Alkene Hydrogenations by Soluble Iron Nanocluster Catalysts

Abstract: The replacement of noble metal technologies and the realization of new reactivities with earth-abundant metals is at the heart of sustainable synthesis. Alkene hydrogenations have so far been most effectively performed by noble metal catalysts. This study reports an iron-catalyzed hydrogenation protocol for tri- and tetra-substituted alkenes of unprecedented activity and scope under mild conditions (1–4 bar H₂, 20°C). Instructive snapshots at the interface of homogeneous and heterogeneous iron catalysis were recorded by the isolation of novel Fe nanocluster architectures that act as catalyst reservoirs and soluble seeds of particle growth.

Catalytic hydrogenations of unsaturated C=C bond systems are pivotal to modern chemical transformations and mostly performed with nickel or platinum group catalysts. While some of the largest technical processes are iron-catalyzed hydrogenations (Haber–Bosch, Fischer–Tropsch), the potential of iron as abundant, non-toxic, and cheap transition metal catalyst for C=C hydrogenations has only very recently been tapped. Significant progress in the design of molecular Fe catalysts was made by the introduction of tridentate bis-(iminopyridine) ligands (PDI) by Budzelaar et al. and Chirik et al. The (PDI)Fe(N₂)₂ pre-catalysts cleanly hydrogenate mono- and di-substituted alkenes under mild conditions and exceed the productivity of some precious metal catalysts. Further improved activities were observed with the related bis(carbene)-pyridine iron(I) complexes (Scheme 1, top). On the other hand, ill-defined or nanoparticulate Fe catalysts were prepared by decompositions of iron carbonyls or by reductions of iron salts with organometallic or hydride reagents but exhibited only moderate hydrogenation activities. While providing an operationally simple access to Fe-based hydrogenation catalysts, the latter approaches provided limited mechanistic insight, often involved precipitation of heterogeneous species especially in the absence of suitable ligands, and generally displayed high catalyst sensitivity and limited scope. From our recent studies into the development of low-valent iron catalysts for hydrogenations, we reasoned that an effective yet operationally simple protocol would fulfill the following criteria: 1) The active catalyst is prepared in situ by the reduction of iron(II) precursors with commercial reductants; 2) the catalyst contains bulky ligands that are cheap, easily available, coordinate iron in various low oxidation states, and prevent unwanted aggregation to larger, catalytically inactive particles; 3) the ligands create a lipophilic periphery that enhances solubilization under the non-polar conditions of alkene hydrogenations; and iv) the catalytic hydrogenation operates under mild conditions without sophisticated additives in common organic solvents. With these framework conditions, we investigated combinations of iron(II) bis(1,1,1,3,3,3-hexamethyl-disilazan-2-ide), Fe(hmds), and various reductants. Documented herein are the benefits of using this simple catalytic system that presents tangible advances over the current state-of-the-art that could not have been predicted: Clean hydrogenations of challenging alkenes (for example, tetra-substituted) proceed under very mild conditions. A most user-friendly protocol can be adopted by simple mixing of the ferrous salt, reductant, and ligand. The isolation of novel soluble Fe nanocluster topologies provides new insight into reductive catalyst formation and cluster aggregation (Scheme 1, bottom).

There are several reports of the coordination chemistry of Fe(hmds), in the presence of various ligands, but only very few applications to catalytic reactions have been demonstrated. The displacement of hmds ligands from Fe(hmds)₂ by formal hydride donors has not received significant attention despite its relevance to the preparation of simple hydridoiron species and hydrogenase model compounds. In the context of alkene hydrogenations, Chaudret et al. prepared catalytically active Fe nanoparticles by thermal decomposition of Fe(hmds), at 150°C in the presence of H₂. We studied the generation of active hydrogenation catalysts from Fe(hmds), and various simple and commercial hydride donors, and the role of hmds ligands.
The mild conditions tolerated fluoride, chloride, bromide, silylenol ether, amine, imide, ester, thioether, and benzyl ether functions. The hydrogenations of some challenging substrates required elevated temperature and/or pressure. Remarkably mild conditions enabled the hydrogenation of tetra-substituted alkenes (1–4 bar H₂, 20°C).[14] The harsher conditions required for complete hydrogenation of 1,2-dimethylindene might be a consequence of the low isomerization activity of the Fe(hmds)/Dibal-H catalyst.[15] Notably, no ring-opening of α-cyclopropyl styrene was observed.[14] With reduced catalyst loadings of 0.5 mol% Fe(hmds) and 1 mol% Dibal-H, turnover frequencies (TOF in h⁻¹) of 660 and 280 were recorded in the hydrogenations of 1-octene and α-methylstyrene, respectively (2 bar H₂, PhMe, 20°C, 5 min). Under the same conditions, conversion of 1-phenyl-1-cyclohexene required 3 mol% catalyst loading which resulted in a TOF of 60 h⁻¹. Alkenes were cleanly reacted to alkanes under identical conditions (Scheme 3).

Kinetic poisoning studies were performed to ascertain the topicity of the operating catalyst species.[15] The addition of sub-catalytic amounts of trimethylphosphine (PMe₃) led to catalyst inhibition already at a catalyst/poison ratio of 10:1 (Scheme 4, top).[16]

Contrary to this, the selective homogeneous catalyst poison dibenzyl-[α,ε]-cyclooctatetraene[17] (dct, 4 equiv per Fe) showed no significant inhibition but was merely a competing substrate for hydrogenation (Scheme 4, bottom). We thus postulate the operation of a heterotopic mechanism by polynuclear low-valent Fe catalysts.

In an effort to identify potential catalytically active species, we investigated the reaction of Fe[N(SiMe₃)₂]₂ with Dibal-H under the conditions of the hydrogenation reactions (toluene or hexane, 20°C). The reaction of Fe[N(SiMe₃)₂]₂ and Dibal-H in a toluene/hexane mixture underwent rapid color change from green to brown–black. Filtration, removal of the solvents, and crystallization from n-hexane afforded the dark crystalline Fe₄ nanocluster Fe₄(hmds),Fe₄(toluene) in 38% yield (Scheme 5, Figure 1).[14] Single crystal structure analysis showed a planar Fe₄ core which is peripherally decorated with four hmds ligands of which two hmds adopt a bridging µ–coordination mode. One Fe atom bears an η¹-toluene. The paramagnetic complex had a melting point of 123°C and exhibited an effective magnetic moment \( \mu_{\text{eff}} = \ldots \).
Two structurally related nanoclusters were isolated by slow solvent evaporation from the reaction of Fe[N(SiMe$_3$)$_2$]$_2$ and Dibal-H in n-hexane. Crystal structure analysis established the dark-red oligohydridoiron clusters Fe$_5$(hmds)$_6$FeH$_5$ (35% yield, 4/1, Scheme 5, Figure 1). The Fe$_5$ cluster is a truncated derivative of the Fe$_7$ cluster and bears one μ$_2$-H and four μ$_3$-H atoms coordinated to iron. The highly symmetrical Fe$_7$ cluster, a low-valent “Fe wheel”, contains six peripheral μ$_2$-hmds ligands and six μ$_3$-H ligands.$^{[19]}$ The composition of the cluster mixture was further verified by X-ray analysis, elemental analysis, and LIFDI-MS (m/z 1301.2287, 1358.1793). The Fe$_5$, Fe$_6$, and Fe$_7$ nanocluster architectures contain multiple iron centers in low oxidation states (formally Fe$^0$, Fe$^I$, Fe$^{II}$) and constitute a distinct class of metallic cluster complexes$^{[20]}$ that adopt...
rare planar Fe₄ geometries and are void of the common carbonyl, nitrido, o xo and carbido ligands. Generally, discrete metallic clusters with direct interactions between the redox centers are considered as materials for optical, magnetic, and catalytic applications. Detail studies of spectroscopic and coordination properties of the Fe nanoclusters are beyond the scope of this catalytic method development but will be reported soon. Preliminary studies proved that the Fe₄ nanocluster is a competent hydrogenation pre-catalyst in the presence of DiBal-H and HN(TMS)₂ (Scheme 6).

Figure 1. Crystal structures (50% probability level, peripheral H atoms omitted) of Fe₄(hmds)₄Fe(toluene), Fe₄(hmds)₄FeH₄, Fe₄(hmds)₄FeH₂ (left to right).

Scheme 6. Catalytic hydrogenation with the isolated Fe₄ nanocluster.

In summary, we have developed an iron-catalyzed hydrogenation protocol that displays unprecedented activity for challenging tri- and tetra-substituted alkenes under very mild reaction conditions. The catalyst is prepared by reaction of Fe[N(SiMe₃)₂]₄ with disobutylaluminum hydride or by a most user-friendly in situ method from FeCl₃. The isolation of novel low-valent nanoclusters with planar Fe₄, Fe₆, and Fe₇ geometries under such conditions provides new insight into the interface of homogeneous/heterogeneous catalysis and the growth of metallic nanoparticle materials. Further studies of the spectroscopic and chemical properties of these and related planar [(amido)Fe]₄ nanoclusters are currently being executed.

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Conflict of interest

The authors declare no conflict of interest.

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