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Iron-Catalyzed, Highly Regioselective Synthesis of α-Aryl Carboxylic Acids from Styrene Derivatives and CO_2

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Supporting Information

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 % $FeCl_2$, bis(imino)pyridine **6** (1 mol %), CO_2 (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 (CO_2).

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 C_1 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-catalyzed 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 -neutral styrene derivatives using a substoichiometric nickel(II) precatalyst (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 hydrometalation step and a copper salt to aid transmetalation to magnesium.

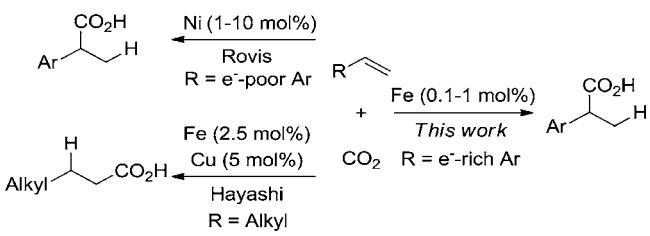

Figure 1. Proposed iron-catalyzed hydrocarboxylation of alkenes.

We sought to develop an iron-catalyzed hydrocarboxylation of alkenes starting from an inexpensive, commercially available, nontoxic, and bench-stable iron(II) precatalyst. The reaction of iron(II) salts with Grignard reagents bearing β-hydrogens results in reduction of the iron center 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 hydrometalation process. The hydrometalated intermediate may then be able to react with carbon dioxide to produce the hydrocarboxylation product.

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] Yet, this yield could not be improved upon. At room temperature, 5 mol % *N*-methylpyrrolidone (NMP) **3** and $FeCl_2$[12] gave a yield of 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 **2α** (α:β >100:1) (entry 8). Isopropylmagnesium chloride gave a similar conversion, however with reduced regioselectivity (α:β 13:1) (entry 9). Ethylmagnesium bromide gave a quantitative conversion to the carboxylic acids **2** (96% isolated yield **2α**) with excellent regioselectivity (α:β 75:1) (entry 10), even when using just 0.1 mol % precatalyst 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]

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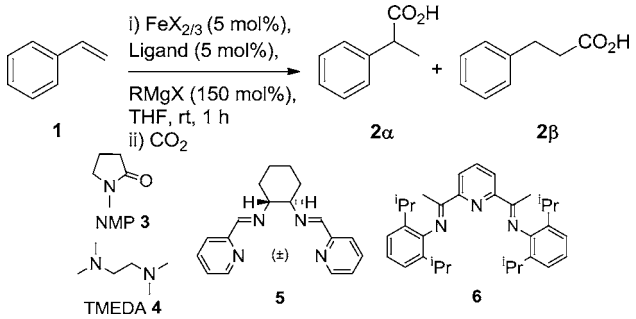
Table 1. Catalyst Identification for the Hydrocarboxylation of Styrene[a]



entry	iron salt	ligand	RMgX	yield (%)[b] 2α	2β
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	$FeCl_2$	$P(n\text{-}Bu)_3$	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*-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	$FeCl_2 \cdot 4H_2O$[j]	**6**[j]	EtMgBr[e]	97	1

[a]Conditions: (i) 0.7 mmol of **1**, 5 mol % iron salt, 5 mol % ligand, THF (0.15 M), 150 mol % RMgX, 1 h, rt; (ii) CO_2, 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 Et_2O. [f]1 M in THF. [g]Isolated yield. [h]2 M in Et_2O. [i]3 h reaction time. [j]1 mol %.

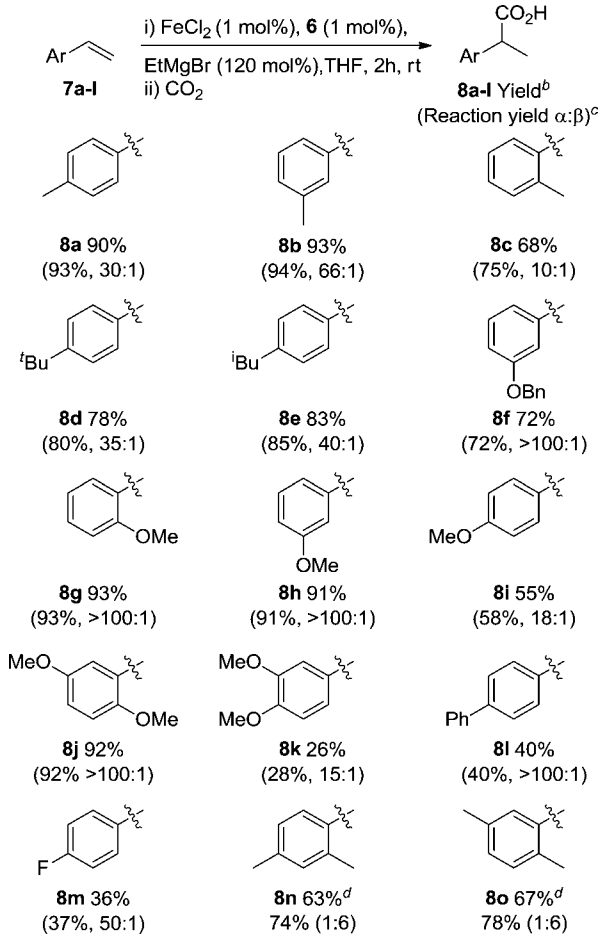
Importantly, in the absence of iron, no hydrocarboxylation was observed and the addition of trace levels of other transition metal salts to the standard reaction conditions did not increase the yield of the reaction. The use of these other transition metal salts in the absence of $FeCl_2$ showed no catalytic activity.[15] High purity $FeCl_2$ (99.99%) also catalyzed the reaction with near-quantitative yields.[15,17]

The scope of the reaction was investigated using a 1 mol % catalyst loading, which was formed *in situ* from $FeCl_2$ 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 was 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 (α:β 10:1). The hydrocarboxylation of isobutylstyrene gave directly the pharmaceutical ibuprofen in excellent yield and regioselectively (α:β 40:1). Benzyl protected phenol derivative **7f** gave the α-carboxylic acid **8f** with no benzyl deprotection observed under the reductive reaction conditions.

The electron-rich *ortho*- and *meta*-methoxystyrene derivatives gave the α-carboxylic acids **8g** and **8h** in excellent yield and

Table 2. Iron-Catalyzed Hydrocarboxylation of Styrene Derivatives: Scope and Limitations[a]

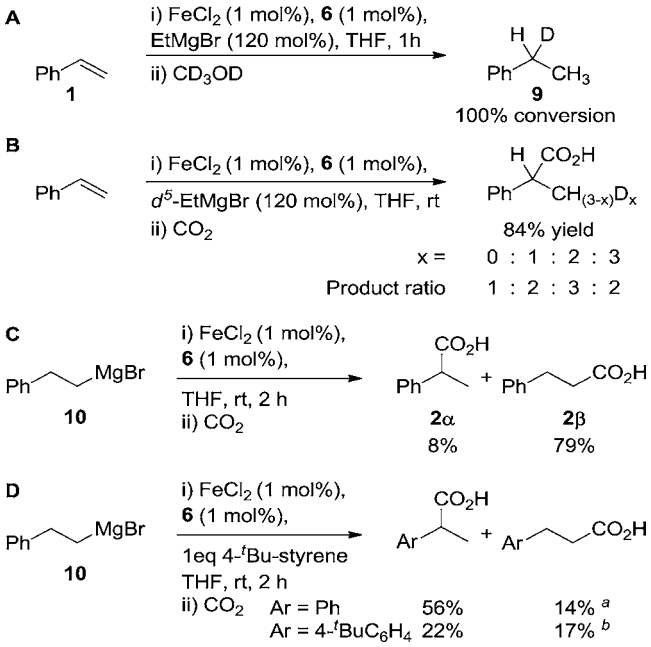


[a]Conditions: 0.7 mmol of **1**, **7a–l**, 1 mol % $FeCl_2$, 1 mol % **7**, THF (0.15 M), rt; (i) 120 mol % EtMgBr (3 M in Et_2O), 2 h; (ii) CO_2, 30 min. [b]Isolated yield of α-product. [c]Reaction yield and regioselectivity determined by ^1H NMR using an internal standard. [d]120 mol % Cyclopentylmagnesium bromide used (2 M in Et_2O); isolated yield of β-product.

regioselectivity (α:β >100:1); however *para*-methoxystyrene gave α-carboxylic acid **8i** in a slightly reduced yield and regioselectivity (58%, α:β 18:1). 2,5-Bismethoxystyene gave α-carboxylic acid **8j** in excellent yield and regioselectivity (92%, α:β >100:1); however 3,4-bismethoxystyrene gave a reduced yield, possibly due to Grignard-mediated demethylation which was enhanced by coordination to the adjacent methoxy group (**8k**). Electron-deficient styrene derivatives showed reduced activity; 4-vinylbiphenyl and *para*-fluorostyrene gave moderate yields of α-carboxylic acids **8l** and **8m**, but with excellent regioselectivity (α:β >50:1).[19] When 2,4-dimethyl and 2,5-dimethyl styrene derivatives were tested a significantly lower regioselectivity was observed (α:β ~1:1). Cyclopentylmagnesium bromide, in place of EtMgBr, gave much higher yields, albeit with a reversal in regioselectivity to the β-product **8nβ** and **8oβ** (74–78%, α:β 1:6). Presumably the change in regioselectivity arises due to the increased steric bulk around the iron catalyst, resulting in a kinetic preference for hydrometalation to give the linear β-product.

When the reaction was quenched with d^4-methanol, complete conversion to (1-deuteroethyl)benzene was observed implying the presence of an intermediate α-aryl organometallic

Scheme 1. Mechanistic Investigations into the Iron-Catalyzed Hydrometallation of Alkenes and Isomerization of Grignard Reagents[a,b]

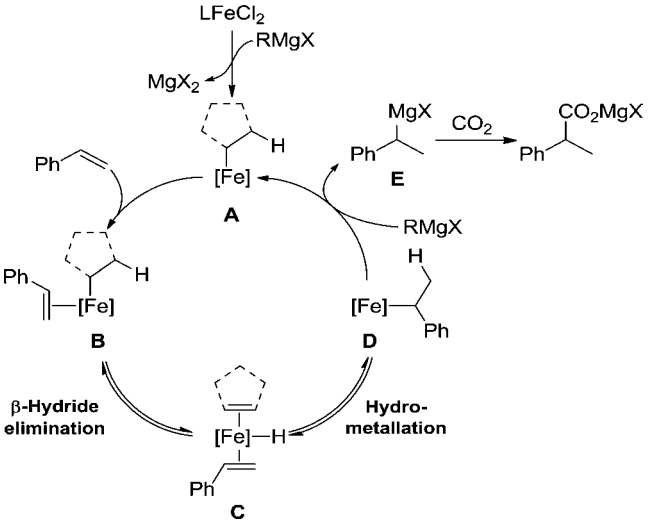


[a]Percentage yields with respect to **10**. [b]Percentage yields with respect to 4-^{t}Bu-styrene.

species (Scheme 1A). To confirm that the incorporated hydride originated from the Grignard reagent, d^5-ethylmagnesium bromide was used in the reaction (Scheme 1B).[20] This gave a complex mixture of β-deuterated products, with zero, one, two, and three deuterium atoms incorporated at the terminal position. This suggests that hydrometalation is both fast and reversible under the reaction conditions. It was calculated that 150 mol % deuterium incorporation had occurred, which is in support of a highly reversible process. No deuterium incorporation was observed at the α-position, suggesting that hydrometalation is highly regioselective in this case.

To investigate whether the α-selectivity originated from a regioselective hydrometalation 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−hydrometalation 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 hydrometalation) and *tert*-butylstyrene (by direct hydrometalation) (Scheme 1D). Considering the rapid rate of β-hydride elimination−hydrometalation with respect to transmetalation or conformational isomerization, and the decrease in regioselectivity (Table 2), it seems likely that *tert*-butylstyrene is coordinated to iron prior to β-hydride elimination of the Grignard reagent **10** or competitively coordinates to iron with the generated styrene.

Scheme 2. Proposed Mechanism for the Iron-Catalyzed Hydrocarboxylation of Alkenes



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 coordination of styrene give an organoferrate complex **B**, which can undergo β-hydride elimination to give an active low-valent iron hydride complex **C**. Hydrometalation of styrene gives the organoferrate complex **D**, which could undergo transmetalation with another equivalent of ethylmagnesium bromide to release the hydromagnesiated product **E**, and reform the initial organoferrate complex **A**.

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 CO_2 as the C_1-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 hydrometalation, followed by transmetalation giving an α-aryl Grignard reagent which reacts with CO_2. This methodology provides a significant advance in the iron-catalyzed functionalization of alkenes using mild and operationally simple conditions.

■ ASSOCIATED CONTENT

Supporting Information

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

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) For reviews of iron catalysis, see: (a) Bolm, C.; Legros, J.; Le Paih, J.; Zani, L. *Chem. Rev.* **2004**, *104*, 6217. (b) Enthaler, S.; Junge, K.; Beller, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3317. (c) Correa, A.; García Mancheño, O.; Bolm, C. *Chem. Soc. Rev.* **2008**, *37*, 1108. (d) Sherry, B. D.; Fürstner, A. *Acc. Chem. Res.* **2008**, *41*, 1500. (e) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. *Chem. Rev.* **2011**, *111*, 1293. (f) Leitner, A. *Iron Catalysis in Organic Chemistry: Reactions and Applications*; Pleitker, B., Ed.; Wiley-VCH: Weinheim, Germany, 2008, p 147.

(2) For recent reviews, see: (a) Huang, K.; Sun, C.-L.; Shi, Z.-J. *Chem. Soc. Rev.* **2011**, *40*, 2435. (b) Cokoja, M.; Bruckmeier, C.; Rieger, B.; Herrmann, W. A.; Kühn, F. E. *Angew. Chem., Int. Ed.* **2011**, *50*, 8510. (c) Riduan, S. N.; Zhang, Y. *Dalton Trans.* **2010**, *39*, 3347.

(3) For reviews, see: (a) Nakamura, E.; Yoshikai, N. *J. Org. Chem.* **2010**, *75*, 6061. (b) Czaplik, W. M.; Mayer, M.; Cvengros, J.; Jacobi von Wangelin, A. *ChemSusChem* **2009**, *2*, 396. (c) García Mancheño, O. *Angew. Chem., Int. Ed.* **2011**, *50*, 2216. (d) Fürstner, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 1364.

(4) For selected recent examples, see: (a) Steib, A. K.; Thaler, T.; Komeyama, K.; Mayer, P.; Knochel, P. *Angew. Chem., Int. Ed.* **2011**, *50*, 3303. (b) Czaplik, W. M.; Mayer, M.; Jacobi von Wangelin, A. *ChemCatChem.* **2011**, *3*, 135. (c) Gulak, S.; Jacobi von Wangelin, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 1357. (d) Mayer, M.; Czaplik, W. M.; Jacobi von Wangelin, A. *Adv. Synth. Catal.* **2010**, *352*, 2147. (e) Bedford, R. B.; Huwe, M.; Wilkinson, M. C. *Chem. Commun.* **2009**, 600. (f) Cahiez, G.; Habiak, V.; Duplais, C.; Moyeux, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 4364. (g) Yoshikai, N.; Mieczkowshi, A.; Matsumoto, A.; Ilies, L.; Nakamura, E. *J. Am. Chem. Soc.* **2010**, *132*, 5568. (h) Ilies, L.; Asako, S.; Nakamura, E. *J. Am. Chem. Soc.* **2011**, *133*, 7672. (i) Moreau, B.; Wu, J. Y.; Ritter, T. *Org. Lett.* **2009**, *11*, 337.

(5) (a) Correa, A.; García Mancheño, O.; Bolm, C. *Chem. Soc. Rev.* **2008**, *37*, 1108. (b) Chen, M. S.; White, M. C. *Science* **2010**, *327*, 566. (c) Paradin, S. M.; White, M. C. *J. Am. Chem. Soc.* **2012**, *134*, 2036. (d) Suzuki, K.; Oldenburg, P. D.; Que, L., Jr. *Angew. Chem., Int. Ed.* **2008**, *47*, 1887.

(6) (a) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 13794. (b) Bart, S. C.; Hawrelak, E. J.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2005**, *24*, 5518. (c) Phua, P. H.; LeFort, L.; Boogers, J. A. F.; Tristany, M.; de Vries, J. G. *Chem. Commun.* **2009**, 3747. (d) Takeuchi, M.; Kano, K. *Organometallics* **1993**, *12*, 2059. (e) Ashby, E. C.; Lin, J. J. *J. Org. Chem.* **1978**, *43*, 2567. (f) Tondreau, A. M.; Atienza, C. C. H.; Weller, K. J.; Nye, S. A.; Lewis, K. M.; Delis, J. G. P.; Chirik, P. J. *Science* **2012**, *335*, 567. (g) Wu, J. Y.; Stanzl, B. N.; Ritter, T. *J. Am. Chem. Soc.* **2010**, *132*, 13214. (h) Wu, J. Y.; Moreau, B.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 12915.

(7) For reviews, see: (a) Junge, K.; Schröder, K.; Beller, M. *Chem. Commun.* **2011**, *47*, 4849. (b) Le Bailly, B. A. F.; Thomas, S. P. *RSC Advances* **2011**, *1*, 1435. (c) Morris, R. H. *Chem. Soc. Rev.* **2009**, *38*, 2282. (d) Chirik, P. J. In *Catalysis without Precious Metals*; Bullock, R. M., Ed.; Wiley-VCH: Weinheim, Germany, 2010, p 83. For selected recent examples, see: (e) Langer, R.; Leitus, G.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2011**, *50*, 2120. (f) Lagaditis, P. O.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 9662. (g) Tondreau, A. M.; Darmon, J. M.; Wile, B. M.; Floyd, S. K.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2009**, *28*, 3928. (h) Shaikh, N. S.; Enthaler, S.; Junge, K.; Beller, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 2497. (i) Casey, C. P.; Guan, H. *J. Am. Chem. Soc.* **2007**, *129*, 5816.

(8) (a) Hoberg, H.; Peres, Y.; Krüger, C.; Tsay, Y.-H. *Angew. Chem., Int. Ed.* **1987**, *26*, 771. (b) Hoberg, H.; Peres, Y.; Milchereit, A. *J. Organomet. Chem.* **1986**, *307*, C38. (c) Hoberg, H.; Jenni, K.; Krüger, C.; Raabe, E. *Angew. Chem., Int. Ed.* **1986**, *25*, 810. (d) Hoberg, H.; Jenni, K.; Angermund, K.; Krüger, C. *Angew. Chem., Int. Ed.* **1987**, *26*, 153.

(9) Williams, C. M.; Johnson, J. B.; Rovis, T. *J. Am. Chem. Soc.* **2008**, *130*, 14936.

(10) Shirakawa, E.; Ikeda, D.; Masui, S.; Yoshida, M.; Hayashi, T. *J. Am. Chem. Soc.* **2012**, *134*, 272.

(11) (a) Aleandri, L. E.; Bogdanović, B.; Bons, P.; Duerr, C.; Gaidies, A.; Hartwig, T.; Huckett, S. C.; Lagarden, M.; Wilczok, U.; Brand, R. A. *Chem. Mater.* **1995**, *7*, 1153. (b) Bogdanović, B.; Schwickardi, M. *Angew. Chem., Int. Ed.* **2000**, *24*, 4610. (c) Fürstner, A.; Marin, R.; Krause, H.; Seidel, G.; Goddard, R.; Lehmann, C. W. *J. Am. Chem. Soc.* **2008**, *130*, 8773.

(12) $FeCl_2$ was chosen, as the background reaction (without ligand) was minimal and due to its low cost and wide availability.

(13) Previously used for the reductive cross-coupling of vinyl halides and Grignard reagents; see: Le Bailly, B. A. F.; Greenhalgh, M. D.; Thomas, S. P. *Chem. Commun.* **2012**, *48*, 1580.

(14) This iron complex was first used by Gibson and Brookhart as a polymerization catalyst; see: (a) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849. (b) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049. It has since used by Chirik as a hydrogenation and hydrosilylation catalyst; see ref 6a, f.

(15) See Supporting Information for details.

(16) No other hydride sources ($NaBH_4$, $LiAlH_4$, $NaHBEt_3$, $LiHBEt_3$, $^iBu_2AlH$, $LiHB^sBu_3$, $Li[Me_2NBH_3]$, ^nBuLi, Et_2Zn, Et_3Al) were found to mediate the hydrocarboxylation.

(17) (a) Buchwald, S. L; Bolm, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 5586. (b) Bedford, R. B.; Hall, M. A.; Hodges, G. R.; Huwe, M.; Wilkinson, M. C. *Chem. Commun.* **2009**, *42*, 6430.

(18) The generation of α-phenylethylmagnesium bromide by reductive insertion of magnesium is procedurally challenging as a Wurtz-type radical homocoupling dominates, resulting in 2,3-diphenylbutane as the major product. See Supporting Information and (a) Stobbe, H.; Posnjak, G. *Liebigs. Ann.* **1909**, *371*, 287. (b) Cohen, H. L.; Wright, G. F. *J. Org. Chem.* **1953**, *18*, 432.

(19) 4-F_3C-, 4-H_3CCO_2-, 4-O_2N-, and 4-NC-styrene were not tolerated under the reaction conditions. Aryl bromides and chlorides underwent proto-dehalogenation; see: Czaplik, W. M.; Grupe, S.; Mayer, M.; Jacobi von Wangelin, A. *Chem. Commun.* **2010**, *46*, 6350.

(20) In addition, methyl- and phenylmagnesium chloride failed to catalyze the reaction.

(21) The hydromagnesiation of styrene by alkylmagnesium halides has been previously reported to be catalyzed by $TiCl_4$ and $NiCl_2$; however in both cases only moderate yields were obtained under forcing conditions. See: (a) Cooper, G. D.; Finkbeiner, H. L. *J. Org. Chem.* **1962**, *27*, 1493. (b) Farády, L.; Bencze, L.; Markó, L. *J. Organomet. Chem.* **1967**, *10*, 505. $FeCl_3$ was also reported to catalyze the reaction albeit in low yield (15%).