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Synthesis and X-ray structures of rhodium complexes with new chiral biaryl-based NHC-ligands

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ABSTRACT

A new series of chiral NHC–rhodium complexes has been prepared from the reactions between $[Rh(COD)Cl]_2$, NaOAc, KI and dibenzimidazolium salt **4a** or monobenzimidazolium salts **4b–d**, which are derived from chiral 2,2′-diamino-6,6′-dimethyl-1,1′-biphenyl, 2,2′-diamino-1,1′-binaphthyl or 6,6′-dimethyl-2-amino-2′-hydroxy-1,1′-biphenyl. The steric and electronic effects of the ligand play an important role in the complex formation. For example, treatment of chiral monobenzimidazolium salt **4b** (with a NMe_2 group) with 0.5 equiv of $[Rh(COD)Cl]_2$ in the presence of NaOAc and KI in CH_3CN at reflux gives a chiral Rh(I) complex **5b**, while chiral monobenzimidazolium salt **4d** (with a MeO group) affords a *racemic* Rh(I) complex **5d**. Under similar reaction conditions, treatment of dibenzimidazolium salt **4a** with 0.5 equiv of $[Rh(COD)Cl]_2$ in the presence of NaOAc and KI gives a *racemic* Rh(III) complex **5a**, while the dibenzimidazolium salt $[C_{20}H_{12}(C_7H_5N_2Me)_2]I_2$ derived from chiral 2,2′-diamino-1,1′-binaphthyl affords a chiral Rh(III) complex $[C_{20}H_{12}(C_7H_4N_2Me)_2]RhI_2(OAc)$. All compounds have been characterized by various spectroscopic techniques, and elemental analyses. The solid-state structures of the rhodium complexes have been further confirmed by X-ray diffraction analyses.

1. Introduction

N-Heterocyclic carbenes ligands (NHCs) have been rapidly developed in recent years due to their stability to air and moisture and their strong σ-donor but poor π-acceptor abilities, and recent efforts have focused on the development of chiral NHC–metal complexes/catalysts for enantioselective reactions [1–19]. Since Herrmann and his co-workers first reported the use of chiral NHCs as ligands in transition-metal catalyzed asymmetric reactions [5] in 1996, examples for the use of chiral NHC-ligands in asymmetric synthesis now range from ruthenium complex catalyzed metathesis [14], iridium complex catalyzed hydrogenation [9] to hydrosilylation reactions catalyzed by rhodium compounds [10,15–16], which have already obtained remarkable achievements. For example, chiral NHC–Rh complexes are useful catalysts for asymmetric hydrosilylation reactions under mild conditions, and in some cases, enantioselectivities up to 99% ee are achieved [15–16]. Chiral NHC–Ru complexes show excellent catalytic activity in asymmetric metathesis reactions, and the enantioselectivity is as high as 90% ee [14]. These excellent enantioselectivities provide clear evidence for the enormous potential of NHC-complexes in enantioselective synthesis. Thus, the development of new NHC-complexes and the exploration of their use in asymmetric reactions are still an open area of research.

In recent years, 2,2′-diamino-6,6′-dimethyl-1,1′-biphenyl as its (*R*) or (*S*) enantiomers has been modified to give variants which bear appropriate structural and electronic features for intended specific reactions, and its derivatives have exhibited good to excellent enantioselectivities in a number of asymmetric transformations [20–25]. However, to our knowledge, no example of chiral NHC–metal complex/catalyst based on 2,2′-diamino-6,6′-dimethyl-1,1′-biphenyl has been reported yet, in contrast to binaphthylamine [15–16]. To explore the chemistry of 2,2′-diamino-6,6′-dimethyl-1,1′-biphenyl in NHC-ligand system, we have recently designed and prepared a new series of bidentate chiral NHC-ligands from 2,2′-diamino-6,6′-dimethyl-1,1′-biphenyl, and found they are useful ligands for metal complexes. We report herein the synthesis of these new ligands and their use in the coordination chemistry of rhodium. For better understanding and comparison, the NHC–rhodium complexes derived from chiral 2-amino-2′-hydroxy-6,6′-dimethyl-1,1′-biphenyl and 2,2′-diamino-1,1′-binaphthyl will also be described.

2. Experimental

2.1. General methods

All chemicals were purchased from Aldrich Chemical Co. and Beijing Chemical Co. used as received unless otherwise noted. (*S*)-2,2′-Diamino-6,6′-dimethyl-1,1′-biphenyl [26], (*S*)-2-

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amino-2′-dimethylamino-1,1′-binaphthyl [27–30], (*R*)-2-amino-2′-dimethylamino-6,6′-dimethyl-1,1′-biphenyl [27–30] and (*R*)-2-amino-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl [31] were prepared according to literature methods. Infrared spectra were obtained from KBr pellets on an Avatar 360 Fourier transform spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 500 spectrometer at 500 and 125 MHz, respectively. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents for proton and carbon chemical shifts. Melting points were measured on an X-6 melting point apparatus and were uncorrected. Optical rotations were measured on a Perkin–Elmer 343 polarimeter. Elemental analyses were performed on a Vario EL elemental analyzer.

2.2. Preparation of **1a–1d**

The preparation of **1a** is representative. Under an argon atmosphere, a mixture of (*S*)-2,2′-diamino-6,6′-dimethyl-1,1′-biphenyl (1.06 g, 5.0 mmol), 2-bromo-nitrobenzene (3.03 g, 15 mmol), $Pd_2(dba)_3$ (0.12 g, 0.125 mmol), bis(2-diphenylphosphinophenyl) ether (DPEphos) (0.20 g, 0.375 mmol), and Cs_2CO_3 (5.20 g, 16 mmol) was stirred in toluene (40 mL) at 80 °C for two days. After the reaction mixture was cooled to room temperature, the reaction was quenched by the addition of 100 mL of H_2O. The mixture was extracted with EtOAc (50 mL × 3), dried over anhydrous Na_2SO_4, and filtered. Removal of the solvent and the residue was purified by flash column chromatography (hexane/ethyl acetate = 6/1) to give **1a** as a red solid. Yield: 2.16 g (95%). M.p.: 113–115 °C, $[\alpha]_D^{20} = +1280$ (*c* 0.38, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 8.87 (s, 2H, N*H*), 7.92 (d, *J* = 8.6 Hz, 2H, aryl H), 7.28–7.24 (m, 4H, aryl H), 7.19–7.12 (m, 4H, aryl H), 7.07–7.04 (m, 2H, aryl H), 6.54 (m, 2H, aryl H), 2.02 (s, 6H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 141.9, 138.6, 136.9, 135.5, 133.5, 130.8, 128.6, 127.0, 126.4, 120.2, 117.5, 115.7, 19.7. IR (KBr, cm^{-1}): ν 3445 (m), 3327 (m), 2920 (w), 2853 (w), 1611 (m), 1575 (s), 1505 (s), 1344 (s), 1254 (s), 1148 (s), 777 (s), 736 (s). Anal. Calc. for $C_{26}H_{22}N_4O_4$: C, 68.71; H, 4.88; N, 12.33. Found: C, 68.81; H, 4.72; N, 12.40%.

1b, yield: 1.77 g (98%). Red crystals, m.p.: 144–146 °C, $[\alpha]_D^{20} = -117.4$ (*c* 0.43, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 9.17 (s, 1H, N*H*), 7.74 (m, 1H, aryl H), 7.25–7.21 (m, 3H, aryl H), 7.17–7.10 (m, 3H, aryl H), 6.89–6.81 (m, 2H, aryl H), 6.57 (m, 1H, aryl H), 2.46 (s, 6H, NMe_2), 2.05 (s, 3H, C*H*$_3$), 1.86 (s, 3H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 152.1, 143.4, 138.9, 137.1, 136.9, 135.7, 135.1, 133.0, 130.7, 128.4, 127.4, 126.5, 124.2, 122.4, 116.6, 116.3, 116.0, 43.8, 20.2, 19.9. IR (KBr, cm^{-1}): ν 3314 (m), 2943 (m), 2829 (m), 2787 (m), 1616 (m), 1513 (s), 1348 (s), 1261 (s), 1148 (s), 790 (s), 747 (s). Anal. Calc. for $C_{22}H_{23}N_3O_2$: C, 73.11; H, 6.41; N, 11.63. Found: C, 72.81; H, 6.62; N, 11.40%.

1c, yield: 1.97 g (91%). Red solid, m.p.: 122–124 °C, $[\alpha]_D^{20} = +80.3$ (*c* 0.38, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 9.46 (s, 1H, N*H*), 7.95–7.83 (m, 4H, aryl H), 7.73–7.71 (m, 1H, aryl H), 7.63–7.60 (m, 1H, aryl H), 7.46–7.43 (m, 1H, aryl H), 7.40–7.36 (m, 1H, aryl H), 7.24–7.20 (m, 3H, aryl H), 7.14–6.95 (m, 3H, aryl H), 6.93–6.56 (m, 1H, aryl H), 6.57–6.52 (m, 1H, aryl H), 2.55 (s, 6H, NMe_2). ^{13}C NMR ($CDCl_3$): δ 135.1, 134.6, 133.5, 133.4, 131.7, 129.7, 128.8, 128.2, 128.0, 126.9, 126.4, 125.4, 125.1, 123.9, 118.6, 117.1, 116.7, 43.9. IR (KBr, cm^{-1}): ν 3321 (m), 3056 (m), 2946 (m), 2837 (m), 1610 (s), 1567 (s), 1493 (s), 1255 (s), 1242 (s), 1147 (s), 817 (s), 738 (s). Anal. Calc. for $C_{28}H_{23}N_3O_2$: C, 77.58; H, 5.35; N, 9.69. Found: C, 77.81; H, 5.62; N, 9.40%.

1d, yield: 1.64 g (94%). Red solid, m.p.: 133–135 °C, $[\alpha]_D^{20} = -276.0$ (*c* 0.45, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 9.02 (s, 1H, N*H*), 7.98 (m, 1H, aryl H), 7.25–7.09 (m, 6H, aryl H), 6.77 (m, 2H, aryl H), 6.56 (m, 1H, aryl H), 3.65 (s, 3H, OC*H*$_3$), 1.97 (s, 3H, C*H*$_3$), 1.87 (s, 3H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 156.6, 143.1, 138.9, 137.6, 137.2, 135.2, 132.9, 128.8, 127.6, 127.0, 126.5, 125.6, 125.3, 122.7, 121.1, 116.8, 116.2, 108.1, 55.5, 19.9, 19.4. IR (KBr, cm^{-1}): ν 3337 (m), 2943 (w), 1614 (s), 1573 (s), 1498 (s), 1253 (s), 1083 (s), 743 (s). Anal. Calc. for $C_{21}H_{20}N_2O_3$: C, 72.40; H, 5.79; N, 8.04. Found: C, 72.31; H, 5.62; N, 8.40%.

2.3. Preparation of **2a–2d**

The preparation of **2a** is representative. Hydrazine hydrate (2 mL of 100%, 40.0 mmol) was added to an ethanol solution (40 mL) of **1a** (2.27 g, 5.0 mmol). Freshly prepared Raney nickel catalyst was added at intervals sufficient to maintain a vigorous reaction without causing excessive frothing. After a short time (about 2 min) the solution became colorless, ammonia began to be evolved also, and the reaction subsided. External heat was applied and the reaction continued until all the hydrazine had decomposed. The catalyst was filtered off and the filtrate was immediately evaporated to give quantitatively **2a** as a white solid. m.p.: 218–220 °C, $[\alpha]_D^{20} = +34.1$ (*c* 0.17, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.07–7.02 (m, 2H, aryl H), 6.96–6.91 (m, 4H, aryl H), 6.74 (d, *J* = 7.4 Hz, 2H, aryl H), 6.68–6.62 (m, 4H, aryl H), 6.46 (d, *J* = 8.80 Hz, 2H, aryl H), 4.89 (s, 2H, N*H*), 3.21 (s, 4H, N*H*$_2$), 2.03 (s, 6H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 143.7, 143.0, 137.9, 128.8, 127.8, 126.8, 126.4, 122.3, 120.8, 119.0, 116.0, 111.0, 19.7. IR (KBr, cm^{-1}): ν 3457 (m), 3419 (m), 3365 (m), 3334 (m), 3020 (m), 2918 (m), 1612 (s), 1574 (s), 1499 (s), 1461 (s), 1300 (s), 772 (s), 751 (s). Anal. Calc. for $C_{26}H_{26}N_4$: C, 79.16; H, 6.64; N, 14.20. Found: C, 78.81; H, 6.62; N, 14.40%.

2b, white solid, m.p.: 134–136 °C, $[\alpha]_D^{20} = +9.2$ (*c* 0.24, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.18 (m, 4H, aryl H), 7.07 (m, 2H, aryl H), 6.96 (m, 2H, aryl H), 6.82 (m, 2H, aryl H), 4.96 (s, 1H, N*H*), 3.44 (s, 2H, N*H*$_2$), 2,38 (s, 6H, NMe_2), 2.10 (s, 3H, C*H*$_3$), 2.06 ((s, 3H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 152.4, 143.4, 143.2, 138.6, 136.9, 130.9, 128.5, 128.1, 127.7, 126.8, 126.2, 126.0, 124.7, 120.8, 118.4, 116.5, 115.6, 111.4, 43.5, 20.0, 19.9. IR (KBr, cm^{-1}): ν 3325 (m), 3182 (m), 2957 (m), 2928 (m), 1605 (s), 1523 (s), 827 (s), 735 (s), 605 (s). Anal. Calc. for $C_{22}H_{25}N_3$: C, 79.72; H, 7.60; N, 12.68. Found: C, 79.81; H, 7.62; N, 12.40%.

2c, white solid, m.p.: 96–98 °C, $[\alpha]_D^{20} = -20.1$ (*c* 0.46, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.87 (d, *J* = 8.8 Hz, 1H, aryl H), 7.77 (d, *J* = 7.96 Hz, 1H, aryl H), 7.70 (s, 2H, aryl H), 7.46 (d, *J* = 8.8 Hz, 1H, aryl H), 7.27 (s, 1H, aryl H), 7.18 (s, 1H, aryl H), 7.14–7.11 (s, 3H, aryl H), 7.02–6.92 (m, 4H, aryl H), 6.66–6.60 (m, 2H, aryl H), 5.01 (s, 1H, N*H*), 3.63–3.67 (br s, 2H, N*H*$_2$), 2,56 (s, 6H, NMe_2). ^{13}C NMR ($CDCl_3$): δ 149.8, 143.1, 141.4, 134.4, 134.0, 130.3, 129.6, 128.8, 128.5, 128.1, 128.0, 126.9, 126.7, 126.4, 126.2, 125.3, 124.8, 124.2, 123.0, 122.3, 119.3, 118.6, 117.0, 116.3, 115.7, 18.4. IR (KBr, cm^{-1}): ν 3458 (m), 3344 (m), 3052 (m), 2939 (m), 2864 (m), 1618 (s), 1595 (s), 1502 (s), 1480 (s), 1416 (s), 1344 (s), 1299 (s), 1130 (s), 814 (s), 749 (s). Anal. Calc. for $C_{28}H_{25}N_3$: C, 83.34; H, 6.24; N, 10.41. Found: C, 83.31; H, 6.32; N, 10.40%.

2d, white solid, m.p.: 133–135 °C, $[\alpha]_D^{20} = +21.3$ (*c* 0.08, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.18 (m, 1H, aryl H), 7.02–6.88 (m, 4H, aryl H), 6.79–6.75 (m, 2H, aryl H), 6.41–6.73 (m, 2H, aryl H), 6.40 (m, 1H, aryl H), 3.66 (s, 3H, OC*H*$_3$), 2.01 (s, 3H, C*H*$_3$), 1.87 (s, 3H, C*H*$_3$); protons of N*H* were not observed. ^{13}C NMR ($CDCl_3$): δ 156.1, 142.2, 140.3, 138.0, 136.3, 128.1, 127.8, 126.9, 126.0, 125.1, 124.3, 122.9, 122.0, 119.5, 118.8, 115.6, 109.9, 107.7, 54.6, 18.8, 18.5. IR (KBr, cm^{-1}): ν 3463 (m), 3373 (m), 3028 (m), 2953 (m), 1615 (s), 1464 (s), 1304 (s), 1254 (s), 1081 (s), 1001 (s), 776 (s), 743 (s). Anal. Calc. for $C_{21}H_{22}N_2O$: C, 79.21; H, 6.96; N, 8.80. Found: C, 79.11; H, 6.82; N, 8.48%.

2.4. Preparation of **3a–3d**

The preparation of **3a** is representative. Compound **2a** (394 mg, 1.0 mmol), *p*-toluenesulfonic acid (20 mg), and triethyl orthofor-

mate [$HC(OC_2H_5)_3$] (10 mL) were heated at 100 °C for one day. 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 **3a** as a white solid. Colorless crystals suitable for X-ray structural analysis were grown from an ethyl acetate solution at room temperature. Yield: 369 mg (89%). M.p.: 216–218 °C, $[\alpha]_D^{20} = -230.6$ (*c* 0.18, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.47 (s, 2H, aryl H), 740 (m, 2H, aryl H), 7.35 (m, 2H, aryl H), 7.19 (s, 2H, NC*H*N), 7.06 (m, 2H, aryl H), 6.90 (m, 2H, aryl H), 6.47 (m, 2H, aryl H), 6.10 (s, 2H, aryl H), 2.31 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 141.4, 139.9, 133.8, 132.2, 130.5, 129.5, 128.6, 126.0, 124.3, 123.8, 122.4, 119.2, 109.3, 20.4. IR (KBr, cm^{-1}): ν 3088 (m), 2962 (m), 1608 (m), 1577 (m), 1485 (s), 1466 (s), 797 (s), 728 (s). Anal. Calc. for $C_{28}H_{22}N_4$: C, 81.13; H, 5.35; N, 13.52. Found: C, 80.81; H, 5.62; N, 13.40%.

3b, yield: 314 mg (92%). Colorless crystals, m.p.: 124–126 °C, $[\alpha]_D^{20} = +93.2$ (*c* 0.24, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.74 (s, 1H, NC*H*N), 7.52–7.49 (m, 3H, aryl H), 7.42–7.40 (m, 1H, aryl H), 7.30–7.25 (m, 3H, aryl H), 7.10–7.07 (m,1H, aryl H), 6.87 (m, 1H, aryl H), 6.60 (m, 1H, aryl H), 2.27 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.01 (s, 6H, NMe_2). ^{13}C NMR ($CDCl_3$): δ 151.7, 142.4, 141.0, 139.6, 137.5, 136.9, 134.8, 134.4, 130.7, 129.7, 128.9, 128.0, 124.7, 124.2, 123.3, 122.4, 119.3, 116.5, 110.6, 42.9, 20.3, 20.0. IR (KBr, cm^{-1}): ν 3045 (m), 2977 (m), 2821 (m), 1605 (m), 1579 (m), 1490 (s), 1462 (s), 761 (s), 739 (s). Anal. Calc. for $C_{23}H_{23}N_3$: C, 80.90; H, 6.79; N, 12.31. Found: C, 80.75; H, 6.85; N, 12.31%.

3c, yield: 355 mg (86%). White solid, m.p.: 168–170 °C, $[\alpha]_D^{20} = -111.0$ (*c* 0.50, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.06 (m, 1H, aryl H), 7.97 (m, 1H, aryl H), 7.72–7.67 (m, 3H, aryl H), 7.60 (m, 1H, aryl H), 7.53 (m, 1H, aryl H), 7.44 (m, 1H, aryl H), 7.34 (m, 1H, aryl H), 7.31 (m, 1H, aryl H), 7.26 (m, 2H, aryl H), 7.18 (m, 1H, aryl H), 7.10 (m, 3H, aryl H), 6.97 (m, 1H, aryl H), 1.85 (s, 6H, NMe_2). ^{13}C NMR ($CDCl_3$): δ 150.0, 142.8, 142.7, 134.8, 134.5, 134.4, 133.3, 133.1, 132.8, 130.0, 129.4, 129.2, 128.4, 127.5, 127.3, 126.8, 126.7, 124.8, 124.7, 123.6, 122.9, 122.0, 121.5, 119.9, 119.0, 110.1, 42.7. IR (KBr, cm^{-1}): ν 3064 (m), 2883 (m), 1612 (m), 1595 (s), 1489 (s), 1283 (s), 1237 (s), 821 (s), 740 (s). Anal. Calc. for $C_{29}H_{23}N_3$: C, 84.23; H, 5.61; N, 10.16. Found: C, 84.21; H, 5.62; N, 10.30%.

3d, yield: 282 mg (86%). Colorless crystals, m.p.: 174–176 °C, $[\alpha]_D^{20} = -128.9$ (*c* 0.31, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.63 (m, 2H, aryl H), 7.39 (s, 2H, aryl H), 7.30–7.28 (m, 2H, aryl H), 7.18 (s, 2H, aryl H), 7.02 (m, 1H, NC*H*N), 6.60–6.56 (m, 2H, aryl H), 3.51 (s, 3H, OCH_3), 2.00 (s, 3H, CH_3), 1.73 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 155.6, 138.7, 136.2, 133.9, 129.4, 128.1, 127.2, 125.1, 123.6, 123.2, 122.3, 121.7, 121.5, 118.7, 109.5, 107.0, 54.3, 19.1, 18.5. IR (KBr, cm^{-1}): ν 3443 (m), 2949 (m), 1579 (s) (m), 1485 (s), 1465 (s), 1258 (s), 1081 (s), 806 (s), 783 (s), 747 (s). Anal. Calc. for $C_{22}H_{20}N_2O$: C, 80.46; H, 6.14; N, 8.53. Found: C, 80.35; H, 5.92; N, 8.43%.

2.5. Preparation of *4a–4d*

The preparation of **4a** is representative. Compound **3a** (414 mg, 1.0 mmol) and CH_3I (0.48 mL, 8.0 mmol) in CH_3CN (10 mL) were stirred at 50 °C for one day. After cooling 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 **4a** as a white solid. Yield: 635 mg (91%). M.p.: 290–292 °C, $[\alpha]_D^{20} = -79.7$ (*c* 0.37, CH_3OH). ^1H NMR (CD_3OD): δ 7.77–7.60 (m, 8H, aryl H), 7.35 (m, 4H, aryl H), 6.90 (s, 2H, aryl H), 6.45 (s, 2H, aryl H), 4.71 (s, 6H, NCH_3), 2.36 (s, 6H, CH_3). ^{13}C NMR (CD_3OD): δ 143.0, 135.0, 133.1, 132.7, 132.2, 131.6, 129.6, 128.9, 126.9, 114.6, 112.7, 34.4, 20.7. IR (KBr, cm^{-1}): ν 3025 (m), 1614 (m), 1561 (s), 1460 (s), 1245 (s), 1135 (s), 753 (s). Anal. Calc. for $C_{30}H_{28}N_4I_2$: C, 51.59; H, 4.04; N, 8.02. Found: C, 51.81; H, 4.22; N, 8.21%. Colorless crystals **4a** · $1.5CH_3CN$ · $1.5H_2O$ suitable for X-ray structural analysis were grown from an CH_3CN solution at room temperature.

4b, yield: 459 mg (95%). Colorless crystals, m.p.: 292–294 °C, $[\alpha]_D^{20} = -23.2$ (*c* 0.76, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 10.35 (s, 1H, aryl H), 9.24 (s, 1H, aryl H), 7.55 (m, 6H, aryl H), 6.99 (m, 2H, aryl H), 6.43 (m, 1H, aryl H), 4.16 (s, 3H, NCH_3), 2.40 (s, 3H, CH_3), 2.21 (s, 6H, NMe_2), 1.60 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 150.9, 143.3, 140.3, 137.1, 133.1, 132.3, 131.2, 130.7, 129.2, 129.0, 127.5, 126.9, 124.7, 115.6, 112.8, 43.0, 34.5, 20.2. IR (KBr, cm^{-1}): ν 3024 (s), 1610 (w), 1560 (s), 1482 (s), 1342 (s), 1242 (s), 1183 (s), 1029 (s), 813 (s), 759 (vs). Anal. Calc. for $C_{24}H_{26}N_3I$: C, 59.63; H, 5.42; N, 8.69. Found: C, 59.72; H, 5.23; N, 8.55%.

4c, yield: 505 mg (91%). White solid, m.p.: 174–176 °C, $[\alpha]_D^{20} = +62.9$ (*c* 0.31, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 10.67 (s, 1H, aryl H), 8.18 (m, 1H, aryl H), 8.04 (m, 1H, aryl H), 7.93 (m, 1H, aryl H), 7.63–7.38 (m, 8H, aryl H), 7.20 (m, 1H, aryl H), 7.06 (m, 1H, aryl H), 6.94 (m, 1H, aryl H), 6.72 (s, 1H, aryl H), 6.57 (s, 1H, aryl H), 4.30 (s, 3H, NCH_3), 2.45 (s, 6H, NMe_2). ^{13}C NMR ($CDCl_3$): δ 147.7, 141.6, 132.6, 131.8, 129.0, 128.6, 127.3, 127.2, 127.0, 126.4, 126.3, 126.2, 125.5, 122.7, 117.8, 116.1, 110.7, 110.2, 41.6, 32.5. IR (KBr, cm^{-1}): ν 3005 (m), 1616 (m), 1562 (s), 1505 (s), 1459 (s), 1337 (s), 1132 (s), 918 (s), 749 (s). Anal. Calc. for $C_{30}H_{26}N_3I$: C, 64.87; H, 4.72; N, 7.57. Found: C, 64.81; H, 4.62; N, 7.40%.

4d, yield: 437 mg (93%). Colorless crystals, m.p.: 276–278 °C, $[\alpha]_D^{20} = -49.7$ (*c* 0.32, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 9.92 (s, 1H, aryl H), 7.55 (m, 7H, aryl H), 6.67 (m, 1H, aryl H), 6.49 (m, 2H, aryl H), 4.21 (s, 3H, NCH_3), 3.30 (s, 3H, OCH_3), 2.03 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 155.0, 140.7, 139.3, 134.2, 132.0, 131.3, 130.5, 130.2, 128.7, 128.0, 127.4, 126.2, 124.9, 123.8, 122.0, 121.9, 112.6, 111.9, 107.0, 54.5, 33.8, 19.0. IR (KBr, cm^{-1}): ν 3026 (m), 2960.3, 2833 (m), 1557 (s), 1466 (s), 1258 (s), 1080 (s), 785 (s), 751 (s). Anal. Calc. for $C_{23}H_{23}N_2IO$: C, 58.73; H, 4.93; N, 5.96. Found: C, 58.64; H, 5.14; N, 5.91%.

2.6. Preparation of *5a–5d*

The preparation of **5a** is representative. A mixture of **4a** (140 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 two days. After cooling to room temperature, removal of the solvent and the residue was purified by flash column chromatography (hexane/ethyl acetate = 1/1) to give **5a** as an orange solid. Orange crystals suitable for X-ray structural analysis were grown from an ethyl acetate solution at room temperature. Yield: 58 mg (67%). M.p.: 188–190 °C, $[\alpha]_D^{20} = 0.0$ (*c* 0.35, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.01 (d, *J* = 8.0 Hz, 2H, aryl H), 7.26–7.14 (m, 6H, aryl H), 7.04–6.95 (m, 4H, aryl H), 6.54 (d, *J* = 8.0 Hz, 2H, aryl H), 4.29 (s, 6H, NCH_3), 1.94 (s, 3H, CH_3), 1.62 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 187.8, 166.6, 135.6, 135.3, 135.1, 134.3, 133.8, 130.2, 129.8, 126.0, 122.5, 121.8, 110.5, 109.0, 37.1, 24.0, 18.3. IR (KBr, cm^{-1}): ν 2962 (s), 1605 (w), 1463 (s), 1261 (s), 1091 (s), 1019 (s), 801 (s). Anal. Calc. for $C_{32}H_{29}N_4I_2O_2Rh$: C, 44.78; H, 3.41; N, 6.53. Found: C, 44.81; H, 3.42; N, 6.40%.

5b, yield: 71 mg (51%). Orange solid, m.p.: 220–222 °C, $[\alpha]_D^{20} = +19.2$ (*c* 0.26, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 9.32 (d, *J* = 7.8 Hz, 1H, aryl H), 7.57 (t, *J* = 7.7 Hz, 1H, aryl H), 7.42 (d, *J* = 7.6 Hz, 1H, aryl H), 6.97 (d, *J* = 8.0 Hz, 1H, aryl H), 6.85 (m, 3H, aryl H), 6.52 (t, *J* = 8.2 Hz, 1H, aryl H), 6.35 (d, *J* = 7.8 Hz, 1H, aryl H), 6.29 (d, *J* = 8.2 Hz, 1H, aryl H), 5.29 (m, 1H, C*H*), 5.16 (m, 1H, C*H*), 4.21 (s, 3H, NCH_3), 3.91 (m, 1H, C*H*), 3.35 (m, 1H, C*H*), 2.15 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 1.86 (s, 6H, NMe_2), 2.39–2.17 (m, 4H, CH_2), 1.82 (m, 2H, CH_2), 1.35 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 151.5, 137.5, 129.1, 127.7, 126.3, 126.0, 125.6, 120.2, 120.0, 115.4, 110.4, 106.9, 95.0, 78.6, 78.5, 68.6, 43.5, 31.1, 30.2, 28.7, 27.5, 26.5, 19.5, 19.4. IR (KBr, cm^{-1}): ν 2930 (s), 2872 (m), 1600

(m), 1475 (s), 1457 (s), 1380 (s), 1336 (s), 1215 (s), 1091 (s), 1016 (m), 912 (m), 734 (vs). Anal. Calc. for $C_{32}H_{37}N_3IRh$: C, 55.42; H, 5.38; N, 6.06. Found: C, 55.31; H, 5.62; N, 6.40%. Orange crystals **5b** · CH_3OH suitable for X-ray structural analysis were grown from a methanol solution at room temperature.

5c, yield: 48 mg (63%). Orange crystals, m.p.: 262–264 °C, $[\alpha]_D^{20} = +56.7$ (*c* 0.21, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 9.79 (d, *J* = 8.8 Hz, 1H, aryl H), 8.23 (d, *J* = 8.7 Hz, 1H, aryl H), 8.04 (d, *J* = 8.2 Hz, 1H, aryl H), 7.55 (d, *J* = 8.9 Hz, 1H, aryl H), 7.50 (m, 1H, aryl H), 7.33 (t, *J* = 7.2 Hz, 1H, aryl H), 7.26 (m, 3H, aryl H), 6.96 (m, 3H, aryl H), 6.85 (d, *J* = 8.9 Hz, 1H, aryl H), 6.72 (t, *J* = 7.6 Hz, 1H, aryl H), 5.93 (t, *J* = 7.6 Hz, 1H, aryl H), 5.71 (d, *J* = 8.3 Hz, 1H, aryl H), 5.41 (m, 1H, C*H*), 5.22 (m, 1H, C*H*), 4.24 (s, 3H, NCH_3), 3.96 (m, 1H, C*H*), 3.44 (m, 1H, C*H*), 2.37–2.13 (m, 4H, CH_2), 1.93 (s, 6H, NMe_2), 1.73 (m, 2H, CH_2), 1.18 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 150.0, 133.6, 133.2, 132.5, 130.4, 129.8, 129.1, 127.3, 127.1, 126.7, 126.6, 125.9, 125.6, 125.5, 125.3, 125.0, 123.5, 120.5, 119.6, 117.5, 110.5, 107.0, 95.3, 95.2, 94.9, 94.8, 70.3, 70.1, 68.7, 68.6, 43.5, 35.3, 32.8, 29.7, 29.1, 27.6. IR (KBr, cm^{-1}): *v* 2932 (m), 2824 (m), 1594 (m), 1505 (s), 1474 (m), 1427 (s), 1383 (s), 1334 (s), 1261 (s), 1092 (vs), 1019 (s), 802 (s), 738 (s). Anal. Calc. for $C_{38}H_{37}N_3IRh$: C, 59.62; H, 4.87; N, 5.49. Found: C, 59.81; H, 4.62; N, 5.40%.

5d, yield: 44 mg (65%). Orange crystals, m.p.: 273–275 °C, $[\alpha]_D^{20} = 0.0$ (*c* 0.46, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 9.16 (d, *J* = 7.6 Hz, 1H, aryl H), 7.57 (m, 1H, aryl H), 7.41 (m, 1H, aryl H), 7.01 (m, 1H, aryl H), 6.88 (m, 3H, aryl H), 6.62 (m, 1H, aryl H), 6.28 (d, *J* = 7.6 Hz, 1H, aryl H), 6.13 (d, *J* = 8.4 Hz, 1H, aryl H), 5.29 (m, 1H, C*H*), 5.16 (m, 1H, C*H*), 4.21 (s, 3H, NCH_3), 3.87 (m, 1H, C*H*), 3.79 (s, 3H, OCH_3), 3.36 (m, 1H, C*H*), 2.15 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.42–2.17 (m, 4H, CH_2), 1.99–1.32 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ 156.5, 139.0, 138.0, 137.8, 134.7, 129.9, 128.6, 127.5,

Table 1
Crystal data and experimental parameters for compounds **1b**, **3a**, **3b**, **3d**, **4a** and **4b**.

compound	**1b**	**3a**	**3b**	**3d**	**4a** · $1.5CH_3CN$ · $1.5H_2O$	**4b**
Formula	$C_{22}H_{23}N_3O_2$	$C_{28}H_{22}N_4$	$C_{23}H_{23}N_3$	$C_{22}H_{20}N_2O$	$C_{66}H_{71}N_{11}I_4O_3$	$C_{24}H_{26}IN_3$
Formula weight	361.43	414.50	341.44	328.40	1573.94	483.38
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P12_11$	$P12_11$	$P12_11$
a (Å)	10.387(1)	7.657(1)	7.984(1)	8.992(1)	10.499(2)	8.001(1)
b (Å)	11.922(1)	14.203(3)	14.144(2)	18.294(2)	15.395(3)	16.272(2)
c (Å)	15.721(1)	20.209(5)	16.473(2)	10.872(1)	21.046(4)	8.434(1)
β (°)	90	90	90	100.64(1)	90.24(3)	100.34(1)
V (Å^3)	1946.7(3)	2197.5(9)	1860.1(3)	1757.8(3)	3385.5(12)	1080.3(2)
Z	4	4	4	4	2	2
$D_{calc.}$ (g/cm^3)	1.233	1.253	1.219	1.241	1.544	1.486
μ(Mo/Kα)$_{calc}$ (mm^{-1})	0.080	0.075	0.073	0.077	1.893	1.496
Size (mm)	0.22 × 0.18 × 0.16	0.18 × 0.12 × 0.10	0.26 × 0.10 × 0.08	0.28 × 0.26 × 0.24	0.22 × 0.20 × 0.14	0.28 × 0.26 × 0.18
F(000)	768	872	728	696	1560	488
2θ range (°)	4.28–55.76	4.94–55.72	5.68–54.56	4.42–55.02	3.88–60.06	4.90–64.62
No. of reflections collected	24631	26507	22394	21476	34505	13687
No. of unique reflections [$R_{(int)}$]	2633 (0.0395)	2971 (0.0434)	2366 (0.0491)	4166 (0.0373)	16998 (0.0347)	6338 (0.0381)
No. of observed reflections	2633	2971	2366	4166	16998	6338
Absorbed corrections (T_{max}, T_{min})	0.99, 0.98	0.99, 0.98	0.99, 0.98	0.98, 0.97	0.78, 0.68	0.77, 0.68
R	0.037	0.044	0.039	0.037	0.034	0.024
R_w	0.091	0.109	0.093	0.093	0.073	0.050
R_{all}	0.041	0.046	0.043	0.040	0.038	0.027
GOF	1.08	1.07	1.07	1.05	1.00	0.95

Table 2
Crystal data and experimental parameters for compounds **4d** and **5a-d**.

Compound	**4d**	**5a**	**5b** · CH_3OH	**5c**	**5d**
Formula	$C_{23}H_{23}N_2O$	$C_{32}H_{29}N_4I_2O_2Rh$	$C_{33}H_{41}N_3IORh$	$C_{38}H_{37}N_3IRh$	$C_{31}H_{34}N_2I_2ORh$
Formula weight	470.33	858.30	725.50	765.52	680.41
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P12_11$	C12/c1	$P12_11$	$P2_12_12_1$	C12/c1
a (Å)	8.292(2)	14.255(2)	8.624(2)	8.548(1)	8.047(1)
b (Å)	29.913(5)	16.678(2)	15.140(2)	15.901(2)	13.402(2)
c (Å)	8.542(2)	12.585(1)	111.703(2)	23.578(4)	25.121(3)
β (°)	101.50(1)	92.46(1)	94.00(1)	90	95.22(1)
V (Å^3)	2076.3(7)	2989.3(5)	1524.3(4)	3204.7(8)	2697.9(6)
Z	4	4	2	4	4
$D_{calc.}$ (g/cm^3)	1.505	1.907	1.581	1.587	1.675
μ(Mo/Kα)$_{calc.}$ (mm^{-1})	1.557	2.673	1.603	1.528	1.804
Size (mm)	0.05 × 0.04 × 0.03	0.16 × 0.12 × 0.10	0.22 × 0.20 × 0.16	0.22 × 0.20 × 0.14	0.22 × 0.20 × 0.18
F(000)	944	1664	732	1536	1360
2θ range (°)	4.86–55.76	3.76–55.74	4.74–55.88	3.46–58.28	4.46–55.72
No. of reflections, collected	19201	14511	14866	27296	26134
No. of unique reflections [$R_{(int)}$]	9702 (0.0481)	3574 (0.0516)	6941 (0.0686)	8620 (0.0465)	6416 (0.0736)
No. of observed reflections	9702	3574	6941	8620	6416
Absorbed corrections (T_{max}, T_{min})	0.95, 0.93	0.78, 0.67	0.78, 0.72	0.81, 0.73	0.74, 0.69
R	0.039	0.041	0.062	0.029	0.069
R_w	0.067	0.082	0.180	0.060	0.133
R_{all}	0.045	0.043	0.069	0.032	0.076
GOF	1.03	1.13	1.06	1.06	1.29

126.8, 126.6, 124.2, 121.4, 120.8, 111.9, 111.4, 108.6, 96.0, 95.4, 94.5, 71.2, 71.1, 69.7, 69.5, 55.2, 36.1, 34.3, 30.4, 28.6, 28.3, 20.4, 19.9. IR (KBr, cm^{-1}): ν 2937 (m), 1576 (m), 1458 (s), 1335 (s), 1255 (s), 1080 (s), 907 (s), 736 (s). Anal. Calc. for $C_{31}H_{34}N_2IORh$: C, 54.72; H, 5.04; N, 4.12. Found: C, 54.81; H, 5.12; N, 4.40%.

2.7. X-ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a Rigaku Saturn CCD diffractometer at 113(2) K using graphite monochromated Mo Kα radiation (λ = 0.71070 Å). An empirical absorption correction was applied using the SADABS program [32]. All structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 program package [33]. All the hydrogen atoms were geometrically fixed using the riding model. The crystal data and experimental data for **1b**, **3a**, **3b**, **3d**, **4a**, **4b**, **4d** and **5a–d** are summarized in Tables 1 and 2. Selected bond lengths and angles for **5a–d** are listed in Table 3.

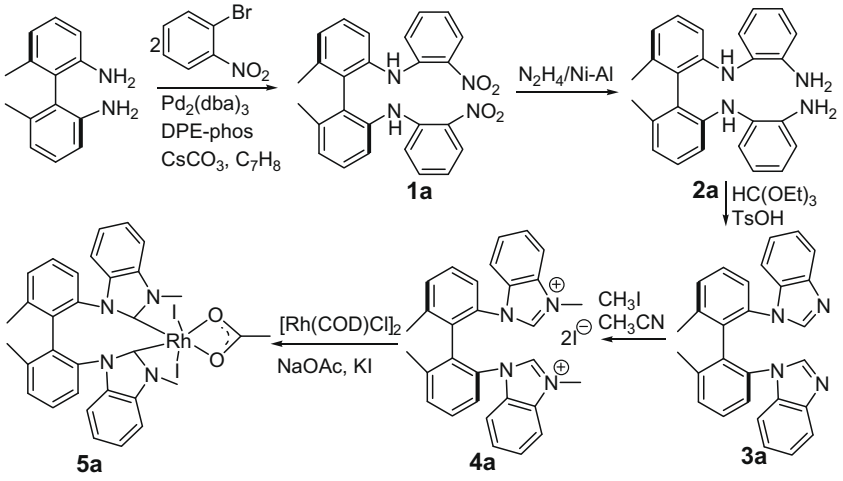
Table 3
Selected bond distances (Å) and bond angles (°) for compounds **5a–d**.

Compound	5a	5b	5c	5d
Rh–C(carbene)	1.985(4)	2.026(9)	2.009(3)	2.013(7)
Rh–C(COD, av.)		2.148(11)	2.171(3)	2.169(7)
Rh–I	2.654(1)	2.694(1)	2.711(1)	2.721(1)
Rh–O	2.153(3)			
C(carbene)–Rh–C(carbene)	99.3(2)			
Torsion (aryl–aryl)	82.2(5)	73.6(9)	71.6(8)	78.9(7)

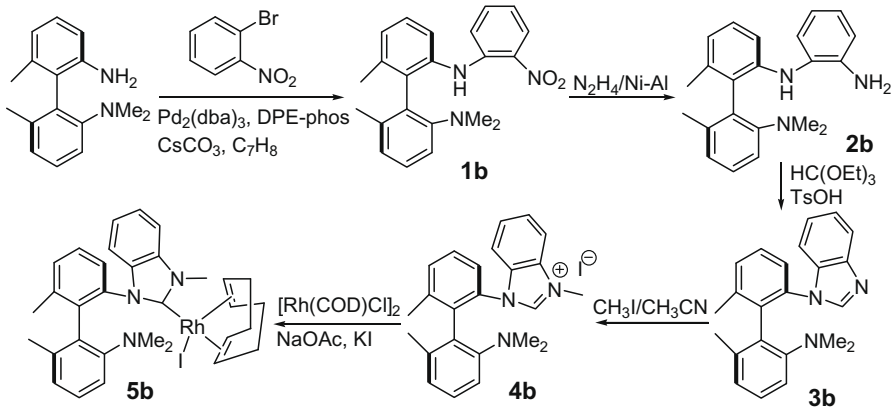
3. Results and discussion

3.1. Synthesis and characterization of ligands

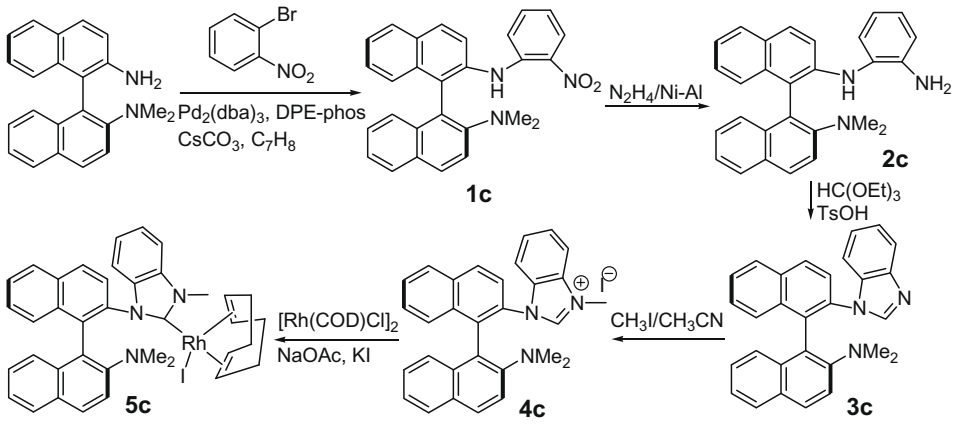
Treatment of (*S*)-2,2′-diamino-6,6′-dimethyl-1,1′-biphenyl, (*R*)-2-amino-2′-dimethylamino-6,6′-dimethyl-1,1′-biphenyl, (*S*)-2-amino-2′-dimethylamino-1,1′-binaphthyl or (*R*)- 2-amino-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl with an excess of 2-bromo-nitrobenzene in the presence of catalytic amount of $Pd_2(dba)_3$ and bis(2-diphenylphosphinophenyl) ether (DPEphos) in toluene at 80 °C gives the nitro compounds **1a–d** in good yields (Schemes 1–4). Reduction of the nitro compounds **1a–d** by hydrazine hydrate in the presence of Raney nickel catalyst quantitatively affords the amino compounds **2a–d** (Schemes 1–4). During the course of the reaction, the conversion can be easily monitored by thin layer chromatography (TLC), and the rings of the naphthyl groups can not be reduced under this reaction condition, in contrast to Pd-C/H_2 catalytic reduction system with high H_2 gas pressure [16,34]. Subsequent cyclization of **2a–d** with triethyl orthoformate in the presence of catalytic amount of *p*-toluenesulfonic acid (TsOH) at reflux gives the dibenzimidazole **3a** and the monobenzimidazoles **3b–d** in good yields (Schemes 1–4). Finally quaternization of the benzimidazole rings of **3a–d** with methyl



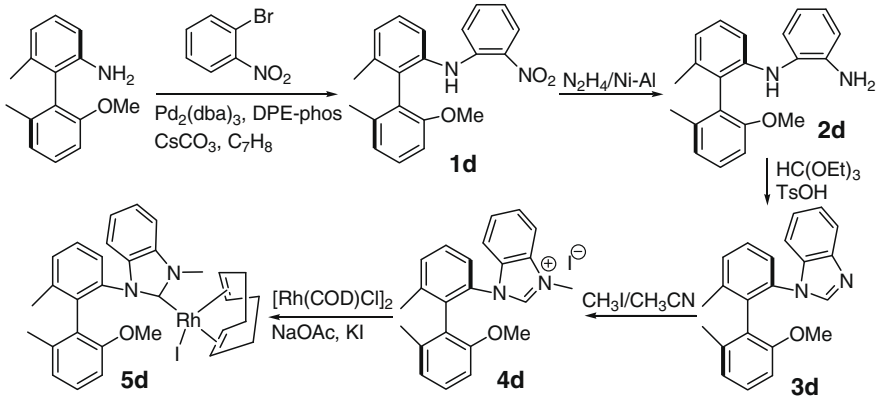
Scheme 1. Synthesis of bis-NHC–Rh(III) complex **5a**.



Scheme 2. Synthesis of NHC–Rh(I) complex **5b**.



Scheme 3. Synthesis of NHC–Rh(I) complex **5c**.



Scheme 4. Synthesis of NHC–Rh(I) complex **5d**.

iodide affords the corresponding dibenzimidazolium salt **4a** and monobenzimidazolium salts **4b–d** in good yields (Schemes 1–4). All the new compounds are air-stable, and they have been characterized by various spectroscopic techniques and elemental analyses. The solid-state structures of compounds **1b**, **3a**, **3b**, **3d**, **4a**, **4b** and **4d** have been further confirmed by X-ray diffraction analyses.

The molecular structures of **4a** and **4d** show that there are two **4a** molecules with three CH_3CN molecules and three H_2O, and two **4d** molecules in the asymmetric unit. The molecular structures clearly show that the biaryl groups of the compounds **1b**, **3a**, **3b**, **3d** and the cations in **4a**, **4b** and **4d** arrange in a staggered geometry (Figs. 1–7). The twisting between the aryl rings of torsion angle is 73.1(2)° for **1b**, 75.8(2)° for **3a**, 72.3(2)° for **3b**, 83.7 (2)° for **3d**, 77.6(4)° for **4a**, 77.2(2)° for **4b**, and 72.8(4)° for **4d**, respectively, which are comparable to those found in (*S*)-2-(Me_2N)-$C_{20}H_{12}$-2′-($NCHC_4H_4N$) (75.6(3)°) [29], (*S*)-2-($NCHC_4H_4N$)-2′-hydroxy-6,6′-dimethyl-1,1′-biphenyl (76.7(2)°) [35], and (*S*)-2-($NCHC_4H_4N$)-2′-methoxy-6,6′-dimethyl-1,1′-biphenyl (83.0(4)°) [31].

3.2. Synthesis and characterization of complexes

It has been reported that treatment of the dibenzimidazolium salt $[C_{20}H_{12}(C_7H_5N_2Me)_2]I_2$ derived from chiral 2,2′-diamino-1,1′-binaphthyl with 0.5 equiv of $[Rh(COD)Cl]_2$ in the presence of NaOAc and KI affords a chiral Rh(III) complex $[C_{20}H_{12}(C_7H_4N_2Me)_2]RhI_2(OAc)$ [16]. However, treatment of dibenzimidazolium salt **4a** with 0.5 equiv of $[Rh(COD)Cl]_2$ in the presence of NaOAc and KI does not give a chiral Rh(III) complex, instead, a *racemic* Rh(III) complex **5a** has been isolated in 67% yield (Scheme 1), which is identified by both optical rotation and X-ray diffraction analyses, and is due to the steric effect of the ligands, *i.e.*, the feature of the bis-NHC-ligand **4a** compared to the bis-NHC-ligand derived from 2,2′-diamino-1,1′-binaphthyl is the less steric hindrance

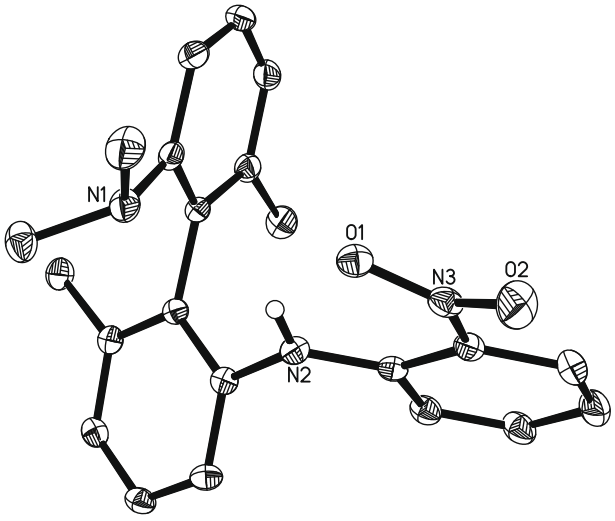


Fig. 1. Molecular structure of **1b** (thermal ellipsoids drawn at the 35% probability level).

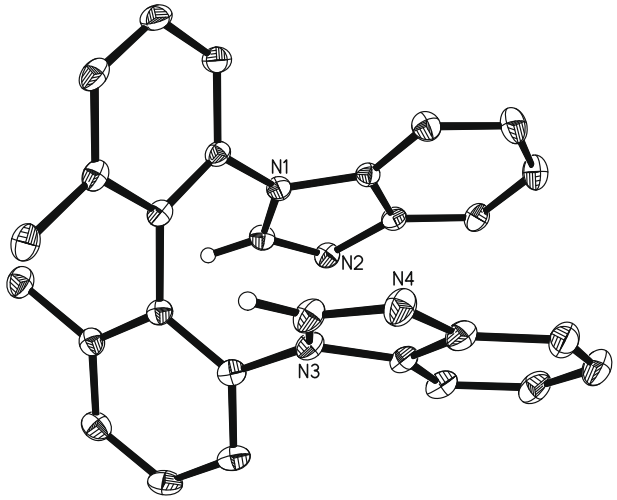


Fig. 2. Molecular structure of **3a** (thermal ellipsoids drawn at the 35% probability level).

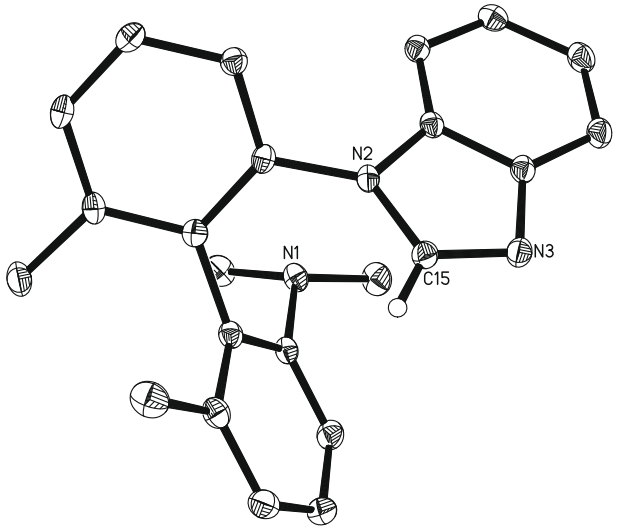


Fig. 3. Molecular structure of **3b** (thermal ellipsoids drawn at the 35% probability level).

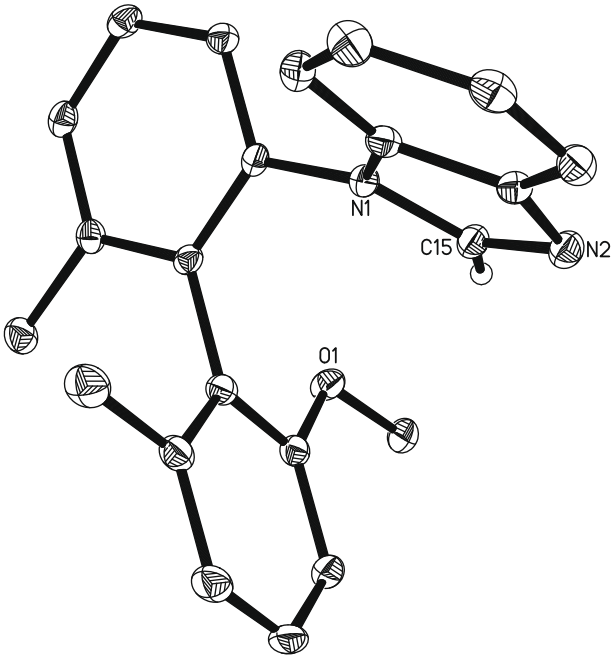


Fig. 4. Molecular structure of **3d** (thermal ellipsoids drawn at the 35% probability level).

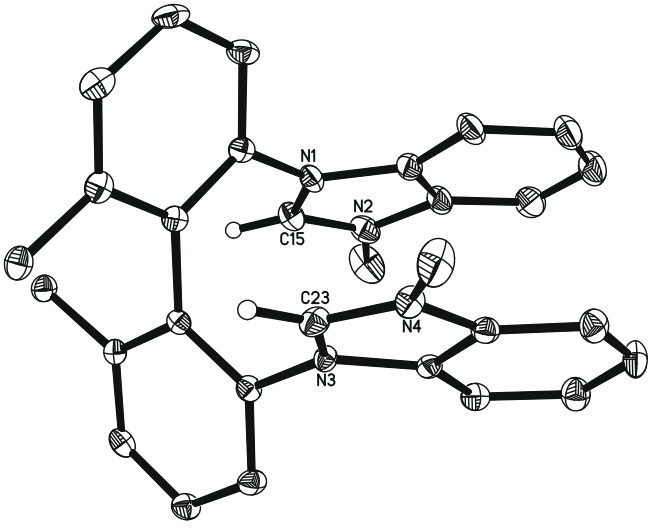


Fig. 5. Molecular structure of the cation in **4a** (thermal ellipsoids drawn at the 35% probability level).

of the biaryl groups, which allowed the C–C bond between the two phenyl rings of the bis-NHC-ligand **4a** rotating more easily. The similar results also have been observed by Seki and his co-workers for racemization of chiral 1,1′-biaryl-2,2′-dicarboxylic acid system, in which the racemization of chiral 6,6′-dimethyl-1,1′-biphenyl-2,2′-dicarboxylic acid occurs at 85 °C, while 1,1′-binaphthyl-2,2′-dicarboxylic acid does not at this temperature [36]. Under similar reaction conditions, treatment of chiral monobenzimidazolium salt **4b** with 0.5 equiv of $[Rh(COD)Cl]_2$ in the presence of NaOAc and KI in CH_3CN at reflux does not expect to give a Rh(III) complex, instead, a chiral Rh(I) complex **5b** has been isolated in 51% yield (Scheme 2), which is due to the electronic effect between rhodium and the NHC-ligands postulated by Peris [37], in which the I^- is oxidized by oxygen (from air) to I_2, followed by oxidatively addition to the Rh(I) compound, and in any case, the high donor abilities of the di-heteroatom-stabilized carbene ligands favor a high-valent metal for bonding [37]. Reaction of the chiral monobenzimidazolium salt **4c** with 0.5 equiv of $[Rh(COD)Cl]_2$ in the presence of NaOAc and KI in CH_3CN at reflux also gives a chiral Rh(I) complex **5c** in 63% yield (Scheme 3), while the chiral monobenzimidazolium salt **4d** affords a *racemic* Rh(I) complex **5d** in 65% yield (Scheme 4), which is also identified by both optical rotation and X-ray diffraction analyses, and is also due to the steric effect of the ligands, *i.e.*, the feature of the mono-NHC-ligand **4d** (biphenyl group coupled with a MeO group) compared to the mono-NHC-ligands **4b** (biphenyl group with a Me_2N group) and **4c** (binaphthyl group coupled with a Me_2N group) is the less steric hindrance of the substituted biaryl groups, which allowed the C–C bond between the two phenyl rings of the mono-NHC-ligand **4d** rotating more easily. These complexes are air-stable, and they are soluble in organic solvents such as THF, DME, pyridine, and CH_3CN, and only slightly soluble in toluene, and benzene, and insoluble in *n*-hexane. They have been characterized by various

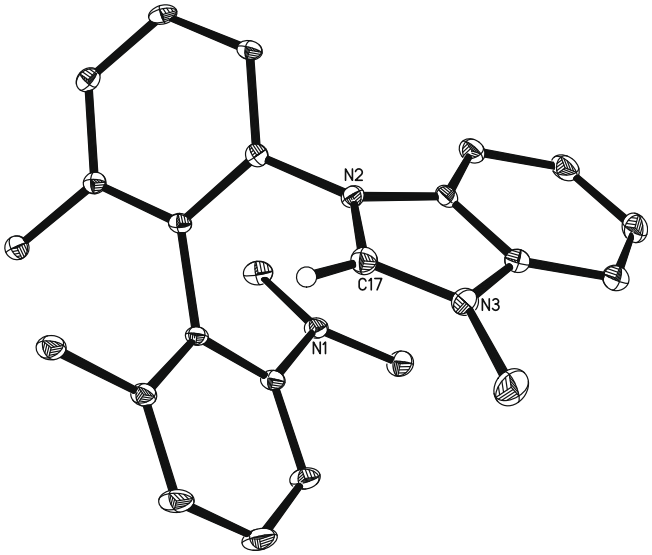


Fig. 6. Molecular structure of the cation in **4b** (thermal ellipsoids drawn at the 35% probability level).

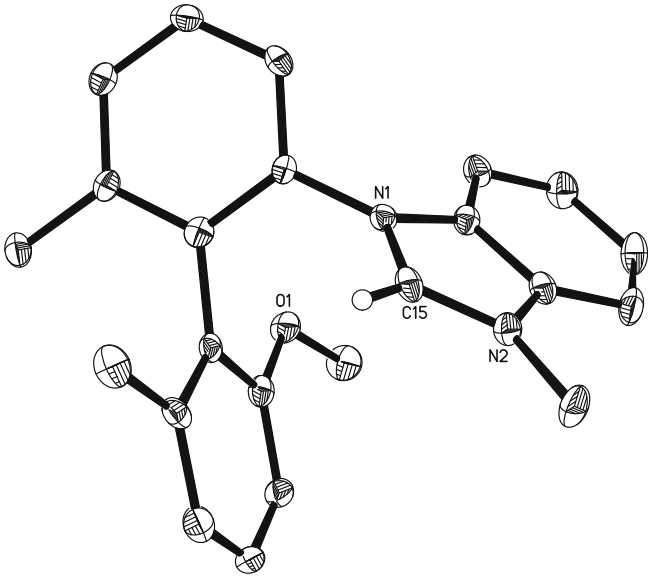


Fig. 7. Molecular structure of the cation in **4d** (thermal ellipsoids drawn at the 35% probability level).

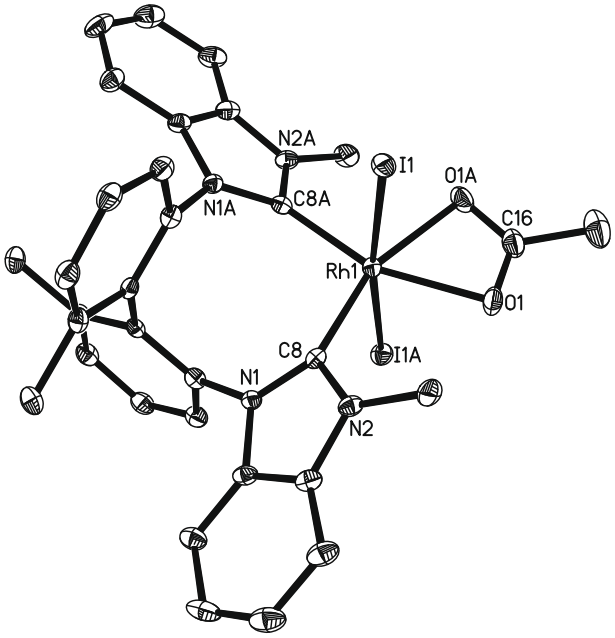


Fig. 8. Molecular structure of **5a** (thermal ellipsoids drawn at the 35% probability level).

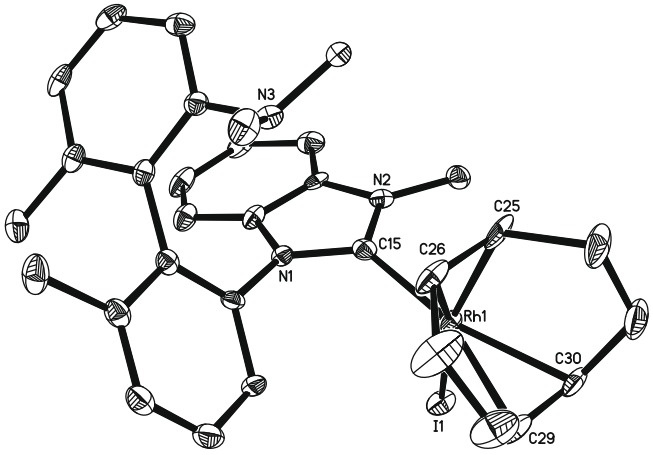


Fig. 9. Molecular structure of **5b** (thermal ellipsoids drawn at the 35% probability level).

spectroscopic techniques, elemental analyses, and single-crystal X-ray diffraction analyses.

The molecular structure of **5a** shows that the Rh(III) is σ-bound to two carbon atoms (carbenes) and two iodine atoms and two oxygen atoms from OAc^- anion in a distorted-octahedral geometry (Fig. 8). The biscarbene moiety is chelating, with a bite angle C(8)–Rh(1)–C(8A) of 99.3(2)°, which is larger than that found in bisimidazol-2-ylidene-phenylene-bridged related complex (C–Rh–C, 92.2°) [38]. The sum of the angles in the equatorial plane containing the acetate and biscarbene ligand is 360.3(2)°, indicating a highly coplanar arrangement. The Rh–C(carbene) distance (1.985(4) Å) is a little shorter than those found in bisimidazol-2-ylidene-phenylene-bridged related complex (1.992(9) and 2.000(10) Å) [38]. The distance is, however, still typical for σ-character bond, indicating that the back-donation is negligible for this compound [37]. The twisting between the phenyl rings of torsion angle is 82.2(5)°, which is larger than those found in **3a** (75.8(2)°) and **4a** (77.6(4)°).

The molecular structure of **5b** shows that there is one **5b** molecule and one methanol molecule in the asymmetric unit. The molecular structures clearly show that the two biaryl groups of the compounds **5b**, **5c** and **5d** arrange in a C_1-symmetric staggered geometry (Figs. 9–11), and the substituted Me_2N or MeO group is far away from the metal center. In each molecule, the Rh(I) is bound to one iodine atom and one carbon atom (carbene) and two alkene groups from COD in a pseudosquare-planar geometry (Figs. 9–11) with the average distance of Rh–C(COD) (2.148(11) Å) for **5b**, (2.171(3) Å) for **5c**, and (2.169(7) Å) for **5d**, and the distance of Rh–I (2.694(1) Å) for **5b**, (2.711(1) Å) for **5c**, and (2,721(1) Å) for **5d**, respectively. The distance of Rh–C(carbene) is (2.026(9) Å) for **5b**, (2.009(3) Å) for **5c**, and (2.013(7) Å) for **5d**, respectively, which again are typical for Rh–C σ-bonds with very little back-donation [37]. The twisting between the aryl rings of torsion angle is 73.6(9)° for **5b**, 71.6(8)° for **5c**, and 78.9(7)° for **5d**, respectively.

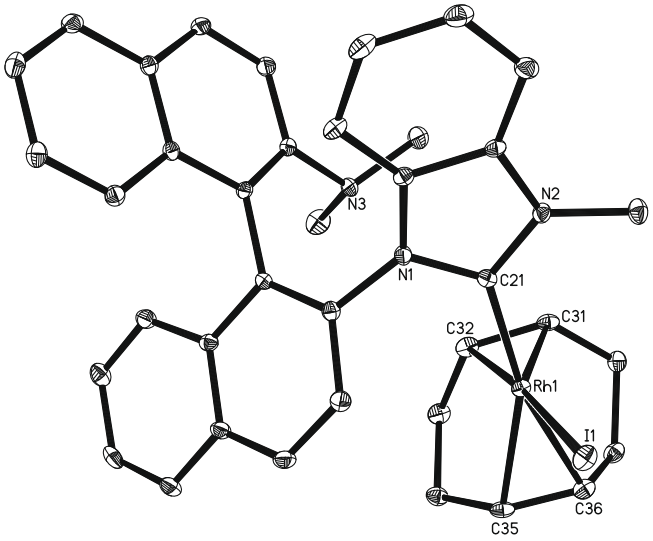


Fig. 10. Molecular structure of **5c** (thermal ellipsoids drawn at the 35% probability level).

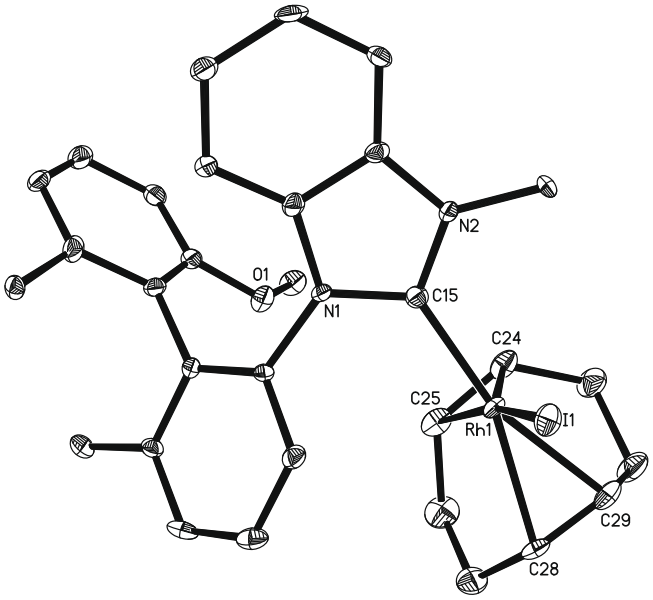


Fig. 11. Molecular structure of **5d** (thermal ellipsoids drawn at the 35% probability level).

4. Conclusions

In conclusion, a new series of chiral NHC–rhodium complexes has been prepared from the reactions between $[Rh(COD)Cl]_2$, NaOAc, KI and dibenzimidazolium salt **4a** or monobenzimidazolium salts **4b–d**. The steric and electronic effects of the ligand play an important role in the formation of these complexes. When changes are made from Me_2N group to MeO group, from binaphthyl to 6,6′-dimethyl-1,1′-biphenyl, and from monobenzimidazolium salts to dibenzimidazolium salts, the benzimidazolium salts exhibit different reactivity patterns. For example, treatment of chiral monobenzimidazolium salt **4b** (with a NMe_2 group) with 0.5 equiv of $[Rh(COD)Cl]_2$ in the presence of NaOAc and KI in CH_3CN at reflux gives a chiral Rh(I) complex **5b**, while chiral monobenzimidazolium salt **4d** (with a MeO group) affords a *racemic* Rh(I) complex **5d**. Under similar reaction conditions, treatment of dibenzimidazolium salt **4a** with 0.5 equiv of $[Rh(COD)Cl]_2$ in the presence of NaOAc and KI gives a *racemic* Rh(III) complex **5a**, while the dibenzimidazolium salt $[C_{20}H_{12}(C_7H_5N_2Me)_2]I_2$ derived from chiral 2,2′-diamino-1,1′-binaphthyl affords a chiral Rh(III) complex $[C_{20}H_{12}(C_7H_4N_2Me)_2]RhI_2(OAc)$ [16]. We are currently concentrating on these transformations, further efforts will focus on the applications of these chiral NHC–rhodium complexes toward asymmetric reactions and the exploration of new NHC–metal complexes based on chiral NHC-ligands.

Acknowledgement

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Appendix A. Supplementary material

CCDC 704981, 704982, 704983, 704984, 704985, 704986, 704987, 704988, 704989, 704990 and 704991 contain the supplementary crystallographic data for **1b**, **3a**, **3b**, **3d**, **4a**, **4b**, **4d**, **5a**, **5b**, **5c** and **5d**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.12.059.

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