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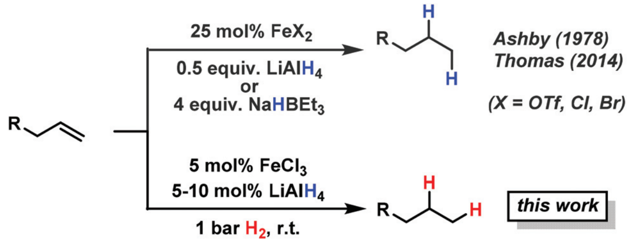
Iron-catalyzed olefin hydrogenation at 1 bar H_2 with a $FeCl_3$–$LiAlH_4$ catalyst†

Tim N. Gieshoff,[a] Matteo Villa,[a] Alice Welther,[a] Markus Plois,[b] Uttam Chakraborty,[b] Robert Wolf[b] and Axel Jacobi von Wangelin*[a]

The scope and mechanism of a practical protocol for the iron-catalyzed hydrogenation of alkenes and alkynes at 1 bar H_2 pressure were studied. The catalyst is formed from cheap chemicals (5 mol% $FeCl_3$–$LiAlH_4$, 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.[1] 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.[2] Homogeneous iron catalysts were mostly reported with phosphine and pyridyl-2,6-diimine ligands, sometimes requiring high pressures of H_2.[3,4] 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.[5] Fe-catalyzed reductions of olefins were recently reported with cheap ferrous salt pre-catalysts FeX_2 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.[6] Reductions of alkenes and alkynes with $LiAlH_4$ in the presence of various transition metal halides ($NiCl_2$, $TiCl_2$, $CoCl_2$, $FeCl_3$) were already reported in the 1960s and postulated to involve metal hydride species that engage in formal hydrometalations of the olefin.[7] 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 ($LiAlH_4$) as catalyst activator under an atmosphere of 1 bar H_2 as stoichiometric hydrogen source (Scheme 1).[7e] This method allows the use of standard (ambient pressure) equipment. H_2 is an abundant raw material; $LiAlH_4$ is an easy-to-handle reductant with numerous applications.[8]



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

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 $FeCl_3$ (Table 1).[9] $LiAlH_4$ displayed excellent selectivity which exceeded that of earlier protocols with Grignard reagents.[5] Isomerization of the terminal double bond into conjugation – which occurred in the related EtMgCl-mediated protocols (entries 2, 4) – was effectively suppressed.[10] $NaBH_4$ was far less active even at elevated temperature and pressure (entries 6, 7). Interestingly, low ratios of $LiAlH_4$–$FeCl_3$ (1/1 to 2/1) fared optimal in the hydrogenation of **1** at 1 bar H_2. When employing a larger excess of $LiAlH_4$ (>2/1), the catalytic activity collapsed.[7e] This stoichiometry differs from literature reports where large excess amounts of hydride reagents effected clean hydrogenations of olefins.[6,7a–c] At 60 °C, the $FeCl_3$–$LiAlH_4$ catalyst decomposed upon decolorization. The catalyst system

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[a] Institute of Organic Chemistry, University of Regensburg, 93040 Regensburg, Germany. E-mail: axel.jacobi@ur.de
[b] Institute of Inorganic Chemistry, University of Regensburg, 93040 Regensburg, Germany

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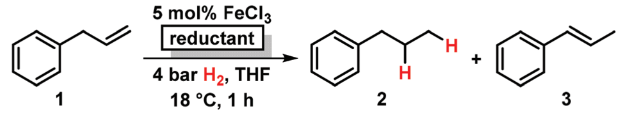
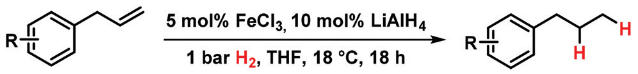
Table 1 Selected optimization experiments[a]

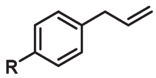
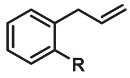
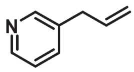
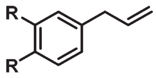


	Reductant (mol%)	Deviation from conditions	2^b (%)	$3^{a,b}$ (%)
1	—	—	0	2
2	EtMgCl (30)	—	42	56
3	EtMgCl (30)	—[b]	16	0
4	EtMgCl (30)	1 bar H_2, 20 h	60	36
5	Et_2Zn (20)	30 bar H_2, 80 °C, 12 h	4	1
6	$NaBH_4$ (100)	50 bar H_2, 24 h	8	0
7	$NaBH_4$ (100)	MeOH–THF (1 : 1), 50 bar H_2, 50 °C, 20 h	45	38
8	$LiAlH_4$ (10)	—	97	3
9	**$LiAlH_4$ (10)**	**1 bar H_2, 20 h**	**98**	**1**
10	$LiAlH_4$ (30)	As entry 9, open to air[c]	95	3
11	$LiAlH_4$ (10)	$FeCl_2$	96	1
12	$LiAlH_4$ (10)	$Fe(acac)_3$	20	15

[a] Conditions: 5 mol% $FeCl_3$ 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_2; [b] Quantitative GC-FID (internal reference); [c] During catalyst preparation.

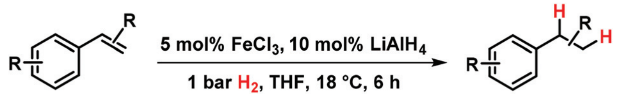
Table 2 Hydrogenation of allylbenzenes at 1 bar H_2

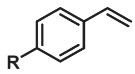
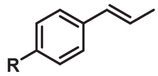
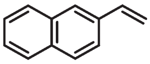
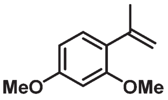
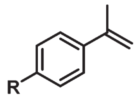
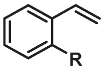
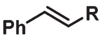
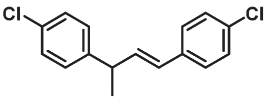
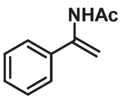
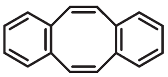
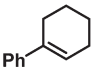


	Allylbenzene	R	Yield[a] (%)
1		H	93
2		Me	79 (92)[b]
3		OMe	84 (89)[c]
4		Me	95
5		OAc	93 (95)[c,d]
6			99
7		OMe	100
8		F	86

[a] Quantitative GC-FID (internal reference); conversion (%) in parentheses if <95%. [b] 7% 1-propen-1-ylbenzene (*E*/*Z* 9/1). [c] 24 h. [d] By NMR (*vs.* CH_2Br_2).

Table 3 Hydrogenation of styrene derivatives



	Styrene	R	Yield[a] (%)
1		H	100
2		Me	98
3		OMe	98
4		Cl	93[b]
5		Br	94[b]
6		F	77[c]
7		OBn	100[d]
8		NH_2	97[c]
9		CO_2Me	97
10		H	100[e]
11		OMe	84
12			100
13			86[d]
14		H	100[d]
15		Cl	85 (89)[f]
16		Br	44 (56)[f]
17		Br	92[c,f]
18		OMe	100[d]
19		Cl	74 (86)[b]
20		OBn	100[d]
21		Ph	100[d]
22		Bn	100[d]
23		CO_2Et	58 (68)[c]
24			48 (54)
25			88[c]
26			33 (58)[e]
27			75[d,g]
28			18 (18)[c]

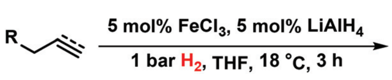
[a] Quantitative GC-FID (internal reference); conversion (%) in parentheses if <95%. [b] <12% ethylbenzene. [c] 20 h, 10 bar H_2. [d] 5 mol% $LiAlH_4$, 3 h. [e] 20 h. [f] <5% cumene. [g] Mixture of partial and full hydrogenation products (~6/1).

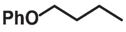
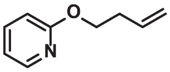
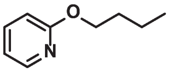
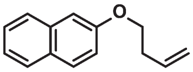
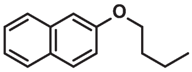
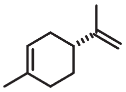
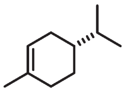
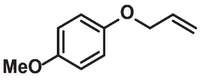
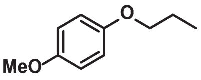
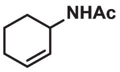
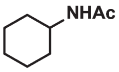
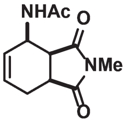
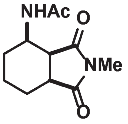
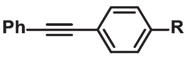
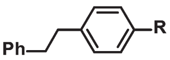
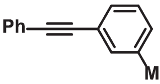
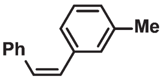
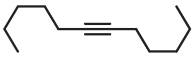
comprises of cheap and easy-to-handle reagents ($FeCl_3$ or $FeCl_2$, $LiAlH_4$, THF); the reaction operates under ambient conditions (1 bar H_2, 20 °C), which make the general protocol practical for every-day use in standard synthesis laboratories. The optimized conditions were applied to functionalized allylbenzenes and styrenes (Tables 2 and 3).[9]

Allylbenzenes underwent only minimal olefin isomerization.[10] 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. Clean hydrogenation was achieved with bulky, *ortho*-substituted, and electron-rich styrenes. For comparison, the $FeCl_3$/EtMgCl-derived catalyst effected undesired dehalogenation (Cl, Br)[11] and allylether cleavage,[12] 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, $pK_a \sim 17$), 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_2).[13]

Hydrogenations of aliphatic alkenes were also catalyzed by $FeCl_3$–$LiAlH_4$ under similar conditions (Table 4).[9] Terminal olefins were only slowly isomerized (~10%).[10] Surprisingly, substrates containing moderately acidic protons ($pK_a \sim 25$)[14] underwent hydrogenation with high selectivity (entries 10–13).[15] Alkynes underwent *Z*-selective semi-hydrogenation,[16] whereas complete hydrogenation to the alkanes was observed at longer reaction times or elevated pressures.

Table 4 Hydrogenation of other alkenes and alkynes

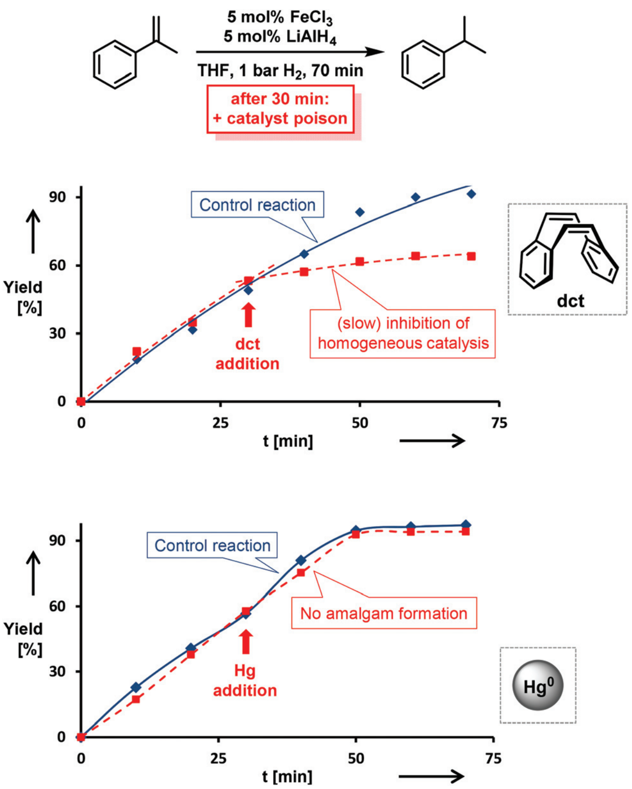


	Substrate	Product		Yield[a] (%)
1				82[b]
2				69[b]
3				82[c]
4				89 (89)[c]
5				65 (65)[c]
6				21 (41)[b]
7				100[d]
8 9				2 (10) 64 (65)[d]
10 11				12 (16) 96[d,e]
12 13				38 (38)[d,e] 69 (69)[d,e,f]
14 15			R = H CO_2Me	100[c] 92[c]
16				75 (80)[g]
17				90[g]

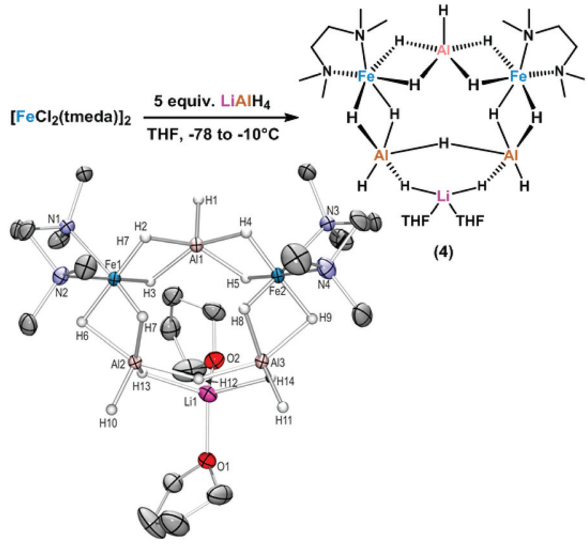
[a] Quantitative GC-FID (internal reference); conversion (%) in parentheses if <95%. [b] Alkene isomers. [c] 20 h. [d] 10 bar, 20 h. [e] 10 mol% $LiAlH_4$. [f] 60 °C. [g] By NMR (*vs.* CH_2Br_2).

Mechanistic studies

The distinction between homogeneous and heterogeneous catalysts is a challenging task.[17] 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 π-acceptor properties.[18] Upon addition of 30 mol% dct (6 equiv. per [Fe]) to the hydrogenation of isopropenylbenzene at 1 bar H_2 after 30 min, the catalyst activity was significantly inhibited (Scheme 2, top).[9,19] A similar conclusion can be derived from a poisoning experiment with 3 equiv. Hg (60 equiv. Hg per [Fe]). A potential amalgam formation[20] was not observed and no significant change of the catalyst activity was observed in comparison with the control reaction (Scheme 2, bottom).[9] 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 $FeCl_3$ with an excess of $LiAlH_4$ ultimately leads to the formation of iron metal and AlH_3 *via* the intermediate



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).

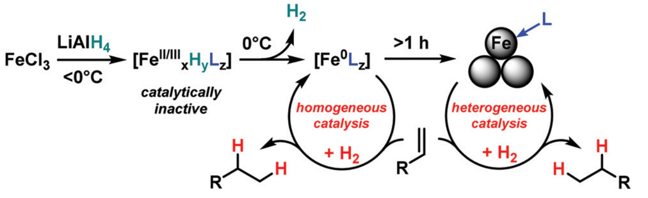


Scheme 3 Synthesis of the soluble LiAlFe-oligohydride complex **4**.

formation of a thermally unstable iron(II) compound with the composition $Fe(AlH_4)_2$.[21,22] In an attempt to gain deeper insight into the catalyst species operating in homogeneous solution, we treated $[FeCl_2(tmeda)]_2$ (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) with $LiAlH_4$ at −70 °C and obtained dark red crystals of the oligohydride compound $[Li(thf)_2\{Fe(tmeda)\}_2(AlH_5)(Al_2H_9)]$ (**4**, Scheme 3).[9] 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 H_2, −10 °C) and maintained its red colour throughout the reaction. Above −10 °C, the complex rapidly decomposed upon H_2 evolution to give a brown paramagnetic species which afforded good yields in hydrogenations at 20 °C and 4 bar 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.[23]

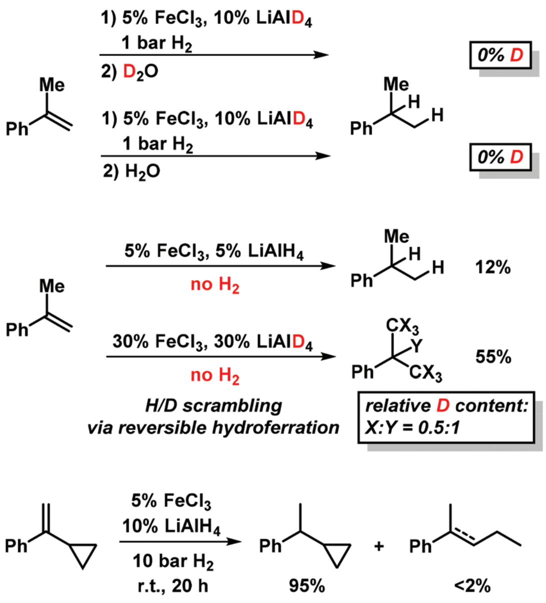
The initially homogeneous dark-brown catalyst species (possibly in the oxidation states 0 and/or +1)[23] experience rapid ageing and particle formation after appr. 1 h under the reductive conditions. Several methods of synthesis and characterization techniques of naked Fe(0) nanoparticles (prepared by reduction of ferric and ferrous halides) have been reported.[5,7,23,24] DLS measurements (dynamic light scattering) of freshly prepared catalyst solutions (5 mol% $FeCl_3$–$LiAlH_4$, 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 ($FeCl_3$–$LiAlH_4$ (1/1) in THF) stored at 0 °C under argon for 6 h, 24 h, and 48 h afforded 42%, 12%, and 5% conversion of α-methylstyrene under standard conditions (see entry 16 in Table 2), respectively.



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

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 $FeCl_3$ (or L_nFeCl_2) with $LiAlH_4$ at above 0 °C and are typically characterized by the dark brown colour. The absence of suitable ligands leads to the formation of Fe(0) nanoclusters[5,22,24] which require higher H_2 pressures than the homogeneous species to maintain catalytic activity.

Deuterium incorporation was observed at higher catalyst concentrations (30 mol% $FeCl_3$–$LiAlD_4$) in the absence of H_2 which gave ~55% hydrogenation product (Scheme 5, center).[9] Such 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).[9] However, the radical mechanism is very unlikely to operate under hydrogenation conditions in the presence of H_2 gas (Scheme 5):[9] reaction work-up with deuterium oxide (D_2O) and employment of lithium aluminium-deuteride ($LiAlD_4$) 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 H_2 (center), and with radical probe (bottom).

radical probe 1-cyclopropyl-1-phenylethylene[25] resulted in less than 2% ring opening (Scheme 5, bottom).[9] The hydrogenation of various styrenes (1 bar H_2) was unaffected by the presence of 1 equiv. 1,1-diphenylethene. On the other hand, the addition of TEMPO (2,2,6,6-tetramethylpiperidinyloxyl, 1 equiv.) inhibited conversion of α-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 $FeCl_3$ in THF (0.50 mL, 0.05 M) and an aliquot of a vigorously stirred suspension of $LiAlH_4$ in THF (0.50 mL, 0.1 M) under an argon atmosphere. After stirring the dark brown mixture for 10 min (during which H_2 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_2 pressures, the vial was transferred to a high pressure reactor (Parr™), the reactor purged with H_2 (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 $NaHCO_3$ (1 mL) and extracted with ethyl acetate (2 × 2 mL). The organic phases were dried (Na_2SO_4) and subjected to flash chromatography (SiO_2, 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_2. This method uses cheap and easy-to-handle reagents ($FeCl_3$, $LiAlH_4$, THF, H_2) 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_2 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.

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