ORGANOMETALLICS

Synthesis, Reactivities, and Catalytic Properties of Iodo-Bridged Polymeric Iridium Complexes with Flexible Carbon Chain-Bridged Bis(tetramethylcyclopentadienyl) Ligands

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Supporting Information

ABSTRACT: Dinuclear iridium complexes $[(C_5Me_4)(CH_2)_{\mu}]$ $(C_{s}Me_{4})$ [Ir(COD)]₂ (2a: n = 2; 2b: n = 3; 2c: n = 4) are obtained from the reactions of the corresponding dilithium salts $\operatorname{Li}_{2}[(C_{s}\operatorname{Me}_{4})(\operatorname{CH}_{2})_{n}(C_{s}\operatorname{Me}_{4})]$ (n = 2-4) with $[\operatorname{Ir}(\mu-\operatorname{Cl})(\operatorname{COD})]_{2}$. Further oxidation of 2 affords iodo-bridged polymeric iridium complexes $[(C_5Me_4)(CH_2)_n(C_5Me_4)(IrI_2)_2]_n$ (3a: n = 2; 3b: n =3; 3c: n = 4). Dinuclear iridium complexes $[(C_5Me_4)(CH_2)_n]$ (C_5Me_4)][IrI₂(PPh₃)]₂ (4a: n = 2; 4b: n = 3; 4c: n = 4) and $[(C_5Me_4)(CH_2)_n(C_5Me_4)][IrI_2(CO)]_2$ (**5b**: n = 3; **5c**: n = 4) are



obtained from the reactions of 3 with PPh₃ and CO, respectively. Dinuclear dicarbonyl iridium complexes $[(C_5Me_4)(CH_2)_n]$ (C_5Me_4)][Ir(CO)₂]₂ (6b: n = 3; 6c: n = 4) are obtained from the reactions of 3 with Zn and CO. Additionally, the cyclometalated dinuclear iridium complexes 7b,c, 8b,c, 9b,c, and 10b,c are obtained from the reactions of 3 with the corresponding nitrogen ligands in the presence of KOH. The molecular structures of complexes 2a, 4a, 5b, 6c, and 7b have been determined by single-crystal X-ray diffraction analysis. Moreover, we found that complexes 3 and 4 are efficient catalysts for the selective amine cross-coupling reaction.

INTRODUCTION

Over the past decades, dinuclear metallocene complexes have attracted significant interest in academic and industrial fields.¹ In these complexes the two metal centers stay in close proximity to offer the opportunity to produce cooperative electronic and chemical interactions, and the complexes have been envisaged to be useful for homogeneous catalysis.^{1b} In 1969 Maitlis's group reported [Cp*IrCl₂]₂ and Cp*Ir(CO)₂ as the first examples of half-sandwich Cp*Ir complexes (Cp* = $C_{s}Me_{s}$).² Recently, Cp*Ir complexes have been widely used in the fields of organometallic chemistry,^{3,4} polymer chemistry,⁵ and organic chemistry,⁶ as fundamental reagents by virtue of their properties. Although bridged cyclopentadienyliridium dinuclear complexes have been reported,⁷ to the best of our knowledge, these complexes have not been applied in catalysis. Introduction of four methyl groups into the Cp rings of these dinuclear complexes could improve their solubility in organic solvents and reactivity. However, there is no report of a dinuclear iridium complex with a bridged ligand connected to the two C₅Me₄Ir fragments (Chart 1). Tethering two iridium atoms to each other via a relatively short linkage might encourage different catalytic properties compared to the unlinked cyclopentadienyl complexes. Because the presence of a carbocyclic structure in the hydrocarbyl chain will make the chain rigid, we hope to use a flexible linear alkanediyl group (E

Chart 1

Cp*lr complex

Bridged C₅Me₄Ir dinuclear complex



not been reported

L = CI, Br, I, CO, PR₃, Py etc.

= $(CH_2)_n$ as a linker to directly connect the two C_5Me_4Ir fragments.

In this paper, iodo-bridged polymeric iridium complexes $[(C_5Me_4)(CH_2)_n(C_5Me_4)(IrI_2)_2]_m$ (n = 2-4) are synthesized successfully. Furthermore, these iridium complexes are used as the starting materials to synthesize a series of dinuclear iridium complexes. Moreover, we studied the catalytic properties of these iodo-bridged polymeric iridium complexes and derivative dinuclear iridium complexes in the selective amine crosscoupling reaction.

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Scheme 1



RESULTS AND DISCUSSION

Preparation of Dinuclear Iridium Complexes $[(C_5Me_4)-(CH_2)_n(C_5Me_4)][Ir(COD)]_2$ (2a: n = 2; 2b: n = 3; 2c: n = 4). To synthesize the iridium complexes, we chose the bifunctional ligands $C_5Me_4H(CH_2)_nC_5Me_4H$ (1a: n = 2; 1b: n = 3; 1c: n = 4) as the starting materials, in which $(CH_2)_n$ was a flexible linker to connect two tetramethylcyclopentadiene fragments. Ligands 1a and 1b were prepared by Nazarov cyclization reaction according to the literature methods.^{8,9} Ligand 1c was prepared by the reaction of Grignard reagent with tetramethylcyclopentenone, followed by hydrolysis and dehydration. Mintz and co-workers also reported the synthesis of ligand 1b.^{10a} Suzuki and co-workers obtained 1c from the reaction of α, ω -dilithioalkane with tetramethylcyclopentenone, and they used this ligand to synthesize bridged tetramethylcyclopenta-

Several dinuclear bis(cyclopentadienyl) iridium cyclooctadiene complexes have been obtained from the reactions of the corresponding dilithium salts with $[Ir(\mu-Cl)(COD)]_2$ in THF at room temperature or refluxing temperature.⁷ However, we failed to isolate the corresponding products from $Li_2[C_5Me_4(CH_2)_nC_5Me_4]$ with $[Ir(\mu-Cl)(COD)]_2$ under these reaction conditions. Fortunately, we obtained the dinuclear iridium cyclooctadiene complexes 2 in refluxing xylene in low to moderate yields (Scheme 1).

In the ¹H NMR spectra of complexes **2**, the signals associated with the methyl protons on the C₅ rings appeared at around 1.8 ppm as two singlet peaks close to each other with an integral intensity of 12H. The structure of **2a** was confirmed by single-crystal X-ray diffraction studies, which is depicted in Figure 1 with selected bond lengths. Complex **2a** possesses two $(C_5Me_4)Ir(COD)$ fragments, linked by a $(CH_2)_2$ chain with *cis*-configuration. In each fragment, the Ir atom is bounded in



Figure 1. ORTEP view of $[(C_5Me_4)(CH_2)_2(C_5Me_4)][Ir(C_8H_{12})]_2$ (2a) showing 60% ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Ir(1)-C(1) 2.106(7), Ir(1)-C(4) 2.103(6), Ir(1)-C(5) 2.119(6), Ir(1)-C(8) 2.099(6), Ir(2)-C(29) 2.117(6), Ir(2)-C(32) 2.115(6), Ir(2)-C(33) 2.101(6), Ir(2)-C(36) 2.119(6), Ir(1)\cdotsIr(2) 6.505.

 η^5 -fashion with the cyclopentadienyl ring and in two η^2 -fashion with cyclooctadiene. The molecular structure is unsymmetrical, and the two cyclopentadienyl rings lie in the same direction.

almost parallel. Preparation of Iodo-Bridged Polymeric Iridium Complexes $[(C_5Me_4)(CH_2)_n(C_5Me_4)(IrI_2)_2]_m$ (3a: n = 2; 3b: n = 3; **3c:** n = 4). Complexes 2 were easily oxidized by iodine in CH₂Cl₂ and gave the dark red diiodo iridium(III) complexes 3 in good yields. The elemental analysis suggested that it should be an organometallic polymer, linked by Ir-I-Ir bridges as shown in Scheme 1. Complexes 3 are almost insoluble in all organic solvents. In the ¹H NMR spectra of 3 in DMSO-D₆ solution, the signals associated with the methyl protons on the C_5 rings appeared at around 1.9 ppm as two singlet peaks close to each other with an integral intensity of 12H. It is possible that DMSO-D₆ could cleave the iodo-bridges to form the dinuclear iridium complexes $[(C_5Me_4)(CH_2)_n(C_5Me_4)]$ - $[IrI_2(DMSO-D_6)]_2$. The reported halogen-bridged polymeric iridium and rhodium complexes show similar insolubility in a wide variety of organic solvents.^{7,11}

The dihedral angle between the two cyclopentadienyl planes is

170.1°, indicating that the two cyclopentadienyl rings are

Preparation of Dinuclear Iridium Complexes $[(C_5Me_4)-(CH_2)_n(C_5Me_4)][Irl_2(PPh_3)]_2$ (4a: n = 2, 4b: n = 3; 4c: n = 4) and $[(C_5Me_4)(CH_2)_n(C_5Me_4)][Irl_2(CO)]_2$ (5b: n = 3; 5c: n = 4). To further characterize complexes 3, we used two different ligands, PPh₃ and CO, to dissociate the iodo-bridged polymeric complexes. As shown in Scheme 2, dinuclear complexes



 $[(C_5Me_4)(CH_2)_n(C_5Me_4)][IrI_2(PPh_3)]_2$ (4a: n = 2; 4b: n = 3; 4c: n = 4) were easily obtained by reactions of 3 with PPh₃ in CH₂Cl₂ at room temperature for 2 h in almost quantitative yield as orange-yellow solids. In the ¹H NMR spectra of complexes 4, the signals associated with the methyl protons on the C₅ rings appeared at around 1.73 and 1.56 ppm as two singlets or doublets with an integral intensity of 12H. The ³¹P{¹H} NMR spectra of 4 showed only one phosphorus at around δ -9.5 ppm, which is similar to the reported mononuclear analogue (C₅Me₄H)IrI₂(PPh₃) (δ -8.2 ppm).¹² The structure of 4a was confirmed by single-crystal X-ray diffraction studies and is depicted in Figure 2 with selected bond lengths and angles. Complex 4a possesses two three-legged half-sandwich (C₅Me₄)IrI₂(PPh₃) fragments linked by a



Figure 2. ORTEP view of $[(C_5Me_4)(CH_2)_2(C_5Me_4)][IrI_2(PPh_3)]_2$ (4a) showing 30% ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)–P(1) 2.316(1), Ir(1)–I(1) 2.6956(7), Ir(1)–I(2) 2.6974(8), Ir(1)…Ir(1A) 7.953, I(1)–Ir(1)–I(2) 93.02(2), I(1)–Ir(1)–P(1) 91.93(3), I(2)–Ir(1)–P(1) 88.85(3).

 $(CH_2)_2$ chain, with C_i symmetry. The $IrI_2(PPh_3)$ fragments are positioned on the Cp faces of the bridging ligand so that interring repulsions are minimized. This results in a long interatomic separation of $Ir(1)\cdots Ir(2) = 7.953$ Å, significantly longer than the corresponding distance in complex **2a** $[Ir(1)\cdots Ir(2) = 6.505$ Å], which may result from steric hindrance of the $IrI_2(PPh_3)$ fragments.

The further reactivity search of complex **3a** was not carried out owing to the very poor yield of **2a**. Similarly, dinuclear complexes $[(C_5Me_4)(CH_2)_n(C_5Me_4)][IrI_2(CO)]_2$ (**5b**,**c**, n = 3, 4) were obtained by reactions of **3** with CO in CH₂Cl₂ at room temperature for 2 h (Scheme 3). Complex **5b** is an orange-red



solid and is easily soluble in halogenated hydrocarbons such as chloroform and dichloromethane. In contrast, complex **5c** is a yellow solid and is barely soluble even in chloroform and dichloromethane. In the ¹H NMR spectra of complexes **5**, the signals associated with the methyl protons on the C_5 rings appeared at around 2.2 ppm as two singlets close to each other with an integral intensity of 12H. Additionally, the IR spectra of **5** show only one absorption peak attributable to stretching vibration of terminal carbonyl absorptions around 2020 cm⁻¹. The structure of **5b** was confirmed by single-crystal X-ray diffraction studies and is depicted in Figure 3 with selected bond lengths and angles.

Preparation of Dinuclear Dicarbonyl Iridium Complexes $[(C_5Me_4)(CH_2)_n(C_5Me_4)][Ir(CO)_2]_2$ (6b: n = 3; 6c: n =4). Graham's group had reported the synthesis of Cp*Ir(CO)_2 from reducing $[Cp*IrCl_2]_2$ with Zn powder in the presence of high-pressure CO.^{3c} This method was applied successfully to synthesize dinuclear dicarbonyl iridium complexes 6 with some improvements. The suspension of complexes 3 and Zn powder in CH₃OH was bubbled by CO at 65 °C for 5 h to give a pale yellow solution. After cooling to room temperature, an aqueous solution of NaOH saturated with NaCl was added. Then the



Figure 3. ORTEP view of $[(C_5Me_4)(CH_2)_3(C_5Me_4)][IrI_2(CO)]_2$ (5b) showing 30% ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)–C(1) 2.106(7), Ir(1)–I(1) 2.7013(6), Ir(1)–I(2) 2.7040(6), Ir(2)–C(2) 1.888(6), Ir(2)–I(3) 2.6846(7), Ir(2)–I(4) 2.6743(6), Ir(1)…Ir(2) 9.001, C(1)–Ir(1)–I(1) 90.8(2), C(1)–Ir(1)–I(2) 88.9(2), I(1)– Ir(1)–I(2) 91.10(2), C(2)–Ir(2)–I(3) 87.7(2), C(2)–Ir(2)–I(4) 88.2(2), I(3)–Ir(2)–I(4) 90.53(2).

resulting mixture was extracted with hexane and dried. Removal of solvent under reduced pressure afforded the dinuclear dicarbonyliridium complexes $[(C_5Me_4)(CH_2)_n(C_5Me_4)]$ [Ir- $(CO)_2$]₂ (**6b**,**c**, n = 3, 4) as yellow microcrystalline solids in good yields (Scheme 4).



In the ¹H NMR spectra of a C_6D_6 solution of complexes **6**, the signals associated with the methyl protons on the C_5 rings appear at around 1.8 ppm as two singlets close to each other with an integral intensity of 12H. The signals around δ 177 ppm in the ¹³C NMR spectra of **6** clearly reveal the presence of terminal carbonyl ligands. The IR spectra of **6** show two absorption peaks attributable to stretching vibration of the terminal carbonyl absorptions around 2000 and 1930 cm⁻¹. The structure of **6c** was confirmed by single-crystal X-ray diffraction studies and is depicted in Figure 4 with selected bond lengths and angles.

Preparation of Cyclometalated Dinuclear Iridium Complexes 7b,c, 8b,c, 9b,c, and 10b,c. The first example



Figure 4. ORTEP view of $[(C_5Me_4)(CH_2)_4(C_5Me_4)][Ir(CO)_2]_2$ (6c) showing 30% ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)-C(1) 1.838(6), Ir(1)-C(2) 1.834(7), $Ir(1)\cdots Ir(1A)$ 10.465, C(1)-Ir(1)-C(2) 89.3(2).

Scheme 5



of the Cp*Ir complex with a cyclometalated nitrogen donor ligand was reported by Beck and co-workers in 1998, using $[Cp*IrCl_2]_2$ and NaOAc.^{4a} After that, $[Cp*IrCl_2]_2$ has been established as a starting material to synthesize many cyclometalated iridium complexes.⁴

Because of the well-established cyclometalated Cp*Ir complex with 2-phenylpyridine,^{4g} our initial study focused on the reactions of complexes 3 with this ligand. However, we failed to obtain the cyclometalated product in the presence of NaOAc. When these reactions were carried out in refluxing CH₃CN in the presence of KOH, the cyclometalated dinuclear iridium complexes 7b,c were obtained as a yellow solid in moderate to good yield (Scheme 5). The ¹H NMR spectra of 7 clearly show eight protons, as expected for the orthometalated ligand, which is similar to that of the reported analogous mononuclear Cp*Ir complex.¹³ The structure of 7b was confirmed by single-crystal X-ray diffraction studies and is depicted in Figure 5 with selected bond lengths and angles. Complex 7b possesses two inequivalent (C_5Me_4) Ir fragments, linked by a $(CH_2)_3$ chain. The (C_5Me_4) Ir fragments adopt a three-legged piano-stool geometry, and the two cyclopentadienyl rings are criss-crossed with each other at a dihedral angle of 72.3°. The Ir–I bond lengths are 2.6895(9) and 2.689(1) Å, the Ir-N bond lengths are 2.079(4) and 2.068(4) Å, and Ir-C (phenyl pyridine) lengths are 2.041(5) and 2.008(2) Å. These values are close to that of the corresponding analogous mononuclear Cp*Ir complex.¹³ The ¹H NMR spectrum of 7b



Figure 5. ORTEP view of 7b showing 30% ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)-N(1) 2.079(4), Ir(1)-C(28) 2.041(5), Ir(1)-I(1) 2.6895(9), Ir(2)-N(2) 2.068(4), Ir(2)-C(39) 2.008(2), Ir(2)-I(2) 2.689(1), $Ir(1)\cdots Ir(2) 7.761$, N(1)-Ir(1)-C(28) 78.6(2), N(2)-Ir(2)-C(39) 77.0(2).

shows several signals in the range δ 1.81–1.69 for the methyl groups, due to its unsymmetrical structure.

Similarly, cyclometalated dinuclear iridium complexes **8b,c**, **9b,c**, and **10b,c** were obtained from the reactions of complexes **3** and the corresponding ligands. The ¹H NMR spectra of complexes **8–10** also agree with the cyclometalated structures. These results indicated that pyridine, imine, and dihydroimidazole can act as good directing groups in the cyclometalated reactions of complexes **3**.

Catalytic Studies. Complexes 3 and $[Cp*IrI_2]_2$ may possess similar catalytic properties owing to their analogous structures. Williams's group reported that $[Cp*IrI_2]_2$ could serve as an efficient catalyst in the selective amine crosscoupling reaction.^{6g} Complexes 3 were evaluated as catalyst precursors in this reaction, and the catalytic results are summarized in Table 1.

Table 1. N-Alkylation of Aniline Catalyzed by Iridium Complexes a

	R NH ₂ 3 equ xylend	at. µiv (ⁱ Pr) ₂ NH e, 155 ℃, 10 h		
entry	cat.	amine substrate	product	yield (%)
1	3a	4-MeOC ₆ H ₄ NH ₂	11	99
2	3b	4-MeOC ₆ H ₄ NH ₂	11	99
3	3c	4-MeOC ₆ H ₄ NH ₂	11	99
4	3b	C ₆ H ₅ NH ₂	12	99
5	3b	4-ClC ₆ H ₄ NH ₂	13	95
6	3b	4-MeC ₆ H ₄ NH ₂	14	99
7	3b	$4-O_2NC_6H_4NH_2$	15	25
8	3b	3-ClC ₆ H ₄ NH ₂	16	96
9	3b	3-MeC ₆ H ₄ NH ₂	17	98
10	3b	$2-MeC_6H_4NH_2$	18	80
11	3b	2-MeOC ₆ H ₄ NH ₂	19	83
12	3b	C ₆ H ₅ CH ₂ NH ₂	20	96
13	$[Cp*IrI_2]_2$	4-MeOC ₆ H ₄ NH ₂	11	99
14	4b	4-MeOC ₆ H ₄ NH ₂	11	96
15	5b	4-MeOC ₆ H ₄ NH ₂	11	31
16	$Cp*Ir(PPh_3)I_2$	4-MeOC ₆ H ₄ NH ₂	11	84
17^{b}	4b	4-MeOC ₆ H ₄ NH ₂	11	96
18^{b}	$Cp*Ir(PPh_3)I_2$	4-MeOC ₆ H ₄ NH ₂	11	65
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^{*a*}Reaction conditions: amine substrate RNH₂ (1 mmol), (iPr)₂NH (3 mmol), xylene (2 mL), catalyst (2 mol % Ir), 155 °C, 10 h. Yields of isolated products are based on amine substrates. ^{*b*}T = 140 °C.

The reactions were carried out using a catalyst loading of 2 mol % Ir in xylene at 155 °C. We first examined the Nalkylation of 4-methoxyaniline with diisopropylamine catalyzed by three iodo-bridged polymeric iridium complexes, 3a-c. Encouragingly, excellent yields were obtained by using any of them. Then we investigated N-alkylation of a range of amines with diisopropylamine by using 3b as the catalyst. In most cases, the N-isopropylamine was isolated in excellent yield. However, the electron-deficient (Table 1, entry 7) and orthosubstituted (Table 1, entries 10, 11) aniline led to a lower yield. Moreover, benzylamine (Table 1, entry 12) could also react nicely with diisopropylamine. These results indicated that the catalytic activities of complexes 3 were similar to that of $[Cp*IrI_2]_2$ (ref 6g and Table 1, entry 13). The catalytic activities of dinuclear complexes 4b and 5b in the N-alkylation of 4-methoxyaniline with diisopropylamine were also studied. The yield using 4b as the catalyst is excellent, while the yield using **5b** as the catalyst is much lower (Table 1, entries 14, 15). Compared to dinuclear complex 4b, the monometallic analogue $Cp*Ir(PPh_3)I_2$ afforded a lower yield (Table 1, entry 16). When the reaction temperature was decreased to 140 °C, the catalytic activity of 4b was significantly better than that of its monometallic analogue (Table 1, entries 17, 18).

When catalysts **3** were used in this reaction, the iridium complex could be removed from the reaction mixture by simple

filtration owing to their very poor solubility. Then we turned our attention to the recyclability. In the N-alkylation of 4methoxyaniline with 3b as the catalyst under the conditions listed in Table 1, the iridium complex can be recycled easily. The initial three cycles afforded the corresponding product in high yields (Table 2). However, the yield dramatically

Table 2. Recycling of Catalyst 3b for N-Alkylation of 4-Methoxyaniline



decreased in the fourth cycle, with most of the iridium complex converted to a black solid. This black solid is not soluble even in DMSO, and it may be formed from decomposition of the iridium catalyst.

CONCLUSION

In summary, iodo-bridged polymeric iridium complexes 3a-c $[(C_5Me_4)(CH_2)_n(C_5Me_4)(IrI_2)_2]_m$ (n = 2-4) were synthesized successfully by the reactions of dilithium salts $Li_2[(C_5Me_4) (CH_2)_n(C_5Me_4)$ with $[Ir(\mu-Cl)(COD)]_2$, followed by oxidation by iodine. Complexes 3 could serve as starting material to synthesize a series of dinuclear iridium complexes $[(C_5Me_4) (CH_2)_n(C_5Me_4)$ [IrI₂(PPh₃)]₂ (4a-c), [(C₅Me₄)(CH₂)_n- (C_5Me_4) [IrI₂(CO)]₂ (**5b**,c), and [(C₅Me₄)(CH₂)_n(C₅Me₄)]- $[Ir(CO)_2]_2$ (**6b**,c). Additionally, the cyclometalated dinuclear iridium complexes 7b,c, 8b,c, 9b,c, and 10b,c could be obtained by the reactions of complexes 3 with corresponding ligands in refluxing CH₃CN in the presence of KOH. Moreover, we found that complexes 3 and 4 could serve as efficient catalysts in the selective amine cross-coupling reaction. The study of recyclability of 3 indicated that the recovered catalyst only had good activity in the initial three cycles. Our further research of these dinuclear iridium complexes both in stoichiometry and in catalysis is still in progress.

EXPERIMENTAL SECTION

General Considerations. Schlenk- and vacuum-line techniques were employed for all manipulations. All solvents were distilled from appropriate drying agents under argon before use. ¹H, ¹³C, and ³¹P NMR spectra were recorded using a Bruker AV400 spectrometer. IR spectra were recorded as KBr disks on a Bruker TENSOR 27 spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. ESI mass spectra were measured on a Finnigan LCQ Advantage instrument. Compounds 1a,⁸ 1b,⁹ and $[Ir(\mu-Cl)(COD)]_2^{14}$ were prepared by literature methods.

Preparation of $(C_5Me_4H)(CH_2)_4(C_5Me_4H)$ (1c). To a 250 mL three-necked flask, equipped with a reflux condenser, a constant pressure funnel, and a large magnetic stirrer bar, were added THF (80 mL) and Mg (1.70 g, 70.0 mmol). Then a mixture of Br(CH₂)₄Br (7.68 g, 35 mmol) and THF (15 mL) was added dropwise to the solution as required for initiation of the Grignard reaction. After the reaction began, this solution was added at a rate that caused reflux of the solvent. The reaction mixture was then heated under reflux for 1 h.

To another 250 mL three-necked flask, equipped with a reflux condenser, a constant pressure funnel, and a magnetic stirrer bar, were added 2,3,4,5-tetramethylcyclopent-2-en-1-one (10.0 g, 72.5 mmol) and THF (30 mL). The reaction mixture was cooled to 0 °C, and the

Grignard reagent was added dropwise to the solution. After the addition was complete, the solution was stirred overnight at room temperature and then refluxed for another 3 h. The resulting suspension was cooled to room temperature and quenched with 6 M HCl aqueous solution (100 mL). The mixture was stirred vigorously for 6 h. The aqueous phase was extracted three times with 50 mL of diethyl ether, and the combined ether fraction was dried over MgSO₄. The solvents and excess tetramethylcyclopentenone were removed in vacuo. The resultant brown, oily product was purified by column chromatography on silica gel with petroleum ether as the eluent. Evaporation of the eluate afforded 1c as a yellow oil (7.5 g, 72%). ¹H NMR (CDCl₃): δ 2.59–2.12 (m, 6H, C₅Me₄CH₂ and C₅Me₄H), 1.82–1.78 (m, 18H, C₅Me₄), 1.3 (m, 4H, CH₂), 1.02–0.86 (m, 6H, C₅Me₄). ESI-MS (m/z): 298 [M]⁺. This spectroscopic data are much closer to that reported by Suzuki.^{10b}

Preparation of Dinuclear Iridium Complexes 2a–c, [(C₅Me₄)-(CH₂)_n(C₅Me₄)][Ir(COD)]₂ (2a: n = 2; 2b: n = 3; 2c: n = 4). A solution of 1b (329 mg, 1.16 mmol) in hexane (20 mL) was treated with 1.03 mL of *n*-BuLi (2.25 M, 2.32 mmol) in 0 °C, and the mixture was refluxed overnight to give a white precipitate. The solvent was removed in vacuo, and then xylene (20 mL) was added. The mixture was cooled to 0 °C, and then [Ir(μ -Cl)(COD)]₂ (779 mg, 1.16 mmol) was added. The reaction mixture was refluxed for 24 h to give a dark solution. The reaction solvent was removed in vacuo, and the residue was chromatographed on a short alumina column with petroleum ether as eluent to give a white solid, 2b (420 mg, 42%). By using similar procedures, 2a and 2c could be obtained in 5% and 36% yields, respectively.

Compound **2a** (n = 2). Mp: 267–268 °C. Anal. Calcd for $C_{36}H_{52}I_{2}$: C, 49.74; H, 6.03. Found: C, 49.66; H, 5.97. ¹H NMR (CDCl₃): δ 2.76 (d, J = 2.8 Hz, 8H, CH(COD)), 2.29 (s, 4H, (CH₂)₂), 2.01–1.98 (m, 8H, CH₂(COD)), 1.86 (s, 12H, C₅Me₄), 1.78–1.76 (m, 8H, CH₂(COD)), 1.75 (s, 12H, C₅Me₄). ¹³C NMR (100 MHz, CDCl₃): δ 95.0 (C_5 (CH₃)₄), 92.2 (C_5 Me₄), 90.3 (C_5 Me₄), 51.8 (CH(COD)), 33.1, 26.0, 8.3 (C_5 Me₄), 7.8 (C_5 Me₄). ESI-MS (m/z): 871 ([M + H]⁺, based on ¹⁹³Ir).

Compound **2b** (n = 3). Mp: 179–180 °C. Anal. Calcd for $C_{37}H_{54}Ir_2$: C, 50.31; H, 6.16. Found: C, 50.25; H, 6.09. ¹H NMR (CDCl₃): δ 2.75 (s, 8H, CH(COD)), 2.19 (t, J = 7.3 Hz, 4H, CH₂CH₂CH₂CH₂), 1.98 (m, 8H, CH₂(COD)), 1.85 (s, 12H, C₅Me₄), 1.78 (m, 20H, C₅Me₄ and CH₂(COD)), 1.54 (m, 2H, CH₂CH₂CH₂CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 96.1 (C_5 Me₄), 92.9 (C_5 Me₄), 91.3 (C_5 Me₄), 52.8 (CH(COD)), 34.2, 33.3, 24.8, 9.3 (C_5 Me₄), 9.0 (C_5 Me₄). ESI-MS (m/z): 885 ([M + H]⁺, based on ¹⁹³Ir).

Compound 2c (n = 4). Mp: 231–232 °C. Anal. Calcd for $C_{38}H_{56}Ir_2$: C, 50.87; H, 6.29. Found: C, 50.94; H, 6.37. ¹H NMR (CDCl₃): δ 2.74 (d, J = 2.7 Hz, 8H, CH(COD)), 2.16 (t, J = 6.9 Hz, 4H, CH₂CH₂CH₂CH₂), 2.00–1.98 (m, 8H, CH₂(COD)), 1.85 (s, 12H, C₅Me₄), 1.79 (s, 12H, C₅Me₄), 1.76 (m, 8H, CH₂(COD)), 1.46 (m, 4H, CH₂CH₂CH₂CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 96.5 (C₅Me₄), 92.8 (C₅Me₄), 91.4 (C₅Me₄), 58.3 (CH(COD)), 52.8 (CH(COD)), 34.1, 31.7, 24.6, 18.3, 9.3 (C₅Me₄), 9.1 (C₅Me₄). ESI-MS (m/z): 899 ([M + H]⁺, based on ¹⁹³Ir).

Preparation of lodo-Bridged Polymeric Iridium Complexes $[(C_5Me_4)(CH_2)_n(C_5Me_4)(Irl_2)_2]_m$ (3a: n = 2; 3b: n = 3; 3c: n = 4). To a solution of 2b (300 mg, 0.340 mmol) in 40 mL of CH_2Cl_2 was added dropwise 175 mg (0.690 mmol) of I_2 in 50 mL of CH_2Cl_2 , and the mixture was stirred for 3 days to give a dark red suspension. The reaction solvent was removed in vacuo, and the residue was washed with CH_2Cl_2 three times to give a dark red solid 3b (351 mg, 88%). By using similar procedures, 3a and 3c could be obtained in 84% and 87% yields, respectively.

Compound **3a** (n = 2). Mp: >300 °C. Anal. Calcd for $C_{20}H_{28}I_4Ir_2$: C, 20.70; H, 2.43. Found: C, 20.83; H, 2.45. ¹H NMR (DMSO- d_6): δ 2.37 (s, 4H, (CH_2)₂), 1.94 (s, 12H, C_5Me_4), 1.91 (s, 12H, C_5Me_4).

Compound **3b** (*n* = 3). Mp: >300 °C. Anal. Calcd for $C_{21}H_{30}I_4Ir_2$: C, 21.47; H, 2.57. Found: C, 21.41; H, 2.63. ¹H NMR (DMSO- d_6): δ 2.33 (t, *J* = 7.8 Hz, 4H, CH₂CH₂CH₂), 1.92 (s, 12H, C₃Me₄), 1.88 (s, 12H, C₅Me₄), 1.56 (m, 2H, CH₂CH₂CH₂). Compound 3c (n = 4). Mp: >300 °C. Anal. Calcd for $C_{22}H_{32}I_4Ir_2$: C, 22.23; H, 2.71. Found: C, 22.29; H, 2.69. ¹H NMR (DMSO- d_6): δ 2.34 (m, 4H, CH₂CH₂CH₂CH₂), 1.93 (s, 12H, C₅Me₄), 1.89 (s, 12H, C₅Me₄), 1.50 (m, 4H, CH₂CH₂CH₂CH₂).

Preparation of Dinuclear Iridium Complexes $[(C_5Me_4)(CH_2)_n-(C_5Me_4)][IrI_2(PPh_3)]_2$ (4a: n = 2, 4b: n = 3; 4c: n = 4). A suspension of 3b (50 mg, 0.0426 mmol) and PPh₃ (23 mg, 0.0877 mmol) in 20 mL of CH₂Cl₂ was stirred for 2 h to give a red solution. After removal of solvent in vacuo the residue was washed with ether three times to give an orange solid, 4b (68 mg, 94%). By using similar procedures, 4a and 4c also could be obtained as orange solids in 95% and 97% yields, respectively.

Compound 4a (n = 2). Mp: >300 °C. Anal. Calcd for $C_{56}H_{58}I_4Ir_2P_2$: C, 39.92; H, 3.47. Found: C, 40.07; H, 3.53. ¹H NMR (CDCl₃): δ 7.76 (s, 4H, Ph-H), 7.60 (m, 8H, Ph-H), 7.46 (m, 12H, Ph-H), 7.26 (s, 6H, Ph-H), 2.17 (s, 4H, (CH₂)₂), 1.78 (s, 12H, C_5Me_4), 1.53 (s, 12H, C_5Me_4). ³¹P NMR (CDCl₃): δ -9.6 (s). ESI-MS (m/z): 1559 ([M - I]⁺, based on ¹⁹³Ir). Compound 4b (n = 3). Mp: 242–243 °C. Anal. Calcd for

Compound **4b** (*n* = 3). Mp: 242–243 °C. Anal. Calcd for $C_{57}H_{60}L_4Ir_2P_2$: C, 40.29; H, 3.56. Found: C, 40.17; H, 3.47. ¹H NMR (CDCl₃): δ 7.77 (s, 4H, Ph-H), 7.59 (t, *J* = 8.2 Hz, 8H, Ph-H), 7.44–7.42 (m, 12H, Ph-H), 7.23 (s, 6H, Ph-H), 2.03 (t, *J* = 7.5 Hz, 4H, CH₂CH₂CH₂), 1.69 (d, *J*_{PH} = 1.4 Hz, 12H, C₅*Me*₄), 1.56 (d, *J*_{PH} = 1.2 Hz, 12H, C₅*Me*₄), 1.42–1.40 (m, 2H, CH₂CH₂CH₂). ³¹P NMR (CDCl₃): δ –9.4 (s). ESI-MS (*m*/*z*): 1573 ([M – -I]⁺, based on ¹⁹³Ir).

Compound 4c (n = 4). Mp: >300 °C. Anal. Calcd for $C_{58}H_{62}I_4Ir_2P_2$: C, 40.66; H, 3.65. Found: C, 40.59; H, 3.70. ¹H NMR (CDCl₃): δ 7.78 (m, 4H, Ph-H), 7.60 (t, J = 8.3 Hz, 8H, Ph-H), 7.44–7.43 (m, 12H, Ph-H), 7.23 (s, 6H, Ph-H), 1.96 (t, J = 6.5 Hz, 4H, CH₂CH₂CH₂CH₂), 1.72 (d, $J_{PH} = 1.9$ Hz, 12H, C_5Me_4), 1.59 (d, $J_{PH} = 1.8$ Hz, 12H, C_5Me_4), 1.31 (m, 4H, CH₂CH₂CH₂CH₂). ³¹P NMR (CDCl₃): δ –9.4 (s). ESI-MS (m/z): 1587 ([M – 1]⁺, based on ¹⁹³Ir).

Preparation of Dinuclear Diiodo(carbonyl) Iridium Complexes $[(C_5Me_4)(CH_2)_n(C_5Me_4)][IrI_2(CO)]_2$ (5b: n = 3; 5c: n = 4). A suspension of 3b (63 mg, 0.0536 mmol) in 15 mL of CH_2Cl_2 was bubbled by CO at room temperature for 2 h to give a red solution. Removal of solvent in vacuo gave an orange-red solid, 5b (63 mg, 96%). By using similar procedures, 5c also could be obtained as a yellow solid in 95% yield.

Compound **5b** (*n* = 3). Mp: 217–218 °C. Anal. Calcd for $C_{23}H_{30}I_4Ir_2O_2$: C, 22.45; H, 2.46. Found: C, 22.63; H, 2.50. ¹H NMR (CDCl₃): δ 2.51 (m, 4H, CH₂CH₂CH₂), 2.26 (s, 12H, C₅Me₄), 2.21 (s, 12H, C₅Me₄), 1.75 (m, 2H, CH₂CH₂CH₂). IR (ν_{CO} , cm⁻¹): 2025 (s).

Compound 5c (n = 4). Mp: >300 °C. Anal. Calcd for $C_{24}H_{32}I_4Ir_2O_2$: C, 23.16; H, 2.59. Found: C, 22.95; H, 2.52. ¹H NMR (CDCl₃): δ 2.44 (m, 4H, CH₂CH₂CH₂CH₂), 2.26 (s, 12H, C₅Me₄), 2.21 (s, 12H, C₅Me₄), 1.68 (m, 4H, CH₂CH₂CH₂CH₂CH₂). IR (ν_{CO} , cm⁻¹): 2022 (s).

Preparation of Dinuclear Dicarbonyl Iridium Complexes $[(C_5Me_4)(CH_2)_n(C_5Me_4)][[Ir(CO)_2]_2$ (6b: n = 3; 6c: n = 4). A suspension of 3b (100 mg, 0.0851 mmol) and Zn powder (60 mg, 0.918 mmol) in 30 mL of CH₃OH was bubbled by CO at 65 °C for 5 h to give a pale yellow solution. After cooling to room temperature, an aqueous solution of NaOH saturated with NaCl (15 mL, argon sparged) was transferred via cannula to the solution, and it was stirred for 20 min. The mixture was extracted with 4×10 mL of hexane. The extracts were combined and dried by MgSO₄ for 2 h. The solution was filtered, and the solvent was removed in vacuo to give a yellow solid, 6b (54 mg, 81%). By using similar procedures, 6c could be obtained as a yellow solid in 78% yield.

Compound **6b** (n = 3). Mp: 88–90 °C. Anal. Calcd for $C_{25}H_{32}Ir_2O_4$: C, 38.45; H, 4.13. Found: C, 38.69; H, 4.22. ¹H NMR (C_6D_6) : δ 2.19 (t, J = 8.1 Hz, 4H, $CH_2CH_2CH_2$), 1.86 (s, 12H, C_5Me_4), 1.80 (s, 12H, C_5Me_4), 1.35 (m, 2H, $CH_2CH_2CH_2$). ¹³C NMR (100 MHz, C_6D_6): δ 177.8 (C \equiv O), 102.4 ($C_5(CH_3)_4$), 97.6 ($C_5(CH_3)_4$), 96.4 ($C_5(CH_3)_4$), 37.3 ($CH_2CH_2CH_2$), 25.0 ($CH_2CH_2CH_2$), 10.3 (C_5Me_4). IR (ν_{C0} , cm⁻¹): 1999 (s), 1926 (s). ESI-MS (m/z): 781 ([M + H]⁺, based on ¹⁹³Ir).

Compound **6c** (n = 4). Mp: 151–152 °C. Anal. Calcd for $C_{26}H_{34}Ir_2O_4$: C, 39.28; H, 4.31. Found: C, 39.53; H, 4.38. ¹H NMR (C_6D_6) : δ 2.18 (t, J = 7.0 Hz, 4H, $CH_2CH_2CH_2CH_2$), 1.87 (s, 12H, C_5Me_4), 1.80 (s, 12H, C_5Me_4), 1.38 (m, 4H, $CH_2CH_2CH_2CH_2$). ¹³C NMR (100 MHz, C_6D_6): δ 176.6 (C=O), 102.4 (C_5Me_4), 96.2 (C_5Me_4), 95.1 (C_5Me_4), 33.1 ($CH_2CH_2CH_2CH_2$), 23.4 ($CH_2CH_2CH_2CH_2$), 9.0 (C_5Me_4). IR (ν_{C0} , cm⁻¹): 2005 (s), 1937 (s). ESI-MS (m/z): 795 ([M + H]⁺, based on ¹⁹³Ir).

Preparation of Cyclometalated Dinuclear Iridium Complexs 7b,c. A solution of 3b (80.0 mg, 0.0681 mmol), 2-phenylpyridine (25.3 mg, 0.163 mmol), and KOH (11.2 mg, 0.200 mmol) in 30 mL of CH₃CN was refluxed for 24 h. After filtration through Celite the filtrate was concentrated and further purified via neutral alumina gel chromatography with CH₂Cl₂ to give a yellow solid, 7b (38 mg, 45%). By using similar procedures, 7c could be obtained as a yellow solid in 51% yield.

Compound **7b** (n = 3). Mp: >300 °C. Anal. Calcd for C₄₃H₄₆I₂Ir₂N₂: C, 42.02; H, 3.77. Found: C, 42.11; H, 3.81. ¹H NMR (CDCl₃): δ 8.67 (d, J = 5.7 Hz, 2H, HC=N), 7.77 (d, J = 8.1 Hz, 2H, Ar-H), 7.67 (dd, J = 7.7, 12.5 Hz, 4H, Ar-H), 7.60 (t, J = 7.7 Hz, 2H, Ar-H), 7.16 (t, J = 7.4 Hz, 2H, Ar-H), 6.98 (dd, J = 6.4, 13.2 Hz, 2H, Ar-H), 2.21–2.05 (m, 4H, CH₂CH₂CH₂), 1.81–1.69 (m, 24H, C₅Me₄), 1.50–1.42 (m, 2H, CH₂CH₂CH₂). ESI-MS (m/z): 1103 ([M – I]⁺, based on ¹⁹³Ir).

Compound 7c (n = 4). Mp: >300 °C. Anal. Calcd for $C_{44}H_{48}I_2Ir_2N_2$: C, 42.51; H, 3.89. Found: C, 42.69; H, 3.95. ¹H NMR (CDCl₃): δ 8.69 (d, *J* = 5.9 Hz, 2H, *HC*==N), 7.79 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.69 (dd, *J* = 7.8, 14.3 Hz, 4H, Ar-H), 7.61 (t, *J* = 7.9 Hz, 2H, Ar-H), 7.16 (t, *J* = 7.1 Hz, 2H, Ar-H), 6.98 (dd, *J* = 7.8, 13.9 Hz, 2H, Ar-H), 2.13–2.10 (m, 4H, CH₂CH₂CH₂CH₂CH₂), 1.80–1.74 (m, 24H, C₅Me₄), 1.43 (m, 4H, CH₂CH₂CH₂CH₂). ESI-MS (*m*/*z*): 1117 ([M – I]⁺, based on ¹⁹³Ir).

Preparation of Cyclometalated Dinuclear Iridium Complexs 8b,c. A solution of 3b (80.0 mg, 0.0681 mmol), N-benzylidenemethylamine (19.4 mg, 0.163 mmol), and KOH (11.2 mg, 0.200 mmol) in 30 mL of CH₃CN was refluxed for 24 h. After filtration through Celite the filtrate was concentrated and further purified via neutral alumina gel chromatography with CH_2Cl_2 to give a yellow solid, 8b (47 mg, 60%). By using similar procedures, 8c could be obtained as a yellow solid in 55% yield.

Compound **8b** (n = 3). Mp: >300 °C. Anal. Calcd for $C_{37}H_{46}I_2Ir_2N_2$: C, 38.41; H, 4.01. Found: C, 38.23; H, 3.89. ¹H NMR (CDCl₃): δ 8.13 (s, 2H, HC=N), 7.66 (d, J = 7.6 Hz, 2H, C_6H_4), 7.52 (t, J = 7.3 Hz, 2H, C_6H_4), 7.10 (t, J = 7.4 Hz, 2H, C_6H_4), 6.92 (t, J = 7.3 Hz, 2H, C_6H_4), 3.94 (s, 6H, NMe), 2.23 (m, 4H, CH₂CH₂CH₂), 1.86–1.78 (m, 24H, C_5Me_4), 1.53 (m, 2H, CH₂CH₂CH₂). ESI-MS (m/z): 1031 ([M – I]⁺, based on ¹⁹³Ir).

Compound 8c (n = 4). Mp: >300 °C. Anal. Calcd for $C_{38}H_{48}I_2Ir_2N_2$: C, 38.97; H, 4.13. Found: C, 38.93; H, 4.12. ¹H NMR (CDCl₃): δ 8.13 (s, 2H, HC=N), 7.68 (d, J = 7.6 Hz, 2H, C₆H₄), 7.52 (t, J = 7.5 Hz, 2H, C₆H₄), 7.10 (t, J = 7.4 Hz, 2H, C₆H₄), 6.92 (t, J = 7.3 Hz, 2H, C₆H₄), 3.94 (s, 6H, NMe), 2.18 (m, 4H, CH₂CH₂CH₂CH₂CH₂), 1.88–1.82 (m, 24H, C₅Me₄), 1.45 (m, 4H, CH₂CH₂CH₂CH₂). ESI-MS (m/z): 1045 ([M – 1]⁺, based on ¹⁹³Ir).

Preparation of Cyclometalated Dinuclear Iridium Complexs 9b,c. A solution of 3b (80.0 mg, 0.0681 mmol), (*E*)-2-styrylpyridine (29.5 mg, 0.163 mmol), and KOH (11.2 mg, 0.200 mmol) in 30 mL of CH₃CN was refluxed for 24 h. After filtration through Celite the filtrate was concentrated and further purified via neutral alumina gel chromatography with $CH_2Cl_2/acetone$ (20:1) to give a yellow solid, 9b (44 mg, 50%). By using similar procedures, 9c could be obtained as a yellow solid in 53% yield.

Compound **9b** (n = 3). Mp: >300 °C. Anal. Calcd for $C_{47}H_{50}I_2Ir_2N_2$: C, 44.06; H, 3.93. Found: C, 44.18; H, 3.90. ¹H NMR (CDCl₃): δ 8.47 (d, J = 5.7 Hz, 2H, HC=N), 7.57 (d, J = 7.5 Hz, 2H, Ar-H), 7.38 (t, J = 8.3 Hz, 2H, Ar-H), 7.29–7.21 (m, J = 8H, Ar-H), 6.94 (s, 2H, Ar-H), 6.71 (t, J = 5.9 Hz, 2H, Ar-H), 1.87 (t, J = 7.9 Hz, 4H, $CH_2CH_2CH_2$), 1.58–1.49 (m, 24H, C_5Me_4), 1.26 (m, 2H, CH₂CH₂CH₂). ESI-MS (m/z): 1155 ([M – I]⁺, based on ¹⁹³Ir).

Compound 9c (n = 4). Mp: >300 °C. Anal. Calcd for $C_{48}H_{52}I_2Ir_2N_2$: C, 44.51; H, 4.05. Found: C, 44.63; H, 4.01. ¹H NMR (CDCl₃): δ 8.49 (d, J = 5.7 Hz, 2H, HC=N), 7.58 (d, J = 7.3 Hz, 2H, Ar-H), 7.40 (t, J = 7.5 Hz, 2H, Ar-H), 7.31–7.19 (m, J = 8H, Ar-H), 6.96 (s, 2H, Ar-H), 6.72 (t, J = 6.4 Hz, 2H, Ar-H), 1.78 (m, 4H, CH₂CH₂CH₂CH₂), 1.63–1.52 (m, 24H, C₅Me₄), 1.22 (m, 4H, CH₂CH₂CH₂). ESI-MS (m/z): 1169 ([M – I]⁺, based on ¹⁹³Ir).

Preparation of Cyclometalated Dinuclear Iridium Complexs 10b,c. A solution of **3b** (80.0 mg, 0.0681 mmol), 2-phenyl-4,5dihydro-1*H*-imidazole (23.8 mg, 0.163 mmol), and KOH (11.2 mg, 0.200 mmol) in 30 mL of CH₃CN was refluxed for 24 h. After filtration through Celite the filtrate was concentrated and further purified via neutral alumina gel chromatography with CH₂Cl₂/acetone (20:1) to give a yellow solid, **10b** (51 mg, 62%). By using similar procedures, **10c** could be obtained as a yellow solid in 58% yield.

Compound **10b** (n = 3). Mp: >300 °C. Anal. Calcd for $C_{39}H_{48}I_2Ir_2N_4$: C, 38.68; H, 3.99. Found: C, 38.40; H, 4.01. ¹H NMR (CDCl₃): δ 7.68 (d, J = 7.5 Hz, 2H, C_6H_4), 7.25 (d, J = 7.6 Hz, 2H, C_6H_4), 7.12 (t, J = 6.9 Hz, 2H, C_6H_4), 6.88 (t, J = 7.1 Hz, 2H, C_6H_4), 5.36 (s, 2H, NH), 3.87 (t, J = 9.3 Hz, 4H, (CH₂)₂), 3.71–3.64 (m, 2H, (CH₂)₂), 3.50–3.45 (m, 2H, (CH₂)₂), 2.19 (m, 4H, CH₂CH₂CH₂), 1.86–1.78 (m, 24H, C_5Me_4), 1.47 (m, 2H, CH₂CH₂CH₂). ESI-MS (m/z): 1085 ([M – I]⁺, based on ¹⁹³Ir).

Compound 10c (n = 4). Mp: >300 °C. Anal. Calcd for $C_{40}H_{50}I_2Ir_2N_4$: C, 39.22; H, 4.11. Found: C, 39.01; H, 3.98. ¹H NMR (CDCl₃): δ 7.70 (d, J = 7.5 Hz, 2H, C_6H_4), 7.19 (d, J = 7.5 Hz, 2H, C_6H_4), 7.19 (d, J = 7.5 Hz, 2H, C_6H_4), 5.11 (s, 2H, NH), 3.96 (t, J = 9.1 Hz, 4H, (CH₂)₂), 3.82 (t, J = 9.1 Hz, 4H, (CH₂)₂), 2.17 (m, 4H, CH₂CH₂CH₂CH₂), 1.87–1.83 (m, 24H, C_5Me_4), 1.45 (m, 4H, CH₂CH₂CH₂CH₂). ESI-MS (m/z): 1099 ([M – I]⁺, based on ¹⁹³Ir).

Preparation of Cp*lr(PPh₃)l₂. A suspension of $[Cp*IrI_2]_2$ (50 mg, 0.0426 mmol) and PPh₃ (23 mg, 0.0877 mmol) in 20 mL of CH₂Cl₂ was stirred for 2 h to give a red solution. After removal of solvent in vacuo the residue was washed with hexane three times to give a red solid (69 mg, 96%). Mp: 238 °C. Anal. Calcd for C₂₈H₃₀I₂IrP: C, 39.87; H, 3.58. Found: C, 39.93; H, 3.55. ¹H NMR (CDCl₃): δ 7.79 (s, 2H, Ar-H), 7.60 (m, 4H, Ar-H), 7.44 (s, 6H, Ar-H), 7.23 (s, 3H, Ar-H), 1.66 (d, J = 2.2 Hz, 15H, C₃Me₅). ³¹P NMR: δ -8.2 (s). ESI-MS (m/z): 717 ($[M - I]^+$, based on ¹⁹³Ir).

General Procedure for Iridium-Catalyzed Selective Amine Cross-Coupling Reaction. Catalyst (2 mol % Ir), amine substrate RNH₂ (1 mmol), diisopropylamine (3 mmol), and xylene (2 mL) was added to a Schlenk tube. The mixture was heated under reflux for 10 h and then cooled to room temperature. The resulting solution was directly purified by column chromatography with petroleum ether/ethyl acetate (4:1) as eluent. The structures of products 11 and 12,^{6g} 13,¹⁵ 14–18,^{6g} 19,¹⁶ and 20^{6g} were confirmed by comparing their ¹H NMR spectra with those in the literature.

Crystallographic Studies. Single crystals of 2a, 4a, 5b, and 7b suitable for X-ray diffraction analysis were grown from a hexane/ CH₂Cl₂ solution at room temperature, while 6c was grown from a hexane/ether solution. Data collection was performed on a Rigaku Saturn 70 diffractometer equipped with a rotating anode system by using graphite-monochromated Mo K α radiation (ω -2 θ scans). Semiempirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by fullmatrix least-squares. All calculations were carried out using the SHELXL-97 program system. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations. The crystal data and summary of X-ray data collection for complexes 2a, 4a, 5b, 6c, and 7b are presented in the Supporting Information. In 7b, the phenyl pyridine and iodine groups attached to one of the iridium atoms are disordered.

ASSOCIATED CONTENT

S Supporting Information

A CIF file giving X-ray structural information for **2a**, **4a**, **5b**, **6c**, and **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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