBr, cm^{-1}):

2966, 1594, 1566, 1499, 1460, 1337, 1279, 1133, 1104, 1029, 1014, 900, 826, 733. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.07–8.26 (m, 2H), 7.83–7.93 (m, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.4 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 5.07 (s, 2H), 4.47 (s, 2H), 4.05 (s, 5H), 2.71 (q, 2H), 1.29 (t, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 159.4, 147.6, 143.7, 138.1, 138.0, 136.6, 129.3, 128.5, 128.3, 127.3, 127.0, 125.0, 119.9, 84.0, 70.5, 69.7, 68.0, 29.8, 15.7. MS (EI) m/z = 418.1 (M+H)$^+$. Elemental analysis calcd (%) for $C_{27}H_{23}FeN$: C 77.71, H 5.56, N 3.36. Found: C 77.79, H 5.43, N 3.43.

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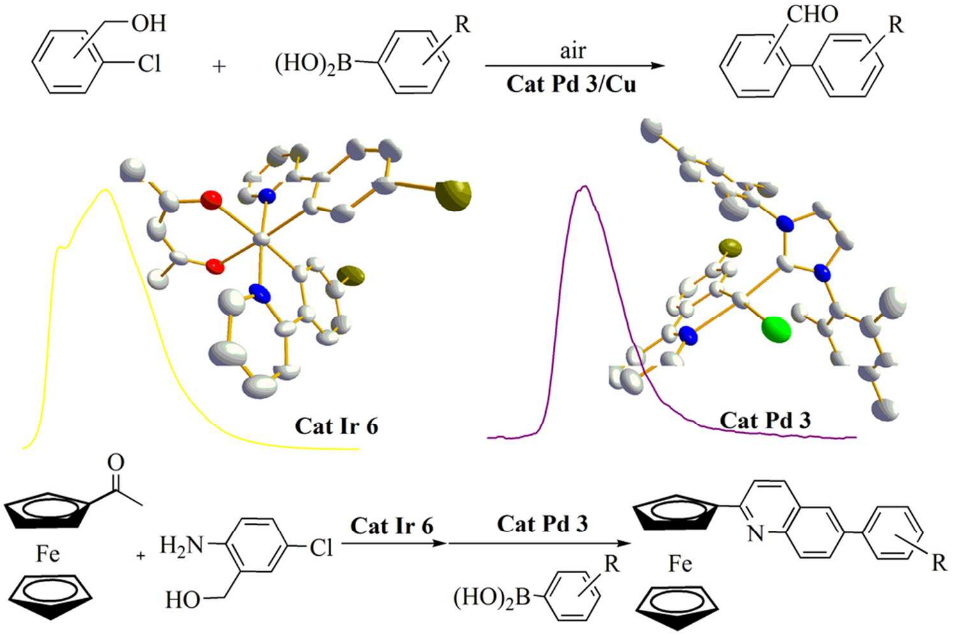

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