Organic & Biomolecular Chemistry

Accepted Manuscript

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DOI: 10.1039/C8OB01997E

Journal Name

ARTICLE

Dirhodium(II)/P(*t*-Bu)$_3$ Catalyzed Tandem Reaction of α,β-Unsaturated Aldehyde with Arylboronic Acids

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

The phosphine ligated dirhodium(II) acetate is advocated as a catalyst for the synthesis of aryl alkyl ketones by the tandem reaction of α,β-unsaturated aromatic or aliphatic aldehydes with arylboronic acids. This tandem procedure included arylation followed by isomerization reaction. This method exhibits good functional group tolerance and has a broad substrate scope. With the conjugated aldehydes, the one-step synthesis of γ,δ-unsaturated ketones was realized through this reaction. It is noteworthy that the length of Rh-P bond is an important factor affecting catalytic reactions. The comparative analysis of the crystal structures of axially alkylphosphane and arylphosphane ligated dirhodium(II) acetate revealed that the shorter Rh-P bond length favors the isomerization process as compared to the longer one. In addition, dirhodium(II) compound can be recovered after completion of the reaction.

Introduction

A high degree of potential cooperativity and electronic communication between the metal-metal covalent bonds lead to the evidence that multi-metallic synergism contributes to the design of new catalysts for their potential use in organic syntheses. To comprehend the functional approach of these catalysts, it is important to understand the multinuclear reaction pathways and to develop the well-defined multinuclear platforms. Dirhodium(II) complexes (Rh_2(II)) possess a dimeric "paddlewheel" structure surrounded by Rh-Rh single bond with four bridging ligands and two axial ligands and hence act as an efficient catalyst for the generation of carbene and nitrene species.[1,2] Although this high symmetrical structure of Rh_2(II) provides two equivalent axial sites as the catalytically active sites, only one of the two rhodium atoms acts as an efficient catalytic site at a time during the reaction.[1,3] Based on this observation, the simple and efficient strategy to enhance the rate and/or selectivity of Rh_2(II)-catalyzed reactions was developed.

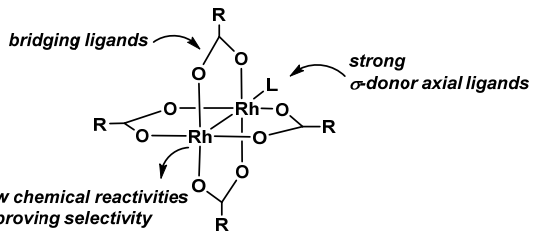

Fig 1. Structure of dirhodium(II) carboxylate catalysts.

By introducing a σ-donating ligand coordinated axially to one of the Rh atoms, the electrophilicity of the other Rh atom was found affected across the Rh-Rh bond (Fig 1).[4] We previously reported the efficient preparation of axially ligated $Rh_2(OAc)_4(P(t\text{-}Bu)_3)_2$ complexes with unusually long Rh-P σ-bond length and achieved their excellent catalytic performance in arylation reactions using arylboronic acids and isatin derivatives.[5] As part of our ongoing studies on a combined approach of alkyl phosphine ligands (PR_3) and Rh_2(II) along with their applicative aspects, the present paper describes the one-pot tandem reaction of α,β-unsaturated aldehyde with arylboronic acids to easily prepare the aryl alkyl ketones in good yields. The resulting aryl-alkyl products are the versatile building blocks for the synthesis of bioactive scaffolds, drugs and natural products.[6] General methods for the synthesis of aryl alkyl ketones include Friedel-Crafts acylation reaction,[7] benzylic oxidation of alkylbenzenes,[8] and the addition of organometallic reagents to benzaldehyde.[9] However, all these methods suffer various disadvantages such as relatively harsh reaction conditions, low yields, limited substrate scope, lack of atomic economy, and complicated workup and purification procedure. Zou *et al.* previously reported the synthesis of aryl alkyl ketones using cinnamaldehyde derivatives with arylboronic acids catalyzed by rhodium complex.[10] In their procedure, only seven examples were reported and the substrates were limited to the use of cinnamaldehyde derivatives only. Herein, we developed the catalytic system that worked very well not only with α,β-unsaturated aromatic but also with the α,β-unsaturated aliphatic aldehydes. The scope of the reaction was much enlarged as other conjugated aldehydes like 2,4-hexadienal was also used. With the conjugated aldehydes, the one-step synthesis of γ,δ-unsaturated ketones were realized. As a key intermediate used in the preparation of heterocyclic compounds, it may take multiple steps to synthesize in the previous reports.[11] In addition, the noble $Rh_2(OAc)_4$ was recovered efficiently after the completion of the reaction.

Results and discussion

Our studies began with the arylation reaction between cinnamaldehyde **1a** and arylboronic acid **2a**. Gois and coworkers

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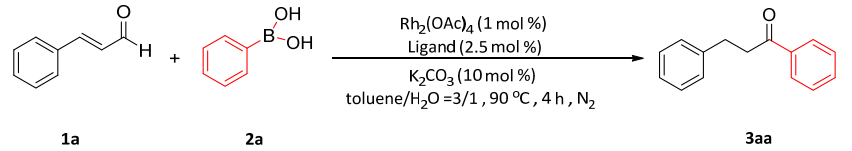
†Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

DOI: 10.1039/C8OB01975E

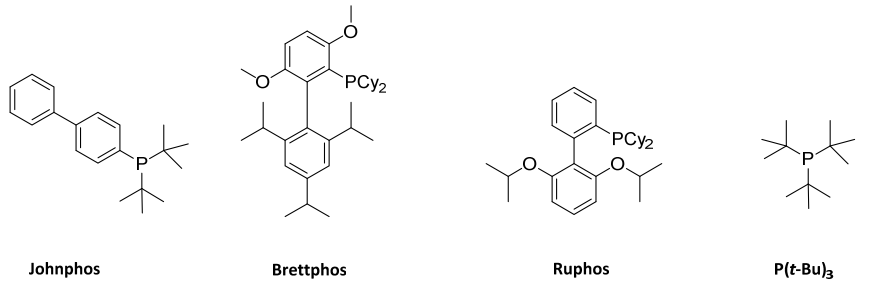
reported the use of Rh_2(II)/N-heterocyclic carbene (NHC) complexes to catalyze the reaction of **1a** with **2a** to obtain the secondary alcohols.[12] Instead of producing secondary alcohols, we found that the reaction between **1a** and **2a** catalyzed by $Rh_2(OAc)_4(PR_3)_2$ in toluene/H_2O under the previously reported conditions gave the 1,3-diphenylpropan-1-one **3aa** as the final product. This result drew our attention and stimulated us to investigate the reaction inside. Various PR_3 ligands were screened in the reaction including selected Buchwald ligands (Ruphos, Breetphos). The bulky alkyl P(*t*-Bu)$_3$ ligand was proved to be the best ligand, resulting in the better yields of **3aa** in shorter time (Table 1, entry 8).

Under optimal reaction conditions, extending the model reaction to other aldehyde substrates (Table 2), it was observed that both electron-rich and electron-poor aryl-substituted cinnamaldehydes **1a-1j** could be successfully converted to the desired products **3** with high yields. A variety of functional groups including nitro, methoxy, halogen group were well tolerated. The steric hindrance of aryl substitution of **1** did not affect the reaction, as both 2-methoxycinnamic aldehyde **1b** and 2-nitrocinnamic aldehyde **1d** gave ketone products **3ba** and **3da** in 87% and 84% yields, respectively. When more substituted α,β-unsaturated aromatic aldehydes were applied in this reaction, the secondary alcohols were obtained as major products and only a very small amounts of aryl alkyl ketones products were detected.

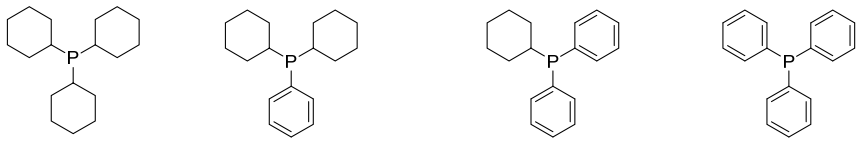
Table 1. Evaluation of various PR_3 ligand [a]



1a **2a** **3aa**



Johnphos Brettphos Ruphos $P(t\text{-}Bu)_3$



PCy_3 PCy_2Ph $PCyPh_2$ PPh_3

entry	ligand	yield/%
1	No Ligand	Trace
2	Johnphos	15
3	PCy_3HBF_4	8
4	PCy_2Ph	5
5	$PCyPh_2$	42
6	PPh_3	49
7	Ruphos	24
8	Brettphos	Trace
9 [b]	$[(t\text{-}Bu)_3PH]BF_4$	88

[a] Unless otherwise noted, all reactions were performed by using 1a (0.50 mmol), 2a (0.55 mmol), $Rh_2(OAc)_4$ (1 mol %), Ligand (2.5 mol %) and K_2CO_3 (10 mol %) in 2 mL of toluene/H_2O (v/v = 3/1) at 90 ℃ for 4 h under N_2. Yield of ^1H NMR. [b] Yield of isolated product.

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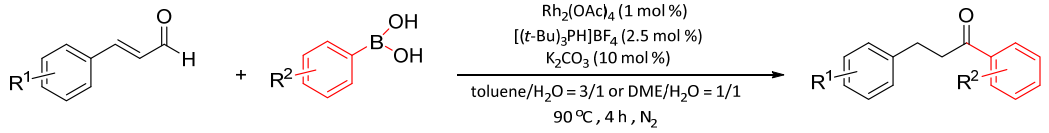
Table 2. The scope of α, β-unsaturated aromatic aldehydes **1** with arylboronic acids **2** [a]



1a-1j **2a-2p** **3ba-3ap**

entry	R^1	R^2	product	yield/%
1	2-OMe (**1b**)	H (**2a**)	**3ba**	87
2	2-Cl (**1c**)	H (**2a**)	**3ca**	85
3	2-NO_2 (**1d**)	H (**2a**)	**3da**	84
4	4-OMe (**1e**)	H (**2a**)	**3ea**	85
5	4-Me (**1f**)	H (**2a**)	**3fa**	89
6	4-Br (**1g**)	H (**2a**)	**3ga**	88
7	4-Cl (**1h**)	H (**2a**)	**3ha**	84
8	4-F (**1i**)	H (**2a**)	**3ia**	82
9	4-NO_2 (**1j**)	H (**2a**)	**3ja**	80
10 [b,c]	H (**1a**)	2-OMe (**2b**)	**3ab**	86
11	H (**1a**)	2-Me (**2c**)	**3ac**	89
12	H (**1a**)	3-OMe (**2d**)	**3ad**	82
13	H (**1a**)	3-Me (**2e**)	**3ae**	87
14 [b]	H (**1a**)	3-NO_2 (**2f**)	**3af**	65
15	H (**1a**)	4-OMe (**2g**)	**3ag**	85
16	H (**1a**)	4-*t*-Bu (**2h**)	**3ah**	86
17	H (**1a**)	4-Me (**2i**)	**3ai**	84
18 [b]	H (**1a**)	4-Ph (**2j**)	**3aj**	84
19	H (**1a**)	4-Cl (**2k**)	**3ak**	89
20	H (**1a**)	4-F (**2l**)	**3al**	87
21 [b]	H (**1a**)	4-CF_3 (**2m**)	**3am**	85
22 [d]	H (**1a**)	1-naphthyl(**2n**)	**3an**	87
23	H (**1a**)	3,5-Me (**2o**)	**3ao**	87
24 [b]	H (**1a**)	3,5-F (**2p**)	**3ap**	67

[a] Unless otherwise noted, all reactions were performed by using α,β-unsaturated aromatic aldehydes 1 (0.50 mmol), arylboronic acids 2 (0.55 mmol), $Rh_2(OAc)_4$ (1 mol %), [(t-Bu)$_3$PH]BF_4 (2.5 mol %) and K_2CO_3 (10 mol %) in 2 mL of toluene/H_2O (v/v = 3/1) at 90 ℃ for 4 h under N_2. Yield of isolated product. [b] The reactions were performed in 2 mL of 1/1(v/v) DME/H_2O. [c] The reaction was performed by using 2b (0.65 mmol) [d] The reaction was performed at 90 ℃ for 8 h under N_2.

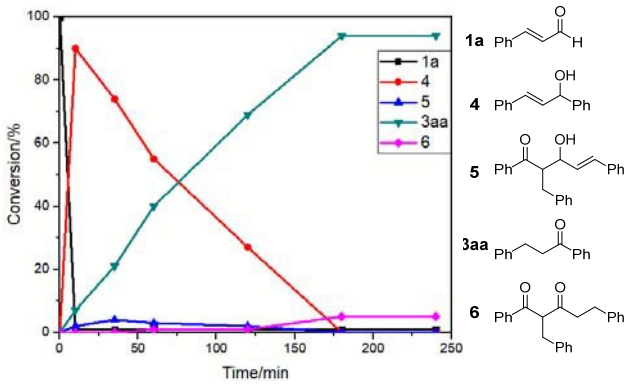
The substrate scope of arylboronic acids **2** was also examined in this reaction. It was noticed that both electron-rich and electron-poor aryl substituents of the **2** reacted smoothly with **1a** to afford the corresponding ketone products **3ab-3ap** (Table 2). It was observed that several arylboronic acids substrates such as **2b**, **2f**, **2j**, **2m** gave fewer yields of the ketone products in toluene/H_2O biphasic solvents. However, when DME/H_2O was used instead of toluene/H_2O, the ketone products (**3ab**, **3af**, **3aj**, **3am**) were obtained in good yields. This could be explained as the solubility of the aforementioned arylboronic acids were not good in toluene/H_2O solvent. Sterically bulkier arylboronic acids such as 1-naphthyphenyl boronic acids **2n** reacted with **1a** to yield the ketones **3an** in 87% yield, albeit in a longer time (8 h). The electron-deficient arylboronic acids such as 3,5-difluorophenylboronic acid **2p** gave the moderate yield of product **3ap** in the DME/H_2O solvent. The boronic acids such as (*E*)-styrylboronic acid, cyclopropylboronic acid et al were also tried in the reactions but gave no products, which indicated the alkenylboronic acids or alkylboronic acids were not suitable substrates for this reaction.

Further studies showed that the aliphatic unsaturated aldehydes were also reacted with **2** to afford the desired products in moderate yields. As shown in Table 3, crotonaldehyde derivatives **1k-1o** reacted smoothly with different aryl substituted boronic acids **2a-2m**. The electron rich arylboronic acids produced better yields as compared to their electron-deficient analogs. It is worth noting that the γ,δ-unsaturated ketones **3na-3oa** were obtained easily when conjugated alkene such as compound **1n** (2*E*,4*E*/2*E*,4*Z* = 86/14) and **1o** (2*E*,4*E*/2*E*,4*Z* = 91/9) were used as substrates in this reaction. The γ,δ-unsaturated ketones act as key substrates for the synthesis of heterocyclic compounds such as *N*-sulfonyl substituted pyrrolidines, polysubstituted tetrahydrofurans, and highly biologically active pyrethridine skeletons.[11] However, several steps or harsh conditions

were required for the synthesis of γ,δ-unsaturated ketones as shown in previous reports.[11b,13] Compared to the reported methods, this streamlined procedure provides a convenient approach to use the readily available material to synthesis these useful molecules.

During the course of our study, we observed accompanying three compounds formed that were believed to be intermediates. Therefore, to elucidate the reaction pathway, we stopped the reaction in the middle that was performed between **1a** and **2a** under optimized conditions. All the intermediates were isolated and characterized using spectroscopic techniques. As shown in scheme 1, the three intermediates are inferred as secondary allylic alcohol **4**, allylic alcohol **5** obtained via aldol reaction from **3aa** with **1a,** and diketone **6**. Considering that the intermediates varied significantly during the reaction, we used ^{1}H NMR to monitor the reaction.

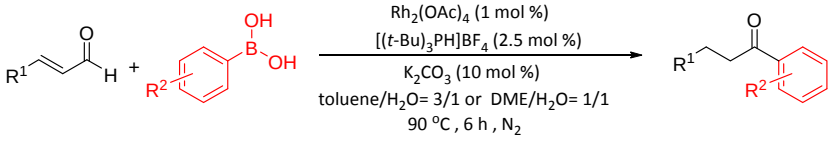
As shown in Scheme 1, we observed the very quick consumption of aldehyde **1a** with concomitant formation of secondary allylic alcohol **4**. After 10 min, the conversion of the compound **4** already achieved 90%. This result was found consistent with our previous study.[5] The aryl reaction was very fast due to longer Rh-P bond distance in the $Rh_2(OAc)_4(P(t\text{-}Bu)_3)_2$, which facilitated the substitution of one of the P(*t*-Bu)$_3$ ligands by the arylboronic acid **2a**. It was interesting to observe that the compound **4** was slowly transformed into ketone product **3aa**. Meanwhile, the aldol products **5** was formed in small amounts and then transformed to diketone **6**. These results indicated that the two catalytic cycles were prevailed in this reaction: firstly, the 1,2-addition of arylboronic acid to aldehyde, followed by isomerization of resulting allylic alcohol intermediate to afford the ketone product.



Scheme 1. Reaction profile of tandem reaction catalyzed by $Rh_2(OAc)_4(P(t\text{-}Bu)_3)_2$

Since the mechanism of arylation catalyzed by $Rh_2(OAc)_4(P(t\text{-}Bu)_3)_2$ complex was already investigated in our previous study,[5] herein, we focused on the procedure of isomerization of an allylic alcohol.

Table 3. The scope of α,β-unsaturated aliphatic aldehydes with **2** [a]



1k-1o **2a-2m** **3ka-3oa**

entry	R^1	R^2	product	yield/%
1	Me (**1k**)	H (**2a**)	**3ka**	58
2	Me (**1k**)	2-Me (**2c**)	**3kc**	57
3	Me (**1k**)	3-OMe (**2d**)	**3kd**	50
4	Me (**1k**)	3-Me (**2e**)	**3ke**	46
5	Me (**1k**)	4-OMe (**2g**)	**3kg**	57
6	Me (**1k**)	4-Me (**2i**)	**3ki**	56
7	Me (**1k**)	4-Cl (**2k**)	**3kk**	41
8	Me (**1k**)	4-F (**2l**)	**3kl**	38
9	Me (**1k**)	4-CF_3 (**2m**)	**3km**	30
10	Et (**1l**)	H (**2a**)	**3la**	54
11	*n*-Pr (**1m**)	H (**2a**)	**3ma**	61
12	CH_3CH=CH (**1n**) *E*/*Z*=86/14	H (**2a**)	**3na** *E*/*Z*=78/22	65
13	CH_3CH=CH (**1n**) *E*/*Z*=86/14	2-Me (**2c**)	**3nc** *E*/*Z* =82/18	70
14	CH_3CH=CH (**1n**) *E*/*Z*=86/14	3-Me (**2e**)	**3ne** *E*/*Z* =79/21	69
15 [b]	CH_3CH=CH (**1n**) *E*/*Z*=86/14	4-OMe (**2g**)	**3ng** *E*/*Z* =84/16	53
16	CH_3CH=CH (**1n**) *E*/*Z*=86/14	4-Me (**2i**)	**3ni** *E*/*Z* =79/21	72
17	CH_3CH=CH (**1n**) *E*/*Z*=86/14	4-Cl (**2k**)	**3nk** *E*/*Z* =83/17	63
18	CH_3CH=CH (**1n**) *E*/*Z*=86/14	4-F (**2l**)	**3nl** *E*/*Z* =87/13	61
19	C_2H_5CH=CH (**1o**) *E*/*Z* =91/9	H (**2a**)	**3oa** *E*/*Z* =88/12	62

[a] Unless otherwise noted, all reactions were performed by using α,β-unsaturated aliphatic aldehydes **1** (1.00 mmol), arylboronic acids **2** (1.10 mmol), $Rh_2(OAc)_4$ (1 mol %), $[(t\text{-}Bu)_3PH]BF_4$ (2.5 mol %) and K_2CO_3 (10 mol %) in 4 mL of 3/1(v/v) toluene/H_2O at 90 ℃ for 4 h under N_2. Yield of isolated product. The *E*/*Z* ratios of commercially available substrates **1n** and **1o** were determined by ^{1}H-NMR spectra. The *E*/*Z* ratio of products **3na**-**oa** were determined by ^{1}H-NMR spectra of the isolated products. [b] The reactions were performed in 4 mL of 1/1(v/v) DME/H_2O.

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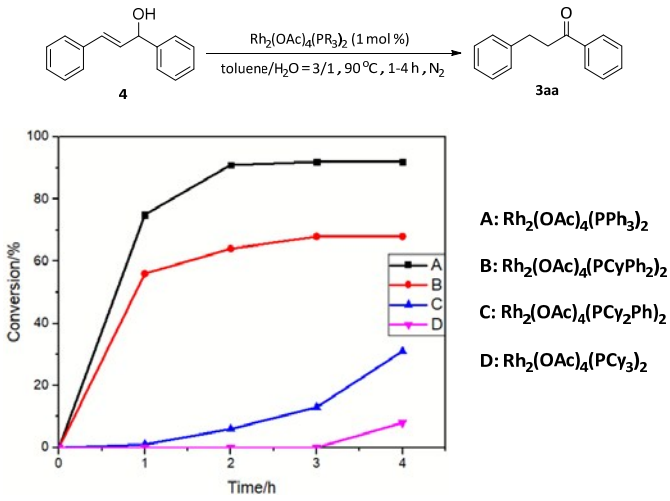
Although, the isomerization of allylic alcohol is a well known procedure, especially catalyzed by the Rh, Ru or Ir metal,[14] but it has never been reported by the dinuclear metal to the best of our knowledge. In this regard, we attempt to understand how the $Rh_2(OAc)_4(P(t\text{-}Bu)_3)_2$ complex catalyzed the isomerization of allyl alcohol along with the effects of axial phosphane ligands on the $Rh_2(OAc)_4$. Therefore, we used the intermediate **4** as starting material to study the isomerization. Unexpectedly, the bulky ligands ligated $Rh_2(OAc)_4(P(t\text{-}Bu)_3)_2$-catalyzed isomerization reaction was slow and the reaction was completed in almost 8 h. To our surprise, the aryl ligands PPh_3 combined with $Rh_2(OAc)_4$ were clearly shown superior to the $Rh_2(OAc)_4(P(t\text{-}Bu)_3)_2$, catalyzing the isomerization reaction to produce the product **3aa** in only 2 h without any base added. However, the $Rh_2(OAc)_4(PPh_3)_2$ complex was proved to be incompetent to catalyze the arylation in our previous work.[5,15] This result suggested that the axial ligands need to be carefully selected when applied in the different reactions. Based on these results, we continued to investigate the performance of different $Rh_2(OAc)_4(PR_3)_2$ complexes such as $PCyPh_2$, PCy_2Ph and PCy_3 in the isomerization reaction to clarify which ligands are optimal.



Scheme 2. Reaction profile of the isomerization of allyl alcohol **4** catalyzed by $Rh_2(OAc)(PR_3)_2$

As shown in the Scheme 2, the rate of isomerization reaction kept on increasing with the increased aryl portion in the ligands. Compared with the reaction catalyzed by PCy_2Ph with only 1% conversion, the conversion of **3aa** reached to 75% conversion after 1h in the reaction catalyzed by $Rh_2(OAc)_4(PPh_3)_2$ complex. According to scheme 2, the sequence of efficient catalysts catalyzed the isomerization reaction are as follows: $Rh_2(OAc)_4(PPh_3)_2$>$Rh_2(OAc)_4(PCyPh_2)_2$>$Rh_2(OAc)_4(PCy_2Ph)_2$>$Rh_2(OAc)_4(PCy_3)_2$.

To understand the catalytic performances of these different complexes towards the isomerization of the allylic alcohol, we prepared the crystals of $Rh_2(OAc)_4(PCyPh_2)_2$ and $Rh_2(OAc)_4(PCy_2Ph)_2$ complexes according to our previous method. Selected data of crystal structures are provided in Fig 2 to compare with other reported structures. From the data, it is obvious that the length of Rh-P bond of $Rh_2(OAc)_4(PPh_3)_2$ complex (2.477Å) was shorter than other complexes, and the situation was same with the Rh-O bond (2.045 Å) (Table 4). As previous research reported,[5] the length of the Rh-P bond was determined by the ability of σ-donating and the steric profile of PR_3 ligands, the short Rh−P bond in $Rh_2(OAc)_4(PPh_3)_2$ complex is the result of strong π back-bonding between Rh and P. As opposed to the previous report that longer Rh−P bond favors the arylation reaction, this structural analysis indicated that the short Rh-P bond facilitated the isomerization reaction.

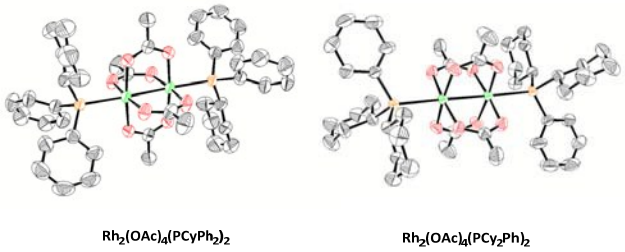


Fig 2. ORTEP crystal structure of $Rh_2(OAc)_4(PCyPh_2)_2$ and $Rh_2(OAc)_4(PCy_2Ph)_2$. The molecular structures are depicted in an ellipsoid style at the 50% probability level.

However, it is inferred from the data shown in Table 1 from the previous studies that the tandem reaction catalyzed by $Rh_2(OAc)_4(PPh_3)_2$ complex gave the product **3aa** in 49% yield only. The studies of the reaction catalyzed by $Rh_2(OAc)_4(PPh_3)_2$ showed that the starting material **1a** was only partial converted to intermediate **4** after 1 h (see ESI), indicating that the arylation catalyzed by the $Rh_2(OAc)_4(PPh_3)_2$ complex was slow. The deboronate reaction occurred under the basic aqueous condition may account for the moderate yield of final product **3aa**.[17] Taken into full consideration, the $Rh_2(OAc)_4(P(t\text{-}Bu)_3)_2$ complex demonstrated its competence to catalyze the two sequential catalytic cycles regardless of catalyzing the isomerization slowly.

Table 4. Selected bond distances from crystal structure data of selected axially ligated dirhodium(II) complexes

entry	$Rh_2(OAc)_2(PR_3)_2$	Rh-Rh (Å)	Rh-O (Å)	Rh-P (Å)
1	$Rh_2(OAc)_4(P(t\text{-}Bu)_3)_2$ [5]	2.454	2.046	2.663
2	$Rh_2(OAc)_2(PCy_3)_2$ [5]	2.457	2.055	2.509
3	$Rh_2(OAc)_2(PCy_2Ph)_2$	2.454	2.050	2.499
4	$Rh_2(OAc)_2(PCyPh_2)_2$	2.451	2.050	2.492
5	$Rh_2(OAc)_2(PPh_3)_2$ [16]	2.451	2.045	2.477

Further, on the basis of the structure information, some experiments were conducted to unravel the mechanism of isomerization. The UV-vis spectral analysis was applied to validate the stability of Rh_2(II) complex as the presence of axial ligands may cause the Rh-Rh bond to undergo oxidative cleavage.[2,18] The mixture was allowed to rest at room temperature after the reaction between **1a** and **2a** was finished, and two layers were separated (toluene and water, respectively). The toluene layer was found to be reddish purple and the UV-vis spectrum showed an absorption peak at 557 nm, indicating the existence of $Rh_2(OAc)_4(P(t\text{-}Bu)_3)_2$ complex (Fig 3). Meanwhile, the light green water layer with absorption peaks at 444 and 587 nm in Uv-vis spectrum indicated the existence of free ligated $Rh_2(OAc)_4$. The absorbance spectral studies confirmed that the Rh-Rh bond still remained intact during this tandem procedure.[19] According to our previously reported method,[5] we successfully recovered the catalyst with 45% recovery rate (see ESI).

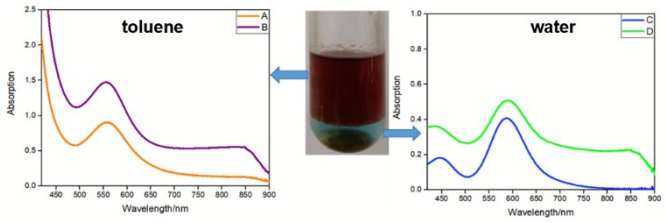
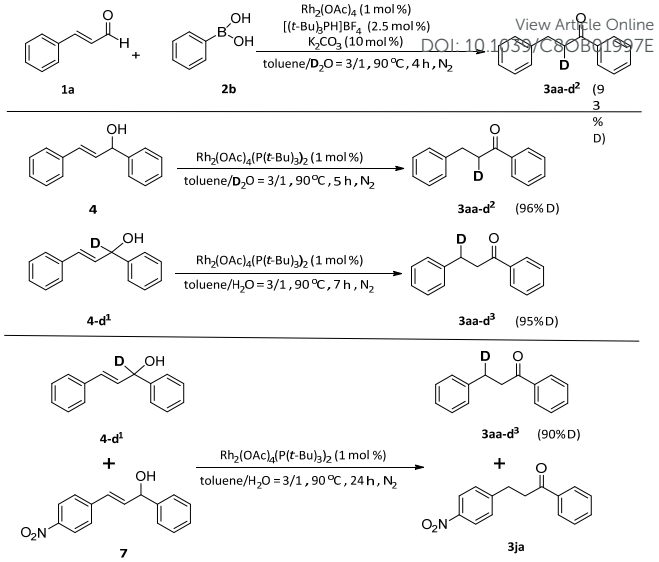


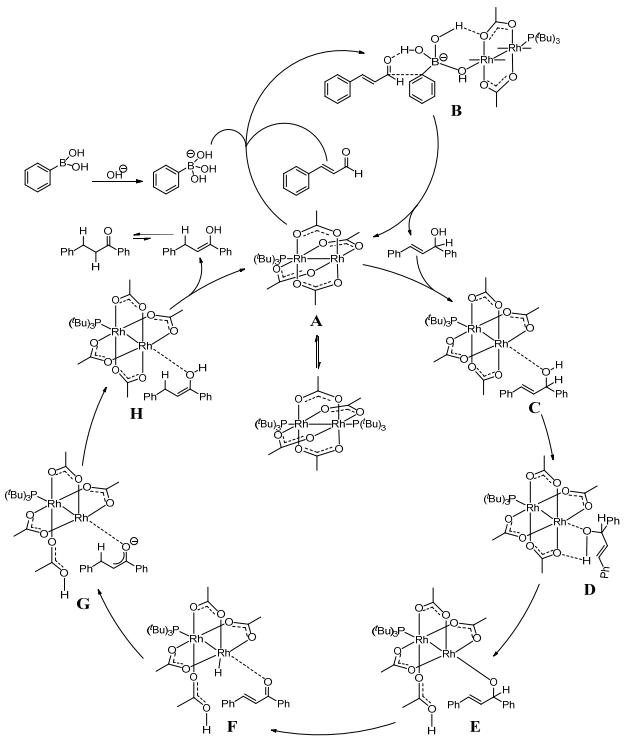
Fig 3. UV-vis spectral analysis of the toluene phase and the water phase. (A) $Rh_2(OAc)_4(P(t\text{-}Bu)_3)_2$ (3 mg) in toluene (2.5 mL) (λ_{max} = 557 nm). (B) The toluene phase (λ_{max} = 557 nm) of the reaction. (C) The water phase (λ_{max} = 444 nm & 587 nm) of the reaction. (D) $Rh_2(OAc)_4(H_2O)_2$ (3 mg) in water (2.5 mL) (λ_{max} = 444 nm & 587 nm).

Essentially, three different mechanisms[14b,20] have been proposed for the isomerization of allylic alcohols catalyzed by metal catalyst, which involve either a metal hydride addition-elimination mechanism, a π-allyl metal hydride mechanism, or a mechanism involving a metal alkoxide. Next, to gain further insights into the mechanism, deuterium labeling and crossover experiments were conducted (Scheme 3). The essential role of H_2O in the mixed solvent of the reaction was probed by performing labeling experiments using D_2O. The reaction in toluene/D_2O resulted in the formation of α monodeuterated product (Scheme 3, **3aa-d²**). Another two reactions with selectively-labeled substrates **4-d¹** were then conducted. The formation of 1,3-deuterium shift ketone product **3aa-d³** was detected, whereas the result of the crossover experiment demonstrated that this 1,3-deuterium shift process was intramolecular since there was no transfer of deuterium between the compounds **4-d¹** and **7**.



Scheme 3. Isotopic labeling studies and crossover experiment

Based on the above information, the mechanism of the two-step catalytic cycle was proposed. The arylation mechanism is similar to that reported in our previous work,[5] as the substrate aldehyde **1** and phenylboronic acid **2** reacted with Rh_2(II) catalyst to form a six-membered ring transition state leading to the arylation reaction. Based on isomerization results and deuterium labeling experiments, we proposed that the mechanism of isomerization was consistent with that of metal alkoxide[21] (Scheme 4). The presence of *trans*-effect[4,22] was found to exist in the $Rh_2(OAc)_4(PR_3)_2$ complex which demonstrated that only one Rh atom out of two Rh atoms of $Rh_2(OAc)_4$ complex serves as the reaction center. First, the oxygen atom of allylic alcohols coordinated axially with the Rh atom, dissociated by the phosphine ligand to form **C**. The hydrogen atom on the hydroxyl of allylic alcohol and the oxygen atom in the bridging ligand of $Rh_2(OAc)_4$ formed hydrogen bond which resulted in a four-membered ring transition state **D**. Further, the Rh-O bond in the **D** was broken to generate **E**.[23] Followed by the β-H elimination, the intermediacy η^1-rhodium hydride ketone complex **F** was generated which underwent 1,4-addition of the hydride to afford **G**. Then, the dissociated acetoxy ligand coordinated with the rhodium atom to regenerate the $Rh_2(OAc)_4$, accompanying the formation of axially coordinated enols. The enols were decomplexed from the $Rh_2(OAc)_4$ during tautomerism to give the saturated ketones product. During the whole catalytic cycle, the axial ligand PR_3 attached with one of the two rhodium atoms, fine-tuned the electrophilicity of the catalytic rhodium atom across the Rh-Rh bond. The detailed explanation of the superiority of PPh_3 as axial ligand compared to the alkyl phosphane ligands require further study.



Scheme 4. Possible mechanism

Conclusions

In conclusion, a strong σ-donating ligand, *tert*-butylphosphine, coordinated to the axial position of $Rh_2(OAc)_4$ acted as an efficient combined catalyst in the tandem reaction of α,β-unsaturated aromatic or aliphatic aldehydes with arylboronic acids to produce various functional ketone derivatives in high yields. The tandem procedure occurred in two steps including arylation and isomerization reactions. This protocol was well tolerated by variously substituted aromatic rings and other functional groups. Especially, the γ,δ-unsaturated ketones were synthesized in a one-pot reaction with great ease using this strategy. The recovery of metal catalyst $Rh_2(OAc)_4$ after the completion of reaction also supports the potential application of this catalyst in organic syntheses. The further investigation will be focused on the detailed explanation of effect of fine tuning of axial PR_3 ligands.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are grateful for the financial support provided by the National Natural Science Foundation of China (21272102).

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View Article Online
DOI: 10.1039/C8OB01997E