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The oxidative coupling between benzaldehyde derivatives and phenylacetylene catalyzed by rhodium complexes via C-H bond activation

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Abstract: This paper reports the use of rhodium (Rh) catalysts for the oxidative coupling reaction between phenylacetylene and benzaldehyde derivatives via C-H bond activation. These reactions were catalyzed by Rh(L-amino acid)(cod) (the L-amino acid is L-phenylalanine, L-valine or L-proline; cod is 1,5-cyclooctadiene) to obtain chromones in 12.7–88.3% yield. These new Rh catalysts have excellent activity for the coupling reaction between phenylacetylene and different benzaldehyde derivatives. It was found that the electronic effects of the benzaldehyde derivative substituent affected the reaction yield, which is in accordance with the proposed mechanism.

Keywords: rhodium catalyst, benzaldehyde derivatives, phenylacetylene, electronic effects

Introduction

In previous studies, rhodium catalysts have been used in many different domains, such as oxidative coupling reactions [1,2], activated chemical bond reactions [3,4], polymerizations [5,6], and asymmetric hydrogenation reactions [7,8]. Rh complexes have shown high catalytic activity, especially in the case of polymerizations of various substituted acetylenes [9,10,11]. We previously reported two kinds of novel Rh complexes containing L-amino acids and 1,5-cyclooctadiene (cod) as ligands to catalyze the helical selective polymerization of m-dihydroxyphenylacetylene, 3,4,5-trisubstituted phenylacetylene, and p-dodecyloxy-m,m-dihydroxyphenylacetylene [11].

Oxidative coupling reactions have been carried out by using Au catalysts [12,13], Fe catalysts [14], Ir catalysts [15,16], Cu catalysts [17,18], Pd catalysts [19,20], and Ru catalysts [21]. Even if Rh catalysts are expensive, they have unique advantages because of their functional group tolerance, wide range of substrate scope, high activity, and selectivity for synthetic transformations [22-26]. Rh catalysts are used by many researchers in C-H activation reactions [27-29]. One kind of Rh catalyst, which contains Cp* (Cp* = 1,2,3,4,5-Pentamethylcyclopentadiene (C_5Me_5) ligands, has been used to catalyze oxidative coupling reactions. For example, Lu *et al.* reported that $[Cp^*RhCl_2]_2$ catalyzed the C-H activation of pyrazolones with symmetric 1,6-enynes to obtain functional products in 34%–72% yield [27]. Krieger's team used $[Cp^*RhCl_2]_2$ to obtain macrocyclic pyridones in excellent yields, and proposed that the catalyst could become more efficient in redox-neutral processes when the *O*-pivaloyl hydroxamate is the directing group [28]. The alkyne annulation with peresters, as the oxidizing directing group, was also catalyzed by $[Cp^*RhCl_2]_2$ via C–H activation [29].

We synthesized Rh(L-amino acid)(cod)s, which are chiral, highly selective and highly active Rh complexes [11]. In this paper, these Rh complexes were used in oxidative coupling reactions between phenylacetylene and benzaldehyde derivatives. However, we did not determine the actual mechanism of the Rh-diene complexes, i.e., Rh(L-amino acid)(cod), in oxidative coupling reactions, but we have discussed a possible mechanism in our

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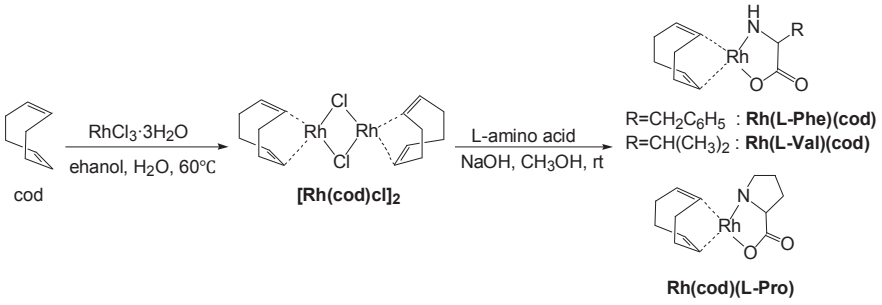
previous articles [30]. In this study, the oxidative coupling reaction between phenylacetylene and benzaldehyde derivatives was catalyzed by Rh with an L-amino acid ligand, plus the catalytic efficiencies and substituent electronic effects are discussed.

Results and discussion

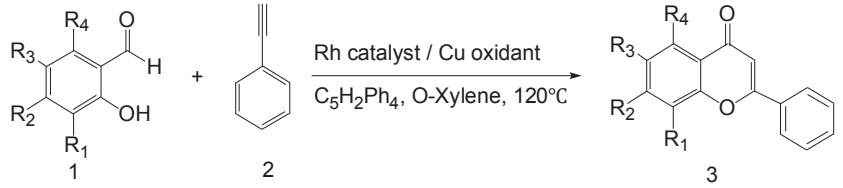
The oxidative coupling reactions between phenylacetylene and the benzaldehyde derivatives (1a-1g) were carried out by using Rh catalysts at 120°C in an o-xylene solution (Scheme 2). The Rh catalysts can activate the C-H bond in compounds 1a-1g to react with the triple bond of phenylacetylene, which produces final compounds (3a-3g). Products were purified by extraction and silica gel column chromatography, before analysis of the product chemical structures by ^{1}H-NMR, ^{13}C-NMR and IR (See SI, Figures S13-S30), it was concluded that the novel compounds (3a-3g) were synthesized successfully.

We hypothesize that the Rh-N bond between the L-amino acid ligand and Rh metal centre is active [26]. Rhodium easily reacts with an atom that has more electrons in its outermost shell to form a new active Rh species [31]. In the oxidative coupling reaction process, the hydroxyl oxygen atom in the benzaldehyde derivative replaces the nitrogen atom of L-amino acid in Rh(L-amino acid)(cod) to coordinate with Rh resulting in intermediate A (Scheme 3). The triple bond of phenylacetylene attacks the Rh centre displacing the L-amino acid ligand, leaving an empty catalytic site (see B in Scheme 3). Then, the triple bond of phenylacetylene inserts into this unoccupied site at Rh to afford ring structure C [30]. Rh(L-amino acid)(cod) is regenerated using a Cu oxidant [32], and the desired product (3a) is obtained. Rh catalyst with a cyclopentadiene ligand and Cu oxidant effectively catalyzes the cyclization reaction of salicylaldehydes and alkynes to produce chromone derivatives [32].

We discussed the influence of L-amino acid ligands for these oxidative coupling reactions [30]. When Rh(L-Phe)(cod) was used as catalyst to obtain the highest yield of 3a (see Table 1), as Rh(L-Phe)(cod) has the best catalytic effect among the obtained Rh complexes. We considered that as L-Phe has a large phenyl group, which can easily dissociate



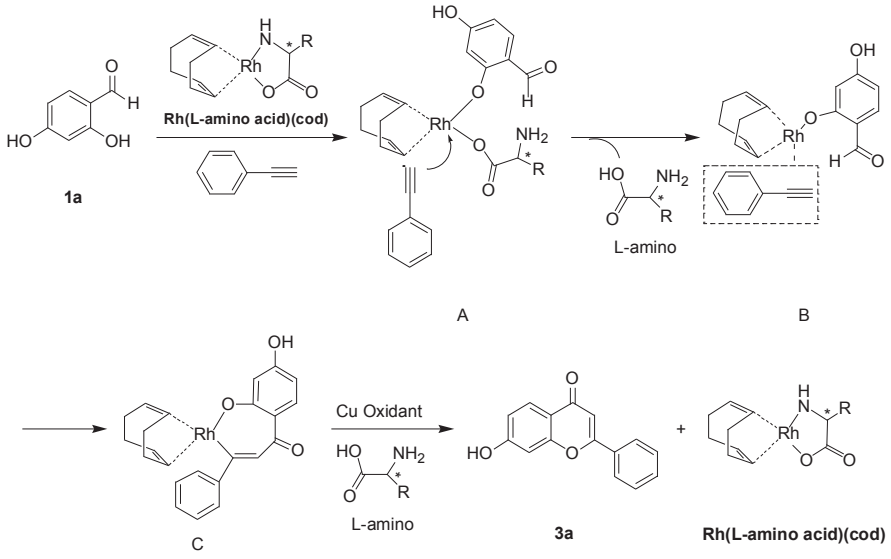
Scheme 1 Synthetic route to **Rh(L-amino acids)(cod)**.



1a: R_1=H R_2=OH R_3=H R_4=H
1b: R_1=H R_2=H R_3=H R_4=H
1c: R_1=OH R_2=OH R_3=H R_4=H
1d: R_1=H R_2=OH R_3=H R_4=OH
1e: R_1=H R_2=H R_3=Cl R_4=H
1f: R_1=H R_2=H R_3=Br R_4=H
1g: R_1=Br R_2=H R_3=Br R_4=H

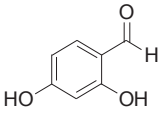
3a: R_1=H R_2=OH R_3=H R_4=H
3b: R_1=H R_2=H R_3=H R_4=H
3c: R_1=OH R_2=OH R_3=H R_4=H
3d: R_1=H R_2=OH R_3=H R_4=OH
3e: R_1=H R_2=H R_3=Cl R_4=H
3f: R_1=H R_2=H R_3=Br R_4=H
3g: R_1=Br R_2=H R_3=Br R_4=H

Scheme 2 Synthetic route to **chromones**.



Scheme 3 Plausible reaction mechanism.

Table 1 Oxidative coupling reactions between dihydroxybenzaldehyde [1a] and phenylacetylene catalyzed by rhodium with amino acid ligands[a]

No.	Reactant	Rh Catalyst	Yield (%)
1		Rh(cod)(L-Phe)	82.9
2		Rh(cod)(L-Val)	63.7
3	**1a**	Rh(cod)(L-Pro)	54.2

[a]In o-xylene at 120°C for 6 h with [1a]/[2]/[Rh catalyst] =1:1:0.001 (in mmol).

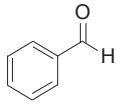
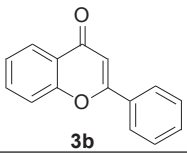
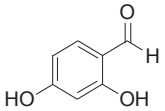
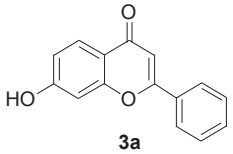
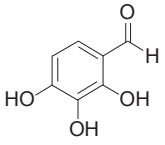
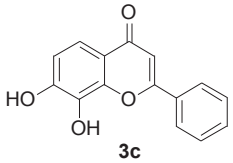
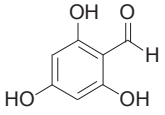
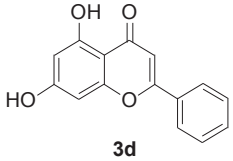
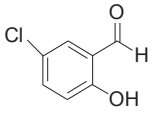
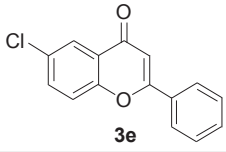
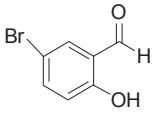
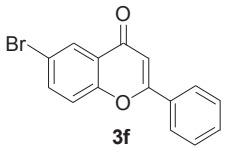
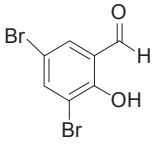
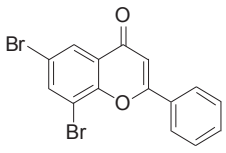
from Rh, providing an empty coordination site at Rh for phenylacetylene insertion, yielding a $Rh^{I}X$ species [30].

To investigate the effect of the benzaldehyde derivatives on the oxidative coupling reaction, seven chemical reactions between 1a-1g and 2 were catalyzed by Rh(L-Phe)(cod), as shown in Table 2. All of these benzaldehyde derivatives (1a-1g) reacted with phenylacetylene to obtain chromones 3a-3g in 12.7%–88.3% yield. These results illustrated that Rh catalysts with L-amino acid ligands have a wide range of applications for different substrates.

The reason for such a wide range of yields in Table 2 can be explained by the role of the substituent effects. Aldehyde groups and hydroxyl groups on the phenyl ring can react with the triple bond of phenylacetylene, therefore the nature and position of ring substituents affects the reactivity of the aromatic compound. The benzaldehyde that has two hydroxyl groups in the ortho- and para-positions (Table 2, 1a) reacted with phenylacetylene to obtain the product in 82.9% yield, which is lower than the yield obtained by unsubstituted benzaldehyde as the substrate (Table 2, 1b, 88.0%) but higher than the yield afforded by the substrate containing three hydroxyl groups (Table 2, 1c and 1d). In particular, 2,4,6-trihydroxybenzaldehyde had the lowest yield of 22.6% (Table 2, 1d). The reason for these results could be that hydroxyl groups in the ortho- or para-position can increase the electron density of the benzene ring. The electronegativity of the carbon atom closest to the aldehyde group is enhanced by the hydroxyl groups (Table 2, 1a, 1c, 1d). As the number of hydroxyl groups increases, the electronegativity of the benzaldehyde also increases. Compound 1d with two ortho and one para hydroxyl group has a higher electronegativity than 1c, in which the ortho-position, meta-position and para-position each contain one hydroxyl group. Therefore, the electronegativity order of the carbon in position 1 is 1d > 1c >1a> 1b (see chart 1), which is contrary to their yield order (1d < 1c <1a < 1b in Table 2). The reason for this phenomenon can be explained as the electronegative triple bond of phenylacetylene can enter into the unoccupied active site on Rh. This sequence results in ring structure formation with the positive carbon atom of the aldehyde group in 1a-1d. The electronegativity of the carbon atom at position 1 is weakened by the positive electricity of carbon in the aldehyde group. This is not beneficial for the formation of ring structures, between benzaldehyde derivative and phenylacetylene in oxidative coupling reactions. Consequently, the yield order is opposite to the number of hydroxyl groups because of the effect of the electron density in the aromatic ring.

There are also similar influences for the oxidative coupling reactions between halogen substituted

Table 2 Oxidative coupling reactions between aldehyde derivatives (1a-1g) and phenylacetylene using Rh(L-Phe)(cod) as the catalyst[a]

No.	Reactants	Aim Structure	Yield (%)
1	 1b	 3b	88.3
2	 1a	 3a	82.9
3	 1c	 3c	69.7
4	 1d	 3d	22.6
5	 1e	 3e	49.5
6	 1f	 3f	29.3
7	 1g	 3g	12.7

[a]In o-xylene at 120°C for 6 h with [1]/[2]/ [Rh catalyst] =1:1:0.001 (in mmol).

benzaldehydes (1e-1g) and phenylacetylene (2). Chlorine and bromine are electron withdrawing groups, as an electronic effect, but are also electron-donating groups via conjugation effects. The conjugation effect of 1g with two bromine groups is stronger than 1e and 1f, and so the electronegativity of carbon in position 1 of 1g is the strongest among 1e-1g. Increasing the electronegativity of the carbon in position 1 is not conducive to form a ring structure between benzaldehyde derivative and phenylacetylene.

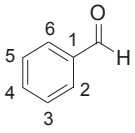


Chart 1 Sequence of carbon in 1a-1g.

So, the yield of 1g is low (12.7%) (Table 2, 7). The carbon atom in position 1 of 1e has a lower electronegativity than those of 1f and 1g, so the yield of 3e was higher than those of 3f and 3g (Table 2, 5-7). However, all of these reaction yields were lower than the yield provided by benzaldehyde and phenylacetylene (Table 2, 1). The reason for this result is that halogen and hydroxyl can weaken the ability of benzaldehyde derivatives to form a ring structure with phenylacetylene.

Conclusions

In summary, the C-H bond activation reaction of benzaldehyde derivatives was demonstrated in the presence of novel Rh catalysts with L-amino acid ligand. Seven kinds of chromones were synthesized. Rh(L-Phe)(cod) had the best catalytic effect among the obtained Rh complexes. L-amino acids containing a large aromatic group can dissociate easily to afford an empty Rh active site, which can improve the catalytic activity of the Rh complexes. The kind of substituent and its position on the aromatic ring of benzaldehyde affects the oxidative coupling reaction by electronic effects.

Experimental

Synthesis of 3-phenyl-7-hydroxy-1H-chromen-4-one (3a): Rh(L-phe)(cod) (1.50mg, 3.98×10^{-6}mol), 1,2,3,4-tetraphenyl-1,3-cyclopentadiene (7.04mg, 1.90×10^{-5}mol) and $Cu(OAc)_2\cdot H_2O$ (200mg, 1.00×10^{-3}mol) were dissolved in o-xylene (2.76mL, 2.29×10^{-5}mol), 2,4-dihydroxybenzaldehyde (6.04×10^{2}mg, 4.37×10^{-3}mol) and phenylacetylene (4.91×10^{-1}mL, 4.47×10^{-3}mol) were added. The mixture was stirred under N_2 at 120°C for 6 h. The product was extracted by ether and water. The final product was isolated in n-hexane and ethyl acetate by silica gel column chromatography. Other chromones were obtained by a similar process as described for 3a.

3-phenyl-7-hydroxy-1H-chromen-4-one (3a): The compound was obtained in 82.9% yield as a brown oil. ^{1}H-NMR (600 MHz, $CDCl_3$, TMS, δ): 7.57, (d, 2H, H-2, H-5, J=1.2Hz), 7.56 (d, 2H, H-6, H-8, J=1.2Hz), 7.40 (t, 1H, H=4',

J=3Hz), 7.39 (t, 1H, H-5', J=6Hz), 7.38 (t, 1H, H-3', J=3Hz), 7.37 (s, 1H, H-1'), 7.36 (s, 1H, H-2'), 7.35 (t, 1H, H-4', J=3Hz). ^{13}C-NMR (150 MHz, $CDCl_3$, TMS, δ): 72.65, 80.54, 120.73, 127.65, 128.19, 131.72 ppm. IR (KBr): 3063, 2964, 2924, 2851, 2218, 1951, 1485, 1023 cm^{-1}. (See Figures S13-S15 of Supporting Information)

3-phenyl-1H-chromen-4-one (3b): The compound was obtained in 88.3% yield as a brown oil. ^{1}H-NMR (600 MHz, $CDCl_3$, TMS, δ): 7.63 (s, 2H, H-2, H-5), 7.62 (d, 3H, H-6, H-7, H-8, J=1.2Hz), 7.52 (t, 1H, H-4', J=3Hz), 7.51 (t, 1H, H-5', J=6Hz), 7.50 (t, 1H, H-3', J=3Hz), 7.47 (s, 1H, H-1'), 7.46 (s, 1H, H-2'), 7.45 (t, 1H, H-4', J=3Hz). ^{13}C-NMR (150 MHz, $CDCl_3$, TMS, δ): 77.24, 81.57, 121.83, 128.46, 129.23, 132.53 ppm. IR (KBr): 3050, 2953, 2926, 2855, 2191, 1741, 1485, 1252 cm^{-1}. (See Figures S16-S18 of Supporting Information)

3-phenyl-7,8-dihydroxy-1H-chromen-4-one (3c): The compound was obtained in 69.7% yield as a brown oil. ^{1}H-NMR (600 MHz, $CDCl_3$, TMS, δ): 7.54 (d, 2H, H-2, H-5, J=2.4Hz), 7.53 (d, 1H, H-6, J=3.6Hz), 7.39 (t, 1H, H=4', J=3Hz), 7.38 (t, 1H, H-5', J=6Hz), 7.37 (t, 1H, H-3', J=3Hz), 7.35 (s, 1H, H-1'), 7.34 (d, 1H, H-2', J=1.2Hz), 7.33 (t, 1H, H-4', J=3.6Hz). ^{13}C-NMR (150 MHz, $CDCl_3$, TMS, δ): 73.91, 81.56, 121.82, 128.45, 129.22, 132.52 ppm. IR (KBr): 3064, 2973, 2918, 2198, 1961, 1487, 1460, 1013 cm^{-1}. (See Figures S19-S21 of Supporting Information)

3-phenyl-5,7-dihydroxy-1H-chromen-4-one (3d): The compound was obtained in 22.6% yield as a brown oil. ^{1}H-NMR (600 MHz, $CDCl_3$, TMS, δ): 7.54, (d, 2H, H-2, J=2.4Hz), 7.53 (d, 2H, H-6, H-8, J=3.6Hz), 7.39 (t, 1H, H=4', J=3Hz), 7.38 (t, 1H, H-5', J=6Hz), 7.37 (t, 1H, H-3', J=3Hz), 7.36 (s, 1H, H-1'), 7.34 (d, 1H, H-2', J=1.2Hz), 7.33 (t, 1H, H-4', J=3Hz). ^{13}C-NMR (150 MHz, $CDCl_3$, TMS, δ): 73.93, 81.57, 121.81, 128.46, 129.23, 132.53 ppm. IR (KBr): 2978, 2931, 2912, 2891, 1714, 1443, 1055, 882 cm^{-1}. (See Figures S22-S24 of Supporting Information)

3-phenyl-6-chloro-1H-chromen-4-one (3e): The compound was obtained in 49.5% yield as a brown oil. ^{1}H-NMR (600 MHz, $CDCl_3$, TMS, δ): 7.55, (s, 2H, H-2, H-5), 7.54 (d, 2H, H-7, H-8, J=1.2Hz), 7.39 (s, 1H, H=4'), 7.38 (s, 1H, H-5'), 7.37 (s, 1H, H-3'), 7.36 (s, 1H, H-1'), 7.35 (s, 1H, H-2'), 7.33 (d, 1H, H-4'). ^{13}C-NMR (150 MHz, $CDCl_3$, TMS, δ): 72.99, 80.54, 118.45, 120.82, 128.26, 127.49, 131.39 ppm. IR (KBr): 3047, 2949, 2921, 2848, 2142, 1951, 1660, 1468 cm^{-1}. (See Figures S25-S27 of Supporting Information)

3-phenyl-6-bromo-1H-chromen-4-one (3f): The compound was obtained in 29.3% yield as a brown oil. ^{1}H-NMR (600 MHz, $CDCl_3$, TMS, δ): 7.54, (s, 2H, H-2, H-5), 7.53 (d, 2H, H-7, H-8, J=1.2Hz), 7.39 (s, 1H, H=4'), 7.37 (t, 1H, H-5', J=6Hz), 7.36 (s, 1H, H-3'), 7.35 (s, 1H, H-1'), 7.34 (s, 1H, H-2'), 7.33 (t, 1H, H-4', J=3Hz). ^{13}C-NMR (150 MHz, $CDCl_3$, TMS, δ): 72.91, 80.47, 118.78, 120.85, 127.42, 128.18, 131.47 ppm. IR (KBr): 3057, 2954, 2912, 2849, 2214, 1951, 1598, 1266 cm^{-1}. (See Figures S28-S30 of Supporting Information)

3-phenyl-6,8-dibromo-1H-chromen-4-one (3g): The compound was obtained in 12.7% yield as a brown oil. ^{1}H-NMR (600 MHz, $CDCl_3$, TMS, δ): 7.54, (s, 2H, H-2, H-5), 7.53 (d, 2H, H-7, J=1.2Hz), 7.39 (s, 1H, H=4'), 7.38 (t, 1H, H-5', J=6Hz), 7.37 (s, 1H, H-3'), 7.36 (s, 1H, H-1'), 7.34 (s, 1H, H-2'), 7.33 (d, 1H, H-4', J=1.2Hz). ^{13}C-NMR (150 MHz, $CDCl_3$, TMS, δ): 72.89, 80.53, 120.86, 127.42, 128.23, 131.44 ppm. IR (KBr): 3053, 2966, 2917, 2857, 2144, 1880, 1484, 1260 cm^{-1}. (See Figures S31-S33 of Supporting Information)

Instruments: The molecular structures of the products were determined by NMR [Bruker, Germany; ^{1}H (600 MHz) and ^{13}C (150 MHz)] and IR [Perkin-Elmer, America; Spectrum One B IR spectrophotometer]. Yield = Actual product weight ÷Theoretical product weight. Theoretical product weight = Theoretical mole number of product × molecular weight of product.

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