Journal of Organometallic Chemistry 695 (2010) 1675–1681

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis of binuclear iridium(III) and rhodium(III) complexes bearing methylnaphthalene-linked *N*-heterocyclic carbenes, and application to intramolecular hydroamination

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ARTICLE INFO

Article history:
Received 9 February 2010
Received in revised form
5 April 2010
Accepted 9 April 2010
Available online 21 April 2010

Keywords:
N-heterocyclic carbene
Iridium complex
Rhodium complex
Binuclear complex
Intramolecular hydroamination

ABSTRACT

New methylnaphthalene-linked imidazolium salts **1** were synthesized through the reaction of 1,8-dibromomethylnaphthalene and *N*-alkylimidazole. On treatment of imidazolium salt **1** with silver oxide followed by $[Cp^*MCl_2]_2$ (M = Ir, Rh), binuclear iridium and rhodium complexes **2** were formed. Reaction of these complexes **2** with $AgPF_6$ afforded Cl-bridged cationic binuclear iridium and rhodium complexes **3**. X-ray crystallographic analysis of **3** revealed that the two imidazole rings of the carbene ligand are in a parallel geometry. The cationic binuclear iridium complexes **3-Ir** could be applied to the intramolecular hydroamination reaction of 2-ethynylaniline to give the corresponding indole compound.

1. Introduction

N-heterocyclic carbenes (NHCs) have emerged as an extremely useful class of ligands for use in transition-metal complexes [1]. It is well recognized that replacement of phosphines by NHCs can provide complexes with enhanced stability and catalytic performance due to the higher electron-donor ability. The majority of NHC ligands used are monodentate, and much fewer complexes are known that include bidentate bis-NHC ligands, in which a pair of NHC groups is joined by an appropriate linker group. The use of chelating bis-NHC and pincer NHC ligands has allowed for the preparation of new complexes which show increased catalytic activity [2] along with improved stability due to the entropic advantages of chelation. In contrast to chelated NHC complexes, the reactivity and catalytic application of binuclear bridging NHC complex has scarcely been studied [3] even though several binuclear complexes with alkyl chain-linked NHC ligand have been prepared [4]. In order to bring the metals together such that cooperative interaction is possible, the bridging NHC complex needs to have short metal–metal separation. In the case of phosphine ligands, various late-transition-metal complexes with short metal–metal separation have been prepared using a bridging diphosphine ligand [5]. However, synthesis of the corresponding bridging bis-NHC complexes such as halogen bridged complex has not been developed in detail. On the basis of this concept, Cowie et al. recently reported on rhodium complexes which were bridged by a bis-NHC ligand and halogen using a bridging dppm ligand as a second bridging group [4e].

In this report, we describe the synthesis of a new flexible bis-NHC ligand linked by a methylnaphthalene unit, which is used to form complexes with iridium and rhodium (Fig. 1). Because the methylnaphthalene-linked ligand is flexible due to rotation around the methylene groups, it is possible to obtain a structural complex with short metal–metal separation. To evaluate the properties of the ligand, we selected a Cp* iridium(III) system as a metal-complex fragment because stable complexes bearing a monodentate NHC ligand had been reported in Ref. [6], and were found to be of application in intramolecular hydroamination of 2-ethynylaniline derivatives.

2. Results and discussion

2.1. Synthesis of imidazolium salts and binuclear neutral iridium(III) and rhodium(III) complexes

The methylnaphthalene-linked imidazolium salts **1a** and **1b** were readily obtained as white powders by the reaction of

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doi:10.1016/j.jorganchem.2010.04.006

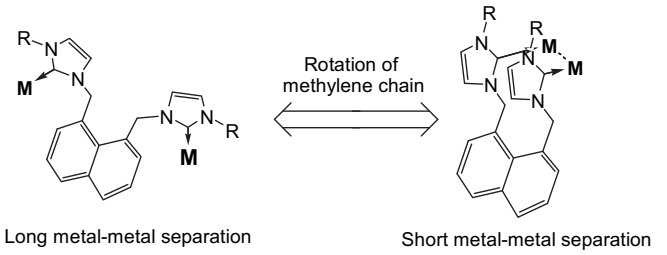


Fig. 1. Methylnaphthalene-linked bis-NHC ligand.

1,8-dibromomethylnaphthalene with *N*-alkylimidazole at 140 °C (Scheme 1). In the ^{1}H NMR spectra of **1a** and **1b**, the characteristic imidazolium proton appeared at 9.98 ppm for **1a** and 10.19 ppm for **1b**.

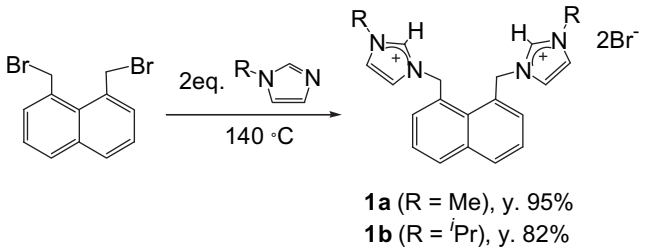
For synthesis of the binuclear carbene complexes, transmetallation from the corresponding silver carbene complexes generated *in situ* was carried out. Transmetallation has proved to be a promising procedure for obtaining *N*-heterocyclic carbene complexes, typically involving treatment of an imidazolium salt with silver oxide to form a silver *N*-heterocyclic carbene complex [7]. Treatment of imidazolium salt **1** with 1 equiv. of silver oxide followed by 1 equiv. of $[Cp^*IrCl_2]_2$ in dichloromethane afforded the binuclear carbene complex **2-Ir** as an orange solid (Scheme 2). In the case of the rhodium complex, the analogous reaction with $[Cp^*RhCl_2]_2$ took place to give **2a-Rh** as a red solid. In the case of the reaction of $[Cp^*IrCl_2]_2$ with 2 equiv. of silver carbene generated by *in situ* reaction of **1a** and silver oxide, the binuclear complex **2a-Ir** was obtained in preference to the mononuclear chelating carbene complex.

The $^{13}C\{^1H\}$ NMR spectra of **2a-Ir**, **2a-Rh** and **2b-Ir** showed signals characteristic of the carbene carbon at 157.3, 170.8 ($J_{RhC} = 58.8$ Hz) and 157.7 ppm, respectively. These carbene signals have the same chemical shifts as those for previously reported neutral Cp* iridium(III) and rhodium(III) complexes bearing a monodentate *N*-heterocyclic carbene ligand [6,8].

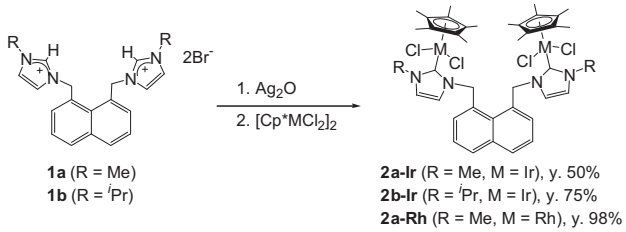
The structure of complex **2b-Ir** was also confirmed by X-ray analysis. The ORTEP drawing of **2b-Ir** is shown in Fig. 2. Selected bond distances and angles are listed in Table 1. The molecule has a dimeric structure connected by the carbene ligand, and the Cp* Ir moieties occupy each side of the naphthalene ring. The two Ir-C(carbene) distances are 2.037(6) and 2.053(5) Å, respectively. These bond distances are the same as those previously reported for a neutral Cp* iridium(III) complex bearing a monodentate *N*-heterocyclic carbene ligand [6].

2.2. Synthesis of Cl-bridged binuclear iridium(III) and rhodium(III) complexes

We next prepared Cl-bridged binuclear iridium and rhodium complexes. The complex **2a** reacted readily with 2 equiv. of $AgPF_6$ at room temperature to afford the Cl-bridged cationic binuclear



Scheme 1. Synthesis of imidazolium salt **1**



Scheme 2. Synthesis of binuclear carbene complex **2**

complex **3a** (Scheme 3). The $^{13}C\{^1H\}$ NMR resonances for the characteristic carbene carbons are observed at 156.9 ppm for **3a-Ir**, and 167.5 ($J_{RhC} = 58.8$ Hz) ppm for **3a-Rh**, which are similar to those reported for similar cationic iridium and rhodium carbene complexes [6]. The complex **3b-Ir** bearing an isopropyl group was also prepared by a similar procedure. In contrast, the reaction of corresponding monodentate *N*-heterocyclic carbene complex ($[Cp^*IrCl_2(I^iPr)]$) with $AgPF_6$ resulted in complex mixture.

Orange single crystals of complex **3a-Ir** suitable for X-ray diffraction were grown from dichloromethane and diethyl ether. The ORTEP drawing of **3a-Ir** is shown in Fig. 3. Selected bond distances and angles are listed in Table 2. X-ray analysis of complex **3a-Ir** revealed the existence of a chloride-bridged binuclear skeleton with a pair of *N*-heterocyclic carbene ligands. The two imidazole rings of the *N*-heterocyclic carbene ligand are parallel to each other. The two Ir-C(carbene) bond distances of **3a-Ir** (2.059(5) and 2.069(5) Å) are slightly longer than those for the neutral complex **2b-Ir**, and are in good agreement with the distances reported for cationic iridium(III) *N*-heterocyclic carbene complexes [6]. The Ir–Ir separation of 3.7701(3) Å corresponds to nonbonding.

Complex **3a-Ir** reacted readily with trimethylphosphite to give the phosphite complex **4a-Ir** (Scheme 4). In contrast, triethylphosphine and triphenylphosphine did not react with complex **3a-Ir**. The ^{31}P NMR spectrum of **4a-Ir** showed a singlet at 78.2 ppm and a septet at −144.5 ppm, assignable to the trimethylphosphite ligand and PF_6 anion, respectively. In ^{13}C NMR, a doublet assignable to the carbene carbon was observed at 161.1 ppm with a coupling constant of 25.2 Hz consistent with coupling to the phosphorus atom of trimethylphosphite. This spectral data suggested a structure in which phosphite was coordinated to the iridium metals, and indicated a weak coordinate bond for the bridging chlorides in complex **3**.

2.3. Application to intramolecular hydroamination

The transition-metal-catalyzed intramolecular hydroamination of 2-ethynylaniline has received much attention as a simple

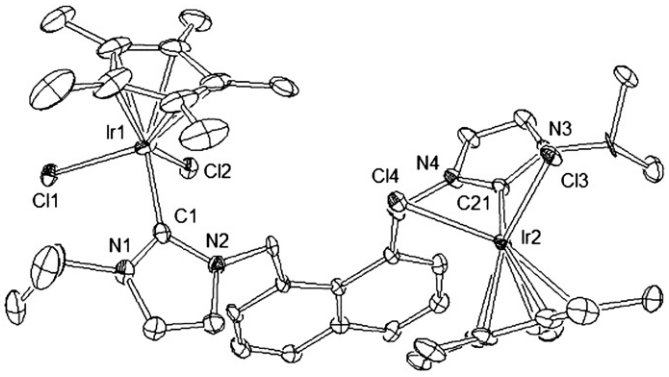


Fig. 2. ORTEP drawing of complex **2b-Ir** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and CH_2Cl_2 molecules are omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) for $[(Cp^*IrCl_2)_2(I^iPrCH_2C_{10}H_6CH_2I^iPr)]\cdot 5CH_2Cl_2$ (**2b-Ir**·$5CH_2Cl_2$)

Ir(1)-Ir(2)	8.1178(2)	Ir(1)-Cl(1)	2.4298(10)
Ir(1)-Cl(2)	2.4055(15)	Ir(1)-C(1)	2.037(6)
Ir(2)-Cl(3)	2.4265(11)	Ir(2)-Cl(4)	2.4520(12)
Ir(2)-C(21)	2.053(5)	N(1)-C(1)	2.037(6)
N(2)-C(1)	1.370(7)	N(3)-C(21)	1.361(5)
N(4)-C(21)	1.350(7)		
Ir(1)-C(1)-N(1)	129.0(4)	Ir(1)-C(1)-N(2)	126.9(3)
Ir(2)-C(21)-N(3)	127.9(3)	Ir(2)-C(21)-N(4)	128.0(3)
N(1)-C(1)-N(2)	103.5(5)	N(3)-C(21)-N(4)	104.0(4)

method for the synthesis of indole compounds. Many late-transition-metal complexes have been used in this reaction [9]. Crabtree et al. recently reported that an iridium(III)-hydride complex effectively catalyzed intramolecular hydroamination of 2-ethynylaniline [9n]. However, intramolecular hydroamination using a cationic iridium(III) catalyst has not been well examined with the exception of this iridium-hydride system. In the following, we describe the intramolecular hydroamination of 2-ethynylaniline using the cationic Cl-bridged iridium (III) complex **3-Ir** (Schemes 5 and 6).

First, catalysts and solvents were screened in the intramolecular hydroamination reaction of 2-aminodiphenyl acetylene (**5a**), as shown in Scheme 5 and Table 3. In the presence of the Cl-bridged iridium complex **3a-Ir** in acetonitrile, the intramolecular hydroamination reaction proceeded effectively under reflux conditions to afford **6a** in good yield (entry 1). While the use of **3b-Ir** and rhodium complex **3a-Rh** resulted in slightly lower yields of **6a** (entries 2 and 3), the neutral iridium complex **2a-Ir** did not catalyze the reaction (entry 4). Other solvents such as propionitrile, 1,2-dichloroethane, THF, 1,4-dioxane, DMF, ^{i}PrOH were significantly less effective (entries 5–10). The reaction using iridium complex bearing monodentate *N*-heterocyclic carbene ligand ($[Cp^*IrCl_2(I^iPr)]$) in the presence of $AgPF_6$ resulted in moderate yield (entry 11). Among the catalysts and solvents screened, the highest yield of the hydroamination product **6a** was achieved using the Cl-bridged cationic iridium complex **3a-Ir** in acetonitrile.

On the basis of the screening results, the iridium complex **3a-Ir** was examined in the catalysis of intramolecular hydroamination of various 2-ethynylanilines **5**, as shown in Scheme 6 and Table 4. The alkyl-substituted alkynes (**5b**, **5c** and **5d**) underwent reaction to the corresponding products in good yields (entries 1–3). Similarly, the use of *o*-, *m*-, and *p*-methyl-substituted aryl alkynes afforded the corresponding products **5** in good yields (entries 4–6). However, the reaction of *p*-methoxy-, trifluoromethyl-, and nitro-substituted aryl alkynes led to lower yields (entries 7–9). Alkyne **5k**, which possesses a pyridyl group, did not undergo reaction (entry 10). In contrast, replacement of the pyridyl group with a thiophenyl group (**5l**) resulted in the formation of the corresponding hydroamination product **6l** in good yield (entry 11).

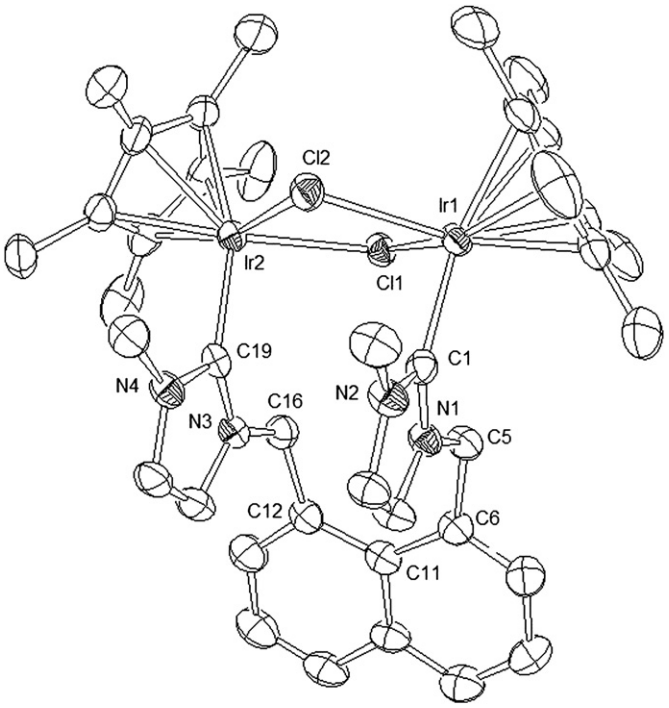


Fig. 3. ORTEP drawing of complex **3a-Ir** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms, PF_6 anions and CH_2Cl_2 molecules are omitted for clarity.

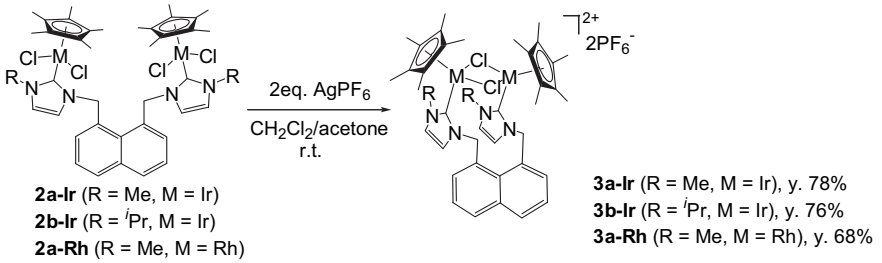
3. Conclusion

Novel binuclear iridium(III) and rhodium(III) complexes bearing methylnaphthalene-linked *N*-heterocyclic carbenes were prepared. The neutral bimetallic iridium and rhodium complexes could easily be converted to cationic Cl-bridged complexes by reaction with 2 equiv. of $AgPF_6$, and the resulting iridium complex reacted with 2 equiv. of trimethylphosphite to yield the phosphite complex by cleavage of the Ir-Cl coordinate bond. These results indicate the flexible nature of the methylnaphthalene-linked *N*-heterocyclic carbene ligand. The Cl-bridged cationic iridium(III) complex was active for catalytic intramolecular hydroamination of 2-ethynylanilines leading to indole compounds. Further investigation into the reactivity of these complexes is underway in our laboratory.

4. Experimental

4.1. General procedures

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under dry nitrogen or argon



Scheme 3. Synthesis of Cl-bridged binuclear complex **3**

Table 2
Selected bond distances (Å) and angles (°) for $[(Cp^*IrCl)_2(IMeCH_2C_{10}H_6CH_2IMe)](PF_6)_2\cdot 2CH_2Cl_2$ (**3a-Ir**$\cdot 2CH_2Cl_2$)

Ir(1)-Ir(2)	3.7701(3)	Ir(1)-Cl(1)	2.4497(12)
Ir(1)-Cl(2)	2.4534(13)	Ir(1)-C(1)	2.059(5)
Ir(2)-Cl(1)	2.4643(12)	Ir(2)-Cl(2)	2.4665(14)
Ir(2)-C(19)	2.069(5)	N(1)-C(1)	1.366(6)
N(2)-C(1)	1.344(6)	N(3)-C(19)	1.358(6)
N(4)-C(19)	1.356(6)		
Ir(1)-C(1)-N(1)	130.0(3)	Ir(1)-C(1)-N(2)	126.0(3)
Ir(2)-C(19)-N(3)	128.1(3)	Ir(2)-C(19)-N(4)	126.3(3)
N(1)-C(1)-N(2)	104.0(4)	N(3)-C(19)-N(4)	104.3(4)

atmosphere, which was purified by SICAPENT (Merck Co., Inc.), by using a standard Schlenk tube or high vacuum techniques. Toluene, hexane, diethyl ether and THF were distilled over Na/benzophenone prior to use. Dichloromethane was distilled over CaH_2 prior to use. 1,8-Dibromomethylnaphthalene [10], $[Cp^*IrCl_2]_2$ [11], alkyne **5a** [12], **5b** [13], **5c** [14], **5d** [13], **5e** [15], **5f** [16], **5g** [17], **5h** [14], **5i** [18], **5j** [19], **5k** [20] and **5l** [21] were prepared according to the literature methods. Other reagents employed in this research were commercially available and used without further purification. The NMR spectra were recorded on JEOL Delta-400 or Varian Mercury 300 spectrometers at ambient temperature. ^{1}H NMR spectra and $^{13}C\{^1H\}$ NMR spectra were measured using Me_4Si as an internal reference. All chemical shifts were recorded in ppm and all coupling constants were recorded in Hz. Elementary analyses were measured on a Perkin-Elmer 240C.

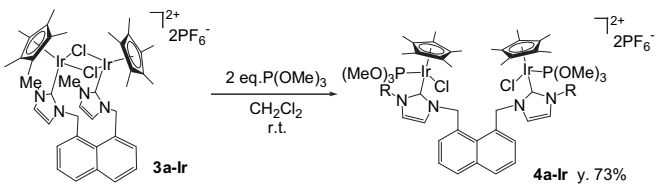
4.2. Preparation of imidazolium salts (*1*)

4.2.1. Preparation of 1,1′-(1,8-dimethylnaphthalene)-3,3′-dimethyldiimidazolium dibromide [$(IMeCH_2C_{10}H_6CH_2IMe)\cdot(HBr)_2$] (*1a*)

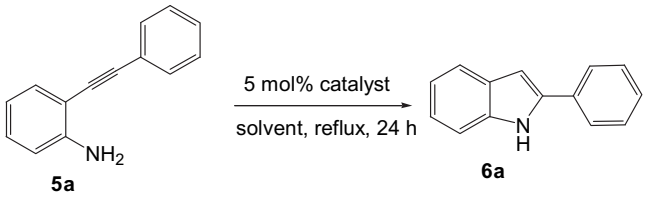
The mixture of 1,8-dibromonaphthalene (250 mg, 0.80 mmol) and *N*-methylimidazole (5mL) charged in Schlenk tube under argon. After stirring for 1 h at 140 °C, the supernatants were removed. The residual solid was washed with toluene (3 × 10 mL) and dried in vacuo to yield **1a** as a white solid (360 mg, 0.753 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.70 (s, CH_3), 6.47 (s, 4H, $-CH_{2-}$), 6.89 (s, 2H, CH═CH), 7.06 (s, 2H, CH═CH), 7.1–8.0 (m, 6H, naphthalene), 9.98 (s, NCHN). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 36.2, 52.7 (s, CH_3, $-CH_{2-}$), 120.7, 122.8, 124.4, 126.0, 128.2, 129.0, 130.1, 131.1, 137.2 (s, CH═CH, naphthalene, NCHN). Anal. Calc. for $C_{20}H_{22}Br_2N_4$: C, 50.23; H, 4.64; N, 11.72. Found: C, 49.36; H, 4.70; N, 11.60%.

4.2.2. Preparation of 1,1′-(1,8-dimethylnaphthalene)-3,3′-diisopropyldiimidazolium dibromide [$(I^iPrCH_2C_{10}H_6CH_2I^iPr)\cdot(HBr)_2$] (*1b*)

The mixture of 1,8-dibromonaphthalene (16 mg, 0.53 mmol) and *N*-isopropylimidazole (5 mL) charged in Schlenk tube under argon. After stirring for 1 h at 160 °C, the supernatants were removed. The residual solid was washed with toluene (3 × 10 mL) and dried in vacuo to yield **1b** as a white solid (230 mg, 0.430 mmol, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.65 (d, J = 6.4 Hz, 12H, ^{i}Pr-CH_3), 4.81 (sep, J = 6.4 Hz, ^{i}Pr-CH), 6.51 (s, 4H, $-CH_{2-}$), 7.2–8.1 (m, 10H, CH═CH, naphthalene), 10.19 (s, NCHN). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 22.9 (s, ^{i}Pr-CH_3), 53.4, 53.7 (s, ^{i}Pr-CH, $-CH_{2-}$), 120.2, 123.0, 125.8, 128.7, 129.7, 129.8, 131.6, 135.6, 135.8 (s, CH═CH, naphthalene, NCHN). Anal. Calc. for $C_{24}H_{30}Br_2N_4$: C, 53.95; H, 5.66; N, 10.49. Found: C, 53.78; H, 5.75; N, 10.53%.



Scheme 4. Reaction of Cl-bridged iridium(III) binuclear complex **3a-Ir** with trimethylphosphite



Scheme 5. Intramolecular hydroamination of **5a**

4.3. Preparation of iridium and Rhodium complexes

4.3.1. Preparation of $[(Cp^*IrCl_2)_2(IMeCH_2C_{10}H_6CH_2IMe)]$ (*2a-Ir*)

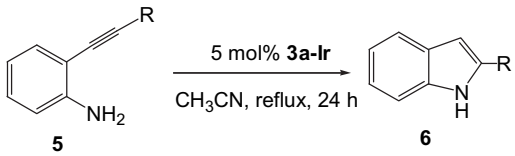
The mixture of 1,1′-(1,8-dimethylnaphthalene)-3,3′-dimethyldiimidazolium dibromide (**1a**) (153 mg, 0.32 mmol), silver(I) oxide (91 mg, 0.39 mmol) and CH_2Cl_2 (5 mL) charged in Schlenk tube under nitrogen and stirring for 2 h. The resulting mixture was added to the CH_2Cl_2 solution (5 mL) of $[Cp^*IrCl_2]_2$ (259 mg, 0.33 mmol). After stirring for 2 h, the mixture was filtrated through celite, and the volatiles were removed under reduced pressure. The residual solid was washed with diethyl ether several times, and then dried in vacuo to give **2a-Ir** as a orange solid (267 mg, 0.24 mmol, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.61 (s, 30H, C_5Me_5), 4.05 (s, 6H, NMe), 5.6 (br, 4H, NCH_2), 7.0–7.8 (m, CH═CH, naphthalene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 9.20 (s, C_5Me_5), 38.7 (s, NMe), 53.4 (s, NCH_2), 89.0 (s, C_5Me_5). 122–135 (s, CH═CH, naphthalene,), 157.3 (s, NCN). Anal. Calc. for $C_{40}H_{50}Cl_4Ir_2N_4\cdot 0.5CH_2Cl_2$: C, 42.90; H, 4.45; N, 4.85. Found: C, 42.33; H, 4.47; N, 4.94%.

4.3.2. Preparation of $[(Cp^*RhCl_2)_2(IMeCH_2C_{10}H_6CH_2IMe)]$ (*2a-Rh*)

Complex **2a-Rh** was prepared from 1,1′-(1,8-dimethylnaphthalene)-3,3′-dimethyldiimidazolium dibromide (**1a**) (262 mg, 0.55 mmol), silver(I) oxide (154 mg, 0.66 mmol), and $[Cp^*RhCl_2]_2$ (340 mg, 0.55 mmol) in the same manner as that for **2a-Ir**. Complex **2a-Rh** was isolated as a orange solid (505 mg, 0.54 mmol, 98%). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 9.49 (s, C_5Me_5), 39.1 (s, NMe), 55.6 (s, NCH_2), 96.3 (d, J = 6.0 Hz, C_5Me_5), 122–135 (s, CH═CH, naphthalene), 170.8 (d, J = 58.8 Hz, NCN). Anal. Calc. for $C_{40}H_{50}Cl_4N_4Rh_2\cdot CH_2Cl_2$: C, 48.31; H, 5.14; N, 5.50. Found: C, 48.31; H, 5.37; N, 5.77%. In the ^{1}H NMR, **2a-Rh** showed broadened signals in the temperature range from −60 °C to 60 °C. The satisfactory ^{1}H NMR data could not be observed.

4.3.3. Preparation of $[(Cp^*IrCl_2)_2(I^iPrCH_2C_{10}H_6CH_2I^iPr)]$ (*2b-Ir*)

The mixture of **1b** (253 mg, 0.47 mmol) and Ag_2O (118 mg, 0.51 mmol) in CH_2Cl_2 was stirred for 1 h at room temperature



Scheme 6. Intramolecular hydroamination of **5**

Table 3
Screening of reaction conditions for intramolecular hydroamination of **5a.**[a]

Entry	Catalyst	Solvent	GC yield (%)
1	**3a-Ir**	CH_3CN	73
2	**3b-Ir**	CH_3CN	55
3	**3a-Rh**	CH_3CN	52
4	**2a-Ir**	CH_3CN	5
5	**3a-Ir**	CH_3CH_2CN	62
6	**3a-Ir**	CH_2ClCH_2Cl	32
7	**3a-Ir**	THF	15
8	**3a-Ir**	1,4-dioxane	19
9	**3a-Ir**	DMF	38
10	**3a-Ir**	^{i}PrOH	33
11[b]	$[Cp^*IrCl_2(I^iPr)]/AgPF_6$	CH_3CN	52

[a] Reaction conditions: carbene complex (0.0125 mmol), alkyne (0.25 mmol), solvent (2 mL).
[b] $[Cp^*IrCl_2(I^iPr)]$ (0.025 mmol), $AgPF_6$ (0.025 mmol)

under argon atmosphere. The resulting solution was added to the solution of $[Cp^*IrCl_2]_2$ (375 mg, 0.471 mmol) in CH_2Cl_2 (5 mL). After being stirred at room temperature for 4 h, the solution was filtered and the filtrate was evaporated off under high vacuum. The residual solid was washed with diethyl ether at several times, and dried in vacuo to give **2b-Ir** (409 mg, 0.35 mmol, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.59 (s, 30 H, Cp*), 1.59 (d, J = 6.4 Hz, 12H, ^{i}Pr-CH_3), 5.35 (sep, J = 6.4 Hz, 2H, ^{i}Pr-CH), 5.58 (d, J = 17.4 Hz, 2H, CH_2), 5.66 (d, J = 17.4 Hz, 2H, CH_2), 6.5–7.9 (m, 10H, C=C, naphthalene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 8.23, 9.13, 13.9 (s, ^{i}Pr, C_5Me_5), 51.6 (s, NCH_2), 89.0 (s, C_5Me_5). 122–135 (s, CH=CH, naphthalene,), 157.7 (s, NCN). Anal. Calc. for $C_{44}H_{58}Cl_4Ir_2N_4\cdot CH_2Cl_2$: C, 43.10; H, 4.82; N, 4.47. Found: C, 43.44; H, 4.96; N, 4.81%.

4.3.4. Preparation of $[(Cp^*IrCl)_2(IMeCH_2C_{10}H_6CH_2IMe)](PF_6)_2$ (**3a-Ir**)

Mixture of complex **2a-Ir** (267 mg, 0.24 mmol), $AgPF_6$ (121 mg, 0.48 mmol), CH_2Cl_2 (5 mL), and acetone (5 mL) were stirred at room temperature. After being stirred for 2 h, the volatiles were removed under reduced pressure. The residue was extracted with CH_2Cl_2 and the volatiles were removed under reduced pressure. The residual solid was washed with diethyl ether several times, and then dried in vacuo to give **3a-Ir** as a orange solid (197 mg, 0.15 mmol, 63%). ^{1}H NMR (400 MHz, acetone-d^6): δ 1.77 (s, 30H, Cp*), 3.88 (s, 6H, NMe), 5.12 (d, J = 14.7 Hz, 2H, NCH_2), 6.28 (d, J = 2.3 Hz, 2H, CH=CH), 7.05 (d, J = 2.3 Hz, 2H, CH=CH), 7.07 (d, J = 14.7 Hz, 2H, NCH_2), 7.70 (dd, J = 8.0, 5.9 Hz, 2H, naphthalene), 7.89 (d, J = 5.9 Hz, 2H, naphthalene), 8.27 (d, J = 8.0 Hz, 2H, naphthalene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 9.67 (s, C_5Me_5), 39.1 (s, NMe), 53.4 (s, NCH_2), 93.3 (s, C_5Me_5). 124.0, 125.1, 126.9, 128.8, 132.4, 134.1, 137.8, 138.0 (s, CH=CH, naphthalene), 156.9 (s, NCN).

Table 4
Intramolecular hydroamination of **5** using iridium complex **3a-Ir**[a]

Entry	**5**	R	**6**	Isolated yield (%)
1	**5b**	$^nC_6H_{13}$	**6b**	80
2	**5c**	Cyclopropyl	**6c**	75
3	**5d**	CH_2Ph	**6d**	69
4	**5e**	o-$CH_3C_6H_4$	**6e**	78
5	**5f**	m-$CH_3C_6H_4$	**6f**	70
6	**5g**	p-$CH_3C_6H_4$	**6g**	68
7	**5h**	p-$CH_3OC_6H_4$	**6h**	37
8	**5i**	p-$CF_3C_6H_4$	**6i**	24
9	**5j**	p-$NO_2C_6H_4$	**6j**	15
10	**5k**	2-Pyridyl	**6k**	0
11	**5l**	2-Thiophenyl	**6l**	76

[a] Reaction conditions: carbene complex (0.0125 mmol), alkyne (0.25 mmol), CH_3CN (2 mL).

$^{31}P\{^1H\}$ NMR ($CDCl_3$) −143.8 (sep, J = 713 Hz, PF_6). Anal. Calc. for $C_{40}H_{50}Cl_2F_{12}Ir_2N_4P_2\cdot 2CH_2Cl_2$: C, 33.59; H, 3.62; N, 3.73. Found: C, 33.81 H, 3.72; N, 3.35%.

4.3.5. Preparation of $[(Cp^*RhCl)_2(IMeCH_2C_{10}H_6CH_2IMe)](PF_6)_2$ (**3a-Rh**)

Complex **3a-Rh** was prepared from **3a** (173 mg, 0.19 mmol), and $AgPF_6$ (94 mg, 0.37 mmol) in the same manner as that for **3a-Ir**. Complex **3a-Rh** was isolated as a orange solid (154 mg, 0.13 mmol, 68%). ^{1}H NMR (400 MHz, acetone-d^6): δ 1.78 (s, 30 H, Cp*), 3.88 (s, 6H, NMe), 5.16 (d, J = 14.6 Hz, 2H, NCH_2), 6.28 (s, 2H, CH=CH), 7.05 (s, 2H, CH=CH), 7.01 (d, J = 14.6 Hz, NCH_2), 7.70 (t, J = 7.6 Hz, 2H, naphthalene), 7.92 (d, J = 6.4 Hz, 2H, naphthalene), 8.28 (d, J = 7.6 Hz, 2H, naphthalene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 9.91(s, C_5Me_5), 39.3 (s, NMe), 55.6 (s, NCH_2), 100.3 (d, J = 8.4 Hz, C_5Me_5). 124.3, 125.6, 126.8, 128.8, 132.2, 133.9, 137.7, 137.9 (s, CH=CH, naphthalene,), 167.5 (d, J = 58.8 Hz, NCN). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −143.8 (sep, J = 713 Hz, PF_6). Anal. Calc. for $C_{40}H_{50}Cl_2F_{12}N_4P_2Rh_2\cdot 2CH_2Cl_2$: C, 38.12; H, 4.11; N, 4.23. Found: C, 38.87 H, 4.16; N, 3.74%.

4.3.6. Preparation of $[(Cp^*IrCl)_2(I^iPrCH_2C_{10}H_6CH_2I^iPr)](PF_6)_2$ (**3b-Ir**)

Complex **3b-Ir** was prepared from **3a** (160 mg, 0.14 mmol), and $AgPF_6$ (69 mg, 0.27 mmol) in the same manner as that for **3a-Ir**. Complex **3b-Ir** was isolated as a orange solid (88 mg, 0.064 mmol, 47%). ^{1}H NMR (400 MHz, acetone-d^6): δ 1.5–2.0 (br, 30 H, Cp*), 1.62 (br-d, J = 5.9 Hz, 12 H, ^{i}Pr-CH_3), 4.85 (br-s, 2H, ^{i}Pr-CH), 6.27 (br, 4H, NCH_2), 7.4–8.2 (m, 10 H, CH=CH, naphthalene). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 9.63 (s, C_5Me_5), 22.6 (s, ^{i}Pr-CH_3), 54.2 (s, NCH_2), 92.2 (s, C_5Me_5), 122.0, 123.8, 126.7, 129.6, 130.5, 131.2, 132.4, 136.2 (s, CH=CH, naphthalene,). $^{31}P\{^1H\}$ NMR ($CDCl_3$) −143.8 (sep, J = 713 Hz, PF_6). Correct elemental analysis data could not be obtained.

4.3.7. Preparation of $[\{Cp^*IrCl(P(OMe)_3)\}_2(IMeCH_2C_{10}H_6CH_2IMe)](PF_6)_2$ (**4-Ir**)

Mixture of complex **3a-Ir** (167 mg, 0.13 mmol), CH_2Cl_2 (5 mL), and trimethylphosphite (30 μl, 0.25 mmol) were stirred at room temperature. After being stirred for 3 h, the volatiles were removed under reduced pressure. The residue was washed with diethylether, and was recrystallized from acetone/hexane. The orange crystal of **3a-Ir** were obtained (79 mg, 0.092 mmol, 73%). ^{1}H NMR (400 MHz, acetone-d^6): δ 1.76 (s, 30H, Cp*), 3.72 (d, J = 11.5 Hz, 18 H, P$(OCH_3)_3$), 3.99 (s, 6H, NMe), 6.2–8.0 (m, 14H, NCH_2, CH=CH, naphthalene). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d^6): δ 9.36 (s, C_5Me_5), 40.0 (s, NMe), 54.6 (d, J = 7.2 Hz, P$(OCH_3)_3$), 56.4 (s, NCH_2), 98.7 (d, J = 3.5 Hz, C_5Me_5). 126.0, 126.4, 126.9, 127.0, 130.2, 130.9, 135.7, 136.7 (s, CH=CH, naphthalene), 161.1 (d, J = 25.2 Hz, NCN). $^{31}P\{^1H\}$ NMR (acetone-d^6): δ 78.2(s, P$(OCH_3)_3$), −144.5 (sep, J = 713 Hz, PF_6). Anal. Calc. for $C_{46}H_{68}Cl_2F_{12}N_4O_3P_4Ir_2\cdot CH_2Cl_2$: C, 33.90; H, 4.24; N, 3.36. Found: C, 33.70 H, 4.35; N, 3.59%.

4.3.8. Preparation of $[Cp^*IrCl_2(I^iPr)]$

The mixture of 1,3-diisopropylimidazolium chloride (150 mg, 0.80 mmol), silver(I) oxide (111 mg, 0.48 mmol) and CH_2Cl_2 (5 mL) charged in Schlenk tube under nitrogen and stirring for 3 h. The resulting mixture was added to the CH_2Cl_2 solution (5 mL) of $[Cp^*IrCl_2]_2$ (317 mg, 0.40 mmol). Ater stirring for 15vh, the mixture was filtrated through celite, and the volatiles were removed under reduced pressure. The residual solid was purified by alumina column chromatography using methanol, and then dried in vacuo to give $[Cp^*IrCl_2(I^iPr)]$ as a yellow solid (99 mg, 0.18 mmol, 23%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.45 (t, J = 6.9 Hz, 12H, ^{i}Pr-CH_3), 1.72 (s, 15 H, Cp*), 4.79 (sep, J = 6.9 Hz, 2H, ^{i}Pr-CH), 6.99 (s, 2H, CH=CH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 9.43 (s, C_5Me_5), 24.0, 25.0 (s, ^{i}Pr-CH_3), 52.1 (s, ^{i}Pr-CH), 85.8 (s, C_5Me_5), 117.6 (s, CH=CH), 160.4 (s, NCN).

4.4. General procedure for intramolecular hydroamination of alkyne

The mixture of iridium complex **3a-Ir** (12 mg, 0.0092 mmol), alkyne **5** (36 mg, 0.18 mmol) and acetonitrile (2 mL) charged in Schlenk tube under nitrogen atmosphere. After stirring for 24 h in reflux conditions, the solution filtered through a small amounts of silica gel using ethyl acetate. The residue was purified by silica gel preparative TLC (hexane/ethyl acetate = 10:1). The solvent was removed to give corresponding indole compound **6** as white solid. The structures of **6a** [22], **6b** [23], **6c** [21], **6d** [24], **6e** [25], **6f** [22], **6g** [25], **6h** [22], **6i** [23], **6j** [19] and **6l** [26] were referred to the reported data.

4.5. X-ray Crystal structure determinations

Suitable single crystals were obtained by recrystallization from CH_2Cl_2/diethyl ether. Crystal of **2b-Ir**·$5CH_2Cl_2$ and **3a-Ir**·$2CH_2Cl_2$ were mounted at the top of nylon loop using liquid paraffin, which was set on a Rigaku Saturn CCD/Rigaku AFC 8 diffractometer and Rigaku RAXIS RAPID diffractometer, respectively. The measurement was made by using Mo Kα radiation ($\lambda = 0.71070$ Å) at −183 °C for under a cold nitrogen stream for **2b-Ir**·$5CH_2Cl_2$ and by using Cu Kα radiation ($\lambda = 1.54187$ Å) at −80 °C for under a cold nitrogen stream for **3a-Ir**·$2CH_2Cl_2$. The crystal-to-detector distances were 39.99 mm for **2b-Ir**·$5CH_2Cl_2$ and 127.40 mm for **3a-Ir**·$2CH_2Cl_2$. A total of 836 oscillation for **2b-Ir**·$5CH_2Cl_2$ and 288 oscillation for **3a-Ir**·$2CH_2Cl_2$ images were collected. Readout was performed in the 0.137 mm pixel mode for **2b-Ir**·$5CH_2Cl_2$ and for 0.100 mm pixel mode for **3a-Ir**·$2CH_2Cl_2$. The crystal parameters along with data collections are summarized in Table 5. These structures were solved by direct methods (SHELX97) [27] for **2b-Ir**·$5CH_2Cl_2$ and (SIR92) [28] for **3a-Ir**·$2CH_2Cl_2$ and expanded using Fourier techniques [29]. All of non-hydrogen atoms were refined anisotropically. All hydrogen atoms **2b-Ir**·$5CH_2Cl_2$ and for **3a-Ir**·$2CH_2Cl_2$ were refined using riding model. All calculations were performed using the CrystalStructure [30] crystallographic software package except for refinement, which was performed using SHELXL-97 [27].

Table 5
Crystal data for $[(Cp^*IrCl_2)_2(I^iPrCH_2C_{10}H_6CH_2I^iPr)]\cdot 5CH_2Cl_2$ (**2b-Ir**·$5CH_2Cl_2$), and $[(Cp^*IrCl)_2(IMeCH_2C_{10}H_6CH_2IMe)](PF_6)_2\cdot 2CH_2Cl_2$ (**3a-Ir**·$2CH_2Cl_2$)

Compound	**2b-Ir**·$5CH_2Cl_2$	**3a-Ir**·$2CH_2Cl_2$
Formula	$C_{49}H_{68}Cl_{14}Ir_2N_4$	$C_{42}H_{54}F_{12}N_4Cl_6Ir_2P_2$
Mol. Wt.	1593.89	1502.00
Crystal color, habit	Yellow, prism	Red, block
Crystal size (mm)	0.44 × 0.38 × 0.35	0.50 × 0.40 × 0.30
Crystal system	Triclinic	Monoclinic
Space group	P$\bar{1}$ (No 2)	$P2_1/n$ (No 14)
a/Å	11.160(3)	12.0378(2)
b/Å	16.506(4)	28.0984(5)
c/Å	18.146(5)	15.8868(3)
α/°	102.504(5)	90.0
β/°	100.806(2)	105.2221(7)
γ/°	108.201(3)	90.0
V/Å	2980.4(13)	5185.05(16)
Z	2	4
D_c (g cm^{-3})	1.776	1.924
μ (Mo Kα) (cm^{-1})	51.367	–
μ (Cu Kα) (cm^{-1})	–	137.018
Reflections measured	34383	95498
2θ (°)	60.2	136.5
Independent reflections (R_{int})	17166 ($R_{int} = 0.038$)	9493 ($R_{int} = 0.143$)
Number of variables	623	614
Reflection/parameter ratio	27.55	15.46
Residuals: R; Rw	0.0539; 0.1439	0.0425; 0.1096
Residuals: R_1	0.0460	0.0417
Number of reflections to calculated R_1	13738 ($I > 2.0\sigma$(I))	9275 ($I > 2.0\sigma$(I))
GOF indicator	1.081	1.109

Acknowledgements

This work is supported by a Joint Research Grant from the Institute of Science and Engineering, Chuo University.

Appendix. Supplementary data

CCDC 760813 for **2b-Ir** and 760814 for **3a-Ir** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at: doi:10.1016/j.jorganchem.2010.04.006.

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