Supporting Information

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Kinetic Studies Prove High Catalytic Activity of a Diene-Rhodium Complex in 1,4-Addition of Phenylboronic Acid to α,β-Unsaturated Ketones

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Supporting Information

\[
\nu = \frac{2k_1[1][\text{Rh}]_{\text{total}}}{1 + \sqrt{1 + 8K_{\text{dimer}}[\text{Rh}]_{\text{total}}}} \quad \text{(eq S1)}
\]

\[
\nu = \frac{2k_1k_2[1][2][\text{Rh}]_{\text{total}}}{(k_1[1] + k_2[2]) + \sqrt{(k_1[1] + k_2[2])^2 + 8K_{\text{dimer}}(k_2[2])^2[\text{Rh}]_{\text{total}}}} \quad \text{(eq S2)}
\]

1. Kinetic Studies for the Reaction of Phenylboronic Acid (1) to Methyl Vinyl Ketone (2a) in the Presence of \([\text{Rh(OH)(cod)}]_2\) (4) at 30 °C

The kinetic behavior was analyzed by using the method of \[\text{“excess”}\] relationship and graphical rate equation developed by Blackmond.\(^1\)\(^2\) The detailed treatments of the data and the rate law of the reactions are similar to those reported in our previous kinetic studies.\(^3\)

\[\]

Figure S1. Comparison of conversion measured by heat flow to the conversion measured by NMR analysis. Reaction conditions: $[1]_0 = 67$ mM, $[2a]_0 = 101$ mM, 1,4-dioxane = 6.0 mL, $H_2O = 0.6$ mL, $[4] = 1.30$ mM Rh, $[B(OH)_3]_0 = 533$ mM.

Common reaction conditions: 1,4-dioxane (3.0 mL), $H_2O$ (0.3 mL), $[B(OH)_3]_0 = 536$ mM at 30 °C

1.1. Same [“excess”]: proving unsteady-state phenomenon

Figure S2. Same [“excess”].
(a) $[1]_0 = 67.9$ mM, $[2a]_0 = 201$ mM, $[Rh] = 2.70$ mM Rh,
(b) $[1]_0 = 98.5$ mM, $[2a]_0 = 234$ mM, $[Rh] = 2.66$ mM Rh.

The two curves overlay exactly one another except during the induction period, which shows that neither catalyst deactivation nor product inhibition takes place during the reaction.
1.2. Different [“excess”]: order in substrates

Figure S3. Different [“excess”].
(a) [1]₀ = 67.9 mM, [2a]₀ = 201 mM, [Rh] = 2.70 mM Rh,
(c) [1]₀ = 66.0 mM, [2a]₀ = 128 mM, [Rh] = 2.60 mM Rh,
(d) [1]₀ = 85.6 mM, [2a]₀ = 200 mM, [Rh] = 2.73 mM Rh,
(e) [1]₀ = 88.6 mM, [2a]₀ = 110 mM, [Rh] = 2.73 mM Rh.

Plotting the graphical rate equation of rate versus [PhB(OH)₂(1)] for these reactions carried out at two different [“excess”] values gives first-order relationship for rate versus [PhB(OH)₂(1)]. The curves a, c, d, and e overlay, which indicates that the reaction follows zero-order kinetics in [MVK(2a)].

1.3. Order in [Rh]_{total}

Figure S4. Order in [Rh]_{total}.
(a) [1]₀ = 67.9 mM, [2a]₀ = 201 mM, [Rh] = 2.70 mM Rh,
(f) [1]₀ = 70.4 mM, [2a]₀ = 200 mM, [Rh] = 1.37 mM Rh,
(g) [1]₀ = 65.8 mM, [2a]₀ = 198 mM, [Rh] = 3.97 mM Rh,
(h) [1]₀ = 65.8 mM, [2a]₀ = 198 mM, [Rh] = 5.33 mM Rh.

The relationship is much clearer in the right graph, which is plotted rate divided by [Rh]^{0.65}_{total} versus [PhB(OH)₂(1)]. Therefore, the reaction follows 0.65-order kinetics in [Rh]_{total} at these rhodium concentrations.
1.4. Fitting the experimental data to kinetic model.

**Figure S5.** Modeling to the experimental data.

Kinetic modeling of the data to fit the proposed rate expression (eq S1) was carried out using the Excel Solver program. Error analysis of the fits was performed using SlovStat (a statistics program purchased with Excel® for Chemists, by E. Joseph Billo). Only data collected between 30-90% conversion were used in modeling because of the presence of the induction period. The data included from these reactions provide over 2000 data pairs (rate, concentration). Solid lines represent the kinetic model given in eq S1.

These data gave good fit, and the kinetic rate constant and equilibrium constant were calculated from the modeling as follows:

\[ k_1 = 1.3 \, \text{M}^{-1}\text{s}^{-1} \, (1\%) \]

\[ K_{\text{dimer}} = 3.8 \times 10^2 \, \text{M}^{-1} \, (3\%) \]

\( (R^2 = 0.996, \, \text{SSE} = 0.0016) \)
2. Kinetic Studies for the Reaction of Phenylboronic Acid (1) to Methyl Vinyl Ketone (2a) in the Presence of [Rh(OH)(cod)]₂ (4) at 50 °C. For a Quantitative Comparison between Diene System and Binap System

Common reaction conditions: 1,4-dioxane (6.0 mL), H₂O (0.6 mL), [B(OH)₃]₀ = 533 mM at 50 °C.

2.1. Same ["excess"]: proving unsteady-state phenomenon

![Graph](image1.png)

**Figure S6** Same ["excess"].
(a) [1]₀ = 33.5 mM, [2a]₀ = 67.0 mM, [Rh] = 1.34 mM Rh,
(b) [1]₀ = 67.0 mM, [2a]₀ = 101 mM, [Rh] = 1.34 mM Rh.

2.2. Different ["excess"]: order in substrates

![Graph](image2.png)

**Figure S7** Different ["excess"].
(a) [1]₀ = 33.5 mM, [2a]₀ = 67.0 mM, [Rh] = 1.34 mM Rh,
(b) [1]₀ = 33.5 mM, [2a]₀ = 101 mM, [Rh] = 1.33 mM Rh,
(d) [1]₀ = 55.5 mM, [2a]₀ = 101 mM, [Rh] = 1.36 mM Rh.
2.3. Order in [Rh]_{total}

**Figure S8.** Order in [Rh]_{total}
(a) [I]_0 = 33.5 mM, [2a]_0 = 67.0 mM, [Rh] = 1.34 mM Rh,
(e) [I]_0 = 33.5 mM, [2a]_0 = 67.0 mM, [Rh] = 2.00 mM Rh,
(f) [I]_0 = 33.5 mM, [2a]_0 = 67.0 mM, [Rh] = 2.71 mM Rh.

2.4. Fitting the experimental data to kinetic model

**Figure S9.** Kinetic modeling to the experimental data.

Determination of the statistically certain values for the diene system at 50 °C failed due to the slight catalyst deactivation and inadequate data points caused by too fast reaction rate. We assumed that the dimerization constant $K_{dimer}$ at 50 °C has the same value ($K_{dimer} = 3.8 \times 10^2$ M$^{-1}$) as at 30 °C, because the reaction order in catalyst at 50 °C was 0.65, which is the same value as at 30 °C. By substituting this $K_{dimer}$ value in equation S1, the rate constant for the transmetalation $k_1$ at 50 °C was estimated to be 6.7 M$^{-1}$s$^{-1}$ from the fitting between the experimental rate data and equation S1.
3. Kinetic Studies for the Reaction of Phenylboronic Acid (1) to 2-Cyclohexen-1-one (2b) in the Presence of [Rh(OH)(cod)]$_2$ (4) at 30 °C. For Determination of Kinetic Constants for $k_1$ and $K_{dimer}$ with 2b

3.1. Fitting the experimental data to kinetic model

![Figure S10](image-url)  
**Figure S10.** Kinetic modeling to the experimental data.  
(a) $[1]_0 = 65.7$ mM, $[2b]_0 = 198$ mM, $[\text{Rh}] = 2.64$ mM Rh,  
(b) $[1]_0 = 97.9$ mM, $[2b]_0 = 231$ mM, $[\text{Rh}] = 2.64$ mM Rh,  
(c) $[1]_0 = 65.3$ mM, $[2b]_0 = 132$ mM, $[\text{Rh}] = 2.64$ mM Rh,  
(d) $[1]_0 = 68.9$ mM, $[2b]_0 = 198$ mM, $[\text{Rh}] = 1.28$ mM Rh,  
(e) $[1]_0 = 66.6$ mM, $[2b]_0 = 198$ mM, $[\text{Rh}] = 3.92$ mM Rh,  
(f) $[1]_0 = 66.6$ mM, $[2b]_0 = 198$ mM, $[\text{Rh}] = 5.33$ mM Rh.

To extract the kinetic constants for $k_1$ and $K_{dimer}$ with 2-cyclohexenone (2b), the method described in Sec 1.4 was applied to the reaction of PhB(OH)$_2$ (1) to 2b instead of MVK (2a). Only data collected between 30-90% conversion were used in modeling because of the presence of the induction period. The data included from these reactions provide over 2400 data pairs (rate, concentration). Solid lines represent the kinetic model given in eq S1.

These data gave good fit, and the kinetic rate constant and equilibrium constant were calculated from the modeling as follows:

\[ k_1 = 1.3 \text{ M}^{-1}\text{s}^{-1} (0.7\%) \]
\[ K_{dimer} = 3.8 \times 10^2 \text{ M}^{-1} (2\%) \]
\[ (R^2 = 0.998, \text{SSE} = 0.0011) \]

These values for $k_1$ and $K_{dimer}$ with cyclohexenone 2b are identical to those with MVK 2a. Thus, the difference of the enones does not affect the transmetalation and the equilibrium between the dimer and monomer.
4. Determination of the Rate Constant for the Fast Insertion

The reactions of PhB(OH)$_2$ (1) with a smaller amount of enones 2 were carried out to observe the influence of the insertion, as described in the main text.

common reaction conditions: 1,4-dioxane (3.0 mL), H$_2$O (0.3 mL), [B(OH)$_3$]$_0$ = 536 mM at 30 °C

![Figure S11](image1.png)

*Figure S11.* Reaction heat flow as a function of time for the reaction of 1 to 2a (left) and 2b (right).

The heat flow for the 1,4-addition was obtained by subtraction of the heat flow of the hydrolysis from the total heat flow. It enabled us to plot the rate vs [PhB(OH)$_2$(1)].

![Figure S12](image2.png)

*Figure S12.* Rate vs [1] for the reactions of 1 with 2a (left) and with 2b (right). The solid lines represent the kinetic model given in eq S1.

As shown in the right graph in Figure S12, the rate constant for the insertion $k_2$ was estimated to be 16 M$^{-1}$s$^{-1}$ from the fitting between the experimental rate data and equation S1, where the values for $k_1$ and
$K_{\text{dimer}}$ in eq S2 were obtained for 2b in Sec 3.

It was difficult to obtain satisfactory data in the case of 2a due to the remarkably fast insertion of 2a compared to 2b. It is likely that it was caused by too rapid change in heat flow at the final stage of the reaction for reaction calorimetry to respond. Actually, the competition experiment of 2a (1 equiv) and 2b (1 equiv) with PhB(OH)$_2$ 1 in the presence of rhodium catalyst 4 resulted in exclusive formation of 1,4-addition product 3a which is derived form more reactive 2a (>100:1, $^1$H NMR analysis). This is in good agreement with the extremely fast insertion of MVK.