A novel glycerol valorization route: chemoselective dehydrogenation catalyzed by iridium derivatives

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Organoiridium derivatives of the type Ir(diene)(N-N)X (diene = 1,5-hexadiene,1,5-cyclooctadiene; N-N = 2,2′-bipyridine, 1,10-phenanthroline and substituted derivatives; X = Cl, I) catalyze the hydrogen transfer reaction from glycerol to acetophenone, yielding dihydroxyacetone and phenylethanol. The catalytic reactions are performed at temperatures of 100 °C or higher, in the presence of a basic cocatalyst. The effect of experimental conditions on overall conversion and catalyst lifetime is discussed, as well as on the degradation of dihydroxyacetone, which can lead to an apparent decrease of selectivity of the catalytic reaction.

Introduction

In recent years sustainability has become an imperative issue, forcing both academic and industrial scientists towards the design of more environmentally friendly and atom efficient chemical processes. A considerable number of new synthetic methods has been proposed which meet the requirements of the twelve principles of green chemistry as stated by Anastas and Kirchoff.[1] One of the crucial points is represented by the use of renewables which are destined to increasingly replace fossil fuels as a carbon source. In this respect, the interest of several scientists has been recently attracted by glycerol, a renewable raw material[2] which is characterized by unique properties: it is a nontoxic, edible and biodegradable compound and its nature as a polyfunctional molecule allows a variety of possible transformations.

At present, the availability of glycerol is increasing due to the expanding manufacture of the biodiesel fuel obtained by methanol transesterification of seed oils, a process which generates about 10% weight of glycerol as a side-product. At the same time, first generation biofuel production from edible seeds is already causing unacceptable consequences on food costs, *i.e.* the food *vs.* fuel dilemma.[3] However, second generation biofuels based on alternative sources (lignocellulosic materials, microalgae, inedible seeds such as *Jatropha curcas*), which combine highly efficient production with environmental and ethical sustainability, are expected to use the same industrial route as the economic feasibility of the direct conversion of biomass to second generation fuels is still far away.

On the whole, the large surplus of glycerol in association with its high functionalization makes it one of the most promising platform chemicals of the near future. Under the influence of suitable catalysts, glycerol can undergo a large number of chemical transformations to products of commercial value. Among the processes under current investigation hydrogenolysis leading to 1,2- or 1,3-propanediol, reforming to CO and H_2, carboxylation to give glycerol carbonate, dehydration to acrolein and oxidation seem the most promising.[4]

Glycerol oxidation can lead to a large variety of products (Scheme 1), many of which have commercial relevance. In most cases, however, the process is far from being satisfactory as the selective transformation of one single hydroxyl group has proven a hard task to be accomplished. Oxidation of the primary hydroxyl groups to form glyceric acid and subsequently tartronic acid is catalyzed by platinum group metals supported over carbon or ceria, however the selectivity observed is often affected by low catalyst stability.[5] Selective oxidation of the secondary hydroxyl group of glycerol yields dihydroxyacetone (DHA), an important synthon in organic synthesis[6] and itself a commercially valuable chemical used as a component in artificial tanning preparations. At present DHA is produced by microbial fermentation of glycerol with *Gluconobacter oxydans*[7] or by electrocatalytic oxidation in the presence of TEMPO,[8] whereas heterogeneous catalysts mostly prefer to affect primary OH groups, with some notable exceptions such as bismuth-promoted platinum.[9] Finally, oxidation of all three alcoholic groups of glycerol yields mesoxalic acid, a reaction which is preferably catalyzed by platinum-based heterogeneous catalysts.[10]

A possible environmentally friendly route to glycerol oxidation is represented by dehydrogenation *via* a hydrogen transfer reaction. In the last few decades, transfer hydrogenation has been developed as an efficient reduction method for organic substrates, generally ketones, aldehydes and imines (Scheme 2).[11] These reactions are homogeneously catalyzed by transition metal derivatives, with the hydrogen donors generally employed being formic acid and 2-propanol.

Glycerol can be envisaged as a disubstituted 2-propanol, therefore we reasoned that it should be possible to perform a transfer dehydrogenation of glycerol in the presence of a suitable catalyst and an appropriate hydrogen acceptor. In principle, both primary and secondary hydroxyl groups of glycerol can undergo

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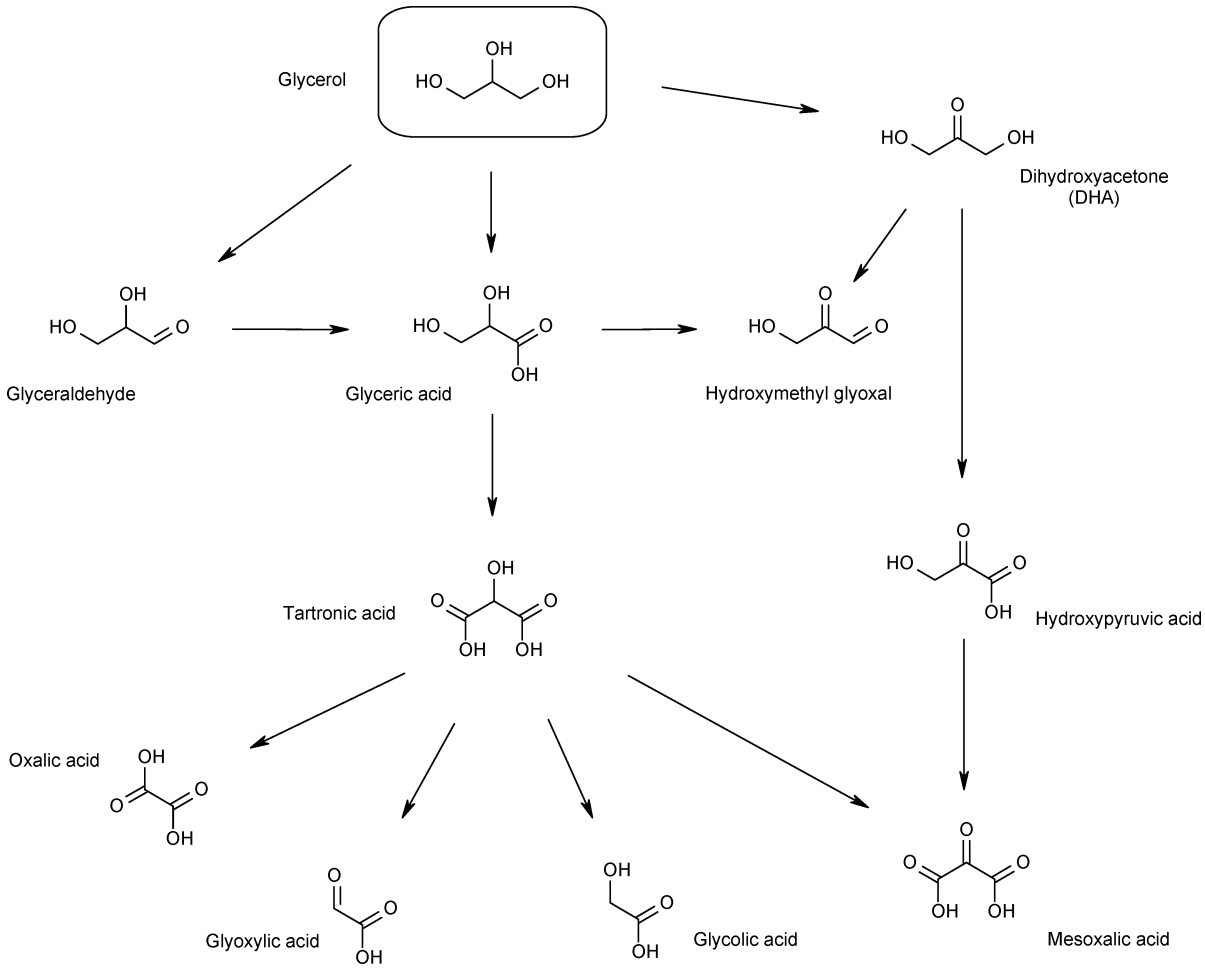
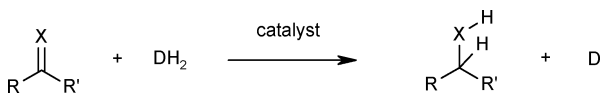


Scheme 1 Products of glycerol oxidation.



Scheme 2 Transfer hydrogenation.

dehydrogenation, however, according to the relative oxidation potentials of secondary *vs.* primary alcohols[12] the hydrogen transfer is expected to selectively occur from the secondary hydroxyl group, yielding DHA as a dehydrogenation product.

To our knowledge, no report regarding transfer dehydrogenation of glycerol has appeared in the literature until now. We therefore applied our previous experience in hydrogen transfer reactions catalyzed by organoderivatives of platinum group metals, especially iridium[13] to study selective glycerol dehydrogenation.

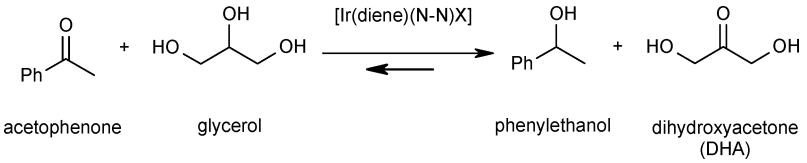
Here we describe the results obtained in the dehydrogenation of glycerol catalyzed by the compounds Ir(diene)(N-N)X (diene = 1,5-hexadiene (hd),1,5-cyclooctadiene (cod); N-N = 2,2′-bipyridine, 1,10-phenanthroline and substituted derivatives; X = Cl, I).

Results and discussion

Iridium derivatives of the type Ir(diene)(N-N)X are well known transfer hydrogenation catalysts for the reduction of various unsaturated substrates. When a ketone is used as a hydrogen acceptor, the hydrogen transfer reaction is actually an equilibrium between the hydrogen donor (an alcohol such as 2-propanol or cyclopentanol) and the acceptor molecule: this equilibrium can be driven to the products side by use of a large excess of one of the reactants, a situation which is generally obtained by using the hydrogen donor (alcohol) as a solvent for the reaction mixture.

In our initial approach to transfer dehydrogenation of glycerol we chose as the acceptor molecule acetophenone, a model substrate which has often been employed in catalytic reduction studies (Scheme 3). Initial tests performed using an excess of glycerol together with a cosolvent (*e.g.* dioxane) gave encouraging results, whereas reactions performed in the absence of a cosolvent evidenced some difficulties concerning, for example, solubility of catalysts. However, as the latter option looked more coherent with the green chemistry principles, we decided to limit our investigations to the reactions performed in the absence of a cosolvent.

A first series of reactions was performed using Ir(diene)(Me_4phen)Cl and Ir(diene)(Me_2bipy)Cl (diene = hd or cod; Me_4phen = 3,4,7,8-tetramethyl-1,10-phenanthroline; Me_2bipy = 4,4′-dimethyl-2,2′-bipyridine) and 2 equivalents of NaOH, the basic cocatalyst generally employed in transfer hydrogenation: after 1 h at 100 °C the analysis of the reaction mixture revealed that glycerol was behaving as a hydrogen



Scheme 3 Transfer dehydrogenation of glycerol.

Table 1 Hydrogen transfer reduction of acetophenone by glycerol catalyzed by Ir(diene)(N-N)Cl[a]

Entry	Catalyst	Conv. (%)[b]
1	Ir(hd)(Me_4phen)Cl	26
2	Ir(cod)(Me_4phen)Cl	4
3	Ir(hd)(Me_2bipy)Cl	25
4	Ir(cod)(Me_2bipy)Cl	6

[a] Experimental conditions: [Ir] = 3.0×10^{-3} M; [acetophenone]/[Ir] = 100; T = 100 °C; reaction time = 1 h; base = NaOH; [base]/[Ir] = 2. [b] Calculated as % acetophenone reduced to phenylethanol.

donor, partially reducing acetophenone to phenylethanol. When the reaction was performed in the absence of either metal catalyst or NaOH, no traces of phenyethanol were observed. These findings confirm on one hand that NaOH does not promote hydrogen transfer from the alcohol to the ketone in the present conditions, on the other the need for the presence of both a catalyst and a base. Notably, the presence of the base also supressed formation of ketals arising from the condensation of acetophenone with glycerol that was observed in the blank experiments. A comparison between cod and hd-derivatives is reported in Table 1: the hexadiene catalysts are superior to those with cyclooctadiene in both cases, with phenylethanol yields of 25–26% (hd catalysts) *vs.* 4–6% (cod catalysts). Such a difference in catalytic activity as a function of the diene is coherent with previously reported trends in transfer hydrogenation of ketones.[13a] On the other hand an effect of the lower solubility in glycerol of the cod complexes compared to the hd ones cannot be disregarded.

In the final reaction mixtures dihydroxyacetone was always detected among the products, however the relative amount was always lower than that of phenylethanol: with 25–26% of acetophenone reduction, DHA yield was only 8% of the initial acetophenone, resulting in a selectivity in DHA of 30%; on the other hand, other dehydrogenation products of glycerol (*e.g.* glyceraldehyde) were never detected in the final reaction mixtures.

As an alternative approach, weaker bases were considered as possible cocatalysts. Actually, a first reaction performed using K_2CO_3 in the place of NaOH gave even better results both as conversion (33 *vs.* 26%) and selectivity in DHA (39 *vs.* 30%). The results of a series of reactions using different bases are reported in Table 2. From these data, apart from entry 2 concerning NaOH, a significant correlation between cocatalyst basicity and conversion is observed, *i.e.* the lower the K_b value, the lower the extent of acetophenone reduction (see Table 2, entries 3–6). On the other hand, the selectivity in DHA formation does not show an analogous, clear correlation upon the strength of the base: apparently the higher the conversion, the lower the DHA selectivity.

Table 2 Hydrogen transfer reduction of acetophenone by glycerol catalyzed by Ir(hd)(Me_4phen)Cl[a]

Entry	Base	K_b	[base]/[Ir]	Conv. (%)[b]	DHA yield (sel.) (%)[c]
1	—		—	0	—
2	NaOH	55	2	26	8 (30)
3	K_2CO_3	2×10^{-4}	2	33	13 (39)
4	$NaHCO_3$	2×10^{-8}	2	21	7 (35)
5	$NaCO_2CH_3$	6×10^{-10}	2	8	6 (76)
6	$Na_2C_2O_4$	2×10^{-10}	2	13	8 (58)
7	K_2CO_3	2×10^{-4}	1	30	10 (34)
8	K_2CO_3	2×10^{-4}	4	35	11 (31)

[a] Experimental conditions: [Ir] = 3.0×10^{-3} M; [acetophenone]/[Ir] = 100; T = 100 °C; reaction time = 1 h. [b] Calculated as % acetophenone reduced to phenylethanol. [c] DHA yield %: calculated on the basis of the initial acetophenone; sel. %: calculated on the basis of the Conversion.

Interestingly, when sodium acetate was used as cocatalyst at 120 °C higher conversion (26%) was achieved, but lower selectivity (52%) compared to the reaction at 100 °C (Table 2, entry 5). With regard to cocatalyst concentration, the data reported in entries 3, 7 and 8 of Table 2 evidence that an increase of [K_2CO_3]/[Ir] ratio produces a moderate increase of conversion, leaving the yield of DHA nearly unaffected.

A comparison of catalytic activity and selectivity using iridium-hexadiene complexes with different ligands was made using K_2CO_3 as a basic cocatalyst. Table 3 reports the data concerning chloro complexes which differ in the nature of the nitrogen ligand (entries 1–4; Me_2phen = 4,7-dimethyl-1,10-phenanthroline; bipy = 2,2′-bipyridine); two results regarding iodo derivatives are included to evaluate the halogen effect (compare entries 1, 5 and 2, 6); in the table conversions and selectivities are shown at two different reaction times (30 and 60 min) to enable easier comparison. Chloro derivatives prove to be more active; on the other hand, selectivity in DHA formation is higher when iodo compounds are employed, *i.e.* once more a lower reaction conversion corresponds to better selectivity. The four chloro complexes with different nitrogen ligands (the derivative with unsubstituted phenanthroline was not examined due to its low solubility) display similar catalytic activities with highest conversion observed with the Me_2phen catalyst (36% conversion in 30 min and 39% in 60 min). In previous studies, the activity of analogous series of catalysts in hydrogen transfer reactions had been shown to be influenced by the donor ability of the nitrogen ligands;[13–15] in other words, better electron releasing ligands gave rise to more active catalysts. In the present studies no such dependence is evidenced as the best donor ligand leads to the lowest conversion, although the differences observed are barely significant. A prompt rationalization of such data is not obvious as several factors are likely to affect the extent of acetophenone reduction, *i.e.* catalyst solubility, the effect of

Table 3 Hydrogen transfer reduction of acetophenone by glycerol catalyzed by Ir(hd)(N-N)X complexes[a]

		30 min reaction time		60 min reaction time	
Entry	Catalyst	Conv. (%)[b]	DHA yeld (sel.) (%)[c]	Conv. (%)[b]	DHA yeld (sel.) (%)[c]
1	Ir(hd)(Me_4phen)Cl	28	13 (47)	33	13 (39)
2	Ir(hd)(Me_2phen)Cl	36	17 (47)	39	13 (34)
3	Ir(hd)(Me_2bipy)Cl	31	13 (41)	33	11 (33)
4	Ir(hd)(bipy)Cl	28	12 (42)	31	12 (38)
5	Ir(hd)(Me_4phen)I	17	11 (68)	21	11 (50)
6	Ir(hd)(Me_2phen)I	13	12 (92)	18	12 (67)

[a] Experimental conditions: [Ir] = 3.0×10^{-3} M; [acetophenone]/[Ir] = 100; T = 100 °C; base = K_2CO_3; [base]/[Ir] = 2. [b] Calculated as % acetophenone reduced to phenylethanol. [c] DHA yield %: calculated on the basis of the initial acetophenone; sel. %: calculated on the basis of the conversion.

ligands steric hindrance on the coordination of the reactants and products, kinetics of catalyst deactivation (*vide infra*) *etc.* A final remark about the data reported in Table 3 regards the selectivity in DHA formation which decreases at longer reaction times.

In order to have a clearer view on the observed trend of DHA selectivity we studied in the detail the evolution of conversion and DHA yield as a function of reaction time and temperature; the results are listed in Table 4.

The data regarding the reactions at 100 °C (Table 4, entries 1–5) clearly show that initially the catalytic reaction is fast and very selective with respect to DHA formation; then, after 15 min a pronounced decrease in rate of acetophenone consumption is observed; no significant acetophenone reduction takes place after 60 min. On the other hand, the conversion is significantly increased by a moderate temperature increase (Table 4, entries 3, 6 and 7) whereas at lower temperature (80 °C) the reaction rate is negligible.

As far as the DHA selectivity is concerned, we observe a different behaviour: at 100 °C (Table 4, entries 1–5 and Fig. 1, (▲) markers) there is nearly linear apparent dependence on the conversion, *i.e.* the higher the conversion, the lower the selectivity.

The same trend in conversion *vs.* DHA selectivity was found (i) for the same reactions carried out at 110 °C (Fig. 1, (●) markers), and (ii) again at 100 °C but with the catalyst Ir(hd)(Me_4phen)I (Fig. 1, (◆) markers). Remarkably, all the trends reported in Fig. 1 clearly suggest a 100% selectivity for DHA formation at initial stages of the reaction.

Table 4 Hydrogen transfer reduction of acetophenone by glycerol catalyzed by Ir(hd)(Me_4phen)Cl[a]

Entry	Reaction time/min	T/°C	Conv. (%)[b]	DHA yield (sel.) (%)[c]
1	5	100	15	11 (77)
2	15	100	26	13 (53)
3	30	100	28	13 (47)
4	60	100	33	13 (39)
5	180	100	34	12 (34)
6	30	110	37	14 (37)
7	30	120	47	12 (24)

[a] Experimental conditions: [Ir] = 3.0×10^{-3} M; [acetophenone]/[Ir] = 100; T = 100 °C; base = K_2CO_3; [base]/[Ir] = 2. [b] Calculated as % acetophenone reduced to phenylethanol. [c] DHA yield %: calculated on the basis of the initial acetophenone; sel. %: calculated on the basis of the conversion.

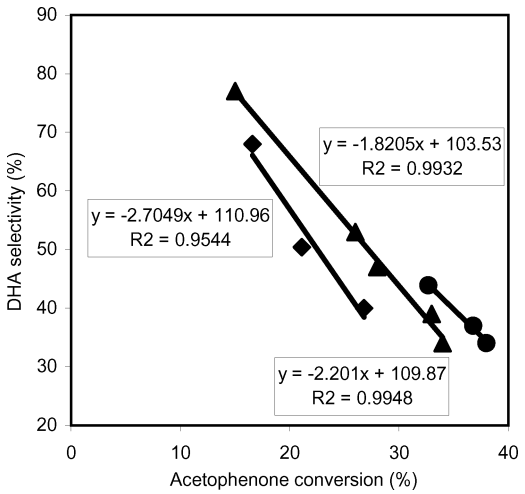


Fig. 1 DHA sel. *vs.* acetophenone conv.; exp. conditions: [Ir] = 3.0×10^{-3} M; [acetophenone]/[Ir] = 100; base = K_2CO_3; [base]/[Ir] = 2; (–▲–): cat. = Ir(hd)(Me_4phen)Cl, T = 100 °C; (–●–): cat. = Ir(hd)(Me_4phen)Cl, T = 110 °C; (–◆–): cat. = Ir(hd)(Me_4phen)I, T = 100 °C; the calculated equations and R^2 for each of the linear correlations are shown in the boxes.

In summary, the above reported data suggest that dehydrogenation of glycerol yields DHA as the only product which, however, partially disappears from the reaction mixture owing to further reactions. Several features suggest the decomposition of DHA, *i.e.*: the trend at low conversion values in Fig. 1; the actual decrease in DHA yield at longer reaction times (Table 3, entries 2 and 3, reaction times 30 and 60 min; Table 4, entries 4 and 5); the analogous behaviour obtained with different catalysts and different temperatures.

The occurrence of DHA decomposition was confirmed by performig a series of test reactions in the same experimental conditions of the catalytic reactions but without a catalyst. In the first test we loaded a Schlenk tube with 0.88 mmols of acetophenone, 0.43 of phenylethanol and 0.43 of DHA: *i.e.*, the amounts calculated on an hypothesis of 33% conversion and 100% DHA selectivity. After 1 h at 100 °C, in the presence of K_2CO_3, we detected only 0.16 mmols of DHA in the reaction mixture which corresponds exactly to what found at the end of the catalytic reaction in the same experimental conditions. In other words, 60% of the initial DHA in the test reaction underwent decomposition. No decomposition products were detected by GC/MS in the final reaction mixture; attempts to

identify the products by NMR spectroscopy were frustrated by the presence of too many resonances.

Further tests were devoted to check the dependence of DHA decomposition on the base strength, showing an increase of decomposition for stronger bases. In the absence of basic cocatalyst at 100 °C only 10% of DHA was lost; however, thermal decomposition was progressively affected by an increase in reaction temperature: up to 90% of DHA was decomposed in 1 h at 160 °C. As in the catalytic reactions, in absence of bases, significant amounts of ketals were detected by the reaction of glycerol with acetophenone.

In summary, DHA decomposition promoted by temperature and a basic cocatalyst explains the DHA selectivity dependence on cocatalyst basicity, [base]/[Ir] ratio, temperature and reaction time and, more generally, the decrease of selectivity with the increase of conversion.

Actually, instability of DHA towards thermal degradation is well known,[16] whereas effects of a strong base on DHA formation were not evidenced,[5a,8] even if condensation reactions of DHA in basic media were previously reported leading to complex mixtures of higher carbohydrates even at temperatures as low as 30 °C;[17] similar condensation reactions are likely to take place also in our hydrogen transfer conditions.

Further comments are due to the observed decrease of acetophenone reduction with time, which can be rationalized in terms of catalyst deactivation. Similar deactivations of iridium-based hydrogen transfer catalysts have been previously observed:[18] they can be explained in terms of irreversible processes caused by either high temperature or reactions with the cocatalyst (or both) and they represent a major weak point of such catalytic systems. Furthermore, also the presence of significant amounts of water in the reaction medium due to the hygroscopicity of the glycerol is expected to have a detrimental effect on the lifetime of the catalyst. Previously reported deactivations caused a less pronouced decrease of catalytic activity, but the experimental conditions used were milder (lower temperature and/or absence of basic cocatalyst) than those employed in the present investigation.

Conclusions

The hydrogen transfer from glycerol to acetophenone is catalyzed by Ir(diene)(N-N)X; the reaction is performed at 100 °C in pure glycerol. As foreseen on the basis of thermodynamic data, glycerol dehydrogenation does selectively occur at the secondary hydroxyl group to give dihydroxyacetone, whereas acetophenone is reduced to phenylethanol. To the best of our knowledge, this study is the first example of a transfer dehydrogenation of glycerol, a reaction which represents an interesting green route to glycerol valorization. However, the selectivity is lowered by further reactions of DHA which are promoted by the basic cocatalyst. Further, thermal degradation of DHA, which becomes significant above 100 °C, prevents the use of higher reaction temperatures which might allow avoidance of the basic cocatalyst. Even though the experimental conditions required by the catalysts used in the present study affect the observed selectivity, we have demonstrated that the route of chemoselective glycerol oxydation *via* hydrogen transfer to a suitable acceptor is feasible, thus opening future perspectives in this field.

Experimental section

General

All the reactions and manipulations were routinely performed under an argon atmosphere using standard Schlenk tube techniques.

Methanol was distilled over CaO; dioxane was distilled over sodium benzophenone ketyl just prior to use. Naphthalene (GC standard) was purified by recrystallization from ethanol. All the other chemicals were reagent grade and were used as received by commercial suppliers.

Iridium chloride hydrate was a loan from Johnson Matthey PLC and it was used as received.

Instrumental

^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX400 spectrometer operating at 399.77 and 100.54 MHz, respectively. Infrared spectra were recorded in Nujol mull on a FT-IR Perkin Elmer System 2000 spectrometer.

Chemical yields of the catalytic reactions were determined by GC on a Hewlett-Packard 5890 Series II gaschromatograph equipped with a Rtx-5 capillary column, using naphthalene as an internal standard. Alternatively, analysis of the reaction products were performed on a Hewlett-Packard 5890 Series II GC instrument coupled to a Hewlett-Packard 5971A Mass Selective Detector equipped with a Rtx-5MS column.

Synthesis of Ir(cod)(N-N)Cl, Ir(hd)(N-N)Cl and Ir(hd)(N-N)I

The compounds were prepared according to previously described methods.[19,13a]

Procedure for the catalytic reactions

The experimental procedure for the hydrogen transfer reactions performed using glycerol as a solvent, without addition of a cosolvent, was carefully set up in order to overcome operative difficulties (*e.g.* high solvent viscosity, low solubility of catalysts and GC standards) and at the same time to guarantee excellent reproducibility.

In a typical catalytic reaction, 4.0 mL of glycerol were introduced in a Schlenk tube equipped with an argon inlet and deaerated by bubbling argon for 15 min. After addition of the catalyst (0.012 mmol), the reaction vessel was closed with a serum cap and heated with vigorous stirring to 100 °C (or other chosen reaction temperature) in a thermostatted oil bath. When the final temperature was reached, addition by microsyringe of 1.2 mmol of acetophenone ([sub]/[Ir] = 100) was followed by addition of 0.024 mmol of $K_2CO_{3(aq)}$ or other basic cocatalyst ([base]/[Ir] = 2), which started the catalytic reaction.

Use of a condenser was avoided in order to minimize evaporation of acetophenone and of its reduction product phenylethanol (as evidenced in preliminary reactions). After the desired reaction time, the Schlenk tube was cooled under

running water and 10 mL of methanol containing the GC standard naphthalene were added. The resulting solution was analyzed as described in the next paragraph.

Determination of the reaction products

Determination of the composition of the final reaction mixture was made by GC and GC/MS. Qualitative analysis was accomplished by GC/MS using where possible authentic samples for comparison. Quantitative evaluation of product distribution was performed by GC with the aid of an internal standard reference (naphthalene), using response factors determined by use of standard solutions; several specimens of such standard solutions at different concentrations allowed quantitative analysis which were reproducible within ±1%.

In the quantitative analysis of the catalytic reactions, the sum of final amounts of acetophenone and phenyethanol exactly corresponded to the amount of acetophenone initially loaded; moreover, no other product derived from acetophenone was detected.

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