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Synthesis of Ir[μ²-(*N*-*N*)]M (M = Ir and Ru) Homo- and Heterobimetallic Complexes through a Condensation Reaction of *N*-Amino and Formyl Groups Bound to Mononuclear (η^n-C_nMe_n)M Units (*n* = 5 for M = Ir; *n* = 6 for M = Ru)

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Reactions of [{Cp*IrCl(μ-Cl)}$_2$] (Cp* = η^5-pentamethylcyclopentadienyl) with bidentate pyridine–imine ligands such as 2-(1-hydrazonoethyl)pyridine (**L**^{1}-NH_2) and 4-({[1-(pyridine-2-yl)ethylidene]hydrazono}methyl)benzaldehyde (**L**^{3}-CHO), followed by salt exchange, afforded the corresponding iridium mononuclear complexes [Cp*IrCl(**L**^{1}-NH_2)][PF_6] (**1a**-PF_6) and [Cp* IrCl(**L**^{3}-CHO)][PF_6] (**6**-PF_6) that bear *N*-amino and formyl functionalities, whereas the reaction of [{Cp*IrCl(μ-Cl)}$_2$] with butane-2,3-diylidenebis(hydrazone) [**L**^{2}-$(NH_2)_2$; 2 equiv.] afforded the half-metallocene iridium complex **2**-PF_6 with two free amino groups at the 2,5-positions of an irida-2,5-diazacyclopentene skeleton. Post-functionalization of the *N*-amino groups of **1a**-PF_6 and **6**-PF_6 was accomplished with 3,5-dimethoxybenzaldehyde in the presence of a catalytic amount of H_2SO_4 in CH_3CN heated at reflux. The condensation reaction proceeded to form *N*-imino-functionalized iridium mononuclear complexes **3**-PF_6 and **4**-PF_6. Dinuclearization of complex **1a**-PF_6 was achieved by a condensation reaction of **1a**-PF_6 with dialdehydes. Reaction of an *N*-amino functional group of **1a**-PF_6 with terephthalaldehyde and isophthalaldehyde in the presence of a catalytic amount of H_2SO_4 gave the corresponding homodinuclear iridium complexes *m*-**5**-PF_6 and *p*-**5**-PF_6 in high yield. The molecular structure of *p*-**5**-PF_6, evaluated by X-ray diffraction study, revealed that two {Cp*IrCl} fragments coordinated to the tetradentate linked hydrazonoethyl skeleton in an *anti* fashion. Furthermore, treatment of the formyl group of iridium complex **6**-PF_6 with the *N*-amino group of ruthenium complex **1b**-PF_6 resulted in the selective formation of an Ir[μ²-(*N*-*N*)]Ru heterobimetallic complex (**7**-PF_6) under similar reaction conditions. The selectivity for the formation of the Ru–Ir heterobimetallic complex was due to the tolerance of the imine moiety to hydrolysis under acidic conditions.

Introduction

Multimetallic complexes have attracted much interest because of their unique and intriguing chemical behaviors, distinct from the corresponding mononuclear complexes,[1,2] which mimic metalloenzymes that contain more than two metals at their active sites,[3] thereby providing suitable molecular sources immobilized on the surface as nanoscale materials and heterogeneous catalysts,[4] and catalyzing unique transformations of organic compounds.[5] For the construction of multimetallic complexes, a rational approach is to design and synthesize the ligand architecture as a key factor for controlling nuclearity as well as the assembly of metal ions. In fact, multidentate ligands have been successfully applied to prepare a diverse array of metal complexes that range from binuclear to larger nuclear complexes.[6–8] Another promising synthetic method is, in principle, a bottom-up approach that uses mononuclear metal species to create multimetallic complexes by means of an intermolecular homo- and cross-coupling reaction of functional groups on each ligand directly bound to the metals.[9,10] Although this method has advantages for synthesizing heterometallic complexes, few examples have been investigated to date.

Herein we report the condensation reactions of *N*-amino and formyl moieties of functionalized hydrazone-based ligands [**L**^{1}-NH_2, **L**^{2}-$(NH_2)_2$, **L**^{3}-CHO in Scheme 1] coordinated to a {Cp*IrCl} fragment; this is exemplified by the reaction of an *N*-amino moiety of a pyridine–imine ligand bound to a {Cp*IrCl} fragment with dialdehydes to give the corresponding homodinuclear iridium complexes. Further extension of the condensation methodology provided access to the synthesis of heteromultimetallic complexes: a formyl group of an iridium complex was treated with an *N*-amino group of a half-metallocene ruthenium complex to afford a Ru–Ir heterobimetallic complex.

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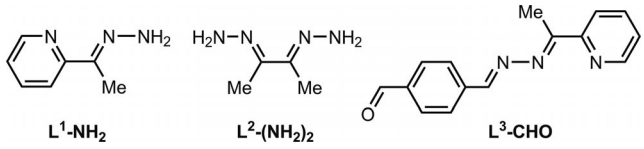
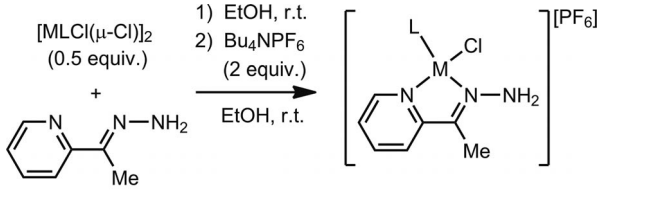


Scheme 1. *N*-Amino- and formyl-functionalized hydrazone-based ligands $\mathbf{L}^1$-NH_2, $\mathbf{L}^2$-$(NH_2)_2$, and $\mathbf{L}^3$-CHO.

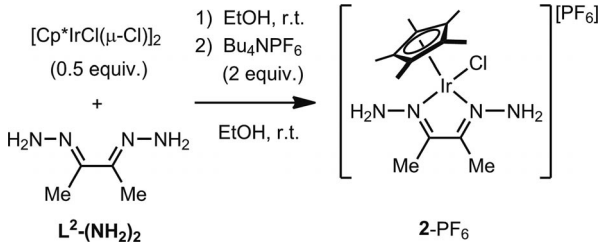
Results and Discussion

A cationic iridium complex, [Cp*IrCl($\mathbf{L}^1$-NH_2)][Cl] (**1a**-Cl), was synthesized by treating [{Cp*IrCl(μ-Cl)}$_2$] with $\mathbf{L}^1$-NH_2 (2 equiv.) [Equation (1)] following the literature procedure to the synthesis of half-metallocene iridium complexes with pyridine-based ligands.[11,12] Subsequently, an anion-exchange reaction of **1a**-Cl with excess amounts of [Bu_4N][PF_6] afforded the corresponding cationic complex with a PF_6 anion, [Cp*IrCl($\mathbf{L}^1$-NH_2)][PF_6] (**1a**-PF_6), which was characterized by ^{1}H and ^{13}C NMR spectra together with combustion analysis. Notable spectroscopic data of **1a**-PF_6 in CD_3CN were a broad singlet at δ_H = 6.61 ppm assignable to a free NH_2 group and a resonance at δ_C = 157.2 ppm due to a ketimine carbon. The C=N stretching frequency (1607 cm^{-1}) shifted to lower field than that of the free ligand (1637 cm^{-1}) in the IR spectrum of **1a**-PF_6, thus indicating the coordination of the imine moiety of the ligand to the iridium metal, and the presence of PF_6 was confirmed by a strong absorption at 840 cm^{-1} due to the intrinsic P–F bond stretching frequency. The solid-state structure of **1a**-PF_6 was determined by single-crystal X-ray analysis, which revealed a three-legged piano-stool geometry around the iridium atom and the presence of a free *N*-amino group, similar to other {Cp*IrCl} complexes with *N*,*N* ligands (Figure 1, Table 1).[11,12] The iridium complex **1a** is an interesting motif to generate an electron-rich {Cp*Ir(α-diimine)} fragment that exhibits strong electronic interaction between the metal center and the π-accepting ligand.[11a,c] Furthermore, by introducing a Ru^{2+} fragment to multimetallic assemblies, it is expected to show unique electronic properties due to the redox processes of $Ru^{2+/3+}$.[13] We thus prepared a ruthenium complex **1b**-PF_6 by the reaction of [{(C_6Me_6)RuCl(μ-Cl)}$_2$] with $\mathbf{L}^1$-NH_2 (2 equiv.), followed by an anion-exchange reaction with [Bu_4N][PF_6].



(1)

The same synthetic strategy could be applied to the reaction of [{Cp*IrCl(μ-Cl)}$_2$] with butane-2,3-diylidenebis(hydrazone) [$\mathbf{L}^2$-$(NH_2)_2$; 2 equiv.] followed by an anion-exchange reaction with [Bu_4N][PF_6] to give complex **2**-PF_6 [Equation (2)], which has two free amino groups at the 2,5-positions of an irida-2,5-diazacyclopentene skeleton. In the ^{1}H NMR spectrum, one broad resonance was observed at δ_H = 6.30 ppm assignable to two –NH_2 groups, and a singlet resonance at δ_C = 154.3 ppm that corresponded to ketimine carbon atoms.



(2)

To check the reactivity of the *N*-NH_2 group of these mononuclear half-metallocene complexes, we performed a post-functionalization reaction of **1a**-PF_6 with 3,5-dimethoxybenzaldehyde. When a mixture of **1a**-PF_6 and excess amounts of 3,5-dimethoxybenzaldehyde (1.5 equiv.) was heated to reflux in CH_3CN in the presence of a catalytic amount of sulfuric acid, the *N*-imino-functionalized product **3**-PF_6 was isolated in 92% yield [Equation (3)]. Notably, this condensation reaction proceeded selectively without any decomposition of **1a**-PF_6, even though H_2SO_4 was used. The formation of the imine moiety of **3**-PF_6 was confirmed by ^{1}H and ^{13}C NMR spectra: a singlet resonance at δ_H = 8.68 ppm and a resonance at δ_C = 162.6 ppm clearly indicated the formation of an aldimine moiety after the condensation reaction.

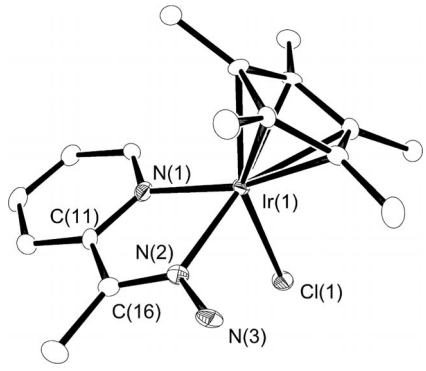
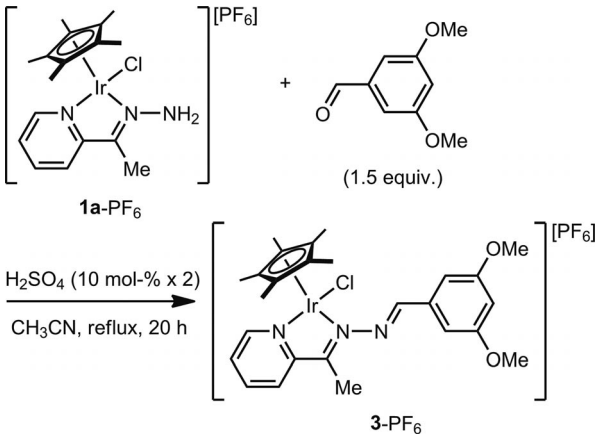


Figure 1. ORTEP drawing of the cationic part of **1a**-PF_6. The thermal ellipsoids are drawn at 30% probability level, and hydrogen atoms and PF_6^- are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] of **1a**-PF_6.

Ir(1)–N(1)	2.097(8)	Ir(1)–N(2)	2.074(8)
Ir(1)–Cl(1)	2.398(3)	N(1)–C(11)	1.361(12)
C(11)–C(16)	1.467(14)	N(2)–C(16)	1.291(13)
N(2)–N(3)	1.387(12)		
N(1)–Ir(1)–N(2)	75.3(3)	N(1)–Ir(1)–Cl(1)	86.3(3)
N(2)–Ir(1)–Cl(1)	84.6(2)		



(3)

Figure 2 shows the molecular structure of **3**-PF_6, and the selected bond lengths and angles are listed in Table 2. The iridium metal adopts a three-legged piano-stool geometry, the same as that observed for **1a**-PF_6. The Ir–N bond lengths [2.104(6) and 2.122(6) Å] are slightly elongated relative to **1a**-PF_6 due to the bulky substituent on the N(2) atom, whereas the angle of N(1)–Ir(1)–N(2) [75.4(2)°] is almost the same as that of **1a**-PF_6. The bond length of N(3)–C(18) [1.266(10) Å] is the same as that of a normal carbon–nitrogen double bond. The 3,5-dimethoxyphenyl group locates *trans* to the {Cp*IrCl} fragment across the N(3)–C(18) double bond.

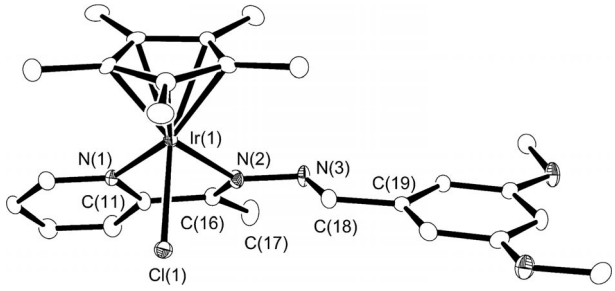
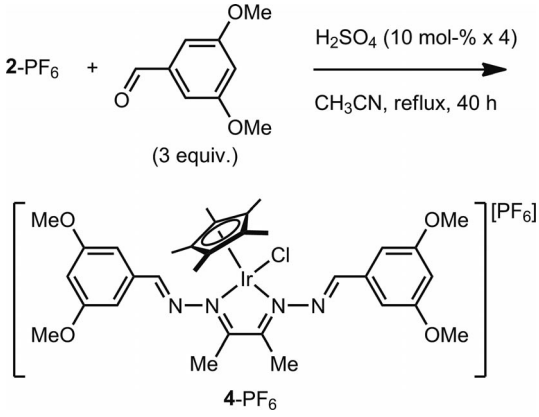


Figure 2. ORTEP drawing of the cationic part of **3**-PF_6. The thermal ellipsoids are drawn at 50% probability level; hydrogen atoms and PF_6^- are omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [°] of **3**-PF_6.

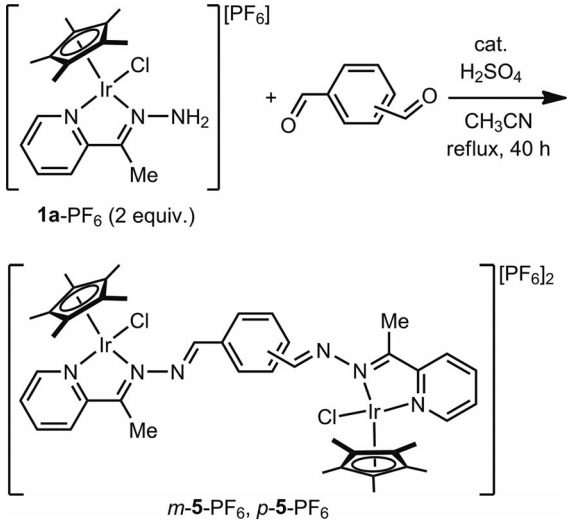
Ir(1)–N(1)	2.104(6)	Ir(1)–N(2)	2.122(6)
Ir(1)–Cl(1)	2.4018(18)	N(1)–C(11)	1.357(9)
C(11)–C(16)	1.468(10)	N(2)–C(16)	1.304(10)
N(2)–N(3)	1.404(8)	N(3)–C(18)	1.266(10)
N(1)–Ir(1)–N(2)	75.4(2)	N(1)–Ir(1)–Cl(1)	86.53(18)
N(2)–Ir(1)–Cl(1)	88.52(18)	N(2)–N(3)–C(18)	113.7(6)
C(19)–C(18)–N(3)	122.4(7)		

Under the optimized conditions established for the synthesis of **3**-PF_6, the reaction of **2**-PF_6, which has two NH_2 groups at the 1,4-positions of the diazabutadiene backbone, with excess amounts (3 equiv.) of 3,5-dimethoxybenzaldehyde was conducted in the presence of a catalytic amount of sulfuric acid. After heating the solution to reflux in CH_3CN for 40 h, two NH_2 moieties of **2**-PF_6 were converted to imine groups to afford **4**-PF_6 in 41% yield [Equation (4)]. In the ^{1}H NMR spectrum of **4**-PF_6, a singlet resonance at δ_H = 8.65 ppm due to imine protons and a singlet at δ_H = 3.88 ppm due to two methoxy protons were observed with a 1:2 relative intensity, thus indicating that **4**-PF_6 has a symmetric structure in solution.



(4)

As the imine moieties of these iridium complexes are stable under acidic conditions, we applied the imine condenstation reaction to prepare homo and hetero dinuclear complexes. First, we conducted a reaction of **1a**-PF_6 with *o*-phthalaldehyde; however, the condensation reaction did not proceed, presumably because of the steric repulsion between the two {Cp*IrCl} moieties. In contrast, the reaction of **1a**-PF_6 with much longer organic spacers such as isophthalaldehyde and terephthalaldehyde, yielded the corresponding dinuclear iridium complexes *m*-**5**-PF_6 and *p*-**5**-PF_6 [Equation (5)]. The ^{1}H NMR spectrum of *m*-**5**-PF_6 at –30 °C displayed two singlet signals at δ_H = 8.76 and 8.80 ppm due to two magnetically inequivalent imine protons, thereby indicating that the complex *m*-**5**-PF_6 has a dissymmetric arrangement for avoiding the steric hindrance between the two {Cp*IrCl} moieties. On the other hand, rather simple resonances due to the symmetric structure of *p*-**5**-PF_6 were observed in the ^{1}H NMR spectrum.



(5)

The solid-state structure of *p*-**5**-PF_6 is depicted in Figure 3, and the selected bond lengths and angles are listed in Table 3. Iridium atoms of *p*-**5**-PF_6 are coordinated to the nitrogen atoms of a Schiff base ligand, terminal chloride atoms, and η^5-pentamethylcyclopentadienyl ligands, thus leading to a typical piano-stool conformation. Two {Cp*IrCl} fragments locate in *anti* fashion to the tetradentate ligand skeleton.[12n] Two metallacycle moieties are parallel, whereas the dihedral angle between one metallacycle that contains Ir(1) and the central aromatic ring is 50.27°. The average distance between the metal atoms and carbon atoms of the Cp* rings is 2.17 Å, comparable to that in related Cp*Ir complexes.[11,12] The Ir–N bond lengths and the angles of N–Ir–N are similar to those of **3**-PF_6. In this case, the short C=N and long C–C bonds for the metallacycle were observed, clearly indicating the neutral coordination of pyridine–imine moiety to the metal center.[11]

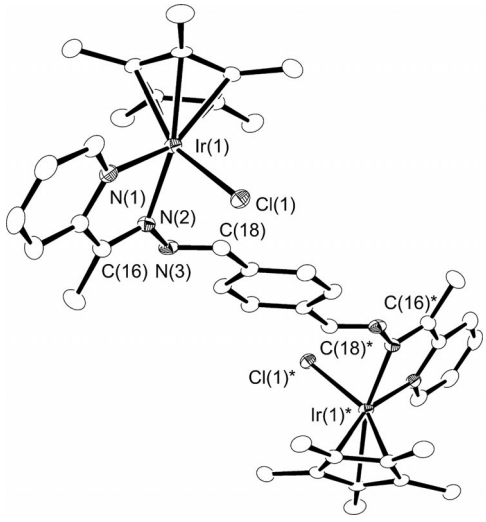
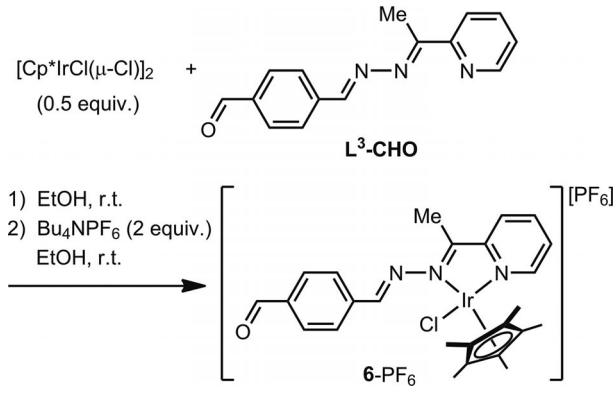


Figure 3. ORTEP drawing of the cationic part of *p*-**5**-PF_6. The thermal ellipsoids are drawn at 50% probability level; hydrogen atoms and $[PF_6]^-$ are omitted for clarity.

Table 3. Selected bond lengths [Å] and angles [°] of *p*-**5**-PF_6.

Ir(1)–N(1)	2.080(5)	Ir(1)–N(2)	2.092(5)
Ir(1)–Cl(1)	2.3878(17)	N(2)–C(16)	1.289(8)
N(2)–N(3)	1.407(7)	C(18)–N(3)	1.280(8)
N(1)–Ir(1)–N(2)	75.73(19)	N(1)–Ir(1)–Cl(1)	85.00(14)
N(2)–Ir(1)–Cl(1)	87.65(14)	C(16)–N(2)–N(3)	116.7(5)
C(18)–N(3)–N(2)	113.5(5)		

To prepare heterobimetallic complexes, we first tried to synthesize an iridium complex with a formyl functionality in the ligand backbone. 4-({[1-(Pyridine-2-yl)ethylidene]-hydrazono}-methyl)benzaldehyde ($\mathbf{L}^3$-CHO) was prepared by a condensation reaction of $\mathbf{L}^1$-NH_2 with 1 equiv. of terephthalaldehyde in Et_2O, and isolated in 54% yield by silica gel column chromatography. Treatment of $[\{Cp^*IrCl(\mu\text{-}Cl)\}_2]$ with $\mathbf{L}^3$-CHO (2 equiv.) followed by an anion-exchange reaction with $[Bu_4N][PF_6]$ gave the iridium complex **6**-PF_6 [Equation (6)]. Complex **6**-PF_6 was characterized by spectroscopic data together with a single-crystal X-ray diffraction study for **6**-PF_6 (Figure 4); selected bond lengths and angles of **6**-PF_6 are listed in Table 4. Notably, the formyl group was observed as a singlet at δ_H = 10.13 ppm, and the aldimine group was observed as a singlet at δ_H = 8.85 ppm in the ^1H NMR spectrum of **6**-PF_6.



(6)

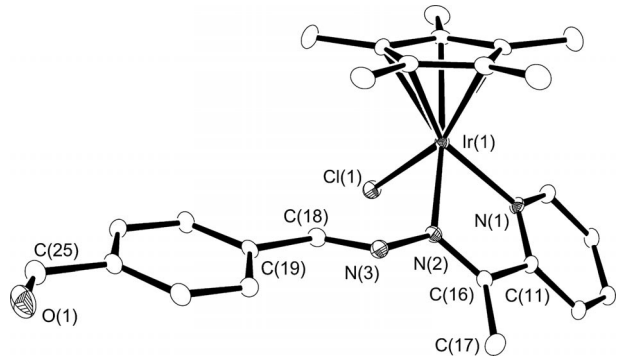


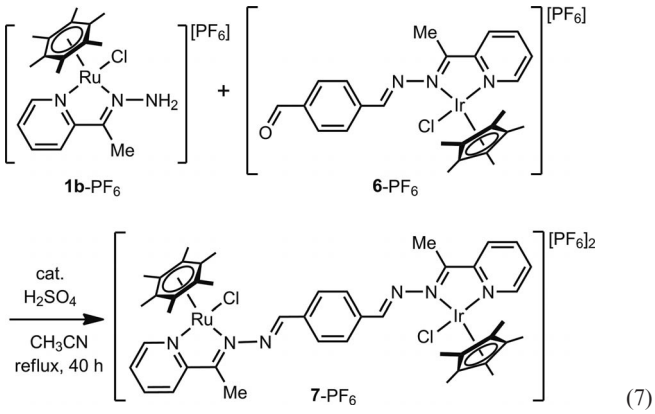
Figure 4. ORTEP drawing of the cationic part of **6**-PF_6. The thermal ellipsoids are drawn at 50% probability level, and hydrogen atoms and $[PF_6]^-$ are omitted for clarity.

Table 4. Selected bond lengths [Å] and angles [°] of **6**-PF_6.

Ir(1)–N(1)	2.086(4)	Ir(1)–N(2)	2.098(4)
Ir(1)–Cl(1)	2.4004(13)	N(1)–C(11)	1.353(6)
C(11)–C(16)	1.471(6)	N(2)–C(16)	1.288(6)
N(2)–N(3)	1.416(5)	N(3)–C(18)	1.270(6)
N(1)–Ir(1)–N(2)	75.16(15)	N(1)–Ir(1)–Cl(1)	85.71(12)
N(2)–Ir(1)–Cl(1)	90.01(12)	N(2)–N(3)–C(18)	113.2(4)
C(19)–C(18)–N(3)	121.8(4)		

We therefore examined the preparation of heterobimetallic complexes by using formyl-substituted complex **6**-PF_6 as a heterobimetallic synthon. Treatment of **6**-PF_6 with $[(C_6Me_6)RuCl(\mathbf{L}^1\text{-}NH_2)][PF_6]$ (**1b**-PF_6) in CH_3CN heated to reflux in the presence of a catalytic amount of H_2SO_4 resulted in the selective formation of Ru–Ir heterobimetallic complex **7**-PF_6 [Equation (7)]. The formation of a new imine moiety in **7**-PF_6 was confirmed by ^1H and ^{13}C NMR spectra. The ^1H NMR spectrum of **7**-PF_6 displayed two sets of resonances assignable to pyridine imine moieties, ald-

imine, and phenyl groups: Two singlet signals were observed at δ_H = 2.60 and 2.74 ppm for the two ketimine groups, δ_H = 8.18 and 8.19 ppm for the phenyl groups, and δ_H = 8.82 and 8.87 ppm for the two aldimine groups.



(7)

Conclusion

We prepared mononuclear half-metallocene iridium complexes with amino and formyl functionalities at the ligand backbone as units for synthesizing bimetallic complexes. Post-functionalization of the *N*-amino groups attached to the {Cp*Ir(Cl)} fragments was accomplished by treatment with 3,5-dimethoxybenzaldehyde in the presence of a catalytic amount of H_2SO_4, and the condensation reaction proceeded to form *N*-imino-functionalized iridium mononuclear complexes. Homobimetallic Ir_2 complexes were isolated by the condensation reaction of an iridium complex with an *N*-amino group and dialdehydes. Heterodinuclearization was accomplished by the condensation reaction of an iridium complex that bore a formyl group with a ruthenium complex that had an *N*-amino moiety. Tolerance of the metal complexes to hydrolysis under acidic conditions was a key factor for the condensation–dinuclearization reaction. We are currently investigating further applications of this reaction for the preparation of multinuclear complexes by means of the condensation reaction of amine and aldehyde groups bound to mononuclear metal complexes.

Experimental Section

General: All manipulations involving air- and moisture-sensitive organometallic compounds were operated using the standard Schlenk techniques under argon. [{Cp*IrCl(μ-Cl)}$_2$],[14] [{(C_6Me_6)RuCl(μ-Cl)}$_2$],[15] **L**^{1}-NH_2, and **L**^{2}-$(NH_2)_2$[16] were prepared according to the literature. Other chemicals were purchased and used without further purification. CH_3CN and CH_2Cl_2 were degassed and stored with activated molecular sieves (3 and 4 Å, respectively). Et_2O and hexane were dried and deoxygenated by distillation with sodium benzophenone ketyl under argon. Methanol and ethanol were distilled from the corresponding magnesium alkoxide under argon. Alternatively, CH_3CN, CH_2Cl_2, THF, Et_2O, and hexane were dried and deoxygenated by using a Grubbs column (Glass Counter Solvent Dispending System, Nikko Hansen & Co, Ltd.). ^{1}H (400 MHz), ^{19}F (376 MHz), and ^{13}C NMR (100 MHz) spectra were measured with Bruker Avance III-400 spectrometers. ^{1}H NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane or referenced to the chemical shifts of residual solvent resonances (CH_3CN was used as internal standard, δ = 1.94 ppm). ^{13}C NMR spectroscopic chemical shifts are reported in ppm (δ) relative to carbon resonances in [D_3]acetonitrile at δ = 1.32 ppm. Assignments for ^{1}H and ^{13}C NMR peaks for some of the complexes were aided by 2D ^{1}H–^{1}H COSY, 2D ^{1}H–^{13}C HMQC, and HMBC spectra. Infrared spectra were recorded with a JASCO FT/IR-410 spectrometer. Mass spectra were obtained with a Bruker Daltonics MicroTOF II-HB and JEOL JMS-700. The elemental analyses were recorded with a Perkin–Elmer 2400 instrument at the Faculty of Engineering Science, Osaka University. All melting points were recorded with a Yanaco micro melting point apparatus. Flash column chromatography was performed using silica gel 60 (230–400 mesh).

Pyridine–Imine Ligand L^3-CHO: A solution of **L**^{1}-NH_2 (329.5 mg, 2.438 mmol) in Et_2O was added dropwise to a solution of terephthalaldehyde (331.9 mg, 2.438 mmol) in Et_2O, and the mixture was stirred at room temperature. After 1.5 h, the solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel (hexane/EtOAc 85:15) to give a yellow powder (54%). ^{1}H NMR (400 MHz, $CDCl_3$, 35 °C): δ = 2.59 (s, 3 H, CH_3), 7.34 (ddd, ^3J = 4.8, 7.8 Hz, ^4J = 1.1 Hz, 1 H, pyridine-H^4), 7.76 (td, J = 7.8, 1.7 Hz, 1 H, pyridine-H^3), 7.96 (d, ^3J = 8.3 Hz, 2 H, Ar), 8.01 (d, ^3J = 8.3 Hz, 2 H, Ar), 8.21 (dt, ^3J = 7.8 Hz, ^4J = 1.1 Hz, 1 H, pyridine-H^2), 8.39 (s, 1 H, NC-H), 8.67 (ddd, ^3J = 4.8 Hz, ^4J = 1.7 Hz, ^5J = 0.9 Hz, 1 H, pyridine-H^5), 10.08 (s, 1 H, CH=O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ = 14.4 (CH_3), 121.6 (pyridine-C^5), 124.7 (pyridine-C^3), 128.9 (*o*-*C* of Ar), 130.2 (*m*-*C* of Ar), 136.4 (pyridine-C^4), 137.9 (*p*-*C* of Ar), 140.1 (*ipso*-*C* of Ar), 149.1 (pyridine-C^2), 155.7 (pyridine-C^1), 156.1 (N=CH), 165.7 (N=*C*CH_3), 191.8 (CH=O) ppm. MS (FAB): *m*/*z* = 252 ([**L**^{3}-CHO + H]$^+$). $C_{15}H_{13}N_3O$ (251.29): calcd. C 71.70, H 5.21, N 16.72; found C 71.63, H 4.88, N 16.81; m.p. 119 °C.

[Cp*IrCl(L^1-NH_2)][PF_6] (1a-PF_6): A mixture of [{Cp*IrCl(μ-Cl)}$_2$] (122 mg, 1.54×10^{-1} mmol) and **L**^{1}-NH_2 (42 mg, 3.1×10^{-1} mmol) in ethanol (10 mL) was stirred at room temperature for 5 min to immediately give an orange solution, to which Bu_4NPF_6 (238 mg, 6.14 mmol) was added, thereby resulting in the precipitation of **1a**-PF_6 as a yellow powder. After filtration, the residue was washed with THF and ether, and then dried in vacuo to give a yellow powder of **1a**-PF_6 (181 mg, 92% yield). ^{1}H NMR (400 MHz, CD_3CN, 35 °C): δ = 1.69 [s, 15 H, $C_5(CH_3)_5$], 2.49 (s, 3 H, CH_3), 6.61 (br. s, 2 H, NH_2), 7.62 (ddd, ^3J = 5.7, 7.6 Hz, ^4J = 1.4 Hz, 1 H, pyridine-H^4), 7.87 (ddd, ^3J = 8.1 Hz, ^4J = 1.4 Hz, ^5J = 0.8 Hz, 1 H, pyridine-H^2), 8.09 (ddd, ^3J = 7.6, 8.1 Hz, ^4J = 1.4 Hz, 1 H, pyridine-H^3), 8.72 (ddd, ^3J = 5.7 Hz, ^4J = 1.4 Hz, ^5J = 0.8 Hz, 1 H, pyridine-H^5) ppm. ^{13}C NMR (100 MHz, CD_3CN, 35 °C): δ = 9.0 [$C_5(CH_3)_5$], 13.5 (CH_3), 90.9 [$C_5(CH_3)_5$], 125.8 (pyridine-C^2), 128.2 (pyridine-C^4), 140.9 (pyridine-C^3), 152.5 (pyridine-C^5), 152.7 (pyridine-C^1), 157.2 (*C*=N) ppm. MS (FAB): *m*/*z* = 498 ([**1a**]$^+$). $C_{17}H_{24}ClF_6IrN_3P$ (643.03): calcd. C 31.75, H 3.76, N 6.53; found C 31.73, H 3.44, N 6.52; m.p. 267 °C (dec.).

[(η^6-C_6Me_6)RuCl(L^1-NH_2)][PF_6] (1b-PF_6): A mixture of [{(η^6-C_6Me_6)RuCl(μ-Cl)}$_2$] (149 mg, 2.22×10^{-1} mmol) and **L**^{1}-NH_2 (61 mg, 4.5×10^{-1} mmol) in ethanol was stirred at room temperature for 30 min to give a red solution, to which Bu_4NPF_6 (344 mg,

8.88×10^{-1} mmol) was added. After all volatiles were removed under reduced pressure, the resulting residue was washed with THF and ether, and then dried in vacuo to give **1b**-PF_6 as a brown powder (84% yield). ^{1}H NMR (400 MHz, CD_3CN, 35 °C): δ = 2.11 [s, 18 H, $C_6(CH_3)_6$], 2.39 (s, 3 H, CH_3), 6.44 (br. s, 2 H, NH_2), 7.53 (ddd, ^3J = 5.7, 7.6 Hz, ^4J = 1.3 Hz, 1 H, pyridine-H^4), 7.75 (ddd, ^3J = 8.1 Hz, ^4J = 1.3 Hz, ^5J = 0.7 Hz, 1 H, pyridine-H^2), 8.02 (ddd, ^3J = 7.6, 8.1 Hz, ^4J = 1.4 Hz, 1 H, pyridine-H^3), 8.75 (ddd, ^3J = 5.7 Hz, ^4J = 1.4 Hz, ^5J = 0.7 Hz, 1 H, pyridine-H^5) ppm. ^{13}C NMR (100 MHz, CD_3CN, 35 °C): δ = 13.4 (CH_3), 15.9 [$C_6(CH_3)_6$], 97.3 [$C_6(CH_3)_6$], 125.1 (pyridine-C^2), 126.4 (pyridine-C^4), 139.9 (pyridine-C^3), 151.4 (pyridine-C^1), 153.9 (pyridine-C^5), 156.4 (C=N) ppm. MS (ESI): m/z = 434 ([**1b**]$^+$). $C_{19}H_{28}ClF_6N_4PRu$ (593.94): calcd. C 39.42, H 4.70, N 7.26; found C 39.60, H 4.52, N 7.13; m.p. 204 °C (dec.).

[Cp*IrCl{L^2-(NH$_2$)$_2$}][PF$_6$] (2-PF$_6$): A mixture of [{Cp*IrCl(μ-Cl)}$_2$] (422 mg, 5.30×10^{-1} mmol) and **L**^{2}-$(NH_2)_2$ (121 mg, 1.06 mmol) in ethanol (20 mL) was stirred at room temperature. Immediately, the solution turned orange. Bu_4NPF_6 (821 mg, 2.12 mmol) was added to the resulting solution, and then all volatiles were removed in vacuo. The resulting residue was extracted with THF, and all volatiles were removed under reduced pressure. The residue was washed with a small volume of THF and ether, and then dried in vacuo to give **2**-PF_6 as a pale yellow powder (411 mg, 62% yield). ^{1}H NMR (400 MHz, CD_3CN, 35 °C): δ = 1.73 [s, 15 H, $C_5(CH_3)_5$], 2.22 (s, 6 H, CH_3), 6.30 (br. s, 4 H, NH_2) ppm. ^{13}C NMR (100 MHz, CD_3CN, 35 °C): δ = 9.1 [$C_5(CH_3)_5$], 15.0 (CH_3), 91.5 [$C_5(CH_3)_5$] 154.3 (C=N) ppm. MS (ESI): m/z = 477 ([**2**]$^+$). $C_{14}H_{25}ClF_6IrN_4P$ (622.01): calcd. C 27.03, H 4.05, N 9.01; found C 27.11, H 3.70, N 8.92; m.p. 245 °C (dec.).

[Cp*IrCl(L^3-CHO)][PF$_6$] (6-PF$_6$): The same operation as **1a**-PF_6 was conducted for a mixture of [{Cp*IrCl(μ-Cl)}$_2$] (98 mg, 1.2×10^{-1} mmol) and **L**^{3}-CHO (62 mg, 2.5 mmol) in ethanol (10 mL). Compound **6**-PF_6 was isolated as a yellow powder (87% yield). ^{1}H NMR (400 MHz, CD_3CN, 35 °C): δ = 1.62 [s, 15 H, $C_5(CH_3)_5$], 2.72 (s, 1 H, CH_3), 7.83 (ddd, ^3J = 5.6, 7.3 Hz, ^4J = 1.8 Hz, 1 H, pyridine-H^4), 8.09 (d, ^3J = 8.4 Hz, 2 H, Ar), 8.18 (d, ^3J = 8.4 Hz, 2 H, Ar), 8.19 (ddd, ^3J = 8.2 Hz, ^4J = 1.8 Hz, ^5J = 0.7 Hz, 1 H, pyridine-H^2), 8.23 (ddd, ^3J = 7.3, 8.2 Hz, ^4J = 1.4 Hz, 1 H, pyridine-H^3), 8.85 (s, 1 H, CH=N), 8.87 (ddd, ^3J = 5.6 Hz, ^4J = 1.4 Hz, ^5J = 0.7 Hz, 1 H, pyridine-H^5), 10.13 (s, 1 H, CH=O) ppm. ^{13}C NMR (100 MHz, CD_3CN, 35 °C): δ = 9.3 [$C_5(CH_3)_5$], 16.2 (CH_3), 91.6 [$C_5(CH_3)_5$], 128.7 (pyridine-C^2), 130.7 (pyridine-C^4), 130.9 (Ar), 131.1 (Ar), 137.5 (Ar), 140.5 (Ar), 141.3 (pyridine-C^3), 152.9 (pyridine-C^5), 156.0 (pyridine-C^1), 162.4 (HC=N), 162.8 (MeC=N), 193.2 (CH=O) ppm. MS (ESI): m/z = 614 ([**6**]$^+$). $C_{25}H_{28}ClF_6IrN_3OP$ (759.15): calcd. C 39.55, H 3.72, N 5.54; found C 39.77, H 3.36, N 5.52; m.p. 210 °C (dec.).

[Cp*IrCl(L^1-N=CHAr)][PF$_6$] [3-PF$_6$; Ar = C$_6$H$_3$(OMe)$_2$-3,5]: A mixture of **1a**-PF_6 (69 mg, 1.1×10^{-1} mmol), 3,5-dimethoxybenzaldehyde (19 mg, 1.6×10^{-1} mmol), and a catalytic amount (10 mol-%) of concentrated H_2SO_4 in acetonitrile (3 mL) was heated to reflux for 10 h. A second portion of concentrated H_2SO_4 (10 mol-%) was added, and then the reaction mixture was heated to reflux for a further 10 h. The solvent was removed in vacuo, and the resulting residue was washed with ethanol and hexane, then dried in vacuo to give **3**-PF_6 as a yellow powder (77 mg, 92% yield). ^{1}H NMR (400 MHz, CD_3CN, 35 °C): δ = 1.62 [s, 15 H, $C_5(CH_3)_5$], 2.71 (s, 3 H, CH_3), 3.87 (s, 6 H, OCH_3), 6.77 (t, ^4J = 2.3 Hz, 1 H, *ortho*-Ar), 7.12 (d, ^4J = 2.3 Hz, 2 H, *para*-Ar), 7.82 (ddd, ^3J = 5.6, 7.4 Hz, ^4J = 1.7 Hz, 1 H, pyridine-H^4), 8.17 (ddd, ^3J = 8.3 Hz, ^4J = 1.7 Hz, ^5J = 0.7 Hz, 1 H, pyridine-H^2), 8.22 (ddd, ^3J = 7.4, 8.3 Hz, ^4J = 1.4 Hz, 1 H, pyridine-H^3), 8.68 (s, 1 H, NC-H), 8.86 (ddd, ^3J = 5.6 Hz, ^4J = 1.4 Hz, ^5J = 0.7 Hz, 1 H, pyridine-H^5) ppm. ^{13}C NMR (100 MHz, CD_3CN, 35 °C): δ = 9.4 [$C_5(CH_3)_5$], 16.2 (CH_3), 56.6 (OCH_3), 91.6 [$C_5(CH_3)_5$], 106.3 (*para*-Ar), 108.0 (*ortho*-Ar), 128.5 (pyridine-C^2), 130.6 (pyridine-C^4), 134.6 (*ipso*-Ar), 141.2 (pyridine-C^3), 152.9 (pyridine-C^5), 156.3 (pyridine-C^1), 162.6 (HC=N), 162.6 (*meta*-Ar), 163.0 (MeC=N) ppm. MS (FAB): m/z = 646 ([**3**]$^+$). $C_{26}H_{32}N_3O_2ClPF_6Ir$: C 39.47, H 4.08, N 5.31; found C 39.21, H 3.89, N 5.34; m.p. 272 °C (dec.).

[Cp*IrCl{L^2-(N=CHAr)$_2$}][PF$_6$] [4-PF$_6$; Ar = C$_6$H$_3$(OMe)$_2$-3,5]: Similarly, a mixture of **2**-PF_6 (26 mg, 4.1×10^{-2} mmol) and 3,5-dimethoxybenzaldehyde (14 mg, 1.2×10^{-1} mmol) in acetonitrile (5 mL) in the presence of a catalytic amount of concentrated H_2SO_4 afforded **4**-PF_6 as an orange powder (16 mg, 41% yield). ^{1}H NMR (400 MHz, CD_3CN, 35 °C): δ = 1.59 [s, 15 H, $C_5(CH_3)_5$], 2.54 (s, 6 H, CH_3), 3.88 (s, 6 H, OCH_3), 6.77 (t, ^4J = 2.3 Hz, 2 H, *para*-Ar), 7.11 (d, ^4J = 2.3 Hz, 4 H, *ortho*-Ar), 8.65 (s, 1 H, NC-H) ppm. ^{13}C NMR (100 MHz, CD_3CN, 35 °C): δ = 9.8 [$C_5(CH_3)_5$], 17.8 (CH_3), 56.6 (OCH_3), 93.4 [$C_5(CH_3)_5$], 106.4 (*para*-Ar), 108.2 (*ortho*-Ph), 134.4 (*ipso*-Ar), 162.6 (HC=N), 162.7 (MeC=N), 168.5 (*meta*-Ar) ppm. MS (FAB): m/z = 773 ([**4**]$^+$). $C_{32}H_{41}ClF_6IrN_4O_4P$ (918.34): calcd. C 41.85, H 4.50, N 6.10; found C 41.84, H 4.34, N 5.96; m.p. 203 °C (dec).

***p*-[Cp*(Cl)Ir(L^1-N=CHC$_6$H$_4$CH=N-L^1)Ir(Cl)Cp*][PF$_6$]$_2$ (*p*-5-PF$_6$):** A mixture of **1**-PF_6 (121 mg, 1.89×10^{-1} mmol) and terephthalaldehyde (13 mg, 9.5×10^{-2} mmol) in acetonitrile (5 mL) in the presence of a catalytic amount of concentrated H_2SO_4 (10 mol-%) was similarly treated to give *p*-**5**-PF_6 as an orange powder (87 mg, 52% yield). ^{1}H NMR (400 MHz, CD_3CN, 30 °C): δ = 1.64 [s, 30 H, $C_5(CH_3)$], 2.74 (s, 6 H, CH_3), 7.85 (ddd, ^3J = 5.6, 7.3 Hz, ^4J = 1.9 Hz, 1 H, pyridine-H^4), 8.19 (s, 4 H, Ph-H), 8.21 (ddd, ^3J = 8.2 Hz, ^4J = 1.9 Hz, ^5J = 0.6 Hz, 1 H, pyridine-H^2), 8.24 (ddd, ^3J = 7.3, 8.2 Hz, ^4J = 1.4 Hz, 1 H, pyridine-H^3), 8.87 (s, 2 H, NC-H), 8.88 (br. d, ^3J = 5.6 Hz, 2 H, pyridine-H_5) ppm. ^{13}C NMR (100 MHz, CD_3CN, 30 °C): δ = 9.4 [$C_5(CH_3)_5$], 16.3 (CH_3), 91.7 [$C_5(CH_3)_5$], 128.7 (pyridine-C^2), 130.8 (pyridine-C^4), 131.1 (Ar), 136.6 (*ipso*-Ar), 141.4 (pyridine-C^3), 153.0 (pyridine-C^5), 156.1 (pyridine-C^1), 162.3 (HC=N), 167.8 (MeC=N) ppm. MS (ESI): m/z = 547 ([*p*-**5**]$^{2+}$). $C_{42}H_{50}Cl_2F_{12}IrN_6P_2$ (1191.95): calcd. C 36.44, H 3.64, N 6.07; found C 36.25, H 3.34, N 6.13; m.p. 258 °C (dec.).

***m*-[Cp*(Cl)Ir(L^1-N=CHC$_6$H$_4$CH=N-L^1)Ir(Cl)Cp*][PF$_6$]$_2$ (*m*-5-PF$_6$):** The same operation was conducted for the mixture of **1a**-PF_6 (102 mg, 1.58×10^{-1} mmol) and isophthalaldehyde (11 mg, 7.9×10^{-2} mmol) to give *m*-**5**-PF_6 as an orange powder (73% yield). ^{1}H NMR (400 MHz, CD_3CN, –30 °C): δ = 1.55 [s, 30 H, $C_5(CH_3)$], 2.65_7 (s, 3 H, CH_3), 2.66_4 (s, 3 H, CH_3), 7.7–7.8 (m, 3 H, py and Ar), 8.1–8.3 (m, 6 H, py and Ar), 8.46 (br. d, J = 16 Hz, 1 H, Ar), 8.76 (s, 1 H, NC-H), 8.80 (s, 1 H, NC-H), 8.81 (br. d, J = 5.6 Hz, 2 H, py) ppm. ^{13}C NMR (100 MHz, CD_3CN, –30 °C): δ = 8.2_7 [$C_5(CH_3)_5$], 8.2_8 [$C_5(CH_3)_5$], 15.2_0 (CH_3), 15.2_1 (CH_3), 90.2_6 [$C_5(CH_3)_5$], 90.2_7 [$C_5(CH_3)_5$], 127.4_6, 127.5_1, 129.6_8, 129.7_2, 130.0, 130.4, 131.0, 132.4_2, 132.4_4, 132.9, 133.3, 140.2, 151.7_5 (pyridine-C^5), 151.7_9 (pyridine-C^5), 154.9_0 (pyridine-C^1), 154.9_1 (pyridine-C^1), 161.0 (HC=N), 161.1 (HC=N), 166.6 (MeC=N), 166.9 (MeC=N) ppm. MS (ESI): m/z = 547 ([*m*-**5**]$^{2+}$). $C_{42}H_{50}Cl_2F_{12}IrN_6P_2$ (1191.95): calcd. C 36.44, H 3.64, N 6.07; found C 36.15, H 3.54, N 6.01; m.p. 235 °C (dec.).

[(η^6-C$_6$Me$_6$)Ru(Cl)(L^1-N=CH-L^3)Ir(Cl)Cp*][PF$_6$]$_2$ (7-PF$_6$): A mixture of **6**-PF_6 (45.2 mg, 59.5 μmol), **1b**-PF_6 (34.5 mg, 59.6 μmol), and a catalytic amount of concentrated H_2SO_4 in acetonitrile was treated in a similar procedure to give **7**-PF_6 as an orange powder (76% yield). ^{1}H NMR (400 MHz, CD_3CN, 30 °C): δ = 1.64 [s, 15

H, $C_5(CH_3)_5$], 2.08 [s, 18 H, $C_6(CH_3)_6$], 2.60 (s, 3 H, CH_3), 2.74 (s, 3 H, CH_3), 7.76 (ddd, ^3J = 5.6, 7.3 Hz, ^4J = 1.5 Hz, 1 H, pyridine-H^4), 7.85 (ddd, ^3J = 5.5, 7.3 Hz, ^4J = 1.8 Hz, 1 H, pyridine-H^4), 8.06 (ddd, ^3J = 7.8 Hz, ^4J = 1.5 Hz, ^5J = 0.6 Hz, 1 H, pyridine-H^2), 8.16 (ddd, ^3J = 7.3, 7.8 Hz, ^4J = 1.4 Hz, 1 H, pyridine-H^3), 8.17 (d, ^3J = 7.2 Hz, 2 H, Ar), 8.19 (d, ^3J = 7.2 Hz, 2 H, Ar), 8.19 (ddd, ^3J = 7.9 Hz, ^4J = 1.8 Hz, ^5J = 0.6 Hz, 1 H, pyridine-H^2), 8.24 (ddd, ^3J = 7.3, 7.9 Hz, ^4J = 1.8 Hz, 1 H, pyridine-H^3), 8.82 (s, 1 H, NC-*H*), 8.87 (s, 1 H, NC-*H*), 8.88 (ddd, ^3J = 5.5 Hz, ^4J = 1.4 Hz, ^5J = 0.6 Hz, 1 H, pyridine-H^5), 8.89 (ddd, ^3J = 5.6 Hz, ^4J = 1.4 Hz, ^5J = 0.6 Hz, 1 H, pyridine-H^5) ppm. ^{13}C NMR (100 MHz, CD_3CN, 30 °C): δ = 9.4 [$C_5(CH_3)_5$], 16.2 (CH_3), 16.3 (CH_3), 16.4 [$C_6(CH_3)_6$], 91.6 [$C_5(CH_3)_5$], 97.8 [$C_6(CH_3)_6$], 128.0 (pyridine-C^2), 128.7 (pyridine-C^2), 129.1 (pyridine-C^4), 130.8 (pyridine-C^4), 130.9 (Ar), 131.0 (Ar), 136.5 (Ar), 136.9 (Ar), 140.4 (pyridine-C^3), 141.3 (pyridine-C^3), 152.9 (pyridine-C^5), 154.4 (pyridine-C^5), 155.4 (pyridine-C^1), 156.0 (pyridine-C^1), 161.0 (HC=N), 162.3 (HC=N), 165.8 (Me*C*=N), 167.8 (Me*C*=N) ppm. MS (ESI): *m*/*z* = 515 ([**7**]$^{2+}$). $C_{42}H_{53}Cl_2F_{12}IrN_6P_2Ru$ (1296.04): calcd. C 40.03, H 4.05, N 6.37; found C 39.71, H 4.12, N 6.22; m.p. 242 °C (dec.).

X-ray Crystallographic Analysis for 1a-PF_6, 3-PF_6, *p*-5-PF_6, and 6-PF_6: All crystals were handled similarly. The crystals were mounted on the CryoLoop (Hampton Research Crop.) with a layer of light mineral oil and in a nitrogen stream at 120(1) K. Measurements were made with a Rigaku Mercury CCD area detector with graphite-monochromated Mo-K_α radiation (λ = 0.71075). Crystal data and structure refinement parameters are summarized in Table SX in the Supporting Information. The structures were solved by direct methods (SIR 92, SIR2008, or SHELXS97) and refined on F^2 by full-matrix least-squares methods by using SHELXL-97.[17] Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\Sigma w(F_o^2 - F_c^2)^2]$ $\{w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]\}$, in which $P = [\max(F_o^2,0) + 2F_c^2]/3$ with $\sigma^2(F_o^2)$ from counting statistics. The functions *R*1 and *wR*2 were $(\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ and $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecule.[18]

CCDC-841812 (for **1a**-PF_6), -841813 (for **3**-PF_6), -841814 (for *p*-**5**-PF_6), and -841815 (for **6**-PF_6) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif..

Supporting Information (see footnote on the first page of this article): A table for crystal parameters for **1a**-PF_6, **3**-PF_6, *p*-**5**-PF_6, and **6**-PF_6 is included.

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