

Dehydrogenation of glycerol to dihydroxyacetone catalyzed by iridium complexes with P–N ligands

Corrado Crotti,^{a,b} Jan Kašpar^{b,c} and Erica Farnetti^{*b,c}

Received 23rd February 2010, Accepted 14th April 2010

First published as an Advance Article on the web 24th May 2010

DOI: 10.1039/c003542d

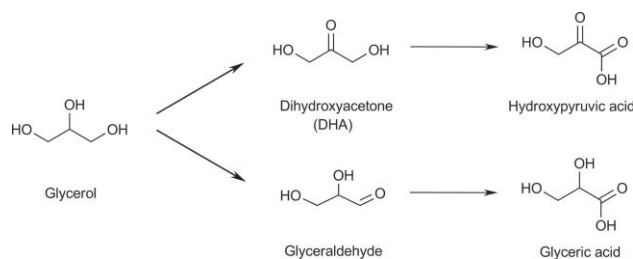
The chemoselective dehydrogenation of glycerol was catalyzed by organoiridium derivatives of the type [Ir(cod)L] (cod = 1,5-cyclooctadiene; L = Prⁿ-N(CH₂CH₂PPh₂)₂, Et₂NCH₂CH₂N(CH₂CH₂PPh₂)₂, *o*-Me₂NC₆H₄PPh₂) using hydrogen acceptors such as acetophenone, cyclohexanone, styrene and benzaldehyde. The catalytic reactions were performed in the absence of a basic cocatalyst in order to avoid decomposition of the desired product, *i.e.* dihydroxyacetone. Acceptor-less dehydrogenation was also observed either in the absence of a hydrogen acceptor, or as a parallel route, when the reaction was performed in the presence of acetophenone.

Introduction

Glycerol is the main byproduct of the biodiesel production process, and its availability has greatly increased in the last decade. Therefore, glycerol is nowadays pointed out as one of the most important renewable raw materials.¹ However, the very reason that makes this molecule an attractive candidate for chemical reactions, *i.e.* its high degree of functionalization, represents a severe limit to its selective transformation. As a matter of fact, the most challenging problem concerning glycerol valorization is represented by selectivity. Moreover, if on one hand glycerol is a very abundant, safe organic building block, on the other its physicochemical properties, such as strong hydrophilicity and high viscosity, greatly increase the experimental difficulties.

Among the most promising glycerol valorization routes² is selective oxidation, which can lead to a variety of target molecules (see Scheme 1), which are either commercially valuable themselves or are interesting building blocks. In fact, so far, the market for these chemicals has been limited because of their high cost. Therefore, efficient, selective processes are needed in order to make them widely and cheaply available. The development of catalytic processes that afford a single oxidation product with a good selectivity is therefore highly desirable. The catalyst must allow the control of glycerol oxidation towards either the primary hydroxyl groups, to produce glyceric acid, or the secondary alcohol function, to give dihydroxyacetone (DHA) and hydroxypyruvic acid. DHA is presently employed in the cosmetics industry as a component in artificial tanning preparations. If available at a lower market price, it would also find various applications as a versatile building block. Previously

reported examples of glycerol oxidation to DHA include microbial fermentation with *Gluconobacter oxydans*,³ which is the currently used method for industrial production, and electrocatalytic oxidation in the presence of TEMPO;⁴ heterogeneously-catalyzed reactions are generally poorly selective,⁵ with the exception of some platinum catalysts developed by Kimura and co-workers.⁶ An efficient, selective, catalytic procedure for glycerol oxidation to DHA is presently lacking.



Scheme 1

We recently proposed a novel route for glycerol valorization⁷ using homogeneous iridium-based catalysts 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) to promote the chemoselective dehydrogenation of glycerol to DHA under hydrogen transfer conditions. The idea was that glycerol would behave as a hydrogen donor, as it can be considered as a disubstituted 2-propanol. Unfortunately, in spite of the excellent chemoselectivity of the catalytic systems employed, the final yields of DHA were lower than expected due to the poor stability of the target molecule in the presence of the necessary basic cocatalyst. It can be recalled that the great majority of transfer hydrogenation catalysts require a basic cocatalyst in order to achieve an appreciable catalytic activity.⁸

In the course of previous studies on hydrogen transfer reactions, in our laboratories, we had developed iridium catalysts with P–N-type ligands that showed the unusual

^aCNR—Istituto Struttura della Materia, Unità staccata di Trieste, S.S.14, Km 163.5, 34149, Basovizza, Trieste, Italy

^bINCA (Interuniversity Consortium “Chemistry for the Environment”), Research Unit of Trieste, Italy

^cDipartimento di Scienze Chimiche, Università di Trieste, Via Giorgieri 1, 34127, Trieste, Italy. E-mail: farnetti@units.it; Fax: +39 040 5583903; Tel: +39 040 5583938

ability to promote the reaction in the absence of a basic cocatalyst.^{9,10} Such complexes, namely [HIr(cod)(PNP)] (PNP = $\text{Pr}^n\text{-N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$), [HIr(cod)(P_2N_2)] (P_2N_2 = $\text{Et}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$) and [HIr(cod)(P-NMe₂)] (P-NMe₂ = *o*-Me₂NC₆H₄PPh₂), appeared to be suitable candidates to study glycerol dehydrogenation in the absence of a basic cocatalyst, with the aim of minimising the decomposition of the DHA product. Here, we report the results obtained by the use of such catalysts, together with those observed with other organoiridium compounds in the base-free hydrogen transfer dehydrogenation of glycerol in the presence of a ketone, olefin or aldehyde as a hydrogen acceptor, as well as some results of acceptor-less glycerol dehydrogenation reactions.

Results

The iridium complexes [HIr(cod)L] (L = PNP (**1**), P_2N_2 (**2**)), which were prepared by the reaction of [Ir(cod)(OMe)]₂ with one equivalent of the phosphine ligand, were in fact isolated as their isomers [Ir($\sigma,\eta^2\text{-C}_8\text{H}_{13}$)L] (see Fig. 1).

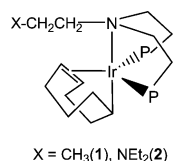


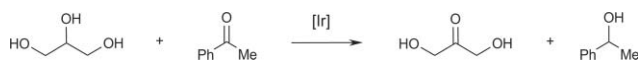
Fig. 1 Structures of compounds **1** and **2**

As evidenced by NMR studies with both P–N ligands, in solution, the hydrido cyclooctadiene compound rearranged to the insertion product with a coordinated cyclooctenyl group; in the resulting equilibrium, at r.t., the latter species was the prevalent one, whereas the amount of hydrido isomer [HIr($\eta^2,\eta^2\text{-C}_8\text{H}_{12}$)L] increased by raising the temperature.

In previous studies, compounds **1** and **2** have proved to be active catalysts for the hydrogen transfer reduction of various ketones, using a secondary alcohol, such as 2-propanol or cyclopentanol, as a hydrogen donor in the absence of a basic cocatalyst.^{9,11}

Catalytic reactions with acetophenone

The hydrogen transfer reactions between glycerol and acetophenone (see Scheme 2) were initially performed using the former as the solvent.



Scheme 2

Compounds **1** and **2**, as well as all the other iridium catalysts tested, proved to be only partially soluble in glycerol, even at temperatures above 100 °C; however, the catalytic reactions were never performed at temperatures higher than 120 °C, as our previous studies⁷ had evidenced that the expected product, DHA, undergoes significant thermal degradation at such temperatures (after 1 h in the absence of catalyst, DHA decomposition was lower than 10% at 100 °C, 20% at 120 °C and 45% at 140 °C).

Table 1 Hydrogen transfer reactions between glycerol and acetophenone catalyzed by iridium complexes^a

Entry	Catalyst	Yield (%) ^b	
		1-Phenylethanol	DHA
1	HIr(cod)(PNP)	8	6
2	HIr(cod)(P_2N_2)	<1	<1
3	HIr(cod)(PCy ₂ Ph) ₂	<1	<1
4	HIr(cod)(dppp)	1	1
5	HIr(cod)(P-NMe ₂)	3	2
6	IrCp*(NHC)Cl ₂	3	1
7	[IrCp*Cl ₂] ₂	1	1

^a Experimental conditions: [Ir] = 3.0×10^{-3} M, [acetophenone]/[Ir] = 100, T = 120 °C, reaction time = 1 h. ^b Based on the initial acetophenone amount.

In the catalytic reaction in the presence of **1** at 120 °C, after 1 h, GC analysis of the reaction mixture showed a conversion of 8%, measured as the decrease in acetophenone concentration and the quantitative formation of the reduction product, 1-phenylethanol. The only glycerol oxidation product detected was DHA, but the yield of the latter compound was not quantitative, probably due to partial thermal degradation. When the same reaction was performed using **2** as the catalyst, only traces of 1-phenylethanol and DHA were detected, even after longer reaction times.

Other selected iridium catalysts, all of which are known to promote hydrogen transfer under baseless conditions, were tested for glycerol dehydrogenation. [HIr(cod)(PCy₂Ph)₂]¹² [HIr(cod)(dppp)] (dppp = 1,3-bis(diphenylphosphino)propane)¹³ and [HIr(cod)(P-NMe₂)]⁹ only gave low conversions (see Table 1, entries 3–5). On the other hand, the complexes [Cp*IrCl₂]₂ (Cp* = pentamethylcyclopentadienyl) and [Cp*Ir(NHC)Cl₂] (NHC = 1,3-di-*n*-butylimidazolylidene)^{14,15} promoted the formation of small amounts of DHA, the main reaction products being, in both cases, mixtures of cyclic ketals formed by glycerol acetalization (see Table 1, entries 6 and 7).

Based on these results, further investigations focused on catalyst **1**. We tested this compound at longer reaction times and obtained only moderate increases of conversion, measured as 1-phenylethanol yield, but lower selectivities of DHA formation. This was because a longer permanence in solution at 120 °C caused a more pronounced degradation of the hydroxyketone. On the other hand, reactions performed at lower temperatures resulted in a worse conversion but a higher selectivity. Interestingly, in some cases, the DHA yield was higher than that of 1-phenylethanol (e.g. at 100 °C, 5% and 3%, respectively) (*vide infra*).

The use of pure glycerol leads to low catalyst solubility. Unfortunately, the alternative use of a glycerol/water mixture caused a remarkable loss of DHA yield, thus ruling out the greenest possible cosolvent. Some organic solvents were then tested (Table 2); toluene and anisole were chosen as possible catalyst protecting agents, since at 100 °C they gave rise to two-phase mixtures, the catalyst being more soluble in the cosolvent. On the other hand, dioxane and *tert*-butanol were selected as they gave rise to homogeneous solutions where the catalyst dissolved more easily than in glycerol alone. In fact, in all cases,

Table 2 Hydrogen transfer reactions between glycerol and acetophenone catalyzed by $\text{HIr}(\text{cod})(\text{PNP})$ in the presence of a cosolvent^a

Entry	Cosolvent	Yield (%) ^b	
		1-Phenylethanol	DHA
1	—	3	5
2	1,4-Dioxane	1	4
3	Toluene	1	6
4	Anisole	1	9
5	<i>tert</i> -Butanol	2	5

^a Experimental conditions: $[\text{Ir}] = 3.0 \times 10^{-3} \text{ M}$, $[\text{acetophenone}]/[\text{Ir}] = 100$, $T = 100^\circ\text{C}$, reaction time = 1 h, glycerol/cosolvent = 3 : 1. ^b Based on the initial acetophenone amount.

the catalyst was completely dissolved by the reaction mixture. For all the reactions with a cosolvent (Table 2, entries 2–5), the conversions (measured as the amount of acetophenone reduced to 1-phenylethanol) did not exceed 2%. Rather surprisingly, the yield of DHA was, in all cases, higher than that of 1-phenylethanol, which could be explained in terms of two parallel reaction paths, *i.e.* a hydrogen transfer between glycerol and acetophenone and a dehydrogenation of glycerol without the participation of a hydrogen acceptor.

Catalytic reactions without a hydrogen acceptor

The acceptor-less dehydrogenation of alcohols is an uncommon reaction, only a few examples having been reported recently.¹⁶ It is needless to point out the importance of this process due to its excellent atom economy and *E* factor.^{1a}

A series of dehydrogenation reactions in the absence of a hydrogen acceptor (see Scheme 3), with or without cosolvent, led to the formation of DHA, thus confirming that catalyst **1** promotes acceptor-less dehydrogenation. Even better yields were achieved using other solvents that featured miscibility with glycerol, low volatility and a negligible hydrogen donor ability: 1,3-dimethoxybenzene and 2-methyl-1-phenyl-2-propanol gave dehydrogenation TONs up to 11 in 1 h at 100°C (compared to a dehydrogenation TON of about 2 obtained in the analogous reaction without cosolvent).

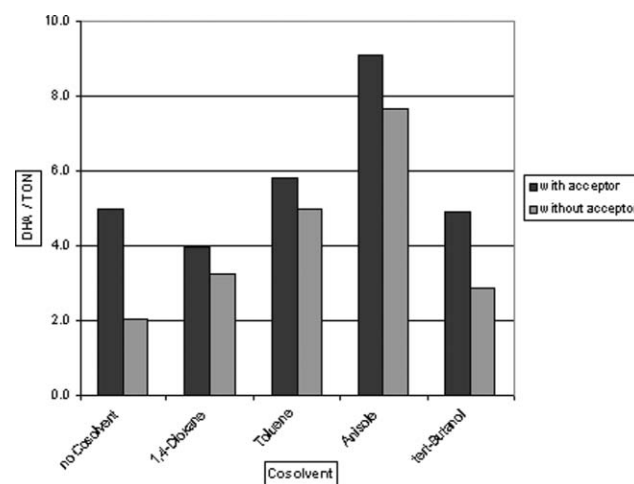
**Scheme 3**

Reaction temperatures either higher or lower than 100°C gave poorer results, as DHA yields were lower *e.g.* at 80°C , whereas at 120°C the final amount of DHA had decreased, probably due to thermal degradation; the latter effect was also observed after longer reaction times. In all cases, a comparison of two similar reactions where the only difference was the presence or absence of acetophenone as a hydrogen acceptor was extremely satisfactory, confirming that, when acetophenone was employed, the final total yield of DHA was the sum of the amount formed *via* hydrogen transfer and that formed *via* dehydrogenation. A graphical comparison of the TONs of the catalytic reactions with and without hydrogen acceptor is shown in Fig. 2.

Table 3 Hydrogen transfer reactions between glycerol and various acceptors catalyzed by $\text{HIr}(\text{cod})(\text{PNP})$ ^a

Entry	Acceptor	Yield (%) ^b	
		Hydrogenated acceptor	DHA
1	Acetophenone	3	5
2	Cyclohexanone	4	5
3	Styrene	6	8
4	<i>trans</i> -Ethylcrotonate	<1	2
5	Benzaldehyde	37	23

^a Experimental conditions: $[\text{Ir}] = 3.0 \times 10^{-3} \text{ M}$, $[\text{acceptor}]/[\text{Ir}] = 100$, $T = 100^\circ\text{C}$, reaction time = 1 h. ^b Based on the initial acceptor amount.

**Fig. 2** Comparison of reaction TONs with and without acetophenone as a hydrogen acceptor in the presence of a cosolvent.

Catalytic reactions with various hydrogen acceptors

In order to assess to what extent the choice of hydrogen acceptor affects the glycerol dehydrogenation, other hydrogen acceptors were investigated, *i.e.* cyclohexanone, an aldehyde (benzaldehyde) and two olefins (styrene and *trans*-ethylcrotonate) (Table 3).

The catalytic reactions performed with the two ketones gave similar results (see Table 3, entries 1 and 2), whereas styrene was superior to the conjugated olefin (Table 3, entries 3 and 4). Notably, when benzaldehyde was employed as a hydrogen acceptor (Table 3, entry 5), DHA yields higher than 20% were obtained. In this case, significant amounts of acetals were also formed. Such compounds have been identified on the basis of GC-MS and NMR data as the cyclic acetals formed from glycerol and benzaldehyde, *i.e.* *cis*- and *trans*-2-phenyl-[1,3]dioxan-5-ol, and *cis*- and *trans*-(2-phenyl-[1,3]dioxolan-4-yl)-methanol.

Catalytic reactions with benzaldehyde

The use of benzaldehyde as a hydrogen acceptor in glycerol dehydrogenation was further investigated. It is noteworthy that for a long time aldehydes have not been considered good candidates as hydrogen acceptors,¹⁷ mainly due to their disposition to undergo decarbonylation, thus forming catalytically-inactive metal carbonyl derivatives; moreover, their low stability under

Table 4 Hydrogen transfer reactions between glycerol and benzaldehyde catalyzed by iridium complexes^a

Entry	Catalyst	Yield (%) ^b		
		Benzyl alcohol	DHA	Acetals
1	HIr(cod)(PNP)	37	23	7
2 ^c	HIr(cod)(PNP)	46	24	16
3 ^d	HIr(cod)(PNP)	18	12	14
4	HIr(cod)(P ₂ N ₂)	5	8	15
5	HIr(cod)(PNMe ₂)	4	7	23

^a Experimental conditions: [Ir] = 3.0×10^{-3} M, [benzaldehyde]/[Ir] = 100, T = 100 °C, reaction time = 1 h. ^b Based on the initial benzaldehyde amount. ^c Reaction time = 3 h. ^d [Benzaldehyde]/[Ir] = 200.

the basic conditions generally required by hydrogen transfer catalysis has made them poorly appreciated substrates in this reaction. Only recently have reports appeared in the literature demonstrating the successful reduction of aldehydes under hydrogen transfer conditions.^{14b,18}

Benzaldehyde was tested as a hydrogen acceptor along with catalyst **1** under a range of different experimental conditions, in addition to other iridium-based catalysts. The data reported in Table 4 show that: (a) once more, longer reaction times led to an increase of the overall conversion without a significant increase in the DHA yield; moreover, when using benzaldehyde as an acceptor, the amount of acetals formed increased with time (see Table 4, entries 1 and 2); (b) higher aldehyde concentrations ([benzaldehyde]/[Ir] = 200 vs. 100) appeared to favour acetalization rather than hydrogen transfer (compare Table 4, entries 1 and 3); (c) other iridium catalysts were less active than **1** with respect to the hydrogen transfer reaction, whereas they appeared to be more efficient in catalyzing the formation of acetals (see Table 4, entries 4 and 5). The excess of benzyl alcohol with respect to DHA (see Table 4, entries 1–3) could be attributed to an iridium-catalyzed benzaldehyde dimerization; consistently, both benzyl alcohol and benzoic acid were detected, allowing benzaldehyde to react in the presence of **1** at 100 °C in wet toluene.

Discussion

The present data confirm the difficulty of catalytic transformations of glycerol when it is used as both a reactant and a reaction medium. In particular, the use of glycerol as a solvent implies a generally low solubility of catalysts and reagents, the unavoidable presence of water, with predictable consequences on organometallic catalysts, and further problems related to its high viscosity. These shortcomings might be overcome by the use of a suitable cosolvent. However, this choice is, in most cases, in contrast with the green chemistry principles stated by Anastas and Kirchhoff.¹⁹ For this reason, in spite of the beneficial effect of a cosolvent, as proved in our studies, no optimization of such reactions was carried out, as our aim was not to tune up at all costs the catalytic reaction, but rather prove that effective, selective reactions can be performed on glycerol by using no other reaction medium than glycerol itself. Furthermore, it turns out that glycerol does not behave as simply a disubstituted secondary alcohol, as proved by the difficult application of known catalytic systems otherwise working for 2-propanol.

With regard to the catalytic reactions reported here, our results confirm that iridium-catalyzed glycerol dehydrogenation selectively occurs at the secondary hydroxyl group, producing DHA as the only product. Unfortunately, the chemical properties of DHA make it susceptible to thermal degradation, thus lowering the effective yields obtained. The need to avoid catalytic systems that require a basic cocatalyst, towards which DHA has been shown to be reactive, severely restricts the choice of catalysts that can be employed. Actually, of the organoiridium compounds tested here, only complex **1** provided good results in glycerol dehydrogenation, whereas the other derivatives tested proved to be less active.

Rather important is the observation that acceptor-less glycerol dehydrogenation does actually work. Even if limited yields of DHA were achieved, the feasibility of the *greenest possible glycerol selective oxidation* has unambiguously been demonstrated.

On the other hand, by an appropriate choice of hydrogen acceptor, significant DHA yields can be produced in the absence of cocatalysts, as well as cosolvents. If the use of either a ketone or an olefin as a hydrogen acceptor only led to limited reaction conversions, when benzaldehyde was employed, the hydrogen transfer reactions occurred with considerable yields. Moreover, with such an acceptor, compounds **2** and [HIr(cod)(P-NMe₂)] also promoted the hydrogen transfer reaction, although with a catalytic activity lower than that of **1**. Therefore, the best results in the present studies were obtained by using benzaldehyde, which is not commonly considered as a first choice hydrogen acceptor.

The DHA yields reported here are quite high as, to our knowledge, only a bismuth-modified optimized platinum catalyst has given better results (37% yield of DHA at 70% conversion).^{20,21} Notably, as we recently reported, in the basic conditions typically required by catalysts [Ir(diene)(N–N)X], the highest DHA yield achieved was 13% at 33% conversion.⁷

Some features of the catalytic reaction are currently the object of more detailed investigations, *i.e.* the reasons for catalyst deactivation, which becomes significant after reaction times of 1–2 h, and the competition after longer reaction times of the acetalization reactions—which are themselves potentially interesting processes.

Conclusions

Glycerol selective dehydrogenation to DHA was achieved under iridium-catalyzed, base-free hydrogen transfer conditions by the appropriate selection of catalyst, hydrogen donor and reaction conditions. Among all of the organoiridium derivatives examined, only [HIr(cod)(PNP)] catalyzed the hydrogen transfer reaction from glycerol to all the acceptors tested. With the use of ketones and olefins, only low conversions were observed, whereas the choice of benzaldehyde as the hydrogen acceptor significantly raised the reaction conversion. DHA once more proved to be an evasive molecule due to its propensity to undergo thermal degradation, thus decreasing the actual yield of the reaction.

The use of organic solvents improved the catalyst performance; however, we preferred to stick to green chemistry principles, so no detailed optimisation of the reactions performed with cosolvents was carried out.

Interestingly, the feasibility of acceptor-less glycerol dehydrogenation was also demonstrated, albeit in limited yield. The development of such reaction would produce the greenest possible route for glycerol dehydrogenation.

Experimental

General

Reactions and manipulations were all performed under an argon atmosphere using standard Schlenk tube techniques.

Toluene was distilled over sodium; dioxane was distilled over sodium benzophenone ketyl immediately before use. The GC standard naphthalene was recrystallized from ethanol. All the other chemicals were of reagent grade and were used as received from their commercial supplier.

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

Instrumental

^1H , ^{13}C and ^{31}P NMR spectra were recorded on a Varian 500 spectrometer operating at 500, 125.68 and 202.28 MHz, respectively.

Infrared spectra were recorded in Nujol mulls on a Perkin-Elmer System 2000 FT-IR spectrophotometer.

The chemical yields of the catalytic reactions were determined by GC using an Agilent 6850 instrument equipped with an Rtx-5 Restek capillary column (30 m length). The analysis of reaction products was periodically sided by a parallel analysis on a Hewlett-Packard 5890 Series II GC instrument coupled to a Hewlett-Packard 5971A Mass Selective Detector equipped with an identical column.

Synthesis of the iridium catalysts

Procedures reported in the literature were followed for the preparation of $[\text{HIr}(\text{cod})(\text{PNP})]$,⁹ $[\text{HIr}(\text{cod})(\text{P}_2\text{N}_2)]$,⁹ $[\text{HIr}(\text{cod})(\text{P}-\text{NMe}_2)]$,¹⁰ $[\text{HIr}(\text{cod})(\text{PCy}_2\text{Ph})_2]$,²² $[\text{HIr}(\text{cod})(\text{dppp})]$,¹³ $[\text{Cp}^*\text{IrCl}_2]$,¹⁴ and $[\text{Cp}^*\text{Ir}(\text{NHC})\text{Cl}_2]$.¹⁵

Procedure for hydrogen transfer reactions without cosolvent

In a typical catalytic reaction, 4.0 mL of glycerol were introduced into a Schlenk tube equipped with an argon inlet and de-aerated by bubbling argon through a needle for 15 min. After the addition of the catalyst (0.012 mmol), the reaction vessel was closed using a serum cap and heated under vigorous stirring to the chosen reaction temperature in a thermostated oil bath. The addition of the hydrogen acceptor (1.2 mmol) by a microsyringe at the reaction temperature started the catalytic reaction.

After the desired reaction time, the Schlenk tube was cooled to r.t. and air let in under stirring. 10 mL of methanol containing the GC standard naphthalene were then added. The resulting solution was further diluted and analyzed by GC.

Procedure for hydrogen transfer reactions with cosolvent

The procedure was identical to that described in the previous paragraph, but for the initial addition of a cosolvent. Typically, the solvent mixture composition was 3.0 mL of glycerol and

1.0 mL of cosolvent. The mixture was de-gassed as described above.

Procedure for dehydrogenation reactions

In a typical acceptor-less dehydrogenation reaction, either 4.0 mL of glycerol or 3.0 mL of glycerol and 1.0 mL of cosolvent were introduced into a Schlenk tube equipped with an argon inlet. The solvent or mixture of solvents was de-aerated by bubbling argon through a needle for 15 min. After the addition of the catalyst (0.012 mmol), the reaction vessel was closed using a serum cap and heated under vigorous stirring to 100 °C (or any other chosen temperature) in a thermostated oil bath. In analogy to the procedure followed for hydrogen transfer reactions, the time when the oil bath reached 100 °C (or any other reaction temperature, respectively) was considered as the start of the catalytic reaction.

After 1 h (or any other reaction time), the Schlenk tube was cooled to r.t. and air let in under stirring. The addition of 10 mL of methanol and the GC standard naphthalene provided the final solution, which was analyzed by GC.

Analysis of the reaction mixtures

The composition of the final reaction mixtures was determined by GC and GC-MS. Qualitative analysis was accomplished by GC-MS using, where possible, authentic samples for comparison. Quantitative evaluation of product distributions were performed by GC with naphthalene as the internal standard, using response factors previously determined by the analysis of standard solutions; the quantitative analysis thus performed allowed a reproducibility within $\pm 1\%$.

The qualitative and quantitative analysis of acetals and ketals formed as by-products in the catalytic reactions was performed by NMR and GC-MS; the data were compared with those of authentic samples obtained by conventional routes (*i.e.* acid-catalyzed acetalization).

Acknowledgements

Johnson Matthey PLC is gratefully acknowledged for the generous loan of iridium chloride. Support from the Interuniversity Consortium "Chemistry for the Environment" (INCA) is acknowledged.

References

- (a) R. A. Sheldon, *Chem. Commun.*, 2008, 3352; (b) P. Gallezot, *Green Chem.*, 2007, **9**, 295.
- (a) A. Behr, J. Eilting, K. Irawadi, J. Leschinski and F. Lindner, *Green Chem.*, 2008, **10**, 13; (b) C.-H. Zhou, J. N. Beltramini, Y.-X. Fan and G. Q. Lu, *Chem. Soc. Rev.*, 2008, **37**, 527; (c) M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi and C. Della Pina, *Angew. Chem., Int. Ed.*, 2007, **46**, 4434.
- D. Hekmat, R. Bauer and V. Neff, *Process Biochem.*, 2007, **42**, 71.
- R. Ciriminna, G. Palmisano, C. Della Pina, M. Rossi and M. Pagliaro, *Tetrahedron Lett.*, 2006, **47**, 6993.
- (a) P. Fordham, M. Besson and P. Gallezot, *Appl. Catal., A*, 1995, **133**, L179; (b) N. Dimitratos, J. A. Lopez-Sanchez, D. Lennon, F. Porta, L. Prati and A. Villa, *Catal. Lett.*, 2006, **108**, 147; (c) S. Carrettin, P. McMorn, P. Johnston, K. Griffin, C. J. Kiely and G. J. Hutchings, *Phys. Chem. Chem. Phys.*, 2003, **5**, 1329; (d) S. Carrettin, P. McMorn, P. Johnston, K. Griffin, C. J. Kiely, C. A. Attard and G. J. Hutchings,

- Top. Catal.*, 2004, **27**, 131; (e) P. Fordham, M. Besson and P. Gallezot, *Catal. Lett.*, 1997, **46**, 195.
- 6 (a) H. Kimura, K. Tsuto, T. Wakisaka, Y. Kazumi and Y. Inaya, *Appl. Catal., A*, 1993, **96**, 217; (b) H. Kimura, *Appl. Catal., A*, 1993, **105**, 147.
- 7 E. Farnetti, J. Kaspar and C. Crotti, *Green Chem.*, 2009, **11**, 704.
- 8 (a) S. Gladiali and E. Alberico, *Chem. Soc. Rev.*, 2006, **35**, 226; (b) G. Zassinovich, G. Mestroni and S. Gladiali, *Chem. Rev.*, 1992, **92**, 1051.
- 9 C. Bianchini, E. Farnetti, M. Graziani, G. Nardin, A. Vacca and F. Zanobini, *J. Am. Chem. Soc.*, 1990, **112**, 9190.
- 10 E. Farnetti, G. Nardin and M. Graziani, *J. Chem. Soc., Chem. Commun.*, 1989, 1264.
- 11 E. Farnetti, N. Verma Gulati and M. Graziani, *Gazz. Chim. It.*, 1993, **123**, 165.
- 12 E. Farnetti, unpublished results.
- 13 M. J. Fernandez, M. A. Esteruelas, M. Covarrubias and L. A. Oro, *J. Organomet. Chem.*, 1986, **316**, 343.
- 14 (a) K. Fujita, S. Furukawa and R. Yamaguchi, *J. Organomet. Chem.*, 2002, **649**, 289; (b) X. Wu, J. Liu, X. Li, A. Zanolli-Gerosa, F. Hancock, D. Vinci, J. Ruan and J. Xiao, *Angew. Chem., Int. Ed.*, 2006, **45**, 6718.
- 15 R. Corberán and E. Peris, *Organometallics*, 2008, **27**, 1954.
- 16 (a) K. Fujita, N. Tanino and R. Yamaguchi, *Org. Lett.*, 2007, **9**, 109; (b) J. van Buijtenen, J. Meuldijk, J. A. J. M. Vekemans, L. A. Hulshof, H. Kooijman and A. Spek, *Organometallics*, 2006, **25**, 873; (c) J. Zhang, M. Gandelman, L. J. W. Shimon, H. Rozenberg and D. Milstein, *Organometallics*, 2004, **23**, 4026.
- 17 S. Gladiali and E. Alberico, in *Transition Metals for Organic Synthesis*, ed. M. Beller and C. Bolm, Wiley-VCH, Weinheim, 2nd edn, 2004, ch. 1.3, pp. 145–166.
- 18 (a) J. R. Miecznikowski and R. H. Crabtree, *Organometallics*, 2004, **23**, 629; (b) A. N. Ajjou and J.-L. Pinet, *J. Mol. Catal. A: Chem.*, 2004, **214**, 203.
- 19 P. T. Anastas and M. M. Kirchhoff, *Acc. Chem. Res.*, 2002, **35**, 686.
- 20 R. Garcia, M. Besson and P. Gallezot, *Appl. Catal., A*, 1995, **127**, 165.
- 21 N. Wörz, A. Brandner and P. Claus, *J. Phys. Chem. C*, 2010, **114**, 1164.
- 22 M. Marigo, D. Millos, N. Marsich and E. Farnetti, *J. Mol. Catal. A: Chem.*, 2003, **206**, 319.