Aromatic C–H Borylation Catalyzed by Iridium/2,6-Diisopropyl-*N*-(2-pyridylmethylene)aniline Complex

Tsuyosi Tagata, Mayumi Nishida*

Koei Chemical Company, Ltd., Kitasode, Sodegaura, Chiba 299-0266, Japan Fax: (+81)-438-63-6876, e-mail: m-nishida@koeichem.co.jp

Received: June 16, 2004; Accepted: September 15, 2004

Abstract: The C–H borylation of aromatic and heteroaromatic compounds, such as benzene, 1,3-dichlorobenzene, 1,3-bis(trifluoromethyl)benzene, 2,6-dichloropyridine, indole, benzothiophene and benzofuran, by bis(pinacolato)diboron or pinacolborane was catalyzed by a 1/2 [IrCl(COD)]₂-2,6-diisopropyl-*N*-(2-pyridylmethylene)aniline complex. The isopropyl groups of the ligand are essential for obtaining the products in high yield. Octane was a suitable solvent for the reactions of the above compounds except for indole. In the case of indole, DME was better than octane and the yield tended to improve with a smaller amount of the catalyst.

Keywords: aromatic C–H borylation; bis(pinacolato)diboron; 2,6-diisopropyl-*N*-(2-pyridylmethylene)aniline; iridium complex; pinacolborane

Aryl- and heteroarylboron compounds are versatile synthons in organic synthesis, especially Suzuki–Miyaura coupling.^[1] There are some well-known synthetic procedures that involve the borylation of lithium intermediates, which are produced by lithium-halogen exchange of aromatic halides^[2] or directed *ortho*-metallation reactions.^[3] In addition to these traditional methods, the direct borylation of arenes by C–H activation reactions





Adv. Synth. Catal. 2004, 346, 1655-1660

DOI: 10.1002/adsc.200404179

has also been recently reported.^[4] The Miyaura–Hartwig team reported that when excess benzene substrate was heated with bis(pinacolato)diboron or pinacolborane at 80 °C for 16 hours in the presence of a mixture of [IrCl(COD)]₂ and bipyridine, the product was obtained in good yield.^[5] We were interested in the diimine moiety of bipyridine. Thus, the feasibility of three types of compounds with a diimine moiety (Types I–III) as a ligand was tested under the conditions mentioned above. We report here aromatic C–H borylation catalyzed by a 1/2 [IrCl(COD)]₂-2,6-diisopropyl-*N*-(2-pyridylmethylene)aniline complex.

Table 1 shows that Type II was the most promising ligand (runs 4-6). Therefore, the influence of the R group (Type II) on the reaction was studied.

To study the electronic effects of the ligand, a methoxy group or a bromide was introduced to the phenyl ring of **2b** (Table 2, runs 1 and 2). However, **2d** and **2e** gave the products in 14% yield, which was almost the same yield as was observed in the reaction with **2b** (Table 1, run 5). Although a mono-alkyl substituent did not improve the yield (Table 2, runs 3-7), a 2,6-dialkyl substitution suc-

Table 1. Influence of ligands of Types I–III on the C–H borylation of benzene.



^[a] Yield was determined by GC. The internal standard was 4,4'-dimethylbiphenyl.

Table 2. C-H borylation using ligand Type II.

| Ligar |) + + | О , В—е О | | 1/2 [I | rCl(COE 80 °C, |))] ₂ -liga 12 h (| and OBO |
|-------|--------|-----------------|--------------|--------------|-------------------|-------------------------------------|--------------------------|
| A | 2b – o | | }—D | | >2p | | |
| Run | Ligand | А | В | С | D | E | Yield [%] ^[a] |
| 1 | 2d | Н | Н | Н | OMe | Н | 14 |
| 2 | 2e | Η | Н | Η | Br | Η | 14 |
| 3 | 2f | Η | Me | Η | Н | Η | 21 |
| 4 | 2g | Η | Et | Η | Н | Η | 19 |
| 5 | 2h | Η | <i>i</i> -Pr | Η | Н | Η | 20 |
| 6 | 2i | Η | t-Bu | Η | Н | Η | 16 |
| 7 | 2j | Η | Ph | Η | Н | Η | 19 |
| 8 | 2k | Η | Et | Et | Н | Η | 32 |
| 9 | 21 | Η | <i>i</i> -Pr | <i>i</i> -Pr | Н | Η | 74 |
| 10 | 2m | Η | <i>i</i> -Pr | <i>i</i> -Pr | Н | Me | 21 |
| 11 | 2n | Η | <i>i-</i> Pr | <i>i</i> -Pr | Н | Ph | 39 |
| 12 | 20 | Me | <i>i-</i> Pr | <i>i</i> -Pr | Н | Η | 78 |
| 13 | 2p | Br | <i>i-</i> Pr | <i>i</i> -Pr | Н | Η | 11 |
| 14 | 2q | | | | | | 14 |

^[a] Yield was determined by GC. The internal standard was 4,4'-dimethylbiphenyl.

cessfully increased the yield (Table 1, run 6, and Table 2, runs 8 and 9). In the reaction with **2l**, the yield was as high as 74% (Table 2, run 9). On the other hand, ligands **2 m** and **2n**, which had a methyl group or phenyl group at position E, gave the product in a low yield (Table 2, runs 10 and 11). While a methyl group at the 6-position of pyridine in **2o** slightly increased the yield (Table 2, run 12), a bromide at this position, as in **2p**, decreased the yield (Table 2, run 13). When the reaction was conducted with **2q**, which had a quinoline moiety, the yield decreased. The reaction may be impaired by the poor coordination ability of ligands **2p** and **2q**. Among the ligands tested above, **2l** and **2o** gave good results. Thus, we used **2l** and **2o** in the reactions of other substrates with pinacolborane.

A mixture of benzene (60 mmol), pinacolborane (2 mmol), $[IrCl(COD)]_2$ (0.015 mmol), and ligand (0.03 mmol) was stirred at 80 °C for 12 h. Both **21** and **20** gave the products in 79% yield (Table 3, runs 1 and 2). In the reaction of 1,3-dichlorobenzene, both bis(pinacolato)diboron and pinacolborane gave the product in over 80% yield (Table 3, runs 3 and 4). When 1,3-bis-(trifluoromethyl)benzene was used as a substrate, pinacolborane gave a higher yield than bis(pinacolato)diboron (Table 3, runs 5–8). The same trend was observed in the reaction of 2,6-dichloropyridine (Table 3, runs 9–

12), where the reaction was conducted in octane according to the conditions reported by Miyaura and Ishiyama.^[6]

However, when the reaction of indole with bis(pinacolato)diboron was carried out in octane, the product was obtained in only 1% yield (Table 4, run 1). To identify better conditions, we examined DME, DMF, and mesitylene as possible solvents. Miyaura and Ishiyama reported that a non-polar solvent was suitable for this reaction.^[7] The reactivity in different solvents was in the order hexane > mesitylene > DME > DMF. However, among the solvents we tested, DME gave a relatively good yield (Table 4, runs 1-4). When the ratio of bis(pinacolato)diboron to indole was changed from 1:4 to 1:2, the yield was increased to 30% (Table 4, run 5). Surprisingly, a smaller amount of the catalyst dramatically improved the yield. When 0.2 mol % of catalyst was used in the reaction, the product was obtained in 91% yield (Table 4, run 7). However, 0.02 mol % of catalyst was too little for the reaction to take place (Table 4, run 8).

To clarify the role of the ligand, two experiments were conducted. First, the reaction was carried out without a ligand. When a mixture of indole, bis(pinacolato)diboron, and [IrCl(COD)]₂ (0.1 mol %) was heated in DME, the product was not obtained. Second, we tested the feasibility of the product as a ligand. When a mixture of indole, bis(pinacolato)diboron, [IrCl(COD)]₂ (0.1 mol %) and **4a** (0.2 mol %) was heated in DME, the product was again not produced. These results showed that the ligand was essential for this reaction and the product did not act as a ligand. The detailed mechanism has not yet been clarified.

The tendency for a smaller amount of catalyst to be associated with an improved yield was not observed when octane was used as a solvent. In fact, the reaction in the presence of 0.2 mol % of catalyst in octane resulted in unsatisfactory conversion (Table 4, run 9).

When the reaction with pinacolborane in the presence of 1.5 mol % catalyst was carried out in DME, the product was obtained in 80% yield (Table 4, run 10). As was seen in the reaction with bis(pinacolato)diboron, 0.1 mol % of catalyst improved the yield to 92% (Table 4, run 11), and 0.01 mol% of catalyst gave the product in only 15% yield (Table 4, run 12). On the other hand, with octane as a solvent, 1.5 mol % and 0.1 mol % of catalyst gave the product in respective yields of 65% and 72% (Table 4, runs 13 and 14). In the case of indole, pinacolborane gave a higher yield than bis(pinacolato)diboron.

We wondered if the same tendency would be observed in the reaction with a 1/2 [IrCl(COD)]₂-bipyridine system in DME.^[8] As shown in Table 5, DME was a better solvent than octane (Table 5, runs 1, 3, 4 and 6) and a smaller amount of catalyst gave a slightly higher yield in DME (Table 5, runs 1, 2, 4 and 5). These trends are the same as those observed in the reaction of indole Table 3. Reactions with pinacolborane.



| Run | Substrate | | Ligand | Pin ₂ B ₂ or PinBH | Product 4 | Yield [%] |
|-----|-----------------|---|--------|--|------------|-------------------|
| | X | Y | | | | |
| 1 | Н | С | 21 | PinBH | 4 a | 79 ^[a] |
| 2 | Н | С | 20 | PinBH | 4 a | 79 ^[a] |
| 3 | Cl | С | 21 | Pin_2B_2 | 4b | 83 ^[b] |
| 4 | Cl | С | 21 | PinBH | 4b | 85 ^[b] |
| 5 | CF ₃ | С | 21 | Pin_2B_2 | 4c | $47^{[a]}$ |
| 6 | CF_3 | С | 20 | Pin_2B_2 | 4c | 6 ^[a] |
| 7 | CF ₃ | С | 21 | PinBH | 4c | 73 ^[a] |
| 8 | CF ₃ | С | 20 | PinBH | 4c | 70 ^[a] |
| 9 | Cl | Ν | 21 | Pin_2B_2 | 4d | 73 ^[b] |
| 10 | Cl | Ν | 20 | Pin_2B_2 | 4d | 71 ^[b] |
| 11 | Cl | Ν | 21 | PinBH | 4d | 93 ^[b] |
| 12 | Cl | Ν | 20 | PinBH | 4d | 90 ^[b] |

^[a] Yields were determined by GC. The internal standard was 4,4'-dimethylbiphenyl.

^[b] Yields were determined by GC. The internal standard was 4,4'-di-t-butylbipyridine.

with 1/2 [IrCl(COD)]₂-2,6-diisopropyl-*N*-(2-pyridylme-thylene)aniline.

We continued to examine the reactions with 1/2 [IrCl(-COD)]₂-**21**. In the reactions of benzothiophene with bis(pinacolato)diboron or pinacolborane, octane was a better solvent than DME (Table 4, runs 15–20). Although the reactions of benzothiophene with bis(pinacolato)diboron in DME (Table 4, runs 15 and 16) did not proceed smoothly, the product was obtained in 86% yield in octane (Table 4, run 17). Pinacolborane in DME gave a better yield than bis(pinacolato)diboron (Table 4, runs 18 and 19). The reaction with pinacolborane in octane gave the product in 94% yield (Table 4, run 20).

In the reaction of benzofuran, octane again acted as a good solvent. Unfortunately, in this case, a regioisomer, which was determined by GC-MS, was found (Table 4, runs 21–26). The reaction with bis(pinacolato)diboron in the presence of 3 mol % of catalyst in octane gave the product in 74% yield with 10% of the isomer (Table 4, run 23). However, the reaction with pinacolborane in octane gave 74% yield with 1% of isomer (Table 4, run 26). In the reaction of benzofuran, pinacolborane resulted in higher yield and selectivity compared to bis(pinacolato)diboron.

Finally, to examine the steric effects of the imine moiety, ligand 2r or 2s was used in the reaction. Compared to the results obtained in the reaction catalyzed by 1/2

Adv. Synth. Catal. 2004, 346, 1655-1660

asc.wiley-vch.de

 $[IrCl(COD)]_2$ -2a (Table 1, run 4), in both cases the yields were improved from 27% to 60% (Table 6). It seemed that steric bulkiness around the imine moiety is important for obtaining the product in high yield. Therefore, 6-diisopropyl-*N*-(2-pyridylmethylene)aniline was also effective.

In conclusion, a 1/2 [IrCl(COD)]₂-2,6-diisopropyl-*N*-(2-pyridylmethylene)aniline complex catalyzed the C–H borylation of aromatic and heteroaromatic compounds. The isopropyl groups of 2,6-diisopropyl-*N*-(2-pyridylmethylene)aniline are indispensable for obtaining the products in high yield. In the reactions of benzene, 1,3-bis(trifluoromethyl)benzene, and 2,6-dichloropyridine in octane, pinacolborane gave a better yield than bis(pinacolato)diboron. In the reactions of benzo-thiophene and benzofuran, octane was also a better solvent than DME, which was consistent with the reactivity reported by Miyaura and Ishiyama. However, in the reaction of indole, DME was the most suitable solvent and the yield was improved with a smaller amount of catalyst. The reason for this trend is under investigation.

Experimental Section

All reactions were conducted under a nitrogen atmosphere. NMR spectra were recorded in CDCl₃ (¹H at 400 MHz and ¹³C at 100 MHz). All starting materials, reagents and solvents

© 2004 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

COMMUNICATIONS

Table 4. Reactions of indole with $1/2 [IrCl(COD)]_2$ -21.



| Run | Z | Solvent | Pin ₂ B ₂ or PinBH | Borane:Substrate (mole ratio) | 1/2 [IrCl(COD)] ₂ -21 (mol %) | Yield [%] ^[a] |
|-----|----|------------|---|----------------------------------|---|-----------------------------|
| 1 | NH | octane | Pin_2B_2 | 1:4 | 3 | 1 |
| 2 | NH | mesitylene | Pin_2B_2 | 1:4 | 3 | 7 |
| 3 | NH | DMF | Pin_2B_2 | 1:4 | 3 | 1 |
| 4 | NH | DME | Pin_2B_2 | 1:4 | 3 | 15 |
| 5 | NH | DME | Pin_2B_2 | 1:2 | 3 | 30 |
| 6 | NH | DME | Pin_2B_2 | 1:2 | 1 | 37 |
| 7 | NH | DME | Pin_2B_2 | 1:2 | 0.2 | 91 |
| 8 | NH | DME | Pin_2B_2 | 1:2 | 0.02 | 1 |
| 9 | NH | octane | Pin_2B_2 | 1:2 | 0.2 | 5 |
| 10 | NH | DME | PinBH | 1:1 | 1.5 | 80 |
| 11 | NH | DME | PinBH | 1:1 | 0.1 | 92 |
| 12 | NH | DME | PinBH | 1:1 | 0.01 | 15 |
| 13 | NH | octane | PinBH | 1:1 | 1.5 | 65 |
| 14 | NH | octane | PinBH | 1:1 | 0.1 | 72 |
| 15 | S | DME | Pin_2B_2 | 1:2 | 3 | 1 |
| 16 | S | DME | Pin_2B_2 | 1:2 | 0.2 | 1 |
| 17 | S | octane | Pin_2B_2 | 1:2 | 3 | 86 |
| 18 | S | DME | PinBH | 1:1 | 1.5 | 59 |
| 19 | S | DME | PinBH | 1:1 | 0.1 | 77 |
| 20 | S | octane | PinBH | 1:1 | 1.5 | 94 |
| 21 | Ο | DME | Pin_2B_2 | 1:2 | 3 | $62 (14^{[b]})$ |
| 22 | О | DME | Pin_2B_2 | 1:2 | 0.2 | $1 (trace^{[b]})$ |
| 23 | Ο | octane | Pin_2B_2 | 1:2 | 3 | 74 (10 ^[b]) |
| 24 | Ο | DME | PinBH | 1:1 | 1.5 | $74(1^{[b]})$ |
| 25 | Ο | DME | PinBH | 1:1 | 0.1 | 77 $(2^{[b]})$ |
| 26 | Ο | octane | PinBH | 1:1 | 1.5 | 82 (1 ^[b]) |

^[a] Yields were determined by GC. The internal standard was 4,4'-di-*t*-butylbipyridine.

^[b] The yield of the isomer was determined by GC-MS.

Table 5. Reaction of indole with 1:2 [IrCl(COD)]₂-bipyridine.



| Run | Ligand | Solvent | Pin ₂ B ₂ or PinBH | Borane : Substrate (mole ratio) | 1:2 [IrCl(COD)] ₂ -Ligand (mol %) | Yield [%] ^[a] |
|-----|--------|---------|---|------------------------------------|---|-----------------------------|
| 1 | 6b | DME | Pin ₂ B ₂ | 1:2 | 3 | 87 |
| 2 | 6a | DME | Pin_2B_2 | 1:2 | 0.2 | 92 |
| 3 | 6a | octane | Pin_2B_2 | 1:2 | 3 | 60 |
| 4 | 6a | DME | PinBH | 1:1 | 1.5 | 67 |
| 5 | 6a | DME | PinBH | 1:1 | 0.1 | 92 |
| 6 | 6a | octane | PinBH | 1:1 | 1.5 | 1 |

[a] Yields were determined by GC. The internal standard was 4,4'-di-t-butylbipyridine.

1658

© 2004 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

asc.wiley-vch.de

Table 6. C-H borylation using ligand Type II.



^[a] Yield was determined by GC. The internal standard was 4,4'-dimethylbiphenyl.

were of commercial grade. All products were known compounds, and identified based on their NMR and GC-mass spectra.

Reactions of Benzene with Bis(pinacolato)diboron in Tables 1, 2, and 6, and of 1,3-Dichlorobenzene or 1,3-Bis(trifluoromethyl)benzene with Bis(pinacolato)diboron in Table 3

A 20-mL tube fitted with a magnetic stirring bar, septum inlet, and condenser was charged with $[IrCl(COD)]_2$ (10.1 mg, 0.015 mmol), ligand (0.03 mmol), and bis(pinacolato)diboron (254 mg, 1.0 mmol), and then flushed with argon. The substrate (60 mmol) was added, and the mixture was stirred at 80 °C for 12 h. The yield was determined by GC. The internal standard was 4,4'-dimethylbiphenyl. Compounds **4a**,^[5] **4b**,^[4j] and **4c**^[4c] are described in the literature.

Reactions of Benzene, 1,3-Dichlorobenzene and 1,3-Bis(trifluoromethyl)benzene with Pinacolborane in Table 3

A 20-mL tube fitted with a magnetic stirring bar, septum inlet, and condenser was charged with $[IrCl(COD)]_2$ (10.1 mg, 0.015 mmol) and ligand (0.03 mmol), and then flushed with argon. The substrate (60 mmol) and pinacolborane (256 mg, 2.0 mmol) were added, and the mixture was stirred at 80 °C for 12 h. The yield was determined by GC. The internal standard was 4,4'-dimethylbiphenyl.

Reactions of 2,6-Dichloropyridine with Bis(pinacolato)diboron in Table 3

A 20-mL tube fitted with a magnetic stirring bar, septum inlet, and condenser was charged with 2,6-dichloropyridine (296 mg, 2.0 mmol), $[IrCl(COD)]_2$ (10.1 mg, 0.015 mmol), ligand **21** or **20** (0.03 mmol), and bis(pinacolato)diboron (254 mg, 1.0 mmol), and then flushed with argon. Octane (5 mL) was added, and the mixture was stirred at 80 °C for 12 h. The yield

Adv. Synth. Catal. 2004, 346, 1655-1660

asc.wiley-vch.de

was determined by GC. The internal standard was 4,4'-di-*t*-bu-tyl-2,2'-bipyridine. Compound **4d**^[4d] is described in the literature.

Reactions of 2,6-Dichloropyridine with Pinacolborane in Table 3

A 50-mL tube fitted with a magnetic stirring bar, septum inlet, and condenser was charged with 2,6-dichloropyridine (1.48 g, 10 mmol), [IrCl(COD)]₂ (50.3 mg, 0.075 mmol) and ligand **2k** or **2n** (0.15 mmol), and then flushed with argon. Octane (25 mL) and pinacolborane (1.28 g, 10 mmol) were then added, and the mixture was stirred at 80 °C for 12 h. The yield was determined by GC. The internal standard was 4,4'-di-*t*-bu-tyl-2,2'-bipyridine.

Reactions of Indole, Benzothiophene and Benzofuran with Bis(pinacolato)diboron or Pinacolborane in Table 4

Borylation of indole, benzothiophene and benzofuran was carried out according to the procedure for the reactions of 2,6-dichloropyridine in Table 3. Besides octane, the other solvents shown in Table 4 were also used in the reaction. The amounts of $[IrCl(COD)]_2$, ligand **21**, and starting material are also shown in Table 4. Compounds **5a**,^[6] **5b**,^[6] and **5c**^[6] are described in the literature.

Reactions of Indole with Bis(pinacolato)diboron or Pinacolborane in the Presence of 1/2 [IrCl(COD)]₂-Bipyridyl in Table 5

Borylation of indole was carried out according to the procedure for the reactions of 2,6-dichloropyridine in Table 3. Besides ligand **21**, **6a** and **6b** were also used as a ligand. The amounts of $[IrCl(COD)]_2$, ligand, and starting material are also shown in Table 5.

Acknowledgements

The authors are grateful for the assistance of Mr. Akira Torii.

References and Notes

- a) A. Suzuki, Acc. Chem. Res. 1982, 15, 178; b) A. Suzuki, Pure Appl. Chem. 1985, 57, 1749; c) A. Suzuki, Pure Appl. Chem. 1991, 63, 419; d) A. Suzuki, Pure Appl. Chem. 1994, 66, 213; e) N. Miyaura, A. Suzuki, Chem. Rev. 1995, 95, 2457; f) V. Snieckus, Chem. Rev. 1990, 90, 879; g) D. S. Matteson, Tetrahedron 1989, 45, 1859; h) N. Miyaura, K Yamada, A. Suzuki, Tetrahedron Lett. 1979, 20, 3437; i) N. Miyaura, T. Yanagi, A. Suzuki, Synth. Commun. 1981, 11, 513; j) S. Saito, M. Sakai, N. Miyaura, Tetrahedron Lett. 1996, 37, 2993.
- [2] a) M. K. Manthy, S. G. Truscott, J. W. Truscott, J. Org. Chem. 1990, 55, 4581–4585; b) J. A. Bryant, R. C. Helge-

son, C. B. Knobler, P. P. DeGrandpre, D. J. Cram, J. Org. Chem. 1990, 55, 4622-4634; c) R. C. Helgeson, B. P. Czech, E. Chapoteau, C. R. Gebauer, K. Anaud. D. J. Cram, J. Am. Chem. Soc. 1989, 111, 6339-6350; d) Y. Yamamoto, T. Seco, H. Nemoto, J. Org. Chem. 1989, 54, 4734-4736; e) U. Schmidt, R. Meyer, V. Leitenberger, A. Lieberknecht, Angew. Chem. 1989, 101, 946-948; f) T. Iihama, J. M. Fu, M. Bourguignon, V. Snieckus, Synthesis 1989, 3, 184-188; g) M. E. Jung, Y. H. Young, Tetrahedron Lett. 1988, 29, 2517-2520.

- [3] a) A. Godard, F. Marsais, N. Ple, F. Trecourt, A. Turck, *Heterocycles* **1995**, 2, 1055–1091 and references cited therein; b) G. Queguiner, F. Marsais, V. Snieckus, J. Epsztajn, *Adv. Hetterocycl. Chem.* **1991**, 52, 187–304 and references cited therein; c) F. Marsais, A. Godard, G. Queguiner, *J. Hetetocyclic Chem.* **1989**, 26, 1589.
- [4] a) C. N. Iverson, M. R. Smith III, J. Am. Chem. Soc. 1999, 121, 7696–7697; b) J.-Y. Cho, C. N. Iverson, M. R. Smith III, J. Am. Chem. Soc. 2000, 122, 12868–12869; c) M. K. Tse, J.-Y. Cho, M. R. Smith III, Org. Lett. 2001, 3, 2831–2833; d) J.-Y. Cho, M. K. Tse, D. Holmes, R. E. Mal-

eczka Jr., M. R. Smith III, Science 2002, 295, 305–308; e) H. Chen, S. Schlecht, T. C. Semple, J. F. Hartwig, Science 2000, 287, 1995; f) H. Chen, S. Schlecht, T. C. Semple, J. F. Hartwig, Angew. Chem. Int. Ed. 1999, 38, 3391–3393; g) S. Shimada, A. S. Batsanov, J. A. K. Hward, T. B. Marder, Angew. Chem. Int. Ed. 2001, 40, 2168–2171; h) T. Ishiyama, N. Miyaura, J. Organomet. Chem. 2003, 680, 3–11 and references cited therein; i) T. Ishiyama, N. Miyaura, The Chemical Record 2004, 3, 271–280 and references cited therein; j) T. Ishiyama, J. Takagi, J. F. Hartwig, N. Miyaura, Angew. Chem. Int. Ed. 2002, 41, 3056–3058.

- [5] T. Ishiyama, J. Takagi, K. Ishida, N. Miyaura, N. R. Anastasi, J. F. Hartwig, J. Am. Chem. Soc. 2002, 124, 390–391.
- [6] J. Takagi, K. Sato, J. F. Hartwig, T. Ishiyama, N. Miyaura, *Tetrahedron Lett.* 2002, 43, 5649–5651.
- [7] T. Ishiyama, Y. Nobuta, J. F. Hartwig, N. Miyaura, *Chem. Commun.* 2003, 2824–2926.
- [8] It was reported that the product was obtained in 92% yield, when **6b** was used as a ligand instead of **6a** in run 3.^[6] Although we carried out the same reaction, the product was obtained in only 58% yield.