

Rh–N-Heterocyclic Carbene (NHC) Complex-Catalyzed Addition of Phenylboronic Acid to N-Sulfonyl and N-Phosphinoyl Aldimines

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Received March 18, 2008; accepted April 22, 2008; published online May 1, 2008

Rh–N-heterocyclic carbene (NHC) complexes were generated *in situ* from imidazolium salts, [RhCl(cod)]₂ and *t*-BuOK in dioxane. In the presence of a catalytic amount of Rh–NHC complexes, the addition reaction of phenylboronic acid to N-sulfonylarylimines and N-phosphinoylarylimines gave the corresponding amines in high yields.

Key words N-heterocyclic carbene; rhodium; phenylboronic acid; addition reaction; N-sulfonylarylimine; N-phosphinoylarylimine

The synthesis, isolation, and characterization of stable N-heterocyclic carbenes (NHCs) first reported by Arduengo *et al.*¹⁾ in 1991, have attracted attention for the use of NHCs as ancillary ligands for transition metal complexes. Due to their strong σ -donating properties, NHCs can form metal complexes that have high stabilities toward heat, moisture, and air, and they have higher catalytic abilities than their phosphine counterparts.^{2–6)} NHCs are now used as ligands for transition metals in many important chemical transformations such as Pd-catalyzed coupling reactions,⁷⁾ Ru-catalyzed olefin metathesis,⁸⁾ Rh-catalyzed hydrosilylations,^{9–11)} and Cu-catalyzed conjugate addition reactions.^{12–14)} Moreover, NHCs have attracted considerable attention as organocatalysts in several reactions such as benzoin condensation,^{15–20)} Stetter reaction,^{21–23)} transesterification/acylation reactions,^{24,25)} and nucleophilic substitution reactions.^{26–28)}

In our study on the use of NHCs as ligands in organic transformations, we have recently reported the addition of diethylzinc to N-sulfonylarylimines catalyzed by Cu–NHC complexes,²⁹⁾ where NHCs exhibit a strong ligand acceleration effect (LAE). This finding has prompted us to investigate the applicability of a similar methodology to the Rh–NHC complex-catalyzed addition of phenylboronic acid to imines.

The addition reaction of organometallic reagents to imines is one of the most efficient procedures for the synthesis of diarylmethylamines, which are important subunits of biologically significant compounds.^{30–33)} Despite many studies on the Rh-phosphine complex-catalyzed addition of arylboronic acids to imines,^{34,35)} there is only one study, *i.e.*, that by Charette and coworkers, in which the Rh–NHC complex is used.³⁶⁾ Here, we report our results on the addition of arylboronic acid to both N-sulfonylarylimines and N-phosphinoylarylimines by using a catalytic amount of Rh–NHC complexes.

Results and Discussion

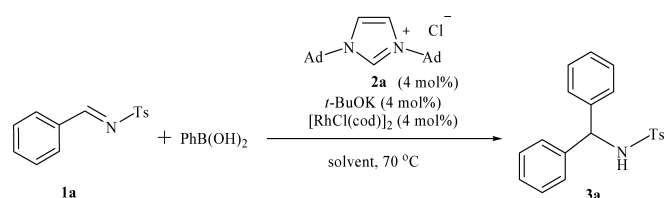
In the study by Charette and coworkers, the Rh–NHC complex was prepared *in situ* using the NHC-transfer reagent Ag–NHC and used as a catalyst in the arylation of *p*-methylphenyl-N-phosphinoylimine with phenylboronic acid.³⁶⁾ They showed only one reaction example. We examined the catalytic ability of the Rh–NHC complex generated *in situ*³⁷⁾ from azolium salts and [RhCl(cod)]₂ for the arylation

of imines. The Rh–NHC complex was prepared from [RhCl(cod)]₂, 1,3-diadamantylimidazolium chloride **2a**, and *t*-BuOK; then, N-sulfonylphenylimine **1a**³⁸⁾ and phenylboronic acid were added to the mixture. The reaction in dioxane at 70 °C for 5 h afforded N-sulfonyldiarylmethylamine **3a** in 91% yield (Table 1, entry 1). The reaction without **2a** in dioxane afforded the desired product **3a** in only 62% yield after 10 h at 70 °C (entry 2). These results showed and indicated that the NHC ligand accelerated the addition reaction. The reaction in THF afforded **3a** in 48% yield, whereas in toluene, the reaction was very sluggish and gave no adducts (Table 1, entries 3–4). On the basis of these results, dioxane was used as a solvent in the later reactions.

The addition reactions of phenylboronic acid to **1a** were carried out using imidazolium salts with mesityl substituent **2b**, triazolium salt **2c**, and thiazolium salt **2d** as ligand precursors. Using imidazolium salt **2b** and triazolium salt **2c**, the addition product was isolated in high yields (Table 2, entries 1 and 2). In the case of thiazolium salt **2d**, only a small amount of addition product was obtained (Table 2, entry 3). From these results, it was found that triazolium salt **2c** also functioned as a potential ligand precursor.

Various N-sulfonylarylimines **1b–h** were subjected to the Rh–NHC complex-catalyzed addition reaction with phenylboronic acid. The substituted phenylimines with both electron-donating and electron-withdrawing groups, **1b–f**, reacted readily with phenylboronic acid in the presence of a

Table 1. Arylation of N-Sulfonylphenylimine **1a** Using Rh–NHC Complex



Entry	Solvent	Time (h)	Yield (%) ^{a)}
1	Dioxane	5	91
2 ^{b)}	Dioxane	10	62
3	THF	5	48
4	Toluene	8	No reaction

a) Isolated yield. b) Without imidazolium salt and base.

Table 2. Arylation of *N*-Sulfonylphenylimine **1a** Using Ligand Precursors **2b–d**

Entry	Azolium salt	Time (h)	Yield (%)
1		5	84
2		6	88
3		6	Trace

Table 3. Arylation of Various *N*-Sulfonylarylimines **1b–h**

Entry	Ar	Time (h)	Yield (%)
1		6	94
2		6	92
3		6	89
4		6	82
5		8	85
6		6	97
7		5	89

catalytic amount of the Rh–NHC complex to give the corresponding amines in high yields (Table 3, entries 1–5). Bulky *N*-sulfonylaryl imines (1-naphthylimine **1g** and 2-trimethylsilylphenylimine **1h**) were also phenylated with phenylboronic acid, affording the corresponding amines in high yields (Table 3, entries 6 and 7).

Next, this procedure was applied to the other substrates, *i.e.*, *N*-phosphinoylarylimines. When the optimal conditions

Table 4. Arylation of *N*-Phosphinoylarylimines **4a–d**

Entry	Ar	Time (h)	Yield (%)
1		5	87
2		6	79
3		6	84
4		6	73

for the addition of phenylboronic acid to *N*-sulfonylarylimines were applied to the reaction of *N*-phosphinoylarylimines, only imine hydrolysis was observed. To overcome this problem, the addition reactions were carried out in the presence of activated, powdered MS 4A. As a result, the addition reaction of phenylboronic acid using a catalytic amount of the Rh–NHC complex was successfully applied to the arylation of *N*-phosphinoylarylimines **4a–d**³⁹ that were derived from benzaldehyde, 4-chlorobenzaldehyde, 4-methylbenzaldehyde, and 2-naphthaldehyde, affording the corresponding addition products **5a–d** in high yields (Table 4, entries 1–4). In the study by Charette *et al.*, **4c** was used as a substrate and the addition product **5c** was obtained in 77% yield after heating for 36 h at 50 °C.³⁶ In our examples, arylation gave better yields and we used the addition reaction in a wide range of substrates.

Conclusion

In conclusion, we have demonstrated a very efficient procedure for the addition of phenylboronic acid to both *N*-sulfonylarylimines and *N*-phosphinoylarylimines. The reaction rate is higher than that in the study by Charette and coworkers, in which the Rh–NHC complex is used as a catalyst.³⁶ The use of a catalytic amount of the Rh–NHC complex enables us to synthesize diarylmethylamines in high yields. In our laboratory, further investigations are in progress for developing an asymmetric version of this addition reaction.

Experimental

General Melting points were determined using the Yazawa micromelting point apparatus without correction. ¹H-NMR (500 MHz) and ¹³C-NMR (126 MHz) spectra were recorded on a JEOL ECA-500 NMR spectrometer. IR spectra were recorded on a Shimadzu IRPrestige-21. FAB-MS spectra were recorded on a JEOL MStation JMS-700 mass spectrometer using *m*-nitrobenzyl alcohol as a matrix. Column chromatography was carried out with silica gel 60 N (spherical, acidic; Kanto Chemical Co., Inc.).

General Procedure for the Preparation of *N*-Sulfonamides **3a–h** To a stirring suspension of azolium salt (4 mol%) and [RhCl(cod)]₂ (3.9 mg, 4 mol%) in 1 ml dioxane, 1 M *t*-BuOK/THF (8 μl, 4 mol%) was added under

argon atmosphere. The mixture was stirred at room temperature for 30 min. Then, the solution of phenylboronic acid (36.6 mg, 0.3 mmol) in 1 ml dioxane and the solution of *N*-sulfonylarylimines **1a–h** (0.2 mmol) in 1 ml dioxane were successively added dropwise to the mixture. After stirring at 70 °C for the indicated time, the mixture was poured into H₂O and extracted with CH₂Cl₂. The organic layer was washed with brine, dried over MgSO₄, and concentrated. The residue was purified by column chromatography (*n*-hexane/ethyl acetate=3:1) to afford the addition products **3a–h**.

N-(Diphenylmethyl)-4-methylbenzenesulfonamide⁴⁰⁾ (**3a**): Colorless powder (recrystallized from *n*-hexane/CH₂Cl₂), 91%, mp 131–133 °C; IR (ATR) cm⁻¹: 3234, 1317, 1157. ¹H-NMR (CDCl₃) δ: 2.37 (3H, s), 5.25 (1H, d, *J*=7.5 Hz), 5.56 (1H, d, *J*=7.5 Hz), 7.07–7.13 (6H, m), 7.18–7.22 (6H, m), 7.55 (2H, d, *J*=8.0 Hz). ¹³C-NMR (CDCl₃) δ: 21.6, 61.4, 127.3, 127.5, 127.7, 128.6, 129.5, 137.4, 140.6, 143.3. MS (FAB) *m/z* 338 (M+1).

N-(4-Chloro- α -phenylbenzyl)-4-methylbenzenesulfonamide⁴⁰⁾ (**3b**): Colorless solid (recrystallized from *n*-hexane/CH₂Cl₂), 94%, mp 115–117 °C; IR (ATR) cm⁻¹: 3234, 1317, 1157. ¹H-NMR (CDCl₃) δ: 2.39 (3H, s), 5.17 (1H, d, *J*=7.0 Hz), 7.03–7.06 (4H, m), 7.14 (2H, d, *J*=8.0 Hz), 7.17 (2H, d, *J*=8.5 Hz), 7.13–7.18 (4H, m), 7.19–7.22 (3H, m), 7.54 (2H, d, *J*=8.0 Hz). ¹³C-NMR (CDCl₃) δ: 21.6, 60.8, 127.3, 127.4, 128.0, 128.7, 128.8, 128.9, 129.5, 133.5, 137.3, 139.1, 140.2, 143.5. MS (FAB) *m/z* 372 (M+1).

N-(2-Chloro- α -phenylbenzyl)-4-methylbenzenesulfonamide⁴⁰⁾ (**3c**): Colorless needles, (recrystallized from *n*-hexane/CH₂Cl₂), 92%, mp 168–170 °C; IR (ATR) cm⁻¹: 3323, 1333, 1153. ¹H-NMR (CDCl₃) δ: 2.37 (3H, s), 5.30 (1H, d, *J*=7.0 Hz), 5.90 (1H, d, *J*=7.0 Hz), 7.05–7.07 (2H, m), 7.13–7.17 (4H, m), 7.21–7.24 (4H, m), 7.33–7.35 (1H, m), 7.61 (2H, d, *J*=8.5 Hz). ¹³C-NMR (CDCl₃) δ: 21.6, 58.7, 127.0, 127.3, 127.4, 128.0, 128.8, 128.9, 129.5, 129.5, 130.0, 132.9, 137.0, 137.6, 139.4, 143.5. MS (FAB) *m/z* 372 (M+1).

N-(4-Methoxy- α -phenylbenzyl)-4-methylbenzenesulfonamide⁴⁰⁾ (**3d**): Colorless solid (recrystallized from *n*-hexane/CH₂Cl₂), 89%, mp 136–139 °C; IR (ATR) cm⁻¹: 3234, 1319, 1157. ¹H-NMR (CDCl₃) δ: 2.37 (3H, s), 3.74 (3H, s), 5.28 (1H, d, *J*=7.5 Hz), 5.51 (1H, d, *J*=7.5 Hz), 6.71 (2H, d, *J*=8.5 Hz), 6.82 (2H, d, *J*=8.5 Hz), 7.09–7.13 (4H, m), 7.17–7.21 (3H, m), 7.54 (2H, d, *J*=8.5 Hz). ¹³C-NMR (CDCl₃) δ: 21.6, 55.4, 60.9, 114.0, 127.3, 127.4, 127.5, 128.6, 128.7, 129.4, 132.9, 137.5, 140.8, 143.2, 159.0.

N-(2-Methoxy- α -phenylbenzyl)-4-methylbenzenesulfonamide⁴⁰⁾ (**3e**): Colorless plates (recrystallized from *n*-hexane/CH₂Cl₂), 82%, mp 124–126 °C; IR (ATR) cm⁻¹: 3302, 1321, 1151. ¹H-NMR (CDCl₃) δ: 2.31 (3H, s), 3.58 (3H, s), 5.64 (1H, d, *J*=9.0 Hz), 5.78 (1H, d, *J*=9.0 Hz), 6.67 (1H, d, *J*=8.6 Hz), 6.77 (1H, t, *J*=7.5 Hz), 6.97 (1H, dd, *J*=7.5, 2.0 Hz), 7.04 (2H, d, *J*=8.0 Hz), 7.13–7.23 (6H, m), 7.50 (2H, d, *J*=8.0 Hz). ¹³C-NMR (CDCl₃) δ: 21.5, 55.3, 59.1, 111.2, 120.7, 126.9, 127.1, 127.2, 127.7, 128.2, 129.0, 129.1, 129.7, 137.6, 140.6, 142.9, 156.4.

N-(4-Methyl- α -phenylbenzyl)-4-methylbenzenesulfonamide³³⁾ (**3f**): Colorless needles (recrystallized from *n*-hexane/CH₂Cl₂), 85%, mp 117–119 °C; IR (ATR) cm⁻¹: 3253, 1317, 1161. ¹H-NMR (CDCl₃) δ: 2.27 (3H, s), 2.38 (3H, s), 5.07 (1H, d, *J*=7.0 Hz), 5.51 (1H, d, *J*=7.0 Hz), 6.96 (2H, d, *J*=8.0 Hz), 7.01 (2H, d, *J*=8.0 Hz), 7.10 (2H, dd, *J*=7.5, 2.0 Hz), 7.13 (2H, d, *J*=7.5 Hz), 7.17–7.21 (3H, m), 7.55 (2H, d, *J*=8.0 Hz). ¹³C-NMR (CDCl₃) δ: 21.1, 21.6, 61.2, 127.3, 127.4, 127.4, 127.6, 128.6, 129.3, 129.4, 137.4, 137.5, 137.7, 140.8, 143.2.

N-(1-Naphthyl)phenylmethyl-4-methylbenzenesulfonamide⁴¹⁾ (**3g**): Colorless granules (recrystallized from *n*-hexane/CH₂Cl₂), 97%, mp 176–178 °C; IR (ATR) cm⁻¹: 3246, 1319, 1150. ¹H-NMR (CDCl₃) δ: 2.35 (3H, s), 5.20 (1H, d, *J*=7.5 Hz), 6.31 (1H, d, *J*=7.5 Hz), 7.05 (2H, d, *J*=8.0 Hz), 7.13–7.15 (2H, m), 7.18–7.21 (3H, m), 7.23–7.30 (2H, m), 7.38 (1H, td, *J*=7.5, 1.0 Hz), 7.44 (1H, td, *J*=7.5, 1.0 Hz), 7.50 (1H, d, *J*=8.5 Hz), 7.72 (1H, d, *J*=8.0 Hz), 7.79–7.82 (2H, m). ¹³C-NMR (CDCl₃) δ: 21.6, 58.6, 123.5, 125.1, 125.8, 126.2, 126.6, 127.2, 127.6, 127.7, 128.7, 128.9, 129.3, 130.5, 134.0, 135.5, 137.3, 140.3, 143.2.

N-(α -Phenyl-2-(trimethylsilyl)-benzyl)-4-methylbenzenesulfonamide³³⁾ (**3h**): Colorless plates (recrystallized from *n*-hexane/CH₂Cl₂), 89%, mp 166–168 °C; IR (ATR) cm⁻¹: 3283, 1317, 1150. ¹H-NMR (CDCl₃) δ: 0.19 (9H, s), 2.35 (3H, s), 5.08 (1H, d, *J*=7.0 Hz), 6.01 (1H, d, *J*=7.0 Hz), 6.97–6.99 (2H, m), 7.08 (2H, d, *J*=8.0 Hz), 7.17–7.20 (7H, m), 7.49 (2H, d, *J*=8.0 Hz). ¹³C-NMR (CDCl₃) δ: 0.6, 21.6, 60.2, 126.8, 127.2, 127.6, 127.8, 128.4, 128.5, 129.3, 135.0, 138.0, 138.6, 141.2, 143.1, 144.5.

General Procedure for the Preparation of *N*-Phosphinic Amides **5a–d**
To a stirring suspension of imidazolium salt (4 mol%) and [RhCl(cod)]₂ (3.9 mg, 4 mol%) in 1 ml dioxane, 1 M *t*-BuOK/THF (8 μ l, 4 mol%) was added under argon atmosphere. The mixture was stirred at room temperature for 30 min. Then, the solution of phenylboronic acid (36.6 mg, 0.3 mmol) in 1 ml dioxane and the solution of *N*-phosphinoylarylimines **4a–d** (0.2 mmol)

in 1 ml dioxane were successively added dropwise to the mixture. Activated MS 4A (powder) was added to this mixture. After stirring at 70 °C for the indicated time, the mixture was filtered through a pad of Celite 545 and the celite cake was washed with CH₂Cl₂. H₂O was added to this mixture; the mixture was then extracted with CH₂Cl₂ and washed with brine. The CH₂Cl₂ layer was dried over MgSO₄ and concentrated. The residue was purified by column chromatography (ethyl acetate) to afford the addition products **5a–d**.

P,P-Diphenyl-*N*-(diphenylmethyl)phosphinic Amide⁴²⁾ (**5a**): Colorless needles (recrystallized from *n*-hexane/CH₂Cl₂), 87%, mp 187–189 °C; IR (ATR) cm⁻¹: 3207, 1182. ¹H-NMR (CDCl₃) δ: 3.64 (1H, dd, *J*=10.0, 7.0 Hz), 5.45 (1H, t, *J*=11.0 Hz), 7.21–7.31 (10H, m), 7.35–7.38 (4H, m), 7.46 (2H, td, *J*=7.5, 1.0 Hz), 7.81–7.85 (4H, m). ¹³C-NMR (CDCl₃) δ: 58.6, 127.3, 127.7, 128.5, 128.6, 132.0 (d, *J*=2.6 Hz), 132.3 (d, *J*=130.0 Hz), 132.4 (d, *J*=9.5 Hz), 132.8, 143.4 (d, *J*=10.2 Hz). MS (FAB) *m/z* 384 (M+1).

P,P-Diphenyl-*N*-(4-chloro- α -phenylbenzyl)phosphinic Amide³⁴⁾ (**5b**): Colorless crystalline powder (recrystallized from *n*-hexane/CH₂Cl₂), 79%, mp 165–167 °C; IR (ATR) cm⁻¹: 3117, 1196. ¹H-NMR (CDCl₃) δ: 3.65 (1H, dd, *J*=10.5, 7.0 Hz), 5.41 (1H, t, *J*=10.5 Hz), 7.19–7.25 (7H, m), 7.30 (2H, t, *J*=8.0 Hz), 7.35–7.39 (4H, m), 7.46 (2H, td, *J*=7.5, 1.0 Hz), 7.78–7.83 (4H, m). ¹³C-NMR (CDCl₃) δ: 58.1, 127.6, 128.5, 128.6, 128.7, 128.7, 129.1, 132.0 (d, *J*=130 Hz), 132.2 (d, *J*=130 Hz), 132.3 (d, *J*=9.5 Hz), 132.4 (d, *J*=9.5 Hz), 133.1, 141.9 (d, *J*=4.9 Hz), 142.9 (d, *J*=5.2 Hz). MS (FAB) *m/z* 418 (M+1).

P,P-Diphenyl-*N*-(4-methyl- α -phenylbenzyl)phosphinic Amide³⁵⁾ (**5c**): Colorless needles (recrystallized from *n*-hexane/CH₂Cl₂), 84%, mp 174–176 °C; IR (ATR) cm⁻¹: 3215, 1435, 1180. ¹H-NMR (CDCl₃) δ: 2.31 (3H, s), 3.64 (1H, dd, *J*=10.5, 7.0 Hz), 5.41 (1H, t, *J*=10.5 Hz), 7.09 (2H, d, *J*=8.0 Hz), 7.14 (2H, d, *J*=8.0 Hz), 7.20–7.30 (5H, m), 7.34–7.39 (4H, m), 7.43–7.48 (2H, m), 7.80–7.85 (4H, m). ¹³C-NMR (CDCl₃) δ: 21.2, 58.4, 127.2, 127.6, 127.6, 128.5, 128.5, 129.3, 131.8 (d, *J*=130.0 Hz), 132.0, 132.4 (d, *J*=9.5 Hz), 132.8 (d, *J*=130.0 Hz), 137.0, 140.5 (d, *J*=9.0 Hz), 143.0 (d, *J*=9.0 Hz). MS (FAB) *m/z* 398 (M+1).

P,P-Diphenyl-*N*-(2-naphthyl)phenylmethylphosphinic Amide (**5d**): Colorless granules (recrystallized from *n*-hexane/CH₂Cl₂), 73%, mp 192–194 °C; IR (ATR) cm⁻¹: 3117, 1506, 1194. ¹H-NMR (CDCl₃) δ: 3.79 (1H, dd, *J*=10.0, 7.0 Hz), 5.62 (1H, t, *J*=11.0 Hz), 7.23–7.48 (13H, m), 7.64 (1H, s), 7.73–7.87 (8H, m). ¹³C-NMR (CDCl₃) δ: 58.8, 125.9, 126.1, 126.3, 127.4, 127.7, 127.8, 128.2, 128.5, 128.5, 128.6, 128.6, 131.7 (d, *J*=130.0 Hz), 132.0, 132.3 (d, *J*=9.0 Hz), 132.4, 132.4, 132.5 (d, *J*=9.0 Hz), 132.9 (d, *J*=130.0 Hz), 133.2, 140.7 (d, *J*=5.8 Hz), 143.3 (d, *J*=5.3 Hz). HR-MS (FAB) Calcd for C₂₉H₂₅NPO (M⁺): 434.1674, Found: 434.1715.

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