

# Homogenous Iridium Catalysts for Biomass Conversion



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**Abstract** The use of biomass as a sustainable feedstock for the production of chemicals has become more and more important in recent years. Homogeneous iridium catalysis offers great opportunities for the conversion of bio-derived platform molecules and even biomass components such as cellulose or lignin, due to the air, water, and acid stability of many iridium complexes. In this chapter, we review the application of iridium catalysts to the transformations of carbohydrate-derived compounds, fatty acids, and lignin.

**Keywords** Biomass conversion · Dehydrogenation · Fatty acids · Glycerol · HMF · Homogeneous catalysis · Hydrogenation · Hydrogen borrowing · Iridium catalysis · Levulinic acid · Lignin · Platform chemicals

## 1 Introduction

The diminishing supply of fossil resources, as well as the climate effects caused by the cumulative release of CO<sub>2</sub> from fossil energy carriers into the atmosphere, forces us to look for more sustainable alternatives. Thus, the conversion of biomass into useful chemicals and fuels has become a very important field of research. Whereas initially most work was focused on the conversion of easily accessible and chemically pure compounds such as sugars and fatty acids, nowadays also direct routes from lignocellulose to some platform chemicals have been established.

Lignocellulosic biomass is generally converted by acid hydrolysis (or in combination with enzymes) into its monomers (sugars from the cellulose and hemicellulose fractions), which are then further converted into a range of small platform molecules (Fig. 1) [1, 2]. Here, there is scope for the use of homogenous catalysis in the further transformation of these molecules into new and known compounds [3]. The great advantage of iridium catalysts in this regard is their high stability towards water, air, and acidic conditions, i.e. the exact conditions present in biomass processing. This opens up the possibility of performing several steps in one pot or at least without extensive and energy intensive purification of intermediates or drying of starting materials. Additionally, many biomass derived compounds are poorly soluble in solvents other than water.

In the following we will discuss the recent work on homogeneous iridium catalysis in the field of biomass conversion. As most current research focusses on the conversion of a few available platform chemicals, the chapter is divided according to the substrates. Most of these are derived from the cellulose/hemicellulose fraction, namely sugars, bio-derived alcohols, furanics (compounds derived from furfural or 5-hydroxymethylfurfural), and small organic acids. Another section deals with iridium-catalyzed transformations of fatty acids, which are derived, together with glycerol, from vegetable oils. Iridium-catalyzed conversion of lignin is discussed in Sect. 6.

Many of the transformations of biomass discussed here are hydrogenation or dehydrogenation reactions. In comparison with oil derived platform chemicals, biomass is highly functionalized with mostly oxygen containing groups. Hydrogenation/dehydrogenation strategies are therefore an efficient way of converting these compounds. The focus with dehydrogenation reactions can be either on the hydrogen generated or on the dehydrogenated product, while of course always both are formed. The generation of hydrogen gas from biomass as a renewable fuel will be discussed in Sect. 5, alongside dehydrogenative strategies for the synthesis of other compounds. Hydrogenation of CO<sub>2</sub> with H<sub>2</sub> gives formic acid, which has been widely researched and proposed as a reversible hydrogen carrier. While we mention the topic of formic acid dehydrogenation in the last section for the hydrogenation of other substrates, a full discussion of CO<sub>2</sub> hydrogenation was deemed out of scope for this chapter. For further information on this topic, we refer to this recent review [4].

## 2 Recent Trends in Iridium-Catalyzed Valorization of Bio-derived Alcohols

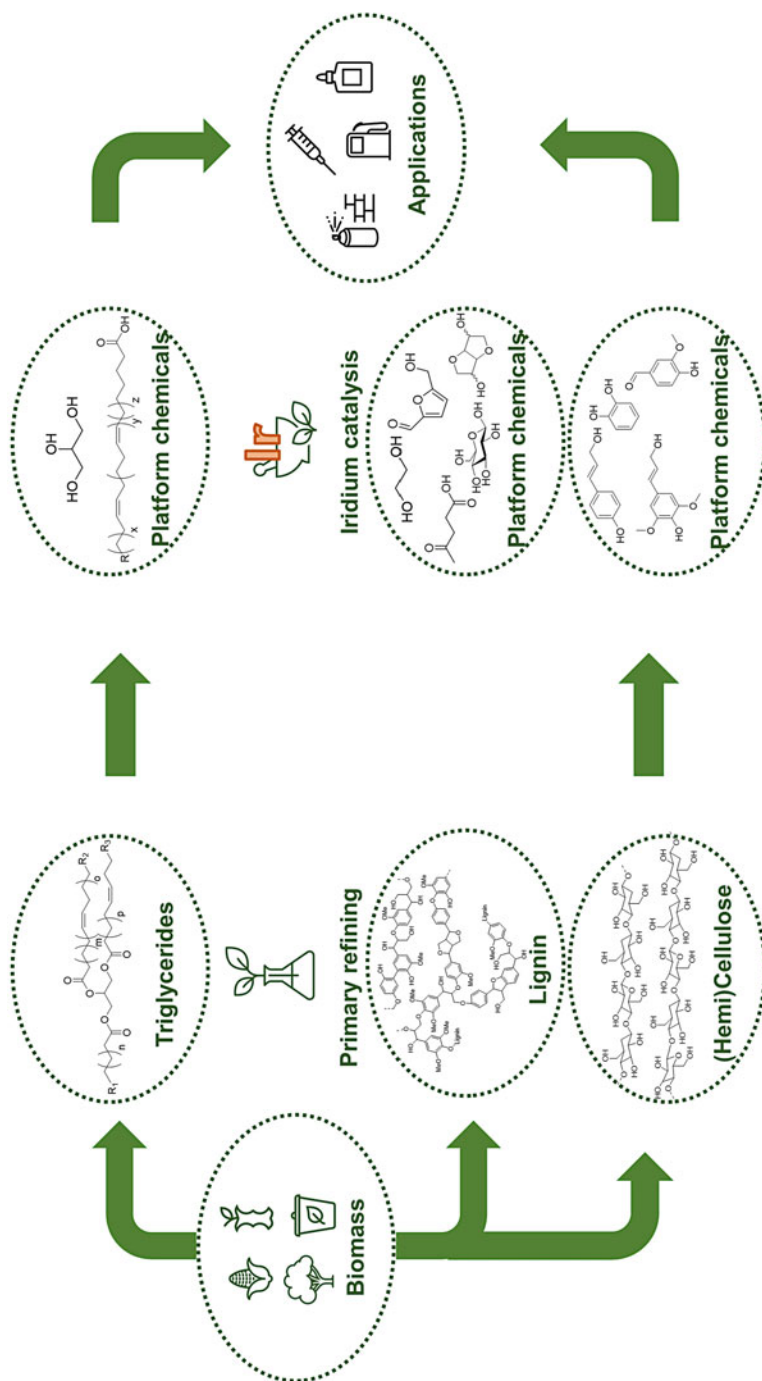
Alcohols, diols, and polyols are indispensable ingredients and reactive materials for polymers, cosmetics, and pharmaceuticals and their wide range of applications makes them one of the largest class of chemicals produced in the world [5]. The C2-C4 diols alone are produced on an annual scale of 18 million tons [6].

In the last two decades, the use of renewable resources for the benign production of industrially relevant alcohols (see Fig. 1) has received significant interest. In this regard, fermentative and catalytic processes were developed to obtain the bio-based versions of the existing fossil-based polyols as well as newly synthesized alcohols, usually not available from fossil feedstock material [6]. For a detailed overview on the production of bio-based alcohols, we refer to the recently published review articles [5, 7]. In this section the use of bio-based polyols in homogeneously iridium-catalyzed reactions is reported.

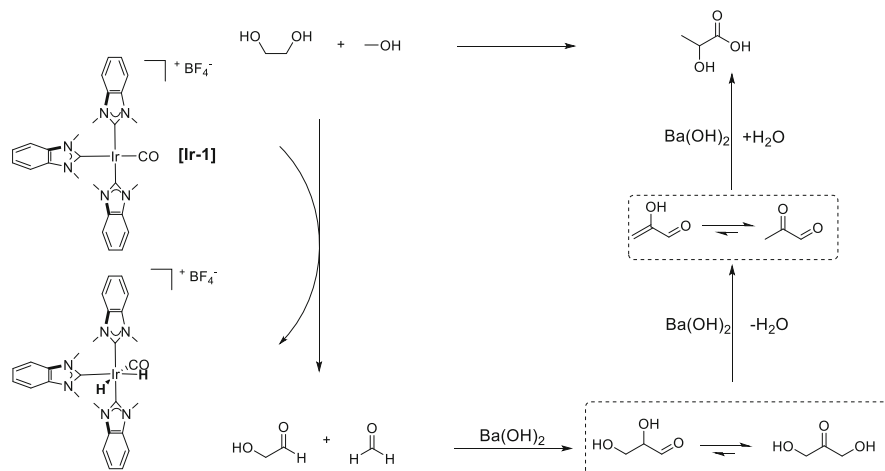
### 2.1 *Iridium-Catalyzed Reactions Using Ethylene Glycol*

#### 2.1.1 Iridium-Catalyzed Selective Cross-Coupling of Ethylene Glycol

Ethylene glycol (EG) is industrially produced from renewable resources on a multiton scale via the hydrogenolysis of sorbitol using a Ni/Ru catalyst [8]. This process leads to a mixture of EG and other bio-based polyols. Furthermore, the dehydration of bio-ethanol to ethylene and its further conversion to EG is an alternative bio-based route according to the conventional petro-based process [8]. Finally, the Dutch company Avantium has recently started to build a demonstration plant where EG will be produced directly from renewable sugars [9]. EG is



**Fig. 1** Conversion of biomass to monomers and platform chemicals



**Scheme 1** Dehydrogenative cross-coupling of EG and MeOH in the presence of a novel iridium-tris-NHC complex

mostly known for its use as anti-freeze ingredient in liquid mixtures [5]. However, extremely relevant is its use as a building block for the synthesis of polyesters. Particularly, polyethylene terephthalate (PET) and, more recently, its green analogue polyethylene 2,5-furandicarboxylate (PEF) are the polyester materials in which EG finds its main use [6]. Additionally, other important derivatives and platform chemicals can be obtained from EG. One of them is lactic acid (LA) which has attracted extensive attention over the last years due to its versatility and the useful properties of its derived polymer, polylactide [10]. Besides the existing conventional processes, based on the fermentation of carbohydrates, several new routes based on renewables have been developed for the production of LA. Tu and coworkers developed a new strategy to synthesize LA which uses bio-derived EG and MeOH as starting materials and a novel iridium complex **[Ir-1]** bearing three N-heterocyclic carbene ligands (NHC) as a catalyst (Scheme 1) [10].

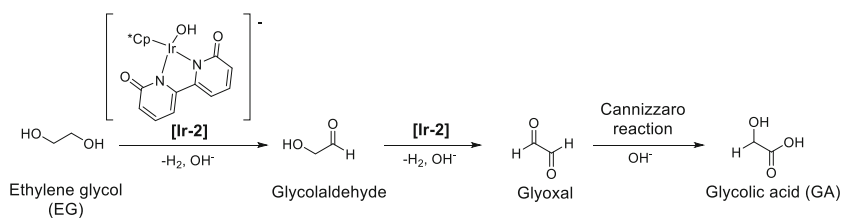
The dehydrogenative cross-coupling between 5 mmol of EG and a large excess of MeOH (2 mL) to quantitatively form LA was performed at 140°C for 1 h in the presence of 500 ppm of **[Ir-1]** and 1.2 equiv. of Ba(OH)<sub>2</sub>·8H<sub>2</sub>O. The use of the base Ba(OH)<sub>2</sub>·8H<sub>2</sub>O is crucial in this reaction since other alkali hydroxides such as calcium hydroxide led to low or no yield of the desired product. When the amount of base was lowered to 1.0 equiv., the yield was only slightly reduced from 100% to 95%. In contrast, by lowering the reaction temperature a significant loss in yield of LA was observed (58% of LA at 120°C for 1 h). Furthermore, the number of NHC ligands coordinated to the metal center is very important as the activity of the iridium (I) catalyst increases as follows: mono-NHC-Ir < bis-NHC-Ir < tris-NHC-Ir [10]. The authors postulated that the increasing number of NHC ligands enhances the steric bulkiness and the electron density which in turn facilitates the oxidation of Ir(I) to Ir(III) and thus improves catalytic performance. In the first step of the

reaction, ethylene glycol is dehydrogenated to glycolaldehyde and methanol is dehydrogenated to formaldehyde. These two products are joined in a base-catalyzed aldol condensation reaction to give glyceraldehyde which is in equilibrium with 1,3-dihydroxyacetone. Further dehydration results in pyruvaldehyde, which undergoes an internal Cannizzaro reaction to form lactic acid (Scheme 1). Interestingly, when EG was replaced by either glycerol or sorbitol, the yield of the reaction remained high and LA was produced with 85% and 99% selectivity, respectively. Finally, strong  $\sigma$ -donating and weak  $\pi$ -acceptor ligands in combination with Ir (I) seemed generally beneficial for the conversion of bio-polyols towards LA.

### 2.1.2 Iridium-Catalyzed Oxidation of Ethylene Glycol Towards Glycolic Acid

Glycolic acid (GA) is a simple  $\alpha$ -hydroxy acid which finds applications in the fields of fine chemicals and pharmaceutical chemistry [11]. Additionally, GA is of interest for the synthesis of polyglycolic acid (PGA), a material which could be a sustainable replacement for traditional plastics, due to its excellent biodegradability and biocompatibility. However, at present, GA is predominantly synthesized via the poorly sustainable process based on the hydrolysis of chloroacetic acid in alkaline solution [11]. In contrast, the synthesis of GA from biomass can be achieved through two different mechanisms both using EG as the starting material. In one method, GA can be synthesized from EG through an oxidation pathway which proceeds via the intermediates glycolaldehyde and glyoxal. However, the synthesis of GA through this process has been so far achieved only by using high temperatures and in the presence of an oxygen enriched atmosphere and metallic oxides [12]. The second strategy, alternative to the oxidation pathway for the conversion of EG into GA, is the use of a dehydrogenation reaction, which is superior to the oxidation pathway, because it avoids overoxidation. Tang and coworkers have used this strategy and developed an iridium-mediated cascade process in alkaline water which consists of two dehydrogenation steps followed by a Cannizzaro reaction (see Scheme 2) which transforms EG into GA [11].

Initially, two different metal catalysts based on Rh and Ir, respectively, were tested for the dehydrogenation of EG. The iridium complex  $[\text{Cp}^*\text{Ir}(\text{bpym})]\text{Cl}_2$



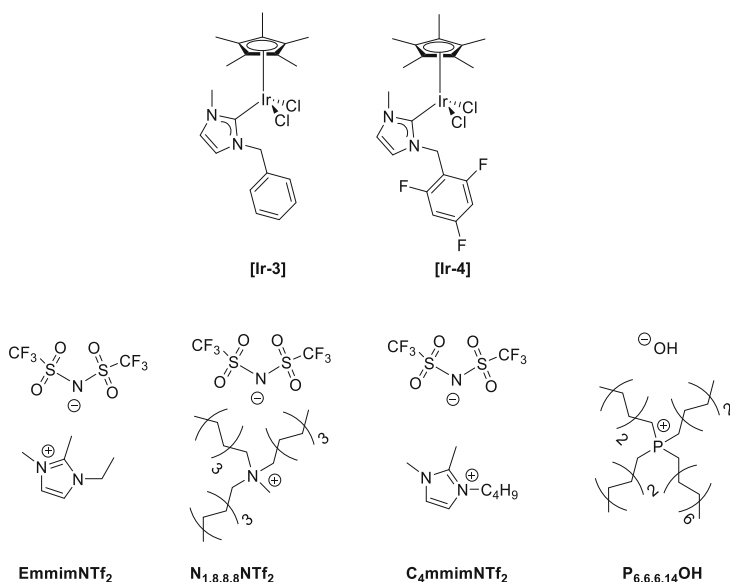
**Scheme 2** Reaction pathway of the conversion of ethylene glycol into glycolic acid catalyzed by  $[\text{Ir-2}]$

(Cp\* = pentamethylcyclopentadienyl; bpym = bipyrimidine) led to yields which were two times higher than the ones obtained using the analogous rhodium complex [Cp\*Rh(bpym)]Cl<sub>2</sub> [11]. For this reason, the authors further explored the reactivity of the iridium complex by replacing the ligands, and when the complex [Cp\*Ir(bpyO)]OH<sup>-</sup> (bpyO =  $\alpha,\alpha'$ -bipyridonate) [**Ir-2**] was used, an excellent conversion of 93% and a GA yield of 76% were obtained (Scheme 2). In order to maximize the concentration of the active dehydrogenation catalyst [**Ir-2**], the pH of the solution was adjusted with a phosphate buffer and additional NaOH was added to compensate the acidifying effect of the produced GA. The best results were obtained (GA yield: 81.5%) when a stoichiometric amount of NaOH was sequentially added to the reaction. Tang and coworkers were also able to reuse the [**Ir-2**] for several catalytic runs, although after the sixth run the conversion of EG and the yield of GA slightly dropped.

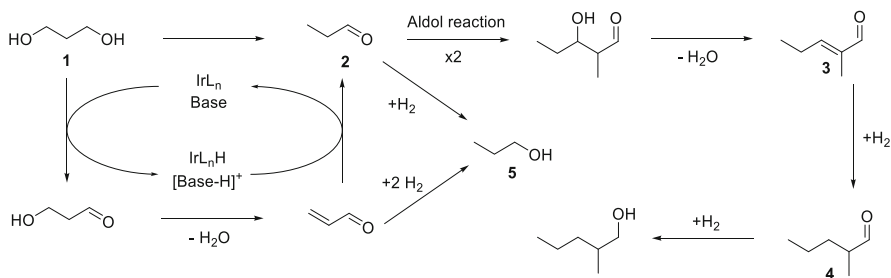
## 2.2 Iridium-Catalyzed Hydrogen Transfer Initiated Dehydration of 1,3-Propanediol to Aldehydes

Aldehydes like propionaldehyde are important intermediates for the production of fragrances, agrochemicals, plasticizers, or drugs [13]. 1,3-Propanediol (1,3-PDO) has been one of the first renewable platform chemicals which is produced by bacterial fermentation of sugars [6, 13]. Due to the relevance of 1,3-PDO, Marr and coworkers became interested in finding new chemocatalytic transformations of this bio-based alcohol into value-added chemicals. During their attempt to aminate 1,3-PDO with a Cp\*Ir(III) N-heterocyclic carbene complex they discovered that, by working in ionic liquids, dehydration of 1,3-PDO occurred [14]. For that reason, the authors decided to use the same iridium catalyst (**Ir-3**, Fig. 2) in ionic liquids for the selective dehydration of 1,3-PDO (**1**) to propionaldehyde (**2**) [13]. This interesting conversion proceeds via a dehydrogenation to 3-hydroxypropionaldehyde, dehydration to acrolein, and hydrogenation to propionaldehyde. The authors refer to the sequence as a hydrogen transfer initiated dehydration (HTID). The reaction was initially tested in the presence of two different ionic liquids (Fig. 2), EmmimNTf<sub>2</sub> or N<sub>1,8,8,8</sub>NTf<sub>2</sub>, respectively, and at temperatures varying between 80°C and 150°C for 6 h. Next to the desired product **2**, side products **3**, **4**, and **5** were found in varying amounts (Scheme 3). The formation of **3** and **4** can be explained by the Aldol reaction of **2** followed by dehydration and consecutive hydrogenation. Hydrogenation of **2** leads to the formation of **5**. In order to prevent the occurrence of aldol condensation reactions, a reduced pressure (0.35 bar) was used to remove the highly volatile propionaldehyde (Schemes 3, 2) which was collected in a cold trap.

The use of EmmimNTf<sub>2</sub> resulted in higher yields and selectivities towards **2** compared to N<sub>1,8,8,8</sub>NTf<sub>2</sub>. Furthermore, the use of ionic liquids led to better results for the dehydration with respect to neat conditions. Finally, it was shown that the base (K<sub>2</sub>CO<sub>3</sub>, KOH, Cs<sub>2</sub>CO<sub>3</sub>) itself had a minor effect on the product distribution



**Fig. 2** Hydrogen borrowing catalysts and ionic liquids used as solvent for the HTID



**Scheme 3** Postulated reaction pathway of the iridium-catalyzed HTID of 1,3-PDO

although its concentration strongly affected the yield of the reaction. Specifically, it was noted that the higher the base concentration was, the lower the yield of **2**. The recyclability of **[Ir-3]** was proven in EmmimNTf<sub>2</sub>, by reusing it for ten cycles in the presence of K<sub>2</sub>CO<sub>3</sub> at 150°C and 0.35 bar [13]. The conversion of 1,3-PDO (75–99%) and the selectivity towards propionaldehyde (65–72%) remained high over all the runs. Both the used ionic liquid and the catalyst **[Ir-3]** exhibited excellent stability towards water, air, and temperature throughout the 10 runs albeit K<sub>2</sub>CO<sub>3</sub> needed to be replenished.

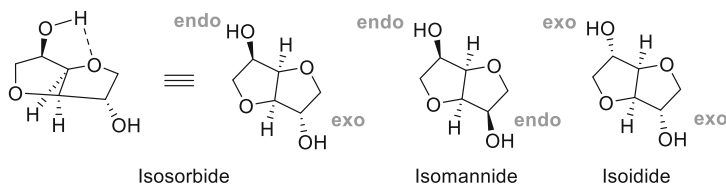
Subsequent work of Marr and coworkers revealed that the use of the fluorinated analogue (**[Ir-4]**, Fig. 2) of their previous reported Ir(III) carbene catalyst **[Ir-3]** improved the conversion (quantitative) and the selectivity towards propanal (87%)



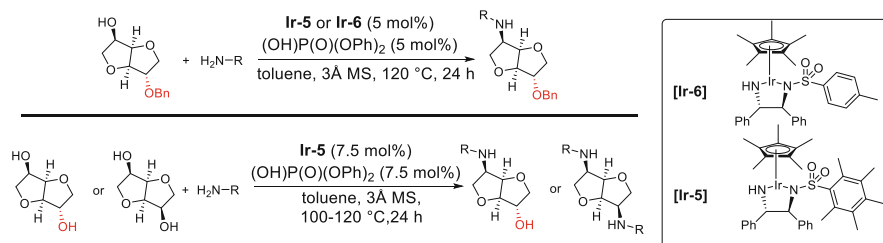
[15]. Intrigued by these promising results, they extended their investigations by using basic ionic liquids gel [16]. In this work, they used mixtures of  $[P_{6,6,6,14}][OH]$  and  $[C_4mmim][NTf_2]$  (Fig. 2) and added tetraethoxysilane which over time cured to form a gel. By using **[Ir-4]** in these gels, high conversions (80–99%) and good yields towards propanal (82–90%) were obtained. A 1:3 ratio of  $[C_4mmim][NTf_2]: [P_{6,6,6,14}][OH]$  was found to be the best mixture which allowed the optimal balance between basicity, stability, and activity with regard to the formation of propanal.

### 2.3 Iridium-Catalyzed Direct Amination of Isohexides

Isohexides like isosorbide and isomannide are produced from sorbitol and mannose, respectively (Fig. 3). They are of high interest for material science applications since their rigid skeleton can boost the glass transition temperature of the polymers in which they are incorporated [17]. Isohexides exist in three diastereomeric forms, but only the isomers isomannide and in particular isosorbide are used for research purposes due to their commercial availability (Fig. 3) [18]. The range of applications of these two diastereomers has been rapidly growing over the last years. Particularly, their corresponding amine derivatives have received a lot of attention in the field of polymer chemistry [19] and for asymmetric induction in organic synthesis [20, 21]. However, the reported synthetic route for isohexide-based amines which consists in the activation of the alcohol by transformation into better leaving groups followed by a substitution reaction with an amine moiety and a final deprotection step, has an overall low atom efficiency and generates large amounts of waste [17]. This problem was recognized by Popowycz and coworkers, who developed the diastereoselective amination of monobenzylated isohexides through a hydrogen borrowing synthetic pathway by using a combination of iridium complex **[Ir-5]** and diphenylphosphoric acid as catalyst (Scheme 4) [18]. The hydrogen borrowing methodology had already been applied for the diamination of isosorbide and isomannide by using homogenous ruthenium catalysts and excellent yields had been achieved [22, 23]. However, the product was obtained as a mixture of three diastereomers. Popowycz and coworkers achieved 60% conversion of the monobenzylated isosorbide and 50% yield of the corresponding amine [18] using diphenylphosphoric acid and **[Ir-6]**, a catalyst system that had been previously



**Fig. 3** Chemical structure of bio-based isohexides



**Scheme 4** Overview of direct amination of isohexides by using iridium catalysts coupled with diphenyl phosphoric acid

developed by Zhao and coworkers (Scheme 4) [24]. The diphenyl phosphoric acid facilitates the condensation of the used (4-methoxyphenyl)methanamine with the intermediate isosorbide ketone. Furthermore, by adding molecular sieves into the reaction mixture and by replacing **[Ir-6]** with **[Ir-5]** a further increase of the amount of amination product was observed (yield 67%). In the end, the best results were obtained with 5 mol% of **[Ir-5]** and 5 mol% of diphenylphosphoric acid in the presence of molecular sieves in toluene at 120°C for 24 h (68% yield; dr > 99:1) (Scheme 4, top). This amination protocol was then successfully applied by using various primary amines. The resulting monobenzylated isohexide amines were obtained in good yields (44–83%) and excellent diastereoselectivities.

DFT calculations revealed that it requires more energy to oxidize the alcohol in the exo-position than the alcohol in the endo-position due to the fact that the hydride that needs to be transferred is inside the envelope which is not easily reached by the bulky catalyst [25]. In agreement with this finding, Popowycz and coworkers experimentally confirmed the mono-amination of isosorbide into a chiral amino alcohol [18]. Intrigued by this first direct and regioselective amination of isosorbide, they further examined the scope of the selective transformation by using the hydrogen borrowing methodology [17]. Their optimization study led to slightly different conditions (7.5 mol% of **[Ir-5]** and diphenyl phosphoric acid) than their previous work (for comparison see Scheme 4). Subsequently, a range of different substituted amines were used for the regioselective amination of isosorbide. Depending on the amine, temperatures between 100°C and 120°C were used to achieve generally high conversions (65–99%) and good selectivities (46–95%) towards the desired chiral amino alcohols. Encouraged by these results, they also developed the first synthesis of the parent amino alcohol (Scheme 4, R = H) which they obtained in 54% yield and of the parent diamine (R = H) in 59% yield. They achieved this via the iridium-catalyzed hydrogen-borrowing reaction with benzylamine and isosorbide and isomannide, respectively, followed by the hydrogenation of the benzyl protecting groups using Pd on carbon [17]. Under the same conditions used for the synthesis of the amino alcohols of isosorbide, isomannide was also converted into a range of different diamines with similar good conversions (78–99%) and selectivities (66–91%).

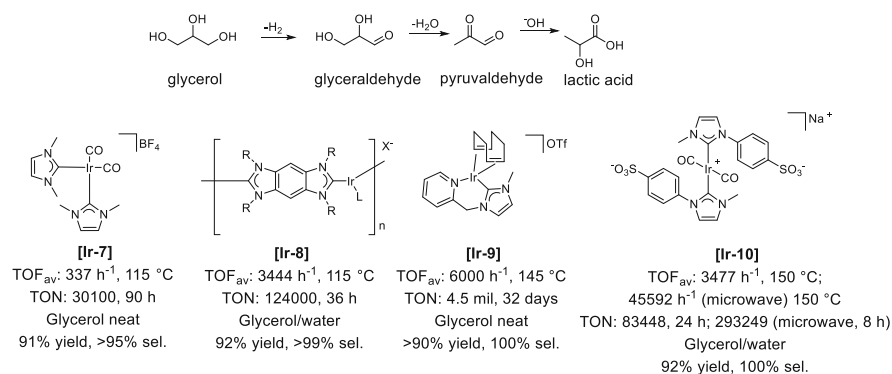
## 2.4 Iridium-Catalyzed Conversion of Glycerol

### 2.4.1 Iridium-Catalyzed Oxidative Conversion of Glycerol

The by-product of the production of biodiesel from fats is glycerol. Thus, glycerol is readily available from biomass, and its use has received a lot of attention, not only with the aim of improving the entire value-chain of biomass transformation, but also as a consequence of the variety of reactions which can be done with this polyol. As mentioned before in Sect. 2.1.1, LA and its derivatives have numerous applications and the demand for polylactide materials is increasing steadily. Currently, lactic acid (LA) is produced via fermentation on a scale of 450,000 tons/year [26]. Nevertheless, the use of a low-value waste product like glycerol as a feedstock material could offer, when catalytically and economically feasible, another scalable and valuable alternative for the synthesis of lactic acid/lactate.

In recent years, several groups investigated the iridium-catalyzed acceptorless dehydrogenation of glycerol to LA. In the seminal work from Crabtree and coworkers the authors used iridium(I) bis NHC complexes for the dehydrogenation of glycerol to form either dihydroxyacetone or glyceraldehyde [27]. Afterwards, the latter products could undergo a dehydration followed by an intramolecular Cannizzaro reaction to afford LA (for comparison, see Scheme 1). They found that **[Ir-7]** (see Fig. 4) was the most active by resulting in high yields (91%) and selectivities (>95%) under solvent-free conditions. The same authors explored the use of sorbitol, mannitol, xylitol, and erythritol as starting materials which are readily available from biomass [28]. Unfortunately, the conversion of these polyols did not even come close to the conversions and selectivities which were obtained with glycerol.

Inspired by these results, Williams and coworkers developed the NHC-pyridine iridium(I) complex **[Ir-9]** which thus far is the most robust and active catalyst for the conversion of glycerol [29]. With this catalyst they were able to reach 4.5 million turnovers in 32 days with an average TOF of 6,000 h<sup>-1</sup> at 145°C under neat

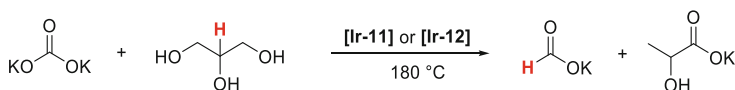
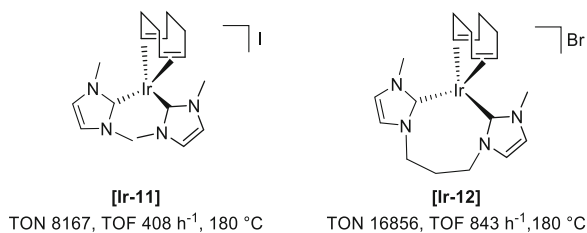


**Fig. 4** Reported iridium catalysts for the acceptorless dehydrogenation of glycerol to lactic acid

conditions. Tu and coworkers developed a polymeric iridium catalyst (**[Ir-8]**, Fig. 4) which allowed the catalyst's recyclability [30]. A maximum turnover number of 124,000 was measured with this catalyst. The extraordinary performance of **[Ir-9]** was explained by the authors as a result of the high stability provided by the bidentate (pyridyl)carbene ligand [29]. In essence, the bidentate coordination mode reduces the probability of ligand scrambling processes which are the major cause of loss of catalytic activity [27]. Subsequently, the group of Voutchkova-Kostal reported other Ir(I)/Ir(III) complexes bearing NHC ligands with attached sulfonate groups [31]. The most active catalyst **[Ir-10]** reached a TOF of  $45,592 \text{ h}^{-1}$  under microwave irradiation at  $150^\circ\text{C}$  and of  $3,477 \text{ h}^{-1}$  when the reaction was conventionally heated at  $150^\circ\text{C}$ .

Jang and coworkers employed various biscarbene Ir(I) complexes (Fig. 5) for the transfer hydrogenation of glycerol with inorganic carbonates in order to obtain both formate and lactate (Scheme 5) [32]. Whereas lactate can be considered as intermediate to access LA and thus polylactic acid, formates are themselves a valuable class of chemicals. The best catalyst **[Ir-12]** reported by Jang and his group was more than two times as efficient than the biscarbene Ir(I) complex **[Ir-11]** of Crabtree [27, 32]. The reason for its superior performance is the high stability of the catalyst at  $180^\circ\text{C}$ , presumably due to the used biscarbene ligand. The latter is a chelating bidentate ligand which inhibits the formation of the inactive tris-carbene-coordinated iridium complexes [29]. Under optimized conditions Jang and coworkers explored the use of  $\text{Na}_2\text{CO}_3$  and  $\text{KHCO}_3$  as alternatives to  $\text{K}_2\text{CO}_3$ . In both cases, TONs with respect to both formate and lactate lower than the ones measured with  $\text{K}_2\text{CO}_3$  were obtained. In the case of  $\text{Na}_2\text{CO}_3$  the lower solubility compared to  $\text{K}_2\text{CO}_3$  was considered responsible for the reduced catalytic performance. In the case of  $\text{KHCO}_3$ , the low pH value of 8.5 in comparison with the pH 11.9 of  $\text{K}_2\text{CO}_3$  in aqueous glycerol was considered the main reason for the drop in TON. As a confirmation of the influence of the pH on catalytic activity, the addition of 2 mmol of KOH to a solution containing 4 mmol of  $\text{KHCO}_3$  led to an increase in TON of more than twice.

**Fig. 5** Iridium catalysts for the transfer hydrogenation of  $\text{K}_2\text{CO}_3$  in glycerol. TON and TOF refer to the formation of formate



**Scheme 5** Transfer hydrogenation of  $\text{K}_2\text{CO}_3$  in glycerol

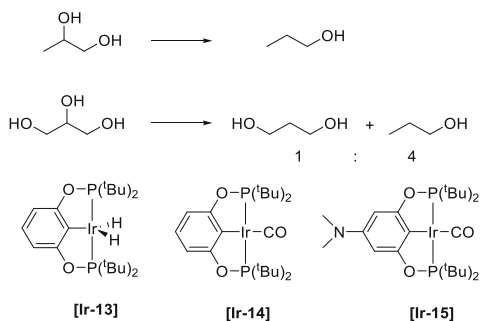
## 2.4.2 Iridium-Catalyzed Deoxygenation of Glycerol

Glycerol is like many other bio-derived chemicals, an oxygen-rich molecule and for this reason deoxygenation/dehydration reactions need to be performed to obtain molecules with low oxygen content. A glycerol derivative of potential interest is, for example, 1,3-propanediol (1,3-PD), a diol commonly used for the synthesis of polymers. The conversion of glycerol to 1,3-PD can be described as a tandem reaction consisting of an initial acid-catalyzed dehydration step followed by a metal catalyzed hydrogenation reaction. For the selective deoxygenation of glycerol mainly heterogenous catalysts are known, also because aqueous acidic conditions and high temperatures are very challenging conditions for many catalytic systems based on well-defined metal complexes. Nevertheless, the groups of Heinekey and Goldberg successfully used iridium pincer complexes (Fig. 6) for the hydrogenolysis of 1,2-propanediol (1,2-PD), a compound that can be made via hydrogenolysis of glycerol, in addition it can be seen as a model reaction for the selective deoxygenation of glycerol [33]. In the presence of 1.04 equivalents of triflic acid and 1.3 mol% **[Ir-13]**, 1,2-PD was effectively hydrogenolyzed using 7 bar of hydrogen to 1-propanol in 95% yield.

As solvent, an acidic aqueous/1,4-dioxane mixture was chosen and the best results were obtained at high water content and low acid concentrations. High acid concentrations or low amount of water led to the formation of several by-products. NMR studies performed after the completion of the reaction revealed that two different iridium species are formed: **[Ir-14]** and **[Ir-14]**-dihydride. Based on this finding, it was proposed that **[Ir-13]** catalyzes the decarbonylation of the intermediate aldehyde and it is presumably transformed in the two observed iridium species. In addition, the authors found that **[Ir-14]** is a catalytically active species that is more stable than the parent complex **[Ir-13]**, since it is still active after storage under air.

Encouraged by these results, the same groups extended their work to the deoxygenation of glycerol [34]. However, complex **[Ir-14]** was poorly soluble in acidic water/1,4-dioxane/glycerol mixtures, also when high temperatures were tested. Therefore, the authors decided to synthesize novel iridium pincer complexes. Complex **[Ir-15]** emerged as a suitable catalyst due to its high solubility in the glycerol containing aqueous dioxane mixture. Particularly, by increasing the amount of

**Fig. 6** Iridium catalysts for the deoxygenation of 1,2-propanediol and glycerol

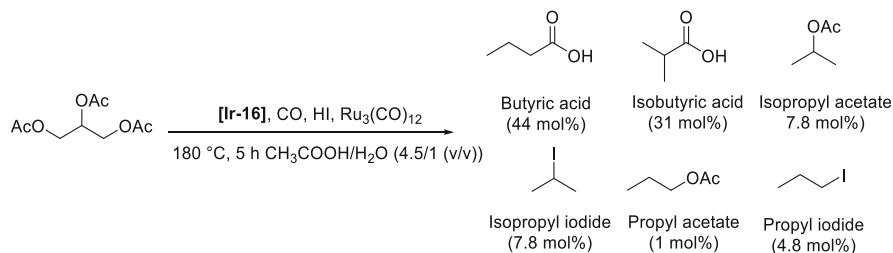


sulfuric acid from 0.25% to 4% (w.r.t. glycerol), the conversion of glycerol increased from 8 to 38% over 24 h at 200°C. However, the increase of the acid concentration was also accompanied by a decrease in selectivity towards 1,3-PD in favor of 1-propanol (1-PO).

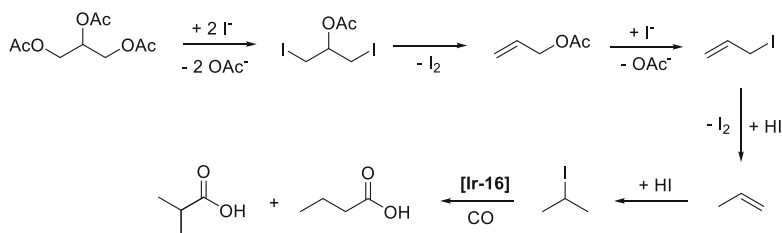
The iridium catalyst was also tested for the direct conversion of crude glycerol generated as a by-product of the biodiesel manufacturing process. Since this material is highly basic, the crude glycerol was acidified with 1 M sulfuric acid prior to reaction. The resulting biphasic system was allowed to settle, the layer of impurities was discarded, and the remaining mixture was used for the reaction. The recycled waste glycerol was deoxygenated in 20% yield after 24 h at 200°C under 80 bar H<sub>2</sub> by using 0.125 mol% of **[Ir-15]** with a high selectivity towards 1-propanol (1-PO: 1,3-PD = 9: 1). The observed selectivity was explained by the high acid concentration which remained after the purification of crude glycerol.

### 2.4.3 Iridium-Catalyzed Carbonylation of Glycerol to Monocarboxylic Acids

A very common deoxygenation approach is the so-called hydro-deoxygenation reaction, in which hydrogen is used as a co-reagent and water is formed as a by-product. In a similar way, CO can be used as a co-reagent instead of hydrogen in a reaction called carbodeoxygenation. Generally, carbonylation reactions are well-established in industry like the production of acetic acid from methanol. However, notwithstanding the progress which has been made in the last decades, the carbonylation of higher alcohols like glycerol using iridium catalysts remains elusive. The latter can be explained by the fact that iridium-based carbonylation catalysts rapidly deactivate due to the formation of  $[\text{Ir}_4(\text{CO})_2]^-$  in the presence of HI as a cocatalyst. As a consequence, a promoter is needed to reversibly bind the iodide and thus to regenerate the active iridium catalyst [35]. To this regard, the group of Britovsek found that by using  $[\text{Ru}_3(\text{CO})_{12}]$  as a promoter in the presence of 0.37 mol% of  $[\text{NBu}_4][\text{IrCl}_2(\text{CO})_2]$  **[Ir-16]** as a catalyst and 48 mol% of HI as a cocatalyst a very good conversion (96%) of triacetin (fully acetylated glycerol) after 5 h at 180°C was achieved (Scheme 6) [36].



**Scheme 6** Iridium-catalyzed carbonylation of triacetin



**Scheme 7** Sequence of intermediates and products in the carbonylation reaction of triacetin

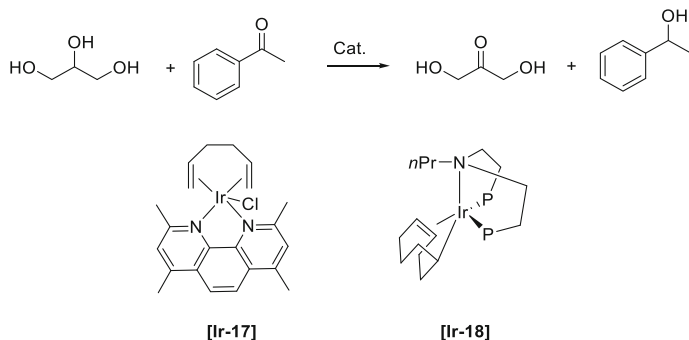
Triacetin was chosen for convenience as the starting material, because it is less viscous than glycerol and because the reaction is carried out in a water/acetic acid mixture which would anyway lead to the formation of a mixture of mono-, di-, and triacetoxiesters of glycerol. The main products of the reaction were butyric acid and isobutyric acid followed by isopropyl iodide and isopropyl acetate (Scheme 6). HI was found to be superior to methyl iodide as a cocatalyst. Additionally, the authors examined the effect of an increasing CO pressure which resulted in an increase of butyric acid while simultaneously the amount of isobutyric acid decreased.

Furthermore, the group was interested in understanding the selectivity to monocarboxylic acids rather than di- or tricarboxylic acids. Therefore, the authors performed their reaction by using DI in  $D_2O$  and  $CD_3COOD$  and they monitored the reaction by  $^1H$  NMR spectroscopy. As a result, they discovered that triacetin undergoes double nucleophilic substitution by HI, which is followed by elimination of iodine and by a subsequent 2,1- shift of the acyl group to the terminal position to give the allyl acetate (Scheme 7). The latter is the key intermediate which subsequently leads via carbonylation of the in situ formed propene to the formation of the monocarboxylic acids butyric acid and isobutyric acid.

#### 2.4.4 Iridium-Catalyzed Chemoselective Dehydrogenation of Glycerol

Glycerol is already widely used as a green solvent to replace other more common but at the same time more hazardous solvents in organic reactions [37]. However, the use of glycerol as a hydrogen donor solvent had remained unexplored until Crotti and coworkers developed a range of iridium complexes bearing a diene unit and a dinitrogen containing ligand, which can catalyze the dehydrogenation of glycerol.

The authors found that **[Ir-17]** was the most active catalyst for the selective dehydrogenation of glycerol towards dihydroxyacetone (Fig. 7) [38]. The selective formation of dihydroxyacetone over glyceraldehyde is important as glyceraldehyde tends to be easily decarbonylated and this could lead to the deactivation of the catalyst due to the formation of a stable carbonyl complex. As a model reaction, the dehydrogenation of glycerol to dihydroxyacetone was coupled with the hydrogenation of acetophenone to phenylethanol. The best results were found in the presence of 1 mol% of **[Ir-17]** and 2 mol% of  $K_2CO_3$  at  $100^\circ C$ . The conversion of acetophenone proceeded albeit slow starting from 15% after 5 min and reaching



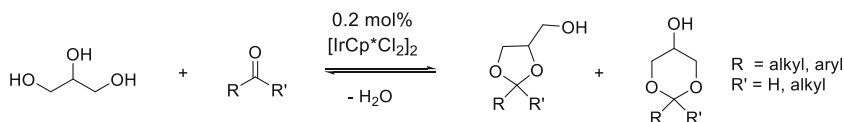
**Fig. 7** Iridium catalysts used for the chemoselective dehydrogenation of glycerol to dihydroxyacetone reported by Farnetti and Crotti

34% after 180 min, while the selectivity of glycerol towards dihydroxyacetone dropped in total by 43% during the same period of time. Raising the temperature could further improve the conversion of acetophenone up to 47%, however again a low yield of dihydroxyacetone of only 12% was obtained. A possible explanation for this poor selectivity to dihydroxyacetone is its further base-catalyzed conversion to lactate, as seen before in several dehydrogenation reactions of glycerol [33]. In order to address this problem, Crotti and co. performed the same reaction in the absence of base and they used a new iridium catalyst bearing a pincer ligand **[Ir-18]** [39]. Different hydrogen acceptors, including acetophenone, were tested at 100°C for 1 h, by using 1 mol% of **[Ir-18]**. As a result, while with acetophenone only 3% yield of the corresponding phenylethanol was achieved, benzaldehyde was converted to benzyl alcohol in 37% yield to form dihydroxyacetone with a selectivity of 23%. Hence, the work of Crotti and Farnetti demonstrated for the first time that glycerol can be used as a solvent, but also as a hydrogen donor leading in this case to the dehydrogenation product dihydroxyacetone. Unfortunately, the latter easily undergoes side reactions at high temperatures. Nevertheless, many researchers have been inspired by the work of Crotti and Farnetti and the use of glycerol as H-donor has been recently reviewed by Crabtree [37]. The latter review article illustrates the progress made in the last decade in this field, and in particular it points out how iridium catalysts bearing carbene ligands emerged as highly stable and active complexes for the dehydrogenation of glycerol.

#### 2.4.5 Iridium-Catalyzed Acetalization of Glycerol

Farnetti and coworkers used  $[\text{IrCp}^*\text{Cl}_2]_2$  **[Ir-19]** as catalyst for the acetalization of glycerol with several ketones and aldehydes [40]. Due to the three hydroxyl groups in glycerol, the products of this reaction can exist in the dioxolane (5-membered ring) or dioxane (6-membered ring) structure (Scheme 8).





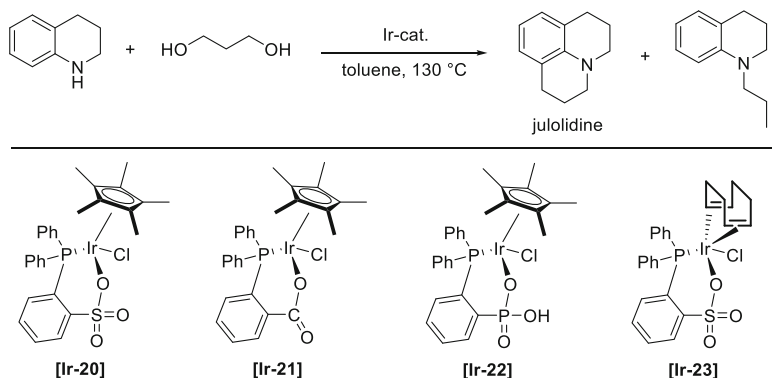
**Scheme 8** Acetalization of glycerol catalyzed by iridium

Cyclic acetals and ketals of glycerol are used, for example, as diesel additives, and for the synthesis of surfactants and scents, flavors, and polymers [41]. The reaction can be catalyzed by acids, however where substrates are acid sensitive or contain other sensitive functional group, a more selective homogeneous catalyst may be the better choice. The authors tested other iridium precursors such as  $[\text{Ir}(\text{COD})\text{Cl}]_2$ , which did not catalyze this reaction, and other iridium complexes, but  $[\text{IrCp}^*\text{Cl}_2]_2$  was by far the most active. With acetone the reaction showed high selectivity (98%) to the dioxolane product with 90% conversion in one hour. With other ketones conversions were a bit lower. The reaction was performed in excess glycerol and excess acetone, with the reaction in acetone giving slightly better conversions. However, using an excess of ketone or aldehyde may not always be possible. The substrate scope was fairly limited, however all ketones tested showed high selectivity towards the dioxolane product after 1 h reaction time. With the two aldehydes tested, the aliphatic aldehyde octanal gave higher conversions than benzaldehyde and also slightly higher selectivity towards the dioxolane. Compared to the ketones the selectivity was lower. This may be due to traces of acid present in the aldehyde which catalyze the reaction unselectively. It is known that the dioxolane is the kinetic product and that with longer reaction times a more equal mixture of the two products is formed [42]. This was also found in this case, when the reaction with benzaldehyde was allowed to proceed for 48 h, after which time the ratio of dioxolane: dioxane was 49:51. In most cases, the dioxane isomer (or one of the two E and Z isomers where applicable) can be isolated by crystallization [43], so that this protocol can be used to selectively synthesize the dioxolane product, and – via long reaction times for isomerization combined with repeated crystallization workup – also the dioxane product. The catalyst was also active for the transacetalization with methanol.

## 2.5 Iridium-Catalyzed Cyclizations of Bio-Derived Alcohols

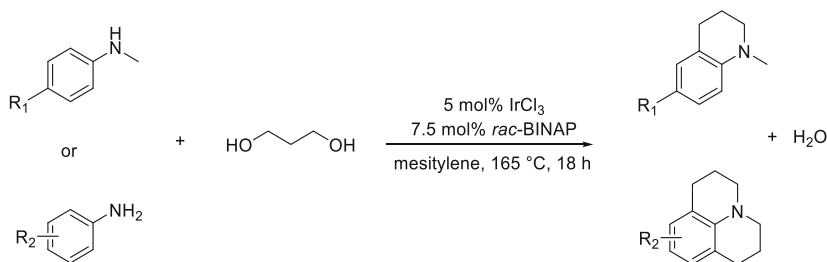
Nitrogen-containing heterocycles are a key structural motif which can be found, for example, in drugs, dyes, and organic electronic materials [44]. Despite their great importance, the conventional synthetic methods of N-heterocycles still often require multiple steps, they sometimes use halogenation reagents, they result in the formation of salt wastes, and they occasionally need oxidants [44].

Bruneau and coworkers used an iridium-catalyzed acceptorless dehydrogenative condensation reaction to prepare julolidines, a class of N-heterocycles with applications in solar cells [45].



**Scheme 9** Synthesis of julolidine catalyzed by different iridium catalysts

Their approach uses bio-derived 1,3-propanediol as a reagent, and it meets several criteria of the twelve principles of green chemistry: it avoids the use of halogenated reagents, it is a catalytic process, and it generates water as an ecofriendly by-product. For their study, they synthesized and tested a range of different well-defined iridium complexes. In particular complexes **[Ir-20-23]** derived from  $[\text{Ir}(\text{Cp}^*)\text{Cl}_2]_2$  were found to be suitable catalysts for the N,C(sp<sup>2</sup>)-dialkylation of tetrahydroquinoline with 1,3-propanediol (see Scheme 9). The reaction proceeds via dehydrogenation of 1,3-propanediol to 3-hydroxy-propanal, which reacts with tetrahydroquinoline to the iminium compound which can be converted to julolidine via three possible pathways. During their optimization, *N*-propyl-tetrahydroquinoline was identified as the main side product of the reaction and its formation was attributed to the acidity of the catalyst or the ligand in the case of **[Ir-22]** which favors a dehydration/reduction pathway [45]. Nevertheless, when the catalysts **[Ir-20]** and **[Ir-21]** were applied, good yields of 72% and 77% of the desired julolidine were observed. Interestingly, the ratio of amine to 1,3-propanediol had a significant impact on the yield which increased from 43% to 72% when the amine/1,3-PDO ratio was changed from 1/1.2 to 2/1. Catalyst **[Ir-21]** was found to be the best catalyst and no significant differences in terms of activity were found when the catalyst was generated in situ by simply mixing 1 mol% of  $[\text{Ir}(\text{Cp}^*)\text{Cl}_2]_2$  and 2 mol% of DPPBA. Furthermore, the use of Butane-1,3-diol, another bio-based polyol, was found to be more challenging than 1,3-PDO, because the dehydration/reduction pathway led mainly to the formation of the undesired *N*-alkylated product (40%), and the julolidine yield was quite low (28%). Finally, since the variety of julolidine derivatives which can be obtained is limited due to the limited number of commercially available 1,3-diols, the authors described the possible post-functionalization of julolidines through hydrogen auto transfer reactions by using aldehydes as electrophiles [45]. The latter led to the  $\beta$ -alkylation of julolidines in a reaction mediated by the same iridium system **[Ir-21]** used for the dehydrogenative condensation step, leading to the possibility for a tandem reaction which combines the synthesis of julolidines with their subsequent  $\beta$ -alkylation.



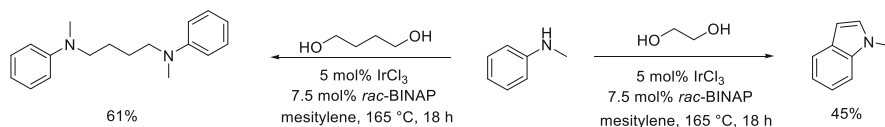
**Scheme 10** Iridium-catalyzed direct cyclization of aromatic amines with diols

The group of Minakawa used anilines for the cyclization with diols [46]. In spite of the limited number of bio-based diols, the access to a wide range of different *N*-heterocycles is possible due to the large number of different substituted anilines available (Scheme 10).

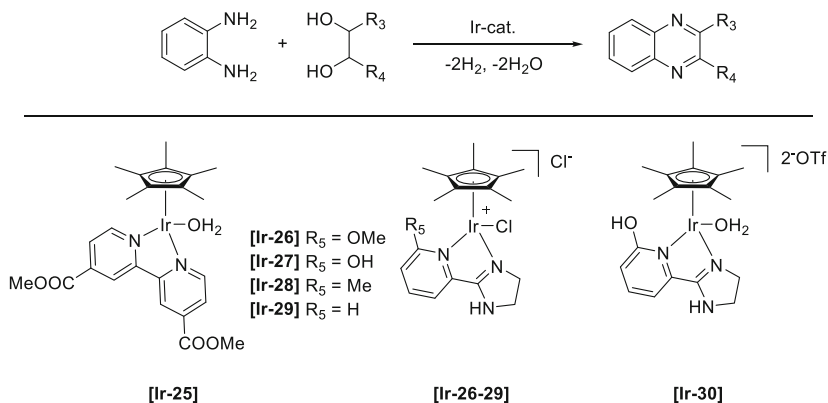
Initially, the direct cyclization of 1,3-propanediol with *N*-methylaniline was studied. After finding the best conditions with 5 mol% of iridium(III) chloride and 7.5 mol% *rac*-BINAP as the ligand [**Ir-24**], a range of different methylated anilines were tested. Uninfluenced by the electron-withdrawing or electron-donating nature of  $R_1$  in the *para*-position, a good isolated yield was obtained (73–83%). Under the same reaction conditions 1,3-propanediol was then reacted with anilines bearing different substituents in the *para*- or *meta*-position to afford various julolidines in moderate yields (26–76%). In contrast, when EG or 1,4-butanediol were reacted with *N*-methylaniline, an indole and a diamine in 45% and 61% yields were found, respectively (Scheme 11) [46].

In a similar fashion, Wan et al. reported the iridium-catalyzed synthesis of quinoxalines using benzene-1,2-diamine and vicinal diols like 1,2-propanediol and 2,3-butanediol [47]. This transformation relies on a dehydrogenation-condensation strategy where first one alcohol group is dehydrogenated by complex [**Ir-25**] whereupon the resulting ketone reacts with one amine of the benzene-1,2-diamine to form an imine. Subsequently, the remaining alcohol is dehydrogenated and reacts in a similar manner with the remaining amine which results in a ring-closure and in the formation of the quinoxaline (Scheme 12).

Both 1,2-propanediol and 2,3-butanediol were successfully used with different substituted aromatic diamines to form the corresponding quinoxalines in generally good yields (56–73%). However, the reported synthetic protocol suffers from the use of a relatively high catalyst loading of 5 mol%, from the use of a large excess of base (3 equiv.  $\text{Cs}_2\text{CO}_3$ ) and from the use of xylene as a non-environmental benign



**Scheme 11** Direct cyclization of different bio-based diols with *N*-methylaniline

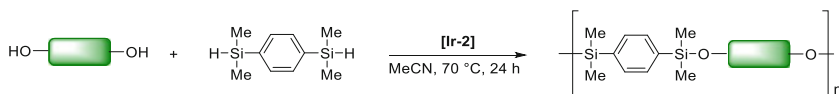


**Scheme 12** Iridium-catalyzed synthesis of quinoxalines by using vicinal bio-derived alcohols

solvent. The latter problem was addressed by Kundu and coworkers who studied the water-soluble iridium catalysts **[Ir-26-30]** for the synthesis of quinoxalines under an atmosphere of air (see Scheme 12) [44]. Complex **[Ir-27]** (2.5 mol%) was found to be the best catalyst in the presence of 1.5 equiv. of KOH at 120°C for 24 h. This synthetic methodology uses not just water as a green solvent instead of xylene, but also it requires a lower amount of base and a shorter reaction time under non-protective atmosphere in comparison with the methodology reported by Wan et al. Furthermore, both 1,2-propanediol and 2,3-butanediol were reacted with a wide range of vicinal aromatic diamines as well as with 2-nitro aniline derivatives. Good yields were obtained with a broad range of substrates (62–90%) [44].

## 2.6 Poly(Silyl Ethers) Via Iridium-Catalyzed Dehydrocoupling Polymerization

In the 2004 DOE report “Top Value-Added Chemicals from Biomass” it was proposed that polymeric materials from renewables should be one of the most desired targets [1]. Bio-based polymers, in fact, are derived from bio-based feedstock materials, and therefore, they allow a reduction of the total greenhouse gas emissions and of the overall carbon footprint of the final products. Bio-based carbon content has thus become an important added value for all companies, who want to improve the sustainability across their entire value chains. Polysilylethers (PSEs) show interesting properties like a low glass transition temperature ( $T_g$ ), good thermal stability, biocompatibility, and high gas permeability but unfortunately, they are not derived from bio-based materials [48]. However, the most frequently used monomers for the synthesis of PSEs are dihydroxy compounds. The latter in turn can be diols which are indeed accessible from renewable feedstock. Driven by this



**Scheme 13** Catalytic dehydrocoupling polymerization for the synthesis of partially bio-based PSEs

knowledge, Zhou and coworkers reported the iridium-catalyzed synthesis of partially bio-based PSEs by using bio-derived diols and a commercially available silane (see Scheme 13) [48].

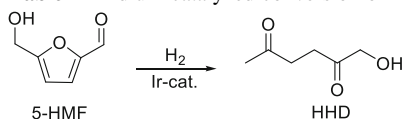
In this protocol the bio-based diols 1,10-decanediol, 1,4-pentanediol, and 1,4-butanediol as BB monomers were reacted with 1,4-bis(dimethyl-silyl)benzene as AA type monomer. The dehydrocoupling polymerization is initiated by an Ir-H species which is presumably formed via a hydrolysis reaction of the hydrosilane with the starting iridium complex [Ir-2]. Subsequently, this newly formed Ir-H species can undergo a metathesis reaction with the bio-based diol that results in the formation of an Ir-alkoxy species which in turn reacts further with the silane to generate the dehydrocoupling product.

For all three diols, high molecular weight polymers were obtained ( $M_n = 24,100\text{--}43,800$ ) in moderate to excellent yields (54–92%). The synthesized PSEs exhibited good thermal stability ( $T_5 = 418^\circ\text{C}$  to  $437^\circ\text{C}$ ) and low glass transition temperatures down to  $-49.6^\circ\text{C}$  [48].

### 3 Iridium-Catalyzed Transformations of Bio-Based Furan Compounds

#### 3.1 Iridium-Catalyzed Synthesis of 1-Hydroxyhexane-2,5-Dione

5-Hydroxymethylfurfural (5-HMF, see Table 1) is a furan compound with both an aldehyde and a hydroxymethyl group and it can be obtained from bio-based feedstock materials like cellulose, glucose, and fructose [54–57]. Although cellulose, starch, or preferably lignocellulose as readily available raw materials are considered more attractive than sugars, high yields of 5-HMF are currently only achieved by acidic treatment of fructose. Unfortunately, this in turn leads to relatively high production costs for 5-HMF. Additionally, the instability of 5-HMF limits its isolation in high yields and hence its current applications. To overcome this problem, the Dutch company Avantium produces the methyl ether of 5-HMF, more stable than 5-HMF itself [58]. Alternatively, Haworth and Jones reported a simple hydrolysis approach (90% yield) from 5-chloromethylfurfural [59], which can be also derived from cheap bulk cellulosic material as shown by Mascal and coworkers [60]. Currently, HMF is produced on relatively small scale by the Swiss company AVA-Biochem. Despite the problems which still need to be solved, the interest in

**Table 1** Iridium-catalyzed conversion of HMF to HHD

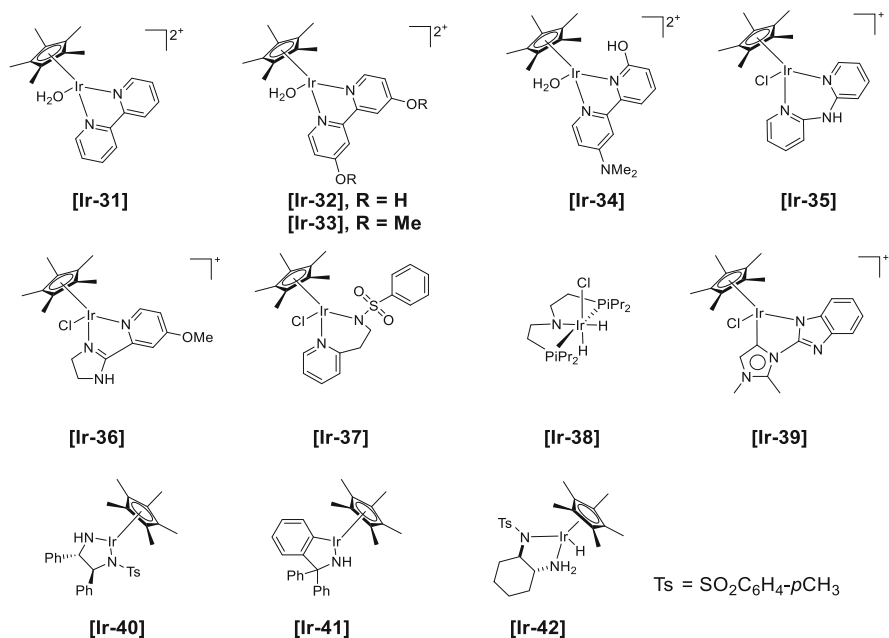
Entry	Catalyst (loading)	Conditions	Conv. [%]	Yield [%]	Ref.
1	[Ir-31] (0.26 mol %)	120°C, H <sub>2</sub> O, 7 bar H <sub>2</sub> , 2 h	100	86	[49]
2	[Ir-32] (0.01 mol %)	130°C, FBS (pH = 2.5), 2 h	100	92(85) <sup>a</sup>	[50]
3	[Ir-32] (0.10 mol %)	130°C, H <sub>2</sub> O, 5 wt% Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> , 30 bar H <sub>2</sub> , 4 h	100	77	[51]
4	[Ir-33] (0.01 mol %)	130°C, FBS (pH = 2.5), 2 h	100	~ 95	[50]
5	[Ir-34] (0.0008 mol %)	120°C, H <sub>2</sub> O (pH = 3.4), 35 bar H <sub>2</sub> , 6 h	88	67	[52]
6	[Ir-35] (0.50 mol %)	120°C, H <sub>2</sub> O, 10 bar H <sub>2</sub> , 2 h	100	76(69) <sup>a</sup>	[53]
7	[Ir-36] (0.075 mol %)	140°C, PBS (pH = 2.5), 60 bar H <sub>2</sub> , 1 h	100	71 <sup>a</sup>	[53]

<sup>a</sup>Isolated yield

the commercialization of 5-HMF is immense, based on the enormous number of publications dealing with its synthesis and derived products [54]. One of the 5-HMF products which has recently received high attention in the field of homogenous iridium catalysis is 1-hydroxyhexane-2,5-dione (HHD, see Table 1), the hydrogenated ring-opened form of 5-HMF [61].

Only a few homogenous iridium catalysts are known for the synthesis of HHD, even though homogenous catalysts seem generally to perform better than heterogeneous systems [61] (Fig. 8). The group of Zhang and coworkers was the first to report an iridium-catalyzed hydrogenation of 5-HMF in aqueous solution in order to synthesize HHD [49]. Bipyridine Cp\*-Ir complexes were found to be efficient catalysts for the selective formation of HHD and [Ir-31] emerged as the best candidate under their optimized conditions (Table 1, Entry 1). Subsequently, Deng, Fu, and coworkers carried out an in-depth investigation on the different parameters of the hydrolytic transfer hydrogenation of HMF, by exploring the effect of electron-donating and electron-withdrawing groups on the bipyridyl ligand, the influence of the temperature and of the pH [50]. The obtained results revealed that temperature and pH are important parameters to maximize catalytic performance. Particularly, full conversions and high selectivities up to 95% were obtained at 130°C in aqueous formate buffer solutions (FBS, pH = 2.5) with catalysts [Ir-32] and [Ir-33] (Table 1, Entries 2 and 4). Moreover, the authors were the first to isolate HHD in 85% yield on a large scale [50].

Unfortunately, attempts to reuse the catalyst resulted in a decrease of catalytic activity and only 70% yield was achieved. The same catalyst [Ir-32] was used by



**Fig. 8** Iridium complexes for the hydrogenation of furan compounds

them to synthesize HHD via hydrolytic hydrogenation (30 bar) with a selectivity of 77% in the presence of 5 wt% of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (Table 1, Entry 3) [51]. Zhang and coworkers tested a new series of Cp\*-iridium(III) complexes bearing different substituted bipyridine ligands [52]. The best catalyst, **[Ir-34]**, has two substituents on the two rings of the bipyridine ligand: on one side it contains an *N*-dimethylamino group as wing-spike, and on the other side it contains a hydroxyl group in ortho-position with respect to the nitrogen. At a comparatively low catalyst loading (0.0008 mol% of **[Ir-34]**) at 120°C in acidic water (pH = 3.4) for 6 h under 35 bar of H<sub>2</sub>, a good conversion (88%) and a reasonably good selectivity towards HHD (67%) were obtained (Table 1, Entry 5). Additionally, the authors compared the performance of the catalyst under transfer hydrogenation conditions with respect to the hydrogenation conditions, by using formic acid as the hydrogen source. In the latter case, the use of 0.005 mol% of **[Ir-34]** with 2 equiv. of formic acid at 120°C led to a yield of 60% in HHD after 2 h of reaction [52]. Two years later de Vries and coworkers investigated new structural motifs in the ligand sphere, finding complexes **[Ir-35]** and **[Ir-36]** to be the best catalysts for the hydrolytic ring-opening of 5-HMF resulting in a selectivity up to 76% in HHD (Table 1, Entries 6–7) [53]. Furthermore, the same authors were able to isolate 69% of HHD and to fully characterize it including by single crystal X-ray analysis. They could further improve the efficiency of **[Ir-36]** by adjusting the pH with a phosphate buffer solution (PBS, pH = 2.5). Under these conditions the catalyst loading was reduced to 0.075 mol% while maintaining the same selectivity towards the formation of HHD. The latter result

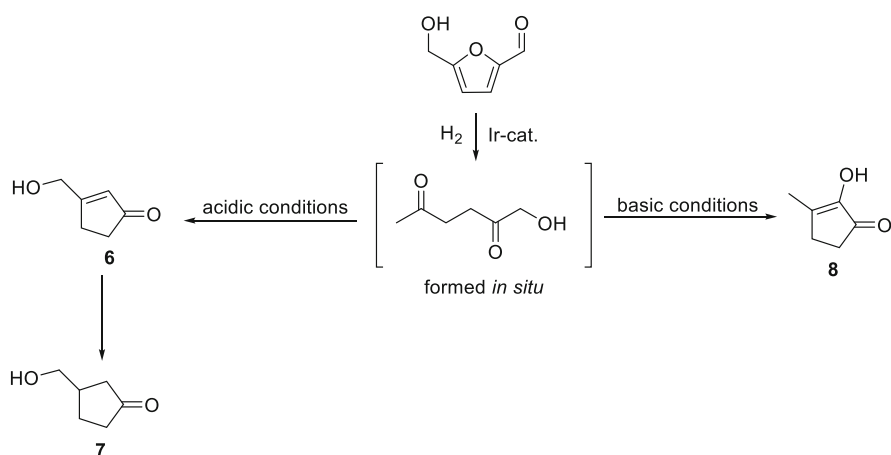
was also used to scale up the reaction in an experiment where 25 g of 5-HMF was used and where HHD was obtained in a good isolated yield of 71% after 1 h [53].

In conclusion, it has been demonstrated that Cp\* iridium complexes bearing additional bidentate ligands show a high activity and a good selectivity in the conversion of 5-HMF into HHD (see Table 1). However, the scalability of the HHD production from 5-HMF through homogenous iridium-catalyzed hydrogenations is still strongly limited by the formation of humins which may be reduced by using high dilutions, and by the poor reusability of the catalysts [61].

### 3.2 Conversion of Furfural Compounds to Ketones

Due to the promising results obtained in the synthesis of HHD from 5-HMF, an increasing interest in the further applications of HHD has emerged. Interestingly, several iridium-catalyzed reactions using 5-HMF as the starting material were reported where HHD was formed in situ and then it further cyclized to two different kinds of cyclopentanones (see Scheme 14) [61].

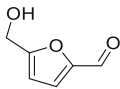
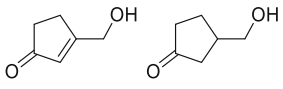
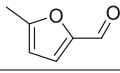
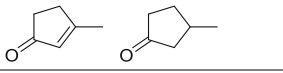
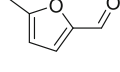
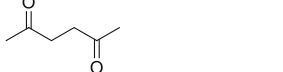
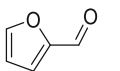
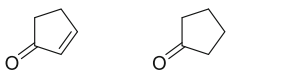
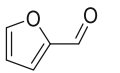
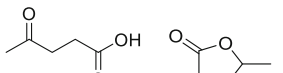
The formation of cyclopentanones is the result of an intramolecular aldol condensation of HHD which, depending on the acidity of the solution, leads to the formation of either 3-hydroxymethyl cyclopentanone (**7**) or 2-hydroxy-3-methylcyclopent-2-enone (**8**), respectively [55]. For the synthesis of **7** only heterogenous catalysts were known till 2017, when the group of Fu investigated for the first time half-sandwich iridium complexes coupled with metal oxides for this reaction [51]. The authors investigated the influence of different parameters like the kind of iridium complex and the kind of Brønsted or Lewis acid used in the reaction. As a conclusion of their study, the best results (100% conversion; 82% of **7**)



**Scheme 14** Intramolecular aldol condensation products starting from 5-HMF



**Table 2** Effect of Lewis acid or Brønsted acid on the iridium-catalyzed conversion of furfural compounds

Entry	Substrate	Acid	Conv. [%]	Yield [%]	Products
1		40 wt% $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	100 <sup>a</sup>	2/82 <sup>a</sup>	
2		45 wt% $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	100 <sup>a</sup>	30/24 <sup>a</sup>	
3		PBS (pH = 1.5)	100 <sup>a</sup>	39 <sup>a</sup>	
4		52 wt% $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	100 <sup>a</sup>	60/~2 <sup>a</sup>	
5		PBS (pH = 1.0)	100 <sup>b</sup>	41/9 <sup>b</sup>	

<sup>a</sup>5-HMF, 5-methyl furfural or furfural aq. (0.067 M, 3 mL), **[Ir-32]** (0.1 mol%), H<sub>2</sub> 30 bar, 130°C, 4 h

<sup>b</sup>Furfural (0.60 mmol), 2 mL pH = 1.0 phosphate buffer solution (0.1 M), **[Ir-32]** (0.0083 mol%), 10 bar H<sub>2</sub>, 120°C, 4 h

were obtained when 0.1 mol% of **[Ir-32]** was used in combination with 40 wt% of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a Lewis acid cocatalyst at 130°C under 30 bar of H<sub>2</sub> for 4 h.

In addition to 5-HMF as a starting material (Table 2, Entry 1), other bio-derived furan compounds like 5-methyl furfural (Table 2, Entries 2–3) and furfural (Table 2, Entries 4–5) could be hydrogenated in the same manner to 3-methyl cyclopentenone and cyclopentenone in 30% and 60% yield, respectively (Table 2). Under Brønsted acid catalysis using a phosphate buffer solution (PBS) 5-methyl furfural (Entry 3) and furfural (Entry 5) were converted to the straight chain ketones 2,5-hexanedione and levulinic acid in moderate yields.

When the intramolecular aldol condensation of HHD is carried out under basic conditions, **8** is formed. The latter is a flavoring agent which is commonly synthesized from adipic acid in a multistep reaction that uses toxic and carcinogenic reactants [61]. For this reason, a catalytic protocol for the synthesis of **8** from benign bio-based materials would be highly desired. The base-promoted formation of **8** by using HHD as a starting material was firstly discovered by Deng, Fu, and coworkers [51]. Later, de Vries and coworkers carried out an in-depth study on the role of the base and of the solvent [53].

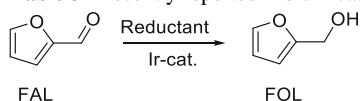
As a conclusion, an isolated yield of 72% of **8** in an aqueous KOH solution at 60°C after 15 min was achieved. Furthermore, the authors decided to combine their previous procedure for the synthesis of HHD mediated by **[Ir-35]** with the KOH-mediated aldol condensation reaction in order to synthesize **8** in a one-pot reaction. Based on this methodology, an overall yield of 55% of **8** was achieved.

### 3.3 Iridium-Catalyzed (Transfer)Hydrogenation of Furfurals

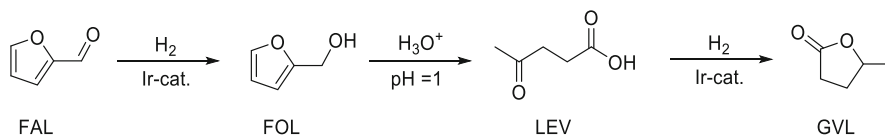
Furfural (FAL) was isolated for the first time by Johann Wolfgang Döbereiner in 1831 and, due to the variety of possible transformations which it can undergo, has become over the last century one of the most important biomass-based C<sub>5</sub>-platform molecules [55]. Its wide range of applications can be found in the recently published review article which summarizes the synthesis of more than 80 chemicals directly or indirectly derived from FAL [62]. The production of FAL is currently carried out in lignocellulosic biorefineries by using agricultural and forestry waste as starting materials. Furfuryl alcohol (FOL) is by far the largest FAL derivative, with 65% of the overall FAL production volume used for its synthesis. FOL is in fact an important intermediate primarily used in the production of resins, pharmaceuticals, and in the manufacture of fragrances. Currently, the gas-phase Cu-catalyzed hydrogenation of FAL is the major route towards FOL, because the reaction in liquid phase is economically unattractive due to the high operating costs of batch reactors [62].

Efficient iridium catalysts for the (transfer)hydrogenation of FAL to FOL were reported by Deng, Fu, and coworkers. Their initial synthetic procedure required the use of semi-sandwich iridium catalysts **[Ir-32]** or **[Ir-33]** in 0.0083 mol% under 10 bar H<sub>2</sub> at 120°C for one hour [63]. Subsequently, the effect of pH (adjusted by a phosphate buffer solution (PBS) and H<sub>3</sub>PO<sub>4</sub>) on catalytic activity for catalysts **[Ir-33]** and **[Ir-32]** was examined. As a result, the highest TOF (1,600 h<sup>-1</sup>) for **[Ir-33]** was found at pH = 3.5, while for **[Ir-32]** the highest TOF (7,340 h<sup>-1</sup>) was achieved at pH = 5. The authors explained the higher activity of catalyst **[Ir-32]** with respect to **[Ir-33]** with its ability to generate an electro-donating aryloxy anion which is crucial for the performance of this type of catalyst. Transfer hydrogenation using formic acid was also examined with these catalysts (Table 3, Entries 1–3). With

**Table 3** Recently reported iridium catalysts for the (transfer)hydrogenation of FAL to FOL



Entry	Catalyst (loading)	Conditions	Yield [%]	TON	TOF [h <sup>-1</sup> ]	Ref
1	<b>[Ir-32]</b> (0.0083 mol%)	H <sub>2</sub> O, 120°C, 1 h, HCOOH	>99	12,067	12,067	[63]
2	<b>[Ir-32]</b> (0.0017 mol%)	H <sub>2</sub> O, 120°C, 1 h, HCOOH	23	13,877	13,877	[63]
3	<b>[Ir-33]</b> (0.0083 mol%)	H <sub>2</sub> O, 120°C, 1 h, HCOOH	30	3,668	3,668	[63]
4	<b>[Ir-37]</b> (1 mol%)	<i>i</i> PrOH, 85°C, 0.5 h	95	95	190	[64]
5	<b>[Ir-39]</b> (0.5 mol%)	EtOH/H <sub>2</sub> O, 30°C, 2 h, 1 bar H <sub>2</sub>	94	470	235	[65]



**Scheme 15** One-pot conversion of FAL to GVL by employing the iridium complexes **[Ir-32]** and **[Ir-33]**

catalyst **[Ir-33]** 30.4% yield was achieved at pH 4 and with catalyst **[Ir-32]** a yield >99% was observed at pH 4.5. Finally, Fu and coworkers also reported the direct conversion of furfural into levulinic acid (LEV) and gamma-valerolactone (GVL) in a one-pot reaction (Scheme 15). Specifically, when furfural was reduced under 10 bar H<sub>2</sub> for 4 h in the presence of 0.0083 mol% of **[Ir-33]** at 120°C in PBS (pH = 1) LEV was produced in 24% yield and GVL in 35% yield. In comparison, by using **[Ir-32]** under the same conditions levulinic acid was obtained in 41% yield and GVL in 9% yield [63].

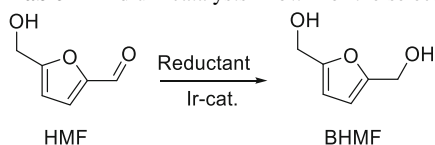
Use of complex **[Ir-37]** was reported by O'Connor and coworkers, who converted FAL into FOL with an excellent 95% yield, by using 1 mol% **[Ir-37]** in combination with isopropanol as the hydrogen source at 85°C for 30 min [64]. Unfortunately, the authors did not investigate lower catalyst loadings, hence a relatively low TON (95) was reported; also, the TOF was only 190 h<sup>-1</sup> (Table 3, Entry 4). Choudhury and coworkers reported the catalyst **[Ir-39]** which they used to hydrogenate FAL to FOL (yield: 94%) under atmospheric hydrogen pressure and under base-free and very mild conditions (Table 3, Entry 5) [65]. The group of Rauchfuss went a step back, to make furfuryl alcohol directly from xylose [66]. Thus in the first step, xylose underwent dehydration catalyzed by 0.1 equiv. of formic acid in DMSO/THF (1/10 v/v), followed by neutralization with 0.1 equiv. of NEt<sub>3</sub> and subsequent addition of 0.5 mol% of **[Ir-40]**. Thereafter, the transfer hydrogenation reaction took place in additional THF with the freshly made furfural and in the presence of replenished formic acid to obtain FOL in 63% isolated yield.

Nielsen and coworkers reported a highly active iridium complex for the hydrogenation of bio-derived 5-methyl furfural (MF) to 5-methyl furfuryl alcohol, a potential biodiesel precursor [67]. In the presence of 0.05 mol% **[Ir-38]** and 2 mol% NaOEt as base in an ethanol/water mixture under 30 bar H<sub>2</sub> pressure at 60°C excellent yields up to 99% were achieved after 150 min. Decreasing the catalyst loading to 0.005 mol% and 0.0005 mol% resulted in 91% yield (5 h) and 56% yield (48 h), respectively, at 120°C under 30 bar H<sub>2</sub> pressure. Finally, the authors performed a scale-up reaction with 7.9 mmol of MF with 0.01 mol% **[Ir-38]** under 30 bar H<sub>2</sub> at 120°C for 2 h which gave an isolated yield of 97%.

### 3.4 Selective Hydrogenation of 5-Hydroxymethyl Furfural to 2,5-Bis(Hydroxymethyl)Furan

2,5-Bis(hydroxymethyl)furan (BHMF) is a key molecule for the preparation of polymers, resins, crown ethers, and rayons and for this reason it is a potentially promising downstream product of biorefineries [68]. Although both homogenous and heterogenous catalysts are known for the selective hydrogenation of 5-HMF to BHMF, the literature about homogeneously catalyzed hydrogenation to form BHMF is scarce [68]. The first example of homogenous iridium catalysts was reported by Rauchfuss and coworkers [66]. The authors tested a range of Cp\* iridium complexes (**[Ir-40-42]**) (0.1–0.5 mol%) all of which hydrogenated 5-HMF quantitatively within a few hours at 40°C in THF (see Table 4, Entries 3–6). The same iridium catalysts were also used for the direct conversion of fructose to BHMF. By performing the reaction at 40°C in the presence of 0.5 mol% of **[Ir-40]** with 2 mmol of D-fructose, 2 mmol of formic acid and 0.2 mmol of base (NaOH or  $\text{NET}_3$ ) in THF, an excellent BHMF yield of 99% was obtained. The effect of the added base was immense: the reaction was completed within 2 h in contrast to 12 h without base (80% yield of BHMF). In order to find a more active system, Deng, Fu, and coworkers carried out an in-depth study of Cp\* iridium complexes bearing a bipyridine moiety. The best results were obtained with **[Ir-32]**, a Cp\*Ir<sup>III</sup> half-sandwich complex able to withstand the acidic reaction conditions (pH 4.0–6.5) (Table 4, Entry 1) [50]. By using an aqueous formate buffer solution (FBS) at 130°C for 2 h and 0.01 mol% of **[Ir-32]**, the formation of BHMF was observed at pH >3. At pH 5.2 BHMF was obtained almost quantitatively. The use of formic acid as the hydrogen source resulted in

**Table 4** Iridium catalysts known for the selective transfer hydrogenation of HMF to BHMF



Entry	Catalyst (loading)	Conditions	Yield [%]	TON	TOF [h <sup>-1</sup> ]	Ref.
1	<b>[Ir-32]</b> (0.01 mol %)	H <sub>2</sub> O, 130°C, 2 h, HCOOH, pH 5–5.5	~98	9,800	4,900	[50]
2	<b>[Ir-37]</b> (1.0 mol %)	<i>i</i> PrOH, 85°C, 0.5 h	99	100	200	[64]
3	<b>[Ir-40]</b> (0.5 mol %)	THF, 40°C, 2 h, HCOOH	99	500	250	[66]
4	<b>[Ir-40]</b> (0.1 mol %)	THF, 40°C, 4 h, HCOOH	70	700	175	[66]
5	<b>[Ir-41]</b> (0.5 M mol%)	THF, 40°C, 1 h, HCOOH	99	500	500	[66]
6	<b>[Ir-42]</b> (0.5 mol %)	THF, 40°C, 1 h, HCOOH	99	500	500	[66]

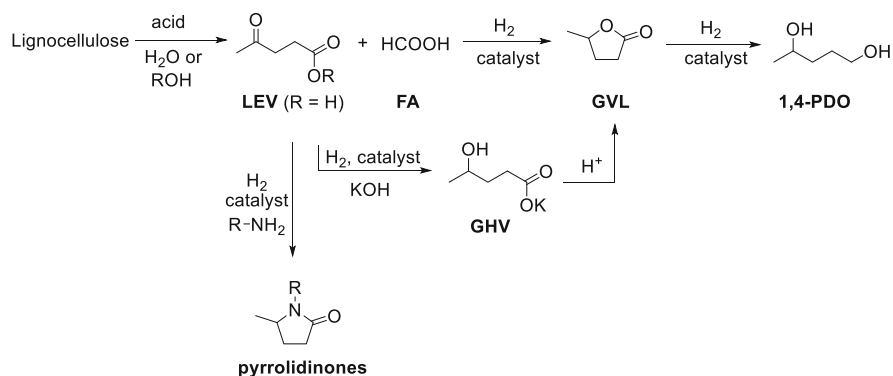
generally higher yields with respect to the use of H<sub>2</sub> (10 bar) in PBS. The latter observation was explained with the high extent of degradation of BHMF in PBS and with the poor solubility of H<sub>2</sub> in water. Additionally, the authors underlined the importance of balancing the acidity of the reaction system. In fact, the presence of FBS leads to a steadily growth in pH during the reaction and at a later stage of the reaction prevents BHMF from degradation. Alternatively, to formic acid, the group of O'Connor and coworkers used isopropanol as a transfer hydrogenation reagent [64]. Under the same conditions used for the transfer hydrogenation of furfural (see Table 3, Entry 4), BHMF was quantitatively formed from 5-HMF after 30 min at 85°C with 1 mol% of [Ir-37] (Table 4, Entry 2). The transfer hydrogenation with [Ir-37] follows an outer sphere mechanism. In contrast, according to Fu and coworkers, catalyst [Ir-32] forms an active hydride species which operates via an inner sphere mechanism.

## 4 Iridium-Catalyzed Conversions of Levulinic Acid

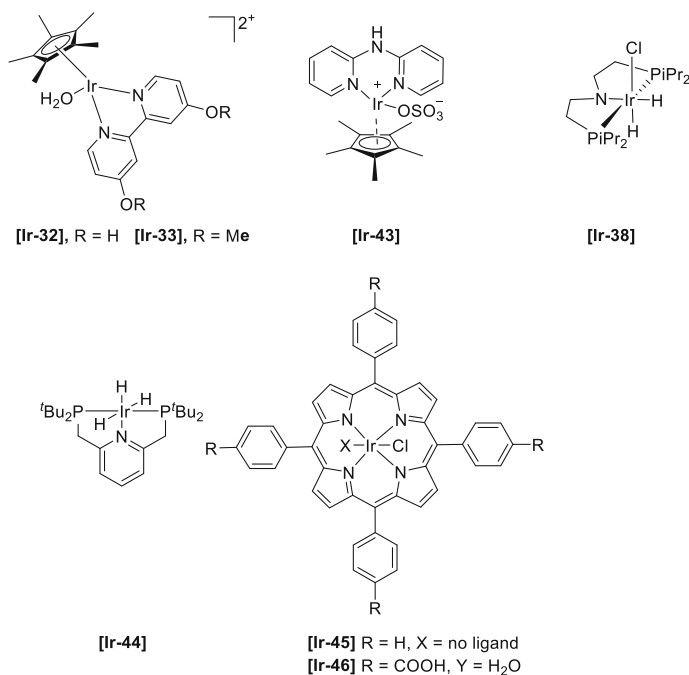
### 4.1 Hydrogenation to GVL

Levulinic acid (LEV) is a platform chemical which can be obtained in high yields from lignocellulose via a simple acid-catalyzed conversion [69]. Hydrogenation of LEV results in gamma-valerolactone (GVL), another very useful platform chemical, which has been investigated for use as a solvent, a fuel additive, as well as a precursor for bulk and fine chemicals (Scheme 16) [70].

To improve the efficiency of this process, a hydrogenation catalyst that can withstand acidic aqueous conditions from the biomass hydrolysis step would be a great advantage. For this reason, Fu and coworkers screened some half-sandwich Iridium catalysts, which were known for the hydrogenation of CO<sub>2</sub> in water [71]. Among these, catalyst [Ir-33] (Fig. 9), with electron-donating methoxy groups



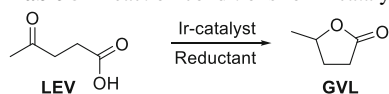
**Scheme 16** The levulinic acid platform



**Fig. 9** Iridium catalysts for the hydrogenation of levulinic acid

on the bipyridine ligand was the most efficient and achieved 98% conversion of LEV to GVL in 4 h at 120°C and 10 bar hydrogen pressure (Table 5, Entry 1). The TON of this catalyst was determined to be 78,000, the highest reported figure for this reaction up to this point. The researchers also tested its activity in the transfer hydrogenation using formic acid (FA), as this compound is a commonly used hydrogen donor in these procedures but is also produced in roughly equal amounts to LEV in the synthesis from biomass. With two equivalents of FA they achieved a yield of 99% GVL under the same reaction conditions (Table 5, Entry 2). Recycling experiments were performed by extracting the GVL from the aqueous reaction mixture followed by the addition of more substrate. After five runs no decrease in yield was detected. After confirming the stability of the catalyst towards sulfuric acid, the researchers also applied their hydrogenation methodology to a mixture of LEV and FA generated by the acid-catalyzed hydrolysis of glucose. The yield of GVL from glucose was 45%. Using cellulose as the starting material, the GVL yield was 34%.

The same group developed a mixed hydrogenation/TH procedure by performing the reaction under 10 bar of hydrogen in a formate buffer (Table 5, Entry 3) [63]. The pH optimum was 4.5 and the contribution of formic acid to the hydrogenation reaction was indicated by comparison to other buffer solutions at the same pH. **[Ir-32]**, which contains 4,4'-hydroxy substituents on the bipyridine ligand, performed better than **[Ir-33]**. The TOF reached 12,200 h<sup>-1</sup>. The authors attributed this to the higher electron-donating ability of the deprotonated hydroxyl groups, present at this pH.

**Table 5** Reaction conditions for Ir-catalyzed hydrogenation of LEV to GVL<sup>a</sup>

Entry	Catalyst (Loading)	Temp	H <sub>2</sub> (bar)	Additive	Yield (%)	TON (TOF) <sup>b</sup>	Ref.
1	[Ir-33] (0.01 mol %)	120°C	10	–	98	78,000 (2,166)	[71]
2	[Ir-33] (0.01 mol %)	120°C	–	2 equiv HCOOH	99	9,900 (2,478)	[71]
3	[Ir-32] (0.0083 mol%)	120°C	10	1M FBS	61	12,200 (12,200)	[63]
4	[Ir-43] (0.05 mol %)	130°C	5	–	99	174,000 (2,418)	[72]
5	[Ir-43] (0.10 mol %)	110°C	–	2 equiv HCOOH	99	9,000 (126)	[72]
6 <sup>c,d</sup>	[Ir-38] (0.05 mol %)	60°C	20	NaOEt (5 mol%)	99	9,300 (390)	[73]
7 <sup>d</sup>	[Ir-44] (0.05 mol %)	100°C	50	LiOH (1.2 equiv)	98	71,000 (1,482)	[74]
8 <sup>e</sup>	[Ir-45] (0.20 mol %)	100°C	10	–	100	1,574 (132)	[75]

<sup>a</sup>Solvent is water except when noted otherwise

<sup>b</sup>TOFs were in most cases calculated by the authors of this chapter from the reported TON values and are given as TOF = h<sup>-1</sup>. They only serve for a rough comparison as they were not calculated at the same degree of conversion

<sup>c</sup>Substrate is ethyl levulinate

<sup>d</sup>Solvent is EtOH

<sup>e</sup>Solvent is DMF

Fischmeister and coworkers developed the Cp\*Ir(SO<sub>4</sub>) complex [Ir-43] containing a bis 2-pyridylamine as ligand which they tested for the reduction of LEV under both hydrogenation and transfer hydrogenation (TH) conditions (Table 5, Entries 4–5) [72]. The researchers found that whereas FA as the hydrogen donor gave full conversion of LEV to GVL, there was no conversion with isopropanol. Control experiments confirmed that [Ir-43] is a very efficient FA dehydrogenation catalyst, causing full dehydrogenation within 1 h under the reaction conditions used for TH. This prompted the authors to investigate the mechanism and it was found that in fact FA is dehydrogenated to form H<sub>2</sub>, which in turn hydrogenates the LEV. Experiments in open versus closed systems showed that there is a combined contribution of TH and dehydrogenation of FA followed by hydrogenation of LEV to the formation of GVL under these conditions. Under hydrogenation conditions full conversion to GVL could be achieved with only 5 bar hydrogen pressure and a maximum TON of 174,000 albeit at longer reaction times. The catalyst loading could be decreased to 0.001 mol% whilst still achieving 97% yield (after 32 h, at 130°C). Recycling experiments demonstrated that the catalyst could be reused three times without loss of activity. The authors also investigated the

reaction starting from glucose via acid hydrolysis. The GVL yield over two steps was 57% using hydrogen gas and 44% under TH conditions using only the FA generated in the reaction as the hydrogen donor.

The Nielsen group investigated the hydrogenation of alkyl levulinates to GVL [73]. These ethyl or methyl esters of LEV are obtained when alcohols are used as the reaction medium for the acid-catalyzed conversion of carbohydrates instead of water and are also produced as a side stream in some processes [76]. Among the range of PNP and SNS pincer catalysts tested, **[Ir-38]** based on the MACHO ligand, earlier developed by Takasago, was the best, able to convert ethyl levulinate to GVL under very mild conditions (20 bar hydrogen and 60°C, neat with only small amounts of alcohol added) (Table 5, Entry 6). In contrast to the previous catalysts, this pincer catalyst requires 5 mol% of base (NaOEt) for activation. The highest TON reached was 9,300. Methyl levulinate reacted faster than the ethyl ester under the same conditions. In a small scale-up the authors tested the catalyst under very mild conditions – 25 bar hydrogen and 25°C. Here they could achieve full conversion with 0.05 mol% of catalyst after 72 h.

Zhou and coworkers screened a range of PNP, PNN, and NNN pincer ligands with iridium in the presence of base. The best catalyst was PNP complex **[Ir-44]**, with the nitrogen analogue also giving high yields [74]. In the optimization of the reaction conditions it was found that base was necessary for the reaction to occur; when it was lowered from 1.2 equiv. to 0.5 equiv., the yield decreased to below 10%. With optimized reaction conditions LEV could be converted to GVL in 98% yield (Table 5, Entry 7). A TON of 71,000 was measured, albeit at quite high hydrogen pressure of 100 bar.

Sakthivel and coworkers synthesized several iridium porphyrin complexes and tested them in the hydrogenation of LEV to GVL and 1,4-pentanediol under base-free conditions [75]. The catalyst with the best performance and selectivity for LEV was **[Ir-45]** (Table 5, Entry 8). The carboxylated version of the catalyst, **[Ir-46]**, was not as efficient as **[Ir-45]**. However, when the authors performed reuse experiments by adding more batches of LEV into the reaction mixture, **[Ir-46]** produced mostly 1,4-pentanediol (1,4-PDO), the further hydrogenation product of GVL, and the yields of 1,4-PDO increased with each cycle, reaching a selectivity of 81% after five runs. For **[Ir-45]** the yield of 1,4-PDO also increased with each run so that the selectivity for LEV was only 66% for run four. The authors attributed this to the buildup of water in the system, but did not perform any control experiments to confirm this or to exclude the formation of nanoparticles.

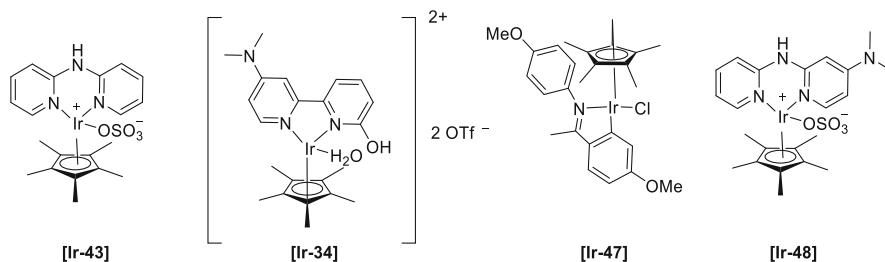
The group of Voutchkova-Kostal employed TH for the hydrogenation of LEV to the potassium salt of gamma-hydroxyvaleric acid (GHV) (Scheme 16) [77]. Under most reaction conditions, even in the presence of base, this compound immediately cyclizes to form the lactone GVL. Based on their efficient NHC iridium complex for the acceptorless dehydrogenation of glycerol (vide supra), glycerol was investigated as the hydrogen donor and a range of NHC-based complexes with pendant sulfonate groups for better water solubility were tested. In the screening, the same complex used in the previous publication, carbonyl complex **[Ir-10]** with two sulfonated NHC ligands, was found to be the most active. Two equivalents of KOH per mol



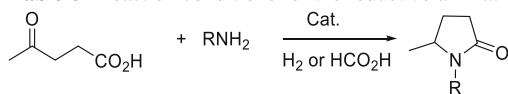
substrate was found to be the optimum amount of additive, while the reaction was carried out in excess glycerol mixed with an equal volume of water. The base is needed to convert the dehydrogenated glycerol to LA, and to stabilize the formed (GHV) as its salt. Coupling these two hydrogenation/dehydrogenation reactions achieves the generation of two valuable products in one pot. The base concentration was adjusted to achieve full conversion of LEV to GHV. Under these conditions, the yield of LA was 2–3 equivalents due to additional acceptorless dehydrogenation of glycerol. With the optimized conditions, quantitative conversion of LEV to GHV as its potassium salt could be achieved at a very low catalyst loading of 1–10 ppm in 2 h at 150°C under microwave heating. The maximum TOF achieved with 1 ppm catalyst was 50,550 h<sup>-1</sup>. As in their previous report [31], these really high turnovers appear to be due to the better heat and mass transfer due to microwave heating. When the experiment was repeated under conventional heating, 24 h was required to reach full conversion. Other hydrogen donors were screened but were not as efficient. Although slower, using (bio-)ethanol, full conversion of LEV could be achieved within 3 h. While this is an interesting report, it is not explained why in this case no GVL is formed, even though it apparently happens in basic conditions in other reports. Attempts were made to separate the two carboxylate products, which were not successful due to the similar properties of the two compounds. However, acidification of the reaction medium led to the cyclization of GHV to GVL which could then be separated from the other product.

## 4.2 Reductive Amination to Pyrrolidinones

The reductive amination of LEV to *N*-substituted 5-methyl pyrrolidinones was also investigated by several groups. These compounds are building blocks for inks, pharmaceuticals, fibers, or surfactants and can be used as solvents, similar to the aprotic polar solvent NMP. The catalysts employed for this transformation are summarized in Fig. 10 and the reaction conditions in Table 6. Building on their previous work for the base-free hydrogenation of LEV to GVL in water (*vide supra*),



**Fig. 10** Catalysts employed for the reductive amination of LA to pyrrolidinones

**Table 6** Reaction conditions for the reductive amination of LEV to pyrrolidinones

Entry	Catalyst (loading)	Temp.	H <sub>2</sub> (bar)	Base/additive	Yield <sup>a</sup>	Ref
1	<b>Ir-43</b> (0.05)	110°C	5	–	90%	[78]
2	<b>Ir-34</b> (0.05)	80°C	20	–	95%	[79]
3	<b>Ir-47</b> (0.05)	80°C	–	FA/formate buffer pH 3.5	91%	[80]
4	<b>Ir-48</b> (0.05)	60°C	–	2 equiv. FA	97%	[81]

<sup>a</sup>Yield is given for the reaction with aniline

Fischmeister and coworkers employed the same catalyst [**Ir-43**] for the reductive amination of LEV with a range of aliphatic and aromatic amines [78]. In neat conditions with 0.05 mol% catalyst loading and 5 bar hydrogen pressure they achieved excellent yields for unhindered substituted anilines, while sterically demanding *ortho*-substituents lowered the yields somewhat (Table 6, Entry 1). Doubly *ortho*-substituted anilines gave moderate yields which could be increased a lot by doubling the catalyst loading. At the reaction temperature of 110°C [**Ir-43**] did not hydrogenate the amido and cyano side chains, acetates however were partially reduced to the alcohol. A range of primary aliphatic and benzylic amines also gave yields of 90% and higher. In addition, the authors performed a process test in which glucose was first hydrolyzed to LEV, and after filtration of insoluble side products and neutralization of the acid, aniline and [**Ir-43**] were added to convert the crude LEV to the pyrrolidinone. The yield over these two steps from glucose was 31%. One of the synthesized compounds, N-Propyl-5-methyl-2-pyrrolidone was assessed as a bio-sourced replacement for the highly regulated and toxic solvent NMP using the Ru-catalyzed arylation of 2-phenylpyridine as a model reaction. While the conversion was slightly lower, the selectivity for the two possible products was different in each solvent, showing that there is scope for tailoring the solvent to a specific reaction. However, as the authors note, in terms of toxicity, there is probably no benefit in using the bio-derived version.

Zhang and coworkers employed catalyst [**Ir-34**] for the reductive amination of LEV (Table 6, Entry 2) [79]. Using 20 bar H<sub>2</sub> at 80°C they achieved good yields in the conversion of a range of electron-rich aryl amines as well as of an aliphatic and a benzylic amine at a catalyst loading of 0.05%.

Xiao and coworkers investigated the reductive amination to pyrrolidinones via transfer hydrogenation from formic acid [80]. They used iridacycle [**Ir-47**] with electron-donating methoxy groups on the ligand in water, but found that it only performed well in a narrow pH range, the optimum being pH 3.5 (Table 6, Entry 3). This necessitated the use of a FA/formate buffer system. With this, they achieved good to very good yields when using various substituted aryl amines with low catalyst loadings of 0.05 mol%. For more challenging substrates like longer chain aliphatic amines the amount of catalyst had to be increased to 0.2 mol%.

The Fischmeister group also recently demonstrated the application of base free transfer hydrogenation for the reductive amination of LEV [81]. Formic acid was used as the renewable hydrogen donor together with an updated version of their catalyst containing an electron-donating dimethylamine group in the ligand (**[Ir-48]**). At a catalyst loading of 0.05 mol% at 60°C using 2 equiv. of FA, a range of aromatic amines with electronically and sterically demanding substituents were converted in good to excellent yields, as well as some aliphatic and benzylic amines (Table 6, Entry 4). Again, the researchers investigated the reaction starting from glucose, using the FA formed as the side product as the hydrogen donor. The yield over these two steps was 23%, which is comparable to other literature reports but a bit lower than using their other hydrogenation procedure. The benefit here however is that no additional hydrogen or hydrogen donor needs to be added.

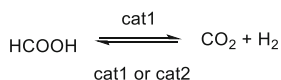
## 5 Iridium-Catalyzed Dehydrogenation of Biomass Compounds

Hydrogen has the potential to become a universal energy carrier in the future as it is light and its combustion only creates water. However, a lot of research remains to be done on the efficient generation and reversible storage of this gas.

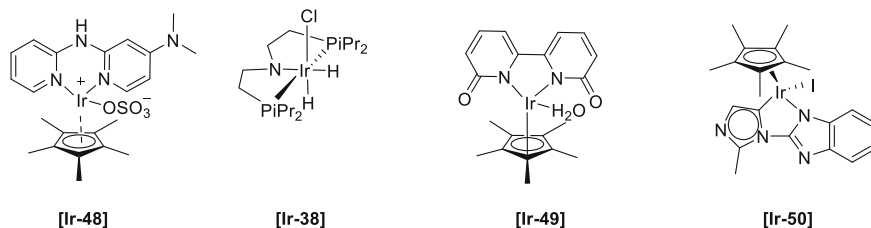
Electrolysis of water is one way to generate renewable hydrogen; however, this is currently still a very energy intensive process, so that researchers have been looking into producing hydrogen from biomass sources via dehydrogenation reactions. In addition, several small molecules are investigated as potential hydrogen carriers. One such molecule is formic acid, which can be made via hydrogenation of CO<sub>2</sub> and is also a side product in the synthesis of LEV (Schemes 16 and 17) [82, 83].

As already mentioned in the introduction, the hydrogenation of CO<sub>2</sub> to generate small molecule hydrogen carriers such as formic acid, methanol, or bicarbonate is a very active area of research with a lot of potential for homogeneous catalysis, including iridium. In this chapter we will not discuss this topic and interested readers are referred to a recent review [1]. One thing to keep in mind however is that the hydrogenation of CO<sub>2</sub> is generally much more difficult than the dehydrogenation of molecules such as FA, due to the stability of the CO<sub>2</sub> molecule.

This section will discuss the recent literature on the dehydrogenation of biomass derived compounds. Depending on the research, the focus here either lies with the production of hydrogen or the synthesis of other compounds. The discussed catalysts are summarized in Fig. 11.



**Scheme 17** Dehydrogenation of FA/hydrogenation of CO<sub>2</sub>



**Fig. 11** Catalysts used for the dehydrogenation of biomass compounds

## 5.1 Hydrogen Generation from Biomass

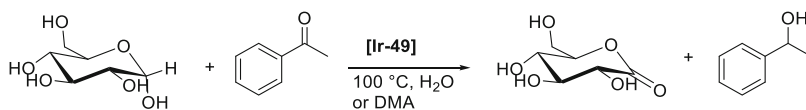
Based on their findings that the TH of LA by formic acid was for a large part due to a hydrogenation reaction after a very fast dehydrogenation of FA, the Fischmeister group investigated their **[Ir-43]** and **[Ir-48]** catalysts (*vide supra*) as well as some related complexes for the dehydrogenation of formic acid under neat and base-free conditions, simulating the conditions needed for fuel cells [84]. Initial ligand screening in aqueous formic acid found that catalyst **[Ir-48]** with an additional electron-donating dimethylamine group on the ligand compared to **[Ir-43]**, and an unsubstituted bridging N-H was the most efficient catalyst for this reaction with a TOF of 12,321 h<sup>-1</sup> at a loading of 0.01 mol% at 80°C in water. pH screening revealed that the catalyst worked best without added base. Based on this result, the reaction was investigated in different concentrations of FA. While it worked in neat FA with a TOF of 4,800 h<sup>-1</sup>, the highest reported value to date, the optimum concentration was 3 M, with a TOF of 13,058 h<sup>-1</sup>. Storage tests of the catalyst in formic acid also revealed that it remained active with only slight decrease in TOF after 10 days.

Beller and coworkers demonstrated that the pincer complex **[Ir-38]** could be used in ppm amounts for hydrogen generation from a range of complex biomass sources including mono- and disaccharides, cellulose, lignocellulose, and even spent cigarette filters (cellulose acetate), which appears to be an important waste stream in Germany [85]. Several catalysts including the commercially available Ru-Macho catalysts were screened, initially using L-fructose as a model substrate. Here it was found that **[Ir-38]** outperformed the Ru catalysts. The optimum amount of base was 1.5 equiv. of NaOH. The role of the base is two-fold: on the one hand, it is needed to activate the pincer complex, and, on the other hand, it traps most of the formed CO<sub>2</sub> as bicarbonate. The protocol was then extended to cellulose and different types of lignocellulose. It was found that for efficient hydrogen generation the biomass first needed to be hydrolyzed into sugars, due to the very low solubility of

(ligno)cellulose. Therefore, a three-step protocol was adopted: First, the biomass was depolymerized in NMP by acid hydrolysis using HCl for 2.5 h at 120°C after which time the reaction mixture was cooled to 95°C, neutralized, and 1.5 eq NaOH were added and in the second step reacted for another hour at 120°C. In the third step, **[Ir-38]** was added for hydrogen generation at the same temperature. With cellulose the catalyst reached at TON of 6,285 after 2 h at 20.3 ppm loading, and with bamboo lignocellulose a TON of 2,844 after 8 h at a loading of 20.9 ppm. Unfortunately, only a small percentage of the sugars was dehydrogenated. When calculated on the total theoretically available hydrogen from the sugar molecule (6), the yield of this process is only around 3.3%. This is much lower than other proposed methods for the generation of renewable hydrogen from biomass, such as aqueous phase reforming. Here a hydrogen yield from glucose of 51% can be achieved, albeit at much higher temperatures [86].

## 5.2 Biomass Molecules as Hydrogen Donors for Transfer Hydrogenation

Another area where dehydrogenation of biomass compounds might be valorized is their use as sacrificial hydrogen donors in transfer hydrogenation. The most commonly used hydrogen donor in TH reactions is isopropanol, which is currently not produced renewably; however, FA is also often employed, as discussed in the chapters above. Fujita and coworkers investigated the use of glucose as a hydrogen donor for the TH of carbonyls to alcohols with Ir catalysts containing different substituents on the bipyridyl ligands [87]. The best catalyst was **[Ir-49]**. Using two equiv. of glucose per mol of substrate and substoichiometric amounts of base in water at 100°C, several acetophenone derivatives could be reduced to the alcohols in good yields using 0.1 mol% of **[Ir-49]** (Scheme 18). However, the reaction required 1 mol% of catalyst for all other aromatic and aliphatic ketones. For acetophenones with methoxy or halide substituents however, ether formation from the resultant alcohols was the main reaction, necessitating a change of solvent. In dimethylacetamide (DMA), good to excellent yields of the desired alcohols could be achieved. Aromatic aldehydes were also reduced to the alcohols. The authors performed experiments to elucidate the mechanism and found that only the anomeric C1 hydroxy group of glucose was dehydrogenated resulting in the formation of gluconolactone; hence, the need for 2 equivalents in order to reach full conversion. Coordination of glucose to the catalyst is facilitated by the carbonyl groups on the ligand.

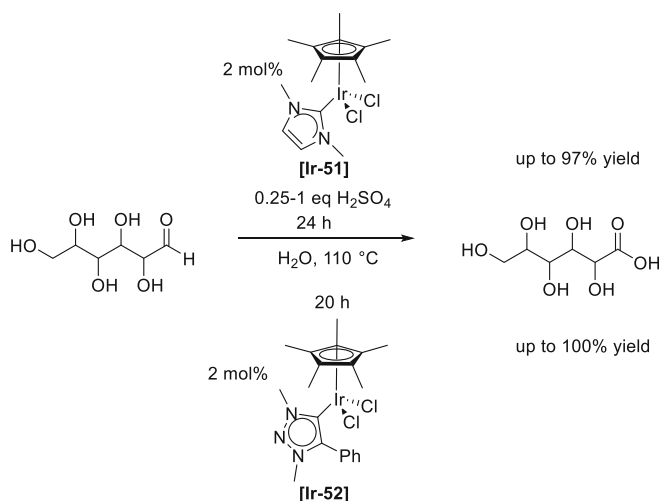


**Scheme 18** Transfer hydrogenation of acetophenone using glucose as hydrogen donor

Choudhury and coworkers employed an iridium catalyst with a strong sigma donating abnormal imidazolydine NHC ligand, **[Ir-50]**, for the transfer hydrogenation of CO<sub>2</sub> to formate, using glycerol as the hydrogen donor [88]. The authors demonstrate that **[Ir-50]** is a very effective catalyst for the TH of CO<sub>2</sub> at ambient pressure. They had previously shown that this catalyst is also very efficient in the same reaction using dihydrogen gas [89]. Glycerol, which is generated as a side product in the transesterification of vegetable oils to biodiesel (*vide infra*), was determined to be the best hydrogen donor, giving better results than the common reductant isopropanol. K<sub>2</sub>CO<sub>3</sub> was found to be a better base than KOH, and control experiments were performed to exclude the generation of formate from K<sub>2</sub>CO<sub>3</sub>. Within 12 h the catalyst reached a TOF of 90 h<sup>-1</sup> at 150°C reaction temperature. In comparison, in their previous publication the same catalyst achieved a TOF of 58 h<sup>-1</sup> under atmospheric pressure and 30°C, while the reverse reaction, the dehydrogenation of formic acid, proceeded with a TOF of 100,000 h<sup>-1</sup> at 90°C. The use of glycerol as a hydrogen donor for TH in combination with iridium and ruthenium catalysts has recently been reviewed [31].

### 5.3 Iridium-Catalyzed Dehydrogenation of Sugars to Sugar Acids

With a focus on the other product, instead of hydrogen, Mata and coworkers employed Cp\*NHC-Ir complex **[Ir-51]** for the selective dehydrogenation of glucose to gluconic acid in water (Scheme 19 top) [90]. This compound is currently produced via enzymatic oxidation in industry. They achieved a yield of 88% with no side



**Scheme 19** Dehydrogenation of sugars to sugar acids

product formation. The reaction was accelerated by the addition of 25 mol% H<sub>2</sub>SO<sub>4</sub>. 1 equiv. of sulfuric acid could increase the yield to 97%. The researchers also applied the reaction to starch as a model carbohydrate. Here two reactions can be performed in one pot as starch hydrolysis is achieved by sulfuric acid in water. After 50 h the yield of gluconic acid was 50%, with 30% glucose and no side product formation. A mechanism was proposed on the basis of ESI-MS experiments combined with DFT calculations. Catalyst precursors containing sulfate or chlorides convert into the active aqua catalyst on dissolution in water. The two water ligands are displaced by glucose in its ring-opened form being bound as a chelate. A nucleophilic attack of H<sub>2</sub>O on the aldehyde group of glucose leads to a gem-diol, which reacts via the release of a proton and beta hydride elimination leading to the release of gluconic acid and the generation of an iridium hydride complex, which takes up the proton and releases hydrogen gas to reform the initial complex. The observed acceleration when acid was added to the system is probably due to the faster protonation of the catalyst in this last step.

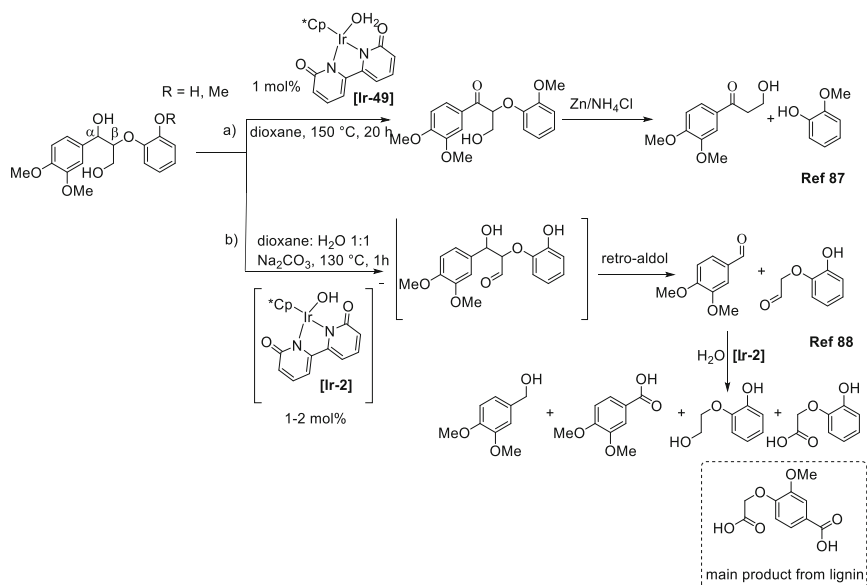
Following on from this initial study, the same group reported a triazole carbene catalyst [**Ir-52**] which could dehydrogenate a range of sugars to their corresponding acids with high selectivity (Schem 19, bottom) [91]. This catalyst did not require acid to work leading to a large improvement over the previous work. The authors tested different *N*-substituents on the triazole ligand (Me, Bu, and glucose) of which the methyl induced the highest yield: quantitative conversion of glucose to gluconic acid could be achieved at a catalyst loading of 2% in water. The glucose substituted catalyst gave high initial rates but then degraded at the optimum reaction temperature of 110°C. Several other sugars were then screened as substrates and most were converted to the corresponding acids in yields of >90%. Catalyst [**Ir-51**] from the group's previous work was screened alongside (with 0.25 eq H<sub>2</sub>SO<sub>4</sub>) and in some cases gave slightly higher yields than [**Ir-52**]. Additionally, the butyl version was also slightly better in some cases. Progress of the reaction was monitored by NMR and was determined to be first order in the catalyst. Again, the authors used ESI-MS for mechanistic studies. Based on these results they postulated that the catalyst forms a dicationic hydride bridged bimetallic complex, which they then synthesized and obtained the X-ray structure for. This dimer appears to be the resting state for the catalyst. The catalytic cycle proceeds as described in the previous publication above. One notable difference is that for the triazolylidene ligand no extra acid is necessary. This is rationalized by the fact that the proton which is released by the rearrangement of the gem-diol can be transported intramolecularly via the N2 of the ligand. This is not possible with NHC ligands and points to a reason for the necessity of acid in the previous work.

## 6 Iridium-Catalyzed Conversion of Lignin

Lignin is the most abundant source of bio-derived aromatics on earth (see Fig. 1), being on average 30% of lignocellulose by weight. However, due to its heterogeneity, it has so far been much more difficult to valorize it compared to the

polysaccharide component of lignocellulose. Lignin contains several different linkages between several aromatic monomers, the composition and ratios of which differ a lot depending on the source. The most common linkage is the  $\beta$ -O-4 aryl ether linkage, which has therefore been the target of most research to date [92]. So far, the focus has been on the generation of (substituted) phenols, and currently the only compound that is produced selectively from lignin in about 3% yield is vanillin [93]. In addition to the variation in composition, the structure and properties of extracted lignins varies depending on the source, and the structure and properties of extracted lignins are very different depending on the method by which they are produced. Due to the mix of monomers and linkages in lignin, the result of lignin depolymerization is always a mixture of compounds. In the following, four recent examples of targeting different parts of the  $\beta$ -O-4 linkage with homogeneous iridium catalysts are discussed.

Fu and coworkers investigated the dehydrogenative oxidation of the  $\alpha$  hydroxyl group to the ketone in a  $\beta$ -O-4 linked model compound (Scheme 20a) [94]. Oxidation to the ketone was reported to lower the bond dissociation energy for the  $\beta$ -O-4 bond and so should facilitate the depolymerization of lignin. A screen of different metal catalysts (Ru, Rh, Ir) revealed that [Ir-49] was by far the best catalyst for this reaction. This catalyst was tested on a range of lignin model substrates under optimized conditions (dioxane, 150°C, 1 mol% catalyst loading, 20 h). Most of these were dehydrogenated to the corresponding ketone in yields around 80%, with a few examples of lower yields. DFT calculations confirmed that the  $\alpha$  keto product is



**Scheme 20** Different reaction pathways on the common  $\beta$ -O-4 linkage in lignin (model compound): (a) selective dehydrogenation of the  $\alpha$ -hydroxyl, (b) selective dehydrogenation of the  $\gamma$ -hydroxyl, followed by base-catalyzed retro-aldol reaction and Ir-catalyzed hydrogenation/dehydrogenation reactions to yield stable alcohols and acids

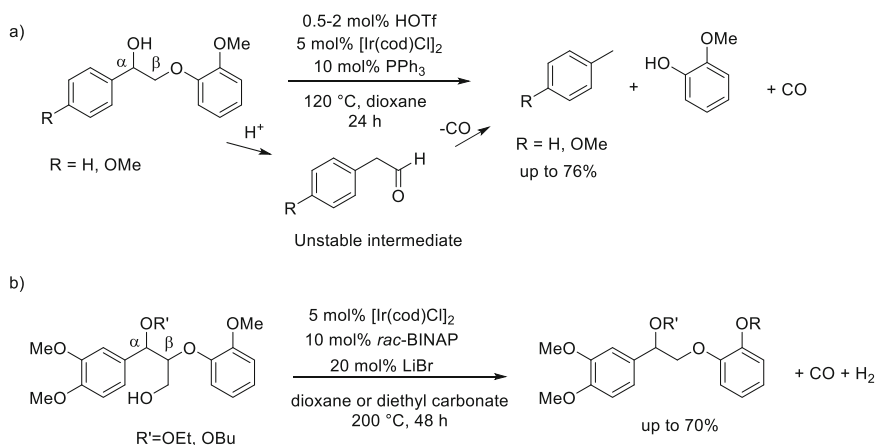


more stable than the gamma. Based on the calculations a mechanism was proposed which proceeds via abstraction of a hydrogen from the carbon by the iridium atom and abstraction of the hydrogen of the hydroxyl group by one of the carbonyl groups of the bipyridine ligand. Following the release of the product, the catalyst returns to its original state by the release of a molecule of H<sub>2</sub>. The authors then applied the catalyst to real lignin, which they extracted with acidic dioxane from birch wood, a source high in  $\beta$ -O-4 linkages. To confirm that the gas released from the reaction is hydrogen, they channeled it into another reaction using a Ru catalyst for the hydrogenation of decene to decane, which was then detected.

In order to depolymerize the Ir-pretreated lignin, first the authors tested a 2-step protocol on the model compound, where the depolymerization was achieved efficiently by Zn/NH<sub>4</sub>Cl. A formate buffer system was also tested, but due to the efficient dehydrogenation of formic acid by the Ir catalyst remaining in solution this was not usable. This procedure was then also applied to real lignin. GPC analysis of lignin samples before and after the treatment steps confirmed that lignin could not be depolymerized by the Zn system without the iridium pretreatment, while after the two steps it showed a decrease in molecular weight.

Two years later the group of Bruijninx employed the anionic version of the bipyridone catalyst [**Ir-49**], [**Ir-2**], to catalyze the conversion of lignin into aromatic diols and diacids via dehydrogenation of the primary ( $\beta$ ) hydroxyl followed by retro-aldol C $\alpha$  – C $\beta$  bond cleavage (Scheme 20b) [95]. This catalyst, [**Ir-2**], was chosen as it was known to be active in primary alcohol dehydrogenation (for example EG, see Sect. 2.1.2). In a basic water/dioxane mixture (pH 11) [**Ir-49**] converted spontaneously into its anionic form [**Ir-2**], and this catalyst system was able to cleave several lignin model compounds, also including phenol-containing ones, efficiently within 1 h. Next, the authors applied their method to real lignin (softwood enzyme), which resulted in an oil in 82% yield, which was confirmed by GPC to have much lower molecular weights. The other 18% were higher molecular weight material. A 2D HSQC NMR analysis showed that there were hardly any  $\beta$ -O-4 linkages left in this material and also the  $\beta$ -5 (phenylcoumaran) linkages were highly reduced. Another type of common linkage in lignin, the resinol ( $\beta$ - $\beta$ ) unit was not touched. Analysis of the oil fraction by GC confirmed the presence of the monomers expected from the model compound experiments. The yield of identified monomers was 3.8 wt% which is about 40% of the theoretical yield. Dioxasolv lignin was also tested and gave a slightly higher yield, mainly due to vanillin derived from the end groups. To simplify the product mixture, the authors refluxed the reaction mixture in air for a further 16 h, which led to the partial conversion of the monomers into a diacid derivative (see Scheme 16) in 2.4% yield, demonstrating that it can be possible to tune the depolymerization reaction to give a few products.

De Vries, Barta, and coworkers investigated iridium-catalyzed decarbonylation as one of the several strategies to prevent recondensation reactions of the aldehyde fragments which are formed by acidolysis of the  $\beta$ -O-4 linkage (Scheme 21a) [96]. In a one-pot reaction they achieved acid-catalyzed cleavage of  $\beta$ -O-4 model compounds by triflic acid and decarbonylation of the resulting aldehydes to methyl aromatics by [Ir(cod)Cl]<sub>2</sub> with triphenylphosphine ligand [**Ir-53**]. They then applied



**Scheme 21** Iridium-catalyzed decarbonylation of  $\beta$ -O-4 lignin model compounds

to methodology to walnut dioxasolv lignin. The content  $\beta$ -O-4 linkages in this type of lignin was determined to be 45% by 2D HMQC NMR. The theoretical maximum monomer yield from breaking  $\beta$ -O-4 bonds connected to monomeric units was 10%. The decarbonylation of lignin yielded 2 wt% of monomers, C1 and C0 phenolics, the latter are probably derived from vanillin-type aldehydes, which are known to form during lignin acidolysis.

Deuss and coworkers recently investigated the acceptorless dehydrogenative decarbonylation of the gamma-carbinol in the  $\beta$ -O-4 linkage (Scheme 21b) [97]. This transformation allows for access to different structures from lignin, whilst at the same time producing syngas (a mixture of CO and H<sub>2</sub>), which is a valuable starting material for the synthesis of alkanes, and which can also be produced via the gasification of biomass. For this purpose the authors choose the catalyst system previously reported by Olsen and Madsen [98] consisting of [Ir(cod)Cl]<sub>2</sub> combined with *rac*-BINAP ligand (**[Ir-54]**) with LiCl (4 eq w.r.t. Ir) as an additive. Using simple model compounds the reaction conditions were optimized in 1,4-dioxane (or diethyl carbonate) as solvent at 190 °C (142 °C inside the reaction vessel). They found that the presence of phenolic residues even enhanced the yield. The generation of syngas was confirmed by GC and the ratio of CO:H<sub>2</sub> was circa 1.1:1. The authors then tested  $\alpha$ -ethoxylated and -butoxylated  $\beta$ -O-4 model substrates, which would be present in lignin extracted with ethanol or butanol, respectively. The reason for using  $\alpha$ -alkoxylated species is to prevent the retro-aldol splitting as in the case of Bruijninx's work. These compounds required higher catalyst loadings and temperature as well as double the reaction time to achieve satisfactory yields. A phenylcoumaran model compound could also be dehydrogenated and decarbonylated under the same conditions. The authors then applied their catalyst system to different types of organosolv lignins and could demonstrate the defunctionalization of these substrates, alongside the production of syngas. However, when using real lignin as the substrate the ratio between CO and H<sub>2</sub> became a

lot higher, indicating that the hydrogen released is reacting with the substrate at other sites under the reaction conditions.

## 7 Iridium-Catalyzed Transformations of Fatty Acids

### 7.1 *Vegetable Oil as a Feedstock*

Vegetable oils, and to a smaller degree animal fats, are a large source of renewable chemicals [99]. In contrast to lignocellulose, vegetable oils are also food products, however currently a lot of oil crops such as rapeseed are grown in large quantities for the production of biodiesel, so that the conversion of a small fraction of these into chemicals will not affect the food production. Additionally, oils can be harvested from algae, which avoids the use of arable land for their production.

For biodiesel production, the triglycerides from vegetable oils are transesterified with methanol to produce fatty acid methyl esters (FAMES), leaving large amounts of glycerol as a side product [100]. Due to this, much research has been done on the valorization of glycerol, including a range of iridium-catalyzed reactions. These are discussed in Sect. 2.4. Additionally, as was already discussed in Sect. 5.2, glycerol is also interesting as a hydrogen donor.

The fatty acids from vegetable oils are mostly unsaturated or polyunsaturated, although saturated fatty acids also exist, for example in coconut and palm oil. Animal fat, on the other hand, contains mostly saturated fatty acids, such as stearic acid.

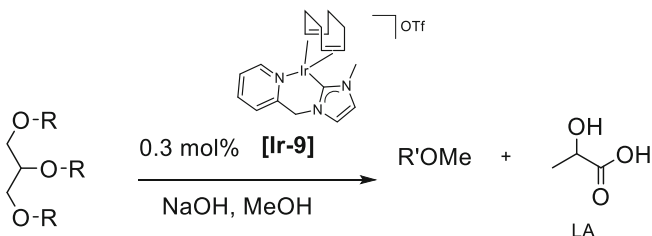
Oleic acid, a monounsaturated omega-9 fatty acid is the most common fatty acid in nature. It is present in up to 70% in canola oil, which is made from rapeseed.

### 7.2 *Iridium-Catalyzed Transformations of Fatty Acids*

#### 7.2.1 Hydrogenation

A high content of polyunsaturated FAMES in biodiesel reduces its performance: the stability and energy density of the fuel are lowered, while viscosity and emission of hydrocarbons are increased. In the USA the main feedstock for producing biodiesel are soybean and corn oil, which are high in polyunsaturated fatty acids, unlike in Europe where high oleic acid content canola oil is most commonly used. Fully saturated FAMES, such as those produced from animal fat, on the other hand, have high melting points and are prone to precipitation in diesel blends [41]. The best performance is achieved by high oleate content.

Williams and coworkers investigated iridium complex [Ir-9] from their previous work on the acceptorless dehydrogenation of glycerol to LA (see Sect. 2.4.1) for the hydrogenation of polyunsaturated FAMES using glycerol and methanol as hydrogen



R = fatty acids from soybean / corn oil  
((poly-)unsaturated/saturated)

R' = oleic acid/saturated fatty acid

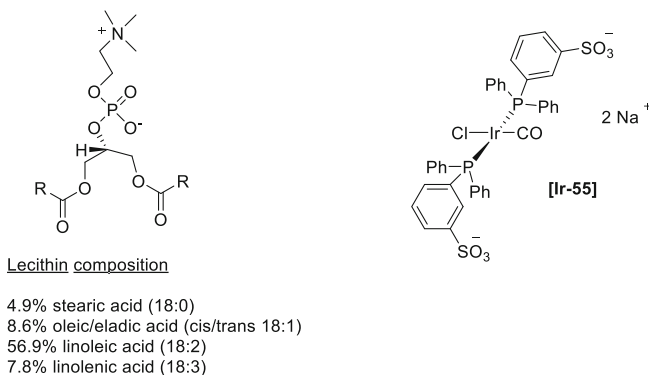
**Scheme 22** Combined methanolysis of vegetable oil, hydrogenation of polyunsaturated fatty acids and conversion of glycerol to lactic acid

donor (Scheme 22) [101]. This reaction could be combined in one pot with the synthesis of FAMES from corn oil and methanol. As one molecule of glycerol can only generate one equivalent of  $\text{H}_2$ , the additional hydrogen was produced by the dehydrogenation of methanol. Under the reaction conditions investigated, full and selective hydrogenation of the polyunsaturated fatty acids to oleate and other monounsaturated acids occurred when using 25 equiv. of methanol on top of the one equivalent of glycerol from the triglyceride. The glycerol was converted into lactate in >99%. Using 25 equivalents of glycerol, hydrogenation also proceeded in >99%. An isolated yield of monounsaturated FAMES of 65% could be achieved. Control experiments demonstrated that a higher methanol loading led to lower conversions due to poisoning of the catalyst. The role of the base in the hydrogenation reaction was investigated and it was found that it was not required for methanol dehydrogenation. However, no lactate was formed from glycerol unless stoichiometric base was present. The reaction was normally performed in closed vessels. To test the contribution of TH, a reaction was performed in an open system. Here the hydrogenation yield was 25%, confirming that most of the hydrogenation was by dihydrogen liberated from the H donors.

Even though not desirable for biodiesel, full hydrogenation of fatty acids was also investigated. By raising the temperature from 120 to 150°C and increasing the catalyst loading substantially from 0.3 to 6 mol%, complete hydrogenation could be achieved in 95%. In an effort to reduce the iridium loading, the authors found that adding Fe-MACHO catalyst in 3 mol% to the original amount of iridium could achieve complete hydrogenation in 90% yield.

Darensbourg and coworkers investigated a water-soluble analogue of Vaska's complex with the ligand (*m*-sulfonatophenyl)diphenylphosphine, [Ir-55], for the hydrogenation and *cis-trans* isomerization of unsaturated (small) carboxylic acids and further applied it to the hydrogenation of soybean lecithin liposomes, as a model for biological membrane modification [102].

Lecithin is a general term for a group of phospholipids. The fatty acid composition of this sample is listed in Fig. 12. Under fairly mild conditions (60°C, 1 bar



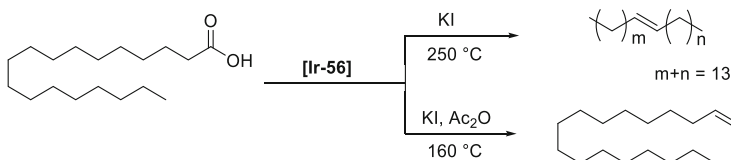
**Fig. 12** Iridium catalyst used in the isomerization of lecithin and lecithin composition

hydrogen) the authors found that even though there was some hydrogenation of the multiple double bonds, the isomerization of the natural *cis* form to the *trans* isomer was much faster. Using 0.01 mmol catalyst/10 mg substrate, the ratio of *cis* to *trans* double bonds in 18:1 fatty acids went from 93.2:6.7 to 58.1:41.9 in just 30 min. At the same time there was only 9.7% of hydrogenation of double bonds. Hydrogenation of *trans* alkenes is much more difficult so that full hydrogenation could not be achieved. Additionally, it might be more difficult for the catalyst to reach the sites due to structural changes in the liposome due to the isomerization. This comparably low activity of the catalyst is however enough to make enough changes to the liposomes for biomedical applications.

### 7.2.2 Decarbonylation

Aliphatic linear alpha olefins (LAOs) are important industrial chemicals, produced on large scale for the synthesis of surfactants and lubricants as well as comonomers in HDPE and linear low density PE, depending on their chain length [103]. Linear internal olefins (LIOs), the isomerization product in this reaction, are also industrially relevant products, mostly used in drilling fluids and paper sizing [104].

Ryu and coworkers applied Vaska's catalyst,  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ , **[Ir-56]**, to the decarbonylation of long chain aliphatic carboxylic acids (Scheme 23) [105]. Using stearic acid from palm oil, they first screened several iridium precursors and

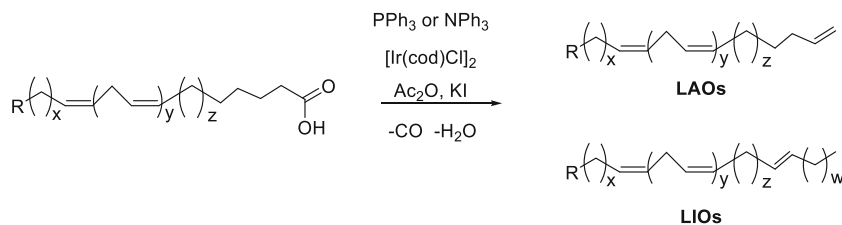


**Scheme 23** Decarbonylation of saturated fatty acids to yield selectively internal or terminal olefins

additives. When using 20 mol% KI as an additive at a reaction temperature of 250°C, internal alkenes were formed with selectivities >98%. A test with the iodine analogue of the iridium catalysts worked equally well, indicating that the KI might activate the catalyst via chloride–iodide exchange. By lowering the temperature to 160°C and adding 2 equivalents of acetic anhydride (Ac<sub>2</sub>O) together with 0.5 eq of KI, it was possible to invert the selectivity to produce the terminal alkenes with 98% selectivity. The methodology was applied to a range of saturated fatty acids, all giving the desired product in >80% yield with 99% selectivity for LIOs and >76% yield and >96% selectivity for LAOs. The proposed mechanism starts by the oxidative addition of an acid anhydride to the iridium. This acid anhydride is either generated from two molecules of carboxylic acid, or by reaction with Ac<sub>2</sub>O, indicating this additive's role in the reaction. The formed acyl complex is then decarbonylated releasing CO. The alkene is released by β-hydride elimination, leaving an iridium hydride complex, which can either release a carboxylic acid and return to the initial state or catalyze the isomerization of the double bond.

Hapiot and coworkers later applied this catalytic system to the decarbonylation of unsaturated fatty acids to produce linear alpha olefins (Scheme 24) [104]. The authors performed extensive screening of reaction conditions with oleic acid as a model substrate. This was chosen for ease of analysis, as it only contains one double bond. In a phosphane ligand screening with [Ir-56] or [Ir(cod)Cl]<sub>2</sub> as the iridium source it was found that the best combination was 3:1 PPh<sub>3</sub>: [Ir(cod)Cl]<sub>2</sub> at 5 mol% loading and 160°C for 5 h ([Ir-57]). Acetic anhydride and potassium iodide were again used as additives. Without Ac<sub>2</sub>O there was hardly any conversion. Just like in Ryu's work, the optimum amounts of the additives for best conversion and selectivity to the terminal alkene were determined to be 2 equiv. Ac<sub>2</sub>O and 0.5 equiv. KI. With [Ir-56], on the other hand, there was good conversion without Ac<sub>2</sub>O, however almost exclusively the internal alkene product was formed. The reaction system was then applied to other unsaturated fatty acids as well as α,ω-diacids. All substrates showed good to very good conversions with selectivities to the terminal alkene of >80%. The catalyst could be recycled by distilling off the product and other components. When fresh substrate was added the conversion and selectivity decreased somewhat. The selectivity could be restored by adding fresh triphenylphosphine; however, the yield was still 10% lower than with fresh catalyst.

A few years later the same group investigated different ligands for this transformation, as phosphane ligands are generally not desirable when not necessary due to



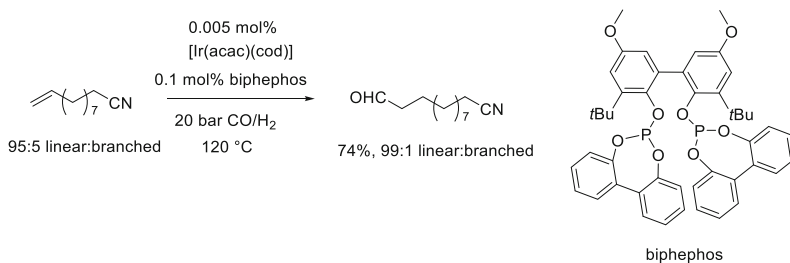
**Scheme 24** Decarbonylation of fatty acids catalyzed by iridium catalysts [Ir-57] and [Ir-58]. The ratio of the two products can be tuned by choice of (a) temperature and additives, and (b) ligand

stability issues [106]. A range of different amine ligands chosen for their air stability were screened with  $[\text{Ir}(\text{cod})\text{Cl}]_2$  under the same reaction conditions as before. Aliphatic tertiary amines gave good conversions, while for aromatic amines and those with delocalized electrons the conversions were much lower, reflecting their weaker binding to the iridium. The best ligand in the screening was the triphenylphosphine analogue  $\text{NPh}_3$ , forming the amine analogue catalyst **[Ir-58]**. However, it could not reach the activity of the  $\text{PPh}_3$  catalyst from the previous publication. While the selectivity for LAOs was much higher with the phosphane ligand, it was found that it was possible to tune the reaction conditions to reach very high selectivity for LIOs with the amine ligands.

### 7.2.3 Hydroformylation

Carpentier and coworkers investigated the use of iridium among other metals for the hydroformylation-isomerization reaction of fatty acid derivatives [107]. The study focused on 10-undecenitrile as the substrate (Scheme 25). This compound can be readily prepared by the reaction of 10-undecenoic acid from castor oil with ammonia and is a precursor to polyamide-12 [108].

Testing the bis-phosphite ligand Biphephos, originally developed by Union Carbide, which they had employed in their previous study with rhodium [109], with other metals, the authors found that with iridium the TOF was only five times slower than that of the rhodium system ( $730$  vs  $3,320 \text{ h}^{-1}$ ). Other metals tested (Pd, Ru) were a lot slower. This is an interesting result, as currently most hydroformylation catalysts are based on rhodium, a very expensive and rare metal, which is considered vastly superior to all others for this reaction. Even though iridium is not cheap either, it is much cheaper than rhodium, making this a potentially viable process. One problem with hydroformylation is isomerization of the double bond of the alkene to internal positions, which then gives rise to undesired branched hydroformylation products. The selectivity to the terminal aldehyde with the iridium catalyst (**[Ir-59]**) in this case was 99:1. Some of the starting material was isomerized to internal alkenes; however, this was only hydroformylated to a minor extent. For 10-undecenitrile, the amount of internal alkenes increased from 5 to 22% during the reaction. Some other fatty acid derivatives were screened and showed the same high selectivity to the linear products. Additionally, the iridium



**Scheme 25** Hydroformylation of fatty acid derivatives with **[Ir-59]**

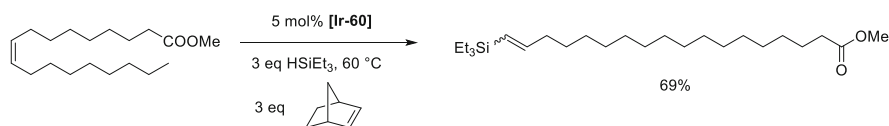
could be reused three times by distilling off the reaction mixture and product and adding more ligand.

### 7.2.4 Trialkylsilylation

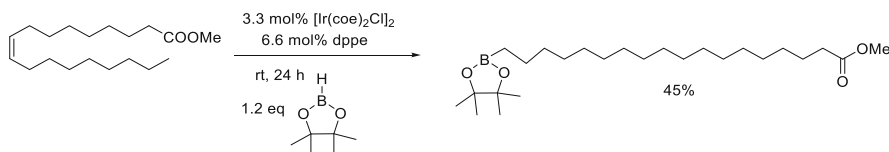
As we have already seen, terminal olefins are often more desired for further functionalization, giving rise to linear, end-functionalized compounds. Riepl and coworkers investigated the iridium-catalyzed isomerizing dehydrogenative silylation of methyl oleate, the most common FAME (Scheme 26) [110]. Silicon containing compounds like this are interesting precursors for industry in the fields of adhesives, lubricants, plasticizers, and polymers. Initially the authors tried to apply an existing methodology for isomerizing silylation to methyl oleate [111]. This consisted of 5 mol%  $[\text{Ir}(\text{OMe})\text{Cl}]_2$ , 10 mol% 2,2'-bipyridine ligand combined with 3 equivalents of norbornene as a hydrogen acceptor, and 3 equivalents of triethylsilane. However, it turned out that the bipyridine ligand was inhibiting the isomerization step, so that very little desired product was formed even after prolonged reaction times. When the ligand was omitted, and  $[\text{Ir}(\text{OMe})(\text{cod})]_2$ , **[Ir-60]**, was used, the yield of the terminal silylated product rose to 69% (Scheme 26). Further changing of reaction conditions, such as increasing the temperature from 60°C led to a deactivation of the catalyst. Sadly, the procedure did not work with other bulkier trialkylsilanes.

### 7.2.5 Hydroboration

Angelici and coworkers employed  $[\text{Ir}(\text{coe})_2\text{Cl}]_2$  in combination with dppe ligand (**[Ir-61]**) for the isomerizing hydroboration of methyl oleate with pinacolborane [112]. In their protocol at room temperature, they achieved a yield of 45% of the desired borylated product, while the main product of the reaction was the hydrogenated FAME methyl stearate with 47% (Scheme 27). The fact that there is so much



**Scheme 26** Iridium-catalyzed trialkylsilylation of methyl oleate



**Scheme 27** Isomerizing hydroboration of methyl oleate catalyzed by **[Ir-61]**



of the hydrogenation product formed, which does not happen with shorter chain internal alkenes under the same conditions, led the authors to conclude that the isomerization step is much slower for this substrate.  $[\text{Ir}(\text{cod})\text{Cl}]_2$  gave no borylation product under the same conditions. When the reaction temperature was increased to  $50^\circ\text{C}$ , a low yield of 25% was achieved, with a large amount of the starting material still present after 24 h.

## 8 Conclusion

In this chapter we have summarized research in the field of iridium-catalyzed biomass conversion. This is a developing field, most of the work discussed here was published in the last 8 years. With the recent progress in the conversion of cellulosic biomass and the availability of several platform chemicals, there is now more and more scope for homogeneous catalysis in this area, due to its generally higher selectivity at milder conditions. We therefore expect to see more publications in this field in the future. One massive advantage of iridium over other metals, especially with regard to biomass, is its excellent stability towards water, air, and acidic conditions. We have seen that a range of useful fine chemicals and precursors, monomers, and even polymers can be synthesized from biomass using iridium catalysis. Mechanistically, many of the reactions discussed are hydrogenation/dehydrogenation reactions. This is an important reaction pathway for biomass, which is highly functionalized and oxygen-rich compared to the well-known oil-based building blocks. Other mechanisms such as decarbonylation/hydroformylation and others have also been applied to bio-based compounds. The valorization of lignin still lags behind the saccharide-based biomass but also here iridium catalysts have shown promising potential in the initial defunctionalization and the selective generation of a few monomers from the complex mixture. We expect to see more research in this direction in the coming years.

Finally, the dehydrogenation of biomass to generate hydrogen, a highly useful product with the potential to be a main energy carrier in the future is also being investigated. With the development of more efficient catalysts, the generation of renewable hydrogen from biomass should soon become cost-effective.

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