

# A Study of Allylboronates as Substrates in Palladium-Mediated Arylation

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Palladium-catalyzed arylation of 4,4,5,5-tetramethyl-2-(2-propenyl)-1,3,2-dioxaborolane (**1a**) in the presence of triethylamine or benzyldimethylamine gives a complex reaction mixture with 3-phenylpropene (**2**), 2-phenylpropene (**3**) and 1,3-diphenylpropene (**4**) as the major products. With tetrabutylammonium chloride and potassium carbonate in DMF, 1-phenylpropene (**5**) is the main product, and with sodium methoxide in refluxing THF, 3-phenylpropene (**2**) is the only isomer formed. Arylation with phenylmercuric salts in the presence of stoichiometric amounts of palladium salts furnishes 3-phenylpropene (**2**) and biphenyl as the main products. A possible involvement of a  $\pi$ -allylpalladium complex is discussed. Arylation of  $\pi$ -allylpalladium chloride dimer with phenylmercuric chloride provides 3-phenylpropene (**2**), 1,3-diphenylpropene (**4**) and biphenyl, in various proportions depending on the conditions.

Alkenylboronates react readily in the presence of palladium catalysts with a variety of organic halides, such as aryl halides,<sup>1,2</sup> and vinylic and acetylenic halides,<sup>2,3</sup> to give cross-coupling products. To our knowledge, no study has been reported on palladium-catalyzed reactions of organic halides with allylboronates, a class of compounds which has taken a prominent place in carbon-carbon bond-forming reactions.<sup>4</sup>

We recently reported that the outcome of the reaction of arylpalladium intermediates with allylsilanes is very dependent on the reaction conditions used.<sup>5</sup> We report here a related study on allylboronates as substrates. The aim of the present investigation was to explore the possibility of extending the very useful Heck arylation<sup>6</sup> to include allylboronates.

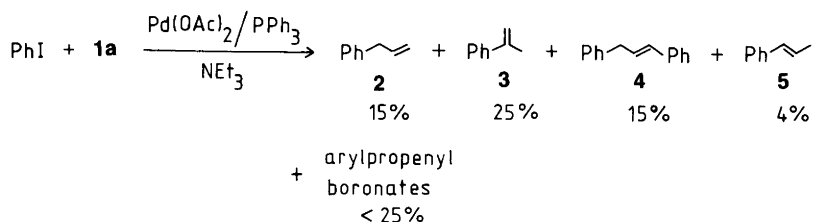
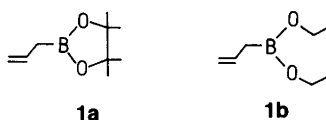
The catalytic reactions were performed with iodobenzene and benzoyl chloride as precursors for the intermediate arylpalladium halide, and alkylamines, sodium acetate, potassium carbonate or sodium methoxide were used as bases. Phenylmercuric chloride or acetate was used in the reactions that were stoichiometric in palladium.

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## Results and discussion

*Catalytic reactions.* Treatment of 4,4,5,5-tetramethyl-2-(2-propenyl)-1,3,2-dioxaborolane (**1a**) with iodobenzene for 25 h at 100 °C in acetonitrile, in the presence of palladium acetate and triphenylphosphine, using triethylamine as base gave a complex reaction mixture. The major components were 3-phenylpropene (**2**), 2-phenylpropene (**3**) and 1,3-diphenylpropene (**4**), formed in 15, 25 and 15 % yield, respectively. In addition, the mixture contained six isomeric arylated propenylboronates in a total yield of less than 25 %, according to a GLC/MS analysis. Smaller amounts of 1-phenylpropene (**5**) (4 %) and biphenyl (4 %) were also formed (eqn. 1). Conducting the reaction in the absence of solvent or at 120 °C influenced the product distribution to only a small extent. A prolonged reaction time altered neither the amount of arylated propenylboronates formed nor the distribution of phenylpropenes. Using diethyl 2-propene-1-boronate (**1b**) as olefin resulted in a similar product distribution, although the consumption of iodobenzene was slower, and less of **3** and somewhat more of **4** were formed.

The reaction of **1a** with benzoyl chloride,<sup>7</sup> and

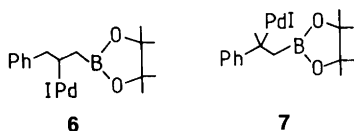


(1)

with benzyltrimethylammonium as base, in the absence of triphenylphosphine as ligand led mainly to deboronation. The deboronation was also found to be favoured by the use of Pd/C instead of Pd(OAc)<sub>2</sub>/2PPh<sub>3</sub>, with iodobenzene as reagent.

Two characteristic features are obvious from the reactions above: (i) a dominant deboronation, and (ii) a higher degree of arylation at the internal carbon of **1a** than would be expected considering that a 80/20 ratio of terminal/internal arylation is achieved with 1-hexene.<sup>6a</sup>

Compound **4** is most likely formed via arylation of **2**. The deboronation that takes place to give **2** and **3** can be explained by assuming that the reaction proceeds via elimination of IPdB< from the palladium intermediates **6** and **7**. An analogous reaction pathway for the arylation of vinylboronates in the presence of triethylamine has been suggested.<sup>8</sup>

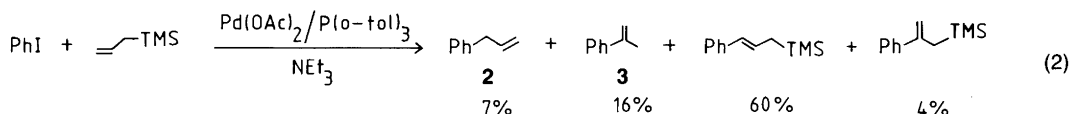


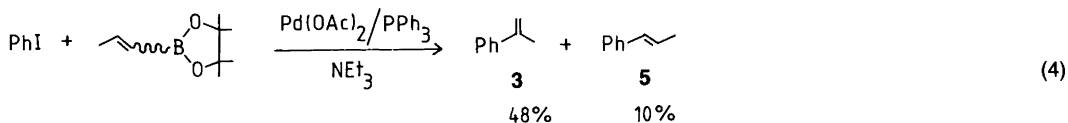
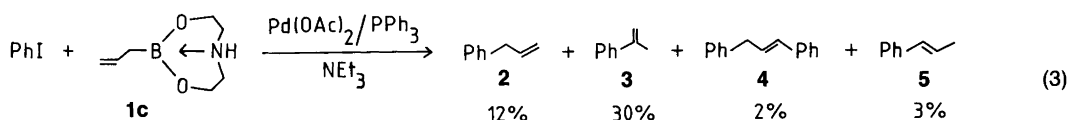
We recently reported that the desilylation which ensues in the arylation of allylsilanes<sup>5</sup> (eqn. 2) and vinylsilanes,<sup>9</sup> particularly favoured in the

absence of a phosphine ligand, could be fully suppressed by the addition of silver nitrate, which probably acts as a halide abstractor. However, we found no effect on the deboronation of **1a** due to the addition of silver nitrate.

There seem to be two reasonable explanations for the high degree of arylation at the internal carbon. First, an isomerisation of **1a** to the corresponding vinylboronate may occur, and thereafter arylation to furnish **3**. Second, a directing effect from the dioxyboron moiety, possibly by means of nitrogen-boron coordination, may account for the observed internal arylation. A reaction of 4,5,7,8-tetrahydro-2-(2-propenyl)-6H-1,3,6,2-dioxaborocine (**1c**) with iodobenzene was found to give a considerable degree (30%) of arylation at the internal carbon (eqn. 3).

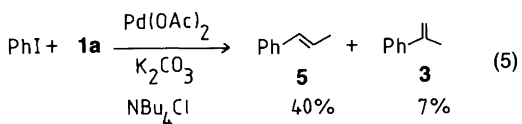
To test whether isomerisation of **1a** to vinylboronates takes place, compound **1a** was subjected to the reaction conditions used above, including the addition of triethylammonium iodide, and with iodobenzene omitted. We found that an isomerisation had indeed occurred, and that **1a** had partly been converted to a 24/10 ratio of (*Z*)-1-propenylboronate and (*E*)-1-propenylboronate after a reaction time of 25 h. To further test the isomerisation/arylation hypothesis, a mixture of the vinylboronates was subjected to Heck arylation conditions, which resulted in a 48% yield of **3** as the major product (eqn. 4). In addition,





10% of **5**, probably derived<sup>8</sup> from an arylation of the boron-substituted carbon, was found. As in the case of **1**, a smaller amount of arylated propenylboronates was observed.

It has recently been reported that tetrabutylammonium chloride and potassium carbonate in DMF is a very efficient combination for the arylation of olefins.<sup>10</sup> Under these conditions, starting with **1a** as olefin, 1-phenylpropene (**5**) was found, surprisingly, to be the major product formed (in 40% yield). Only 7% of **3**, 5% of biphenyl and traces of **2** were detected (eqn. 5).

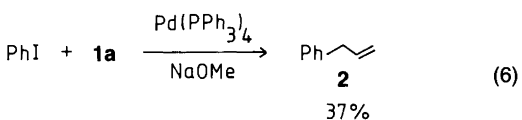


An explanation for the formation of **5** (in eqn. 5) is not obvious. The possibility that **5** could result from isomerisation of **2** seems unlikely, since in a separate experiment **2** remained intact when subjected to the same reaction conditions (tetrabutylammonium chloride, potassium carbonate and DMF). Traces of iodobenzene were added in this experiment to ensure that an active catalyst had been formed. Furthermore, the formation of **5** via arylation of propene is also unlikely since the latter is not formed from **1a** under the reaction conditions used.

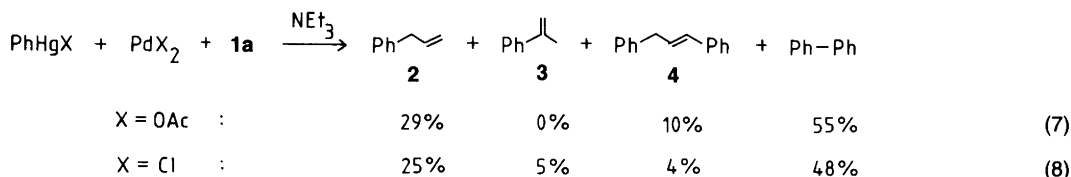
Palladium-catalyzed arylation of **1a** with sodium acetate as base in DMF at 100°C<sup>11</sup> was found to be slow, and most of the iodobenzene was recovered unchanged after two days.

The application of typical conditions used in the cross-coupling of alkenylboronates with orga-

nohalides,<sup>3</sup> i.e. sodium methoxide in THF under reflux in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub>, provided **2** (37% yield) as the only isomer (eqn. 6). No arylated propenylboronates, biphenyl or 1,3-diphenylpropene (**4**) were formed. However, in spite of the use of a two-fold excess of **1a**, the latter was consumed and 50% of the iodobenzene remained after a reaction time of 2.5 h. It is noteworthy that iodobenzene does not react with **2** to form **4** under these conditions, and we assume that **2** is formed in a reaction related to the cross-coupling of alkenylboronates.



*Stoichiometric reactions.* Reaction of **1a** with phenylmercuric acetate and a stoichiometric amount of palladium acetate in acetonitrile at 50°C with triethylamine as the base afforded 29% of 3-phenylpropene (**2**), 10% of 1,3-diphenylpropene (**4**) and 55% of biphenyl as the only products detectable by combined GLC/MS analysis after a reaction time of 2 h (eqn. 7). No 2-phenylpropene (**3**) was observed. Furthermore, arylation with phenylmercuric acetate in the presence of a large excess of **1a** (10 equiv.) resulted in 45% of **2** and 44% of biphenyl. Arylation of **1a** with phenylmercuric chloride/palladium chloride proceeded similarly, although the reaction was somewhat more sluggish, and 5% of 2-phenylpropene (**3**) was formed in addition to 25% of **2**, 4% of **4** and 48% of biphenyl (eqn. 8). The isomer 1-phenylpropene (**5**), frequently seen in



the arylation of allyl chloride,<sup>12</sup> could not be detected in any of the reaction mixtures.

While the deboronation is predominant with arylmercuric salts and **1a**, no desilylation occurs in the reaction of arylmercuric acetate with allylsilane under similar conditions.<sup>13</sup>

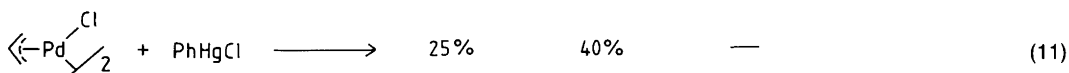
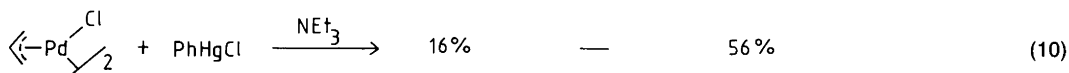
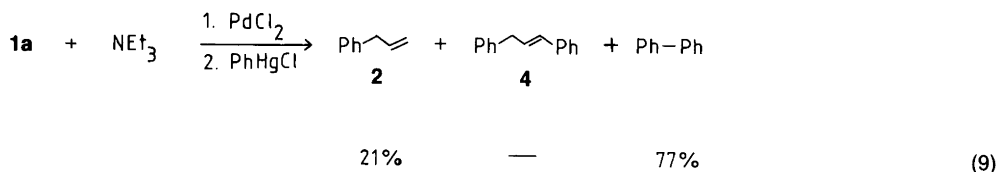
Although the formation of 3-phenylpropene (**2**) is probably analogous to the formation of **2** from allyl chloride,<sup>12</sup> i.e. involves addition of the arylpalladium salt across the double bond followed by palladium halide elimination, we cannot exclude the possibility that the arylation has occurred via a cross-coupling process.<sup>3</sup> Two alternative explanations have been considered as well: one involves an allylpalladium complex and the other an allylmercury complex.

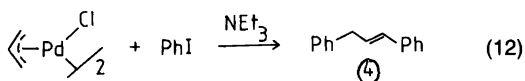
It was reported by Heck that 1-methyl- $\pi$ -allylpalladium chloride dimer reacts with diphenylmercury to produce mainly crotylbenzene and biphenyl.<sup>14</sup> The fact that biphenyl formation is predominant in the reaction of **1a** with phenylmercury compounds in the presence of palladium salts led us to examine the possible involvement of a  $\pi$ -allylpalladium complex in these reactions. We conducted an experiment in which **1a** was treated with palladium chloride in triethylamine for 4 h (**1a** was consumed after this time according to GLC), whereupon phenylmercuric chloride was added. An analysis revealed that 21 % of

**2** and 77 % of biphenyl had been formed (eqn. 9). A similar product distribution, 16 % of **2** and 56 % of biphenyl, was obtained after treatment of  $\pi$ -allylpalladium chloride dimer with phenylmercuric chloride in triethylamine (eqn. 10). It is remarkable that the absence of triethylamine suppresses biphenyl formation, and **2** and **4** are then formed in 25 % and 40 % yield, respectively (eqn. 11). It has been suggested that non-stabilized nucleophilic organometallics, such as methyl, allyl, vinyl and aryl derivatives of tin,<sup>15</sup> zinc,<sup>16</sup> aluminium<sup>17</sup> and zirconium,<sup>17,18</sup> react with  $\pi$ -allylpalladium intermediates by a mechanistic pathway involving transmetalation followed by reductive elimination of the two carbon ligands.

However, the long reaction time (4 h) required to achieve complete conversion of **1a** makes it unlikely that a  $\pi$ -allylpalladium compound is involved in the arylation of **1a** when the reaction mixture is stoichiometric in palladium (eqns. 7 and 8).

The second alternative is based on the fact that alkylboron compounds react with mercuric salts.<sup>19</sup> We assumed that **2** could, at least partly, be derived from coupling of phenylpalladium chloride with an allylmercury species, the latter being formed from **1a** and mercuric chloride (formed *in situ*). Two equivalents of **1a** were consumed after treatment with mercuric chloride for





1 h. Addition of a reaction mixture formed from phenylmercuric chloride and palladium chloride results in only 3 % of **2** and 23 % of biphenyl, indicating that this mechanism is unlikely to operate for the formation of **2** in the addition of **1a** (eqns. 7 and 8).

Furthermore, we have conducted a reaction of  $\pi$ -allylpalladium chloride dimer with iodobenzene in the presence of triethylamine for 3 days, resulting in 38 % of **4** as the major product and 7 % of **2**. No biphenyl was formed and 31 % of the iodobenzene remained unchanged (eqn. 12).

## Conclusion

Arylation of **1** under Heck conditions is accompanied by a high degree of deboronation in all of the reactions studied, and furnishes propenylbenzenes. We have discussed various reaction paths for the formation of some of these isomers and found that the distribution is considerably dependent on the reaction conditions. The deboronation is more predominant than the desilylation that occurs in the palladium-catalyzed arylation of allylsilanes. While the latter reaction provides a convenient preparation of various arylallyl and arylvinylsilanes,<sup>5</sup> the synthetic value of allylboronates, exemplified by **1**, as substrates in the Heck arylation reaction seems to be limited.

## Experimental

**Materials.** Palladium acetate, allylpalladium chloride dimer, and iodobenzene were obtained from Janssen Chimica. Palladium on charcoal (10 % Pd) was purchased from Riedel de Haën and palladium chloride from Johnson Matthey Chemicals. Triphenylphosphine and silver nitrate were obtained from Merck-Schuchardt, phenylmercuric chloride from EGA-Chemie and phenylmercuric acetate from Sigma Chemical Company. Tetrakis(triphenylphosphine)palladium was prepared by a known procedure.<sup>20</sup> 4,4,5,5-Tetramethyl-2-(2-propenyl)-1,3,2-dioxaborolane was prepared according to the method described by Hoffmann.<sup>21</sup> Diethyl 2-propene-1-boronate was also prepared by this method, using triethyl

borate instead of 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. 4,5,7,8-Tetrahydro-2-(2-propenyl)-6H-1,3,6,2-dioxazaborocine was generously supplied by Professor R. W. Hoffmann. The triethylamine was distilled and stored over 3 Å molecular sieves. THF was purified by distillation from sodium under a nitrogen atmosphere, and the other solvents were dried with appropriate molecular sieves. All other chemicals obtained from commercial sources were used as received.

**General.** <sup>1</sup>H NMR spectra of deuteriochloroform solutions of the compounds were recorded on a Varian XL 300 spectrometer. Mass spectra were obtained on a Finnigan 4021 (Data System Incos 2100) gas chromatograph-mass spectrometer. Quantitative gas chromatographic analyses were performed on a Varian 1400 instrument equipped with a 2 m column of 3 % Carbowax 20M on Supelcoport 100/120. GLC yields were determined using 2,3-dimethylnaphthalene as internal standard. All reactions in the temperature range between 100 and 120 °C were run in a 100 ml heavy-walled, thin-necked Pyrex tube fitted with a Teflon stopcock. Reactions at 50 °C were run in a round-bottomed flask with magnetic stirring.

**Reaction of 4,4,5,5-tetramethyl-2-(2-propenyl)-1,3,2-dioxaborolane (1a) (eqn. 1) or diethyl 2-propene-1-boronate (1b) or 4,4,5,5-tetramethyl-2-(1-propenyl)-1,3,2-dioxaborolane (eqn. 4) with iodobenzene and with triethylamine as base.** A mixture of 13.5 mg (0.06 mmol) of palladium acetate, 31.5 mg (0.12 mmol) of triphenylphosphine, 408 mg (2.0 mmol) of iodobenzene, 4.0 mmol of the boronate, 242 mg (2.4 mmol) of triethylamine, 52.0 mg of 2,3-dimethylnaphthalene and 30 ml of acetonitrile (when present) was placed in a Pyrex tube. The tube was flushed with nitrogen, capped, and heated in an oil bath at 100 °C for 25 h. A sample was partitioned between diethyl ether and water, and the organic phase was analyzed by GLC/MS. The reaction with **1a** at 100 or 120 °C yielded 15 % of 3-phenylpropene (**2**), 25 % of 2-phenylpropene (**3**), 15 % of 1,3-diphenylpropene (**4**), 4 % of 1-phenylpropene (**5**), 4 % of biphenyl and less than 25 % of six isomeric arylated propenylboronates. A similar product distribution was obtained in the absence of solvent, except for **2** being formed in 10 % yield. The reaction with diethyl 2-prop-

ene-1-boronate (**1b**) gave 10% of **2**, 10% of **3**, 20% of **4**, 7% of **5**, 7% of biphenyl, less than 20% of arylated propenylboronates, and 8% of recovered iodobenzene. The reaction of 4,4,5,5-tetramethyl-2-(1-propenyl)-1,3,2-dioxaborolane (eqn. 4) resulted in 48% of **3**, 10% of **5** and 17% of arylated propenylboronates.

*Reaction of 1a with palladium-on-charcoal as catalyst.* The reaction was carried out as above, employing 128 mg (0.12 mmol) of palladium-on-charcoal instead of palladium acetate and triphenylphosphine. The reaction yielded less than 10% of arylated propenylboronates.

*Reaction of 1a in the presence of silver salt.* The same procedure as in the first reaction described, except for the addition of 340 mg (2.0 mmol) of silver nitrate. The reaction mixture contained less than 20% of arylated propenylboronates, and 26% of the iodobenzene was recovered.

*Reaction of 1a with benzoyl chloride.* A mixture of 22.4 mg (0.10 mmol) of palladium acetate, 281 mg (2.0 mmol) of benzoyl chloride, 671 mg (4.0 mmol) of **1a**, 338 mg (2.5 mmol) of benzyltrimethylamine, 51.0 mg of 2,3-dimethylnaphthalene and 5 ml of *p*-xylene was placed in a round-bottomed flask equipped with a reflux condenser, a drying tube, and magnetic stirring. The flask was flushed with nitrogen and the mixture was heated under reflux in an oil bath for 24 h. A sample was partitioned between diethyl ether and water, and the organic phase was analyzed by GLC. The reaction gave less than 10% of arylated propenylboronates.

*Reaction of 4,5,7,8-tetrahydro-2-(2-propenyl)-6H-1,3,6,2-dioxazaborocine (1c) with iodobenzene and with triethylamine as base (eqn. 3).* A mixture of 13.5 mg (0.06 mmol) of palladium acetate, 31.5 mg (0.12 mmol) of triphenylphosphine, 408 mg (2.0 mmol) of iodobenzene, 619 mg (4.0 mmol) of **1c**, 242 mg (2.4 mmol) of triethylamine, 52.0 mg of 2,3-dimethylnaphthalene and 30 ml of acetonitrile was placed in a Pyrex tube. The tube was flushed with nitrogen, capped, and heated in an oil bath at 100°C for 18 h. A sample was partitioned between diethyl ether and water, and the organic phase was analyzed by GLC. The reaction yielded 12% of **2**, 30% of **3**, 2% of **4**, 3% of **5** and 7% of biphenyl.

The amount of arylated propenylboronates was not determined.

*Isomerisation of 1a to 1-propenylboronates.* A mixture of 6.7 mg (0.03 mmol) of palladium acetate, 15.7 mg (0.06 mmol) of triphenylphosphine, 336 mg (2.0 mmol) of **1a**, 229 mg (1.0 mmol) of triethylammonium iodide, 20 mg (0.2 mmol) of triethylamine, 290 mg of 2,3-dimethylnaphthalene and 15 ml of acetonitrile was placed in a Pyrex tube. The tube was flushed with nitrogen, capped, and heated in an oil bath at 100°C for 25 h. The reaction was analyzed by GLC. A yield of 15% of a 24/10 mixture of (*Z*)-1-propenylboronate and (*E*)-1-propenylboronate was obtained.

*Reaction of 1a with iodobenzene under solid-liquid phase transfer conditions (eqn. 5).* A mixture of 13.5 mg (0.06 mmol) of palladium acetate, 408 mg (2.0 mmol) of iodobenzene, 671 mg (4.0 mmol) of **1a**, 691 mg (5.0 mmol) of potassium carbonate, 555 mg (2.0 mmol) of tetrabutylammonium chloride and 54.0 mg of 2,3-dimethylnaphthalene in 30 ml of DMF was placed in a round-bottomed flask fitted with a stopper and with magnetic stirring. The flask was flushed with nitrogen and the solution was heated in an oil bath at 50°C for 35 h. A sample was partitioned between diethyl ether and water, and the organic phase was analyzed by GLC. The reaction yielded 2% of **2**, 7% of **3**, 40% of **5** and 5% of biphenyl.

*Attempted isomerisation of 3-phenylpropene (2) under solid-liquid phase transfer conditions.* A mixture of 4.7 mg (0.02 mmol) of palladium acetate, 8.0 mg (0.04 mmol) of iodobenzene, 242 mg (1.8 mmol) of potassium carbonate, 194 mg (0.70 mmol) of tetrabutylammonium chloride, 83.0 mg (0.70 mmol) of **2** and 73.0 mg of 2,3-dimethylnaphthalene in 5 ml of DMF was placed in a round-bottomed flask with magnetic stirring. The flask was flushed with nitrogen and the solution was heated in an oil bath at 50°C for 35 h. A sample was partitioned between diethyl ether and water, and the organic phase was analyzed by GLC. All the 3-phenylpropene (**2**) was recovered unchanged.

*Reaction of 1a with sodium acetate as base.* The reaction was performed as in the first reaction described, using 180 mg (2.2 mmol) of sodium

acetate in DMF instead of 242 mg (2.4 mmol) of triethylamine in acetonitrile. The reaction gave 15 % of **2**, 5 % of **3**, 8 % of **4**, 9 % of **5**, 5 % of arylated propenylboronates, and 35 % of the iodobenzene was recovered.

*Reaction of 1a with Pd(PPh<sub>3</sub>)<sub>4</sub> as catalyst and sodium methoxide as base (eqn. 6).* The experiment was carried out under a nitrogen atmosphere. In a dry 25 ml flask equipped with magnetic stirring and a reflux condenser was placed 34.6 mg (0.03 mmol) of Pd(PPh<sub>3</sub>)<sub>4</sub>. The flask was flushed with nitrogen and charged with 204 mg (1.0 mmol) of iodobenzene, 37.0 mg of 2,3-dimethylnaphthalene and 3 ml of dry THF. After the solution had been stirred for 30 min at room temperature, 302 mg (1.8 mmol) of **1a**, 1 ml of a 2M solution of sodium methoxide in methanol, and 2 ml of dry THF were added, and the reaction mixture was then heated under reflux for 2.5 h. A sample was partitioned between diethyl ether and water, and the organic phase was analyzed by GLC. The reaction yielded 37 % of **2**, and 50 % of the iodobenzene was recovered.

*Reaction of 1a with stoichiometric amounts of palladium acetate and phenylmercuric acetate, or of palladium chloride and phenylmercuric chloride (eqns. 7 and 8).* A mixture of 225 mg (1.0 mmol) of palladium acetate or 177 mg (1.0 mmol) of palladium chloride, and 337 mg (1.0 mmol) of phenylmercuric acetate or 313 mg (1.0 mmol) of phenylmercuric chloride, respectively, together with 336 mg (2.0 mmol) of **1a**, 101 mg (1.0 mmol) of triethylamine, 33.0 mg of 2,3-dimethylnaphthalene and 15 ml of acetonitrile was placed in a round-bottomed flask with magnetic stirring and stopper. The flask was flushed with nitrogen and the solution was heated in an oil bath at 50 °C for 2 h. A sample was distributed between diethyl ether and water, and the organic phase was analyzed by GLC/MS. With two equiv. of **1a**, palladium acetate, and phenylmercuric acetate, the reaction gave 29 % of **2**, 10 % of **4** and 55 % of biphenyl (eqn. 7). The addition of ten equiv. of **1a** furnished 45 % of **2** and 44 % of biphenyl. Two equiv. of **1a** with palladium chloride and phenylmercuric chloride gave 25 % of **2**, 5 % of **3**, 4 % of **4** and 48 % of biphenyl (eqn. 8).

*Reaction of 1a with palladium chloride, and subsequent reaction with phenylmercuric chloride*

(eqn. 9). A solution of 336 mg (2.0 mmol) of **1a**, 355 mg (2.0 mmol) of palladium chloride, 243 mg (2.4 mmol) of triethylamine and 15 ml of acetonitrile was placed in a round-bottomed flask with magnetic stirring and stopper. The flask was flushed with nitrogen and heated in an oil bath at 50 °C for 4 h. Half of the reaction mixture was worked up by dilution with water and subsequent extraction with three portions of chloroform. The combined extracts were dried over magnesium sulfate, and the solvent was evaporated under reduced pressure at room temperature. A 300 MHz NMR spectrum showed the presence of  $\pi$ -allylpalladium chloride dimer. To the other half of the mixture was added 313 mg (1.0 mmol) of phenylmercuric chloride and 80.0 mg of 2,3-dimethylnaphthalene in 6 ml of acetonitrile, whereupon the heating was continued at 50 °C for 2 h. A sample was partitioned between diethyl ether and water, and the organic phase was analyzed by GLC. The reaction gave 21 % of **2** and 77 % of biphenyl.

*Reaction of  $\pi$ -allylpalladium chloride dimer with phenylmercuric chloride in the presence or absence of triethylamine (eqns. 10 and 11).* A mixture of 183 mg (0.50 mmol) of  $\pi$ -allylpalladium chloride dimer, 313 mg (1.0 mmol) of phenylmercuric chloride, 111 mg (1.1 mmol) of triethylamine (when present), 30.0 mg of 2,3-dimethylnaphthalene and 13 ml of acetonitrile was placed in a round-bottomed flask with magnetic stirring and stopper. The solution was heated in an oil bath at 50 °C for 2.5 h. A sample was distributed between diethyl ether and water, and the organic phase was analyzed by GLC/MS. In the presence of triethylamine the reaction gave 16 % of **2** and 56 % of biphenyl, and in the absence of triethylamine 25 % of **2** and 40 % of **4**.

*Reaction of 1a with mercury(II) chloride, and subsequent addition of a mixture of phenylmercuric chloride and palladium chloride.* A mixture of 83.9 mg (0.50 mmol) of **1a**, 67.9 mg (0.25 mmol) of mercury(II) chloride, 45.0 mg of 2,3-dimethylnaphthalene and 2 ml of acetonitrile was placed in a round-bottomed flask with magnetic stirring and stopper. The flask was flushed with nitrogen and heated in an oil bath at 50 °C for 1 h. A solution of 78.3 mg (0.25 mmol) of phenylmercuric chloride, 44.3 mg (0.25 mmol) of palladium chloride and 28.0 mg (0.28 mmol) of

triethylamine in 3 ml of acetonitrile was added and the heating was continued at 50 °C for 2 h. A sample was partitioned between diethyl ether and water, and the organic phase was analyzed by GLC. The reaction gave 3 % of **2** and 23 % of biphenyl.

*Reaction of  $\pi$ -allylpalladium chloride dimer with iodobenzene (eqn. 12).* A mixture of 91.5 mg (0.25 mmol) of  $\pi$ -allylpalladium chloride dimer, 102 mg (0.50 mmol) of iodobenzene, 56.0 mg (0.60 mmol) of triethylamine, 51.0 mg of 2,3-dimethylnaphthalene and 6 ml of acetonitrile was placed in a round-bottomed flask with magnetic stirring and stopper. The solution was heated in an oil bath at 50 °C for 3 days. A sample was partitioned between diethyl ether and water, and the organic phase was analyzed by GLC. The reaction gave 38 % of **4**, 7 % of **2**, and 31 % of the iodobenzene was recovered.

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