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Iron-catalyzed, Highly Regioselective, Synthesis of α -Aryl Carboxylic Acids from Styrene Derivatives and CO₂**

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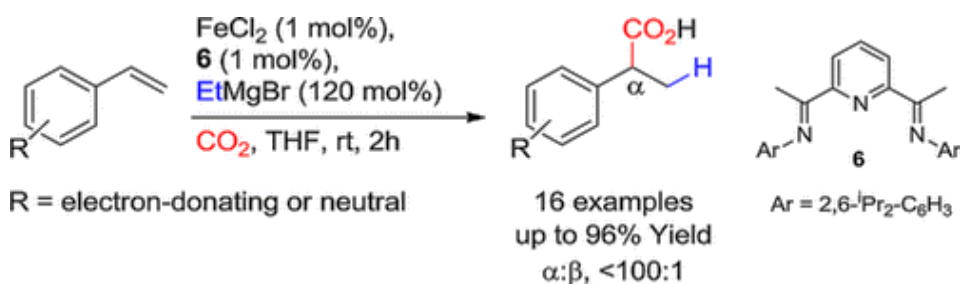
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Supporting information:

Full experimental procedures and analytical data are available. This material is available free of charge via the Internet at <http://pubs.acs.org>

Graphical abstract:



Abstract

The iron-catalyzed hydrocarboxylation of aryl alkenes has been developed using a highly active bench-stable iron(II) precatalyst to give α -aryl carboxylic acids in excellent yields and with near-perfect regioselectivity. Using just 1 mol % FeCl₂, bis(imino)pyridine **6** (1 mol %), CO₂ (atmospheric pressure), and a hydride source (EtMgBr, 1.2 equiv), a range of sterically and electronically differentiated aryl alkenes were transformed to the corresponding α -aryl carboxylic acids (up to 96% isolated yield). The catalyst was found to be equally active with a loading of 0.1 mol %. Preliminary mechanistic investigations show that an iron-catalyzed hydrometalation is followed by transmetalation and reaction with the electrophile (CO₂).

Main text

Iron-catalyzed processes have become increasingly important in the construction of complex molecular frameworks due to the environmental, health and cost benefits of using iron in place of traditionally used transition metals.¹ Carbon dioxide is an attractive carbon source for organic synthesis due to its low cost, low toxicity and ease of handling. Despite the extensive use of carbon monoxide in homo- and heterogeneous catalysis as a C₁ feedstock, e.g. hydroformylation, methodology to utilize carbon dioxide under mild conditions remains underdeveloped.² Iron-catalyzed processes offer an economical and environmentally benign alternative to the transition metals traditionally used in homogeneous catalysis.³⁻⁷ Herein we report the highly regioselective iron-catalyzed synthesis of carboxylic acids from alkenes and carbon dioxide; overall, an iron-catalysed hydrocarboxylation (Figure 1).

Hoberg reported the reaction of carbon dioxide with stoichiometric low-valent nickel- and iron-alkene complexes to give carboxylic acids.⁸ Rovis developed Hoberg's nickel-mediated carboxylation into a reductive carboxylation of electron-deficient and electron-neutral styrene derivatives using a sub-stoichiometric nickel(II) pre-catalyst (Figure 1).⁹ Hayashi and Shirakawa recently reported a cooperative iron-copper catalyzed hydromagnesiation of terminal alkenes by alkene-Grignard exchange (Figure 1).¹⁰ The process required an iron salt for the hydrometallation step and a copper salt to aid transmetalation to magnesium.

We sought to develop an iron-catalyzed hydrocarboxylation of alkenes starting from an inexpensive, commercially available, non-toxic and bench-stable iron(II) precatalyst. The reaction of iron(II) salts with Grignard reagents bearing β -hydrogens results in reduction of the iron centre to give a low-valent, highly reactive, 'inorganic Grignard' species.¹¹ The proposed reduction pathway involves the formation of transient low valent iron-hydride species, which we aimed to exploit by trapping with a

suitable alkene in a hydrometallation process. The hydrometallated intermediate may then be able to react with carbon dioxide to produce the hydrocarboxylation product.

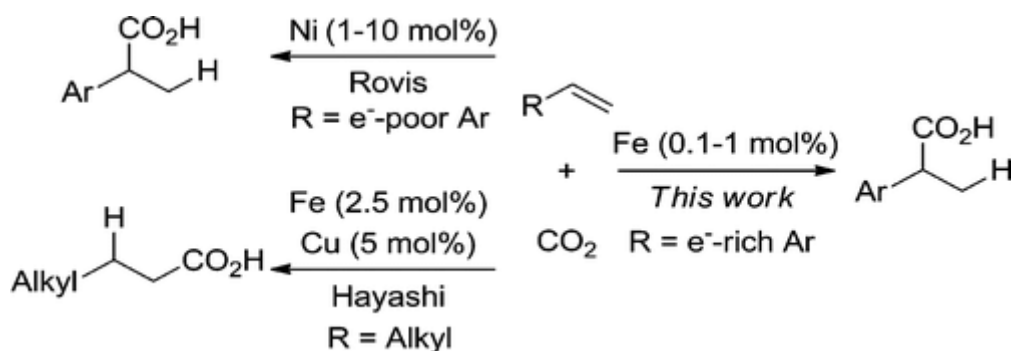
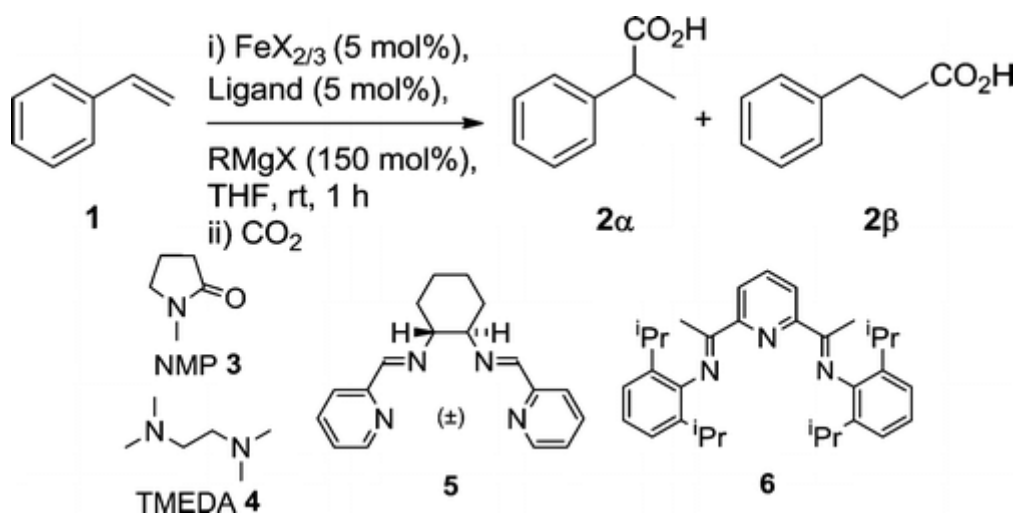


Figure 1. Proposed iron-catalyzed hydrocarboxylation of alkenes.

Initial studies focused on the hydrocarboxylation of styrene using 5 mol% of a simple iron salt with ethylmagnesium chloride as the hydride source. At room temperature very low yields of the carboxylic acid product **2** were observed (Table 1, entries 1-2), however upon heating the reaction at reflux, Fe(OTf)₂ was found to catalyze the reaction to an equal extent as that reported by Rovis (entry 3),⁹ however this yield could not be improved upon. At room temperature, 5 mol% *N*-methylpyrrolidone (NMP) **3** and FeCl₂¹² gave a reaction yield to 27% (entry 4). *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) **4**, tri(*n*-butyl)phosphine, and tetradentate amine ligand **5**¹³ all showed moderate reactivity and regioselectivity (entries 5-7). The most active catalyst was formed using bis(imino)pyridine ligand **6**¹⁴ which gave a yield of 85% and near-perfect regioselectivity for the α -carboxylic acid **2 α** (α : β >100:1) (entry 8). iso-Propylmagnesium chloride gave similar conversion, however with reduced regioselectivity (α : β 13:1) (entry 9). Ethylmagnesium bromide gave quantitative conversion to the carboxylic acids **2** (96% isolated yield **2 α**) with excellent regioselectivity (α : β 75:1) (entry 10), even when using just 0.1 mol% pre-catalyst or the hydrated iron salt (entries 12-14). Cyclopentylmagnesium bromide also gave good conversion; however the use of a secondary Grignard reagent, again, resulted in a lower regioselectivity (α : β 14:1) (entry 11). The hydrocarboxylation reaction showed reduced activity in other solvent systems and at lower temperatures.^{15,16}

Importantly, in the absence of iron, no hydrocarboxylation was observed and the addition of trace levels of other transition metal salts to the standard reaction conditions did not increase the yield of the reaction. The use of these other transition metal salts in the absence of FeCl₂ showed no catalytic activity.¹⁵ High purity FeCl₂ (99.99%) also catalyzed the reaction with near quantitative yields.^{15,17}



entry	Iron salt	Ligand	RMgX	Yield (%) ^b	
				2 α	2 β
1	FeCl ₂	-	EtMgCl ^c	<1	0
2	FeCl ₃	-	EtMgCl ^c	2	0
3	Fe(OTf) ₂ ^d	-	EtMgCl ^c	59	2
4	FeCl ₂	NMP 3	EtMgCl ^c	27	<1
5	FeCl ₂	TMEDA 4	EtMgCl ^c	62	<1
6	FeCl ₂	P(<i>n</i> -Bu) ₃	EtMgBr ^e	66	2
7	FeCl ₂	5	EtMgCl ^c	66	0
8	FeCl ₂	6	EtMgCl ^c	85	<1
9	FeCl ₂	6	<i>i</i> -PrMgCl ^f	79	6
10	FeCl ₂	6	EtMgBr ^e	98 (96) ^g	1
11	FeCl ₂	6	Cyclopentyl-MgBr ^h	87	6
12 ⁱ	FeCl ₂ (1 mol%)	6 (1 mol%)	EtMgBr ^e	97	1
13	FeCl ₂ (0.1 mol%)	6 (0.1 mol%)	EtMgBr ^e	97	1
14	FeCl ₂ ·4H ₂ O ^j	6 ^j	EtMgBr ^e	97	1

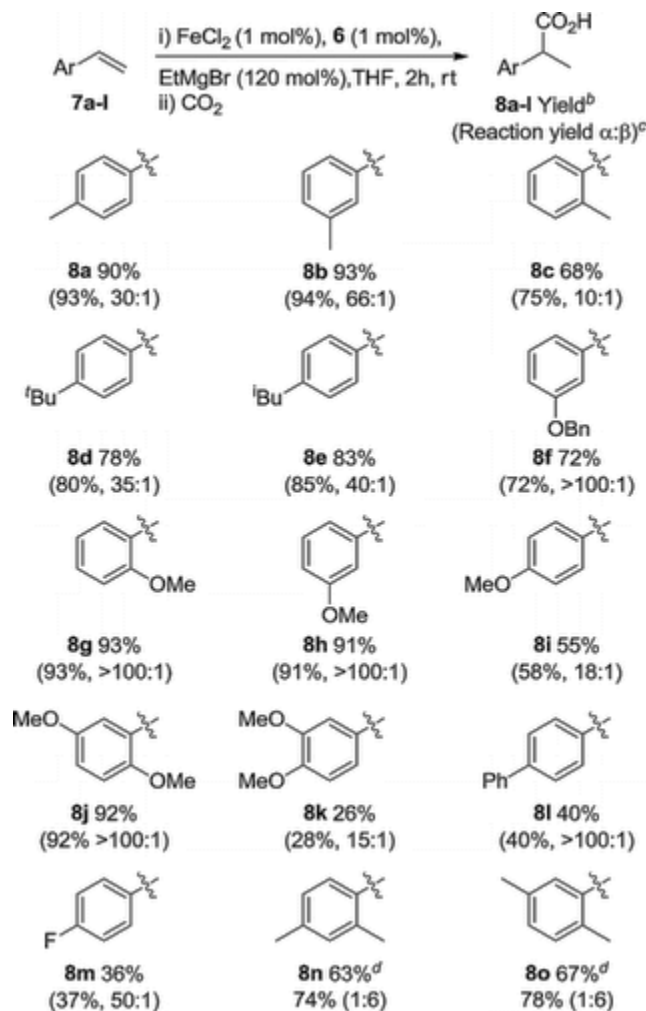
^a Conditions: 0.7 mmol **1**, 5 mol% iron salt, 5 mol% ligand, THF (0.15 M), 150 mol% RMgX, 1 h, r.t. (ii) CO₂, 30 min. ^b Yield determined by ¹H NMR using an internal standard. ^c 2 M in THF. ^d Heated at reflux. ^e 3 M in Et₂O. ^f 1 M in THF. ^g Isolated yield. ^h 2 M in Et₂O. ⁱ 3 h reaction time. ^j 1 mol%.

Table 1. Catalyst identification for the hydrocarboxylation of styrene^a.

The scope of the reaction was investigated using a 1 mol% catalyst loading, which was formed in situ from FeCl₂ and bis(imino)pyridine ligand **6** (Table 2). Pleasingly, it was found that the developed methodology worked most efficiently for styrene derivatives bearing electron-donating groups, demonstrating the complementary nature of this method to those of Rovis and Hayashi and Shirakawa (Figure 1).^{9,10,18}

Alkyl substitution in all positions on the aromatic ring were well tolerated (Table 2, **8a-e**), giving the α -carboxylic acids **8a-d** in excellent yield, with only *ortho*-methyl styrene showing a slightly reduced

regioselectivity ($\alpha:\beta$ 10:1). The hydrocarboxylation of iso-butylstyrene gave directly the pharmaceutical ibuprofen in excellent yield and regioselectively ($\alpha:\beta$ 40:1). Benzyl protected phenol derivative **7f** gave the α -carboxylic acid **8f** with no benzyl deprotection observed under the reductive reaction conditions.



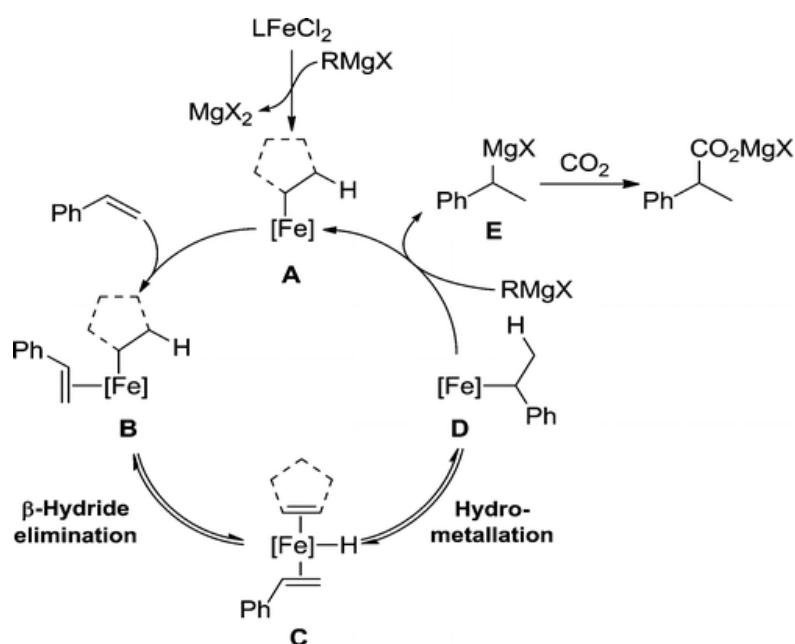
^a Conditions: 0.7mmol **1**, **7a-l**, 1 mol% FeCl₂, 1 mol% **7**, THF (0.15M), rt, (i) 120 mol% EtMgBr (3M in Et₂O), 2h (ii) CO₂, 30 min. ^b Isolated yield of α -product. ^c Reaction yield and regioselectivity determined by ¹H NMR using an internal standard. ^d 120 mol% Cyclopentylmagnesium bromide used (2M in Et₂O), Isolated yield of β -product.

Table 2. Iron-catalyzed hydrocarboxylation of styrene derivatives: scope and limitations^a.

The electron-rich *ortho*- and *meta*-methoxystyrene derivatives gave the α -carboxylic acids **8g** and **8h** in excellent yield and regioselectivity ($\alpha:\beta$ >100:1), however *para*-methoxystyrene gave α -carboxylic acid **8i** in slightly reduced yield and regioselectivity (58%, $\alpha:\beta$ 18:1). 2,5-bismethoxystyrene gave α -carboxylic acid **8j** in excellent yield and regioselectivity (92%, $\alpha:\beta$ >100:1), however 3,4-

To investigate whether the α -selectivity originated from a regioselective hydrometallation or by isomerization of an intermediate Grignard reagent to the thermodynamically more stable α -Grignard, the β -Grignard reagent **10** was independently synthesized and exposed to the standard reaction conditions (Scheme 1C). Very little isomerization to the α -Grignard reagent was observed, suggesting the β -hydride elimination-hydrometallation process is faster than the conformational isomerization of the intermediate iron-hydride-styrene species needed to produce the α -product **2**. However, the addition of an equivalent of *tert*-butylstyrene showed isomerization of the β -Grignard **10** to give a majority of the α -carboxylic acids arising from both the Grignard **10** (by β -hydride elimination, conformational isomerization and hydrometallation) and *tert*-butylstyrene (by direct hydrometallation) (Scheme 1D). Considering the rapid rate of β -hydride elimination-hydrometallation with respect to transmetallation or conformational isomerization, and the decrease in regioselectivity (Table 2), it seems likely that *tert*-butylstyrene is co-ordinated to iron prior to β -hydride elimination of the Grignard reagent **10** or competitively coordinates to iron with the generated styrene.

Thus our suggested mechanism is based on the iron-catalyzed formation of a hydromagnesiated intermediate species capable of reaction with carbon dioxide (Scheme 2).²¹ Alkylation of the iron precatalyst and co-ordination of styrene gives an organoferrate complex **B**, which can undergo β -hydride elimination to give an active low-valent iron hydride complex **C**. Hydrometallation of styrene gives the organoferrate complex **D**, which could undergo transmetallation with another equivalent of ethylmagnesium bromide to release the hydromagnesiated product **E**, and reform the initial organoferrate complex **A**.



Scheme 2. Proposed mechanism for the iron-catalyzed hydrocarboxylation of alkenes.

In summary, an operationally simple, highly active, iron-catalyzed hydrocarboxylation of aryl alkenes has been developed for the synthesis of α -aryl carboxylic acids using CO₂ as the C₁-feedstock. Excellent yields have been achieved for alkyl substituted styrene derivatives with excellent control of regioselectivity. Significantly, styrene derivatives bearing electron-donating groups, which have proved difficult previously, were successfully hydrocarboxylated with good yields and excellent regioselectivity. Mechanistic investigations showed the reaction proceeds by a highly regioselective and reversible iron-catalyzed hydrometallation, followed by transmetallation giving an α -aryl Grignard reagent which reacts with CO₂. This methodology provides a significant advance in the iron-catalyzed functionalization of alkenes using mild and operationally simple conditions.

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