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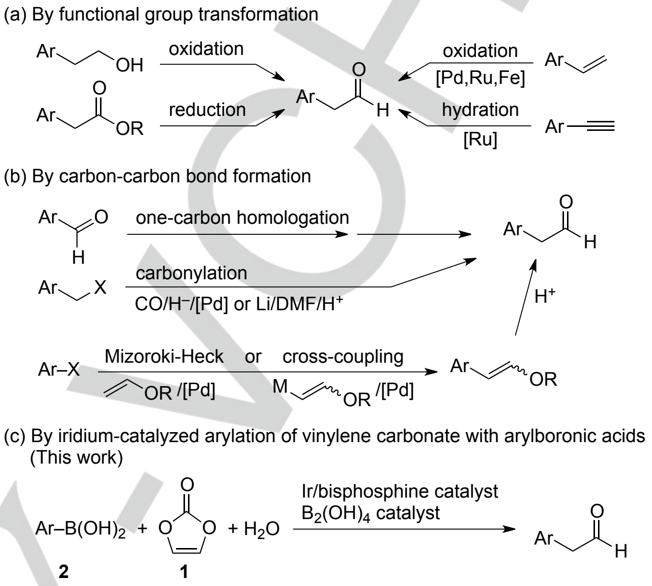
Synthesis of Arylacetaldehydes by Iridium-Catalyzed Arylation of Vinylene Carbonate with Arylboronic Acids[**]

Zhe Wang, Fei Xue, and Tamio Hayashi*

Abstract: One-step synthesis of arylacetaldehydes by carbon-carbon bond formation between formylmethyl and aryl groups has been realized by the reaction of vinylene carbonate with arylboronic acids in the presence of an iridium/bisphosphine catalyst and a catalytic amount of tetrahydroxydiboron.

There has been a considerable interest in synthesis of arylacetaldehydes ($ArCH_2CHO$) because of their valuable synthetic utility.[1] Approaches to the arylacetaldehydes[2] are classified into two reaction types: One is functional group transformation of compounds bearing Ar-C-C carbon skeleton (Type 1, Scheme 1a), and the other is carbon-carbon bond formation by introduction of a formyl group into arylmethyl unit or that of a formylmethyl group (or its synthetic equivalent) into aryl unit constructing the Ar-C-C skeleton (Type 2, Scheme 1b). Selective partial oxidation of alcohols[3] and partial reduction of carboxylic acids[4] are common routes to arylacetaldehydes in Type 1. Oxidation of styrene derivatives[5,6] and hydration of arylacetylenes,[7,8] which are catalyzed by late transition metals, have been also reported to produce arylacetaldehydes. Of Type 2 reactions, one-carbon homologation of aromatic aldehydes[9] and formylation of benzylic halides[10] are typical examples of one-carbon extension route. As for their synthesis through extension of two carbons, Mizoroki-Heck type reaction of aryl halides with vinyl alkyl ethers catalyzed by a palladium complex giving β-alkoxystyrenes has been most extensively studied where the efforts for higher linear/branch selectivity have been made mainly by modifying the alky moiety of vinyl alkyl ethers and screening the solvents.[11] Palladium-catalyzed cross-coupling of aryl halides with β-alkoxyvinylmetals is another way to produce β-alkoxystyrenes by two carbons extension.[12] These routes through β-alkoxystyrenes require one more step, acidic hydrolysis, before reaching the target arylacetaldehydes. We herein report a new one-step reaction pathway where the reaction of arylboronic acids ($ArB(OH)_2$ **2**) with vinylene carbonate[13] (**1**) directly produces the arylacetaldehydes in the presence of a catalytic amount of a bisphosphine/iridium complex and tetrahydroxydiboron ($B_2(OH)_4$) (Scheme 1c). Because of the ready availability of the starting materials including vinylene carbonate (**1**) and mild reaction conditions, the present new reaction provides an alternative route to the synthesis of arylacetaldehydes.



Scheme 1. Synthesis of arylacetaldehydes.

During our studies on the rhodium- and iridium-catalyzed addition of aromatic metal reagents to carbon–carbon multiple bonds,[14,15] we envisioned that vinylene carbonate (**1**) is an interesting compound which would participate in the arylation reaction as a two-carbon extension unit with high functionality.[13] After extensive screening it was found that the vinylene carbonate realizes formylmethylation of arylboronic acids giving arylacetaldehydes in the presence of an iridium catalyst. Thus, the reaction of vinylene carbonate (**1**) with 5 equiv of 3,4-$(OCH_2O)C_6H_3B(OH)_2$ (**2a**) in the presence of tetrahydroxydiboron ($B_2(OH)_4$, 5.5 mol%) and an iridium catalyst generated in situ from $[IrOMe(cod)]_2$ (5.0 mol% Ir) and an electron-rich bisphosphine ligand dppp-OMe (5.5 mol%) in $ClCH_2CH_2Cl/H_2O$ (10:1) at 90 °C for 1 h gave the arylacetaldehyde **3a** in 75% yield (entry 1 in Table 1).

Table 1 summarizes the results obtained at optimization of the reaction conditions. The presence of $B_2(OH)_4$[16,17] in the catalytic amount (5.5 mol%) is essential for the production of arylacetaldehyde. Without $B_2(OH)_4$ under otherwise the same conditions, the yield of **3a** is merely 19% with a low conversion of vinylene carbonate (**1**) (entry 2). The role of $B_2(OH)_4$ in the present reaction is proposed to accelerate the transmetalation of aryl group from boron to iridium in the catalytic cycle (*vide infra*). A more amount (25 mol%) of $B_2(OH)_4$ did not improve the yield of **3a** (entry 3). Bis(pinacolato)diboron ($B_2(pin)_2$) was not effective for the present reaction, the yield of **3a** being essentially the same as that without $B_2(OH)_4$ (entry 4). The phosphine ligand on iridium is crucial for the high yield of aldehyde **3a**. The highest yield was obtained with the electron-rich dppp ligand (dppp-OMe) (entry 1). Although the difference is not very large, the yield is lower with regular dppp and with the electron-poor dppp ligand (dppp-CF_3) (entries 5 and 6). The

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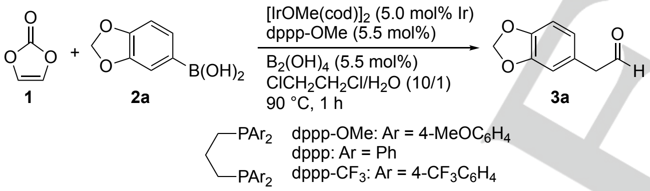
dppp skeleton where two phosphino groups are connected through trimethylene backbone is better than other bisphosphine ligands. For examples, the yields of **3a** were much lower with dppe, dppb, and PPh_3 (entries 7, 8 and 9). The solvent system consisting of 1,2-dichloroethane and a protic solvent is important for the present reaction. Use of toluene or 1,4-dioxane as a main component of solvent greatly lowered the yields of **3a**. (entries 10 and 11). Water or methanol is a protic solvent of choice, a mix solvent of 1,2-dichloroethane/methanol giving **3a** in the same yield as the standard condition using water (entry 12). The yield was lower with t-butyl alcohol as a protic solvent (entry 13). The difference between conversion of **1** (>99%) and yield of **3a** (75%) is ascribed to self decomposition of **1** giving a mixture of polymeric compounds under the reaction conditions. The reaction at a lower temperature (70 °C), which was performed to retard the decomposition, did not improve the yield (entry 14). The use of a large excess (5 equiv) of arylboronic acid under the standard condition is due to its hydrolysis which is a main side reaction also catalyzed by the iridium complex. The amount of arylboronic acid **2a** can be decreased to 3 or 2 equiv with a slight loss of the yield of **3a** (entries 15 and 16). The yield was much lower with $ArBF_3K$ (entry 17). Interestingly, the present reaction is not catalyzed by a rhodium complex which is analogous to the iridium complex used here. In the presence or absence of $B_2(OH)_4$, a rhodium complex generated from $[Rh(OH)(coe)_2]_2$ and dppp-OMe did not produce **3a** at all (entries 18 and 19).

Table 1. Iridium-catalyzed arylation of vinylene carbonate (**1**) with 3,4-(methylenedioxy)phenylboronic acid (**2a**).[a]

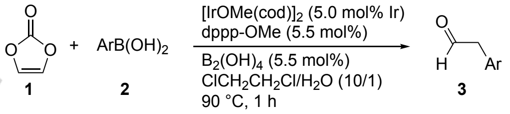


Entry	Variations from standard conditions	Conv (%)[b] of **1**	Yield (%)[b] of **3a**
1	None	>99	76 (75)
2	without $B_2(OH)_4$	40	19
3	$B_2(OH)_4$ (25 mol%)	98	60
4	B_2pin_2[c] (5.5 mol%)	48	23
5	dppp	>99	67 (67)
6	dppp-CF3	98	63
7	dppe[d]	31	2
8	dppb[e]	60	23
9	PPh_3 (0.044 mmol)	80	<2
10	toluene/H_2O (2.0/0.2 mL)	64	16
11	dioxane/H_2O (2.0/0.2 mL)	48	6
12	$ClCH_2CH_2Cl$/MeOH (2.0/0.2 mL)	>99	75 (75)
13	$ClCH_2CH_2Cl$/*t*BuOH (2.0/0.2 mL)	90	56
14	at 70 °C	93	64
15	$ArB(OH)_2$ (3 equiv)	>99	68
16	$ArB(OH)_2$ (2 equiv)	92	62
17	$ArBF_3K$ (5 equiv)	85	7
18	$[Rh(OH)(coe)_2]_2$/dppp-OMe with $B_2(OH)_4$	27	<1
19	$[Rh(OH)(coe)_2]_2$/dppp-OMe without $B_2(OH)_4$	26	<1

[a] Reaction conditions: **1** (0.40 mmol), **2a** (2.0 mmol), $B_2(OH)_4$ (0.022 mmol, 5.5 mol%), $[\{IrOMe(cod)\}_2]$ (0.010 mmol, 5.0 mol% of Ir), dppp-OMe (0.022 mmol), $ClCH_2CH_2Cl$ (2.0 mL), and H_2O (0.2 mL) at 90 °C for 1 h. [b] The conversion and yield were determined by ^1H NMR of the crude reaction mixture using hexamethylbenzene as an internal standard. Isolated yields are shown in parentheses. [c] B_2pin_2, bis(pinacolato)diboron. [d] dppe, 1,2-bis(diphenylphosphino)ethane. [e] dppb, 1,4-bis(diphenylphosphino)butane.

The scope of the arylboronic acids **2** for the iridium-catalyzed formylmethylation with vinylene carbonate (**1**) is summarized in Table 2. The reaction of several arylboronic acids with *para*- or *meta*-substituted aryl groups (**2a**-**2k**) all gave the corresponding arylation products **3** in the yields higher than 70% with a few exceptions (entries 1-11). The yields are not obviously dependent on the electronic properties of the substituents. The present reaction is also applicable to 1-naphthylboronic acid (**2l**), where the sterically hindered *ortho*-substituted aryl group participated in the reaction (entry 12). It is noted that the yield was lower for unsubstituted phenylboronic acid (**2m**), although it was improved to some extent by use of dppp ligand in place of dppp-OMe in this particular case (entry 13).[18]

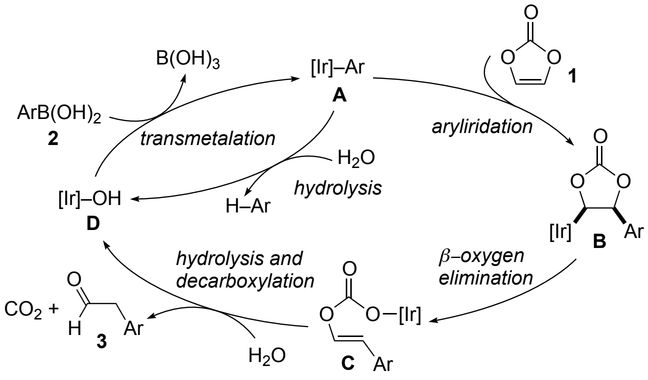
Table 2. Iridium-catalyzed arylation of vinylene carbonate (**1**) with arylboronic acids (**2**) producing arylacetaldehydes **3**.[a]



Entry	**2**: Ar	Yield [%][b] of **3**
1	**2a**: 3,4-$(OCH_2O)C_6H_3$	76 (75)
2	**2b**: 4-$MeOC_6H_4$	75 (72)
3	**2c**: 4-MeC_6H_4	75 (72)
4	**2d**: 4-BrC_6H_4	73 (70)
5	**2e**: 3-$MeOC_6H_4$	73 (70)
6[c]	**2f**: 3-MeC_6H_4	74 (72)
7[c]	**2g**: 3,5-$Me_2C_6H_3$	73 (73)
8	**2h**: 3-$Me_3SiC_6H_4$	83 (80)
9[c]	**2i**: 3-FC_6H_4	74 (70)
10	**2j**: 3-BrC_6H_4	65 (64)
11[d]	**2k**: 2-naphthyl	73 (72)
12[e]	**2l**: 1-naphthyl	68 (68)
13[c]	**2m**: Ph	57(53), 66 (63)[f]

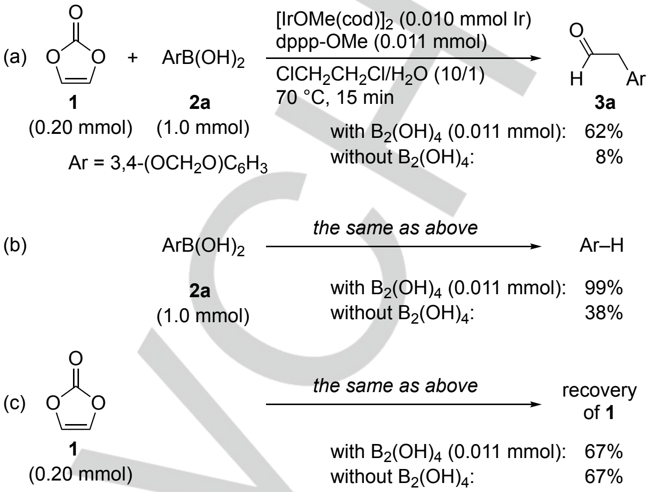
[a] Reaction conditions: **1** (0.40 mmol), arylboronic acids **2** (2.0 mmol), $B_2(OH)_4$ (0.022 mmol), $[\{IrOMe(cod)\}_2]$ (0.010 mmol, 5.0 mol% of Ir), dppp-OMe (0.022 mmol), $ClCH_2CH_2Cl$ (2.0 mL), and H_2O (0.2 mL) at 90 °C for 1 h. [b] Yields were determined by ^1H NMR of the crude reaction mixture using hexamethylbenzene as an internal standard. Isolated yields are shown in parentheses. [c] $B_2(OH)_4$ (0.044 mmol). [d] At 80 °C, $B_2(OH)_4$ (0.044 mmol). [e] At 80 °C, $B_2(OH)_4$ (0.10 mmol). [f] Ligand is dppp instead of dppp-OMe.

The catalytic cycle of the present iridium-catalyzed arylation of vinylene carbonate (**1**) with arylboronic acid **2** giving arylacetaldehyde **3** is proposed as shown in Scheme 2. Thus, an aryl-iridium species [Ir]–Ar **A**, which is generated by transmetalation of Ar group from boron to iridium,[15d,15f] adds to vinylene carbonate (**1**) to give an alkyl-iridium intermediate **B**. Under the present conditions, **B** undergoes β-oxygen elimination to form iridium carbonate of 2-arylethenyl alcohol **C**. Subsequent hydrolysis and decarboxylation followed by the keto-enol tautomerization produces arylacetaldehyde **3** and regenerates [Ir]–OH species **D**.



Scheme 2. Proposed catalytic cycle for the reaction of vinylene carbonate (**1**) with arylboronic acid **2** giving arylacetaldehyde **3**.

Several experiments were conducted to gain an insight into the role of $B_2(OH)_4$[16,17,19,20] as an additive in a catalytic amount in the present iridium-catalyzed reaction (Scheme 3). The reaction of vinylene carbonate (**1**) with arylboronic acid **2a** was repeated both with and without $B_2(OH)_4$ at 70 °C for 15 min. The lower temperature and shorter reaction time than those for standard condition is to make their difference more obvious. As shown in Scheme 3a, the reaction with $B_2(OH)_4$ gave 62% of arylacetaldehyde **3a**, while the reaction without $B_2(OH)_4$ gave merely 8% of **3a**. The big difference is as expected from the results obtained at screening of the reaction conditions (entries 1 vs 2, Table 1). In the absence of vinylene carbonate (**1**), arylboronic acid **2a** was subjected to the reaction conditions for the iridium-catalyzed arylation of **1** (Scheme 3b). It is interesting to observe that all the boronic acid **2a** was hydrolyzed to give arene Ar–H with $B_2(OH)_4$ as an additive while the hydrolysis is much slower in the absence of $B_2(OH)_4$. It was also confirmed that the hydrolysis of boronic acid **2a** does not take place in the absence of the iridium catalyst irrespective of with or without $B_2(OH)_4$. These results clearly indicate that $B_2(OH)_4$ promotes the iridium-catalyzed protodeboronation of $ArB(OH)_2$ giving Ar–H. It follows that transmetalation and/or hydrolysis steps in the catalytic cycle (**D**→**A** and/or **A**→**D** in Scheme 2) are promoted by $B_2(OH)_4$. Considering that the high yield of **3a** is observed with $B_2(OH)_4$, the promotion of hydrolysis step by $B_2(OH)_4$ is less likely. It would be reasonable to understand that $B_2(OH)_4$ promotes the transmetalation step, although its mechanism remains to be clarified. The decomposition of **1** giving a mixture of polymers is not related to the with or without $B_2(OH)_4$ issue, which was shown by the reactions where **1** was exposed to the reaction conditions in the absence of arylboronic acid **2a** (Scheme 3c). The recovery yield of **1** is the same with and without $B_2(OH)_4$.



Scheme 3. Effects of $B_2(OH)_4$ as an additive on the present iridium-catalyzed arylation of vinylene carbonate (**1**) with arylboronic acid **2a**.

In conclusion, we have developed a new synthetic route to arylacetaldehydes, which was realized by the arylation of vinylene carbonate with arylboronic acids in the presence of an iridium/bisphosphine catalyst. In addition to its synthetic utility, the present reaction is interesting as a new type of iridium-catalyzed carbon-carbon bond forming reaction which is promoted by tetrahydroxydiboron as a cocatalyst.

Keywords: arylation • arylacetaldehyde• iridium catalysis • vinylene carbonate • arylboronic acid

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[19] For recent examples on its use as a reducing reagent, see: a) D. Pi, H. Zhou, Y. Zhou, Q. Liu, R. He, G. Shen, Y. Uozumi, *Tetrahedron* **2018**, *74*, 2121; b) D. Chen, Y. Zhou, H. Zhou, S. Liu, Q. Liu, K. Zhang, Y. Uozumi, *Synlett* **2018**, *29*, 1765; c) W. Kong, Q. Wang, J. Zhu, *Angew. Chem. Int. Ed.* **2017**, *56*, 3987; *Angew. Chem.* **2017**, *129*, 4045; d) S. P. Cummings, T.-N. Le, G. E. Fernandez, L. G. Quiambao, B. J. Stokes, *J. Am. Chem. Soc.* **2016**, *138*, 6107; e) Q. Xuan, Q. Song, *Org. Lett.* **2016**, *18*, 4250; f) V. Gurram, H. K. Akula, R. Garlapati, N. Pottabathini, M. K. Lakshman, *Adv. Synth. Catal.* **2015**, *357*, 451; g) A. T. Londregan, D. W. Piotrowski, J. Xiao, *Synlett* **2013**, *24*, 2695.

[20] For recent examples on its use as a borylating reagent, see: a) J.-J. Zhang, X.-H. Duan, Y. Wu, J.-C. Yang, L.-N. Guo, *Chem. Sci.* **2019**, *10*, 161; b) J. Zhao, S. J. T. Jonker, D. N. Meyer, G. Schulz, C. D. Tran, L. Eriksson, K. J. Szabó, *Chem. Sci.* **2018**, *9*, 3305; c) A. Zernickel, W. Du, S. A. Ghorpade, D. N. Sawant, A. A. Makki, N. Sekar, J. Eppinger, *J. Org. Chem.* **2018**, *83*, 1842; d) D. Hu, L. Wang, P. Li, *Org. Lett.* **2017**, *19*, 2770; e) A. M. Mfuh, J. D. Doyle, B. Chhetri, H. D. Arman, O. V. Larionov, *J. Am. Chem. Soc.* **2016**, *138*, 2985; f) K. Chen, S. Zhang, P. He, P. Li, *Chem. Sci.* **2016**, *7*, 3676; g) J. Magano, S. Monfette, *ACS Catal.* **2015**, *5*, 3120; h) W. Erb, M. Albini, J. Rouden, J. Blanchet, *J. Org. Chem.* **2014**, *79*, 10568.

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Page No. – Page No.

Synthesis of Arylacetaldehydes by Iridium-Catalyzed Arylation of Vinylene Carbonate with Arylboronic Acids

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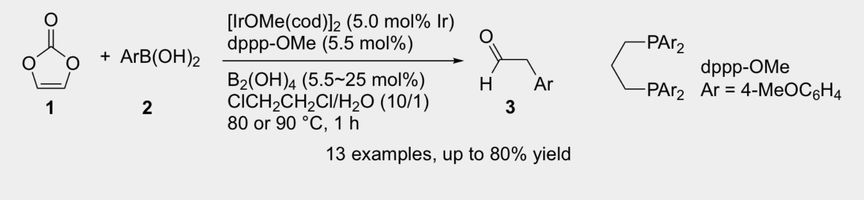

Direct synthesis of arylacetaldehyde through carbon-carbone bond forming reaction has been realized by Iridium-catalyzed hydroarylation of readily available vinylene carbonate (VC) with arylboronic acids.

*Zhe Wang, Fei Xue, and Tamio Hayashi**

Page No. – Page No.

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