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Synthesis of New Chiral Benzimidazolylidene–Rh Complexes and Their Application in Asymmetric Addition Reactions of Organoboronic Acids to Aldehydes

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Academic Editor: Georgiy B. Shul'pin
Received: 29 July 2016; Accepted: 25 August 2016; Published: 3 September 2016

Abstract: A series of novel chiral *N*-heterocyclic carbene rhodium complexes (NHC–Rh) based on benzimidazole have been prepared, and all of the NHC–Rh complexes were fully characterized by NMR and mass spectrometry. These complexes could be used as catalysts for the asymmetric 1,2-addition of organoboronic acids to aldehydes, affording chiral diarylmethanols with high yields and moderate enantioselectivities.

Keywords: *N*-heterocycliccarbene; benzimidazolium; Rh-catalyzed; asymmetric 1,2-addition

1. Introduction

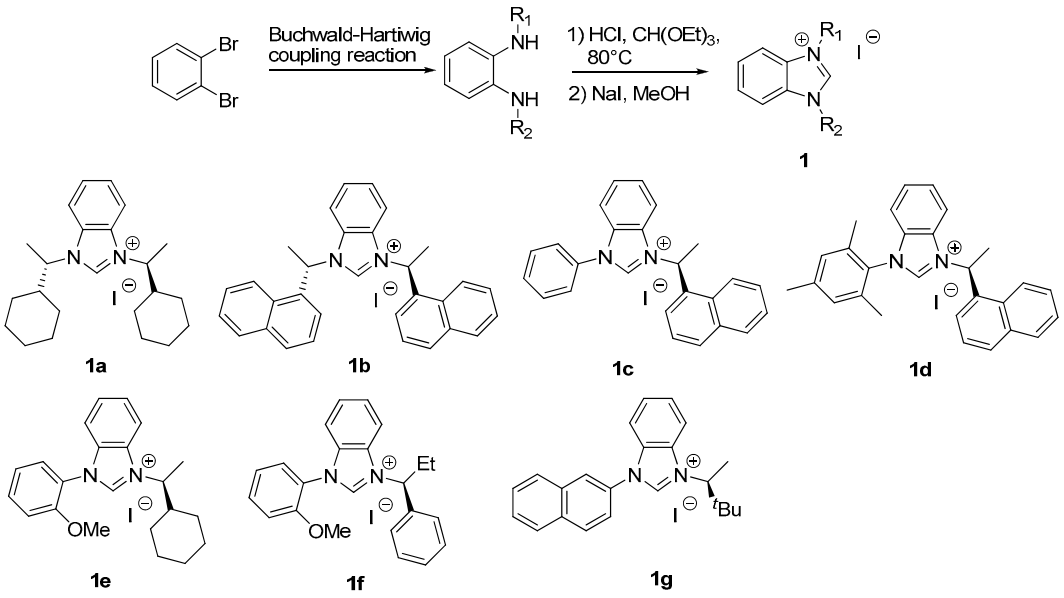
Since *N*-heterocycliccarbenes (NHCs) are excellent σ-donors, and their metal complexes show higher air and thermal stability than phosphane ligands. NHCs are now well established as efficient alternatives to phosphane ligands [1–10]. Much work has been devoted to the design and development of carbene compounds with new structures to tune their steric and electronic properties, and also to their application in organometallic catalysis. As excellent ligands for transition metals, NHCs have found multiple applications in some of the most important catalytic transformations in the chemical industry. As a logical extension of this development, chiral NHC ligands and their application in asymmetric catalysis are receiving increasing attention [11–16]. Despite considerable efforts devoted to this field, the design and synthesis of novel chiral NHCs to enhance their enantioselectivity is still a challenge.

Enantioenriched diarylmethanols are the structural core unit in a considerable number of bioactive compounds and pharmaceuticals [17–20]. The Rh-catalyzed enantioselective arylation of aromatic aldehydes with organoboronic acids has emerged as a direct and economical route for the synthesis of enantiomerically-enriched diarylmethanols [21]. In 1998, Miyaura and co-workers initially reported the enantioselective Rh-catalyzed addition of phenylboronic acid to naphthaldehyde by using the (*S*)-MeO–MOP ligand, giving naphthyphenylmethanol in 78% yield and 41% ee [22]. Since then, considerable efforts have been made in this type of reaction [23–30]. However, examples of using chiral *N*-heterocycliccarbenes in the ligand-catalyzed asymmetric arylation of aldehydes are rare [31–35]. Therefore, developing new chiral *N*-heterocycliccarbene ligands for the asymmetric 1,2-addition of

organoboronic acid to aldehydes is an important synthetic goal. The above-mentioned findings, and our interests in NHCs and C–C forming reactions triggered our efforts to develop new NHC ligands for application in homogeneous catalysis. After our recent report of the synthesis of several chiral benzimidazolium salts for the in situ Rh-catalyzed asymmetric arylation of aldehydes [36], we herein report the synthesis of a series of new NHC–Rh complexes based on benzimidazole and their application in the asymmetric 1,2-addition of arylboronic acids to aldehydes.

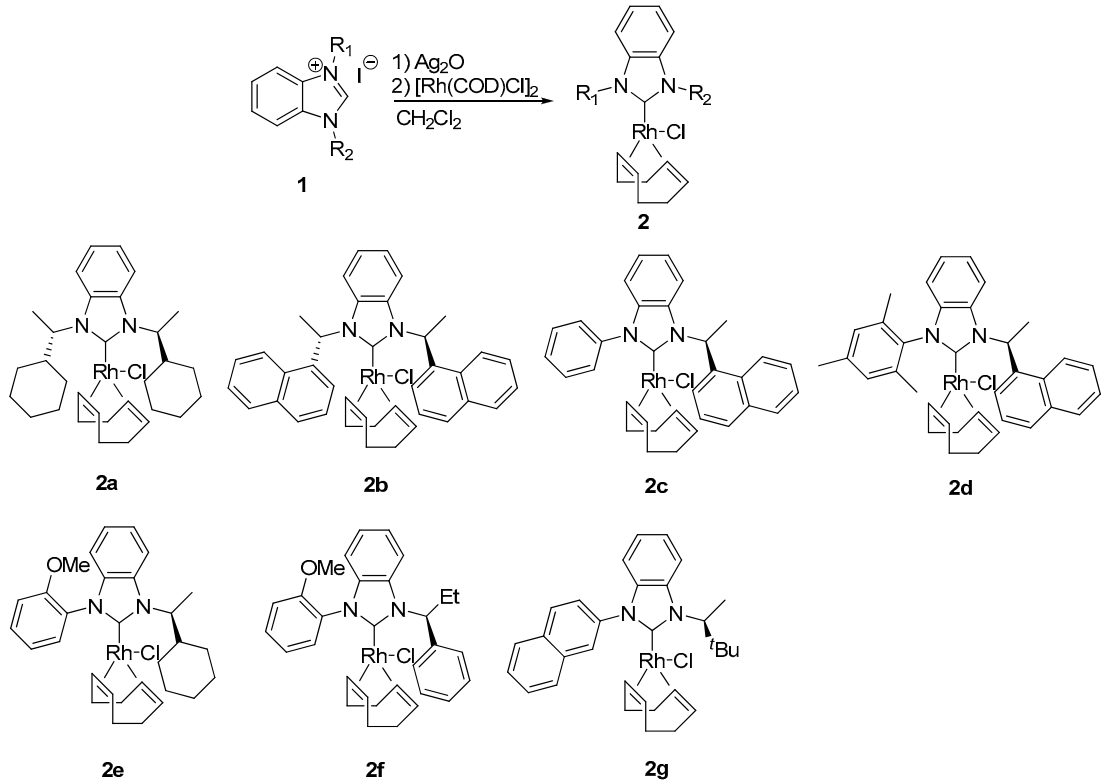
2. Results

The synthetic route to the new NHC–Rh complexes based on the benzimidazole skeleton is shown in Schemes 1 and 2. The NHC complexes were synthesized from enantiomerically-pure benzimidazolium salts (**1a**–**g**), which in turn can be prepared by following our previous articles [36,37]. Among the NHC precursors prepared, compounds **1c** and **1d** were new and are reported for the first time in this paper. In the next step, the mild transmetalation developed by Wang and Lin was adopted to prepare rhodium(I) complexes of **1a**–**g**. According to this strategy, the benzimidazolium salts **1** were treated with Ag_2O in anhydrous CH_2Cl_2 at room temperature in the darkness. Then direct addition of $[Rh(COD)Cl]_2$ to the freshly prepared solution of silver complexes yielded the corresponding chiral complexes **2a**–**g** upon workup, which could be purified by chromatography on silica gel (Scheme 2). The complexes were characterized by ^{1}H NMR, ^{13}C NMR, and high-resolution mass spectrometry (HRMS), and the absence of an N–C_{NHC}–N resonance in the ^{1}H NMR spectra confirmed the formation of the carbene complexes.



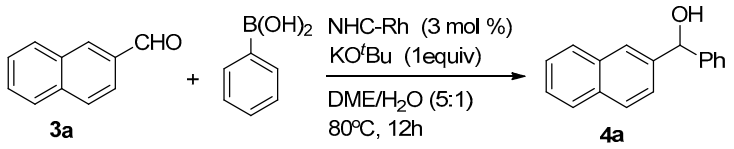
Scheme 1. Synthesis of benzimidazolium salts **1a**–**g**.

With the chiral NHC–Rh complexes in hand, we examined their application in the asymmetric addition of organoboronic acids to aldehydes. Firstly, all of the NHC–Rh complexes were tested in enantioselective phenylation of 2-naphthaldehyde (**3a**) with $PhB(OH)_2$. The reaction was performed with 3.0 mol % of NHC–Rh complex in DME/H_2O (5:1) at 80 °C for 12 h. As shown in Table 1, diarylmethanol **4a** was obtained in high yield with each of the NHC–Rh complexes, and compound **2g** gave the best result (18% ee).



Scheme 2. Synthesis of *N*-heterocyclic carbene–rhodium NHC–Rh complexes **2a**–**g**.

Table 1. Comparison of NHC–Rh complexes.

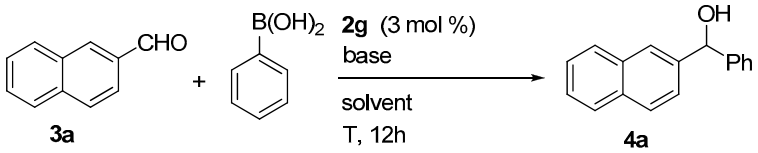


Entry [a]	Ligand	Yield (%) [b]	ee (%) [c]
1	2a	99	3
2	2b	99	1
3	2c	99	6
4	2d	98	17
5	2e	99	3
6	2f	98	3
7	2g	99	18
8	no catalyst	–	–

[a] Reaction condition: ligand (3 mol %), KO^{t}Bu (1 equiv.), arylboronic acids (2 equiv.), N_2, DME/H_2O (5:1), 80 °C, 12 h; [b] Isolated yields; [c] Determined by chiral HPLC (CHIRALCEL OD Column) analysis.

We then optimized the experimental conditions using **2g** as catalyst. By screening bases in DME/H_2O (5:1), we found that the addition of excess KF (6.0 equiv.) significantly improved the enantioselectivity as well as yield (Table 2, entry 6). Next, variation of the solvent indicated that the 5:1 mixture of EtOH/DME was the best choice of solvent (Table 2, entry 16). Further screening of reaction temperature showed that lower temperature afforded the product with similar enantioselectivities but inferior yields (Table 3, entries 20–22).

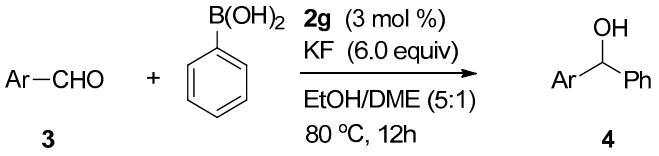
Table 2. Optimization of the reaction conditions.



Entry [a]	Base	Solvent	Temperature (°C)	Yield (%) [b]	ee (%) [c]
1	NaO^{t}Bu	DME/H_2O (5:1)	80	99	18
2	LiO^{t}Bu	DME/H_2O (5:1)	80	42	29
3	LiOH	DME/H_2O (5:1)	80	99	17
4	KF (1 equiv.)	DME/H_2O (5:1)	80	70	32
5	KF (3 equiv.)	DME/H_2O (3:1)	80	80	32
6	KF (6 equiv.)	DME/H_2O (5:1)	80	99	32
7	KF (6 equiv.)	DME/H_2O (10:1)	80	99	14
8	KF (6 equiv.)	DME/H_2O (3:1)	80	99	18
9	KF (6 equiv.)	Toluene/H_2O (5:1)	80	99	22
10	KF (6 equiv.)	MeOH/DME (5:1)	80	99	25
11	KF (6 equiv.)	*t*-BuOH/MeOH (5:1)	80	99	24
12	KF (6 equiv.)	MeOH	80	99	21
13	KF (6 equiv.)	*i*-PrOH	80	99	34
14	KF (6 equiv.)	*t*-BuOH/EtOH (5:1)	80	99	25
15	KF (6 equiv.)	DME	80	93	9
16	KF (6 equiv.)	EtOH/DME (5:1)	80	99	35
17	KF (6 equiv.)	EtOH	80	99	32
18	KF (6 equiv.)	Dioxane	80	94	17
19	KF (6 equiv.)	*i*-PrOH/DME (5:1)	80	99	34
20	KF (6 equiv.)	EtOH/DME (5:1)	50	–	–
21	KF (6 equiv.)	*i*-PrOH	50	43	33
22	KF (6 equiv.)	*i*-PrOH/DME (5:1)	50	47	36

[a] Reaction condition: **2g** (3 mol %), base (1 equiv.), arylboronic acids (2 equiv.), N_2, 80 °C, 12 h; [b] Isolated yields; [c] Determined by chiral HPLC (CHIRALCEL OD Column) analysis.

Table 3. Scope of methodology.



Entry [a]	Ar_1	Yield (%) [b]	ee (%) [c]
1	1-Naphthyl **3b**	97 **4b**	43
2	2-MeOPh **3c**	99 **4c**	37
3	4-MeOPh **3d**	85 **4d**	46
4	4-CF_3Ph **3e**	94 **4e**	40
5	3,4-DiMePh **3f**	99 **4f**	28
6	4-EtPh **3g**	99 **4g**	36
7	2-FPh **3h**	93 **4h**	38
8	3,5-DiFPh **3i**	88 **4i**	28
9	4-NO_2Ph **3j**	94 **4j**	28
10	2-thienyl **3k**	99 **4k**	18
11	2-furyl **3l**	98 **4l**	19

[a] Reaction condition: **2g** (3 mol %), KF (6.0 equiv.), arylboronic acids (2 equiv.), EtOH/DME (5:1), N_2, 80 °C, 12 h; [b] Isolated yields; [c] Determined by chiral HPLC (CHIRALCEL OD or AD Column) analysis.

Having optimized reaction conditions, we examined the reactions with various aldehydes, and the results are summarized in Table 3. The arylations with either electron-rich or electron-deficient benzaldehydes proceeded smoothly to afford the corresponding diarylmethanols in excellent yields and moderate enantioselectivities. The best enantioselectivity was obtained starting from *o*-anisaldehyde (46% ee, entry 3).

3. Materials and Methods

3.1. General

MS spectra were measured on a Finnigan LCQDECA XP instrument (ThermoFinnigan Co., California, CA, USA) and an Agilent Q-TOF 1290LC/6224 MS system (Aglient Technologies Inc., California, CA, USA); ^{1}H and ^{13}C NMR spectra were obtained on Bruker AVANCE III 500 MHz and 600 MHz spectrometers (Bruker Co., Faellanden, Switzerland) with TMS as the internal standard; silica gel GF_{254} and H (10–40 mm, Qingdao Marine Chemical Factory, Qingdao, China) were used for TLC and CC. Unless otherwise noted, all reactions were carried out under an atmosphere of argon or nitrogen.

3.2. Preparation of Benzimidazolium Salt **1a–g**

The NHC precursors **1a–g** were synthesized following our previous paper [36], and the ^{1}H NMR spectra of **1a–b** and **1e–f** were identical to those reported in the literature [36,37]. **1c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 11.18 (s, 1H), 8.24–7.08 (m, 14H), 2.53 (d, J = 6.9 Hz, 3H), 2.39 (s, 3H), 2.07 (s, 3H), 2.00 (s, 3H). **1d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 10.73 (s, 1H), 8.21–7.42 (m, 16H), 7.11 (q, J = 6.8 Hz, 1H), 2.56 (d, J = 6.8 Hz, 3H).

3.3. Preparation of NHC–Rh Complexes **2a–g**

To a solution of imidazolinium salt **1a** (364.0 mg, 1.00 mmol) in CH_2Cl_2 (25 mL) was added silver(I) oxide (115.9 mg, 0.50 mmol) in one portion. The suspension was stirred for 3 h in the darkness, during which the black color gradually diminished. The reaction mixture was filtered through a small pad of Celite, $[Rh(COD)Cl]_2$ (246.5 mg, 0.50 mmol) was added in one portion, and the reaction mixture was stirred for an additional 16 h. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel with CH_2Cl_2 as eluent. After evaporation of volatiles, the residue was purified by column chromatography (CH_2Cl_2) to give **2a** (515.0 mg, 88% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.52–7.43 (m, 2H), 7.19–7.08 (m, 2H), 5.86 (m, 1H), 5.73 (m, 1H), 5.18 (m, 1H), 5.04 (m, 1H), 3.66 (t, J = 7.2 Hz, 1H), 3.41 (d, J = 7.5 Hz, 1H), 2.58–1.79 (m, 15H), 1.71 (m, 6H), 1.52–0.86 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 134.17, 133.92, 121.77, 121.53, 112.10, 112.01, 98.81, 98.76, 98.66, 98.61, 77.28, 76.78, 68.79, 68.67, 67.40, 67.28, 63.73, 62.82, 42.57, 42.35, 33.29, 32.35, 32.07, 31.93, 31.34, 30.68, 30.37, 29.70, 29.36, 28.23, 26.53, 26.42, 26.40, 26.37, 26.05, 25.94, 22.70, 19.06, 18.43, 14.12; HR-ESIMS: m/z 549.2792 $[M–Cl]^+$ (calcd. for $C_{31}H_{46}N_2Rh$, 549.2716).

Analogous compounds **2b–g** were prepared according to the similar procedure for **2a**. HR-ESIMS, ^{1}H and ^{13}C NMR data see Supplementary Materials. **2b**: 97% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.08 (q, J = 7.3 Hz, 1H), 8.57 (m, 2H), 8.03–7.51 (m, 9H), 7.36 (m, 5H), 7.18 (m, 2H), 7.11–7.00 (m, 1H), 5.16 (m, 1H), 5.03 (m, 1H), 3.38 (s, 1H), 3.02 (t, J = 7.2 Hz, 1H), 2.67 (d, J = 7.2 Hz, 3H), 2.35 (m, 1H), 2.25 (d, J = 7.3 Hz, 3H), 2.15–1.98 (m, 1H), 1.96–1.77 (m, 2H), 1.55 (m, 1H), 1.51–1.41 (m, 1H), 1.20 (d, J = 10.3 Hz, 1H), 0.95–0.88 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.83, 136.20, 135.84, 134.96, 134.13, 134.06, 130.80, 130.03, 129.10, 129.03, 128.77, 128.01, 127.07, 126.59, 126.12, 126.03, 125.21, 125.14, 124.19, 123.90, 123.73, 122.35, 122.32, 122.24, 113.93, 112.26, 99.20, 97.82, 77.28, 76.78, 70.74, 70.62, 67.45, 67.33, 61.11, 56.76, 32.68, 31.94, 31.75, 29.71, 29.35, 27.39, 22.70, 22.33, 20.83, 14.13; HR-ESIMS: m/z 529.1152 $[M–Cl–COD]^+$ (calcd. for $C_{31}H_{26}N_2Rh$, 529.1151). **2c**: 91% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.76–8.56 (m, 2H), 8.21 (d, J = 5.5 Hz, 2H), 7.96 (d, J = 8.1 Hz, 1H), 7.78 (m, 3H), 7.61 (m, 4H), 7.44 (d, J = 8.0 Hz, 1H), 7.39–7.24 (m, 4H), 5.01 (s, 2H), 2.60–2.52 (m, 1H), 2.48 (m, 1H), 2.31 (d, J = 7.4 Hz, 3H), 1.91–1.80 (m, 1H), 1.70–1.61 (m, 1H), 1.55–1.40 (m, 2H), 1.31 (m, 2H), 1.09–0.99 (m, 1H), 0.65 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 139.48, 138.06, 136.15, 134.82, 133.99, 130.09, 129.10, 128.97, 128.52, 127.98, 127.29, 126.78, 126.14, 125.25, 123.87, 123.01, 122.74, 122.15, 113.24, 111.01, 99.67, 99.62, 98.81, 98.76, 77.28, 76.77, 69.64, 69.53, 68.89, 68.77, 59.83, 53.42, 31.98, 31.77, 29.70, 28.07, 27.96, 20.95; HR-ESIMS: m/z 559.2367 $[M–Cl]^+$ (calcd. for $C_{33}H_{32}N_2Rh$, 559.1621). **2d**: 89% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.91 (q, J = 7.3 Hz, 1H), 8.65 (d, J = 8.6 Hz, 1H), 7.96 (d, J = 8.1 Hz, 1H), 7.85–7.69

(m, 3H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.33–7.27 (m, 2H), 7.24–7.11 (m, 3H), 7.01–6.86 (m, 2H), 4.98 (m, 1H), 4.89–4.78 (m, 1H), 3.07–2.93 (m, 1H), 2.72 (t, *J* = 7.2 Hz, 1H), 2.51 (s, 3H), 2.43 (s, 3H), 2.37 (d, *J* = 7.3 Hz, 3H), 2.02–1.88 (m, 1H), 1.65 (m, 4H), 1.54–1.28 (m, 4H), 1.10 (s, 1H), 0.67 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 140.28, 139.09, 138.04, 136.73, 135.17, 134.61, 134.05, 132.92, 130.17, 130.04, 128.93, 128.37, 127.78, 126.65, 126.11, 125.33, 124.15, 122.82, 122.70, 121.60, 113.30, 110.80, 98.82, 98.77, 98.48, 98.42, 77.29, 76.78, 69.57, 69.45, 67.98, 67.86, 59.99, 32.79, 31.94, 31.32, 29.70, 29.67, 29.37, 28.96, 27.19, 22.70, 21.18, 21.06, 19.68, 17.72, 14.12; HR-ESIMS: *m*/*z* 601.4336 $[M–Cl]^+$ (calcd. for $C_{36}H_{38}N_2Rh$, 601.2090). **2e**: 83% yield; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.45 (m, 1H), 7.60–7.47 (m, 2H), 7.29 (m, 1H), 7.22–7.08 (m, 3H), 6.95 (d, *J* = 7.9 Hz, 1H), 5.74–5.64 (m, 1H), 5.03–4.88 (m, 2H), 3.78 (d, *J* = 6.1 Hz, 3H), 3.56 (s, 1H), 2.89 (s, 1H), 2.44–2.16 (m, 4H), 1.98–1.61 (m, 11H), 1.47–1.34 (m, 4H), 1.19–1.05 (m, 2H), 0.89 (t, *J* = 6.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 154.29, 136.69, 133.17, 132.68, 130.21, 126.85, 122.06, 121.99, 121.09, 111.75, 111.69, 111.55, 110.98, 110.91, 98.84, 98.79, 98.09, 98.04, 77.28, 76.77, 68.84, 68.72, 67.61, 67.49, 64.12, 63.25, 55.59, 55.42, 42.65, 42.18, 33.21, 32.88, 31.93, 31.66, 31.16, 30.96, 29.70, 29.66, 29.37, 28.60, 28.51, 28.35, 26.58, 26.48, 26.39, 26.25, 25.92, 22.70, 18.94, 18.03, 14.12; HR-ESIMS: *m*/*z* 545.2188 $[M–Cl]^+$ (calcd. for $C_{30}H_{38}N_2ORh$, 545.2039). Complex **2f** is a known compound, and the NMR and high-resolution mass spectrometry of this compound were identical to those reported in the literature [36]. **2g**: 90% yield; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.04 (m, 4H), 7.63 (m, 4H), 7.40–7.30 (m, 1H), 7.25–7.07 (m, 3H), 6.16 (m, 1H), 5.05 (m, 2H), 3.75–3.55 (m, 1H), 2.54–2.15 (m, 3H), 1.92 (s, 1H), 1.81 (d, *J* = 7.2 Hz, 3H), 1.74–1.67 (m, 1H), 1.51–1.41 (m, 2H), 1.31 (s, 9H), 1.21–1.05 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 135.28, 133.64, 132.76, 128.65, 128.46, 127.81, 126.98, 126.86, 122.47, 122.39, 122.35, 122.24, 113.83, 113.35, 110.93, 110.79, 99.59, 98.86, 97.91, 77.28, 76.77, 70.21, 67.97, 67.36, 67.18, 66.97, 66.86, 36.00, 35.64, 32.68, 32.06, 31.83, 31.27, 29.70, 29.49, 29.39, 29.32, 29.06, 27.72, 27.22, 15.73, 15.14, 14.12; HR-ESIMS: *m*/*z* 539.2090 $[M–Cl]^+$ (calcd. for $C_{31}H_{36}N_2Rh$, 539.1934).

3.4. Representative Procedure for the Rh-Catalyzed Asymmetric Arylation of Aldehyde

The NHC–Rh complex **2g** (2.2 mg, 0.00375 mmol) was weighted into 1 mL of DME/H_2O (5:1) under N_2. After stirring at room temperature for 5 min, KF (43.6 mg, 0.75 mmol), phenylboronic acid (30.5 mg, 0.25 mmol), and 2-naphthaldehyde (19.5 mg, 0.125 mmol) were added successively. The resulting mixture was stirred at 80 °C for 12 h. After usual work-up, purification by silica gel column (petroleum/ethyl acetate = 9/1) afforded **4a** as a colorless oil (99% yield, 35% ee). The spectral data were comparable to those reported [38]. The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/Pr^{i}OH = 90/10, flow rate = 0.8 mL/min, t_r (minor) = 19.03 min, t_r (major) = 22.46 min).

Analogous compounds **4b**−**l** were prepared according to the similar procedure for **4a**. **4b**: 97% yield, 43% ee. The spectral data were comparable to those reported [24]. The ee was determined by HPLC analysis with Daicel Chiralcel AD-H (hexane/Pr^{i}OH = 90/10, flow rate = 0.8 mL/min, t_r (minor) = 15.0 min, t_r (major) = 16.5 min). **4c**: 99% yield, 37% ee. The spectral data were comparable to those reported [36]. The ee was determined by HPLC analysis with Daicel Chiralcel AD-H (hexane/Pr^{i}OH = 90/10, flow rate = 0.8 mL/min, t_r (minor) = 11.9 min, t_r (major) = 12.8 min). **4d**: 85% yield, 46% ee. The spectral data were comparable to those reported [24]. The ee was determined by HPLC analysis with Daicel Chiralcel AD-H (hexane/Pr^{i}OH = 90/10, flow rate = 0.8 mL/min, t_r (major) = 14.0 min, t_r (minor) = 15.1 min). **4e**: 94% yield, 40% ee. The spectral data were comparable to those reported [24]. The ee was determined by HPLC analysis with Daicel Chiralcel AD-H (hexane/Pr^{i}OH = 90/10, flow rate = 0.8 mL/min, t_r (major) = 7.5 min, t_r (minor) = 8.8 min). **4f**: 99% yield, 28% ee. The spectral data were comparable to those reported [36]. The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/Pr^{i}OH = 90/10, flow rate = 0.8 mL/min, t_r (minor) = 10.6 min, t_r (major) = 12.4 min). **4g**: 99% yield, 36% ee. The spectral data were comparable to those reported [36]. The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/Pr^{i}OH = 90/10, flow rate = 0.8 mL/min, t_r (minor) = 9.8 min, t_r (major) = 10.2 min). **4h**: 93% yield, 38% ee. The spectral data were comparable to those reported [36]. The ee was determined

by HPLC analysis with Daicel Chiralcel OD-H (hexane/Pr^{i}OH = 90/10, flow rate = 0.8 mL/min, t_r (major) = 8.6 min, t_r (minor) = 9.2 min). **4i**: 88% yield, 28% ee. The spectral data were comparable to those reported [36]. The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/Pr^{i}OH = 90/10, flow rate = 0.8 mL/min, t_r (major) = 11.2 min, t_r (minor) = 13.2 min). **4j**: 94% yield, 28% ee. The spectral data were comparable to those reported [36]. The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/Pr^{i}OH = 90/10, flow rate = 0.8 mL/min, t_r (major) = 21.5 min, t_r (minor) = 23.8 min). **4k**: 99% yield, 18% ee. The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/Pr^{i}OH = 90/10, flow rate = 0.8 mL/min, t_r (minor) = 11.8 min, t_r (major) = 12.6 min). **4l**: 98% yield, 19% ee. The ee was determined by HPLC analysis with Daicel Chiralcel OD-H (hexane/Pr^{i}OH = 85/15, flow rate = 0.8 mL/min, t_r (minor) = 8.6 min, t_r (major) = 9.9 min).

4. Conclusions

In conclusion, seven NHC–Rh complexes (**2a**–**f**) have been prepared. Their applicability in the asymmetric arylation of aromatic aldehydes has been demonstrated, and the corresponding diarylmethanols were obtained with high yields and moderate enantiomeric excesses (up to 46%). Further work is in progress to utilize these complexes in asymmetric 1,2-addition reactions of arylboronic acids with ketones, as well as their applications in fields of nanoscience [39,40].

Supplementary Materials: The following are available online at www.mdpi.com/2073-4344/6/9/132/s1, Figure S1: ^{1}H and ^{13}C NMR Spectra of compounds **2a**–**g**, Figure S2: HR-MS Spectra for Compounds **2a**–**g**, Figure S3: HPLC data of **4a**–**l**.

Acknowledgments: We are grateful to the National Natural Science Foundation of China (81302668) and Hangzhou Science and Technology Information Institute of China (20150633B45).

Author Contributions: Jie Li and Jianyou Shi conceived and designed the experiments; Weiping He and Bihui Zhou performed the experiments and analyzed the data; Jie Li and Jianyou Shi wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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