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Rh(I)-Catalyzed regioselective arylcarboxylation of acrylamides with arylboronic acids and CO_2†

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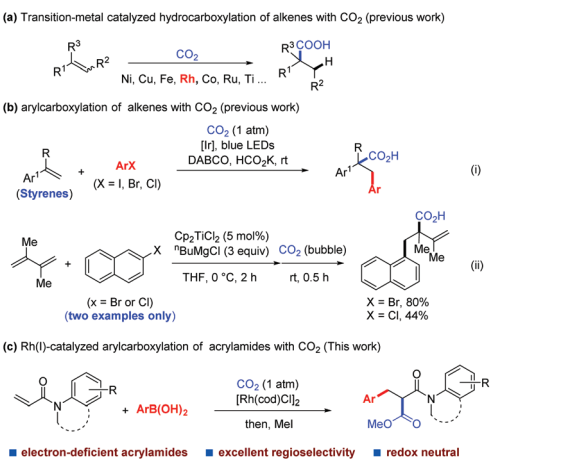
The first Rh(I)-catalyzed regioselective arylcarboxylation of electron-deficient acrylamides with arylboronic acids under atmospheric pressure of CO_2 has been developed. A range of acrylamides and arylboronic acids were compatible with this reaction under redox-neutral conditions, leading to a series of malonate derivatives that are versatile building blocks in organic syntheses.

In recent years, numerous transformations for fine chemical synthesis have been achieved through the use of carbon dioxide (CO_2), which is nontoxic, low cost, abundant, and sustainable, and is often considered an ideal one-carbon (C1) building block.[1] In particular, notable achievements have been made in the functionalization of alkenes with CO_2 *via* hydrocarboxylation with transition-metal catalysis and/or photocatalysis,[2] including a few examples using Rh(I)-catalysis[2d,g,l,r,t] (Scheme 1a). Difunctionalization of alkenes with CO_2, in contrast, has been less explored,[3–5] although several elegant transformations of this kind have been achieved by Xi's,[5a,g] Popp's,[5b,h] Martin's,[5c] Yu's[5d,f] and Wu's[5e] groups. To date, however, only a single method of arylcarboxylation of alkenes is available through visible-light-driven reductive arylcarboxylation with CO_2 and aryl halides, and has been demonstrated by our group recently [Scheme 1b(i)],[6] besides two isolated examples of titanocene-catalyzed arylcarboxylation of dienes reported by Xi's group [Scheme 1b(ii)].[5g] However, the substrates of this photocatalytic method were limited to styrenes and not applicable to electron-deficient α,β-unsaturated substrates such as acrylamides. Therefore, a complementary method that could overcome this limitation is highly desirable.

As part of our continuing interest in developing Rh-catalyzed carboxylation using CO_2,[7] we considered whether it is possible to achieve a Rh-catalyzed difunctionalization of α,β-unsaturated compounds with CO_2.[8] Compared with the Rh-catalyzed 1,4-addition of α,β-unsaturated compounds with organometallic reagents, Rh-catalyzed difunctionalization of these compounds is much less documented and the corresponding arylcarboxylation has not been achieved to date with Rh catalysis.[9] Herein, we report the first Rh(I)-catalyzed arylcarboxylation of acrylamides with arylboronic acids and CO_2.

After extensive investigation of reaction conditions (see also the ESI†), a set of promising reaction conditions were revealed by using *N*-methyl-*N*-phenylacrylamide **1a** and phenylboronic acid **2a** as the model substrates with $[Rh(cod)Cl]_2$ as the catalyst in the presence of Cs_2CO_3 under CO_2 (1 atm) in DMA. Pleasingly, 40% of the desired phenylcarboxylation product **3a** was detected, while 25% of Heck-type product **4** through a β-H elimination process and 7% of 1,4-addition product **5** were also identified as the major side products (Table 1, entry 1). It should be noted that traces of hydrocarboxylation and alkene reduction products could also be detected. Moreover, for the



Scheme 1 Carboxylation of alkenes with CO_2.

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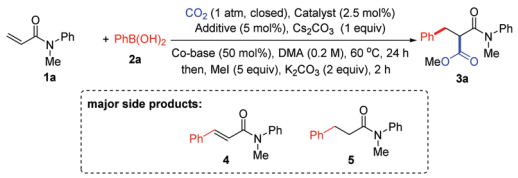
Table 1 Optimization of reaction conditions[a]



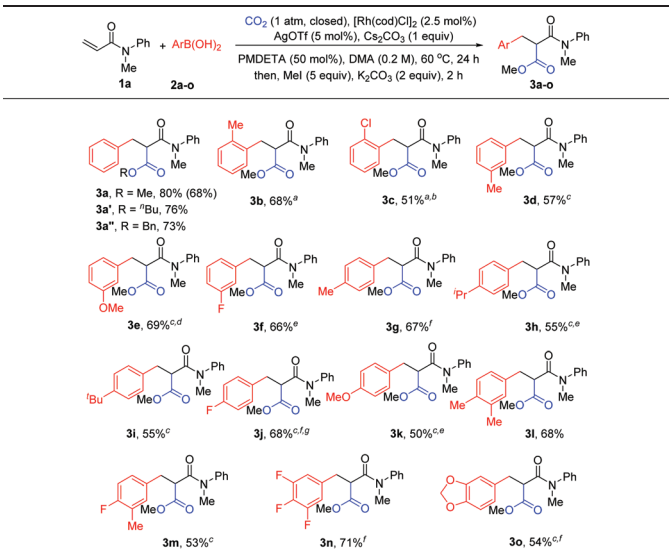
Entry	Catalyst	Co-Base	Additive	Yield[b] (%) (**3a**/**4**/**5**/**1a**)
1	$[Rh(cod)Cl]_2$	—	—	40/25/7/—
2[c]	$[Rh(cod)Cl]_2$	—	—	43/18/16/—
3[d]	$[Rh(cod)Cl]_2$	—	—	36/23/5/—
4	$[Rh(cod)Cl]_2$	**B1**	—	47/27/6/—
5	$[Rh(cod)Cl]_2$	**B2**	—	49/27/3/—
6	$[Rh(cod)Cl]_2$	**B2**	AgF	73/5/14/—
7	$[Rh(cod)Cl]_2$	**B2**	Ag_2O	75/6/13/—
8	$[Rh(cod)Cl]_2$	**B2**	AgCl	77/6/13/—
9	**$[Rh(cod)Cl]_2$**	**B2**	**AgOTf**	**83/6/5/—**
10	$[Rh(cod)Cl]_2$	**B2**	CuCl	58/18/7/—
11[e]	$[Rh(cod)Cl]_2$	**B2**	AgOTf	13/14/57/2
12[f]	$[Rh(cod)Cl]_2$	**B2**	AgOTf	43/14/12/—
13[g]	$[Rh(cod)Cl]_2$	**B2**	AgOTf	19/9/52/—
14[h]	$[Rh(cod)Cl]_2$	**B2**	AgOTf	15/9/73/—
15	$Rh(cod)_2OTf$	**B2**	AgOTf	59/16/8/—
16	$[Rh(CO)_2Cl]_2$	**B2**	AgOTf	—/10/—/81
17	$[Rh(cod)OH]_2$	**B2**	AgOTf	80/9/11/—
18	$[Rh(coe)_2Cl]_2$	**B2**	AgOTf	—/—/—/84
19[i]	$[Rh(cod)Cl]_2$	**B2**	AgOTf	46/14/3/18
20	$[Rh(cod)Cl]_2$	—	AgOTf	46/17/13/—
21	—	**B2**	AgOTf	—/—/—/53
22[j]	$[Rh(cod)Cl]_2$	**B2**	AgOTf	—/8/70/—

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), CO_2 (1 atm, closed), catalyst (2.5 mol%), ligand (5 mol%), Cs_2CO_3 (0.2 mmol), additive (5 mol%), Co-base (50 mol%), and DMA (1 mL), 60 °C, 24 h. [b] Yield was determined by ^1H NMR with CH_2Br_2 as the internal standard. [c] dppe (5 mol% was added as a ligand, dppe: 1,2-bis(diphenylphosphino)ethane). [d] IPr·HCl (5 mol% was added, IPr·HCl: 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride. [e] CsF (0.2 mmol) as a base. [f] KO^{t}Bu (0.2 mmol) as a base. [g] DMF as solvent. [h] NMP as solvent. [i] $[Rh(cod)Cl]_2$ (1 mol%) as a catalyst. [j] Ar (1 atm, closed) was used instead of CO_2. **B1**: *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA). **B2**: *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA).

ease of reaction result analysis, the initial carboxylic acid products were converted into their ester counterparts after the phenylcarboxylation reaction ceased. In order to suppress the formation of side products **4** and **5** and increase the desired product, ligands such as dppe and IPr·HCl were added to tune the reactivity of the Rh catalyst (entries 2 and 3, see also the ESI† for more ligands used). Unfortunately, no significant improvement was observed. To our delight, however, the yield of the desired product was slightly increased when an organic base TMEDA (**B1**) or PMDETA (**B2**) was introduced into the reaction (entries 4 and 5). Subsequently, different silver salts, which are often used to increase the reactivity of Rh catalysts, were extensively investigated as additives for the reaction (entries 6–9; see also the ESI†), and it was found that AgOTf was the best choice to produce the best yield of **3a**, leading to the least yield of **4** and **5** (entry 9). Comparing the results of entry 5 and entries 6–8, it appears that the silver salt mainly inhibited the formation of side product **4**. However, the exact role of the silver salt is not clear at present.[10] Notably, the amine additive (PMDETA) might also be a potential tridentate ligand to form a silver complex in the solution to increase the solubility of the silver salts such as AgCl.[11,10c] Interestingly, CuCl could also slightly improve the reaction (entry 10, see also the ESI†). Other bases or solvents were also evaluated, but no increase in the yield of the desired product was observed (entries 11–14). Other Rh catalysts were then tested (entries 15–18), and only $[Rh(cod)OH]_2$ could lead to rather high yield of the product (entry 17). Importantly, the efficiency of the reaction was reduced evidently with a lower loading of the $[Rh(cod)Cl]_2$ catalyst (entry 19) or without **B2** (entry 20). Moreover, no product was received without the Rh catalyst (entry 21). Finally, when the reaction was run under argon instead of CO_2, no desired product was found, indicating that CO_2 was not generated *in situ* from caesium carbonate (entry 22).

With the optimized reaction conditions in hand, the method was then tested with a range of arylboronic acids (Table 2). First, good isolated yields were obtained with model phenylboronic acid through esterification with different aryl halides (**3a**′ and **3a**″). To our delight, arylboronic acids with electron-rich or electron-deficient substituents at the *ortho*- or *meta*-position of the phenyl group were tolerated, providing moderate to good yields of malonates (**3b–3f**). It was also found that several types of substituents at the *para*-position were suitable for the reaction (**3g–3k**). It is worth noting that multisubstituted phenylboronic acids could also react with **1a** to produce the desired products in acceptable yields (**3l–3o**). It should also be mentioned that the formation of the side pro-

Table 2 Substrate scope of arylboronic acids



Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol, 1.5 equiv.), CO_2 (1 atm, closed), $[Rh(cod)Cl]_2$ (2.5 mol%), Cs_2CO_3 (0.2 mmol), AgOTf (5 mol%), PMDETA (50 mol%), and DMA (1 mL), 60 °C, 24 h; then MeI, or BuBr, or BnBr (1 mmol), and K_2CO_3 (0.4 mmol). Isolated yields; the yield of **3a** in parentheses is that of 1 mmol (**1a**) scale reaction. [a] Ag_2O (5 mol%) as an additive. [b] KO^{t}Bu (0.6 mmol) as a base. [c] Cs_2CO_3 (0.6 mmol) as a base. [d] **2** (0.4 mmol) was used. [e] AgCl (5 mol%) as an additive. [f] AgF (5 mol%) as an additive. [g] $[Rh(cod)Cl]_2$ (5 mol%) as a catalyst.

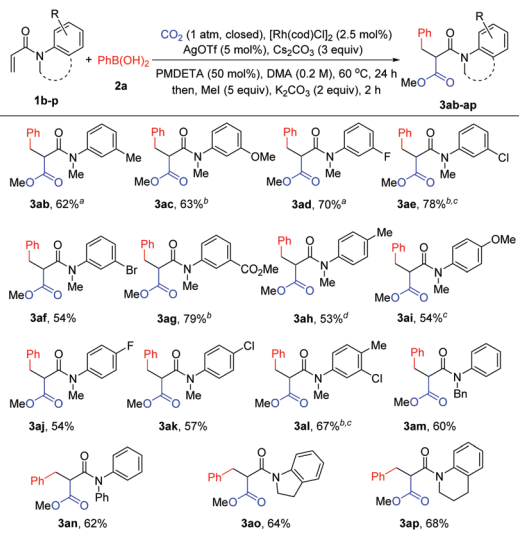
ducts from Heck-type coupling or 1,4-addition could not be suppressed completely for the above examples (see the ESI† for details).

The scope of acrylamides was then examined. As shown in Table 3, acrylamides with electron-donating and electron-withdrawing groups at the *meta*- or *para*-position of the aryl group of acrylamides were well tolerated (**3ab**–**3ak**), affording the desired products smoothly. Unfortunately, acrylamides bearing substituents at the *ortho*-position of the acrylamide's aryl group exhibited low reactivity, which is possibly due to the increased steric hindrance. Moreover, a di-substituted acrylamide was also a viable substrate for this reaction (**3al**). When replacing the *N*-protecting group Me with Ph and Bn (**3am** and **3an**), the corresponding products were still generated. Notably, indoline- and tetrahydroquinoline-derived acrylamides were compatible with the reaction, yielding the desired products in good yields (**3ao** and **3ap**). In addition, it is noteworthy that the side products from Heck-type coupling or 1,4-addition were also present and were hard to suppress for these examples (see the ESI† for details).

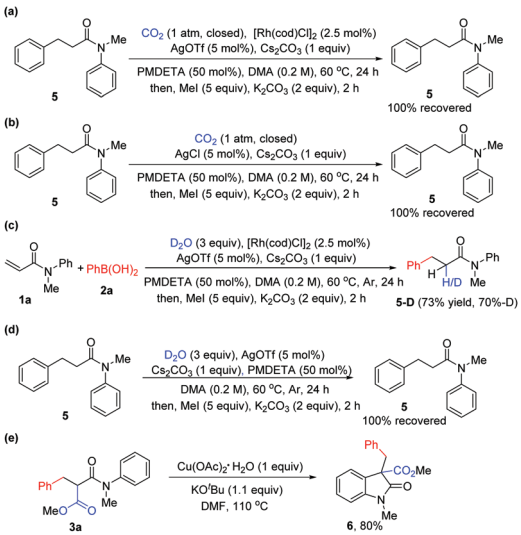
To gain insight into this novel arylcarboxylation method, some control experiments were performed. As shown in Scheme 2, subjecting side product **5** to standard conditions could not lead to the desired product **3a** (Scheme 2a). No **3a** could be formed without adding the Rh catalyst under standard conditions and with AgCl as the additive which could be formed from $[Rh(cod)Cl]_2$ and AgOTf in the reaction (Scheme 2b). These two experiments indicated that the conjugate addition and the nucleophilic addition of CO_2 by the rhodium enolate should occur sequentially without the hydrolysis of the rhodium enolate,[9d] and that the weakly basic conditions of the reaction were not sufficient to induce carboxylation of the α-position of the amide **5**. Further experiments also indicated the presence of a rhodium enolate (Scheme 2c) and its importance for the second functionalization after conjugate addition (Scheme 2d). Finally, the product could be elaborated to generate oxindole-type compounds which are versatile building blocks for organic synthesis and are often found as the core structure of natural products and molecules of medicinal importance (Scheme 2e).[12]

Based on the above results, a plausible mechanism is proposed (Scheme 3). First, ligand exchange converts the $[Rh(cod)Cl]_2$ catalyst to an active rhodium species **A**, which undergoes transmetalation with arylboronic acids **2**, leading to a [Rh]–Ar species **B**. Coordination of **B** onto **1a**, followed by a regioselective addition, produces a rhodium enolate **D**. This key intermediate **D** will attack CO_2 to afford the carboxylate intermediate **E**, which ultimately leads to the desired product **3a**. On the other hand, rhodium enolate **D** can also undergo

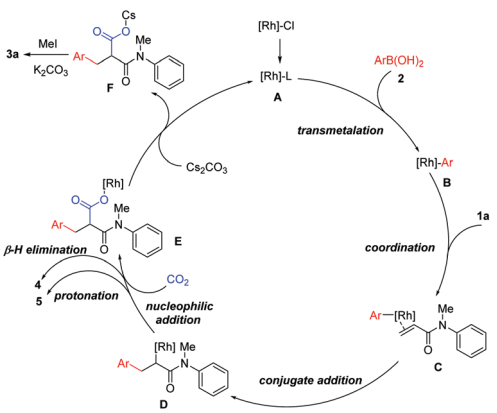
Table 3 Substrate scope of acrylamides



Reaction conditions: **1** (0.2 mmol), **2** (1.5 equiv.), CO_2 (1 atm, closed), $[Rh(cod)Cl]_2$ (2.5 mol%), Cs_2CO_3 (0.6 mmol), AgOTf (5 mol%), PMDETA (50 mol%), and DMA (1 mL), 60 °C, 24 h. Isolated yields. [a] Cs_2CO_3 (0.2 mmol) as a base. [b] $[Rh(cod)Cl]_2$ (5 mol%) as a catalyst. [c] AgF (5 mol%). [d] AgCl (5 mol%).



Scheme 2 Control experiments and product elaboration.



Scheme 3 Proposed catalytic cycle.

either β-H elimination to produce side product **4** or direct protonation to produce side product **5**, respectively.

Conclusions

In summary, we have developed the first Rh(I)-catalyzed regioselective arylcarboxylation of electron-deficient acrylamides with CO_2 under redox-neutral conditions. A range of acrylamides and arylboronic acids were suitable for this reaction, leading to a series of malonate derivatives that could be converted into other important structures such as oxindoles. Preliminary mechanistic studies indicated the importance of the rhodium enolate. Further investigation of the Rh-catalyzed carboxylation strategy with CO_2 is underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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