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Rhodium-Catalyzed Enantioposition Selective Hydroarylation of Divinylphosphine Oxides with Arylboroxines

Zhe Wang and Tamio Hayashi*

Abstract: Rhodium-catalyzed hydroarylation of divinylphosphine oxides (RP(O)(CH=CH_2)$_2$, **1**) with arylboroxines ((ArBO)$_3$, **2**) gave high yields of monoarylation products (RP(O)(CH=CHAr)CH_2CH_3, **3**), where one of the two vinyl groups in **1** underwent oxidative arylation and the other was reduced to ethyl. The reaction in the presence of (*R*)-DTBM-segphos/Rh proceeded with high enantioposition-selectivity to give *P*-stereogenic monoarylation products **3** with high enantioselectivity.

There have recently been considerable interests in catalytic asymmetric synthesis of chiral phosphorus compounds with a stereogenic center on the phosphorus atom.[1,2] One of the extensively studied reactions for their catalytic asymmetric synthesis is desymmetrization of symmetrically substituted phosphine oxides RP(O)*AA* where one of the two enantiotopic substituents *A* is converted into *B* leaving the other *A* unchanged (Scheme 1a). Typical examples are those by asymmetric cycloaddition of dialkynylphosphine oxides[3] and C-H activation of diarylphosphine oxides.[4] One drawback on this type of asymmetric transformation is over-reaction of RP(O)*AB* resulting in RP(O)*BB* which is achiral. Here we wish to report a new type of desymmetrization where one of the two enantiotopic substituents *A* in RP(O)*AA* is converted into *B* and the other *A* is converted into a different group *C* giving rise to a chiral product RP(O)*BC* (Scheme 1b), which was realized by rhodium-catalyzed asymmetric reaction of divinylphosphine oxides with arylboroxines.

Rhodium-catalyzed asymmetric conjugate arylation of electron deficient olefins has been recognized to be one of the most efficient and reliable methods of introducing aromatic groups with high enantioselectivity.[5] In most cases, the asymmetric conjugate arylation has been used for creation of new stereogenic centers at benzylic position by the addition to β-substituted electron-deficient olefins, typically β-substituted α,β-unsaturated carbonyl compounds. Several examples have been also reported in the reaction of β-substituted nitro- and sulfonyl-olefins.[5] To the contrary, the conjugate addition to alkenylphosphine oxides has not been well developed[6] irrespective of the importance of the enantioenriched organophosphorus compounds.[1,2] This is mainly because β-substituted alkenylphosphorus compounds, which would generate new stereogenic center at the β-position, are not very reactive towards the rhodium-catalyzed conjugate arylation. In the present desymmetrization reaction of divinylphosphine oxides, high reactivity is anticipated because the arylation takes place on the unsubstituted vinyl group.

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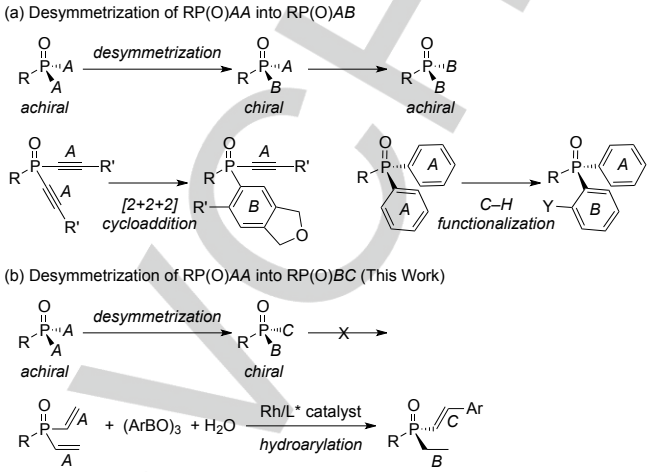
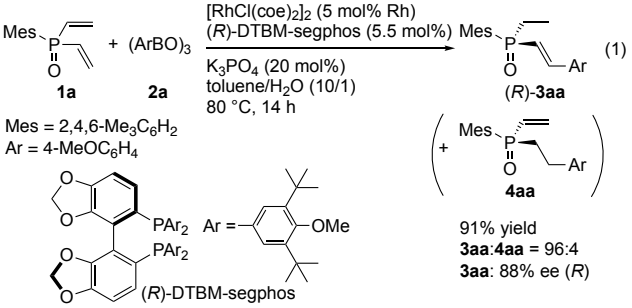
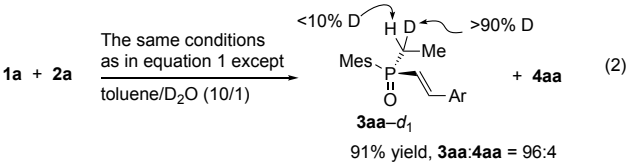


Scheme 1. Asymmetric synthesis of *P*-stereogenic phosphorus compounds by desymmetrization.

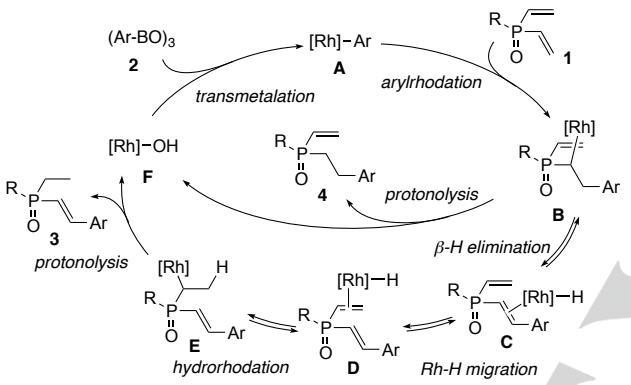
During our studies on the rhodium-catalyzed conjugate arylation of olefins activated by a phosphinyl group, we found that a new type of desymmetrization takes place in the reaction of divinylphosphine oxide **1** with arylboron reagent **2**, which selectively yields the product **3** bearing ethyl and 2-arylethenyl groups on the phosphorus atom. Thus, the reaction of mesityldivinylphosphine oxide (**1a**) with (4-$MeOC_6H_4BO)_3$ (**2a**) in the presence of K_3PO_4 and 5 mol% of a rhodium catalyst coordinated with (*R*)-DTBM-segphos[7] in toluene/H_2O (10/1) at 80 °C for 14 h gave 91% yield of hydroarylation products consisting of mesityl(2-(*E*)-arylethenyl)ethylphosphine oxide (**3aa**) and mesityl(2-arylethyl)vinylphosphine oxide (**4aa**) in a ratio of 96:4 (equation 1 and entry 1 in Table 1). The main product **3aa** was determined to be an *R* isomer[8] of 88% ee .





The reaction in D_2O instead of H_2O (equation 2) gave the deuterated product **3aa**-d_1 where one of the two diastereotopic hydrogens at the α-position of ethyl group is selectively deuterated. The product **3** is proposed to be formed through the

catalytic cycle shown in Scheme 2, which is based on the catalytic cycles reported for the rhodium-catalyzed hydroarylation of conjugate enones and related olefinic substrates.[5,9] Thus, the addition of an Ar–Rh intermediate **A** to one of the two enantiotopic vinyl groups on **1** generates alkyl-Rh species **B**. Protonolysis of **B** would give the product **4** which is a minor product under the present conditions. Instead, β-hydrogen elimination of **B** takes place to form H–Rh complex coordinated with the 2-arylethenyl group **C**. Intramolecular migration of a H–Rh species to the neighboring unsubstituted vinyl group giving another olefin complex **D**. Hydrorhodation of **D** followed by protonolysis of alkyl-rhodium intermediate **E** produces the main product **3**. The deuterium labeling study (equation 2) shows that addition of the H–Rh species to the unsubstituted vinyl group in **D** takes place selectively from one of the two diastereotopic olefin faces, indicating that the H–Rh migration is an intramolecular event.

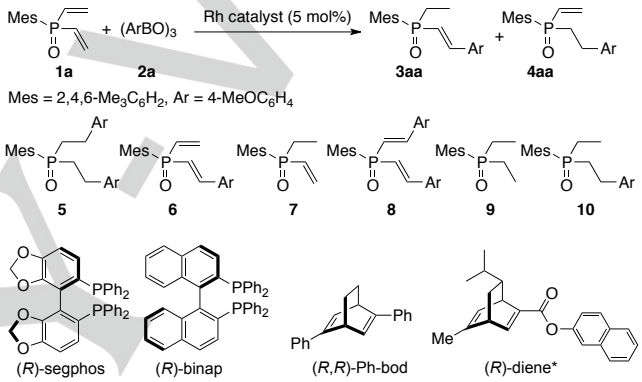


Scheme 2. Catalytic cycle for the reaction of divinylphosphine oxide **1** with arylboron reagent **2** giving product **3**.

Table 1 summarizes the results obtained at optimization of the reaction conditions. The reaction giving **3aa** also proceeded with high chemoselectivity and enantioselectivity with $ArB(OH)_2$ (Ar = 4-$MeOC_6H_4$), although the conversion of **1a** was lower (entry 2). With $ArBF_3K$, the reaction was accompanied by formation of a minor amount (7%) of bishydroarylation product **5** (entry 3). The selectivity producing **3aa** is also high with (*R*)-segphos[7] and (*R*)-binap[10] instead of (*R*)-DTBM-segphos ligand, but the enantioselectivity was much lower (entries 4 and 5). With DTBM-binap ligand, the hydroarylation reaction did not take place (entry 6). Dienes are not the ligands of choice for the present reaction. The starting divinylphosphine oxide **1a** was all consumed, but the selectivity in giving **3aa** or **4aa** was very low with Ph-bod ligand[11] (entry 7). Main products are monoarylated-diolefin **6** (33%) and reduced product **7** (37%). It is probable that **6** and **7** were formed through dissociation of the H–Rh species from **D** (in Scheme 2) followed by its addition to the starting divinylphosphine oxide **1**. In addition, small amounts of diarylated diolefin **8** and diethylphosphine oxide **9** were also formed. A similar result giving various products was observed with (*R*)-diene* ligand[12] (entry 8). The products **6**–**9** are all formed through the intermolecular H–Rh shift, and it may be concluded that the dissociation of olefin from rhodium is more facile with diene ligands than with bisphosphine ligands.

With keeping DTBM-segphos as a ligand on Rh, the effects of bases and solvents on the chemoselectivity were also studied. The selectivity in giving **3aa** was high with Cs_2CO_3 as a base instead of K_3PO_3, albeit in a slightly lower yield (entry 9). The reaction was much slower with KOH, leaving most of the starting **1a** unreacted (entry 10). The solvent system consisting of toluene and H_2O is very important for the selective formation of **3aa**. The selectivity was much lower in dioxane/H_2O (10/1), which is one of the most commonly used solvent systems for the rhodium-catalyzed asymmetric arylation reactions.[5] In addition to **3aa** and **4aa** (38% total yield), other products **6**–**10** were formed non-selectively in the dioxane/H_2O solvent (entry 11). The reaction at a lower temperature (60 °C) did not improve the enantioselectivity (entry 12).

Table 1. Rhodium-catalyzed hydroarylation of mesityldivinylphosphine oxide (**1a**) with 4-methoxyphenylboroxine (**2a**).[a]



Entry	Variations from standard conditions (equation 1)	Conv (%)[b] of **1a**	Yield (%)[c] of **3aa+4aa**	Ratio[b] of **3aa:4aa**	% ee[d] of **3aa**
1	None	>99	91	96:4	88 (*R*)
2	4-$MeOC_6H_4B(OH)_2$	87	78	93:7	87 (*R*)
3	4-$MeOC_6H_4BF_3K$	>99	83[e]	95:5	89 (*R*)
4	(*R*)-segphos	>99	92	98:2	43 (*R*)
5	(*R*)-binap	>99	86	93:7	63 (*R*)
6	(*R*)-DTBM-binap	24	<3	—	—
7	(*R*,*R*)-Ph-bod[f]	>99	15[g]	84:16	3 (*S*)
8	(*R*)-diene*[h]	>99	16[i]	81:19	8 (*R*)
9	Cs_2CO_3 instead of K_3PO_4	94	84	93:7	87 (*R*)
10	KOH instead of K_3PO_4	36	28	94:6	84 (*R*)
11	dioxane/H_2O (0.50/0.05 mL)	>99	35[j]	88:12	73 (*R*)
12	at 60 °C	93	84	97:3	88 (*R*)

[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.13 mmol, 0.40 mmol B), K_3PO_4 (0.040 mmol, 20 mol%), $[\{RhCl(coe)_2\}_2]$ (0.005 mmol, 5 mol% of Rh), (*R*)-DTBM-segphos (0.011 mmol), toluene (0.50 mL), and H_2O (0.05 mL) at 80 °C for 14 h. [b] The conversion and ratio were determined by ^{31}P and ^{1}H NMR of the crude reaction mixture. [c] Isolated yield. [d] The % ee was determined by HPLC on a chiral stationary phase column. [e] **5** (7%) was formed. [f] $[\{RhCl((R,R)\text{-Ph-bod})\}_2]$. [g] **6** (33%), **7** (37%), **8** (9%), and **9** (2%) were formed. [h] $[\{RhCl(diene^*)\}_2]$. [i] **6** (31%), **7** (38%), **8** (10%), and **9** (2%) were formed. [j] **6** (14%), **7** (27%), **8** (3%), **9** (2%), and **10** (8%) were formed.

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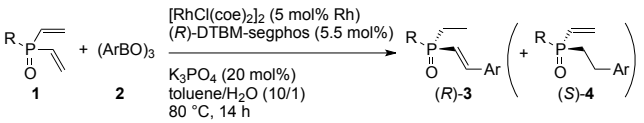
Table 2. Rhodium-catalyzed asymmetric hydroarylation of divinylphosphine oxides **1** with arylboroxines **2**.[a]

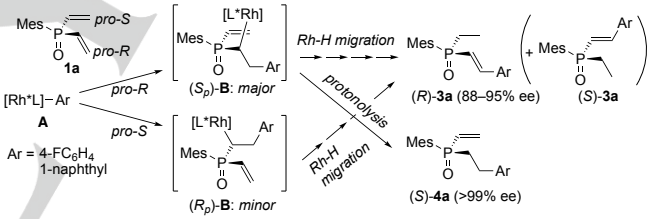


Entry	**1**: R	**2**: Ar	Yield[b] of **3**+**4**, Ratio[c] of **3**:**4**	Ee (%) of **3**[d]
1	**1a**: 2,4,6-$Me_3C_6H_2$	**2a**: 4-$MeOC_6H_4$	91%, 96:4	88 (*R*)
2	**1b**: 2,6-$Me_2C_6H_3$	**2a**	87%, 93:7	88
3	**1c**: 2-methyl-1-naphthyl	**2a**	86%, 92:8	88
4	**1d**: 1-naphthyl	**2a**	91%, 96:4	76
5	**1e**: Ph	**2a**	85%, 96:4	60
6	**1f**: tBu	**2a**	81%, >99:1	83
7	**1a**: 2,4,6-$Me_3C_6H_2$	**2b**: Ph	87%, 92:8	85
8	**1a**	**2c**: 4-FC_6H_4	87%, 81:19	88[e]
9	**1a**	**2d**: 3,5-$Me_2C_6H_3$	86%, 92:8	88
10	**1a**	**2e**: 3-$MeOC_6H_4$	87%, 88:12	84
11	**1a**	**2f**: 3-FC_6H_4	82%, 88:12	86
12[f]	**1a**	**2g**: 3-$Me_3SiC_6H_4$	71%, 85:15	88
13[f]	**1a**	**2h**: 3,4-$OCH_2OC_6H_3$	73%, 91:9	87
14	**1a**	**2i**: 2-naphthyl	88%, 98:2	86
15[f]	**1a**	**2j**: 2-MeC_6H_4	74%, 72:28	93
16[f]	**1a**	**2k**: 1-naphthyl	75%, 54:46	95[e]
17	**1a**	**2l**: 2-FC_6H_4	80%, 19:81	94[e]

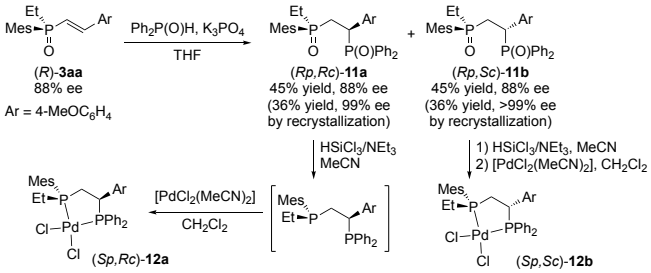
[a] Reaction conditions: **1** (0.20 mmol), arylboroxine **2** (0.13 mmol, 0.40 mmol of B), K_3PO_4 (0.04 mmol), [{RhCl(coe)$_2$}$_2$] (0.005 mmol, 5 mol% of Rh), (*R*)-DTBM-segphos (0.011 mmol), toluene (0.50 mL), and H_2O (0.05 mL) at 80 °C for 14 h. [b] Isolated yield. [c] The ratio was determined by ^{31}P NMR of the crude reaction mixture. [d] The % ee was determined by HPLC on chiral stationary phase columns. [e] The ee of **4ac**, **4ak**, and **4al** are 99.9%, 99.9%, and 99.8%, respectively. [f] K_3PO_4 (0.10 mmol).

The condition optimized for the reaction shown in equation 1 was applied to several other divinylphosphine oxides **1** and arylboroxines **2**. The results are summarized in Table 2. High enantioselectivity was observed in the reactions of arylboroxine **2a** with divinylphosphine oxides **1** bearing a sterically demanding substituent. Those substituted with 2,6-dimethylphenyl (**1b**) and 2-methyl-1-naphthyl (**1c**) gave the corresponding hydroarylation products with 88% ee in high yields (entries 2 and 3). The enantioselectivity was lower with less bulky aromatic groups, 1-naphthyl (76% ee) and unsubstituted phenyl (60% ee) (entries 4 and 5). *Tert*-butyl group can be also used as the substituent on divinylphosphine oxide. The chemoselectivity giving product **3** is very high, although the enantioselectivity is somewhat lower (83% ee) (entry 6). The reaction of divinylphosphine oxide **1a** with arylboroxines where the aryl groups are para- or meta-substituted phenyls all gave the corresponding arylation products **3** in high yields with the **3**:**4** selectivity higher than 8:2 irrespective of the electronic characters of the substituents. The para- and meta-substituents did not have a significant effect on the enantioselectivity, the % ee of **3** being kept as 84–88% (entries 7–14). The reaction with ortho-substituted phenyboron reagents **2j**, **2k**, and **2l**, proceeded with higher enantioselectivity to give the corresponding arylation products **3** with 93–95% ee, while the selectivity in giving **3** over **4** was lower (entries 15–17). The ratio of **3**:**4** was about 1:1 with 1-naphthyl, and it was reversed with 2-FC_6H_4 to give **4** as a main product (**3**:**4** = 19:81).

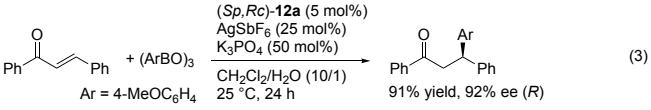
Interestingly, the absolute configuration of the side products **4** is *S*[13] with very high enantiomeric purity (>99% ee), which was determined for **4ac** and **4ak** (entries 8 and 16). The difference of % ee between **3** and **4** indicates that a kinetic resolution took place in the catalytic cycle (Scheme 3). Thus, the Ar-Rh intermediate **A** coordinated with (*R*)-DTBM-segphos ligand adds mainly to *pro-R* vinyl group of divinylphosphine oxide **1a** to generate alkyl-Rh species (*Sp*)-**B** as a major diastereomeric intermediate. The sequence of reactions involving β-hydrogen elimination followed by Rh-H migration gives the product **3a** with *R* configuration. The intermediate (*Sp*)-**B** also undergoes protonolysis to give **4a** with *S* configuration, the selectivity in giving **3a** or **4a** being dependent on the Ar group. On the other hand, the other alkyl-Rh intermediate (*Rp*)-**B**, which is generated as a minor diastereoisomer, does not undergo the protonolysis giving (*R*)-**4a** but exclusively undergoes the reactions starting with β-hydrogen elimination to give (*S*)-**3a**, resulting in a high (>99) % ee of (*S*)-**4a**. It follows that the enantiomeric purity of **3a** is lower than the selectivity at the arylrhodation forming intermediate **B** and that of **4a** is higher.



Scheme 3. Kinetic resolution of the aryl-rhodium intermediates **B** to give the product (*S*)-**4a** of very high % ee.



Scheme 4. Conversion of the hydroarylation product (*R*)-**3aa** into chiral bisphosphines with both *P* and *C* stereogenic centers.



(3)

Taking advantage of the structural features of the arylation product **3**, that is, the double bond in **3** is activated by phosphine oxide for Michael addition, (*R*)-**3aa** (88% ee) was subjected to the conjugate addition of diphenylphosphine oxide[14] (Scheme

4). The addition proceeded smoothly without racemization to give a mixture (1/1) of two diastereoisomers **11a** and **11b** in high yields. Separation of the isomers followed by enhancement of the enantiomeric purity by recrystallization led to (R_p,R_c)-**11a**[15] (99% ee) and (R_p,S_c)-**11b** (>99% ee). Chiral bisphosphines obtained by reduction of the phosphine oxides with $HSiCl_3$[16] were isolated as their palladium complexes **12**. The bisphosphines are unique in that they have both *P*- and *C*-stereogenic centers.[17] The palladium complex (S_p,R_c)-**12a**[15] demonstrated its high catalytic activity and enantioselectivity in the asymmetric conjugate addition of arylboroxin[18] (eq 3).

Acknowledgements

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Keywords: desymmetrization • *P*-stereogenic center • asymmetric hydroarylation • chiral phosphine • rhodium catalyst

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Rhodium-Catalyzed Enantioposition Selective Hydroarylation of Divinylphosphine Oxides with Arylboroxines

Layout 2:

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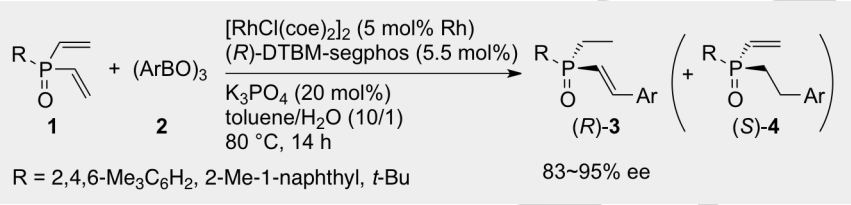

Rhodium-catalyzed hydroarylation of divinylphosphine oxides ($RP(O)(CH=CH_2)_2$, **1**) with arylboroxines ($(ArBO)_3$, **2**) gave high yields of monoarylation products ($RP(O)(CH=CHAr)CH_2CH_3$, **3**), where one of the two vinyl groups in **1** underwent oxidative arylation and the other was reduced to ethyl. The reaction in the presence of (*R*)-DTBM-segphos/Rh proceeded with high enantioposition-selectivity to give *P*-stereogenic monoarylation products **3** with high enantioselectivity.

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