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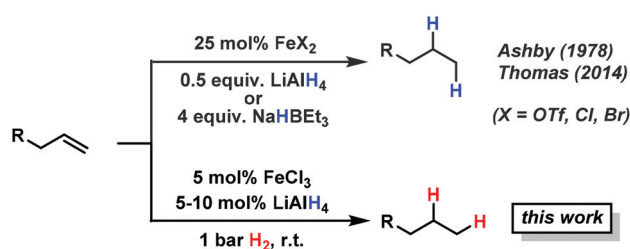
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## Iron-catalyzed olefin hydrogenation at 1 bar H<sub>2</sub> with a FeCl<sub>3</sub>–LiAlH<sub>4</sub> catalyst†

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The scope and mechanism of a practical protocol for the iron-catalyzed hydrogenation of alkenes and alkynes at 1 bar H<sub>2</sub> pressure were studied. The catalyst is formed from cheap chemicals (5 mol% FeCl<sub>3</sub>–LiAlH<sub>4</sub>, THF). A homogeneous mechanism operates at early stages of the reaction while active nanoparticles form upon ageing of the catalyst solution.

Catalytic hydrogenations of olefins constitute one of the strongholds of transition metal catalysis within organic synthesis and technical processes.<sup>1</sup> The majority of methods involve noble metal catalysts based on Pd, Pt, Rh, Ir or toxic metals such as Ni or Co. Iron-catalyzed hydrogenations of olefins have only recently attracted great interest due to their expedient economic and environmental qualities.<sup>2</sup> Homogeneous iron catalysts were mostly reported with phosphine and pyridyl-2,6-diimine ligands, sometimes requiring high pressures of H<sub>2</sub>.<sup>3,4</sup> Nanoparticle Fe catalysts could be prepared by reduction of iron salts with Grignard reagents in the absence of a suitable ligand or by decomposition of iron carbonyls.<sup>5</sup> Fe-catalyzed reductions of olefins were recently reported with cheap ferrous salt pre-catalysts FeX<sub>2</sub> in the presence of an excess of lithium *N,N*-dimethylaminoborohydride (10 equiv.) or sodium triethylborate (4 equiv.) and required a high catalyst loading or the addition of tetra-dentate ligands.<sup>6</sup> Reductions of alkenes and alkynes with LiAlH<sub>4</sub> in the presence of various transition metal halides (NiCl<sub>2</sub>, TiCl<sub>2</sub>, CoCl<sub>2</sub>, FeCl<sub>3</sub>) were already reported in the 1960s and postulated to involve metal hydride species that engage in formal hydrometalations of the olefin.<sup>7</sup> Here, we wish to present a synthetic and mechanistic study on a hydrogenation protocol using catalytic amounts of a cheap Fe salt and catalytic amounts of lithium aluminiumhydride (LiAlH<sub>4</sub>) as catalyst activator under an



**Scheme 1** Iron-catalyzed reductions of olefins: hydride vs. hydrogen methods.

atmosphere of 1 bar H<sub>2</sub> as stoichiometric hydrogen source (Scheme 1).<sup>7e</sup> This method allows the use of standard (ambient pressure) equipment. H<sub>2</sub> is an abundant raw material; LiAlH<sub>4</sub> is an easy-to-handle reductant with numerous applications.<sup>8</sup>

## Reaction conditions and substrate scope

Initial experiments with the model substrate allylbenzene (**1**) aimed at the identification of a suitable catalytic reductant which assists the formation of a low-valent iron catalyst (with dark brown colour) from the commercial pre-catalyst FeCl<sub>3</sub> (Table 1).<sup>9</sup> LiAlH<sub>4</sub> displayed excellent selectivity which exceeded that of earlier protocols with Grignard reagents.<sup>5</sup> Isomerization of the terminal double bond into conjugation – which occurred in the related EtMgCl-mediated protocols (entries 2, 4) – was effectively suppressed.<sup>10</sup> NaBH<sub>4</sub> was far less active even at elevated temperature and pressure (entries 6, 7). Interestingly, low ratios of LiAlH<sub>4</sub>–FeCl<sub>3</sub> (1/1 to 2/1) fared optimal in the hydrogenation of **1** at 1 bar H<sub>2</sub>. When employing a larger excess of LiAlH<sub>4</sub> (>2/1), the catalytic activity collapsed.<sup>7e</sup> This stoichiometry differs from literature reports where large excess amounts of hydride reagents effected clean hydrogenations of olefins.<sup>6,7a–c</sup> At 60 °C, the FeCl<sub>3</sub>–LiAlH<sub>4</sub> catalyst decomposed upon decolorization. The catalyst system

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Table 1 Selected optimization experiments<sup>a</sup>

Reductant (mol%)	Deviation from conditions	2 <sup>b</sup> (%)	3 <sup>a,b</sup> (%)
1	—	0	2
2	EtMgCl (30)	42	56
3	EtMgCl (30)	16	0
4	EtMgCl (30)	60	36
5	Et <sub>2</sub> Zn (20)	4	1
6	NaBH <sub>4</sub> (100)	8	0
7	NaBH <sub>4</sub> (100)	45	38
8	LiAlH <sub>4</sub> (10)	97	3
9	<b>LiAlH<sub>4</sub> (10)</b>	<b>98</b>	<b>1</b>
10	LiAlH <sub>4</sub> (30)	95	3
11	LiAlH <sub>4</sub> (10)	96	1
12	LiAlH <sub>4</sub> (10)	20	15

<sup>a</sup> Conditions: 5 mol% FeCl<sub>3</sub> in THF (0.5 mL) under argon, addition of reductant at r.t., after 10 min addition of 1, after 1 min exchange of Ar with 4 bar H<sub>2</sub>; <sup>b</sup> Quantitative GC-FID (internal reference); <sup>c</sup> During catalyst preparation.

Table 2 Hydrogenation of allylbenzenes at 1 bar H<sub>2</sub>

Allylbenzene	R	Yield <sup>a</sup> (%)	
1	H	93	
2	Me	79 (92) <sup>b</sup>	
3	OMe	84 (89) <sup>c</sup>	
4	Me	95	
5	OAc	93 (95) <sup>c,d</sup>	
6		99	
7	OMe	100	
8	F	86	

<sup>a</sup> Quantitative GC-FID (internal reference); conversion (%) in parentheses if <95%. <sup>b</sup> 7% 1-propen-1-ylbenzene (*E/Z* 9/1). <sup>c</sup> 24 h. <sup>d</sup> By NMR (vs. CH<sub>2</sub>Br<sub>2</sub>).

comprises of cheap and easy-to-handle reagents (FeCl<sub>3</sub> or FeCl<sub>2</sub>, LiAlH<sub>4</sub>, THF); the reaction operates under ambient conditions (1 bar H<sub>2</sub>, 20 °C), which make the general protocol practical for every-day use in standard synthesis laboratories. The optimized conditions were applied to functionalized allylbenzenes and styrenes (Tables 2 and 3).<sup>9</sup>

Allylbenzenes underwent only minimal olefin isomerization.<sup>10</sup> Styrenes exhibited low propensity to undergo polymerization (entry 13, Table 3). The general protocol is compatible with several functional groups including F, Cl, Br, allyl and benzyl ethers, esters, carboxamides, pyridines and anilines.

Table 3 Hydrogenation of styrene derivatives

Styrene	R	Yield <sup>a</sup> (%)	
1	H	100	
2	Me	98	
3	OMe	98	
4	Cl	93 <sup>b</sup>	
5	Br	94 <sup>b</sup>	
6	F	77 <sup>c</sup>	
7	OBn	100 <sup>d</sup>	
8	NH <sub>2</sub>	97 <sup>c</sup>	
9	CO <sub>2</sub> Me	97	
10	H	100 <sup>e</sup>	
11	OMe	84	
12		100	
13		86 <sup>d</sup>	
14	H	100 <sup>d</sup>	
15	Cl	85 (89) <sup>f</sup>	
16	Br	44 (56) <sup>f</sup>	
17	Br	92 <sup>c,f</sup>	
18	OMe	100 <sup>d</sup>	
19	Cl	74 (86) <sup>b</sup>	
20	OBn	100 <sup>d</sup>	
21	Ph	100 <sup>d</sup>	
22	Bn	100 <sup>d</sup>	
23	CO <sub>2</sub> Et	58 (68) <sup>c</sup>	
24		48 (54)	
25		88 <sup>c</sup>	
26		33 (58) <sup>e</sup>	
27		75 <sup>d,g</sup>	
28		18 (18) <sup>c</sup>	

<sup>a</sup> Quantitative GC-FID (internal reference); conversion (%) in parentheses if <95%. <sup>b</sup> <12% ethylbenzene. <sup>c</sup> 20 h, 10 bar H<sub>2</sub>. <sup>d</sup> 5 mol% LiAlH<sub>4</sub>, 3 h. <sup>e</sup> 20 h. <sup>f</sup> <5% cumene. <sup>g</sup> Mixture of partial and full hydrogenation products (~6/1).

Clean hydrogenation was achieved with bulky, *ortho*-substituted, and electron-rich styrenes. For comparison, the FeCl<sub>3</sub>/EtMgCl-derived catalyst effected undesired dehalogenation (Cl, Br)<sup>11</sup> and allylether cleavage,<sup>12</sup> and showed no activity in the presence of carboxylates or cinnamates. Catalyst decomposition was effected by nitro groups, iodides, nitriles, ketones, and acidic protons (*e.g.* alkanols, pK<sub>a</sub> ~ 17), presumably by



oxidation to catalytically incompetent Fe(II) species (decolorization). Tri-substituted styrenes gave low conversions. In general, bulky and functionalized substrates were more reactive at elevated pressures (10 bar H<sub>2</sub>).<sup>13</sup>

Hydrogenations of aliphatic alkenes were also catalyzed by FeCl<sub>3</sub>–LiAlH<sub>4</sub> under similar conditions (Table 4).<sup>9</sup> Terminal olefins were only slowly isomerized (~10%).<sup>10</sup> Surprisingly, substrates containing moderately acidic protons (pK<sub>a</sub> ~ 25)<sup>14</sup> underwent hydrogenation with high selectivity (entries 10–13).<sup>15</sup> Alkynes underwent Z-selective semi-hydrogenation,<sup>16</sup>

whereas complete hydrogenation to the alkanes was observed at longer reaction times or elevated pressures.

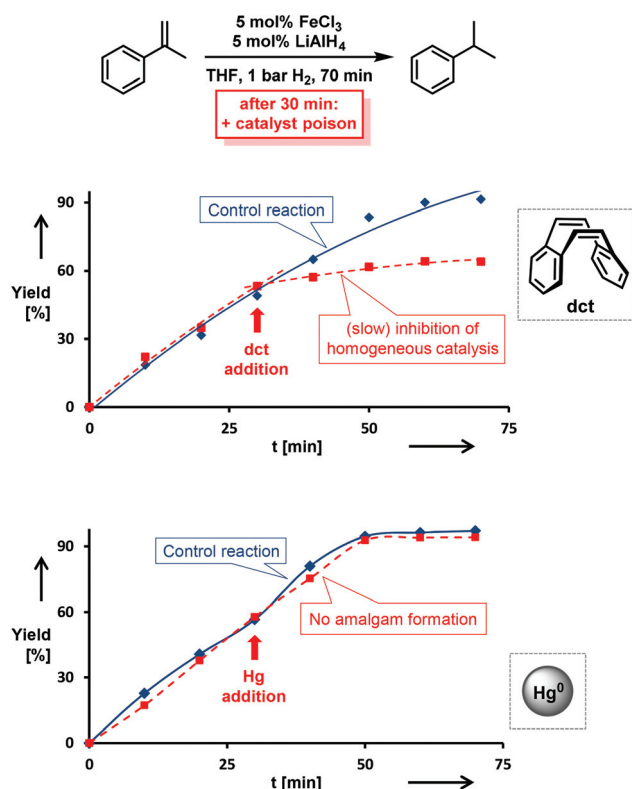
## Mechanistic studies

The distinction between homogeneous and heterogeneous catalysts is a challenging task.<sup>17</sup> However, kinetic experiments with selective poisons can provide valuable information on the topicity of the catalyst species. We have performed two sets of poisoning experiments which appear to support a homogeneous mechanism. Dibenzo[*a,e*]cycloocta-tetraene (dct) is a selective ligand for homogeneous metal species due to its rigid tub-like structure and  $\pi$ -acceptor properties.<sup>18</sup> Upon addition of 30 mol% dct (6 equiv. per [Fe]) to the hydrogenation of isopropenylbenzene at 1 bar H<sub>2</sub> after 30 min, the catalyst activity was significantly inhibited (Scheme 2, top).<sup>9,19</sup> A similar conclusion can be derived from a poisoning experiment with 3 equiv. Hg (60 equiv. Hg per [Fe]). A potential amalgam formation<sup>20</sup> was not observed and no significant change of the catalyst activity was observed in comparison with the control reaction (Scheme 2, bottom).<sup>9</sup> These results suggest the operation of a homogeneous catalyst species during the early stage of the catalytic hydrogenation. Previous studies showed that the reaction of FeCl<sub>3</sub> with an excess of LiAlH<sub>4</sub> ultimately leads to the formation of iron metal and AlH<sub>3</sub> *via* the intermediate

**Table 4** Hydrogenation of other alkenes and alkynes

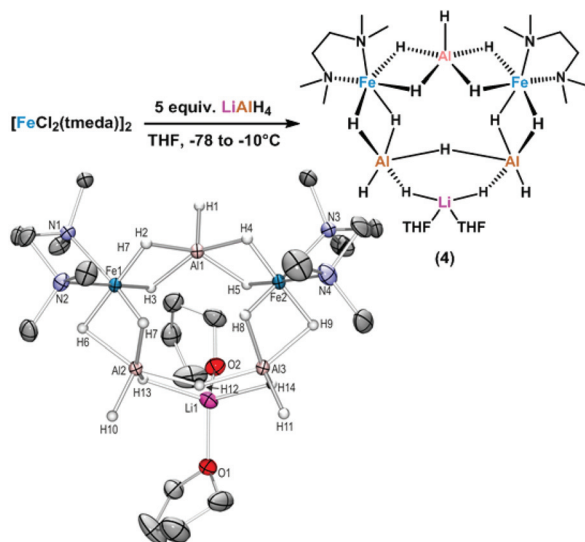
$\text{R}-\text{CH}=\text{CH}_2 \xrightarrow[1 \text{ bar H}_2, \text{ THF, 18 }^\circ\text{C, 3 h}]{5 \text{ mol\% FeCl}_3, 5 \text{ mol\% LiAlH}_4} \text{R}-\text{CH}_2-\text{CH}_3$		
Substrate	Product	Yield <sup>a</sup> (%)
1		82 <sup>b</sup>
2		69 <sup>b</sup>
3		82 <sup>c</sup>
4		89 (89) <sup>c</sup>
5		65 (65) <sup>c</sup>
6		21 (41) <sup>b</sup>
7		100 <sup>d</sup>
8		2 (10)
9		64 (65) <sup>d</sup>
10		12 (16)
11		96 <sup>d,e</sup>
12		38 (38) <sup>d,e</sup>
13		69 (69) <sup>d,e,f</sup>
14		100 <sup>c</sup>
15		92 <sup>c</sup>
16		75 (80) <sup>g</sup>
17		90 <sup>g</sup>

<sup>a</sup> Quantitative GC-FID (internal reference); conversion (%) in parentheses if <95%. <sup>b</sup> Alkene isomers. <sup>c</sup> 20 h. <sup>d</sup> 10 bar, 20 h. <sup>e</sup> 10 mol% LiAlH<sub>4</sub>. <sup>f</sup> 60 °C. <sup>g</sup> By NMR (vs. CH<sub>2</sub>Br<sub>2</sub>).



**Scheme 2** Top: poisoning experiment with 30 mol% dibenzo[*a,e*]cyclooctatetra-ene (dct, dashed curve) vs. control reaction (solid line). Bottom: poisoning with 3 equiv. Hg (dashed) vs. control reaction (solid line).



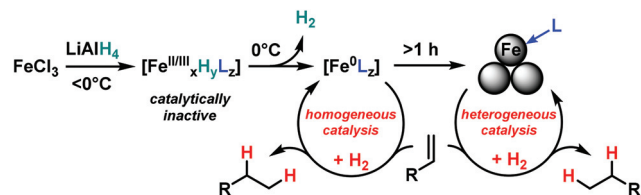


**Scheme 3** Synthesis of the soluble LiAlFe-oligohydride complex **4**.

formation of a thermally unstable iron(II) compound with the composition  $\text{Fe}(\text{AlH}_4)_2$ .<sup>21,22</sup> In an attempt to gain deeper insight into the catalyst species operating in homogeneous solution, we treated  $[\text{FeCl}_2(\text{tmeda})]_2$  ( $\text{tmeda} = N,N,N',N'$ -tetramethylethylenediamine) with  $\text{LiAlH}_4$  at  $-70^\circ\text{C}$  and obtained dark red crystals of the oligohydride compound  $[\text{Li}(\text{thf})_2\{\text{Fe}(\text{tmeda})_2(\text{AlH}_5)(\text{Al}_2\text{H}_9)\}]$  (**4**, Scheme 3).<sup>9</sup> The hexa-metallic macrocyclic cage contains 14 bridging hydrido ligands and two Fe atoms with distorted octahedral coordination geometries. Unfortunately, the thermal instability prevented further spectroscopic characterization.

However, complex **4** showed no activity in hydrogenations of styrenes (1–10 bar  $\text{H}_2$ ,  $-10^\circ\text{C}$ ) and maintained its red colour throughout the reaction. Above  $-10^\circ\text{C}$ , the complex rapidly decomposed upon  $\text{H}_2$  evolution to give a brown paramagnetic species which afforded good yields in hydrogenations at  $20^\circ\text{C}$  and 4 bar  $\text{H}_2$ . The crystallographic characterization of **4** documents that this or similar oligonuclear Fe(II) aluminohydride complexes may be intermediates *en route* to the formation of catalytically active low-valent iron species.<sup>23</sup>

The initially homogeneous dark-brown catalyst species (possibly in the oxidation states 0 and/or +1)<sup>23</sup> experience rapid ageing and particle formation after appr. 1 h under the reductive conditions. Several methods of synthesis and characterization techniques of naked Fe(0) nanoparticles (prepared by reduction of ferric and ferrous halides) have been reported.<sup>5,7,23,24</sup> DLS measurements (dynamic light scattering) of freshly prepared catalyst solutions (5 mol%  $\text{FeCl}_3\text{--LiAlH}_4$ , THF, r.t., 10 min, then 100 nm nanofiltration) documented the presence of poly-disperse particles of 250–1500 nm size after 30 min of ageing under anaerobic conditions in the absence of substrates. The aged species are much less catalytically active than their homogeneous counterparts. Catalyst solutions ( $\text{FeCl}_3\text{--LiAlH}_4$  (1/1) in THF) stored at  $0^\circ\text{C}$  under argon for 6 h, 24 h, and 48 h afforded 42%, 12%, and 5% conversion of

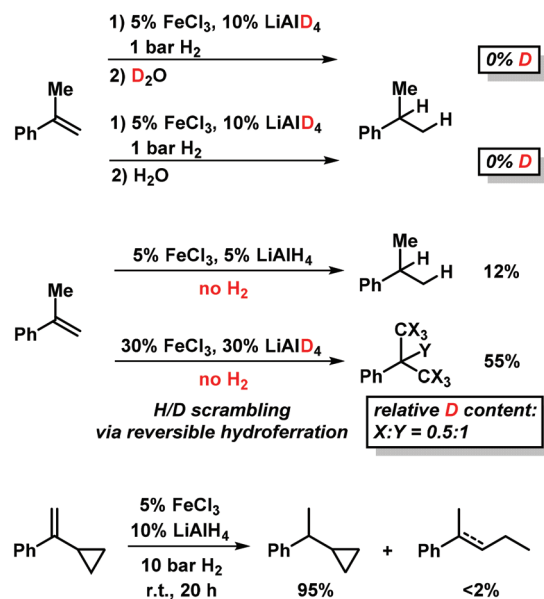


**Scheme 4** Proposed formation and catalysis of low-valent iron species.

$\alpha$ -methylstyrene under standard conditions (see entry 16 in Table 2), respectively.

We postulate a homogeneous mechanism of soluble, low-valent iron catalyst in the initial stage of the hydrogenation reactions (Scheme 4). Such species form by reduction of  $\text{FeCl}_3$  (or  $\text{L}_n\text{FeCl}_2$ ) with  $\text{LiAlH}_4$  at above  $0^\circ\text{C}$  and are typically characterized by the dark brown colour. The absence of suitable ligands leads to the formation of Fe(0) nanoclusters<sup>5,22,24</sup> which require higher  $\text{H}_2$  pressures than the homogeneous species to maintain catalytic activity.

Deuterium incorporation was observed at higher catalyst concentrations (30 mol%  $\text{FeCl}_3\text{--LiAlD}_4$ ) in the absence of  $\text{H}_2$  which gave ~55% hydrogenation product (Scheme 5, center).<sup>9</sup> Such  $\text{H}_2$ -free conditions can effect H/D scrambling in the starting material and product (*via* reversible hydroferration) and the formation of radical intermediates (with participation of THF as H donor).<sup>9</sup> However, the radical mechanism is very unlikely to operate under hydrogenation conditions in the presence of  $\text{H}_2$  gas (Scheme 5):<sup>9</sup> reaction work-up with deuterium oxide ( $\text{D}_2\text{O}$ ) and employment of lithium aluminium-deuteride ( $\text{LiAlD}_4$ ) showed no deuterium incorporation into the products, respectively (Scheme 5, top right). Further, the intermediacy of free C-radicals is unlikely: employment of the



**Scheme 5** Mechanistic studies with deuterated reagents (top), in the absence of  $\text{H}_2$  (center), and with radical probe (bottom).





radical probe 1-cyclopropyl-1-phenylethylene<sup>25</sup> resulted in less than 2% ring opening (Scheme 5, bottom).<sup>9</sup> The hydrogenation of various styrenes (1 bar H<sub>2</sub>) was unaffected by the presence of 1 equiv. 1,1-diphenylethene. On the other hand, the addition of TEMPO (2,2,6,6-tetramethylpiperidinyloxy, 1 equiv.) inhibited conversion of  $\alpha$ -methylstyrene (no TEMPO adduct detected), possibly by irreversible catalyst oxidation as indicated by the decolorization of the solution.

## General procedure

A 10 mL vial was charged with a freshly prepared solution of FeCl<sub>3</sub> in THF (0.50 mL, 0.05 M) and an aliquot of a vigorously stirred suspension of LiAlH<sub>4</sub> in THF (0.50 mL, 0.1 M) under an argon atmosphere. After stirring the dark brown mixture for 10 min (during which H<sub>2</sub> evolution can be observed), the alkene (0.50 mmol) was added and the vial purged with dihydrogen gas (1 min). For reactions under higher H<sub>2</sub> pressures, the vial was transferred to a high pressure reactor (Parr<sup>TM</sup>), the reactor purged with H<sub>2</sub> (1 min), sealed, and the internal pressure adjusted to 1 bar. After 3–20 h at room temperature, the reaction was quenched with saturated aqueous NaHCO<sub>3</sub> (1 mL) and extracted with ethyl acetate (2 × 2 mL). The organic phases were dried (Na<sub>2</sub>SO<sub>4</sub>) and subjected to flash chromatography (SiO<sub>2</sub>, pentane/ethyl acetate) or analyzed by quantitative GC-FID analysis vs. pentadecane as internal reference.

## Conclusions

In summary, we have studied the iron-catalyzed hydrogenation of various styrenes, alkenes, and alkynes under an atmosphere of 1 bar H<sub>2</sub>. This method uses cheap and easy-to-handle reagents (FeCl<sub>3</sub>, LiAlH<sub>4</sub>, THF, H<sub>2</sub>) which allow facile implementation in standard synthesis labs. Alkynes underwent Z-selective semi-hydrogenation. Sterically hindered and functionalized olefins showed higher conversions at elevated H<sub>2</sub> pressures. Mechanistic studies support the notion of a homogeneous catalyst species at the outset of the hydrogenation reactions (<1 h) while catalyst ageing results in the formation of particles which exhibited somewhat lower catalytic activity. The crystallographically characterized homogeneous Fe(II) oligohydride complex **4** can serve as starting point for further model catalyst preparations.

## Acknowledgements

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## Notes and references

- (a) *Catalytic Hydrogenation*, ed. L. Cervený, Elsevier, Amsterdam, 1986; (b) *The Handbook of Homogeneous Hydrogenation*, ed. J. G. de Vries and C. J. Elsevier, Wiley-VCH, Weinheim, 2007; (c) S. Nishimura, *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*, Wiley, New York, 2001.
- (a) K. Junge, K. Schröder and M. Beller, *Chem. Commun.*, 2011, **47**, 4849; (b) B. A. F. Le Bailly and S. P. Thomas, *RSC Adv.*, 2011, **1**, 1435.
- (a) E. J. Daida and J. C. Peters, *Inorg. Chem.*, 2004, **43**, 7474; (b) C. Bianchini, A. Meli, M. Peruzzini, P. Frediani, C. Bohanna, M. A. Esteruelas and L. A. Oro, *Organometallics*, 1992, **11**, 138.
- (a) R. P. Yu, J. M. Darmon, J. M. Hoyt, G. W. Margulieux, Z. R. Turner and P. J. Chirik, *ACS Catal.*, 2012, **2**, 1760; (b) R. J. Trovitch, E. Lobkovsky, E. Bill and P. J. Chirik, *Organometallics*, 2008, **27**, 1470; (c) S. C. Bart, E. Lobkovsky and P. J. Chirik, *J. Am. Chem. Soc.*, 2004, **126**, 13794; (d) T. S. Carter, L. Guet, D. J. Frank, J. West and S. P. Thomas, *Adv. Synth. Catal.*, 2013, **355**, 880.
- (a) P. H. Phua, L. Lefort, J. A. F. Boogers, M. Tristany and J. G. de Vries, *Chem. Commun.*, 2009, 3747; (b) M. Stein, J. Wieland, P. Steurer, F. Tölle, R. Mülhaupt and B. Breit, *Adv. Synth. Catal.*, 2011, **353**, 523; (c) A. Welther, M. Bauer, M. Mayer and A. Jacobi von Wangelin, *ChemCatChem*, 2012, **4**, 1088; (d) R. Hudson, A. Rivière, C. M. Cirtiu, K. L. Luska and A. Moores, *Chem. Commun.*, 2012, **48**, 3360; (e) A. Welther and A. Jacobi von Wangelin, *Curr. Org. Chem.*, 2013, **17**, 326; (f) R. Hudson, G. Hamasaka, T. Osako, Y. M. A. Yamada, C. J. Li, Y. Uozumi and A. Moores, *Green Chem.*, 2013, **15**, 2141.
- (a) B. A. F. Le Bailly, M. D. Greenhalgh and S. P. Thomas, *Chem. Commun.*, 2012, **48**, 1580; (b) D. J. Frank, L. Guet, A. Käslin, E. Murphy and S. P. Thomas, *RSC Adv.*, 2013, **3**, 25698.
- LiAlH<sub>4</sub> as hydride source in metal-catalyzed reductions: (a) G. Dozzi, S. Cucinella and A. Mazzei, *J. Organomet. Chem.*, 1979, **164**, 1; (b) E. C. Ashby and J. J. Lin, *J. Org. Chem.*, 1978, **43**, 2567; (c) E. C. Ashby and J. J. Lin, *Tetrahedron Lett.*, 1977, **51**, 4481. For early reports of H<sub>2</sub> evolution from iron hydride species and catalytic olefin hydrogenations, see: (d) Y. Takegami, T. Ueno and T. Fujii, *Kogyo Kagaku Zasshi (J. Chem. Soc. Jpn., Ind. Chem. Sect.)*, 1964, **67**, 1009; (e) Y. Takegami, T. Ueno and T. Fujii, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 1279.
- (a) Technical production and use of H<sub>2</sub>; H.-J. Arpe, *Industrial Organic Chemistry*, Wiley-VCH, Weinheim, 2010; (b) Selected applications of LiAlH<sub>4</sub>: S. Yaragorla, *Synlett*, 2008, 3073.
- Please see ESI† for detailed experimental and analytical data.
- Olefin isomerization with iron carbonyls: (a) J. V. Crivello and S. Kong, *J. Org. Chem.*, 1998, **63**, 6745; (b) M. R. Reddy and M. Periasamy, *J. Organomet. Chem.*, 1995, **491**, 263; (c) P. A. Tooley, L. W. Arndt and M. Y. Darensbourg, *J. Am. Chem. Soc.*, 1985, **107**, 2422; (d) R. Jennerjahn, R. Jackstell, I. Piras, R. Franke, H. Jiao, M. Bauer and M. Beller, *ChemSusChem*, 2012, **5**, 734; (e) Naked Fe(0) species: M. Mayer,



- A. Welther and A. Jacobi von Wangelin, *ChemCatChem*, 2011, **3**, 1567. Allylbenzenes were prepared according to: (f) M. Mayer, W. M. Czaplik and A. Jacobi von Wangelin, *Adv. Synth. Catal.*, 2010, **352**, 2147.
- 11 (a) F. Alonso, I. P. Beletskaya and M. Yus, *Chem. Rev.*, 2002, **102**, 4009; (b) W. M. Czaplik, S. Grupe, M. Mayer and A. Jacobi von Wangelin, *Chem. Commun.*, 2010, **46**, 6350.
  - 12 D. Gärtner, H. Konnerth and A. Jacobi von Wangelin, *Catal. Sci. Technol.*, 2013, **3**, 2541.
  - 13 (a)  $\alpha$ -Methylstyrene was hydrogenated at 4 bar  $H_2$  in the presence of various functionalized additives (1 equiv.). No decrease of hydrogenation selectivity was observed when adding PhCl, PhBr, PhCO<sub>2</sub>Me, PhNH<sub>2</sub>, PhCONH<sub>2</sub>, and 1,1-diphenylethylene, respectively. With PhNO<sub>2</sub>, PhCN, PhI, and MeCN, no conversion of methylstyrene was observed, respectively, neither was the additive significantly consumed (<5%); (b) At 1–2 bar  $H_2$ , much lower tolerance of functional groups was observed. We assume that the presence of functionalized substrates or polar moieties enhances catalyst ageing and formation of a heterogeneous species which appeared to somewhat less active. It should also be noted that sporadic cases of somewhat lower reproducibilities of reactions at 1 bar  $H_2$  pressure were observed with substrates bearing polar functional groups.
  - 14 N-Methylacetamide (AcNHMe), pK<sub>a</sub> 25.9. F. G. Bordwell, J. A. Harrelson and T.-Y. Lynch, *J. Org. Chem.*, 1990, **55**, 3337.
  - 15 N-Acetylamino-cyclohexenes were prepared according to: (a) D. Strübing, H. Neumann, A. Jacobi von Wangelin, S. Klaus, S. Hübner and M. Beller, *Tetrahedron*, 2006, **62**, 10962; (b) S. Hübner, H. Neumann, A. Jacobi von Wangelin, S. Klaus, D. Strübing, H. Klein and M. Beller, *Synthesis*, 2005, 2084; (c) S. Klaus, S. Hübner, H. Neumann, D. Strübing, A. Jacobi von Wangelin, D. Gördes and M. Beller, *Adv. Synth. Catal.*, 2004, **346**, 970; (d) A. Jacobi von Wangelin, H. Neumann, D. Gördes, A. Spannenberg and M. Beller, *Org. Lett.*, 2001, **3**, 2895.
  - 16 Fe-catalyzed Z-selective semihydrogenation of alkynes: (a) S. Enthaler, M. Haberberger and E. Irran, *Chem. – Asian J.*, 2011, **6**, 1613; (b) L. Ilies, T. Yoshida and E. Nakamura, *J. Am. Chem. Soc.*, 2012, **134**, 16951; (c) C. Belger and B. Plietker, *Chem. Commun.*, 2012, **48**, 5419; (d) T. N. Gieshoff, A. Welther, M. T. Kessler, M. H. G. Prechtel and A. Jacobi von Wangelin, *Chem. Commun.*, 2014, **50**, 2261.
  - 17 (a) J. A. Widegren and R. G. Finke, *J. Mol. Catal. A: Chem.*, 2003, **198**, 317; (b) D. Astruc, F. Lu and J. Ruiz Aranzaes, *Angew. Chem., Int. Ed.*, 2005, **44**, 7852; (c) R. H. Crabtree, *Chem. Rev.*, 2012, **112**, 1536.
  - 18 (a) D. R. Anton and R. H. Crabtree, *Organometallics*, 1983, **2**, 855; (b) G. Franck, M. Brill and G. Helmchen, *J. Org. Chem.*, 2012, **89**, 55; (c) J. F. Sonnenberg and R. H. Morris, *Catal. Sci. Technol.*, 2014, **4**, 3426.
  - 19 The observation of a partial inhibition by dct results from a superposition of an effective catalyst inhibition by the presence of dct and (a slower) hydrogenation of dct as substrate itself (see entry 27 in Table 3).
  - 20 Iron forms only metastable alloys with mercury (amalgam). The maximum concentration of Fe(0) in Hg was reported to be 2–3 wt%. (a) S. Mørup, S. Linderroth, J. Jacobsen and M. Holmblad, *Hyperfine Interact.*, 1991, **69**, 489; (b) S. Linderroth and S. Mørup, *J. Phys.: Condens. Matter*, 1992, **4**, 8627.
  - 21 (a) G. W. Schaeffer, J. S. Roscoe and A. C. Stewart, *J. Am. Chem. Soc.*, 1956, **78**, 729; (b) H. Neumaier, D. Büchel and G. Ziegelmaier, *Z. Anorg. Allg. Chem.*, 1966, **345**, 46; (c) M. E. Kost and A. L. Golovanova, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1957, **5**, 991.
  - 22 The stable low-spin iron(II) aluminohydride complex [(Me<sup>3</sup>tacn)<sub>2</sub>Fe<sub>2</sub>(μ-AlH<sub>6</sub>)]<sup>+</sup> has recently been reported (tacn = 1,4,7-triazacyclononane): M. Oishi, T. Endo, M. Oshima and H. Suzuki, *Inorg. Chem.*, 2014, **53**, 5100.
  - 23 (a) A. Fürstner, R. Martin, H. Krause, G. Seidel, R. Goddard and C. W. Lehmann, *J. Am. Chem. Soc.*, 2008, **130**, 8773; (b) A. Hedström, E. Lindstedt and P.-O. Norrby, *J. Organomet. Chem.*, 2013, **748**, 51.
  - 24 (a) C. Rangheard, C. de Julian Fernandez, P.-H. Phua, J. Hoorn, L. Lefort and J. G. de Vries, *Dalton Trans.*, 2010, **39**, 8464; (b) R. Schoch, W. Desens, T. Werner and M. Bauer, *Chem. – Eur. J.*, 2013, **19**, 15816; (c) V. Kelsen, B. Wendt, S. Werkmeister, K. Junge, M. Beller and B. Chaudret, *Chem. Commun.*, 2013, **49**, 3416.
  - 25 (a) D. Griller and K. U. Ingold, *Acc. Chem. Res.*, 1980, **13**, 317; (b) M. Newcomb, *Tetrahedron*, 1993, **49**, 1151.

