

Synthesis of new NHC–rhodium and iridium complexes derived from 2,2′-diaminobiphenyl and their catalytic activities toward hydrosilylation of ketones

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Abstract—Four new *N*-heterocyclic carbene (NHC)–rhodium and iridium complexes derived from 2,2′-diaminobiphenyl have been successfully synthesized and their structures have been unambiguously characterized by X-ray diffraction. Their catalytic activities for hydrosilylation of ketones with diphenylsilane were investigated. It was found that NHC–rhodium complex (**6**) is the best one among the four catalysts for the reduction of ketones.

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1. Introduction

N-Heterocyclic carbene ligands (NHCs), first reported by Öfele¹ and Wanzlick and Schönherr,² and later isolated and characterized in the stable free state by Arduengo³ and co-workers, have been developed rapidly in the latest decade due to their stability to air and moisture and their strong σ -donor but poor π -acceptor abilities.⁴ Transition-metal complexes with the NHCs have been proven to be effective catalysts for the Suzuki and Heck reaction,^{5,6} aryl amination,⁷ hydrosilylation,⁸ olefin metathesis,⁹ and methane oxidation.¹⁰

In addition to excellent catalytic activity in some reactions, NHC catalysts can also tolerate high reaction temperature since they decompose at slower rates than other ligands such as tertiary phosphines. The use of polydentate NHC ligands has allowed the preparation of new metal complexes whose stabilities are further improved by the chelating effect. Most polycarbene reported so far are bidentate and pincer-type biscarbene ligands that were first used to coordinate to Pd and later were applied to other transition metals such as Rh and Ir. These chelated bis-NHCs not only yield more stable metal complexes, but also give interesting features. These features can provide fine-tuning of topological properties such as steric hindrance, bite angles, and

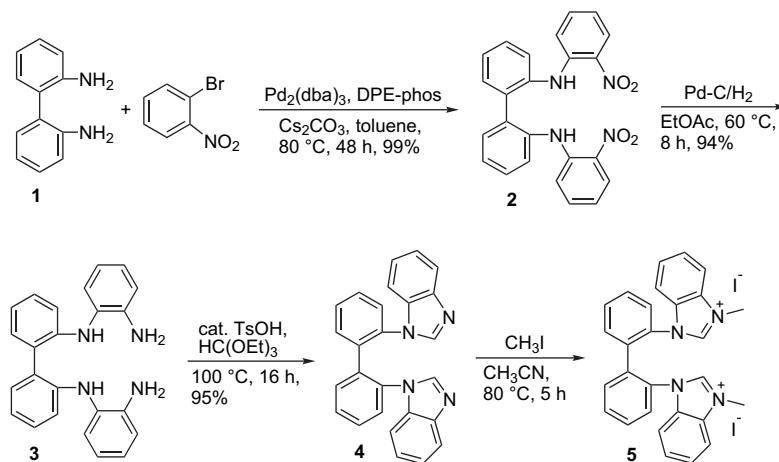
chirality.^{11,12} RajanBabu reported the first chelated bis-NHC complexes of Pd(II) and Ni(II) derived from 2,2′-bis-bromomethyl-[1,1′]binaphthalenyl, in which the two chelating *N*-heterocyclic carbenes oriented in a trans-geometry.¹³ In 2005, Crabtree synthesized a new chiral bis-NHC ligand from (*S*)-1,1-bisnaphthalenyl-2,2′-diamine (BINAM) in two steps.¹⁴ Recently, novel Pd(II) complexes bearing a seven-membered *N*-heterocyclic carbene ligand from 2,2′-diaminobiphenyl were disclosed by Stahl et al.¹⁵ Previously, we also reported the preparation of bis-NHC–Rh(III) and bis-NHC–Pd(II) complexes derived from optically active BINAM, and demonstrated their high catalytic activities and chiral induction abilities in asymmetric reduction of ketones with diphenylsilane and oxidative kinetic resolution of secondary alcohols using molecular oxygen as a terminal oxidant.¹⁶ On the basis of these backgrounds, we tried to explore more such bis-NHC ligands from other diamine sources. In this paper, we wish to report the synthesis of four new *N*-heterocyclic carbene (NHC) rhodium and iridium complexes based on a new bis-NHC ligand from 2,2′-diaminobiphenyl and their application to the hydrosilylation of ketones with diphenylsilane. These interesting bis-NHC–metal complexes have been unambiguously characterized by X-ray diffraction.

2. Results and discussion

The synthesis of bis-NHC ligand **5** is shown in Scheme 1. Using 2,2′-diaminobiphenyl as the starting material to react

Keywords: *N*-Heterocyclic carbene complexes; Rhodium; Iridium; 2,2′-Diaminobiphenyl; Hydrosilylation; Ketones.

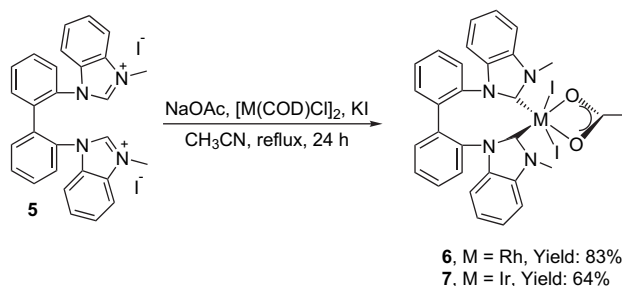
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Scheme 1. Synthesis of bis-NHC ligand **5**.

with 2-bromo-nitrobenzene in toluene at 80 °C, product **2** was given in 99% yield after 48 h. Reduction of **2** by means of Pd/C–H₂ in ethyl acetate at 60 °C produced compound **3** in 94% yield. Subsequent cyclization with triethyl orthoformate catalyzed by toluenesulfonic acid (TsOH) at 100 °C afforded benzimidazole **4** in 95% yield after 16 h. Quaternization of the benzimidazole ring of **4** with methyl iodide gave the corresponding dibenzimidazolium salt **5** as a solid.

Different from the preparation of an axially chiral bis-NHC–Rh complex reported previously by us,^{8b} it was found that upon treatment of the dibenzimidazolium salt **5** with [Rh(COD)Cl]₂ in a similar procedure, the corresponding cis-chelated bis-NHC–Rh(III) complex **6** was exclusively obtained in high yield. Complex **6** could be isolated by silica gel column chromatography as an orange solid in 83% yield (Scheme 2). In addition, cis-chelated bis-NHC–Ir(III) complex **7** could be obtained in 64% yield with the same procedure. This procedure was unsuccessful on the preparation of the bis-NHC–Ir(III) complex using bis-NHC ligand derived from BINAM.¹⁷ Complexes **6** and **7** were stable at ambient atmosphere and their structures are determined by spectroscopic data, microanalysis, and X-ray diffraction (Figs. 1 and 2).^{18,19} The special feature of the bis-NHC ligand **5** compared to bis-NHC ligand derived from BINAM is the less steric hindrance of the biaryl groups, which allowed the C–C bond between the two phenyl rings of the bis-NHC ligand **5** rotating more easily. In turn, this flexible rotation facilitated the formation of the cis-chelated bis-NHC–metal complexes.



Scheme 2. Synthesis of bis-NHC–Rh(III) and bis-NHC–Ir(III) complexes **6** and **7**.

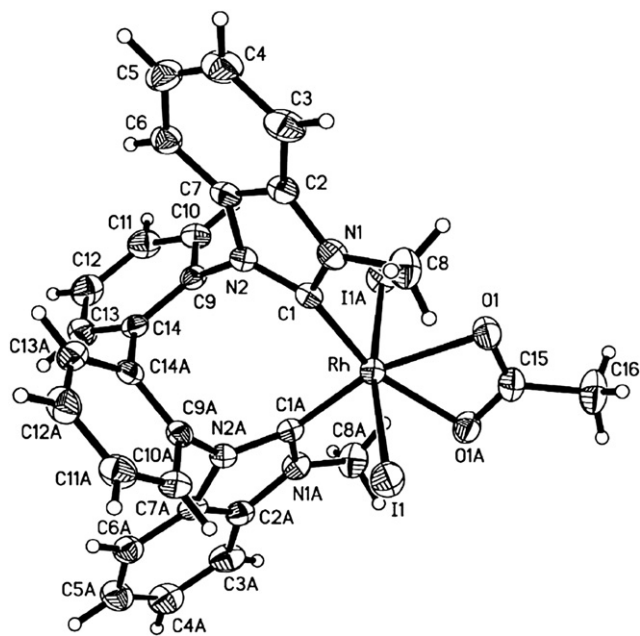


Figure 1. ORTEP drawing of bis-NHC–Rh(III) complex **6**.

Interestingly, upon treatment of the dibenzimidazolium salt **5** with [Rh(COD)Cl]₂ or [Ir(COD)Cl]₂ in tetrahydrofuran (THF) under reflux in the presence of KO^tBu, NHC–Rh(I) complex **8** and NHC–Ir(I) complex **9** were produced in 14% and 12% yields, respectively, along with some unidentified by-products (Scheme 3). Presumably, the (*N*-heterocyclic carbene) intermediate was oxidized to urea by trace of oxygen in the reaction system.²⁰ These complexes were stable under ambient atmosphere and their structures were determined unambiguously by X-ray diffraction. The ORTEP drawing of **8** and **9** are shown in Figures 3 and 4.^{21,22}

Next, these four new NHC–Rh and Ir complexes **6**, **7**, **8**, and **9** were investigated as potential catalysts in the hydrosilylation of ketones. Initial studies on the reaction conditions were carried out with acetophenone **10a** as a substrate in a variety of solvents. The results of these experiments are summarized in Table 1. Catalysts **6** and **8** showed good catalytic activities to give the corresponding reduction product **11a** in 90% and 83% yields using 2.0 mol % of catalyst, respectively (Table 1,

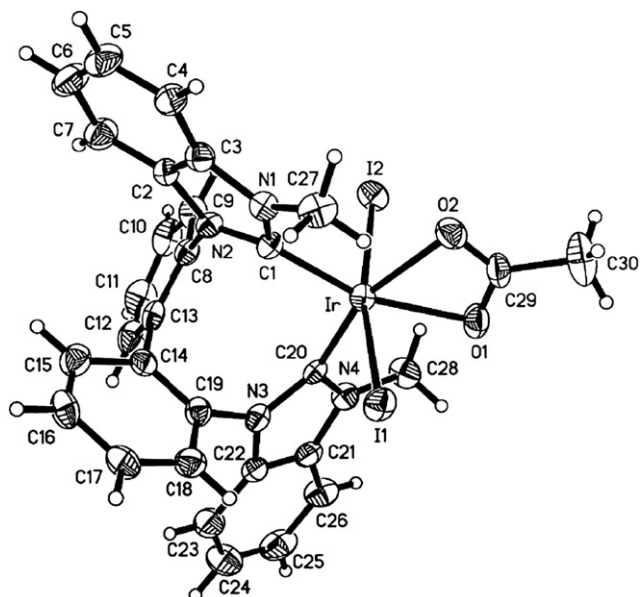
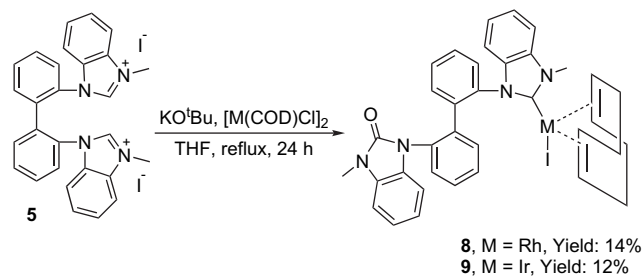


Figure 2. ORTEP drawing of bis-NHC–Ir(III) complex **7**.



Scheme 3. Synthesis of NHC–Rh(I) and NHC–Ir(I) complexes **8** and **9**.

entries 1 and 3). Catalyst **9** showed a moderate activity (Table 1, entry 4). While the NHC–Ir(III) complex **7** showed low catalytic activity, only giving **11a** in 10% yield after 48 h (Table 1, entry 2). Toluene (PhMe) was found to be the best solvent compared to CH_2Cl_2 , CH_3CN , Et_2O , and THF, affording **11a** in 92% yield using 1.0 mol % of catalyst **6** at room temperature (Table 1, entries 7 and 8).

With the optimized conditions in hand, we subsequently investigated the substrate scope of the hydrosilylation of

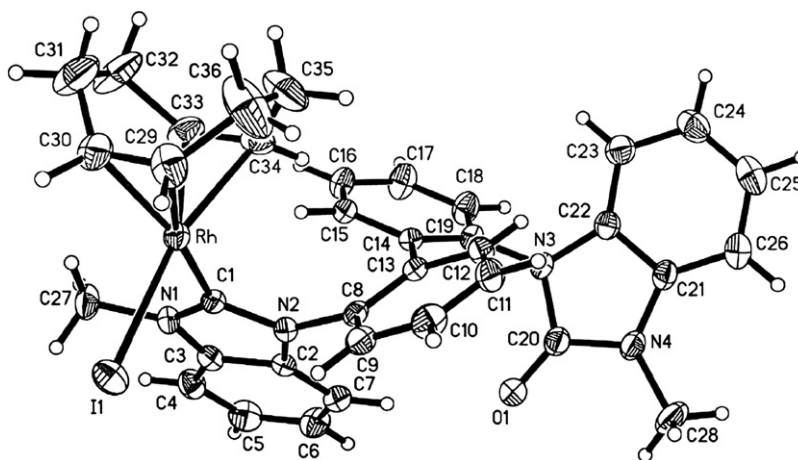


Figure 3. ORTEP drawing of NHC–Rh(I) complex **8**.

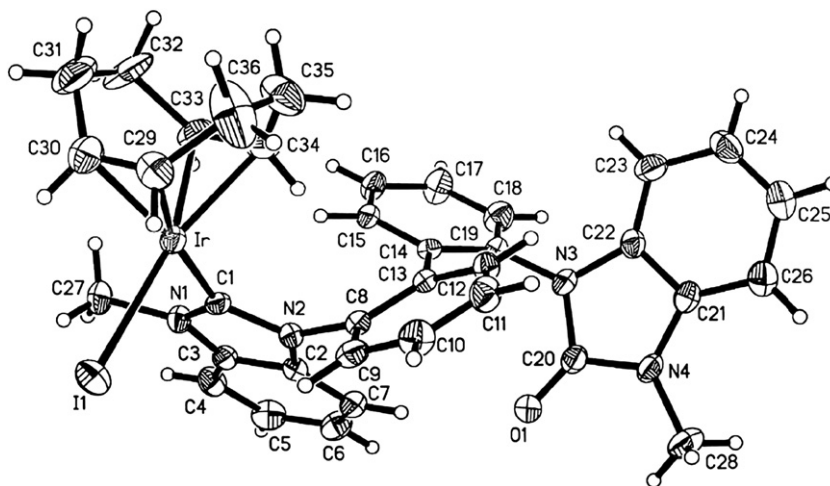
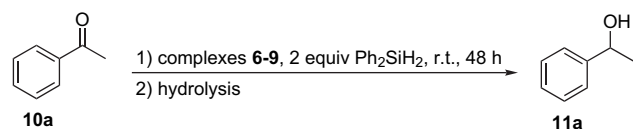


Figure 4. ORTEP drawing of NHC–Ir(I) complex **9**.

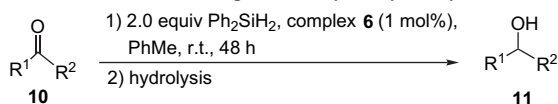
Table 1. NHC–Rh or Ir complexes catalyzed hydrosilylation of ketones

Entry ^a	Catalyst	Solvent	Yield ^b (%) (11a)
1	6 (2 mol %)	THF	90
2	7 (2 mol %)	THF	10
3	8 (2 mol %)	THF	83
4	9 (2 mol %)	THF	58
5	6 (2 mol %)	CH ₂ Cl ₂	44
6	6 (2 mol %)	CH ₃ CN	27
7	6 (2 mol %)	PhMe	95
8	6 (1 mol %)	PhMe	92
9	6 (1 mol %)	Et ₂ O	71
10	6 (1 mol %)	THF	69

^a The reaction was carried out with acetophenone (0.5 mmol), 1 or 2 mol % of catalyst, and 2 equiv of Ph₂SiH₂ in 2 mL of solvent at room temperature for 48 h and then hydrolyzed by MeOH and 1 N HCl.

^b Isolated yields.

ketones **10** using bis-NHC–Rh(III) complex **6**. Various ketones **10** with electron-rich, electron-neutral, and electron-poor substituents on the benzene ring can be smoothly reduced to the corresponding alcohols **11** in good to high yields under mild conditions (Table 2, entries 1–8), whose results were consistent with the previously reported ones

Table 2. Bis-NHC–Rh(III) complex **6** catalyzed hydrosilylation of ketones

Entry ^a	10 (R ¹ /R ²)	Products	Yield ^b (%)
1	10b (C ₆ H ₅ /Et)	11b	83
2	10c (4-ClC ₆ H ₄ /Me)	11c	91
3	10d (4-BrC ₆ H ₄ /Me)	11d	93
4	10e (3-FC ₆ H ₄ /Me)	11e	85
5	10f (4-MeC ₆ H ₄ /Me)	11f	87
6	10g (4-MeOC ₆ H ₄ /Me)	11g	88
7	10h (2-naphthyl/Me)	11h	92
8	10i (C ₆ H ₅ /CH ₂ Cl)	11i	79
9	10j	11j	67
10	10k	11k	73
11	10l	11l	90
12	10m	11m	89
13	10n	11n	93

^a All of the reactions were carried out under the optimized reaction conditions: 1 mol % bis-NHC–Rh(III), 2 equiv Ph₂SiH₂, in PhMe at room temperature for 48 h and then hydrolyzed by MeOH and 1 N HCl.

^b Isolated yields.

by us.^{8b} For α,β -unsaturated ketone **10j** and 1-tetralone **10k**, 67% and 73% yields can be obtained, respectively (Table 2, entries 9 and 10). Dialkyl ketones **10l**, **10m**, and **10n** also can be reduced in high yields under identical conditions (Table 2, entries 11–13).

In conclusion, we have synthesized four new *N*-heterocyclic carbene complexes of rhodium and iridium from a new bis-NHC ligand based on 2,2'-diaminobiphenyl. Among them, the bis-NHC–Rh(III) complex **6** was found to be a fairly effective catalyst for the hydrosilylation of ketones with diphenylsilane to give the corresponding alcohols in moderate to high yields. Efforts to modify the biaryl backbone for asymmetric catalysis are currently in progress.

3. Experimental section

3.1. General remarks

CH₂Cl₂ and CH₃CN were freshly distilled from calcium hydride under argon (Ar) atmosphere; THF, PhMe, and Et₂O were distilled from sodium (Na) under argon (Ar) atmosphere. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. ¹H NMR spectra were recorded on a Varian Mercury vx 300 MHz spectrometer for solution in CDCl₃ with tetramethylsilane (TMS) as an internal standard; coupling constants *J* are given in hertz. ¹³C NMR spectra were recorded on a Varian Mercury vx 75 MHz spectrophotometers with complete proton decoupling spectrophotometers (CDCl₃: 77.0 ppm). Infrared spectra were recorded on a Perkin–Elmer PE-983 spectrometer with absorption in cm⁻¹. Flash column chromatography was performed using 300–400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF₂₅₄) were used. Elementary analysis was taken on Elementar vario EL III. Mass spectra were recorded by EI, and HRMS was measured on a HP-5989 instrument. [Rh(COD)Cl]₂²³ and [Ir(COD)Cl]₂²⁴ were prepared employing the published procedures.

3.1.1. Synthesis of compound 2. Under argon atmosphere, a mixture of 2,2'-diaminobiphenyl (0.92 g, 5 mmol), 2-bromo-nitrobenzene (3.03 g, 15 mmol), Pd₂(dba)₃ (0.12 g, 0.125 mmol), bis(2-diphenylphosphinophenyl) ether (DPEphos) (0.20 g, 0.375 mmol), and Cs₂CO₃ (5.20 g, 16 mmol) was stirred in toluene (40 mL) at 80 °C for 48 h. After the reaction mixture was cooled to room temperature, the reaction was quenched by the addition of 100 mL of H₂O. The mixture was extracted with EtOAc (3×50 mL), dried over anhydrous Na₂SO₄, and filtered. The solvent was removed under reduced pressure and the residue was purified by silica gel flash column chromatography, eluting first with petroleum ether/ethyl acetate (20:1) to remove excess raw material, and then eluting with petroleum ether/ethyl acetate (4:1) to give **2** as a red solid; yield: 2.1 g (99%). Mp 191–192 °C; IR (CH₂Cl₂): ν 3347, 3085, 2925, 1615, 1577, 1505, 1448, 1345, 1255, 1148, 1037, 766 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 6.51–6.54 (m, 2H, ArH), 7.08–7.13 (m, 4H, ArH), 7.29–7.33 (m, 2H, ArH), 7.39–7.43 (m, 6H, ArH), 7.87 (d, *J*=6.3 Hz, 2H, ArH), 9.18 (s, 2H, NH); ¹³C NMR (75 MHz, CDCl₃): δ 114.8, 117.4, 123.7, 125.8, 126.2, 129.0, 132.0, 132.9, 135.4, 136.6, 141.9; MS (EI)

m/z (%): 426 (M^+ , 100), 344 (M^+-82 , 12), 255 (M^+-171 , 13), 241 (M^+-185 , 9); Anal. Calcd for $C_{24}H_{18}N_4O_4$ requires: C, 67.70; H, 4.25; N, 13.14%. Found: C, 67.41; H, 4.01; N, 13.31%.

3.1.2. Synthesis of compound 3. A mixture of **2** (852 mg, 2 mmol), 10% Pd-C (100 mg) in 100 mL of EtOAc was stirred under H_2 atmosphere (15 atm) at 60 °C for 8 h. After cooling to room temperature, Pd-C was removed by filtration. The solvent was evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate 4:1–1:1) to give **3** as a white solid; yield: 688 mg (94%). Mp 235–237 °C; IR (CH_2Cl_2): ν 3329, 3281, 2926, 2319, 1727, 1616, 1507, 1262, 999, 748 cm^{-1} ; 1H NMR (300 MHz, DMSO- d_6): δ 4.71 (br, 4H, NH_2), 5.99 (br, 2H, NH), 6.50–6.57 (m, 4H, ArH), 6.69–6.72 (m, 2H, ArH), 6.81–6.92 (m, 6H, ArH), 7.12–7.21 (m, 4H, ArH); MS (EI) m/z (%): 366 (M^+ , 100), 259 (M^+-107 , 46), 166 (M^+-200 , 15); HRMS (EI) calcd for $C_{24}H_{22}N_4$ (M^+) requires 366.1844, found: 366.1850.

3.1.3. Synthesis of compound 4. Compound **3** (366 mg, 1.0 mmol), toluenesulfonic acid (20 mg), and triethyl orthoformate [$HC(OC_2H_5)_3$] (10 mL) were heated at 100 °C for 16 h. After the reaction mixture was cooled to room temperature, 40 mL of petroleum ether was added to precipitate white solid, filtered, and the precipitate was washed with light petroleum ether to give **4** as a white solid; yield: 365 mg (95%). Mp 166–167 °C; IR (CH_2Cl_2): ν 3430, 3054, 2925, 2844, 1712, 1614, 1492, 1227, 1009, 787, 737 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$, TMS): δ 6.51 (d, 2H, $J=8.1$ Hz, ArH), 6.77 (t, 2H, $J=7.5$ Hz, ArH), 7.01 (t, 2H, $J=7.5$ Hz, ArH), 7.21 (s, 2H, NCHN), 7.26–7.28 (m, 2H, ArH), 7.47–7.53 (m, 4H, ArH), 7.55–7.60 (m, 2H, ArH), 7.71 (d, $J=7.5$ Hz, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 109.2, 119.4, 122.3, 123.3, 125.9, 128.6, 129.6, 132.5, 132.8, 133.5, 133.6, 141.7, 142.4; MS (EI) m/z (%): 386 (M^+ , 100), 268 (M^+-118 , 51), 193 (M^+-193 , 5); Anal. Calcd for $C_{26}H_{18}N_4$ requires: C, 80.81; H, 4.69; N, 14.50%. Found: C, 80.48; H, 4.53; N, 14.40%.

3.1.4. Synthesis of dibenzimidazolium salt 5. Compound **4** (386 mg, 1.0 mmol) and CH_3I (0.48 mL, 8.0 mmol) in CH_3CN (10 mL) were stirred at 80 °C for 5 h. After cooling to room temperature, volatiles were removed under reduced pressure and the obtained solid compound **5** was used for the next reaction without further purification. MS (ESI) m/z : 543.1 (M^+-I), 208.1 (M^+-2I)/2.

3.1.5. Synthesis of bis-NHC–Rh(III) complex 6. A mixture of **5** (134 mg, 0.20 mmol), $[Rh(COD)Cl]_2$ (48 mg, 0.10 mmol), NaOAc (134 mg, 1.60 mmol), and KI (66 mg, 0.40 mmol) was stirred in CH_3CN (12 mL) under reflux for 24 h. After cooling, volatiles were removed under reduced pressure and the residue was purified by silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate 1:1) to give an orange solid, bis-NHC–Rh(III) complex **6**. Yield: 137 mg (83%). A single crystal suitable for X-ray crystal analysis was obtained by recrystallization from a saturated solution of petroleum ether/ethyl acetate (1:1). Mp >250 °C (dec); IR (CH_2Cl_2): ν 3063, 2949, 2376, 1464, 1332, 1220, 1095, 949, 743 cm^{-1} ; 1H NMR (300 MHz,

$CDCl_3$, TMS): δ 2.03 (s, 3H, Me), 4.35 (s, 6H, Me), 6.56 (d, $J=8.1$ Hz, 2H, ArH), 6.70 (d, $J=7.2$ Hz, 2H, ArH), 7.07 (t, $J=7.2$ Hz, 2H, ArH), 7.15 (t, $J=7.2$ Hz, ArH), 7.22–7.39 (m, 6H, ArH), 8.17 (d, $J=8.1$ Hz, 2H, ArH); MS (EI) m/z (%): 703 (M^+-127 , 9), 644 (M^+-186 , 25), 576 (M^+-254 , 11), 517 (M^+-313 , 100), 268 (M^+-562 , 17); Anal. Calcd for $C_{30}H_{25}I_2N_4O_2Rh$ requires: C, 43.40; H, 3.04; N, 6.75%. Found: C, 43.72; H, 3.04; N, 6.27%.

3.1.6. Synthesis of bis-NHC–Ir(III) complex 7. A mixture of **5** (134 mg, 0.20 mmol), $[Ir(COD)Cl]_2$ (67 mg, 0.10 mmol), NaOAc (134 mg, 1.60 mmol), and KI (66 mg, 0.40 mmol) was stirred in CH_3CN (12 mL) under reflux for 24 h. After cooling, volatiles were removed under reduced pressure and the residue was purified by silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate 1:1) to give a yellow solid, bis-NHC–Ir(III) complex **7**. Yield: 117 mg (64%). A single crystal suitable for X-ray crystal analysis was obtained by recrystallization from a saturated solution of petroleum ether/ethyl acetate (1:1). Mp >250 °C (dec); IR (CH_2Cl_2): ν 3058, 2950, 2374, 1711, 1474, 1326, 1094, 954, 744 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.05 (s, 3H, Me), 4.24 (s, 6H, Me), 6.52 (d, $J=8.1$ Hz, 2H, ArH), 6.67 (dd, $J=7.2$, 1.5 Hz, 2H, ArH), 7.03–7.11 (m, 4H, ArH), 7.18 (t, $J=7.2$ Hz, 2H, ArH), 7.24–7.27 (m, 2H, ArH), 7.35 (dt, $J=7.2$, 1.5 Hz, 2H, ArH); MS (EI) m/z (%): 920 (M^+ , 11), 793 (M^+-127 , 38), 733 (M^+-186 , 9), 666 (M^+-254 , 30), 607 (M^+-313 , 100); Anal. Calcd for $C_{30}H_{25}I_2IrN_4O_2$ requires: C, 39.18; H, 2.74; N, 6.09%. Found: C, 39.37; H, 2.51; N, 5.81%.

3.1.7. Synthesis of NHC–Rh(I) complex 8. A mixture of **5** (134 mg, 0.20 mmol), $[Rh(COD)Cl]_2$ (48 mg, 0.10 mmol), KO^tBu (50 mg, 0.45 mmol), and KI (66 mg, 0.40 mmol) was stirred in THF (12 mL) under reflux for 24 h. After cooling, volatiles were removed under reduced pressure and the residue was purified by silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate 5:1–3:1) to give an orange solid, Rh(I) complex **8**. Yield: 22 mg (14%). A single crystal suitable for X-ray crystal analysis was obtained by recrystallization from a saturated solution of petroleum ether/ethyl acetate (4:1). Mp >250 °C (dec); IR (CH_2Cl_2): ν 3061, 2956, 2925, 2317, 1722, 1494, 1384, 1338, 1081, 963, 746 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$, TMS): δ 0.83–0.98 (m, 2H, CH_2), 1.07–1.15 (m, 1H, CH_2), 1.38–1.53 (m, 3H, CH_2), 1.69–1.71 (m, 1H, CH_2), 1.78–1.91 (m, 1H, CH_2), 2.16–2.23 (m, 1H, CH), 2.52–2.65 (m, 1H, CH), 3.33 (s, 3H, Me), 4.20 (s, 3H, Me), 4.78–4.79 (m, 1H, CH), 4.88–4.92 (m, 1H, CH), 6.37–6.53 (m, 1H, ArH), 6.87–6.93 (m, 2H, ArH), 7.04–7.09 (m, 4H, ArH), 7.15–7.23 (m, 5H, ArH), 7.46–7.51 (m, 2H, ArH), 8.06–8.21 (m, 1H, ArH), 8.74–8.76 (m, 1H, ArH); MS (ESI) m/z : 641.2 (M^+-I); HRMS (ESI) calcd for $C_{36}H_{34}IrN_4O$ (M^+-I) requires 641.1788, found: 641.1753.

3.1.8. Synthesis of NHC–Ir(I) complex 9. A mixture of **5** (134 mg, 0.20 mmol), $[Ir(COD)Cl]_2$ (67 mg, 0.10 mmol), KO^tBu (50 mg, 0.45 mmol), and KI (66 mg, 0.40 mmol) was stirred in THF (12 mL) under reflux for 24 h. After cooling, volatiles were removed under reduced pressure and the residue was purified by silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate 4:1–3:1) to

give a yellow solid, Ir(I) complex **9**. Yield: 21 mg (12%). A single crystal suitable for X-ray crystal analysis was obtained by recrystallization from a saturated solution of petroleum ether/ethyl acetate (4:1). Mp > 250 °C (dec); IR (CH₂Cl₂): ν 3057, 2955, 2926, 2030, 1721, 1494, 1386, 1205, 1081, 966, 746 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 0.85–0.93 (m, 2H, CH₂), 1.07–1.15 (m, 1H, CH₂), 1.38–1.53 (m, 3H, CH₂), 1.64–1.70 (m, 1H, CH₂), 1.81–1.86 (m, 1H, CH₂), 2.11–2.22 (m, 1H, CH), 2.55–2.61 (m, 1H, CH), 3.33 (s, 3H, Me), 4.19 (s, 3H, Me), 4.78–4.79 (m, 1H, CH), 4.88–4.92 (m, 1H, CH), 6.42–6.48 (m, 1H, ArH), 6.87–6.93 (m, 2H, ArH), 7.05–7.09 (m, 4H, ArH), 7.16–7.23 (m, 5H, ArH), 7.46–7.51 (m, 2H, ArH), 8.03–8.23 (m, 1H, ArH), 8.74–8.77 (m, 1H, ArH); MS (EI) *m/z* (%): 858 (M⁺, 0.8), 729 (M⁺–129, 46), 623 (M⁺–235, 100); HRMS (ESI) calcd for C₃₆H₃₄IrN₄O (M⁺–I) requires 731.2362, found: 731.2325.

3.2. Representative procedure for bis-NHC–Rh(III)-catalyzed hydrosilylation of ketones

In a flame-dried Schlenk flask was placed bis-NHC–Rh(III) (0.005 mmol, 1 mol %) under argon. Anhydrous toluene (2 mL) and then acetophenone (0.5 mmol) were added by syringe through a septum, diphenylsilane (1 mmol) was added slowly, and the reaction mixture was stirred at room temperature for 48 h. After 48 h, hydrolysis was performed by the addition of MeOH (2 mL) and 1 N HCl (2 mL). The resulting aqueous solution was stirred for 2 h at room temperature and extracted with Et₂O (3 × 10 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate 15:1–10:1) to give the corresponding 1-phenyl-ethanol.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.03.150.

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- The crystal data of **6** have been deposited in CCDC with number 632167. Empirical formula: C₃₂H₂₇Cl₆I₂N₄O₂Rh; formula weight: 1068.99; crystal color, habit: colorless, prismatic; crystal system: monoclinic; lattice type: primitive; lattice parameters: *a* = 13.9748(11) Å, *b* = 23.3683(18) Å, *c* = 11.7901(9) Å, α = 90°, β = 95.0670(10)°, γ = 90°, *V* = 3835.2(5) Å³; space group: *C2/c*; *Z* = 4; *D*_{calcd} = 1.851 g/cm³; *F*₀₀₀ = 2064; diffractometer: Rigaku AFC7R; residuals: *R*; *R*_w: 0.0482, 0.1340.
- The crystal data of **7** have been deposited in CCDC with number 632169. Empirical formula: C₃₃H₃₂I₂IrN₄O₂; formula weight: 962.63; crystal color, habit: colorless, prismatic; crystal system: monoclinic; lattice type: primitive; lattice parameters: *a* = 8.8851(7) Å, *b* = 21.4149(18) Å, *c* = 17.3292(15) Å, α = 90°, β = 100.698(2)°, γ = 90°, *V* = 3240.0(5) Å³; space group: *P2(1)/c*; *Z* = 4; *D*_{calcd} = 1.973 g/cm³; *F*₀₀₀ = 1828; diffractometer: Rigaku AFC7R; residuals: *R*; *R*_w: 0.0537, 0.1188.
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21. The crystal data of **8** have been deposited in CCDC with number 632168. Empirical formula: $C_{36}H_{34}IN_4ORh$; formula weight: 768.48; crystal color, habit: colorless, prismatic; crystal system: monoclinic; lattice type: primitive; lattice parameters: $a=14.7269(10)$ Å, $b=13.2489(9)$ Å, $c=16.7079(12)$ Å, $\alpha=90^\circ$, $\beta=101.136(2)^\circ$, $\gamma=90^\circ$, $V=3198.6(4)$ Å³; space group: $P2(1)/n$; $Z=4$; $D_{\text{calcd}}=1.596$ g/cm³; $F_{000}=1536$; diffractometer: Rigaku AFC7R; residuals: R; R_w : 0.0482, 0.1095.
22. The crystal data of **9** has been deposited in CCDC with number 632170. Empirical formula: $C_{36}H_{34}IrN_4O$; formula weight: 857.77; crystal color, habit: colorless, prismatic; crystal system: monoclinic; lattice type: primitive; lattice parameters: $a=14.7020(9)$ Å, $b=13.2513(9)$ Å, $c=16.7290(11)$ Å, $\alpha=90^\circ$, $\beta=101.0960(10)^\circ$, $\gamma=90^\circ$, $V=3198.2(4)$ Å³; space group: $P2(1)/n$; $Z=4$; $D_{\text{calcd}}=1.781$ g/cm³; $F_{000}=1664$; diffractometer: Rigaku AFC7R; residuals: R; R_w : 0.0491, 0.1040.
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