



Cite this: *RSC Adv.*, 2019, 9, 31217

Received 22nd August 2019  
 Accepted 25th September 2019

DOI: 10.1039/c9ra07604b

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# Iron-catalysed allylation–hydrogenation sequences as masked alkyl–alkyl cross-couplings†

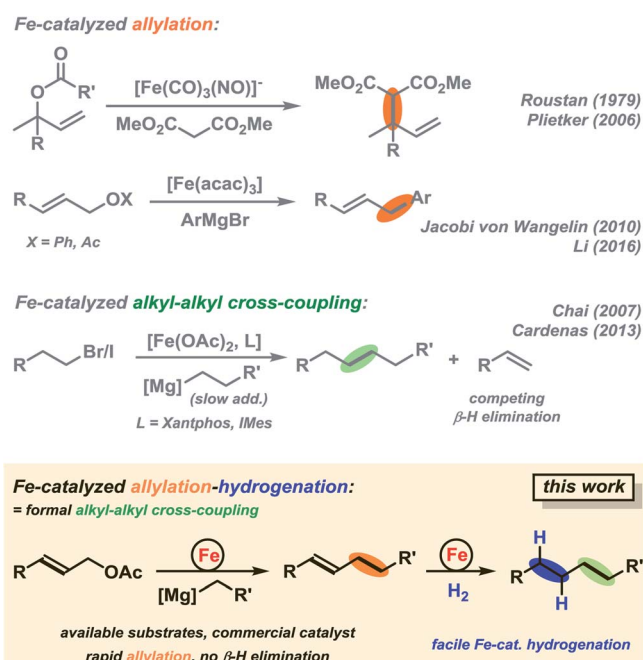
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An iron-catalysed allylation of organomagnesium reagents (alkyl, aryl) with simple allyl acetates proceeds under mild conditions ( $\text{Fe}(\text{OAc})_2$  or  $\text{Fe}(\text{acac})_2$ ,  $\text{Et}_2\text{O}$ , r.t.) to furnish various alkene and styrene derivatives. Mechanistic studies indicate the operation of a homotopic catalyst. The sequential combination of such iron-catalysed allylation with an iron-catalysed hydrogenation results in overall  $\text{C}(\text{sp}^3)\text{--}\text{C}(\text{sp}^3)$ -bond formation that constitutes an attractive alternative to challenging direct cross-coupling protocols with alkyl halides.

## Introduction

The development of transition metal-catalysed cross-coupling reactions has propelled the art of C–C bond formation like no other new methodology in the past decades.<sup>1,2</sup> Among them, Pd and Ni catalysts have clearly dominated the field by virtue of their high versatility and chemoselectivity.<sup>3</sup> However, noble and toxic metal catalysts (e.g. Pd, Rh, Ir, Ni and Co) have high costs and/or exhibit significant levels of toxicity which limit their general applicability under modern sustainability criteria. Iron-catalysed cross-coupling reactions have recently been developed to great maturity and now constitute a powerful alternative to the established noble metal systems.<sup>4–10</sup> Most protocols utilize organic halides as electrophiles (mostly I, Br); only very few reactions involve activated ester derivatives (triflates, tosylates, phosphonates).<sup>11–14</sup> Iron-catalysed cross-couplings reactions at alkenyl acetates were only recently reported.<sup>15–17</sup> Allyl alcohols constitute one of the most easily accessible classes of electrophiles by numerous substitution or reduction methods from abundant starting materials (allyl halides,  $\alpha,\beta$ -unsaturated carbonyls). However, there is no concise report of iron-catalysed reactions of simple allyl alcohol derivatives with organometallic reagents. A handful of iron-catalysed allylations have been reported.<sup>18–20</sup> The Hieber-type salt  $\text{Na}[\text{Fe}(\text{CO})_3(\text{NO})]$  (which is iso-electronic to  $\text{Pd}^0$ ) was especially competent in the catalytic allylation of malonates (Scheme 1, top).<sup>21</sup> Xu and Zhou later reported similar reactions with the stable tetrabutylammonium salt in a CO atmosphere.<sup>22</sup> Plietker *et al.* performed similar reactions in the presence of phosphine ligands that prevented the formation of inactive catalyst derivatives.<sup>18</sup> Substitutions of allyl carbonates with *N*-, *O*-, *S*-nucleophiles and stereoselective

reactions were reported under such conditions.<sup>23–26</sup> Arylations of selected allyl alcohol derivatives with aryl-Grignard reagents have been reported by Li and coworkers and us.<sup>15,27</sup> We envisioned the development of an Fe-catalysed cross-coupling between alkylmagnesium reagents and diverse allyl acetates that benefits from the intrinsic properties of allyl acetates as activated C-electrophiles and the utility of the pendant alkene moiety for further manipulation. While being a formal  $\text{sp}^3$ -electrophile, allyl-X substrates exhibit strikingly different reactivity patterns than alkyl-electrophiles due to the vicinal alkenyl moiety, the absence of  $\beta$ -hydrogen atoms, and the ability to engage in  $\eta^3$ -coordination to transition metals. In comparison



Scheme 1 Iron-catalysed allylic substitutions.<sup>15,18,21,27–29,31</sup>

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9ra07604b

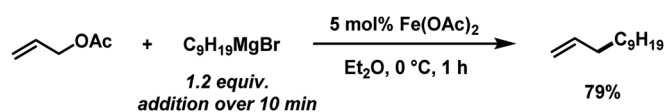


with allyl-X electrophiles, alkyl-X electrophiles exhibit a low propensity to undergo oxidative addition to transition metal complexes, engage in rapid side reactions ( $\beta$ -H elimination, rearrangement), and undergo slow reductive elimination. Consequently, there are very few literature reports on iron-catalysed alkyl-alkyl cross-couplings which exhibit only moderate yields, limited substrate scope (few examples, alkyl-Br/I), and require special conditions (slow addition over 7 h) and/or expensive ligands (Xantphos, IMes; Scheme 1, center).<sup>28–30</sup> We surmised that the combination of an effective allylation reaction with a subsequent hydrogenation reaction would constitute an attractive alternative to the challenging alkyl-alkyl cross-coupling reactions (Scheme 1, bottom).<sup>15</sup> Such method utilizes the wide availability and easy preparation of alkyl-Grignard reagents. The success of the cross-coupling with substituted allyl acetates relies on the strict control of chemoselectivity as the nucleophilic Grignard reagent may readily undergo direct attack at the carboxyl function under thermodynamic control. Iron-catalysed hydrogenations have been reported for a variety of olefins.<sup>31</sup> There are a handful of powerful homogeneous iron catalysts based on pincer-type ligands<sup>32,33</sup> and heterogeneous catalysts derived from the reduction of iron salts with organometallic or hydride reagents.<sup>34–37</sup> With regard to the latter catalyst class, we surmised that the iron catalyst that formed under the conditions of the cross-coupling reaction with the organomagnesium halide might also be competent in the subsequent alkene hydrogenation (Scheme 1, bottom right).<sup>15</sup>

## Results and discussion

### Initial optimizations

The envisaged sequence of an iron-catalysed allylation of organomagnesium halides and an iron-catalysed hydrogenation required the development of a robust allylation reaction with alkylmagnesium halides. From a rapid survey of various catalyst precursors, additives, solvents, and conditions, reactions between allyl acetate and a very low excess of the *n*-alkylmagnesium bromide (1.2 equiv., addition over 10 min) with the commercial pre-catalyst iron(II) acetate (5 mol% Fe(OAc)<sub>2</sub>) in diethylether were identified as being most effective (Scheme 2).<sup>38</sup> Importantly, Fe(OAc)<sub>2</sub> effectively inhibited the competing formal  $\beta$ -H elimination of the Grignard reagent.<sup>39</sup> Other solvents like THF, toluene, *N*-methyl-2-pyrrolidinone (NMP), and 1,2-dimethoxyethane (DME) afforded much lower yields. Toluene/Et<sub>2</sub>O mixtures and ethyl acetate gave similar results. The addition of ligands (amines, *N*-heterocyclic carbenes) showed no significant effect on the reaction outcome, whereas phosphines led to complete catalyst inhibition.<sup>38</sup> The major side



Scheme 2 Optimized conditions for iron-catalysed alkylation of allyl acetate.

reactions observed were the formation of homocoupling products from the Grignard reagent<sup>29</sup> and the nucleophilic attack at the carbonyl group. The composition of the Grignard reagent (RMgX, X = Cl, Br, I; RMgX vs. R<sub>2</sub>Mg) and the choice of solvent exerted a strong influence on the reaction selectivities, most likely as a direct consequence of the Schlenk equilibrium (Table 1).<sup>40</sup> The alkyl-magnesium chloride and the dialkylmagnesium in Et<sub>2</sub>O predominantly afforded the carboxylate substitution product from the uncatalyzed background reaction (entries 1 and 8). The alkyl-magnesium bromide (in Et<sub>2</sub>O) and its LiCl-adduct (in THF) gave highest conversions (entries 4–6).

With substituted allyl acetates bearing alkyl groups, the iron-catalysed allylation was slowed and the formation of the tertiary alcohol was observed as main product. High cross-coupling yields were re-established by slow addition of the Grignard reagent (over 1–6 h). An alternative procedure involved addition of 50 mol% chloroform to the reaction which allowed Grignard addition over only 45 min. A similar protocol was reported but the role of chloroform remained unclear.<sup>12</sup> We speculate that chloroform buffers high concentrations of Grignard reagent and thereby prevents over-reduction of the catalyst to naked Fe(0) species which would rapidly aggregate to inactive particles.<sup>41,42</sup> A similar effect should be observed with electrophilic additives that react with the Grignard reagent in slower rates than the desired cross-coupling but sufficiently rapid to prohibit catalyst reduction. Consistent with this hypothesis, a brief evaluation of electrophiles revealed beneficial effects of the presence of esters, organochlorides, and air under the reaction conditions (Scheme 3; see also Scheme 5B).<sup>38</sup>

### Substrate scope

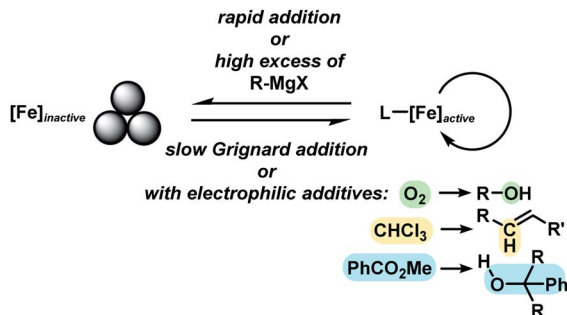
We then explored the substrate scope of the iron-catalysed allylation of alkylmagnesium bromides under the optimized conditions (condition A, see Table 2). The reaction proceeds

Table 1 Variation of Grignard reagents<sup>a</sup>

Entry	X	Solvent (RMgX)	1 [%]	2 [%]	3 [%]
1	Cl	Et <sub>2</sub> O	0	<1	52
2	Cl	THF	37	12	11
3	Cl · LiCl	THF	54	5	2
4	Br	Et <sub>2</sub> O	76	11	<1
5	Br	THF	69	6	2
6	Br · LiCl	THF	77	5	2
7	I	Et <sub>2</sub> O	32	35	0
8 <sup>b</sup>	<i>n</i> -C <sub>9</sub> H <sub>19</sub>	Dioxane	1	<1	48

<sup>a</sup> Yields were determined by quantitative GC-FID vs. internal *n*-pentadecane. <sup>b</sup> MgBr<sub>2</sub> was filtered off prior to Grignard reagent addition.





Scheme 3 Catalyst activity and effect of reaction additives.

with very high regiocontrol most likely through a  $\pi$ -allyliron intermediate as alkylation selectively occurred at the less hindered allyl termini. This is exemplified by the identical product (and yield) that was obtained from prenyl acetate and 2-methylbut-3-en-2-yl acetate, respectively (entries 4 and 5). Bulky allyl acetate derivatives required slow Grignard addition and higher catalyst loading to give moderate yields. Primary, secondary, and tertiary allyl acetates underwent alkylation

Table 2 Iron-catalysed alkylations of allyl acetates (condition A)

Entry	Allyl acetate	Product	R'	Yield <sup>a</sup> [%]
1			H	85
2			Me	72
3			<i>n</i> C <sub>6</sub> H <sub>13</sub>	67
4				61 (< <sup>5b</sup> )
5				59
6			Me	80
7			Cl	0
8			Br	0
9				37 <sup>c</sup>
10				53 <sup>c</sup>
11				16 <sup>c</sup>
12				64

<sup>a</sup> Isolated yields; *E/Z* product ratios >50/1. <sup>b</sup> C<sub>9</sub>H<sub>19</sub>MgCl·LiCl was used. <sup>c</sup> 10 mol% Fe(OAc)<sub>2</sub>, RMgBr addition over 1 h.

under the same conditions. The (*E*)-alkene isomers were formed in all cases with *E/Z* stereoselectivities of >50/1. Halide substituents were not tolerated in the 2-allyl position (entries 7 and 8). A screening of functional additives documented moderate compatibility with nitriles and good tolerance of esters and amines (Table 3). Alcohols required the addition of an extra equivalent Grignard reagent.

In an effort to further expand the scope of this allylation reaction, we employed aryl-substituted allyl acetates (Table 4). Enhanced selectivities were obtained from the use of Fe(acac)<sub>2</sub> as pre-catalyst (acac = acetylacetonato). The presence of CHCl<sub>3</sub> or slow addition of the Grignard reagent did not show any improvements (condition B). Again, increased steric hindrance of the substrates led to lower reactivities.

Finally, we employed different Grignard reagents in reactions with various allyl acetate derivatives (Table 5). Higher yields were obtained with catalytic Fe(acac)<sub>2</sub> when aryl groups were present in the allyl acetate or Grignard reagents. Primary and secondary alkyl-magnesium bromides and arylmagnesium bromides afforded good to very good yields of the cross-coupling products. It is important to note that the conditions A and B exhibited distinct reactivities: condition A, in the presence of CHCl<sub>3</sub> and with catalytic Fe(OAc)<sub>2</sub>, facilitated reactions with sterically demanding allyl acetate derivatives. Condition B (no CHCl<sub>3</sub>, with Fe(acac)<sub>2</sub>) gave higher selectivities for aryl-containing substrates. Allylmagnesium bromide underwent carboxylate substitution (entry 2). 1,3-Dioxolane-2-methylmagnesium bromide was unreactive (entry 15).

### Mechanistic studies

The clear distinction whether homogeneous or heterogeneous catalysis is operating can be intricate, as the catalysts can be

Table 3 External functional group test

Entry	Additive	Additive conversion <sup>a</sup> [%]	Yield <sup>a</sup> [%]
1	—	—	77
2	PhCN	0	21
3	<i>n</i> -C <sub>3</sub> H <sub>7</sub> CN	9	49
4	PhNO <sub>2</sub>	90	<1
5	EtNO <sub>2</sub>	87	8
6	PhNH <sub>2</sub>	77	9
7	<i>n</i> -C <sub>6</sub> H <sub>13</sub> NH <sub>2</sub>	0	80
8	PhCHO	100	16
9	PhCO <sub>2</sub> Me	0	82
10	<i>n</i> -C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> Me	4	72
11	PhOH	0	75 <sup>b</sup>
12	<i>n</i> -C <sub>5</sub> H <sub>11</sub> OH	6	79 <sup>b</sup>

<sup>a</sup> Yields were determined by quantitative GC-FID vs. internal *n*-pentadecane. <sup>b</sup> 2.2 equiv. *n*-C<sub>9</sub>H<sub>19</sub>MgBr.



Table 4 Iron-catalysed alkylations of aryl-substituted allyl acetates (condition B)

Entry	Acetate	Product	X	Yield <sup>a</sup> [%]
1			H	72 (39 <sup>b</sup> )
2			OMe	65
3			Cl	44
4			Me	57
5				17
6				68
7				51
8				56 <sup>c</sup>

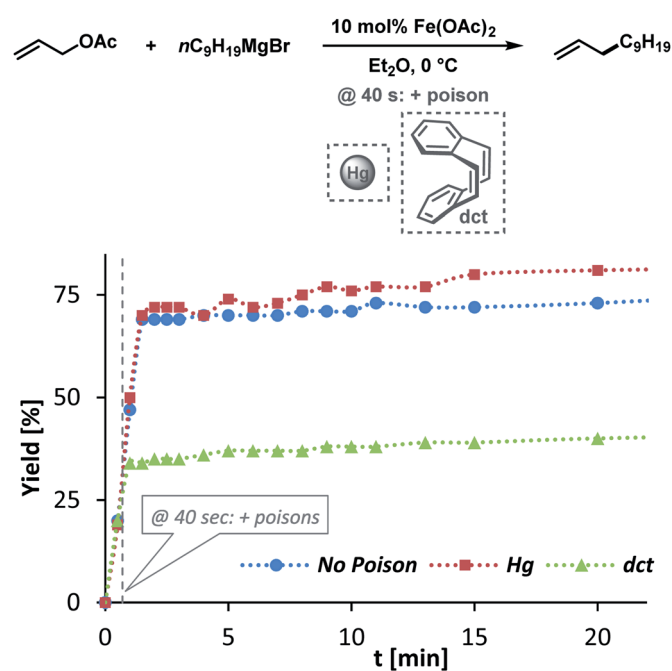
<sup>a</sup> Isolated yields; *E/Z* of products >50/1. <sup>b</sup> With C<sub>9</sub>H<sub>19</sub>MgCl·LiCl. <sup>c</sup> *E/Z* 25/1.

part of an equilibrium between several species and the spectroscopic tools often perturb the system under investigation. We performed Maitlis' hot filtration test which showed comparable catalytic activity in both the filtrate and filter phases.<sup>43</sup> The most reliable insight can be derived from kinetic experiments that are conducted *in operando* under the catalytic reaction conditions.<sup>43,44</sup> Reaction progress analyses showed no sigmoidal curvature that would have been indicative of an initial catalyst nucleation and particle growth. On the contrary, the highest catalyst activity was recorded at the onset of conversion within the first 30 s of the reaction. Furthermore, kinetic poisoning experiments were conducted (Scheme 4). Amalgamation of a potential Fe(0) catalyst was not observed upon addition of 100 equiv. Hg per Fe.<sup>45,46</sup> The addition of dibenzo[*a,e*]cyclooctatetraene (dct, 2 equiv. per Fe),<sup>16,47,48</sup> a selective homotopic poison of low-valent late transition metals, resulted in immediate and complete inhibition of catalytic activity. This observation constitutes a strong indication of a homogeneous catalysis mechanism. We have collected further mechanistic insight from a set of key experiments: the strongly reducing conditions in the presence of a large excess of Grignard reagent led to rapid deactivation of the catalyst,<sup>41</sup> an effect that already became apparent from the adaptation of slow-addition protocols (*vide supra*). Stoichiometric reactions between all components of this allylation protocol provided further insight (Scheme 5A). No direct reaction between allyl acetate and Fe(OAc)<sub>2</sub> occurred so that an allyliron or reduced iron species (both form in the presence of the Grignard reagent)

Table 5 Variation of the Grignard reagents (conditions A and B)

Entry	RMgBr	R'	Yield <sup>a</sup> [%]	
			A	B
1	MeMgBr	Ph	—	68
2		Ph	0	0
3		Ph	—	68
4		H	76	—
5		Ph	—	65
6		H	—	64
7		Ph	—	75
8		H	—	71
9	PhMgBr	Ph	11	64
10	PhMgBr	H	17	65
11	PhMgBr	Ph	—	77
12		H	22	82
13		nC <sub>6</sub> H <sub>13</sub>	<5	<5
14		Ph	—	42
15		Ph	0	0

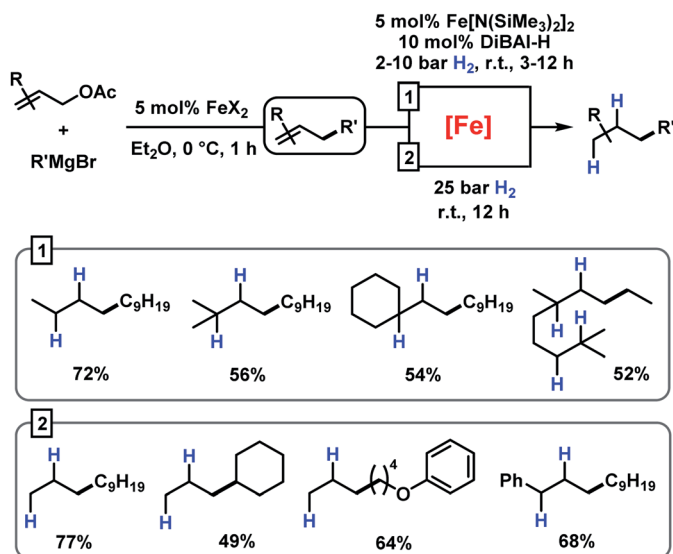
<sup>a</sup> Isolated yields; *E/Z* of products >50/1.



Scheme 4 Poisoning experiments with Hg (100 equiv. per Fe) and dct (2 equiv. per Fe).







Scheme 6 Sequential iron-catalysed allylation and hydrogenation.

## Conclusions

The iron-catalysed allylation of alkyl and aryl Grignard reagents with allyl acetate derivatives operates under very mild conditions with a commercial catalyst. Kinetic experiments suggest a highly active homotopic catalyst. Slow Grignard addition protocols or the presence of electrophilic additives (e.g. chloroform) enhanced catalyst activity and lifetime. The sequential combination of the iron-catalysed allylation of alkyl-magnesium halides with an iron-catalysed hydrogenation of the resultant alkenes results in a formal  $sp^3$ - $sp^3$ -cross-coupling that proved otherwise challenging. The presence of high bromide concentrations inhibited the hydrogenation step.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was generously supported by the European Research Council (CoG 683150) and the University of Hamburg.

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