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Palladium-catalyzed reductive electrocarboxylation of allyl esters with carbon dioxide†

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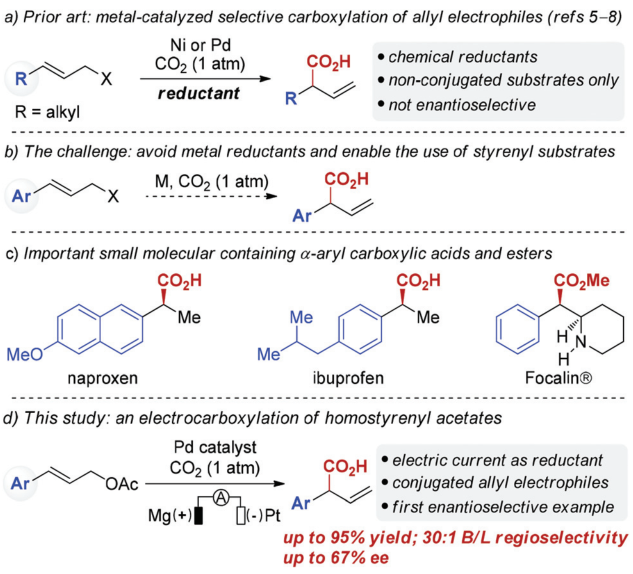
Palladium-catalyzed regioselective electrocarboxylation of homostyrenyl acetates with CO_2 has been successfully developed, providing α-aryl carboxylic acids with good selectivity and yield. In addition, the catalytic asymmetric carboxylation of cinnamyl acetate has been demonstrated, despite moderate enantioselectivity.

Introduction

Catalytic carbon–carbon (C–C) bond forming reactions that utilize carbon dioxide (CO_2) to directly access carboxylic acids have received extensive attention in the past decades due to the attractiveness of CO_2 as a C1 synthon.[1,2] In particular, transition metal-catalyzed allylation of carbon dioxide has emerged as a promising tool to construct β,γ-unsaturated carboxylic acids.[3] Most allylic carboxylation reactions that incorporate CO_2 require highly reactive substrates such as allylstannanes or allylboron reagents, which is due to both the thermodynamic stability and kinetic inertia of CO_2.[4] Recently, Martin and co-workers elegantly demonstrated Ni-catalyzed carboxylation of allyl acetates with CO_2 utilizing Mn as a reducing agent (Scheme 1a).[5] Similarly, Sato and co-workers have successfully developed Pd-catalyzed carboxylation of allylic alcohols using Et_2Zn as a reducing agent.[6] More recently, the Martin group[7] and our group[8] independently reported Ni-catalyzed carboxylation of allyl alcohols using Mn powder. Unfortunately, the use of super-stoichiometric amounts of reducing agents like Mn or Et_2Zn is a drawback of these reactions. Furthermore, these developed protocols are not suitable for homostyrenyl electrophiles (Scheme 1b). Enantio- and regioselective carboxylations of homostyrenyl electrophiles are needed as an efficient way to deliver α-aryl carboxylic acids, which are found in numerous medicines (Scheme 1c). Toward that end, the development of catalytic carboxylation reactions using more environmentally benign reducing agents is highly desirable.[9]

Electrochemistry has been demonstrated to be an efficient and environmentally friendly approach for organic chemistry that employs electrons as redox reagents.[10–12] As part of our ongoing interest in using electric currents as redox reagents in palladium catalyzed reactions,[13] we questioned whether catalytic carboxylations of allyl acetates could be achieved using electric current as a reducing agent.[14] Herein, we describe the first Pd-catalyzed regioselective carboxylation of homostryrenyl acetates utilizing electric current as the reductant, thus providing an environmentally benign method for accessing α-aryl



Scheme 1 Catalytic carboxylation of allyl electrophiles.

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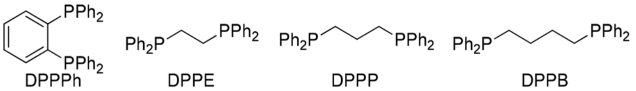
carboxylic acids. In addition, we demonstrate the first catalytic asymmetric carboxylation of cinnamyl acetate, which provides a heretofore unavailable opportunity to construct chiral phenyl acetic acids from homostyrenyl acetates (Scheme 1d).

Results and discussion

Our initial studies focused on Pd-catalyzed carboxylation of (*E*)-3-(4-bromophenyl)allyl acetate **1a** with CO_2 (Table 1). We chose **1a** as the model substrate because it contains relatively reactive C–Br and C–O bonds, which may have different reactivities under electrochemical conditions, and the retained bromide may be subsequently elaborated into useful products by employing various metal-catalyzed cross-coupling reactions.[15] To our delight, at 30 °C, using $Pd(OAc)_2$ as catalyst and 1,2-bis(diphenylphosphino)benzene (DPPPh) as ligand, with Et_4NOTs as electrolyte, EtOH as an additive, and DMF as solvent, the reaction of **1a** with CO_2 gave 81% isolated yield of branched product **2a** with 20 : 1 regioselectivity under constant current electrolysis conditions at 8.0 mA ($J = 8.0$ mA cm^{-2}) at 3 F mol^{-1} (entry 1). Lower regioselectivity was observed when other phosphine ligands were used, including PPh_3, and bidendate DPPE, DPPP, DPPB (entries 2–5). Without EtOH, the regioselectivity and yield were significantly reduced (entry 6). Decreasing or increasing the amount of EtOH to 0.5 or 5.0 equivalents resulted in a slight decrease in yield (entries 7 and 8). Cathodic reduction of EtOH could take place to stabilize the reaction system, although the real role of EtOH is not clear at this stage. Furthermore, both $Pd(OAc)_2$ and phosphine ligand are required for achieving regioselective carboxylation (entries 9 and 10). Finally, a control experiment gave the results that no reaction was observed in the absence of electric current (entry 11). It is worth noting that chemical reductant such as Mn or Zn is not suitable for this carboxylation reaction (entry 12). This implies that electrochemistry could provide unique reactivity by enhancing the nucleophilicity of resulting palladium species (*vide infra*).

Table 1 Reaction optimization with substrate **1a**[a]

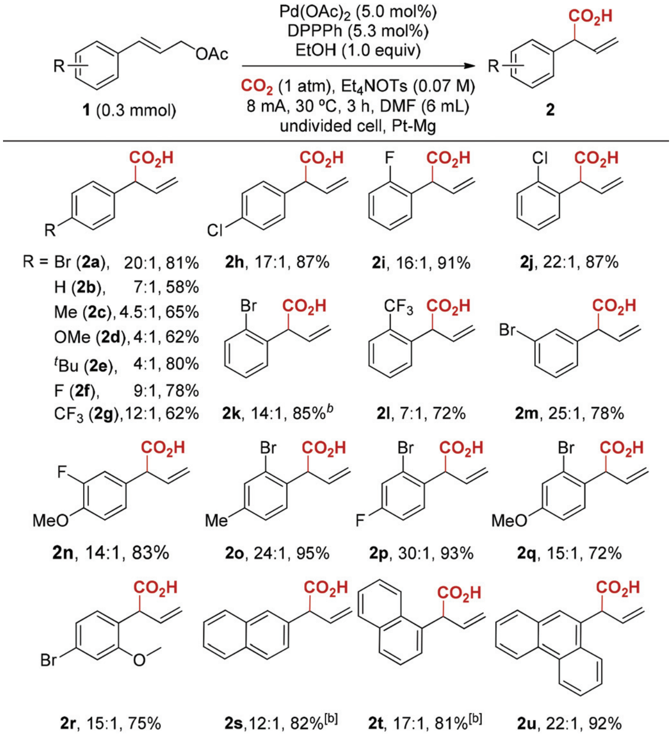
Entry	Deviation from above conditions	F mol^{-1}	Conv.[b] (%)	Yield[b] (%)	2a/2aa[c]
1	None	3	100	85 (81)[d]	20 : 1
2	PPh_3 (12 mol%) in lieu of DPPPh	3	79	36	2 : 1
3	DPPE in lieu of DPPPh	3	85	70	15 : 1
4	DPPE in lieu of DPPPh	3	81	65	18 : 1
5	DPPE in lieu of DPPPh	3	68	51	6 : 1
6	No EtOH	3	38	21	2 : 1
7	EtOH (0.5 equiv.)	3	94	64	20 : 1
8	EtOH (5.0 equiv.)	3	81	59	11 : 1
9	no $Pd(OAc)_2$	3	32	19	2 : 1
10	no DPPPh	3	72	38	3 : 1
11	no electric current	—	0	NP	—
12	Mn or Zn in lieu of electric current	—	0	NP	—



[a] Reaction conditions: **1a** (0.3 mmol), $Pd(OAc)_2$ (5.0 mol%), DPPPh (5.3 mol%), Et_4NOTs (0.15 g, 0.07 M) and EtOH (1.0 equiv.), DMF (6 mL) in an undivided cell with a platinum electrode and a magnesium rod as sacrificial anode. [b] The ratio of B/L products was determined by ^1H-NMR. [c] The yields were determined by ^1H-NMR with CH_2Br_2 as the internal standard. [d] Isolated yield of **2a**.

With the optimized reaction conditions in hand, we next investigated the scope of this reductive electrocarboxylation reaction (Table 2). In addition to Br, our conditions were compatible with numerous other functional groups, including F, Cl, Me, OMe, *t*-Bu, and CF_3 (**2a–2r**). Substrates containing electron-withdrawing groups (**2a**, **2f–2h**) deliver better regioselectivity than electronrich ones (**2b–2e**). Interestingly, this electronic factor is different from Pd-catalyzed allylic alkylation, in which electron-withdrawing groups on aryl rings reduce formation of the branched product.[16] It is worth emphasizing that polysubstituted arenes also deliver high regioselectivity (**2n–2r**). Finally, substrates bearing polycyclic

Table 2 Substrate scope[a]



[a] Yields of the indicated major product were reported. Regioselectivities were determined by crude ^1H-NMR analysis. [b] DPPE was used as the ligand.

aromatics such as naphthalene and anthracene were well tolerated in the reaction (**2s**–**2u**). Unfortunately, alkyl-substituted allylic esters or 3,3-disubstituted allylic esters are not effective at current reaction conditions.

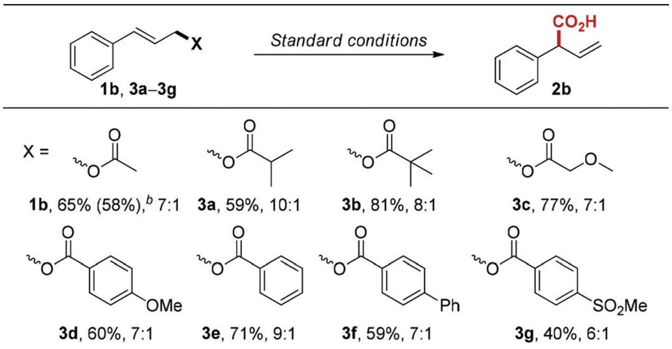
Next, we examined the influence of the leaving group on the reaction, since many allylic compounds with appropriate leaving groups can form π-allylpalladium intermediate *via* oxidative addition to Pd(0) under mild conditions.[17] Unsurprisingly, the different leaving groups influence reaction performance under the optimized conditions (Table 3). Among the esters we tested, cinnamyl isobutyrate (**3a**) gave the best regioselectivity (10 : 1). However, cinnamyl pivalate (**3b**) provided the best yield (81%) with slightly lower regioselectivity (8 : 1). We also investigated the electronic influence of substituted benzoate leaving groups (**3d**–**3g**), but we did not observe any correlation between Hammett values and regioselectivity.

The enantioselective carboxylation of allylic acetates is a major challenge.[18] To our delight, chiral bidentate triarylphosphine ligands were found to be efficient for this catalytic asymmetric carboxylation, and moderate enantioselectivity (67% ee) was achieved (Scheme 2). Interestingly, chiral bidentate phosphine ligands are known to be inactive in Pd-catalyzed allylation of aldehydes.[19]

To gain insight into the reaction mechanism, a cyclic voltammogram (CV) was conducted. The CV of [(*R*)-BINAP]Pd$(OAc)_2$ in DMF reveals one irreversible reduction wave at −0.60 V *vs.* Ag/AgI, corresponding to the reduction of Pd(II) to Pd(0) (b, Fig. 1). The addition of homostyrenyl acetate **1b** causes an increase in the peak current, which indicates oxidative addition of Pd(0) to allyl acetate **1b** (c, Fig. 1). Furthermore, we also observed the second reduction wave at −0.90 V, which is tentatively assigned to the reduction of the resulting allylPd(II) species (c, Fig. 1). The further increase of peak currents (both around −0.65 V and −1.05 V) after the addition of CO_2 suggests that the carboxylation takes place (d, Fig. 1).

Based on Wendt's and Hazari's elegant studies on η^1-allylPd species reacting with CO_2 and our observation, a plausible mechanism for this Pd-catalyzed carboxylation reaction *via* electrochemical reduction is proposed in Scheme 3.[4] Initially, oxidative addition of Pd(0) to the allyl electrophile generates a cationic π-allylpalladium(II) complex (**A**) with leaving group (OAc) as the counteranion,[20] which is in equilibrium to the terminal η^1-allylpalladium(II) species (**B** and **C**).[4] The formation of species **C**, which leads to linear carboxylation product, is less favored due to the steric hindrance between catalyst and aryl group. Next, complex **B** is directly reduced at the cathode to form an anionic η^1-allylpalladium(0) species (**D**) by overall two-electron transfer, which is consistent with the studies on carboxylation of aryl halides by Amatore, Jutand and co-workers.[21] Finally, the nucleophilic complex **D** reacts with CO_2 at the γ-position to deliver product **E** in the presence

Table 3 Leaving group influence[a]



1b, 65% (58%),[b] 7:1 **3a**, 59%, 10:1 **3b**, 81%, 8:1 **3c**, 77%, 7:1

3d, 60%, 7:1 **3e**, 71%, 9:1 **3f**, 59%, 7:1 **3g**, 40%, 6:1

[a] Yields and regioselectivities were determined by crude ^{1}H-NMR analysis. [b] Isolated yield in parentheses.

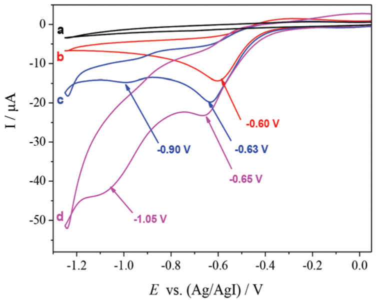
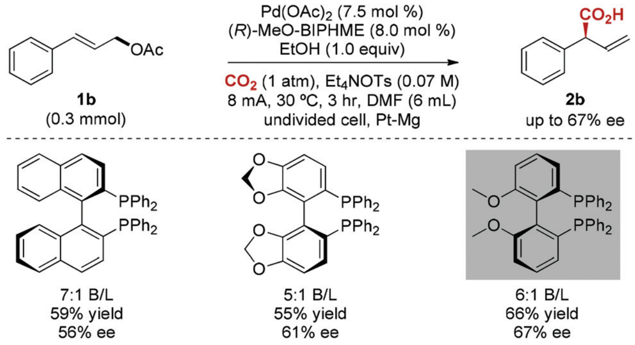
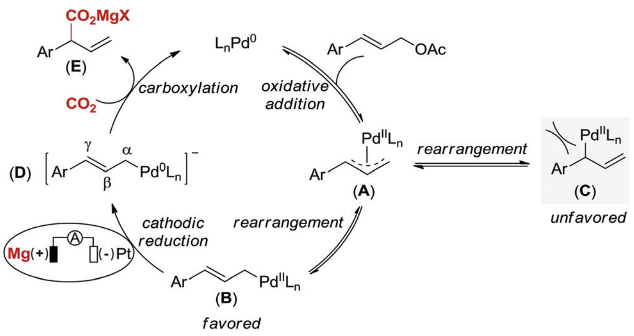


Fig. 1 Cyclic voltammograms recorded on a Pt electrode at 100 mV s^{-1} in: (a) DMF containing 0.07 M Bu_4NPF_6; (b) solution (a) after addition of 2 mM [(*R*)-BINAP]Pd$(OAc)_2$; (c) solution (b) after addition of 20 mM **1b**; (d) solution (c) saturated with CO_2.



Scheme 2 Enantioselective carboxylation.



Scheme 3 Proposed reaction mechanism.

of Mg^{2+} derived from anodic oxidation, thus regenerating Pd(0). Since carboxylation did not occur in the absence of electric current, the terminal η^1-allylpalladium(II) species (**B**) attack CO_2 directly to deliver the palladium(II) carboxylate is not likely in our reaction system.[22]

Conclusions

In summary, we have demonstrated the first example of Pd(0)-catalyzed regioselective carboxylation reaction of homostyrenyl acetates under electrochemical reduction. Compared to established catalytic methods, we employed raw electrons to facilitate this transformation. In addition, an enantioselective carboxylation was also realized *via* Asymmetric Organometallic Electrochemistry (AOE). These findings provide a new avenue for transition metal-catalyzed electrochemical reactions using chiral ligands. Investigations aimed at understanding the reaction mechanism and further increasing the scope of these reactions are currently underway in our laboratory.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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