Synthesis of novel N-heterocyclic carbene-Rh complexes derived from L-proline and their catalysis in the addition of arylboronic acids to aldehydes

Weifeng Zhang, Yuancheng Qin, Sujuan Zhang, and Meiming Luo*

Key Laboratory of Green Chemistry & Technology of Ministry of Education at Sichuan University, College of Chemistry, Sichuan University, Chengdu 610064, P. R. China
E-mail: luom2@yahoo.com.cn

Abstract
Novel chiral imidazolium salts and a stable N-heterocyclic carbene-Rh complex derived from L-proline have been synthesized. The N-heterocyclic carbene-Rh complexes either generated *in situ* or pre-synthesized are active catalysts for the addition reaction of arylboronic acids to aldehydes affording the corresponding secondary alcohols in excellent yields.

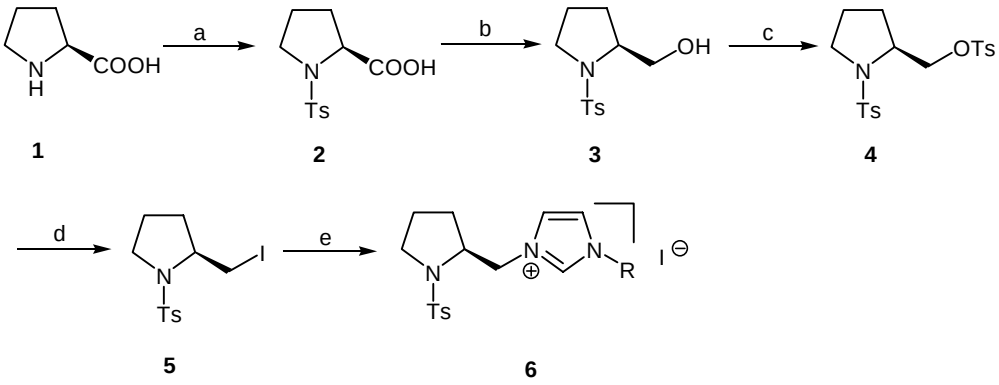
Keywords: N-Heterocyclic carbene, L-proline; chiral, arylboronic acid, aldehyde

Introduction

In recent years, the chemistry of N-heterocyclic carbenes (NHCs) and their transition-metal complexes have attracted much attention because these carbenes are readily generated from the corresponding imidazolium salts[1] and act as efficient ligands in a great variety of catalytic processes including alkene metathesis[2], hydrogenation[3], and C-C[4] and C-N[5] bond construction. On the other hand, although a few examples of chiral NHC-metal complexes have proven exhibiting good or excellent enantioselectivities[6-10], chiral NHC-metal complex as catalyst has not been extensively investigated to date[11]. For instance, as good chiral sources, proline and their derivatives have been widely applied in asymmetric catalysis[12], however, to the best of our knowledge, neither chiral NHC nor its metal complex based on proline has been documented in literature. We report herein the synthesis of novel chiral imidazolium salts (precursor of NHC) and a chiral NHC-Rh complex derived from L-proline, and an investigation of their applications in the catalytic addition of arylboronic acids to aldehydes.

Results and Discussion

The synthesis of the desired imidazolium compounds started from enantiopure L-proline **1**, which was treated with 4-toluenesulfonyl chloride and Na_2CO_3 in water giving **2** in 94% yield (Scheme 1). Reduction of **2** with $NaBH_4$ and $BF_3{\cdot}Et_2O$ at room temperature followed by quenching the reaction with methanol gave (2*S*)-2-(hydroxymethyl)-1-(4-tolylsulfonyl)pyrrolidine **3** in 81% yield. The resulting alcohol reacted with pyridine/TsCl affording the corresponding ester **4** in 83% yield, which then reacted with KI in acetone giving iodide **5** in 74% yield. After heating the mixture of iodide **5** and 1-substituted imidazole in MeCN, the desired imidazolium salts **6** were obtained in yields ranging from 50 to 62%. Their characteristic ^{1}H NMR chemical shifts at = 9.9-10.4 ppm are consistent with the proposed structure N-C*H*-N in imidazolium ring.[6]

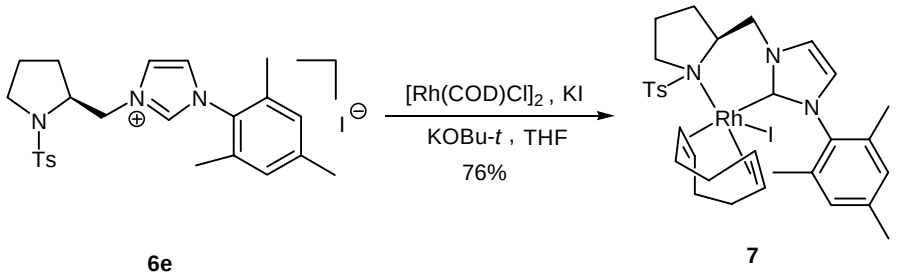


1 **2** **3** **4** **5** **6**

6a: R = Methyl, 62%; **6b**: R = Ph, 57%; **6c**: R = *p*-Methyl-Ph, 53%;
6d: R = *o*-Methyl-Ph, 51%; **6e**: R = 2, 4, 6-trimethyl-Ph, 50%.

Scheme 1. Synthesis of chiral imidazolium salts **6.** (a) TsCl, Na_2CO_3, H_2O, rt, 48h, 94%. (b) $NaBH_4$/ $BF_3{\cdot}Et_2O$, THF, rt, 18 h, 81%. (c) TsCl, pyridine, 0 ^oC, 20 h, 83%. (d) KI, acetone, reflux, 3 d, 74%. (e) 1-substituted imidazoles, MeCN, 80 ^oC, 2 d.

Next, we turned to the preparation of chiral NHC-Rh complex. $[Rh(COD)Cl]_2$ was treated with KOBu-*t* in THF, and subsequently reacted with imidazolium salt **6e** and KI giving the NHC-Rh complex **7** in 76% yield (Scheme 2). It is a yellow, air-stable solid. The ^{1}H NMR spectra confirmed the structure that the low field absorption at δ 9.98 vanished, which is found in imidazolium salt **6e**. The more direct evidence of the metalation of the ligand comes from ^{13}C NMR, which shows the carbene signal at 181.7 ppm and a coupling constant that is diagnostic of direct Rh binding ($^1J_{Rh\text{-}C}$ = 49.4 Hz). HRMS also confirmed the proposed structure. **6e** was selected for the synthesis of NHC-Rh complex because it has a bulky mesityl group on N-atom which had previously been shown to be superior over other substituents in catalysis[9].



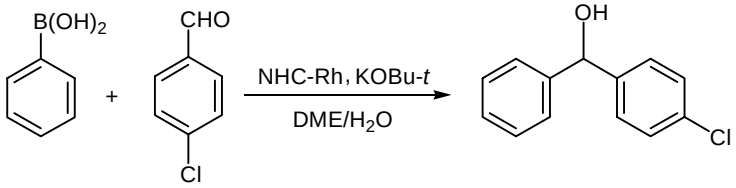
Scheme 2. Synthesis of NHC-Rh complex **7**.

The addition of organometallic reagents to aldehydes has been one of the general methods for the synthesis of secondary alcohols. Of these reagents, organolithium and organomagnesium compounds are most frequently used for this purpose, but tolerate only a few electrophilic groups on themselves.[13] Examples of using other functionalized organometallic species such as organocopper, chromium, tin, especially organozinc[14], have been described. However, those organometallic regeants are usually toxic and sensitive to moisture. The progress that has been achieved by recent publications describing the addition of arylboronic acid derivatives to aldehydes in the presence of catalytic amounts of Rh (I) and phosphine[15], nitrogen[16], especially NHC ligands[17] deserve particular mention. These methods combine a high efficiency with a reasonable tolerance towards polar substituents in the substrates and benefit from the stability and readily accessibility of the nontoxic boron derivatives. Nevertheless, reports on the asymmetric version of this protocol are scare. So far, only two examples have been documented in literature[15, 16]. One is the asymmetric addition of phenylboronic acid to 1-naphthaldehyde catalyzed by a chiral phosphine-Rh complex giving rise to (*R*)-(+)-(1-naphthyl)(phenyl)methanol in 41% *ee*. Another is the rhodium-catalyzed addition of arylboronic acids to aldehydes in the presence of enantiopure amine ligands, but leading to little enantioselectivity (<10% *ee*). To our knowledge, chiral NHC ligands have not been applied in the catalytic addition of arylboronic acids to aldehydes.

A combination of the ligand precursor **6e** with Rh was then tested as catalyst for the catalytic addition of phenylboronic acid to *p*-chlorobenzaldehyde in dimethoxyethane (DME)-H_2O (3:1) solution using KOBu-*t* as a base. The results are shown in Table 1. In the absence of NHC ligand, no product formation was observed (Table 1, entries 1, 3). The reaction was sensitive to changes in rhodium source. With 1 mol% of **6e** and 0.5 mol% rhodium salt as the catalyst, $[Rh(COD)Cl]_2$ gave the alcohol in 95% yield (Table 1, entry 5), while $RhCl_3 \cdot 3H_2O$ led to the alcohol only in 21% yield (Table 1, entry 2). Temperature has significant effect on yield. At room temperature, a catalyst system of **6e** (1 mol%) and $[Rh(COD)Cl]_2$ (0.5 mol %) gave only 23% yield (Table 1, entry 7). However, the yield increased to 95% when the reaction was performed at 80 ^oC (Table 1, entry 5). Reaction temperature at either 60 ^oC or 90 ^oC resulted in lower yield (Table 1, entries 8, 9). The catalyst loading has also important effect on yield. The catalyst loading of 1 mol% of **6e** and 0.5 mol% of $[Rh(COD)Cl]_2$ gave excellent result, whereas the other catalyst loading turned out to be less efficient (Table 1, entries 4-6).

The activity evaluation of ligand precursors **6a-d** was also carried out under comparable conditions. As can be seen from Table 1, all of the imidazolium salts in combination with $[Rh(COD)Cl]_2$ showed good catalytic activity in the addition reaction of phenylboronic acid to 4-chlorobenzaldehyde. The imidazolium salt **6e** bearing bulky substituent on its N-atom exhibited the best results (Table 1, entries 4, 10-13). Apparently, steric factor played a major role as indicated by the significant variation in yields when the R group changed from methyl to mesityl. The pre-synthesized NHC-Rh complex **7** also demonstrated excellent activity (Table 1, entries 14, 15), but did not show better result than the catalyst generated *in situ* from **6e** and $[Rh(COD)Cl]_2$. Around 20% ee value which is comparable with that reported in literature[15, 16] was obtained in the addition of phenylboronic acid to 4-chlorobenzaldehyde, suggesting further structural modifications will be necessary to increase enantioselectivity.

Table 1. Rhodium-catalyzed addition of phenyl boronic acid **8** to 4-chlorobenzaldehyde **9**[a]



8 **9** **10**

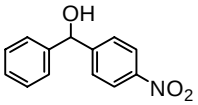
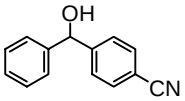
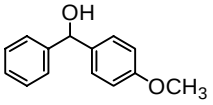
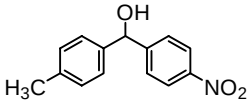
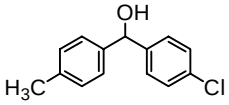
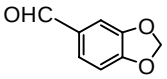
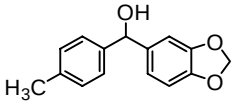
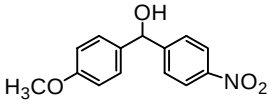
Entry	Metal salt (mol%)	Imidazolium salt (mol%)	T (^oC)	Yield (%)[b]	% *e e*
1	$RhCl_3 3H_2O$ (1.0)		80		nd[c]
2	$RhCl_3 3H_2O$ (1.0)	**6e**/1.0	80	21	nd
3	$[Rh(COD)Cl]_2$ (0.5)		80		nd
4	$[Rh(COD)Cl]_2$ (0.25)	**6e**/0.5	80	76	19[d]
5	$[Rh(COD)Cl]_2$ (0.5)	**6e**/1.0	80	95	17
6	$[Rh(COD)Cl]_2$ (1.0)	**6e**/2.0	80	75	19
7	$[Rh(COD)Cl]_2$ (0.5)	**6e**/1.0	rt	23	22[e]
8	$[Rh(COD)Cl]_2$ (0.5)	**6e**/1.0	60	70	0
9	$[Rh(COD)Cl]_2$ (0.5)	**6e**/1.0	90	87	nd
10	$[Rh(COD)Cl]_2$ (0.5)	**6a**/1.0	80	68	nd
11	$[Rh(COD)Cl]_2$ (0.5)	**6b**/1.0	80	82	nd
12	$[Rh(COD)Cl]_2$ (0.5)	**6c**/1.0	80	75	nd
13	$[Rh(COD)Cl]_2$ (0.5)	**6d**/1.0	80	86	nd
14		**7**/1.0	80	93	17[f]
15		**7**/1.0	60	96	21[f, h]

[a] Reaction conditions: phenylboronic acid (2 mmol), aldehyde (1mmol), KOBu-*t* (1 equivent) in aqueous DME (DME 3 ml/H_2O 1ml) under Ar, 24 h. [b] Isolated yield was based on aldehyde. [c] nd: Not determined [d] Absolute configration (*R*) was assigned by comparison with literature value[18]. [e] 72 h. [f] without addition of KOBu-*t*. [h] 60 h.

Table 2 summarizes the addition of other arylboronic acids to various aldehydes catalyzed by $[Rh(COD)Cl]_2$/**6e**. The results reveal the wide scope of this method that is compatible with nitro, cyano, methoxy, chloro in aldehydes. All of the aldehydes investigated here reacted with arylboronic acids cleanly in excellent yields.

In summary, we have synthesized a series of novel chiral imidazolium salts derived from L-proline, which reacted with $[Rh(COD)Cl]_2$ to form chiral NHC-Rh complexes. These NHC-Rh complexes are highly active catalysts for the addition of arylboronic acids to aldehydes.

Table 2. Rhodium-catalyzed addition of arylboronic acids to aldehydes[a]

Entry	Boronic acid	Aldehyde	Product	Yield[b] (%)
1	$C_6H_5B(OH)_2$	*p*-NO_2-C_6H_5CHO		98[c]
2		*p*-CN-C_6H_5CHO		96[c]
3		*p*-OCH_3-C_6H_5CHO		95
4	*p*-CH_3-$C_6H_5B(OH)_2$	*p*-NO_2-C_6H_5CHO		97[d]
5		*p*-Cl-C_6H_5CHO		99
6				92
7	*p*-CH_3O-$C_6H_5B(OH)_2$	*p*-NO_2-C_6H_5CHO		99[d]

[a] Reaction conditions: arylboronic acid (2 mmol), aldehyde (1mmol), $[Rh(COD)Cl]_2$ (0.5 mol %), imidazolium salt **6e** (1.0 mol %) and KOBu-*t* (1 equivent) in aqueous DME (DME 3 ml/H_2O 1 ml) under Ar, 24 h, 80 ^oC. [b] Isolated yield was based on aldehyde. [c] 18 h. [d] 12 h.

Experimental Section

General Procedures. Melting points were determined with XRC-1 melting point apparatus and were uncorrected. ^1H NMR spectra were recorded on Brucker 300 MHz or Varian INOVA 400 MHz spectrometer. ^{13}C NMR spectra were recorded on Bruker AC-E 200 MHz spectrometer. Mass spectra were obtained by using Bruker Daltonics Data Analysis 3.2. The DME and THF

were dried by Na, CH_2Cl_2 by CaH_2 under inert gas Ar prior to use, respectively. All other reagents were used as they were received without any purification unless noted otherwise.

1-(4-Tolylsulfonyl)-L-proline (2). To a solution of L-proline (**1**) (2.88 g, 25 mmol) in H_2O (25 mL) were added Na_2CO_3 (5.57 g, 52.5 mmol) at 0 ^oC and 4-toluenesulfonyl chloride (5.72 g, 30 mmol) in three portions over a period of 1 h. The slurry were then warmed to room temperature and allowed to stir for 48 h. The reaction mixture was acidified with concentrated aqueous HCl solution to pH 2, and the product was isolated via filtration. The filter cake was washed with pH 2 buffer and dried in a vacuum oven at 60 ^oC for 12 h to give **2** (6.3 g, 94%) as a colorless solid; mp 42-44 ^oC (literature[19], 41-43 ^oC).

(2*S*)-2-(Hydroxymethyl)-1-(4-tolylsulfonyl)pyrrolidine (3). Sodium borohydride (3.6 g, 92.6 mmol) was added to dry THF (80 ml), and the mixture was cooled 10 ^oC before borontrifluoride etherate (15.6 mL, 121mmol) was added dropwise over a period of 1h. Then 1-(4-tolylsulfonyl)-L-proline (**2**) (12.5 g, 46.3 mmol) in THF (60 mL) was added carefully, and the mixture was allowed to stir for 18 h. The reaction was quenched with methanol. 10% Aqueous HCl solution (50 ml) was added, and the mixture was gently heated to 60 ^oC for 1 h. The reaction mixture was adjusted to neutral with 50% aqueous NaOH solution, and the volatiles were evaporated under reduced pressure. The product was then isolated via filtration. The filter cake was washed with water, dried *in vacuo* at 60 ^oC for 12 h yielding **3** (9.48 g, 81%) as a white solid; mp 86-88 ^oC, $[\alpha]_D^{20}$ -62.5 ^{o} (c,1.0, $CHCl_3$) (literature[20], 87-88 ^oC, $[\alpha]_D^{20}$ -62.7 ^{o}).

(2*S*)-1-(4-Tolylsulfonyl)-2-[(4-tolylsulfonyl)oxy]pyrrolidine (4). To an ice-cold solution of (2*S*)-2-(hydroxymethyl)-1-(4-tolylsulfonyl)pyrroline (**3**) (5.1 g, 20 mmol) in pyridine (30 mL) was added 4-toluenesulfonyl chloride (5.6 g) in three portions in 1 h, and the reaction was kept at 0 ^oC for 12 h. Additional 4-toluenesulfonyl chloride (2.0 g) was then added, and the mixture was allowed to stir at 0 ^oC for additional 8 h. The mixture was then cooled with ice bath, and 10% aqueous HCl solution (180 mL) was carefully added. A white precipitate formed which was isolated via filtration and then taken in ethanol (60 mL) and heated to reflux for 0.5 h. The mixture was then cooled, and the solid were filtered and dried *in vacuo* to give **4** (6.8 g, 83%); mp 92-94 ^oC, $[\alpha]_D^{20}$-122.8 ^{o}(c, 1.4, benzene) (literature[21], mp 94-95 ^oC, $[\alpha]_D^{20}$-123.2 ^{o}).

(2*S*)-2-(Iodomethyl)-1-(4-tolylsulfonyl)pyrrolidine (5). KI (3.3 g, 20 mmol) was added to a solution of (2*S*)-1-(4-tolylsulfonyl)-2-[(4-tolylsulfonyl)oxy]pyrrolidine (**4**) (4.09 g, 10 mmol) in acetone (50 mL). Then the mixture was heated to reflux for 6 days. After cooling to room temperature, the solvent was removed under reduced pressure. The residual solids were then washed with toluene (30 mL) for 5 times. After evaporation of toluene under reduced pressure, the residue was then purified by column chromatography on silica gel to afford **5** (2.70 g, 74%) as a colorless prism; mp 103-105 ^oC, $[\alpha]_D^{20}$-148.0 ^{o}(c, 2.0, benzene) (literature[22], mp104-106, $[\alpha]_D^{20}$-148.0 ^{o}).

General procedure for preparation of imidazolium iodide (6)

The iodide (**5**) (2 mmol) and 1-substituted imidazole (2 mmol) were added to a Schlenk tube and the vessel was evacuated and flushed with Ar three times. MeCN (10 mL) was syringed in and the mixture was heated to 80 ^{o}C for 2 days. The solvent was then removed under vacuum. The residual solid was washed with Et_2O and recrystallized from CH_2Cl_2/Et_2O. The product (**6)** was obtained in yields ranging from 50% to 62%.

1-{(*2S*)-2-[1-(4-Tolylsulfonyl)pyrrolidinomethyl]}-3-methylimidazolium iodide (6a). The above procedure was followed using (**5**), 1-methylimidazole and MeCN. A white crystal was obtained in 62% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.00 (s, 1H), 7.76 (br, s, 1H), 7.69-7.71 (d, *J* = 8.0 Hz, 2H), 7.42 (s, 1H), 7.34-7.36 (d, *J* = 8.0 Hz, 2H), 4.73-4.77 (m, 1H), 4.51-4.57(m, 1H), 4.10-4.11 (m, 1H), 4.06 (s, 3H), 3.45-3.51 (m, 1H), 3.09-3.15 (m, 1H), 2.43 (s, 3H), 1.72-1.80 (m, 3H), 1.44-1.45 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ =144.4, 137.4, 132.8, 130.1, 127.7, 123.9, 122.7, 59.8, 53.0, 49.5, 36.9, 29.0, 23.9, 21.5. HRMS (ESI): *m/z* calcd for $C_{16}H_{22}N_3O_2S$ $[M-I]^+$: 320.1427. Found 320.1436.

1-{(*2S*)-2-[1-(4-Tolylsulfonyl)pyrrolidinomethyl]}-3-phenylimidazolium iodide (6b). The above procedure was followed using **5**, 1-phenylimidazole and MeCN. A yellow crystal was obtained in 57% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.36 (s, 1H), 8.02 (s, 1H), 7.63-7.70 (m, 4H), 7.63 (s, 1H), 7.53-7.55 (m, 3H), 7.29-7.33 (s, 2H), 4.90-4.93 (m, 1H), 4.67(m, 1H), 4.31 (s, 1H) 3.61 (m, 1H), 3.12-3.14 (m, 1H), 2.41 (s, 3H), 1.83-1.99 (m, 1H), 1.72-1.83 (m, 1H), 1.60-1.72 (m, 1H), 1.43-1.55(m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ =144.0, 135.3, 134.3, 132.8, 130.3, 129.8, 127.5, 124.7, 122.1, 120.3, 60.0, 52,9, 49.3, 28.6, 23.8, 21.3. HRMS (ESI): *m/z* calcd for $C_{21}H_{24}N_3O_2S$ $[M-I]^+$: 382.1584. Found 382.1587.

1-{(*2S*)-2-[1-(4-Tolylsulfonyl)pyrrolidinomethyl]}-3-(4-methylphenyl)imidazolium iodide (6c). The above procedure was followed using **5**, 1-(4-methylphenyl)imidazole and MeCN. A light yellow crystal was obtained in 53% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.31 (s, 1H), 8.02 (s, 1H), 7.68-7.70 (d, *J* = 8.0 Hz, 2H), 7.58 (m, 1H), 7.55-7.57 (d, *J* = 8.0 Hz, 2H), 7.29-7.33 (m, 4H), 4.89-4.94 (m, 1H), 4.65-4.71 (m, 1H), 4.29-4.33 (m, 1H), 3.58-3.64 (m, 1H), 3.09-3.16(m, 1H), 2.41 (s, 3H), 2.39 (s, 3H), 1.86-1.96 (m, 1H), 1.72-1.84 (m, 1H), 1.63-1.72 (m, 1H), 1.47-1.52 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.8, 140.2, 134.9, 132.8, 131.8, 130.6, 129.7, 127.3, 124.4, 121.7, 120.2, 59.9, 52.7, 49.2, 28.4, 23.7, 21.2, 20.8. HRMS (ESI): *m/z* calcd for $C_{22}H_{26}IN_3O_2S$ $[M-I]^+$: 396.1740. Found 396.1759.

1-{(*2S*)-2-[1-(4-Tolylsulfonyl)pyrrolidinomethyl]}-3-(2-methylphenyl)imidazolium iodide (6d). The above procedure was followed using **5**, 1-(2-methylphenyl)imidazole and MeCN. A light yellow crystal was obtained in 51% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.90 (s, 1H), 8.10-8.11 (m, 1H), 7.68-7.70 (m, 2H), 7.44-7.47 (m, 2H), 7.32-7.39 (m, 5H), 4.97-5.01 (m, 1H), 4.65-4.71 (m, 1H), 4.33-4.38 (m, 1H), 3.01-3.65 (m, 2H), 2.42 (s, 3H), 2.35 (s, 3H), 1.90-1.98 (m, 1H); 1.76-1.80 (m, 1H), 1.63-1.70 (m, 1H), 1.47-1.53 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ =144.1, 136.9, 133.4, 131.9, 130.9, 130.0, 127.6, 126.4, 124.3, 122.4, 60.3, 53.1, 49.4, 28.8, 23.9, 21.4, 17.8. HRMS (ESI): *m/z* calcd for $C_{22}H_{26}N_3O_2S$ $[M-I]^+$: 396.1740. Found 396.1728.

1-{(*2S*)-2-[1-(4-Tolylsulfonyl)pyrrolidinomethyl]}-3-mesitylimidazolium iodide (6e). The above procedure was followed using **5**, 1-mesitylimidazole and MeCN. A light yellow crystal was obtained in 51% yield. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.79 (s, 1H), 8.10 (s, 1H), 7.65-7.67 (d, *J* = 8.1, 2H), 7.29-7.32 (d, *J* = 8.1, 2H), 7.14 (s, 1H), 6.97 (s, 2H), 4.96-5.00 (m, 1H), 4.80-4.83(m, 1H), 4.27 (s, 1H), 3.51-3.55 (m, 1H), 3.10-3.11 (m, 1H), 2.40 (s, 3H), 2.30 (s, 3H), 2.11 (s, 6H), 1.72-1.86 (m, 3H), 1.43-1.46 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ =144.2, 141.1, 137.3, 134.5, 133.1, 130.7, 130.0, 129.8, 127.7, 124.8, 122.5, 60.0, 53.1, 49.4, 28.8, 24.0, 21.5, 21.0, 17.8. HRMS (ESI): *m/z* calcd for $C_{24}H_{30}N_3O_2S$ $[M-I]^+$: 424.2053. Found 424.2079.

(η^4-1,5-Cyclooctadiene){1-{(*2S*)-2-[1-(4-tolylsulfonyl)pyrrolidinomethyl]}-3-mesityl imidazolin-2-ylidene} rhodium (I) iodide (7). $[Rh(COD)Cl]_2$ (0.5 mmol) was added to a Schlenk tube along with 3 equivalents of KO^{t}Bu. The vessel was evacuated and flushed with Ar three times. THF (30 mL) was syringed in and the solution was stirred at room temperature for 2 h before KI (4 equivalents) and imidazolioum salt (**6e**) (0.5 mmol) was added. The mixture was stirred at room temperature for 20 h and heated to reflux for additional 20 h. After cooling to room temperature, the volatiles were removed *in vacuo*, and the solid residue was extracted with CH_2Cl_2 (20 mL) for three times. The CH_2Cl_2 solution was combined, and the volatiles evaporated *in vacuo*. The obtained solid was purified with short column chromatography on silica gel. A yellow product (**7**) was obtained in 76% yield. ^{1}H NMR ($CDCl_3$, 400MHz): δ =7.71-7.78 (d, *J* = 8.3, 2H), 7.36 (d, *J* = 1.74, 1H), 7.32 (d, *J* = 8.3, 2H), 7.04 (s, 1H), 6.92 (s, 1H), 6.80 (d, *J* = 1.74, 1H), 5.52-5.57 (m, 1H), 5.10-5.14 (m, 1H), 5.00-5.13 (m, 1H), 4.40-4.46 (m, 1H), 4.12-4.18 (m, 1H), 3.93-3.96 (m, 1H), 3.51-3.54 (m, 1H), 3.39-3.43 (m, 1H), 3.30-3.33 (m, 1H), 2.47 (s, 3H), 2.44 (s, 3H), 2.37 (s, 3H), 2.26-2.33 (m, 1H), 2.11-2.18 (m, 2H), 1.95-1.98 (m, 2H), 1.93 (s, 3H), 1.88-1.92 (m, 1H), 1.70-1.78 (m, 2H), 1.65-1.67 (m, 2H), 1.41-1.43 (m, 1H), 1.26-1.27 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 181.7 (d, $^1J(^{103}Rh, ^{13}C)$ = 49.4 Hz), 143.8, 138.6, 136.8, 136.2, 135.3, 134.9, 134.6, 134.3, 129.9, 129.6, 129.5, 127.6, 123.7, 122.9, 95.1 (d, $^1J(^{103}Rh, ^{13}C)$ = 5.7 Hz), 94.9 (d, $^1J(^{103}Rh, ^{13}C)$ = 6.7 Hz), 72.0 (d, $^1J(^{103}Rh, ^{13}C)$ = 11.4 Hz), 71.0 (d, $^1J(^{103}Rh, ^{13}C)$ = 11.4 Hz), 60.7, 56.3, 48.6, 33.7, 30.9, 29.9, 29.1, 28.8, 24.2, 21.9, 21.6, 21.1, 17.9. HRMS (ESI): *m/z* calcd for $C_{32}H_{41}N_3O_2RhS$ $[M-I]^+$: 634.1969. Found 634.2004.

Representative procedure for the rhodium-catalyzed addition of arylboronic acids to aldehydes; (4-chlorophenyl)phenylmethanol (10). Phenylboronic acid (**8**) (244 mg, 2 mmol), 4-chlorobenzaldehyde (**9**) (140 mg, 1 mmol), KO^{t}Bu (112 mg, 1 mmol), imidazolium iodide (**6e**) (5.5 mg, 0.01 mmol), $[Rh(COD)Cl]_2$ (2.5 mg, 0.005 mmol) were successively added to a Schlenk tube and the vessel was evacuated and flushed with Ar three times. DME (3 mL) and H_2O (1 mL) was syringed in and the mixture was heated to 80 ^{o}C for 24 h. After cooling to ambient temperature, the reaction mixture was diluted with ethyl acetate (30 mL) and washed with water (5 mL). The organic phase was dried (Na_2SO_4) and evaporated *in vacuo.* The solid residue was purified by column chromatography (petrol ether/ethyl acetate, v/v, 12/1) affording the title compound **10** as colorless syrup that slowly crystallized upon standing at ambient temperature; yield: 210 mmg (95%).

The analytical and spectroscopic data of all products of addition reaction were in agreement with those of authentic samples prepared according to literature procedures.

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References and Footnotes

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