

Review

Iron-catalyzed reduction of carboxylic and carbonic acid derivatives



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ABSTRACT

This review presents recent advances in reduction of carboxylic and carbonic derivatives by means of iron catalysis. It reveals the strong efforts, which have been devoted to the discovery of new ligands and catalysts during the last decade.

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1. Introduction

Reduction of functional groups plays a pivotal role in fine chemistry, both on the laboratory and industrial scale [1]. Well-known and often used reductions with stoichiometric amounts of metal hydride reagents, such as LiAlH_4 or borohydrides, prevail but these methods generate waste and have a detrimental environmental impact, besides toxicity [2]. Silane derivatives are a first alternative to these metal hydride reagents. Thanks to a low bond dissociation energy (92 kcal mol^{-1} in SiH_4 vs. $104 \text{ kcal mol}^{-1}$ in H_2), the reaction conditions are often mild. Moreover, the reactivity of the silanes can be tuned by changing the silicon substituent. These advantages make hydrosilylation a good starting point to develop reactions with new organometallic catalytic species [3] and may also lead to compounds not accessible with other reducing agents (*vide infra*). However, the use of silanes results in some drawbacks. The low Si–H energy bond brings about lower stability than hydrogen and consequently some problems to control the reactivity. Finally, catalytic hydrosilylation reactions generate also many by-products. Then, to overcome the problem of wastes, catalytic reactions with molecular hydrogen are the next attractive step. They are economically viable methods for reduction and both hydrogen atoms are added to the substrates. Heterogeneous catalysts promote hydrogenation under quite harsh conditions that can lead to some problems of chemoselectivity [4]. Homogeneous, well-defined, organometallic complexes usually react under milder conditions, and then are more selective. In the recent years, tremendous progress has been made in the area of hydrogenation of polarized C=X bonds (such as aldehydes, ketones and imines) [5], but also of carboxylic derivatives (esters, amides and nitriles) and carbonic acid compounds, albeit to a lower extent [6]. Indeed, such reductions furnish high-value intermediates for the bulk and fine chemistry, pharmaceutical and agrochemical industries. Carbonic compounds, such as carbon dioxide, carbonates, carbamates, are sources of C_1 in synthesis (alternative to phosgene or carbon monoxide), and thus sources of valorization of carbon feedstock. These compounds offer new routes to the synthesis of methanol or formic acid [7]. Selective hydrogenation of polar C=X bonds (ketones, imines) with homogeneous chiral catalysts is also nowadays a mature area of research and excellent enantioselectivities and high efficiencies can be reached [5,8]. On the contrary, despite its great interest on industrial scale and the exciting challenge, due to the lower electrophilic character of the carbonyl function and to the complexity of the reaction (this is not a simple transfer/addition of one molecule of hydrogen), the hydrogenation of carboxylic or carbonic derivatives suffers from little progress. However, some organometallic complexes have been developed in the last decade to achieve such a reaction and some recent reviews highlight these advances [6,7]. But all these efficient catalysts are mainly based on noble metals such as ruthenium and iridium.

Environmental concerns in chemistry increase the demand for the replacement of these noble metals by Earth-abundant ones. Iron-catalyzed reduction of polarized C=X bonds is a flourishing research area and some complexes compete with the noble metal ones [9]. Hydrogenation of less active functions in the presence of iron complexes is still in its infancy compared to the hydrogenation with ruthenium complexes but some recent results demonstrate the high potential of this chemistry. This review highlights the recent efforts directed to homogeneous iron-catalyzed transformation of carboxylic and carbonic acid derivatives with silanes and molecular hydrogen.

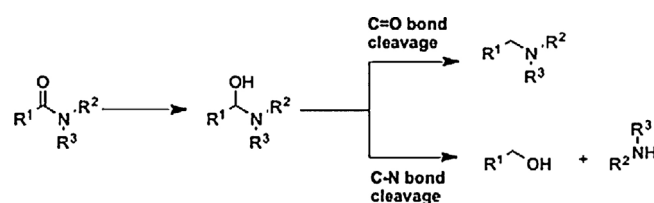
2. Iron-catalyzed hydrosilylation of carboxylic acid derivatives

2.1. Hydrosilylation of amides

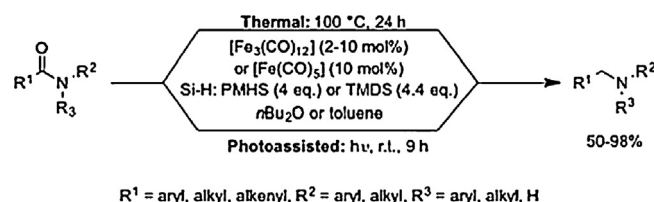
Several challenges have to be faced with the reduction of amides. Beside the high thermodynamic stability, the reduction can lead either to the C–N or C=O bond cleavage, furnishing the amine or alcohol (Scheme 1) [6c]. Contrary to the ruthenium complexes [6g], iron complexes display complete chemoselectivity in favor of the reduction of the C=O bond cleavage, and secondary and tertiary amides furnish exclusively the corresponding amines. Furthermore the primary amides are less reactive and tend to dehydrate to form nitriles [3,10].

The first general iron-catalyzed hydrosilylation of amides generate amines was reported simultaneously by Beller and Nagashima in 2009 [11,12]. In the presence of commercially available $[\text{Fe}_3(\text{CO})_{12}]$ or $[\text{Fe}(\text{CO})_5]$ as pre-catalysts, poly(methylhydrosiloxane) (PMHS) or 1,1,3,3-tetramethyldisiloxane (TMDS) as hydride sources, at high temperature (100°C) in di-*n*-butyl ether or toluene, tertiary amides were reduced to the corresponding amines in moderate to excellent yields (50–98%, Scheme 2). Interestingly, Nagashima noted that the reduction proceeds similarly under irradiation (with a 400 W high-pressure mercury lamp) but at room temperature in shorter reaction time (9 h vs. 24 h). Both reaction procedures (at 100°C or room temperature) are more industrially viable than the low temperature conditions usually required with metal hydride reagents. This system is also nicely tolerant toward various functional groups including halide, ether, cyclopropane, and alkene groups but with ketoamides a mixture of compounds is obtained. Heteroaromatic and heterocyclic amides are reduced to the corresponding amines in high yields (80–94%). However, the catalyst appeared to be sensitive to steric hindrance on both the carbonyl and the amine side. Higher catalyst loading and higher amount of silane are required to achieve full conversion for these substrates. By replacing PMHS by PhSiH_3 (2.5 equiv.), not only tertiary but also secondary amides can be reduced [11]. For example, *N*-methylbenzamide, in the presence of $[\text{Fe}_3(\text{CO})_{12}]$ (4 mol%), afforded the corresponding amine in 99% yield.

Noteworthy, complete chemoselectivity was observed with aromatic amides having a nitro function. The nitro group is reduced whilst the amide group remains intact (Scheme 3) [12]. Nagashima



Scheme 1. Possible reduction pathways from amides.



Scheme 2. Iron-catalyzed reduction of tertiary amides [11,12].

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